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Influence of sodium hydroxide solution on the physico-mechanical parameters of limestone and dolostone on the concrete durability

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Abstract

The main purpose of this study is to create models that can predict how much concrete with alkali-reactive particles will expand and also study the physical and chemical properties of aggregates at the age of 270 days immersed in tap water and the durability of concrete containing aggregates against 1N of sodium hydroxide solution at the age of 9 months to determine the extent of the effect of alkali on aggregates and their ability to resist. The physico-mechanical properties of four aggregates, two of them were limestone (E) collected from the El Alameen area and the other part were dolostone (A) collected from Ataqaa area and the effect of alkali-reactive siliceous limestone and dolostone recovered on concrete prism test (CPT) under the conditions of ASTM standard test C1293 are investigated in this research. The aggregates studied have a more compacted interface transition zone, according to SEM photographs (ITZ). Samples (E1) and (A1) gave the least linear expansion of the concrete prism test at 9 months, thus these samples achieved the highest improvement of physico-mechanical properties. Samples (E2) and (A2) caused increasing in the linear expansion in the concrete prism and therefore caused a reduction of concrete compressive strength due to the high content of silica gel. All E and A samples showed the low resistivity in 1N NaOH up to 9 months of immersion and the results of SEM examination proved that the interfacial transition zone (ITZ) of E1 and A1 is stronger than the other samples. Concretes composed of limestone (E) aggregates seems to have a greater influence on enhancing mechanical properties than concretes formed of dolostone (A) aggregates. Limestone aggregate appears to be the best choice for improving concrete's physico-mechanical properties and alkali aggregate reactivity, according to the findings.
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Keywords: Alkali aggregate reaction, Expansion, Siliceous limestone, Compressive strength

1. Introduction

The alkali-silica reaction (ASR) happens in concrete when alkali metal ions and hydroxyl ions, typically from the cement, react with specific forms of silica found in the aggregate. A hydrated ASR gel is produced because of the procedure, which typically contains calcium. Swelling pressure, expansion, fissures, and strength loss in concrete structures are all influenced by the gel's ability to absorb water and expand. Three criteria are widely acknowledged as necessary for ASR to occur in the real world [Stark et al., (1993)]: a) An amount of reactive silica, which is usually produced from aggregate. b) An amount of alkali (Na and/or K), which is usually obtained from the cement paste. c) At minimum 80% relative humidity in the pore spaces. An expansion is being rejected if either of these following conditions aren't

satisfied. Despite the fact that ASR has been the subject of worldwide research since it was first discovered and characterized, and the extant literature on it is substantial, the molecular and microstructural mechanisms that cause it are extremely generally complex. The hydroxyl ion attacks and dissolves the silica in the aggregates to begin the process. The reactions can then be transformed into an ASR gel. Prior to the development of an ASR gel, the reactivity of calcium silicate hydrate in the mixture is sometimes higher than at environmental temperature. Only later, when ASR has sufficiently developed, do the ASR products release the aggregates, absorb calcium, and approach the C–S–H composition [Katayama, T., (2010)], [Thaulow, et al., (1996)] and [Leemann, et al., (2013)]. Obtained from laboratory observations with specimens, Hou and colleagues

[Hou, et al., (2004),], [Hou, et al., (2005)], [Li, et al., (2014)] and [Hou, et al., (2013)] in our lab identified the following process for ASR binding. Silica dissolves and interacts with calcium hydroxide to generate depolymerized, calcium-silicate-hydrate until the surrounding CH is consumed because to hydroxyl ion attacks. At this point, the C–S–H is becoming increasingly polymerized and silica-rich. After that, a hydrous ASR gel begins to form. Taylor's (1997) conclusion that the chemical composition of ASR is basically just like that of a cementation's material is supported by this research. Li, et al., (2014) recently established these reaction processes and shown that the consumption of CH and the reaction of C–S–H in the paste leading to the formation of ASR gel can be higher at 80°C than at room temperature. The alkali gel that forms in concrete as a result of water absorption and immersion in water and sodium hydroxide solution at high temperatures, as well as the presence of moisture and relative humidity, all of these factors contribute to cracks and negative effects that cause internal stress and increase porosity in the concrete, lowering compressive strength.

2. Experimental Techniques
2.1. Materials
The materials used in this paper include aggregates, Ordinary Portland Cement (CEM I), and sand. Two aggregates are from the El- Alameen area of Egypt (E1&E2), while others come from the Attaqa area of Egypt (A1&A2). The cement is ordinary Portland cement with a grade of 42.5 (Suez Cement Company) of Egypt. Sand is collected in Cairo's open quarries along the El-Wahat El-Baharaya Road of Egypt. The chemical and mineralogical constitution of CEM I and sand are included in Table (1). Table (2) and figure (1) respectively give the chemical and mineralogical compositions of

aggregate samples collected in the El- Alameen area. Table (3) and figure (2) together give the chemical and mineralogical components of the Attaqa region. The X-ray fluorescence (XRF) and the x-ray diffraction (XRD) techniques are used to analyze the chemical composition of the starting components. Table (4) displays the physio-mechanical properties of limestone and dolostone aggregates.
2.2. Methods
2.2.1. Alkali silica reaction (CPT)
 In this test, sodium hydroxide was added to the water to raise the alkali concentration to 1.25 percent by weight of the portland cement, with a concrete mixture of 420 kg/m^3 and an alkali concentration of 0.8 to 1.0 percent. The prisms are moulded into (75 X 75 X 285 cm) cubic steal moulds by refilling the moulds. And cured for around 24 hours at 23°C before being stored over water at 38°C by one year if no SCMs were used where the examination showed highest expansion around 0.04 % and two years if Supplementary cementation materials were used in in the specimens. After a year, that is measured at regular intervals in order to estimate the expansion at a certain moment in time.
    2.2.2. Concrete mix design
All of the coarse and fine aggregate specimens are placed in the pan. The aggregates are soaked in half of the entire amount of water. In the pan, the cement is placed over through the aggregates. The concrete examples are poured and molded inside (10 X 10 X 10) cm^3 steal moulds after being mixed. Concrete samples are kept at 23°C and 100% moisture content for 24 hours. The concrete samples are cured by immersing them in tap water for 270 days and then immersing a portion of them in sodium hydroxide for 9 months. Cubes achieved the improvement of compressive strength and water absorption. The concrete mixture design Kg/m^3 have been shown in the table (5).
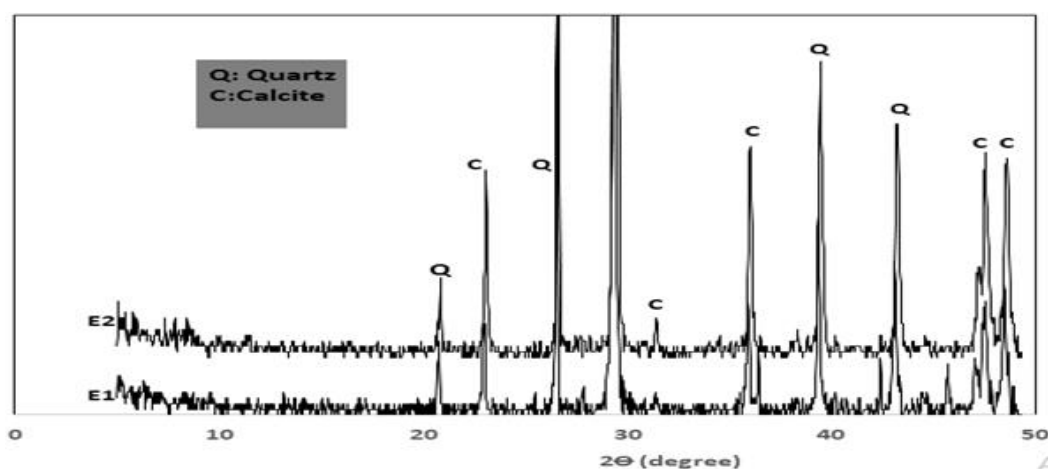

Figure (1): XRD patterns of limestone samples

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Table (1): CEM Ⅰ and sand chemical and mineralogical compositions

Oxide content	Cement	Sand
L.O.I	2.92	1.04
MgO	1.45	0.12
SiO_2	20.47	93.8
Al_2O_3	4.48	1.43
P_2O_5	0.19	0.18
SO_3	2.80	0.45
Cl^-	0.03	0.53
K_2O	0.29	0.34
CaO	60.88	1.02
C_3S	46.32	-
Fe_2O_3	5.49	0.73
Na_2O	0.33	0.22
TiO_2	0.41	0.09
C_2S	23.82	-
Mn_2O_3	0.20	-
Total	99.90	99.95
Ins. Res	0.58	-
Cl^-	0.07	-
Na_2Oeq	0.53	-
L.S.F	0.89	-
C_3A	2.59	-

Table (2): Chemical and mineralogical compositions of aggregate samples from El- Alameen area

Oxide content	E1	E2
SiO_2	16.30	8.79
Al_2O_3	1.41	1.39
P_2O_5	0.04	0.03
SO_3	0.16	0.27
K_2O	0.36	0.31
La_2O_3	0.08	-
TiO_2	0.28	0.22
SrO	0.04	0.05
CaO	48.30	53.60
Fe_2O_3	1.19	0.93
MgO	1.52	0.92
Na_2O	0.43	0.16
Cl^-	0.03	0.02
Y_2O_3	0.01	-
ZrO_2	0.03	0.01
Cr_2O_3	-	0.03
HgO	-	0.02
L.O.I	29.80	33.20
Total	99.99	99.90

E= El- Alameen, E1 is the first sample from El- Alameen area and E2 is the second sample from El- Alameen area.

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Table (3): Chemical and mineralogical compositions of aggregate samples from El- Attaqa area

Oxide content	A1	A2
SiO_2	3.03	4.45
Al_2O_3	0.86	1.13
P_2O_5	0.03	0.09
SO_3	0.69	0.18
K_2O	0.10	0.11
La_2O_3	-	0.16
TiO_2	0.09	-
SrO	-	0.03
CaO	36.50	46.78
Fe_2O_3	0.62	1.13
MgO	13.90	6.02
Na_2O	0.27	0.18
Cl^-	0.21	0.06
MnO	-	0.06
L.O.I	43.60	39.60
Total	99.94	99.98

A= Attaqa, A1 is the first sample from Attaqa area and A2 is the second sample from Attaqa area.
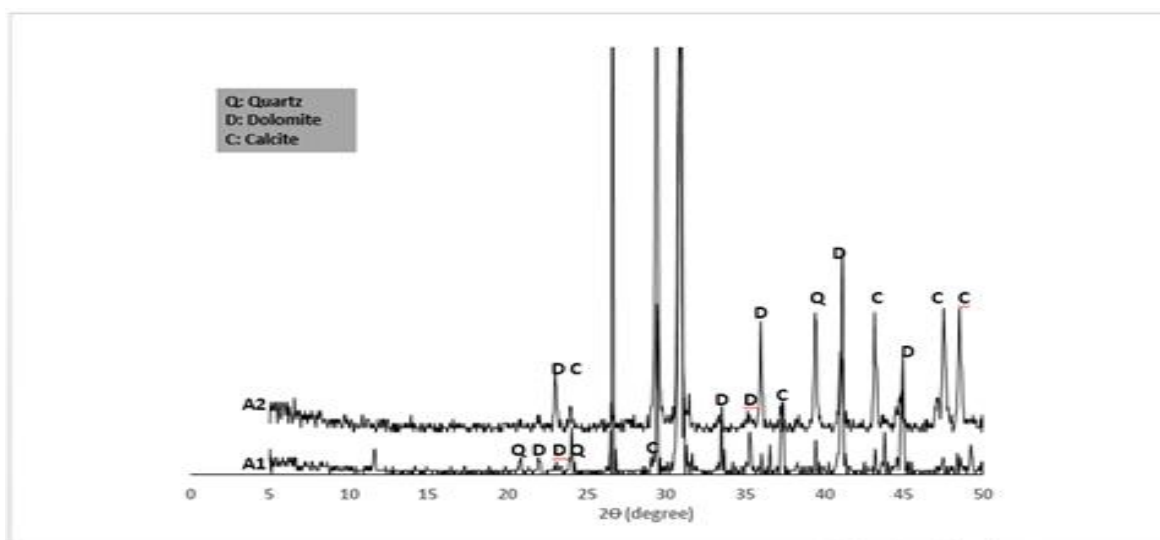
Figure (2): XRD patterns of dolostone samples

Table (5): Mixes proportions Kg / m³

Mix No	Mix Name	Aggregate	CEM I	Sand	W
1	E1	1055	350	703	200
2	E2	1053	350	701	210
3	A1	1054	350	702	196
4	A2	1054	350	702	190

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Table (4): physico mechanical properties of limestone and dolostone

Physical parameters	E1	E2	A1	A2
Water absorption (W_a)%	0.91%	3.4%	1.36%	2.08%
Specific gravity (G_{od})	2.6	2.9	2.78	2.84
Aggregate impact value (AIV)%	11.4%	22.6%	11%	15.08%
Flakiness index (I_F)%	17.65%	38.9%	19.24%	31%
Elongation index (I_E)%	15.23%	34%	16.42%	32%
Los Angeles abrasion value (LAV)%	15.93%	40.2%	14.06%	36.32%

W_a, G_{od}, AIV, I_F, I_E, and LAV have all been physical properties to their own minimum, maximum, and mean values measured in Table (4), Limits of roads and concrete aggregates are defined by BS and ASTM specifications, and also related BS and ASTM standards. According to ASTM-127, the W_a content of aggregate used in cement concrete will be less than 2.5 percent. This means these limestones meet the water absorption requirements for cement concrete. Calcite crystals have a specific gravity of 2.60 to 2.78, while concrete blocks require a lower limit around 2.60. It signifies that the specific gravity results from these stones are in the limits of ASTM C127.The physical qualities of flakiness and elongation index are connected to the geometry of aggregate fragments. High values cause reduced strength and anisotropic properties if used as aggregates in roadway and cement construction. The I_F and I_E value of the limestones vary around (12.20–1930) and (10.10–28.91), respectively, and are constrained by (BS 882 and 812:105. 2.) AIV is an indicator method for testing the compaction resistivity of an aggregate to rapid stress (Smith, Collis 2001). The range of *LAV* for these limestones is 14.08–25.12%, less than 40% as specified by ASTM C-131, which implies that these rocks can be used as road aggregate.

3. Results and discussion
3.1. Concrete Prism Test (CPT)
ASTM C 1293 (Concrete Prism Test) The concrete prism test is thought to be more accurate than the ASTM C 1260, but it has some problems, including a long testing time (1 year or longer) and alkali dissolving throughout the test period, which causes prisms to not expand as they should. According to (Thomas et al. (2006)), over 35% of the total alkali in concrete leaches out during this process, resulting in samples not expanding as they should if the alkali does not leach out, and within the first 90 days, approximately 20% seeped away. The production of ASR gel in concrete is caused by the reaction of alkaline solutions with reactive silica. Chemical composition, crystalline structure, and silica solubility in alkaline (high-pH) concrete pore solution are all factors that influence aggregate

reactivity. In addition, the inner crystal size of the aggregate is inversely proportional to the surface area of silica damaged by alkali assault. Because of their larger surface area, fine particles are hypersensitive towards ASR. The longer test period is one of this test theory's two primary limitations. When working on short-term projects, exposing the concrete prism to water for a year is difficult for filtering aggregates and determining ASR. Alkali leakage is the other limiting. Scientists concluded that during the course of the first year, roughly 35% of the hydroxides initially in the concrete prism leached into the storage of water, with about 20% leaking during 90 days [M.D.A. Thomas, et al., (2012)], [P.Rivard, et al., (2007)] and [P.Rivard, et al., (2003)]. When assessing the length variation after a year, similar leakage could result in an unfavorable lower ASR. Limited the testing technique to 13 or 26 weeks was proposed by Thomas et al. (2006) and Ideker et al. (2010) because of alkali leakage and the longer testing duration. Table (6) gives the linear expansion values of concrete, which are plotted as a relation of curing time in Figure (3). The rate of expansion increased from 7 days to 270 days in sample (E1), and the expansion continued without shrinkage at all other ages, but the expansion reached to 0.029% which this percentage not represented to maximum of expansion. Sample (E2) expanded until it achieved 28 days, then decreased until it obtained 90 days, and then increased again till it expanded more than the allowable expansion at the age of one year until it achieved 270 days, indicating that it is highly reactive. The sample (A1) showed expansion on 7days, kept stable on 28 days, continues to rise slightly until 56days, and then exhibited a noticeable expansion till 270 days. Evidently, the sample (A2) expanded from 7 days until it obtained the age of 56 days, then decreased till it managed to arrive the result of expansion at the age of 7 days, and then rapidly expanded to increase larger than the permitted expansions at the age of one year till it's approached 270 days, implying that it is capable of reactive.
3.2. Physico-mechanical properties of concrete
3.2.1. Water absorption
When CEM I is introduced to non-reactivity aggregates in a very alkali pore solution, silica is

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produced. The reaction of hydroxides with reactive silica in concrete results in the formation of ASR gel. When non-reactive aggregates are used, the cement interacts with Portlandite ($Ca(OH)_2$) to produce higher volumes of calcium silicate hydrates (CSH), which fill open holes and lower pore volume, reducing water absorption. However, when the duration of the samples immersed in water grows, the porosity and water absorption improve too though. Table (7) gives water absorption values of mixes content up to 270 days of curing with the values graphically shown in Figure (4).

Table (6): Linear expansion values of mixes content up to 270 days of curing

Curing time, day Mix notation	Linear expansion, %					
	7	28	56	90	180	270
E1	0.004	0.006	0.021	0.019	0.029	0.029
E2	0.007	0.007	0.003	0.006	0.020	0.161
A1	0.003	0.003	0.005	0.021	0.020	0.033
A2	0.003	0.010	0.004	0.008	0.012	0.093
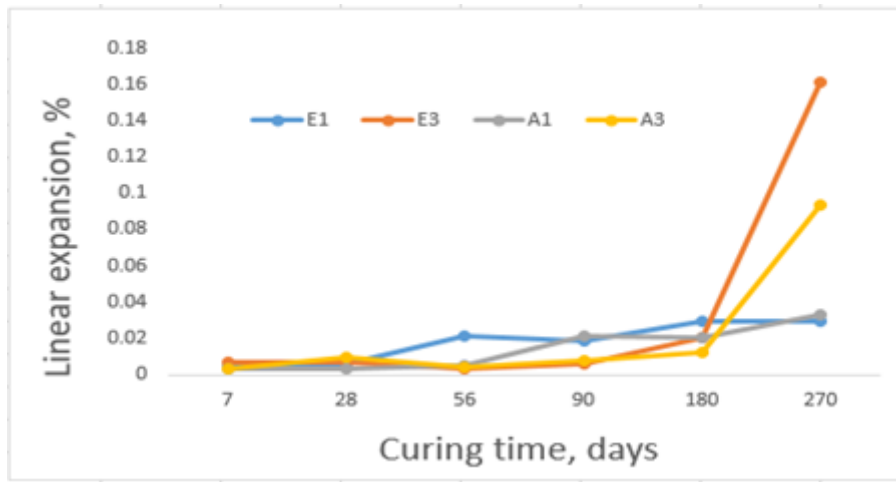
Figure (3): Linear expansion values of mixes content up to 270 days of curing
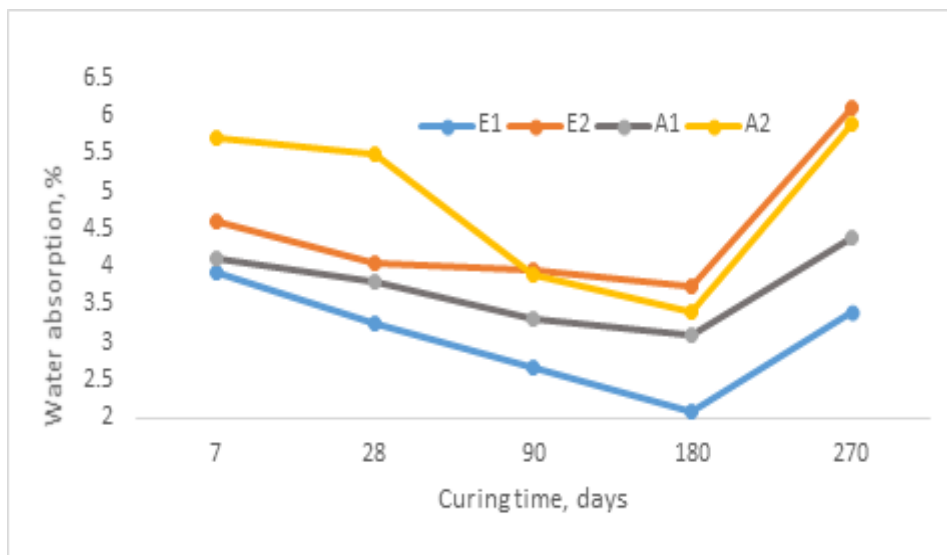
Figure (4): Water absorption values of mixes content up to 270 days of curing

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Table (7): Water absorption values of mixes content up to 270 days of curing

Curing time, day Mix notation	Water absorption, %				
	7	28	90	180	270
E1	3.92	3.24	2.68	2.08	3.4
E2	4.61	4.06	3.96	3.74	6.1
A1	4.1	3.8	3.3	3.1	4.4
A2	5.7	5.5	3.9	3.4	5.9

3.2.2. Compressive strength

The compressive strength values of concrete are listed in Table (8), with the values graphically displayed in Figure (5). Adding cement to non-reactive aggregates improves concrete's compressive strength at all hydration ages up to 180 days. This showed that aggregate is capable of absorbing free lime and producing more CSH. When reactive aggregates are applied such as (E2&A2), therefore, the rate of free lime consumption reduces, resulting in a low CSH concentration that can't cover a considerable percentage of the pore system.

3.2.2. Microstructure and morphology

Figures (6, 7) show scanning electron microscope micrographs of E1, E2, A1, and A2. The SEM data indicated varied microstructures after 28 days of cure. The micrographs of E1 and A1 mixtures appear being more compressed as well as dense than either E2 or A2 mixtures, with extremely high levels of microcrystalline CSH visible.

Table (8): Compressive strength values of mixes content up to 270 days of curing

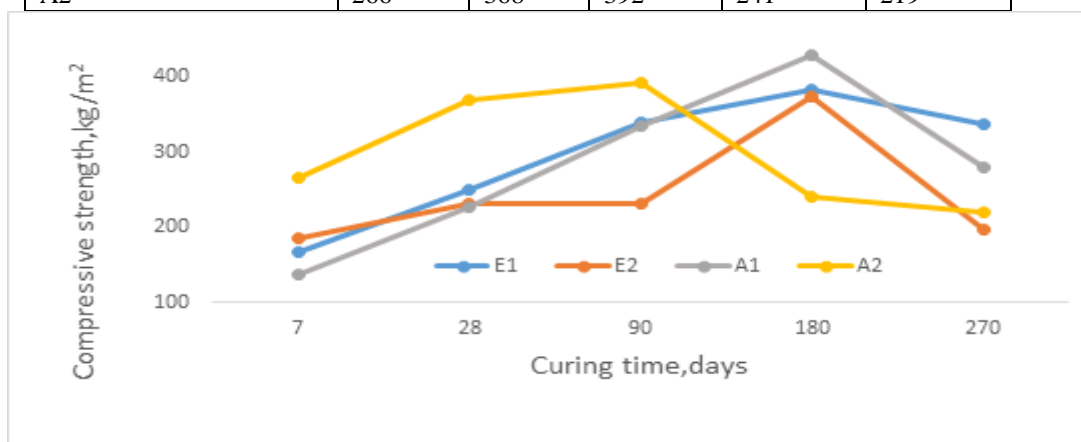| Curing time, day Mix notation	Compressive strength, kg/cm^2				
	7	28	90	180	270
E1	168	250	340	382	337
E2	185	231	232	374	196
A1	137	226	335	429	280
A2	266	368	392	241	219

Figure (5): Compressive strength values of mixes content up to 270 days of curing

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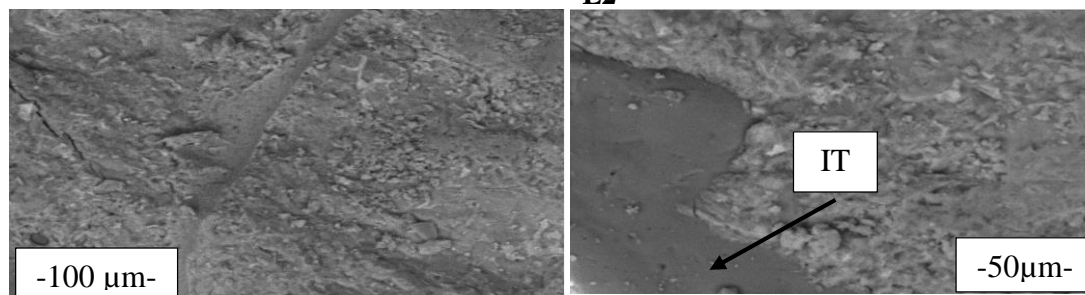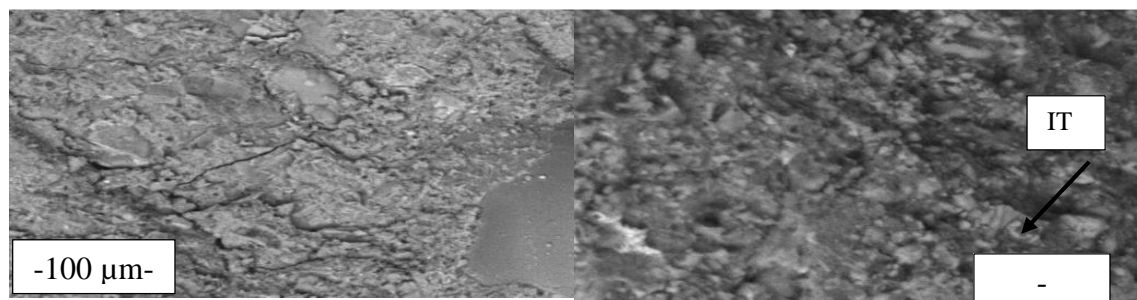
E1
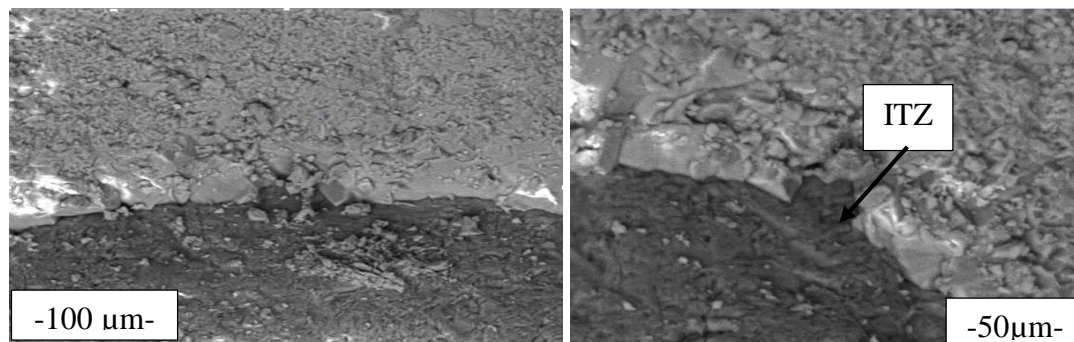
E2

Figure (6): SEM photography of E1 and E2 at 28 days of curing
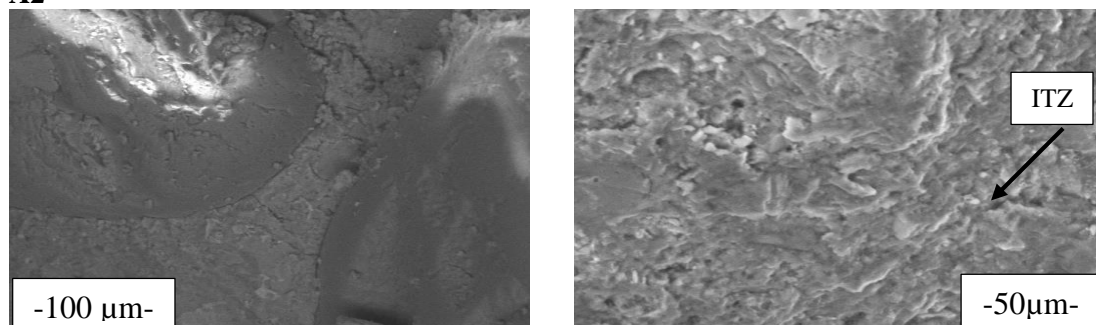
A1

A2

Figure (7): SEM photography of A1 and A2 at 28 days of curing

3.3. Resistance of Concrete to immersion in 1N NaOH

3.3.1. Water absorption

The water absorption values of concrete up to 9 months of immersion are showed in Table (9) and the results are graphically represented in Figure (8). The water absorption values of preferring cured specimens in concrete mixes decrease as the immersion period in 1N NaOH increases till 6 months, but the volume of pores increases after 9 months. This is related to the absence of hydration products accumulating as a result of the activation interruption, indicating that NaOH has a negative impact on water absorption. Furthermore, these results suggested that these values have not been resistant to the alkaline silica reaction.

Table (9): Water absorption values of mixes immersed in 1N NaOH up to 9 months

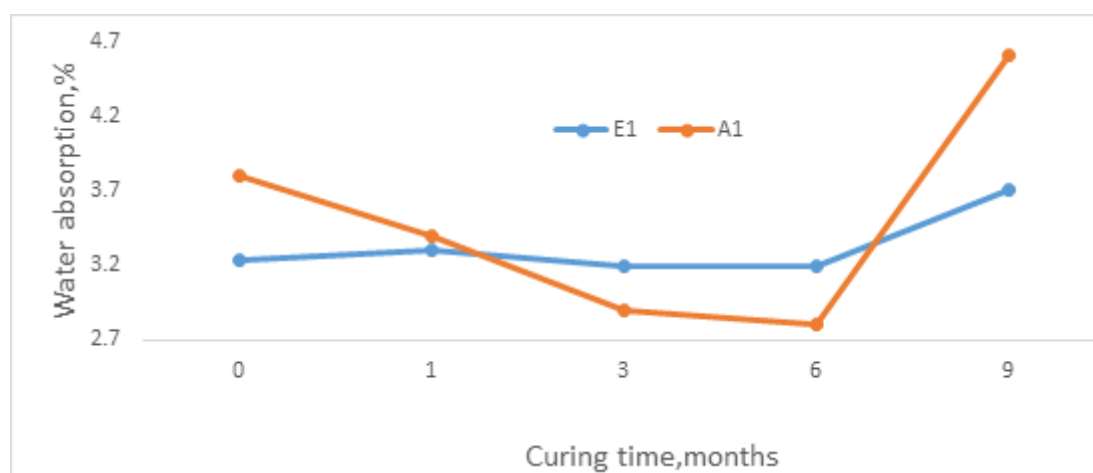| Immersion time, (months) Mix notation	Water absorption, %				
	0	1	3	6	9
E1	3.24	3.3	3.2	3.2	3.7
A1	3.8	3.4	2.9	2.8	4.6

Figure (8): Water absorption values of mixes immersed in 1N NaOH up to 9 months

3.3.2. Compressive strength

The compressive strength values of concrete up to 9 months of immersion are tabulated in Table (10) and the results are plotted represented in Figure (9). When the immersion time in 1N NaOH is exceeded until 6 months, the compressive strength of the cured preferring samples in concrete mixtures improves, but subsequently decreases. This is due to the lack of hydration products accumulated as just a consequence of the activation delay, implying that NaOH reduces compressive strength.

These results also reveal that these values have not been resistive to the alkaline silica reaction.

Table (10): Compressive Strength values of mixes immersed in 1N NaOH up to 9   months

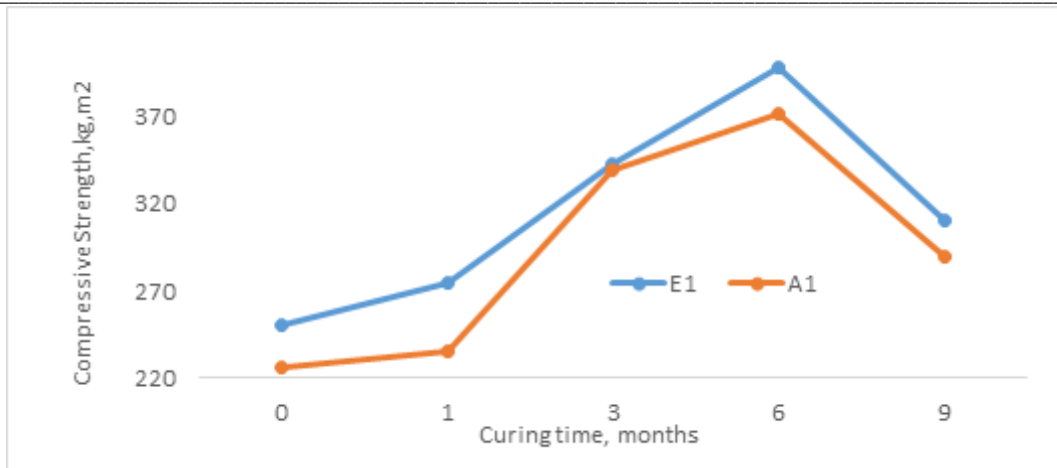| Immersion time, (months) Mix notation	Compressive strength, kg/cm^2				
	0	1	3	6	9
E1	250	275	343	398	311
A1	226	235	339	372	290

Figure (9): Compressive Strength values of mixes immersed in 1N NaOH up to 9 months

3.3.3. Microstructure and morphology

The selection the two best samples for the electron microscope scan though the samples have few pores. Figure (10) shows SEM pictures of E1 and A1 after 270 days of 1N NaOH curing. E1 samples seem being more compacted as A1 mix microstructures. This may be shown by the reducing the calcium hydroxide peaks to generate extra calcium silicate hydrate peak since the quantity of CSH rises, the interfacial transition zone (ITZ) shows harder. In which the E1 mix's (ITZ) is more than the A1 mix's.
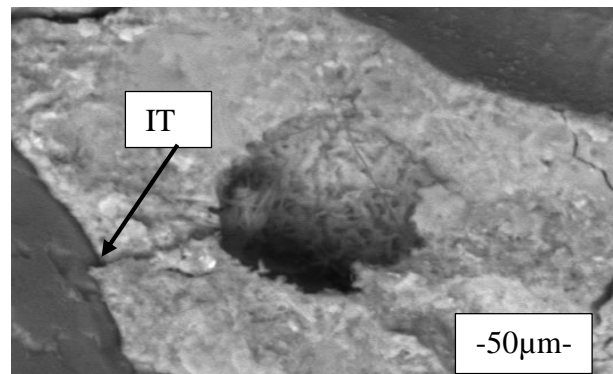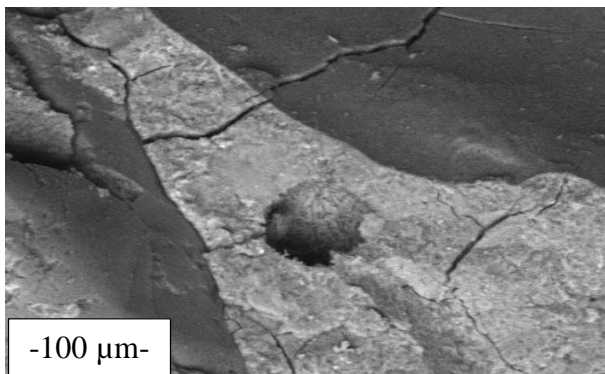
E1
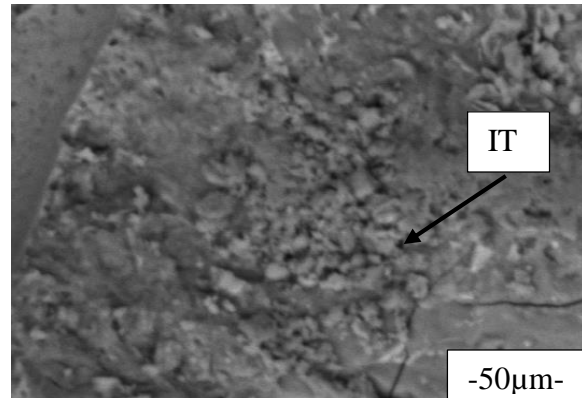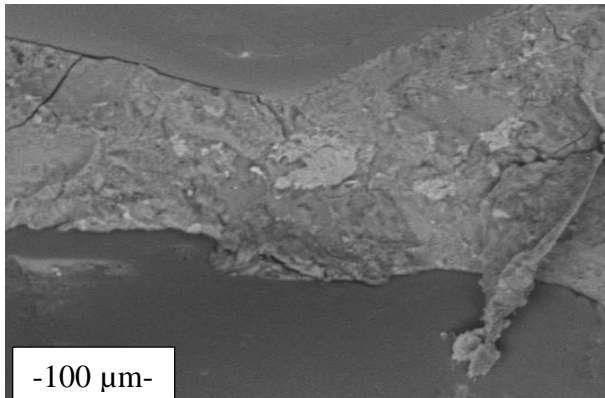
A1

Figure (10): SEM photography of E1 and A1 up to 9 months immersed in 1N NaOH

4. Conclusions

The limestone aggregate has the ability to increase the physical and chemical properties of concrete, according to alkali aggregate reaction of concrete and SEM. The dolostone aggregate decreases the concrete specimen's strength and the increases the expansion of alkali aggregate rection of concrete. Up to nine months, E1 and A1 have greater physico-mechanical and compressive strength durability against to 1N NaOH. The (E) has a higher compressive strength development than the (A). SEM showed that the interfacial transition zone (ITZ) of (E) admixed concrete was harder than that of (A) concrete. Limestone aggregate appears to be the best choice for improving concrete's physico-mechanical properties and alkali aggregate reactivity, according to the findings.

List of Abbreviations

Sodium Hydroxide	NaOH
Ordinary Portland Cement	CEM I
Calcium silicate hydrate	CSH
Portlandite	$Ca(OH)_2$
Quartz	Q
Calcite	C
Dolomite	D
Portlandite	$Ca(OH)_2$
Interfacial Transition Zone	ITZ
X-Ray Diffraction	XRD
X-Ray Fluorescence	XRF
Scanning Electron Microscope	SEM
El-Alameen area	E
Attaqqa area	A
Water absorption	W_a
Specific gravity	G_{od}
Aggregate impact value	AIV
Flakiness index	I_F
Elongation index	I_E
Los Angeles abrasion value	LAV

Declaration

Ethics approval and consent to participate: Not applicable" in this section.

Consent for publication: Not applicable" in this section.

Availability of data and material: All data generated or analyzed during this study are included in this published article [and its supplementary information files.

Competing Interests: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the paper.

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