Behaviour of sustainable concretes modified with mineral admixtures and Nano-silica against aggressive media attacks

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Abstract. The goal of this study is to see how the effect of recycled concrete aggregate admixed with mineral admixtures and Nano-silica on concrete's durability after being exposed to aggressive media attacks. The coarse aggregates applied in the concrete were dolomite (control) and recycled concrete aggregate with the addition of various mineral admixtures such as ground granulated blast slag (GGBFS), granite, and Nano-silica. To lower the water/cement ratio, a superplasticizer (SP)-type (F) was used. The physical and mechanical properties of commonly used raw materials such as aggregates and other various concrete kinds were investigated. The effects of saltwater and 3% sodium chloride on concrete mechanical and microstructures properties were investigated. The slump values of dolomite concrete were found to be lower than those of recycled aggregate concrete. The concrete mix using recyclable aggregate has the highest compressive strength, according to the results. In terms of compressive strength, the addition of 1% NS (Nano-silica) and 15% slag increased both mechanical and durability properties of the recycled aggregate concrete in aggressive media.

1. Introduction

Concrete is a common building material used for concrete structures all over the world. The global concrete industry consumes approximately 1.6 billion tonnes of cement, ten billion tonnes of aggregate, and one billion tonnes of mixing water each year. The concrete industry is clearly the largest consumer of natural resources among manufacturing industries worldwide [1-2]. Simultaneously, it produces massive amounts of construction and demolition waste, which is traditionally disposed of in landfills, causing serious environmental issues. Based on the raw materials available in the area, several varieties of concrete have been made by modifying the aggregate used in concrete. Aggregates make up the majority of normal concrete (about 70-80 percent of the total weight). To improve the properties of concrete, various natural and artificial aggregates are used [3-4].

Due to potential usage in eco-friendly concrete structures, recycled aggregate obtained from construction and demolition waste has received a lot of attention. Furthermore, the lack of natural aggregates in various regions of the world leads to require the development of recycled aggregates as a substitute. Several studies discussed the topic of recycling waste from building demolition in the concrete industry [5-6], as it can leads to environmental advantages (i.e., natural resource conservation, energy savings, reduced demand for land for waste disposal, and reduced pollution [7]).

Concrete is the most common and adaptable building material, and it's often utilised to overcome compressive forces. The various properties of concrete, such as workability, durability, strength, crack
resistance, and permeability, can be improved by adding pozzolanic materials such as slag, silica fume, and fly ash [8]. Many modern concrete mixes include admixtures that improve the microstructure while also lowering the calcium hydroxide concentration by consuming it through a pozzolanic reaction. Fine pozzolanic particles disperse in the paste, creating a high number of nucleation sites for the hydration products to precipitate. As a result of this process, paste becomes more homogenous.

This is caused by an interaction between the pozzolanic material’s amorphous silica and the calcium hydroxide formed during the cement hydration processes. Furthermore, the fine grain’s physical action allows for dense packing within the cement and reduces the wall effect in the paste-aggregate transition zone. [9-13].

Nanotechnology has gained popularity in cement and concrete research in recent years, notably in the formation of Nano-composites with superior physical and mechanical qualities [14-16]. Various types of nanoparticles have been effectively used in concrete to increase mechanical qualities and durability. Silica nanoparticles have been successfully employed as cement paste reinforcements, providing exceptional mechanical qualities. The surrounding sea environment causes concrete structures to deteriorate in numerous circumstances. The chloride ion entered the concrete in a coastal environment either by water or through coastal areas carrying salt ions that destroyed the concrete [17-20].

Many studies have been conducted on the effect of recycled aggregate, mineral admixtures, and Nano silica on the mechanical properties and durability of concrete after immersion in aggressive medium. The recycled aggregate concrete mixtures containing slag gave the best overall performance, according to (Riad et al. 2021; Berndt 2009) [21-22]. When recycled aggregate was used in concrete, durability tests revealed small improvements in coefficients of permeability and chlorine diffusion coefficient. Corinaldesi, Letelier, and Moriconi (2011) and Corinaldesi and Moriconi (2010) conducted experiments on concrete specimens made by completely replacing aggregates with recycled aggregates containing minerals admixture of slag, fly ash, and silica fume, and found that with proper selection and proportioning of the mineral materials in the concrete, satisfactory concrete properties can be developed[23-24].

Elsheikh et al. 2020 discovered that replacing OPC with 5% and 10% silica fume reduced the detrimental effects of chloride and sulphate ions. Furthermore, the blended cement paste containing 10% silica fume was shown to be more resistant to saltwater than the other pastes [25]. Yousef 2021, and Elshami et al. 2021, discovered that the main cause of concrete deterioration in the marine environment is chloride ion penetration, which causes rebar corrosion, which leads to concrete cracking and fragmentation[26-27]. When subjected to coastal media, this work gives a detailed investigation on the influence of Nano-silica, granite, and slag on the physical and mechanical characteristics of concrete produced by recycling coarse aggregates. Cement replacement levels of 15% slag, 10% granite, and 1% Nano-silica were used in concrete mixtures, since they are the most prevalent amounts utilized in reality.

Experimental techniques

1.1. Materials

The concrete mix design was utilized using CEM1- 42.5 N, Ordinary Portland cement (OPC). And blast furnace slag (BFS) provided by [Iron and Steel Factory- Helwan, Egypt]. The chemical characteristics of raw materials are presented in Table (1), in addition to raw materials such as Granite dust and Nano-silica. The coarse aggregates used in this study as a control coarse aggregate, crushed dolomite [Ca Mg (CO3)2] from the Attaka district of Suez, Egypt, was employed. After testing, recycled concrete aggregate (RCA) was obtained by crushing old concrete cubes. According to ESS 1109 [28] and ASTM C637 [29], coarse aggregate were manually sieved into various fractions of size (5-20 mm). Local sand was used for the fine aggregate, which was cleaned on site to eliminate harmful elements and chloride contamination. Figure (1) shows the grading curves for coarse and fine aggregates. The chemical compositions of coarse and fine aggregates are given in Table (2). The physical and mechanical
properties of coarse aggregates and its fine portion shown in Table (3) were evaluated according to the limits specified by the ESS 1109 and ASTM C637. A super plasticizer was added to the concrete mixture to maintain high workability with constant slump of 10 ± 2 cm at a significant reduction of the amount of water in the concrete mix design. Table (4) lists the concrete mix components.

1.2. Casting, curing and testing

A 180 kg pan mixer was used to mix the concrete. The following is a description of the mixing procedure: For around 15 minutes, the aggregates were blended (2 min.). Within the following 15 seconds, half of the total amount of water was added. Three minutes were spent mixing the components. The super plasticizer and binder material (OPC+ admixtures) were equally distributed over the aggregate in the pan, and mixing was maintained for 30 seconds. The mixer was turned off, and then, within the following 30 seconds, the mixing was repeated and the remaining water was added. After all of the components had been added, the mixing continued for another 3 minutes. The concrete was moved over a few times in the pan mixer using a trowel after it was finished mixing to guarantee homogeneity.

2. Fresh mixtures were slump tested according to ASTM C143, [30], and then all concrete specimens were cast into 10×10×10 cm cubes steel moulds by filling the moulds in about two equal layers and compacting each layer with a vibrating table. After concrete casting, the specimens were covered using a plastic sheet and stored for 24 hours temperature of 23 ± 2 °C and 100% RH. Specimens were put in water after demoulding until they were tested. Curing was carried out in accordance with ASTM C511, [31]. The cubes were submerged in saltwater and sodium chloride after curing in tap water for 28 days, and compressive strength tests were taken after 1, 3, 6, and 9 months. The crushed samples at each hydration period were ground first, then stopped the hydration process using a 1:1 by volume combination of acetone and methanol, followed by drying at 80 C for 24 hours to avoid extra hydration, and then the samples were retained in desiccators for future investigation.

Chemical analysis was done with an Axios (PW4400) WD-XRF Sequential Spectrometer, and compressive strength tests were done with a five-ton German Brüf pressing machine at a loading rate of 100 kg/min, as determined by (ASTM-C109 M) [32]. Alkali-Aggregate Reaction, was tested according to ASTM C1260, [33] using three mortar bars from each mix with dimensions 25 x 25 x 275 mm. After demoulding, specimens were immersed in water at 80±2°C for 24 hours followed by immersion in 1N NaOH solution for 14 days at 80±2°C after measuring the starting specimen’s lengths, and recording the change in lengths during the test.

Table 1. Chemical composition of OPC, NS, granite and slag (wt. %).

| Oxide content, (%) | OPC   | Nano silica | Granite | Slag  |
|-------------------|-------|-------------|---------|-------|
| SiO₂              | 21.33 | 95.22       | 69.50   | 36.66 |
| AL₂O₃             | 3.99  | 0.32        | 14.50   | 10.32 |
Fe2O3  3.15  0.85  3.01  0.52  
CaO   62.04  0.26  3.0  38.88  
MgO   2.52  0.55  0.64  1.70  
SO3   2.70  0.20  0.19  2.16  
LOI   3.74  1.51  0.65  0.13  
Na2O  0.26  0.37  3.46  0.45  
K2O   0.22  0.51  4.29  1.02  
Cl-   0.01  0.05  0.11  0.05  
TiO2  -     -     0.37  0.56  
TOTAL 99.95 99.98 99.99 99.97  
Ins. Res 0.66 -     -     -     
Na2OEq. 0.41 -     -     -     
L.S.F  0.90 -     -     -     
C3A   5.22 -     -     -     
C3S   51.40 -     -     -     
C2S   22.47 -     -     -     
C4AF  9.59 -     -     -     

| Oxides, (%) | Dolomite | Recycled dolomite aggregate | Sand |
|-------------|----------|-----------------------------|------|
| SiO2        | 1.67     | 19.10                       | 93.40|
| Al2O3       | 0.07     | 2.45                        | 2.03 |
| Fe2O3       | 0.01     | 1.50                        | 0.98 |
| CaO         | 35.54    | 37.61                       | 0.71 |

**Table 2.** Chemical analysis of raw materials, (wt. %).
|        | Sand | Coarse aggregates | Limits of coarse aggregates |
|--------|------|-------------------|-----------------------------|
|        | Dolomite | Recycled aggregate | dolomite |
| MgO    | 17.51  | 8.87  | 0.25 |
| SO$_3$- | 0.13  | 1.51  | 0.30 |
| Cl-$^-$ | -     | 0.13  | 0.08 |
| Na$_2$O | 0.04  | 0.49  | 0.38 |
| K$_2$O | 0.02  | 0.16  | 0.64 |
| TiO$_2$ | 0.01  | 0.19  | 0.17 |
| BaO    | -     | -     | -   |
| P$_2$O$_5$ | 0.01 | -     | 0.06 |
| MnO    | -     | -     | 0.03 |
| (L.O.I) | 44.99 | 27.83 | 0.74 |
| Total  | 99.97 | 99.97 | 99.92 |

Table 3. Physical and mechanical properties of coarse aggregates and their fine portions.
Water absorption, (%) - 1.09 4.49 ≤ 2.5(1)
Flakiness Index, (%) - 15.12 18.70 ≤ 25(2)
Elongation Index, (%) - 13.79 9.20 ≤ 25(2)
Abrasion resistance, (%) - 19.32 25.84 ≤ 30(2)
Impact value, (%) - 15.52 19.31 ≤ 45(1)

1) According to (Egyptian Standard Specification No. 1109 2002).
(2) According to (Egyptian Code of Practice for Reinforced Concrete No. 203 2017).
(3) According to (ASTM C637 2009).

Figure 1. Sieve analysis of coarse and fine aggregates

Table 4. Mix proportions for concrete per (1m³).

| Composition | OPC | Slag | Granite | Nano silica | W | Fine aggregates | Coarse aggregates | Sp. |
|-------------|-----|------|---------|-------------|---|----------------|------------------|-----|
|             |     |      |         |             |   | Sand           | D               | W   |
| D100        | 450 | -    | -       | -           | 173| 772            | 1544             | 8.1 |
| D70W30      | 450 | -    | -       | -           | 173| 772            | 1081             | 463 | 9.7 |
| D70W30-10G  | 450 | -    | 45      | -           | 173| 772            | 1081             | 463 | 9.5 |
3. Results and Discussion

3.1. Workability

The slump is the easiest test that may be employed for the determination of workability. The fall of practically all combinations was in the range of 10-12 cm. The slump values of new concrete mixes comprising dolomite and recycled concrete aggregate as coarse aggregates as well as 10% granite, 15% slag and 1% Nano-silica as a partial addition to OPC are presented in Figure (2). The findings reveal that concrete containing dolomite aggregate has a higher slump value than concrete containing recycle aggregate. This is because dolomite aggregate has a lower water absorption value, whereas recycled aggregate is more porous and absorbs more water of contents Table (3). The slump value of recycled aggregate concrete made with 10% granite, 15% slag, and 1% NS increased, according to the findings. Because of its spherical structure and smoother shapes, partially adding slag or granite to OPC reduces the water demand.

![Figure 2. Slump values for concrete mixes (cm).](image)

3.2. Alkali-aggregate reaction

Alkali-aggregate reactivity is one of the main challenges in concrete industry. As a result, it's critical to ensure that the subsequent alkali-aggregate reaction doesn't destroy the new structures, especially if novel types of aggregates are used. In concrete, the alkali-aggregate reaction (AAR) happens when the cement by-product alkalis or product from an external source react with particular aggregates to generate chemicals that are harmful to the concrete in some way. The reaction between these alkalis and the free
silica from aggregates resulted in an alkali-silica gel \([N (K)-S-H]\) to form. This Alkali-silica reaction (ASR) tended to damage the concrete [34].

The growth of the mortar bars owing to the alkali-silica reaction is seen in Figure (3). After 14 days of curing under test circumstances, the expansion varied from 0.053 % to 0.071%, which was within the ASTM C1260 Specifications' allowed limit of 0.1%. This demonstrates the harmless behaviour of the used aggregates, indicating that even when recycled aggregates are utilised as coarse aggregate, no potentially harmful expansion owing to alkali-silica interaction would be caused.

![Figure 3. Linear expansion (%) of coarse aggregate after immersion in alkali for 14 days.](image)

3.3. Effect of aggressive media on the aging of concrete

3.3.1. Compressive strength

Figures (4, 5) show the compressive strength of concrete cubes made with dolomite and recycle aggregate, as well as concrete containing 10% granite, 15% slag, and 1% Nano-silica as a partial replacement of ordinary Portland cement, and cured in tap water for up to 28 days, then immersed in sea water and 3% sodium chloride for 1, 3, 6, and 9 months. The results show that the compressive strength of recycled aggregate concrete is higher than that of dolomite aggregate. This is owing to the physico-mechanical qualities of recycled aggregate, which improved interlocking between the porous textures of the aggregate and the cement paste. On the other side, the results show that adding 10% granite, 15% slag, and 1% Nano-silica to D70W30-10G, D70W30-15S, D70W30-10G-1N, D70W30-15S-1N increases compressive strength by 13.1 %, 17.4 %, 39.2 %, and 45.6 %, respectively, when compared to the concrete control D70W30. This is mostly owing to the physical and chemical impacts of granite, slag, and Nano-silica, which offer a filler and a pozzolanic effect, triggering the pore enhancement process, due to their fineness and high amorphous silica concentration. The conversion of lime formed from cement hydration into extra binding elements via the lime-pozzolanic reaction, which precipitate in open pores to provide a more compact closed body structure, causes this refinement.
Figures (4, 5) show an increase in the compressive strength for different concrete mix proportions after 3 months of immersion in sea water and 3 % sodium chloride, then decreases after 9 months of immersion. The enhancement in compressive strength with early immersion time is primarily due to hydration progressing with curing time and pozzolanic reactivity, which causes pore refinement in the transition zone between the mortar and coarse aggregates. As a result, compressive strength improves. The aggressive attack of chloride and sulphate ions, as well as the creation of harmful voluminous expanding compounds such as gypsum and ettringite, may explain the loss in compressive strength with extended immersion duration in sea water and 3 % Na Cl up to 9 months. The results show that when concrete mixes are immersed in 3 % sodium chloride, their compressive strength deteriorates more than when they are immersed in sea water. This is mostly due to the rapidity with which chlorine ions enter concrete and attack the C3A of cement pastes, resulting in chloroaluminate hydrates, which soften the concrete. Magnesium chloride interacts with the Ca (OH) ₂ generated to form CaCl₂ and Mg (OH) ₂. Calcium chloride combines with calcium aluminate hydrates to form calcium chloroaluminate hydrates (Freidel's salt), which has a negative effect on cement concrete and may explain the 9-month continuous drop in compressive strength.

Figure 4. Compressive strength of concrete mixes immersed in sea water up to 9 months.
3.3.2. Scanning electron microscopy (SEM) investigation:

Figure (6) shows SEM micrographs of concrete constructed with dolomite (D100) and recycled aggregate (D70W30), as well as a concrete mix including 15% slag and 1% Nano-silica (D70W30-15S-1N) as a partial addition and curing in tap water for 28 days, then immersed in 3 percent NaCl for 6 months.

The concrete mixes (D100), (D70W30), and (D70W30-15S-1N) were micrographed after 28 days of curing in tap water. Figure (6 a, b, c), show a moderately thick and compact microstructure after 28 days of curing in tap water. This is related to an increase in the amount of CSH phase and the rise of hydration products. In comparison to the other mixes, SEM micrographs of concrete mix (D70W30-15S-1N) revealed a comparatively thick and compact microstructure. This is owing to amorphous Nano-strong silica's pozzolanic activity, which reacts with Ca(OH)2 generated during hydration process to make extra quantities of CSH gel, which then deposits in the pore system. The SEM micrographs of concrete mixes made of (D100) and (D70W30) after 6 months immersion in 3 % Na Cl revealed micro-cracks to be formed in the concrete mortar, predominantly at the interfacial transition zone (ITZ) between the aggregate particles and cement paste (Figure 6 d, e, f). In contrast, the micrographs of the concrete mix (D70W30-15S-1N) showed little change in the concrete mortar, especially at the zone between the aggregates and cement paste. The existence of sulphate and chloride ions in the cementitious material interacts with hydrated cement particles to create spread-out products, resulting in a minor reduction in compressive strength.
4. Conclusions

From the above investigation we can conclude that:

1. When compared to recycling aggregate concrete, the slump values of dolomite concrete decrease.

2. When 1% NS and 15% slag are added to Portland cement, the slump values of the concrete mixtures improve.

3. The used aggregate has a strong resistance to alkali silica reaction, with expansion values (alkali silica reaction) of 0.053, 0.071, and 0.080% for concrete including dolomite and recycling aggregates following immersion in (1N) NaOH, respectively.

4. The compressive strength of a concrete mix including recycled aggregate is the highest.

5. After immersion in aggressive media, the addition of 1% NS and 15% slag enhanced both mechanical and durability qualities of the recycled aggregate concretes.

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