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SULFATE ATTACK ON CONCRETE WITH MINERAL ADMIXTURES

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ABSTRACT

The sulfate resistance of concretes containing fly ash, natural pozzolan and slag is investigated in a field test in which concrete specimens were half-buried in sulfate soil for five years. Mineral admixtures were used as a partial replacement for ordinary portland cement (C_3A = 8.5%), and the progress of sulfate attack was evaluated by several methods (visual rating, loss in mass, dynamic modulus, strength, x-ray analysis). Results of this study show that mineral admixtures improved the sulfate resistance when the concrete is buried in the soil. However, concretes with high content of mineral admixtures exhibit a greater surface scaling over soil level due to the sulfate salt crystallization. In this zone, capillary suction of concrete is the main mechanism of water and salt transportation. Concrete with 20% fly ash provides an integral solution for half-buried structures.

Introduction

The durability of concrete in sulfate environment depends on several factors, such as the permeability of the concrete, the type of structure, the concentration and type of sulfate, the water table and the mobility of the groundwater[1]. On the other hand, the sulfate attack on concrete is a complex phenomenon, where chemical and physical aspects should be considered. According to Calleja[2], the mechanism of sodium sulfate attack can be divided into ettringite formation, gypsum formation, and salt crystallization. All products occupy a greater space than the original compounds causing expansion, disruption and cracking. For gypsum and ettringite formation, the volume increases about 1.2 and 2.5 times, respectively[3], whereas the crystallization of $Na_2SO_4 \cdot 10H_2O$ causes expansion about 4 or 5 times the original volume[4].

During the 1970's, there was great interest in the use of mineral admixtures in concrete due to economic and ecological reasons, and their beneficial effects on concrete properties were rediscovered. In sulfate attack, the contribution of mineral admixtures can be summarized as: calcium hydroxide reduction, permeability reduction and C_3A dilution[5]. In the last years, most laboratory studies[6-8] reporting an improvement in the sulfate resistance of portland cement by the addition of mineral admixtures have been carried out with test methods using totally immersed specimens. Under these conditions of exposure, salt crystallization cannot occur. On the other hand, longtime studies[9,10] have focused on measuring the changes in the basic engineering properties—expansion, mass loss, strength and stiffness- and the performance of admixtures has been judged by this partial information.

Concrete in service is subjected to a variety of conditions of exposure, such as frequency of drying and wetting cycles, different temperatures, superficial carbonation, and drying shrinkage. These conditions influence the mode of attack and it is generally recognized that they cannot be exactly duplicated in the laboratory.

This paper examines the changes in the engineering properties and mineralogical characteristic of concretes containing mineral admixtures, when they were exposed half-buried to a sulfate soil for five years.

Experimental

Materials and Mix Proportions. A portland cement with 8.5% C_3A was used to make concretes with natural pozzolan, fly ash or slag. In addition, a low C_3A (about 2%) portland cement was used to make a sulfate resistant concrete for comparative purpose. Fly ash and natural pozzolan were used as 20 and 40 percent weight replacement for portland cement. According to ASTM C 618, the fly ash and the natural pozzolan used in this study are classified as Class F and Class N pozzolans, respectively. Blast furnace slag was used as 80 percent weight replacement for portland cement. The chemical and physical properties of these materials are summarized in Table 1. All formulated blended cements have demonstrated to be sulfate resistant according to Koch and Steinegger test[11].

For all concretes, coarse aggregate was a granitic crushed stone with a maximum size of 25 mm, and fine aggregate was natural sand with a fineness modulus of 2.75. Concrete proportions were adjusted to give a slump of 70 ± 20 mm. The sand-aggregate ratio was 0.58, the water-cementitious ratio was 0.52, and the cementitious content remained (300 ± 20 kg/m^3). For H2 concrete, the air content was 4.4%, obtained by a neutralized vinsol air entraining agent. Concrete mix proportions and properties of fresh concrete are given in Table 2.

TABLE 1
Prorerties of Mineral Admixtures

	Fly Ash	**Pozzolan**	**Slag**
Chemical composition, %			
SiO_2	59.60	76.90	33.20
Al_2O_3	24.00	9.80	13.30
Fe_2O_3	6.90	3.60	4.10
CaO	4.90	1.80	39.30
SO_3	0.59	-.-	-.-
MgO	2.06	0.50	6.20
Na_2O	0.84	3.70	0.28
K_2O	0.31	1.40	0.80
LOI	0.72	2.40	-.-
S+A+F	90.50	90.30	-.-
[C+A+M]/S	-.-	-.-	1.77

	Fly Ash	**Pozzolan**	**Slag**
Physical Characteristics			
Specific gravity	1.92	2.41	2.91
Fineness (Blaine) m^2/kg	286	630	268
Retained on sieve, % weight			
300 µm (No 50)	1.4	0.0	0.0
150 µm (No 100)	5.2	0.0	4.2
75 µm (No 200)	26.4	3.0	12.6
45 µm (No 325)	41.0	7.6	32.4
Pozzolanic index with portland cement, %	76	92	-.-

TABLE 2
Mix Proportions in kg/m^3 and Properties of Fresh Concrete

				Fine	Coarse	Slump	Unit Weight	Air	Bleeding	
Mix	Water	Cement	Addition	Agg	Agg	(mm)	(kg/m^3)	%	Capacity(%)	Rate*
H1 Type I	167	314	-	703	1215	70	2404	1.3	7.4	47
H2 Type I+air	155	293	-	697	1206	60	2354	4.4	4.4	25
H3 20% Fly Ash	162	245	61	699	1209	65	2378	1.4	6.5	65
H4 40% Fly Ash	158	182	121	689	1195	50	2345	1.8	6.7	66
H5 20% N. Pozz.	161	246	61	702	1210	60	2382	1.7	6.1	30
H6 40% N. Pozz.	159	184	123	699	1198	70	2364	1.8	4.8	18
H7 80% Slag	167	63	253	698	1207	80	2389	1.2	-	-
H8 Type V	163	308	-	704	1214	75	2389	1.5	-	-

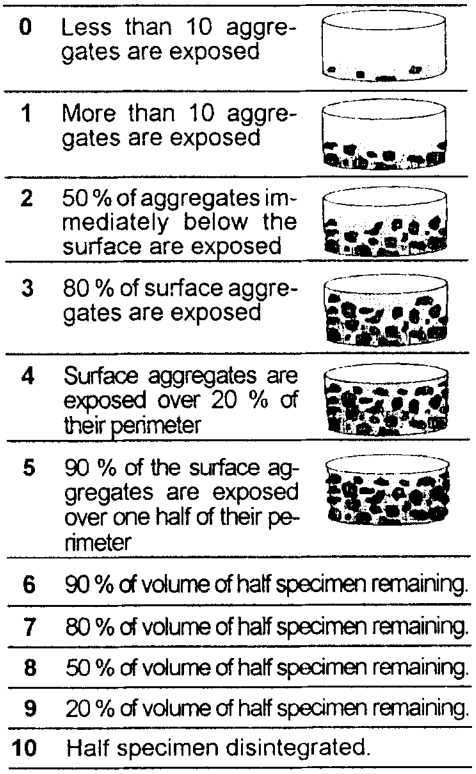
* expressed in 10^{-6} cm/s

Specimen Curing and Exposure Conditions. For each concrete, thirty 150 × 300 mm cylinders were cast with two layers and each layer was compacted with an immersion vibrator. After casting, all specimens were cured in the molds during 24 hours (48 hours for H7 concrete) and then moist cured at 21 °C. After 28 days, cylinders were buried at half height in a soil containing approximately 1% of sodium sulfate (see Figure 1), and two cylinders of each mix were stored in the laboratory as control. The soil was classified as sandy mud and the concentration of ions in soil is given in Table 3.

During the five years reported, weather conditions at the exposure site are described by the following parameters: an annual rainfall of 900 mm, highest temperature of 34 °C in summer and lowest of 0 °C in winter. Specimens are exposed to about fifteen to twenty cycles of wetting and drying per year, due to the periodicity of precipitations. There was no freezing and thawing.

Inspection Tests and Results. The progress of deterioration of each specimen was monitored by the following methods of evaluation:

FIG. 1.
View of concrete specimens in the field.



0	Less than 10 aggregates are exposed	
1	More than 10 aggregates are exposed	
2	50 % of 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	90 % of volume of half specimen remaining.	
7	80 % of volume of half specimen remaining.	
8	50 % of volume of half specimen remaining.	
9	20 % of volume of half specimen remaining.	
10	Half specimen disintegrated.	

FIG. 2.
Visual rating system used to judge specimens in the top and bottom half height of cylinders.

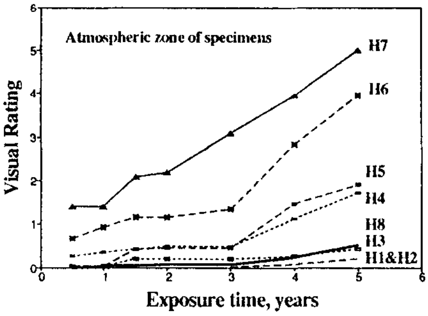


FIG. 3.
Evolution of visual rating at the atmospheric zone of concretes.

Visual observation: The external condition of specimens was judged by a visual rating (Figure 2) based on the rating system proposed by Malhotra et al.[12]. Due to the characteristics of the attack, specimens were evaluated at top and bottom-half height. For each concrete a photograph of a representative specimen was taken at each annual inspection. The evolution of visual rating of top-half height is shown in Figure 3. For H3 through H8 concretes, the visual rating of bottom-half height of specimens was zero at five-year' inspection; whereas it was 0.3 and 0.6 for H1 and H2 concretes, respectively.

TABLE 3

Concentration of Ions in Soil at Springtime, in Percent

	1988 (0y)	1991 (3y)	1995 (5y)
SO_4^{2-}	0.97	1.02	0.93
Mg^{2+}	0.25	0.23	0.21
Cl^-	0.03	0.05	0.06
Na^+	0.35	0.30	0.32
pH	7.5	7.8	8.1

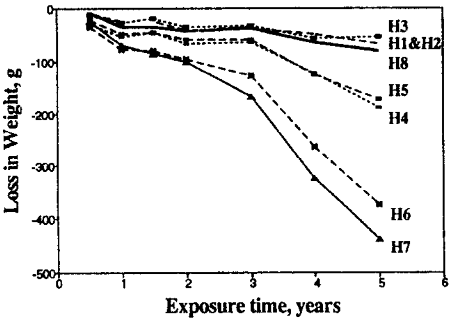


FIG. 4.
Effect of sulfate exposure on loss in weight of concretes.

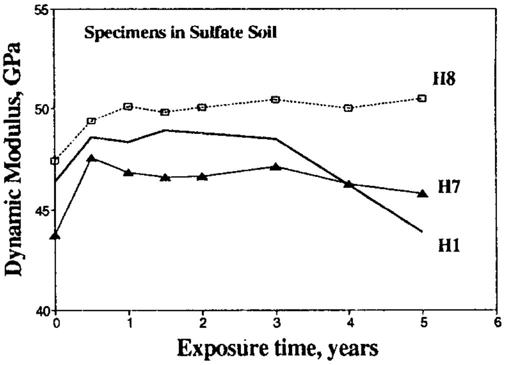


FIG. 5.
Evolution of dynamic modulus for H1 (Type I), H7 (80% slag) and H8 (Type V) concretes.

Loss in weight: All specimens were weighed prior to beginning sulfate exposure. At each inspection, the change in weight was computed as the difference between actual and initial weight. Figure 4 presents the average value of all specimens for each concrete. For concretes H3 through H8, the mass loss occurred in the top-half height of specimens.

Dynamic modulus (Ed). It was determined on cylindrical specimens according to ASTM C

TABLE 4

Compressive Strength in MPs and Elastic Modulus in GPa

		28 Days	1 Year	5 Years
H1	fc	23.97	36.47 (+52)	44.86 (+87)
	E	35.14	41.48 (+18)	30.08 (-14)
H2	fc	22.60	32.57 (+44)	39.95 (+77)
	E	31.90	40.96 (+28)	26.80 (-16)
H3	fc	21.87	37.20 (+70)	43.27 (+98)
	E	36.43	43.68 (+20)	42.19 (+16)
H4	fc	16.13	29.93 (+86)	39.37 (+144)
	E	31.38	42.05 (+34)	40.87 (+30)
H5	fc	22.90	41.07 (+79)	49.43 (+116)
	E	35.13	42.02 (+20)	40.98 (+17)
H6	fc	20.93	35.43 (+69)	44.89 (+114)
	E	37.40	41.37 (+11)	39.46 (+6)
H7	fc	18.05	26.15 (+45)	32.85 (+82)
	E	25.64	31.19 (+22)	34.68 (+35)
H8	fc	31.30	43.39 (+39)	52.57 (+68)
	E	38.81	43.26 (+11)	42.62 (+10)

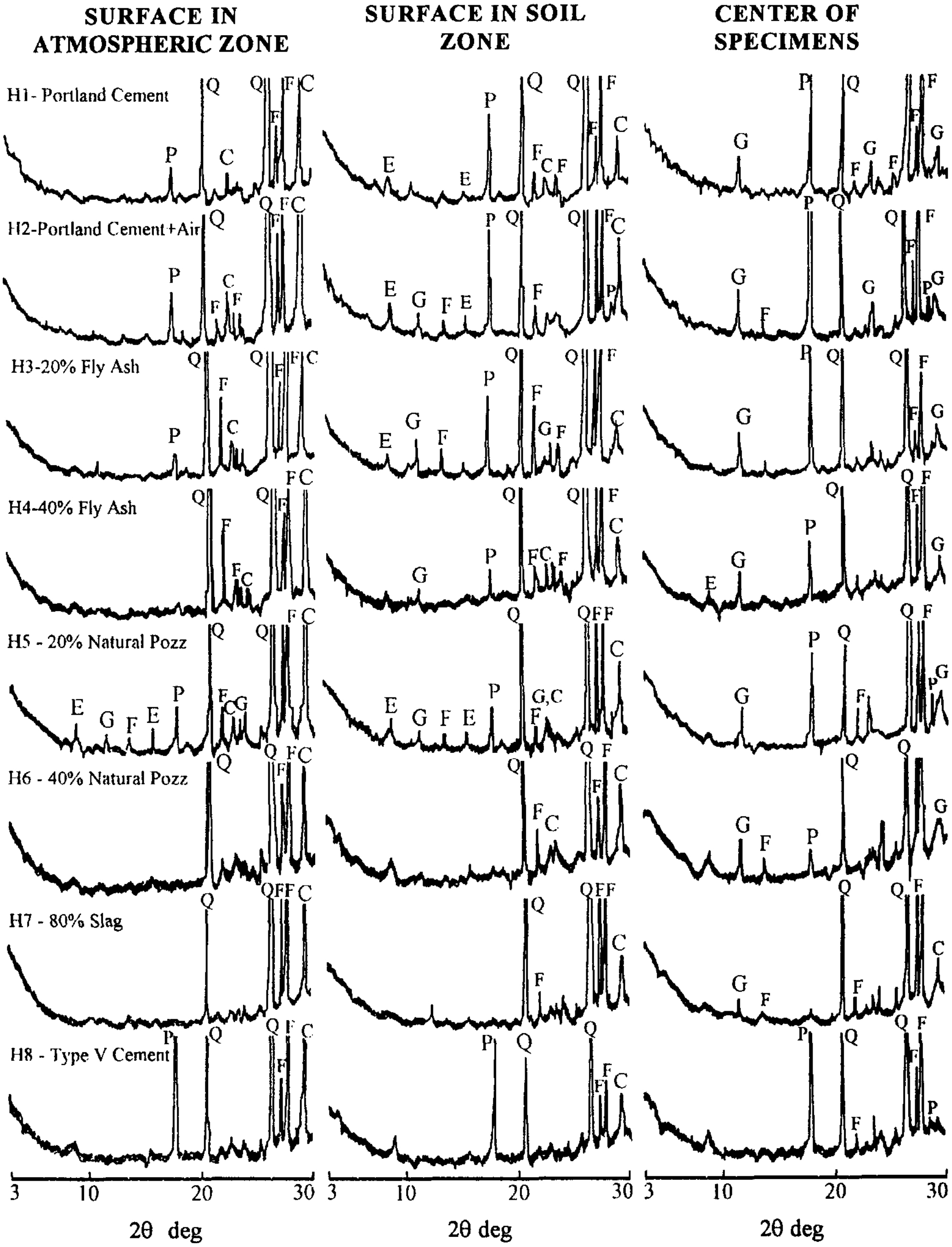


FIG. 6.

XRD-patterns of all concretes at five years (P = portlandite, G = gypsum, C = calcite, E = ettringite, Q = quartz, F = feldspar).

215. For H3 through H8 concretes, there is very small change in the values of E_d after a six-month storage in water or sulfate soils. Only, concretes H1 and H2 showed a drop (about 10%)

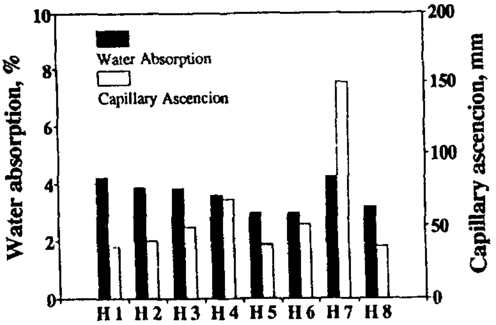


FIG. 7.
Water absorption and capillary ascension for concretes.

in the dynamic modulus. It is not essential to give here the complete data of E_d determination for all concretes analyzed. For the purpose of illustration, Figure 5 shows E_d evolution for H1, H7 and H8 concretes.

Compressive strength and elastic modulus. At five years of exposure, two specimens were tested to evaluate static elastic modulus and compressive strength. The mean values of these tests are reported in Table 4. The numbers in parentheses indicate percent of strength and odulus based on 28-day values.

XRD analysis. A complete XRD study was carried out on a specimen broken under compression after five years. Concretes were crushed to remove coarse aggregate and the remaining mortar was ground to 75μm (N° 200) sieve for X-ray analysis. Samples were taken from either the surface at 50 mm from top and bottom of the specimen, and from the core into top and bottom-half height of specimen. All concretes exhibited a similar XRD pattern of both core samples. Figure 6 shows X-ray analyses of the superficial samples and the core sample in the buried zone.

Discussion

For the exposure conditions of the specimens, the effect of sulfate attack must be examined in two zones: a) the zone where the concrete is in contact with the atmosphere and b) the zone where the concrete is buried in sulfate soil. The external appearance of concrete containing mineral admixtures was entirely different in both zones.

Atmospheric Zone. The evolution of visual aspect (Figure 3) shows that, whereas no significant deterioration (visual rating less than 1) occurred for plain concretes (H1, H2 and H8) after five years, concretes with high content of mineral admixtures (H4, H6 and H7) suffer an undesirably high degree of disintegration within a short exposure time (6 to 12 months). The degradation of concrete in this zone is attributed mainly to the physical attack of sulfate. This mechanism has been described by Reading[13]: the sulfate solution rises into the dryer portion of the specimens by capillary action, where the water evaporates easily. Thus, when the concentration of solute exceeds the saturation concentration, salt crystallization takes place and produces internal stresses in concrete pores, which are large enough to cause concrete cracking[14].

Repetitive crystallization cycles by drying and wetting of concrete cause progressive flaking off in concrete specimens. At first, the outer layer of paste comes off and the surface of specimens has a sandy appearance. Then, the mortar over the aggregates is removed with a plane of weakness at the paste-aggregate interface leading to expose coarse aggregates and the loss in weight increases. Later, a deeper layer is subjected to a similar attack and so the deterioration progresses.

In this zone, the degradation process is closely related with the capillary suction of concrete[15,23]. To examine this assumption, the water absorption and the capillary suction of concrete was determined on specimens (400 × 100 × 70 mm) stored during one year in laboratory as control. Specimens were weighed and a line along the greater dimension was marked in each face. Then, they were immersed vertically in water 50 mm deep during 48 hours. At this time, the height of water risen into the dry portion by capillarity was measured on each face and the specimens were weighed. Thereafter, the specimens were totally immersed in water and the water absorption was determined according to ASTM C 642. Figure 7 shows the mean results for theses tests. The height of capillary suction for concretes containing mineral admixtures increases with an increasing of replacement level. However, water absorption is lower than or equal to that of plain concretes. The higher capillary suction of concretes with mineral admixtures is due to the process of pore size refinement that results from the addition of pozzolan or slag[16]. This process is beneficial for concretes immersed in sulfate solution because the diffusion rate of ions decreases[17]. But, it is harmful in the atmospheric zone because the pore radius governs the water movement by capillarity[18].

Figure 8 shows a specimen detail of H4, H6 and H7 concretes at six-months' inspection. It is observed that extensive damage has occurred at soil level, because concrete has been affected by a major number of crystallization cycles. In this field test, the severity of attack in the atmospheric zone is aggravated due to the contact of specimens with groundwater and the high permeability of the soil. Another cause for poor durability would be the lower maturity of concretes containing mineral admixtures when exposed to first crystallization cycles.

The increase in visual rating (Figure 3) and loss in weight (Figure 4) for H4 through H8 concretes can be justified by the mechanism described above. In fact, both parameters are closely related.

At the outer layer in the atmospheric zone, XRD analyses reveal the presence of a strong calcite peak ($2\theta = 29.4$) and the consequent reduction of calcium hydroxide peak for all concretes. However, both typical compounds associated with sulfate attack (gypsum and ettringite) cannot be detected in the XRD-pattern, except for H5 concrete. The reasons suggested for these absences are: ettringite is unstable when pH is reduced and is decomposed by carbonation[19]; the combination of CH with atmospheric CO_2 is previous than the CH combination to form ettringite and gypsum; and the flaking-off of the concrete layer expels the material where this formation occurs.

Depending on the phase of wetting and drying cycle, a white substance was either observed or absent on the surface of concrete over the soil level. Novak and Colville[20] reported the same observation in concrete foundations in Southern California and all efflorescent samples contained crystals of sodium sulfate salt. Figure 9 show the XRD-pattern of the efflorescence collected from specimens. The main compound found was thenardite (Na_2SO_4), as product of sodium sulfate crystallization under dry condition[20]. For concrete material of the outer layer, XRD analyses (Figure 6) indicate that it is without sulfate salt. This may be due to the cleaning operation used before testing the specimens.

For the dry portion of concrete, its physical characteristics (porosity, capillary suction and tensile strength) prevail over the chemical protection that mineral admixtures provide. The

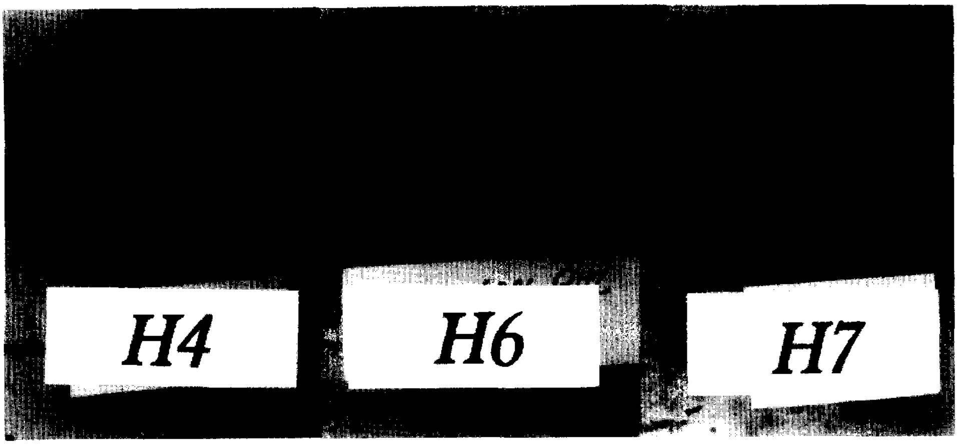


FIG. 8.
Details of specimens of H4, H6 and H7 concretes at soil level after six months of exposure.

primary mechanism of water penetration is capillary suction and the permeability is not relevant.

Deterioration due to sulfate salt crystallization occurs in desert terrains and has been reported in many regions of the world including the Middle East[21], alkali soil in Canada and USA[22], South Australia[23] and Argentine saline dry-lake[24]. The construction codes[1,25] advise of the most severe attack for this condition and recommend the use of sulfate resistant cement plus pozzolan, but only Biczok[26] warns of the high capillary suction of concrete containing mineral admixtures and he recommends an adequate surface protection. A field test carried out in Argentine[24] during 1976–1981 showed similar behavior to that described in this section for rich concretes with Type V cement and natural pozzolan (420 to 440 kg/m^3) and a low water-cement ratio (0.40).

Buried Zone. In the zone where the concrete is in contact with soil, the proper chemical sulfate attack takes place. The deterioration begins particularly at the end of specimens causing swelling, softening and cracking. Later, the spalling of concrete leads to loss in weight and the aggregates are exposed.

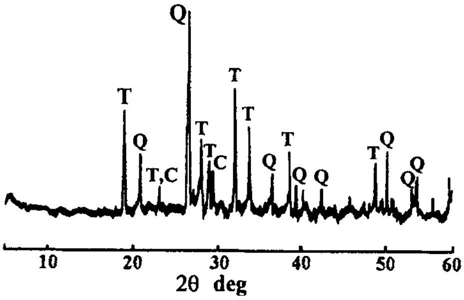


FIG. 9.
XRD pattern of wither efflorescence (T = thenardite, Q = quartz and C = calcite).

For H1 and H2 concretes, visual signs of cracking due to sulfate attack were found at two and three-years' inspections. However, these show no appreciable loss in weight (less than 1%) up to five years of exposure. Concretes containing 20% of fly ash and 20% of natural pozzolan show slight cracks and swelling in the bottom zone at four and five-years' inspection, respectively. On the other hand, concretes containing 40% of fly ash, 40% of natural pozzolan, 80% of slag and Type V portland cement performed satisfactorily after five years, with no damage at the surface of specimens.

The diffractograms of samples taken at the surface layer of specimens (Figure 6) show the presence of ettringite and gypsum for H1 to H5 concretes. For concretes with high replacements of pozzolan, fly ash and slag, the CH is removed, and ettringite and gypsum formation does not occur. For Type V concrete (H8), the gypsum formation is not detected in spite of an abundant presence of CH. Several authors[27,28] have reported that for Type V cement the reduction of large pores after sulfate immersion plays a decisive role in reduction of ion diffusion and decreases its sulfate susceptibility.

The carbonation in this surface zone, judging by the intensity of the calcite peak ($2\theta = 29.4$), is lower than that in the atmospheric zone.

Core Zone. The presence of CH at the core of specimens is quite evident from its characteristic peak at 18° deg 2θ for concretes containing fly ash, natural pozzolan and portland cement. This indicates that pozzolanic reaction converts only part of the CH derived from cement hydration. Only, replacement of slag by cement effectively converts CH, and ettringite and gypsum are absent from the diffraction pattern.

The existence of gypsum was detected with different intensity of principal peak at 11.67 deg 2θ for all concretes, except for Type V cement, while ettringite was not detectable in this zone. This presence reveals a deep penetration of sulfates into the concrete mass of specimens, instead of permeability reduction by pozzolans.

After five years in sulfate soil, compressive strength of all concretes was higher (15 to 30%) than one-year's strength. This observation seems to suggest that all specimens are sound into the core zone and the attack is localized at surface. However, the decrease in dynamic and static elastic modulus for H1 and H2 concretes revels the evidence of the sulfate attack into the core. These E-values indicate the presence of microcracking into the specimens. The strain-stress relationship is greatly affected by the properties of paste-aggregate zone[29]. For portland cement, several studies[30,31] have reported that gypsum is localized preferably at the interface leading to the increase of cracking in this zone and the consequent decrease of modulus. The sulfate attack progressed from the outer layer to the center of specimens, and the deterioration with softening or spalling was not reflected by the compressive strength.

For H3 through H8 concretes, the core of specimens shows no signs of distress based on the evolution of dynamic and static elastic modulus. There is no influence on compressive strength and elastic modulus due to the superficial damage in the atmospheric zone.

Conclusion

Result of this field test show that the attack on concretes half-buried in sulfate permeable soil is a complex phenomenon. Over the soil level, the mechanism of attack is attributed mainly to the sulfate salt crystallization, which causes a progressive scaling of concrete surface. For concrete in contact with soil, the attack is attributed to the chemical reaction between sulfates ions and cement paste compounds to form ettringite and gypsum. External evidences of this attack are cracking, crumbling and softening.

The mineral admixtures used for partial replacement of ordinary portland cement showed a greater sulfate resistance than plain concrete in the buried zone judged by visual, mechanical and mineralogical characteristics. However, the blended cement with Type I cement did not match the performance of Type V cement concrete, which maintained its integrity and there was no evidence of gypsum formation into the specimens.

The extensive damage observed in concretes with high content of mineral admixtures in the atmospheric zone is attributed to the high capillary suction. In this zone, capillary suction of concrete is the main mechanism of water and salt transportation.

For all concretes, there is no correlation between the increase in compressive strength and damage level. The elastic and dynamic modulus appear as more sensible parameters to evaluate the progress of internal attack.

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