Durability of GCB concrete exposed to sea water sulphates in the region of Jijel – Algeria

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Abstract**—**Significant deterioration has been observed on marine structures in the Jijel region, due to the low quality of the concrete produced and the aggressive nature of the external environment. The aim of this work is to study on concrete durability the grooved cubic blocks (GCB) immersed in the seawater near the North West pier of the port of DjenDjen under the effect of sulphates. On will retrieving cores from GCB immersed in sea water for 25 years at DjenDjen and the results obtained will compare with control specimens. Based on this study, it was concluded that the GCB concrete exhibited weak mechanical characteristics compared to the control specimens concrete, and a relatively slow penetration of the aggressive agents; as well as a significant reduction in compressive strength by 45 % of cores; and by 7 % for speed of sound at the age of 25 years. At the same age the carbonation depth test reached to 117.00 mm.

Keywords**—**Durability, sulphate resisting cement (SRC), grooved cubic block (GCB), seawater, sulphates.

I. INTRODUCTION

External sulfate attack on concrete is commonly observed durability problem in concrete structures exposed to the seawater, soils groundwater containing high concentrations of sulfate attack, and occurs after a series of chemical reactions between sulfate ions, cement paste and moisture [1]. The factors influencing the rate of external attack are: the measure of sulfate ions, the sulfates penetrated into the concrete and the percent of C_3A in the cement [2].

Sulfate resisting cement (SRC) use in structures exposed to sulfate action, the ion content increased to cut of content the tri-calcium aluminate (C_3A) to below 3.5 w_t % and adjusting (SO_3) to 2.5 w_t % [3].

DjenDjen at the Mediterranean coast 285 km east of Algiers and 10 km east of Jijel, the main town of the region; the port site is about 1 km east of the mouth of the Wadi DjenDjen. The construction of the port of DjenDjen began in 1983. Originally, it was mainly designed as a steel port, but now it operated as a freight port (vehicles, tubes, general cargo) [4]. The coronation of pier at the port of DjenDjen protected by large grooved cubic blocks (GCB) of 4 m^3 made of unreinforc-ed concrete as shown in Figure 1. Several physicochemical degradations have been observed on the maritime structures in Jijel. These structures cannot withstand the aggressive chemical agents of the external environment, such as: Corrosion of reinforced concrete reinforcement of guard walls, or structural elements due to chlorides (Cl^-) of seawater and very high relative humidity. The submerged part of the discard can be attacked by the sulphates (Na^+, Mg^{+2}, SO_4^{-2}, ...etc.) or alkali-aggregate reactions. These degradations lead to the change of the slope and the geometry of the shell in GCB or rip rap, which modifies the reflection and the propagation of the swell in front of the structure [5]. Sulfate ions (SO_4^{-2}) are reacted with hydrated cement products. This reaction is reprensted by volume increasing which denoted as sulfate attack on concrete. The study is required when the range of Sulfate concentrations are between 150 and 6000 ppm [6].

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Fig. 1 shelling GCB at the coronation of the pier North West of the port DjenDjen.

Mediterranean waters are moderately aggressive and have a high degree of salinity. The attack of the concrete by the only sulfate done by the expansive ettringite formation, resulting from the gypsum ($CaSO_4.2H_2O$) and C_3A. The gypsum is formed by the reaction between portlandite ($Ca(OH)_2$) and external sulfates [7]. In itself, sulfate attack of cementation materials can also lead to significant mechanical damage, related by precipitation of secondary phases within the porous network, such as ettringite and/or gypsum [8]. One of the examples of early ettringite formation is the reaction between calcium sulfate dehydrate and tricalcium aluminates with water, as shown in the Eq. (1), Eq. (2) and Eq. (3): [9]

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4.2H_2O + 2NaOH \quad (1)$$

$$Ca(OH)_2 + MgSO_4 + 2H_2O \rightarrow CaSO_4.2H_2O + Mg(OH)_2 \quad (2)$$

$$C_3A + 3CaSO_4.2H_2O + 26H_2O \rightarrow C_3A.3CaSO_4.32H_2O \quad (3)$$

Thaumasite can be formed in both concrete and mortar. If the temperature environments which were lower than 15 ° C, the thaumasite ($CaSiO_3.CaCO_3.CaSO_4.15H_2O$) was formed by sulphate attack. The latter is the product of reactions between the hydrated calcium silicate (C-S-H), sulfates and carbonates ions according to Eq. (4). Thaumasite can also be formed from ettringite and be associated with the formation of gypsum. The concrete degradation linked to thaumasite training so comes from degradation of hydrated calcium silicate (C-S-H) [10], [11].

$$SO_4^{-2} + 3Ca^{+2} + 3CO_3^{-2} + 3SiO_3^{-2} + 15H_2O \rightarrow 3CaOSiO_2.CO_2.SO_3.15H_2O \quad (4)$$

The carbon dioxide dissolved in water of presence in humidity and it formed of carbonic acid (H_2CO_3) [12]. The carbonic acid reacted with portlandite and form of calcium carbonate ($CaCO_3$), as a product according to the Eq. (5) [13]. The depth of carbonation is greatest when the relative humidity is between 40 to 80 % [14]. Specimens removed and carbonation depths measured by spraying a 1 % phenolphthalein solution dissolved in 70 % ethylic alcohol and 30 % distilled water and by checking the carbonated (white color) and non-carbonated (pink color) areas [15]. The bright pink colored area when the (pH) is greater than 9 or non-carbonated and carbonated areas remaining unstained (pH below 9) [16]. The reduction of curing time for concrete increases the carbonation depth. The diffusion of carbon dioxide into the concrete in the liquid state is ten thousand times (10^4) slower than the diffusion in the dry state. [12]

$$Ca(OH^-)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O \quad (5)$$

The carbonation depth values of (CEM I) concrete specimens with W/C = 0.75 is than higher to specimens with W/C = 0.45 and 0.6 after 12 weeks. Carbonation occurred rapidly at the lower relative humidity of 80 %, due to availability of CO_2 to the dissolved calcium hydroxide. From Mmusi the above findings it suggested that 80 % RH is the critical moisture content for carbonation [17]. They registered after 180 days of exposure, a minimum carbonation depth and of a maximum compressive strength for specimens concrete**.** mixture were of natural aggregates compared to specimens concrete which were mixture of recycled coarse aggregate, natural sand and Supplementary Cementing Material. These samples (150.150.500) cm^3 prismatic beams were placed in a chamber with constant parameters: temperature (28 ± 1°C), relative humidity (70 ± 3 %), CO_2 concentration (6 ± 0.1%) and pressure (14 psi) according to Arredondo-Rea [18].

The OPC cement paste specimens of ratio water - cement (0.25) prepared by mixing of cement with sodium sulfate salt; sodium sulfate salt is adding by 5000 ppm, 10000 ppm and 15000 ppm. The images of SEM for cement pastes with different concentrations of sodium sulfate show the micro cracks in the structure. The cracks increased with the higher concentrations of sodium sulfate in the samples due to gypsum formation expansion which would be related to a volume increase upon transformation of solid calcium hydroxide to gypsum upon reaction with sulfate ions [1]. Specimens of portland cement mortars prepared of water-to-cement ratios as 0.4, 0.6, and 0.8. These specimens immersed a 455 days of solution the sodium sulfate with concentration of 3 % and 8 %. They obtained the decrease of flexure strength of cement mortar depends on concentration of sulfate solution and the water-to cement ratio of the specimen. When concentration of the solution or the water-to-cement ratio increase, the flexure strength quickly decrease. The flexure strength decreases due to the damage evolution caused by the delayed ettringite [19]. From Naik the cylindrical cement paste samples exposed in Na_2SO_4 and $MgSO_4$ solutions with sulfate concentration of 33,800 ppm for 10 weeks. The compressive strength for those specimens decreased after 2 weeks of exposure, and the peak in the maximum compressive strength was greater and occurred at a later under sodium sulfate attack as compared to magnesium sulfate attack [20]. Three types of concrete specimens exposed to 4 % Na_2SO_4 sulphate solutions, the compressive strength for SRC concrete specimens reduced of 5 % than for OPC and BFSC (Granulated blast furnace slag) specimens it was 8 % after 180 days [7]. From Preeti, the OPC mortar cubes were mixing and cured in lab for 28 days. The strength of mortar cubes cast and cured in salt water increased as compared to those of cast and cured in fresh water at all ages of curing. The percentage increase in strength ranges from 8.33 % to 9.09 %; at 7 and 28 days [21]. Suleiman realized of sixty concrete (OPC cement and fly ash) cylinders 100 mm diameter and 200 mm height after treatment of surface by four different types materials, it immersed in a 5% of sodium sulfate solution. They obtained of reducing the w/c ratio improved on performance of concrete exposed to physical sulfate attack since less salt growth can form through the concrete pore space leading to less damage [22]. From Akinsola after immersed of concrete specimens the water cement ratio (0.41) in various environments and an during of 150 days, it obtained the slowly increase in strength for sample cast and cured with both lagoon and ocean water. And these values of compressive strength for concrete cube casted with ocean water and cured with ocean water reduced compared to concrete cube casted with fresh water and cured with fresh water; the percentage decrease in strength is from 24 % at 150 days of immersion. [23]

II. EXPERIMENTAL PROGRAM

Chemical analysis of seawater near the city of Jijel illustrated in Table I.

Table I. Chemical analysis the seawater of Jijel-Algeria.

Composition	Values
pH	8.06
Ca^{+2} (mg/l)	475
Mg^{+2}(mg/l)	1366
K^{+}(mg/l)	460
Na^{+}(mg/l)	10400
SO_4^{-2}(mg/l)	1449
Cl^{-}(mg/l)	20346
Conductivity (µs/cm)	7170
Salinity(mg/l)	4700

The primary chemical constituents of seawater are the ions of chloride, sodium, magnesium, calcium and potassium. According to the European standard NF P 18-011, the water is aggressive since they have a sulfate (SO_4^{-2}) and magnesium ($Mg^{+\ 2}$) content of between 600 and 1500 mg/l. These waters are slightly basic and characterized by a high salinity level, and also by very high conductivity values. Therefore, these values show the existence of very high concentrations of soluble mineral salts. Moreover, these waters characterized by a high concentration of chlorides which makes them aggressive introducing a high risk with regard to reinforcement corrosion in concrete structures.

Table II. Chemical analysis of cement SRC.

Composition	Percentage (%)
C_3S	57,90
C_2S	19,40
C_3A	2,70
C_4AF	14,00
CaO.L	1,00
Gypsum	5,00

In this study, a grooved cubic concrete block (GCB) having a volume of 4 m^3 was chosen. This block had been continually immersed in seawater for a period of 25 years to protect the North West jetty of the port of Djen Djen, and the removal of the GCB executed by a crane. These GBC manufactured in the early 1989 (Fig. 2); by Using of SRC (Sulphate Resistant Cement) concrete (CEM I 42.5 N-ES) from the LAFARGE factory; physical and chemical properties of the used cement illustrated in Tables II. With an adjuvant superplasticizer between 0.7 - 0.9 % of and fine aggregate (the nominal largest size of fine aggregate or sand used was 5 mm), and coarse aggregate (the nominal maximum size of coarse aggregate used was 25 mm). Table III summarizes the concrete GCB mixture compositions.

Table III. Mixtures the concrete of GCB.

Composition	Mass per volume (Kg/m^3)
Cement	275
Fine aggregate (Sand)	582.30
Coarse aggregate	1048.00
Ratio W / C	0.45
Adjuvant super plasticizer (%)	0.7 – 0.9

Typically, the GCB concrete gives a class C25 indicating an average compressive strength of 25 MPa. The coring performed on the non-contact part to the swell (See Fig. 3) according to European standard NF EN 12504-1, and finally these carrots cut in the form of cylinders 50 mm in diameter and 100 mm in length (See Fig. 4). Thereupon the surfaces of these cylindrical specimens are pre-treated for mechanical, physical and chemical tests.

Fig. 2 GCB of 4 m^3 retrieved from seawater.

Fig. 3 GCB coring in concrete.

Fig. 4 concrete cylinders (carrots).

Fig. 5 compressive strength test of carrot.

III. RESULTS AND DISCUSSION

A. *Mechanic test*

The aim of the experimental work is to study the degradation mechanism physic-chemical in concrete specimens immersed in the real aggressive environment (Seawater) for a 25 years (See Fig. 5). Compression test carried out in the lab by using concrete cylindrical specimens of dimensions (D = 50 mm, H = 100 mm) according to European standard NF EN 12390-3. The results of the compressive strength for carrots and for references specimens illustrated in Fig. 6.

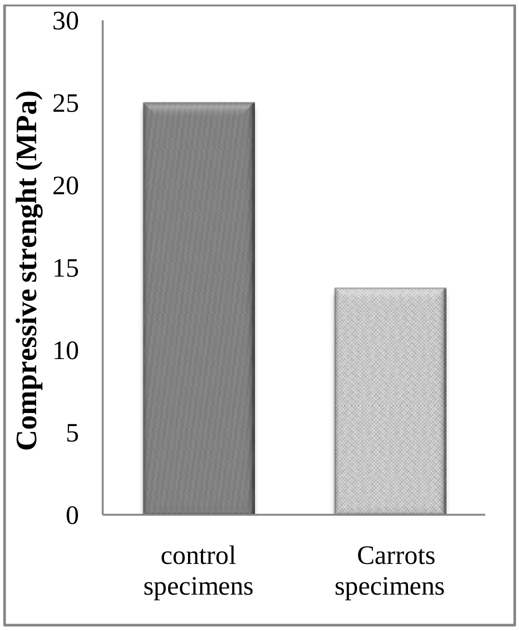

Fig. 6 compressive strength of GCB concrete and control specimens.

The purpose of UPV (Ultrasonic Pulse Velocity) test is to decide the propagation speed of sound waves in concrete carrots specimens according to European standard P 18-418 using ultrasonic equipment. The results of the UPV test for carrots specimens and references specimens presented in Fig. 7.

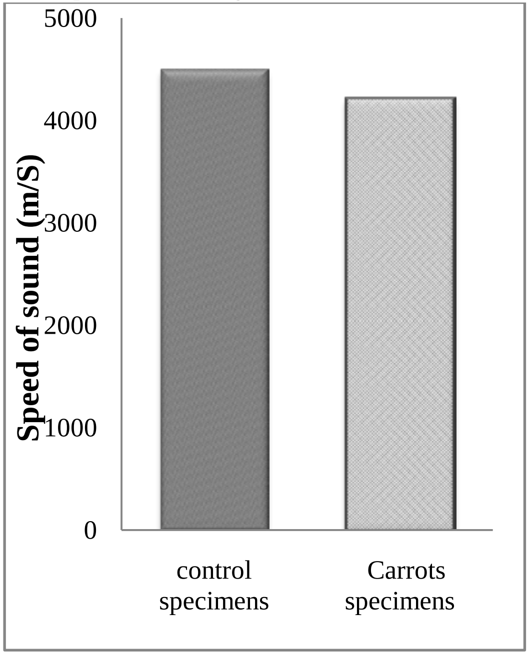

Fig. 7 speed of sound for GCB concrete and control specimens.

From Figure 6, these values of compressive strength for carrots of GCB concrete immersed in sea water are lower than to control specimens, and they decreased continuously up to 25 years; where the value of strength most is 13.73 Mpa, which represent reduction of strength to 45 % at the age of 25 years compared to control specimens. This result demonstrates the negative effect of sulfates in seawater on SRC cement-based concrete. These results are in accordance with the literature review [19], [23]. Where it is concluded that the mechanism of sulfate attack of cementitious materials can also lead to significant mechanical damage, related to precipitation of secondary phases within the porous network, such as ettringite and/or gypsum [8]. The expandable action of gypsum is responsible for the progressive cracks of the structure of the material by dislocation of its surface. The surface attack causes a reduction in the cross-section of the test pieces. Moreover, in presence of magnesium, sodium and calcium sulfate, the mechanism of deterioration is due to dissolution of Na^{+2} and Mg^{+2} resulting from reaction of portlandite with sulfate in accordance with the chemical Eq. (1), Eq. (2) and Eq. (3) [9]. For specimens control, the continuous hydration of the concrete under the effect of wet curing and formation of hydrated calcium silicates (C-S-H), which minimizes permeability of concrete according to Buil and Olivier [12] is the increase of the value of compressive. From Figure 7, the speed of sound for control specimens is higher than that carrots specimen after being immersed in seawater for a period of 25 years; and the value of speed most is 4211.04 m/S or reduction of 7 % than specimens control. These results confirmed the results obtained by compressive test.

B. *Carbonation depth test*

This test conducted in the lab by using of cylindrical carrot specimens concrete, and it performed on the fresh fracture face of specimens in a same conditions (Show Fig. 8); which used an alcoholic solution of phenolphthalein [15].

Fig. 8 test to measure the depth of carbonation of carrots specimens.

The results of carbonation depth of the carrots specimens are 117.00 mm after being immersed in seawater for 25 years. The carbonation depth for GCB concrete immersed in seawater increased with time, confirming the slower rate of diffusion of carbon dioxide within the pore of concrete in seawater according to Mmusi [18]. This indicates that the rate of penetration of carbon dioxide is ten thousand times (10^4) higher in air than in water [17]. This explains diffusion of carbonic acid from seawater (H_2CO_3) inside the pores of concrete, formation of calcium carbonates ($CaCO_3$) and the decrease in pH of the concrete [13], [14].

C. *Chemical analysis of skin specimens*

The results of X-ray diffraction analyses the skin of GCB carrot concrete immersed in sea water of 25 years is presented in Fig. 9.

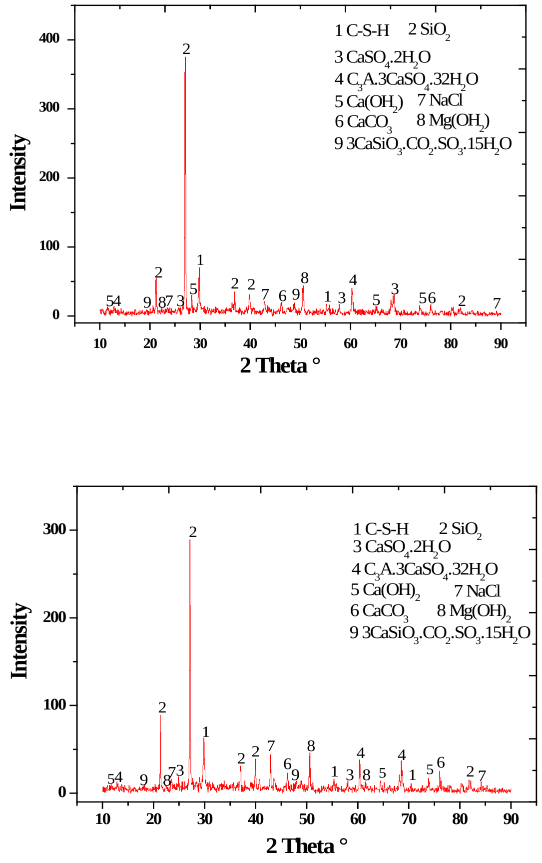

Fig. 9 XRD powder for skin concrete specimens carrot after 25 years of immersion in sea water.

They indicated for two samples the trace of ettringite crystalline, gypsum, $Ca(OH)_2$, $CaCO_3$, thaumasite and NaCl. Several peaks detected of ettringite type, this explained by the fact that part of $Ca(OH)_2$ was used for forming ettringite. This reaction between calcium sulfate dehydrate and tricalcium aluminates with waters shown in the Eq. (3) [9], [11]. The peaks of $CaCO_3$ type detected can be explained by the fact that part of $Ca(OH)_2$ was used for forming calcium carbonate ($CaCO_3$) [12], [15]. Finally, these results confirm the results obtained in mechanical tests.

The morphology of degradation concrete samples surface observed by scanning electron microscopy (SEM) in Fig. 10 after 25 years of immersion in sea water.

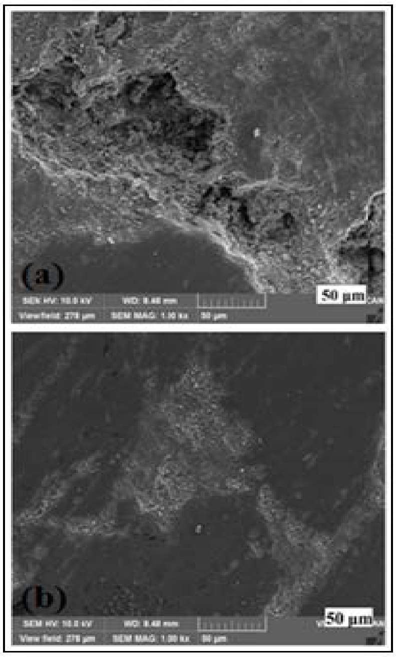

Fig. 10 typical SEM micrographs for surface GCB carrot specimens.

The gypsum ($CaSO_4.2H_2O$), thaumasite ($CaSiO_3.CaCO_3.CaSO_4.15H_2O$), calcium carbonate ($CaCO_3$) and ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$) are precipited as surface to product on the concrete sample surface by electron microscopy and detected by DRX analysis as it illustrated in Figure 10 (a) and Figure 10 (b). It can found that the microstructure is very loose; it can followed that the ingress of sulfate solution into concrete results of degradation in concrete by the chemical action and physical crystallization. Which includes the change of microstructures, cracking of concrete. The mechanism of deterioration is due to the Ca^{2+} dissolution resulting from reaction of portlandite with sulphate or carbonic acid (H_2CO_3) according to the chemical Eq. (3), Eq. (4) and Eq. (5) [7], [12].

IV. CONCLUSION

Chemical attack by aggressive acid sulphuric sulphate is one of the factors responsible for damaging cement pastes. The grooved cubic blocks (GCB), made of SRC concrete immersed in the seawater of the port of DjenDjen for a period of 25 years exhibited weak mechanical characteristics compared to the control specimens concrete, and a relatively slow penetration of the aggressive agents, as well as a significant reduction in compressive strength by 45 % recorded and by 7 % for speed of sound.

Carbon dioxide (CO_2) diffused in pores of GCB concrete is higher than control specimens. Based on this study of durability the cement concrete for maritime works in the Jijel region, it recommended using the proper proportion of mineral additions, e.g. silica fume, puzzolans and slag, reduction of water to cement ratio and an increase of the cement dosage, and a long curing time of the concrete elements.

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