



Mechanical and durability behaviour of concrete with granite waste dust as partial cement replacement under adverse exposure conditions

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HIGHLIGHTS

- Using up to 20% GWD as cement replacement does not significantly affect the mechanical properties of concrete.
- Chloride attack, unlike acid attack, does not degrade the mechanical properties of concrete.
- Using 20% GWD as cement replacement showed the least mass loss.
- Using 10% and 20% GWD as cement replacement led to higher values of OCP and corrosion resistance.
- The H₂SO₄ solution is less aggressive than the NaCl solution in terms of corrosion behavior.

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ABSTRACT

In this research, the effect of granite waste dust (GWD) as partial replacement of cement (up to 20%) on the mechanical and durability behaviour of concrete mixes under adverse exposure conditions was investigated. The specimens were tested after 28 days of curing in lime-saturated water and 91 days of exposure to 5% by weight of NaCl and H₂SO₄ solutions. Compressive and splitting tensile strength, resistance to acid attack, water absorption, open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) tests and Scanning Electron Microscopy (SEM) analysis were performed. The compressive and tensile strength results showed that using up to 20% GWD as cement replacement does not significantly affect the mechanical properties of concrete mixes. However, the concrete mix with 10% GWD displayed the highest strength of all. It was also revealed that the concrete mix with 20% GWD showed a higher resistance to acid and chloride attack than the others. GWD did not have a significant effect on the water absorption of the concrete mixes. OCP and EIS measurements revealed that 10% and 20% GWD as cement replacement significantly improved the corrosion resistance of concrete.

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1. Introduction

In recent years, sustainable construction became a big challenge for civil and environmental engineers because the construction industry is one of the main consumers of natural resources and also a massive waste producer [1,2]. Because most of these waste materials have serious environmental impacts, many researchers have recently tried to come up with much needed sustainable solutions [3]. The granite processing industry generates a large amount

of granite waste, which form a colloidal waste in contact with water during the production process of these stones. As this wet slurry loses its water content due to the water evaporation, it generates fine dry particle waste dust, which is blown away by wind and causes serious environmental impacts. GWD eventually settles down on the vegetation and crops around the granite processing industries and threaten the ecology of the environment [4]. In addition, the ground water level and surface waters are also affected by the GWD due to the prevention of water from reaching the ground water table and the pollution of surface waters, respectively [4].

Concrete is one of the most important materials in the building construction and other infrastructures around the world and it is reported as the second most widely used material by mankind

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[5,6]. Its production led to huge consumption of natural resources and great environmental degradation due to the use of natural aggregates and cement as binder. Cement, as the primary component of concrete, is considered one of the main causes of air pollution due to CO₂ emissions. It was reported that more than 5% of the global carbon dioxide annual emissions are linked to concrete production. This is due to the raw materials calcination for cement clinker production and the burning fuel that is used to keep the high temperatures in a kiln.

Therefore, recycling and reusing waste materials can be considered an effective way to reduce environmental impacts and prevent depletion of natural resources. For this purpose, a wide range of waste materials have been used in concrete production: glass waste, demolition waste, rubber tires, metal-based furnace slag, marble and granite waste dust, silica fume, fly ash and limestone filler [7–15]. Previous researches reported that the use of these waste materials in concrete production significantly reduces its cost and also leads to an improvement of the mechanical, workability and durability properties of concrete mixes [16–22]. In recent years, granite aggregates and powder have been widely used in a variety of applications such as ceramic bricks and tiles, clay materials, concrete bricks and infiltration materials, as partial replacement of natural aggregates or cement in reinforced and mass concrete production [22–30].

It was reported that the use of GWD at cement replacement ratios from 20% to 50% significantly reduces the compressive strength of concrete while the effects on tensile strength were negligible [26]. Divakar et al. [31] showed that the compressive strength of concrete increases about 22% by using fine granite particles as partial replacement of natural sand at 35%. Garas et al. [32] showed that concrete with 30% GWD as cement replacement displayed a higher strength, workability and surface finish than the control mix. It was also reported that the replacement of natural fine aggregates up to 15% with GWD in concrete production does not significantly affect the mechanical and durability properties [33]. Other researchers also reported that using 25% GWD as an addition in the production of concrete has a positive effect on the strength and durability properties [34,35]. Flexikala and Partheeban [36] revealed that replacing natural fine aggregates with GWD in concrete has a positive effect on the mechanical properties. They also showed that both the plastic and drying shrinkages of concrete with GWD were equal to those of the control mix. Ramos et al. [37] reported that there was no need of superplasticizer in concrete mortars with GWD as partial replacement of cement. Thus, using GWD could be considered an economic advantage in concrete production. Aarthi and Arunachalam [38] showed that the resistance of concrete mixes against acid attack and chloride penetration were improved by the use of GWD.

The corrosion of steel rebars embedded in reinforced concrete (RC) members is a serious issue caused by aggressive external agents, namely atmospheric carbon dioxide, chloride ions and sulphate ions [39]. The corrosion of RC members is considered one of the most significant durability problems in structures, resulting in their deterioration particularly in environments where chloride penetration and carbonation risk exists [40,41]. Steel rebars in RC members are normally in a passive state due to a very thin, dense, and stable iron-oxide film called passive layer, which plays a key role in corrosion protection of the steel rebars by reducing the ion mobility between the steel rebar surface and the surrounding concrete. When the chloride content at the steel rebar surface exceeds a critical value, the corrosion process takes place [42]. The corrosion of RC members depends on several factors, such as chloride content, concrete properties, concrete pH, the chemical composition of the steel rebar, the existence of voids between the steel rebar and the concrete interface and the electrochemical potential of the steel rebar surface [42]. Abd Elmoaty [8] reported

that using GWD increased the corrosion cracking time of the concrete mixes and no significant reduction in cracking time was observed for GWD contents greater than 5.0%. Matos et al. [43] also reported that using GWD can originate a denser cement matrix and improve the durability of concrete mixes without affecting the fresh behaviour or strength of the mixes. Since there is an insufficient information on the influence of GWD as partial replacement of cement on the mechanical and durability (corrosion) behaviour of concrete mixes exposed to 5% by weight of NaCl and H₂SO₄ solutions, the aim of this study is to evaluate that influence by conducting compressive and splitting tensile strength, resistance to acid and chloride attack, water absorption, open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) tests, as well as Scanning Electron Microscopy (SEM) analysis.

2. Experimental study

2.1. Materials

In this study, in order to produce concrete mixes Portland cement (Type II), water, (0.3–4.75 mm) and coarse aggregates (5–25 mm) were used.

The coarse and aggregate used in this study were crushed limestone and natural river sand acquired locally. The sieve analysis and physical data of the coarse and aggregates are given in Tables 1 and 2, respectively. The GWD used in this study as partial cement replacement came from a local factory near Mashhad city. Since the GWD was collected wet, it was first completely oven-dried at a temperature of 105 °C in order to control the W/C ratio. The specific gravity of GWD was 2.61. To determine the chemical composition of GWD, the XRD test was carried out. The XRD results and particle size distribution of GWD (taken from [44]) are shown in Table 3 and Fig. 1, respectively. As seen in Table 3, GWD is mostly comprised of silica and alumina. Portland cement Type II manufactured by Mashhad Cement Company, with specific gravity of 3.2 as per ASTM C150, was used as binder. The chemical composition and particle size distribution of cement are given in Table 3 and Fig. 1, respectively. The water used in this study for the preparation and curing of the concrete mixes was regular tap water from the laboratory. In order to determine the corrosion behaviour of steel rebars embedded in RC specimens after exposure to 5% by weight NaCl and H₂SO₄ solutions, 16 mm (A615) rebars were used.

2.2. Experimental design

The experimental program intends to investigate the effect of different ratios (0%, 5%, 10% and 20%) of GWD on the mechanical and durability properties of fresh concrete. With this aim, the experimental program was divided into two parts. The first one covered the effect of GWD as cement replacement on the mechanical properties, namely compressive and splitting tensile strength, and water absorption of concrete mixes after curing in lime-saturated water and exposure to 5% by weight NaCl and H₂SO₄ solutions. The second part addressed the durability behaviour of concrete mixes modified with GWD as partial replacement of cement by conducting a mass loss test for a period of 119 days (28 days of exposure to lime-saturated water and 91 days of exposure to a 5% by weight H₂SO₄ solution). A set of electrochemical tests, namely OCP and EIS, were also carried out in order to determine the corrosion behaviour of steel rebars embedded in RC specimens after exposure to 5% by weight NaCl and H₂SO₄ solutions. The main factors considered in the study were the cement replacement ratio with GWD and the duration of exposure to the NaCl and H₂SO₄ solutions.

Table 1
Sieve analysis data of the coarse and fine aggregates.

	Sieve size (mm)	Passing percentage (%)
Coarse aggregate	37.5	100
	25	91
	19	61.5
	12.5	23
	9.5	5.5
	4.75	0
Fine aggregate	4.75	100
	2.36	83.5
	1.18	58.25
	0.6	28.75
	0.3	4.75
	0.15	0.6
	0.075	0.05

Table 2
Physical properties of the fine and coarse aggregates.

Properties	Fine aggregates	Coarse aggregates
Water absorption (%)	3.75	1.75
Moisture content (%)	2.65	0.7
Relative density	2.63	2.7
Oven dry density (kg/m ³)	1660	1625
Finess modulus	3.24	–

2.3. Specimens preparation

In order to prepare the concrete mixes, the coarse and fine aggregates were first mixed inside the drum mixer. Next the cement was added and mixed for about 2 min. Then, the water was added and mixed until reaching a homogeneous mixture. Then the mix was cast in steel moulds. The concrete specimens were demoulded after 24 h and cured by immersing in lime-saturated water and kept at room temperature for 28 days. The mix proportions of concrete mixes are presented in Table 4.

2.4. Testing

2.4.1. Compressive strength

In order to determine the compressive strength of the concrete mixes, cylindrical moulds with 150 mm diameter and 300 mm height were used according to ASTM C39. The specimens were cast in steel moulds, demoulded after 24 h and cured by immersing in lime-saturated water and kept at room temperature for 28 days. Afterwards, in order to determine the compressive strength of specimens exposed to harsh environments, they were immersed in 5% by weight NaCl and H₂SO₄ solutions for 91 days. The specimens were tested 7, 14, 28, 35, 56 and 119 days after the casting date. The mean value of at least three specimens was reported as the compressive strength of each mix.

2.4.2. Splitting tensile strength

The splitting tensile strength of the concrete mixes was determined according to ASTM C496. A similar preparation method to that of the compressive strength test was used for the splitting tensile strength specimens. The specimens were cast in steel moulds, demoulded after 24 h and cured by immersing in lime-saturated water and kept at room temperature for 28 days. The mean value of at least three specimens was reported as the splitting tensile strength. The specimens were tested 7, 14 and 28 days after the casting date.

2.4.3. Mass loss

In order to determine the resistance of concrete mixes to a 5% by weight H₂SO₄ solution, 100 mm cubic moulds were used. The specimens were first cured for 28 days by immersing in lime-saturated water. Afterwards, they were exposed to a 5% by weight H₂SO₄ solution with pH 1.0 for 91 days. The H₂SO₄ solution was monitored and refreshed weekly in order to keep the pH constant for a duration of 13 weeks at room temperature. The specimens were removed from the solution weekly, washed with regular tap water to remove loose reaction products. Afterwards, specimens were dried at room temperature for an hour before measuring the mass loss of the specimens. The mean value of three specimens was reported as the mass loss of each mix. The mass loss percentage of each specimen was calculated by using the following equation:

$$\text{Mass loss}_t (\%) = ((M_t - M_i) / M_i) \times 100$$

where M_t : mass of the specimens at time t (g), M_i : initial mass of the specimens before exposure to H₂SO₄ solution (g).

2.4.4. Water absorption

To determine the water absorption of concrete mixes, cylindrical moulds with 150 mm diameter and 300 mm height were used according to ASTM C642. The water absorption of specimens immersed in lime saturated water was tested 7, 14 and 28 days after the casting date. After 28 days of curing in lime-saturated water, so as to determine the water absorption of specimens exposed to harsh environments, they were immersed in 5% by weight NaCl and H₂SO₄ solutions. The

water absorption of the specimens was tested 7, 28 and 91 days after immersing in NaCl and H₂SO₄ solutions. The water absorption was reported as the mean value of three specimens.

2.4.5. Open circuit potential

Measuring OCP or half-cell potential as described in ASTM C 876 is the most simple and preliminary electrochemical experiment in order to evaluate the corrosion state of steel rebars in RC members [45]. However, the OCP measurement does not provide information about the rate of corrosion. Therefore, it is better to use it with other monitoring methods such as the EIS technique. In order to determine the corrosion behaviour of steel rebars embedded in concrete mixes using the OCP method, cylindrical moulds with 100 mm diameter and 200 mm height were used and a 200 mm long steel rebar with 16 mm diameter was placed in the middle of each specimen. After 28 days of curing in lime-saturated water, the corrosion resistance of RC specimens was evaluated by immersing the RC specimens in 5% by weight NaCl and H₂SO₄ solutions. The OCP of concrete mixes was measured for a period of 119 days (28 days in lime saturated water and 91 days in 5% by weight NaCl and H₂SO₄ solutions) using a saturated calomel electrode (SCE) as a reference electrode.

2.4.6. Electrochemical impedance spectroscopy

EIS is a powerful tool and technique to characterize a wide variety of electrochemical systems and detect small corrosion occurrences in the metallic parts [46]. It is also a common technique and tool for evaluation and study of corrosion in RC members [46–48]. Therefore, in order to determine the corrosion behaviour of steel rebars embedded in concrete mixes using the EIS method, similar cylindrical moulds with 100 mm diameter and 200 mm height were used and a 200 mm long steel rebar with 16 mm diameter was placed at the middle of each specimen. The EIS test was applied using Zive Lab Potentiostat along with the conventional three electrode setup (a rebar segment was employed as a working electrode and a platinum wire and the SCE were used as a counter and reference electrode respectively). The EIS value of RC specimens was evaluated after 91 days of exposure to 5% by weight NaCl and H₂SO₄ solutions. The EIS test was repeated 3 times for each testing day in order to insure reproducibility.

3. Results and discussion

3.1. Compressive strength

3.1.1. Effect of GWD on compressive strength before exposure to H₂SO₄ and NaCl solutions

The compressive strength of the concrete mixes with GWD as partial cement replacement after 7, 14 and 28 days of curing in lime-saturated water is shown in Fig. 2. Fig. 2 shows that the compressive strength of specimens with 10% GWD is higher than that of the other specimens at all ages. This result is in good agreement with previous studies [30,49], which reported an improvement in the compressive strength of concrete specimens by using 10% GWD [30,49] as cement replacement. In this case, the increment in compressive strength was about 14%, 16% and 11% after 7, 14 and 28 days of curing in lime-saturated water, respectively, relative to the control specimens. This higher compressive strength may be due to the pore filling effect of very fine GWD that enhances the properties of the hard density of the interfacial transition zone product. The same factor explains the trend on the other mechanical properties namely splitting tensile strength. As seen in Fig. 2, the largest decrease in compressive strength after 7, 14 and 28 days was 5.5%, 6.0% and 3%, respectively, for the concrete mix with 20% GWD. This means that the compressive strength of concrete mixes with excessive content of GWD decreases due to the reduction of cement content as binder of the cement paste, as reported previously [26,37,49]. The same factor explains the trend on the other mechanical properties namely

Table 3
Chemical composition of cement and GWD [44].

Material	Chemical composition (%)									
	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	Na ₂ O	CL	LOI
Cement (Type II)	21.4	63.6	4.5	3.5	2.1	2.5	0.5	0.5	0.07	1.9
Granite	70.2	3.7	15.8	1.9	0.6	0.6	3.7	2.1	0.02	1.6

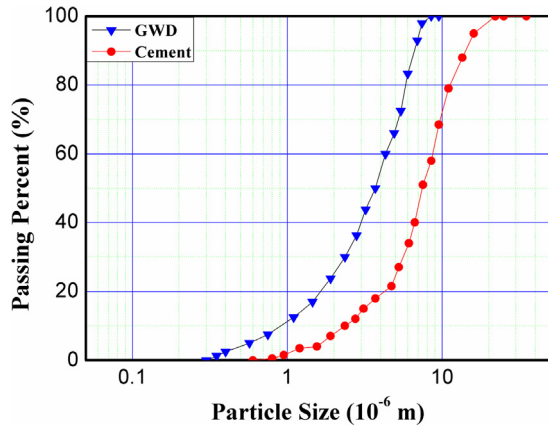


Fig. 1. Particle size distribution of GWD [44] and cement.

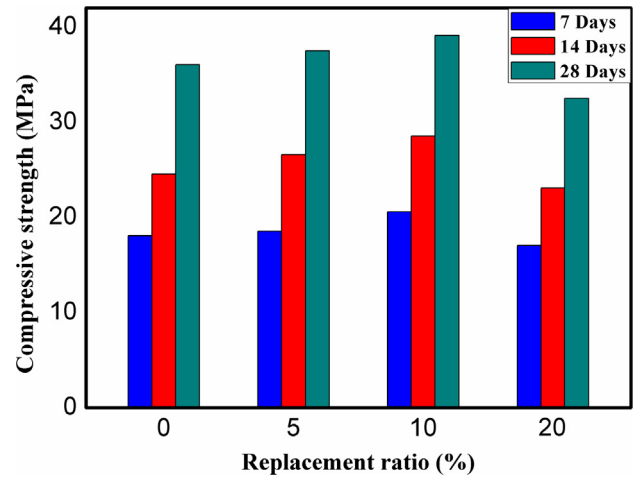


Fig. 2. Compressive strength of concrete mixes with GWD as partial cement replacement after 7, 14 and 28 days of curing in lime-saturated water.

splitting tensile strength. Finally, Fig. 2 shows that, as curing continued, the compressive strength of all concrete mixes increased but the rate of increase varied as reported in previous researches [50,51].

3.1.2. Effect of GWD on compressive strength after exposure to a H_2SO_4 solution

The absolute value and percentage changes in compressive strength of the concrete mixes with GWD as partial cement replacement after 7, 28 and 91 days of exposure to a 5% by weight H_2SO_4 solution are shown in Fig. 3. The percentage change of each mix was determined by comparing the compressive strength of specimens after 7, 28 and 91 days of exposure to the H_2SO_4 solution with the compressive strength of specimens after curing in lime-saturated water for 28 days.

As seen in Fig. 3, the compressive strength of all concrete mixes exposed to a H_2SO_4 solution decreases. However, the rate of decrease depends on the time of exposure. The maximum loss in compressive strength of all concrete mixes was observed after 91 days of exposure to the H_2SO_4 solution, as expected. This loss was roughly about 50% for all concrete mixes. This result is in good agreement with a previous study [4]. As seen in Fig. 3 and similarly to Fig. 2 specimens with 10% GWD displayed the highest compressive strength after 7, 28 and 91 days of exposure to the H_2SO_4 solution. This may be attributed to the micro-filler action and enhanced bonding capability of very fine GWD particles, which resulted in the microstructure improvement of the concrete matrix. On the other hand, the specimens with 20% GWD showed the lowest strength after exposure to the H_2SO_4 solution. This means that an excessive content of GWD as cement replacement decreases the compressive strength, as reported previously [38,49]. This may also be attributed to the poorer microstructure of concrete with higher GWD replacements [4].

The reduction in compressive strength of the mixes may also be related to the reaction of sulphuric acid with $Ca(OH)_2$ [52]. Other

researchers also reported that, when the concrete specimens are exposed to a H_2SO_4 solution, extensive formation of gypsum in the regions close to the surfaces is expected [40]. The specimens with 20% GWD displayed a lower loss in compressive strength of 25.5%, 20% and 9% after 7, 28 and 91 days exposure to the H_2SO_4 solution, respectively, compared to the control mix. This result is in good agreement with a previous study [38]. This may be attributed to the more compact and dense microstructure of concrete matrix due to the micro-filler effect of the GWD particles, as reported by Singh et al. [4]. In addition, it was reported that the porosity of concrete mixes with GWD as partial cement replacement, for ratios of 7.5%, 10.0% and 15.0%, increases [22]. Consequently, the probability of degradation by acid attack increases and makes these mixes more vulnerable to acid attack.

3.1.3. Effect of GWD on compressive strength after exposure to a NaCl solution

The absolute value and percentage changes in compressive strength of concrete mixes with GWD as partial cement replacement after 7, 28 and 91 days of exposure to a 5% by weight NaCl solution are shown in Fig. 4. Similarly to the previous section, the percentage change of each mix was determined by comparing the compressive strength of specimens after 7, 28 and 91 days of exposure to the NaCl solution with the compressive strength of specimens after 28 days of curing in lime-saturated water. As seen in Fig. 4, the compressive strength of all concrete mixes increases as immersion time in a 5% by weight NaCl solution increases. This means that, in contrast with the results of the H_2SO_4 solution, the immersion of concrete specimens in the NaCl solution does not have a harmful effect on the compressive strength. Therefore, it can be concluded that the chloride attack, unlike the acid attack, is not aggressive and does not deteriorate concrete and decrease its compressive strength. As shown in Fig. 4, similarly to the results

Table 4
Composition of the concrete mixes.

Mix No.	Composition (kg/m^3)					
	Granite (%)	Granite	Cement	Water	Fine*	Coarse**
1	0	0	400	200	715	1000
2	5	20	380	200	710	995
3	10	40	360	200	710	995
4	20	80	320	200	700	990

* Fine aggregates.

** Coarse aggregates.

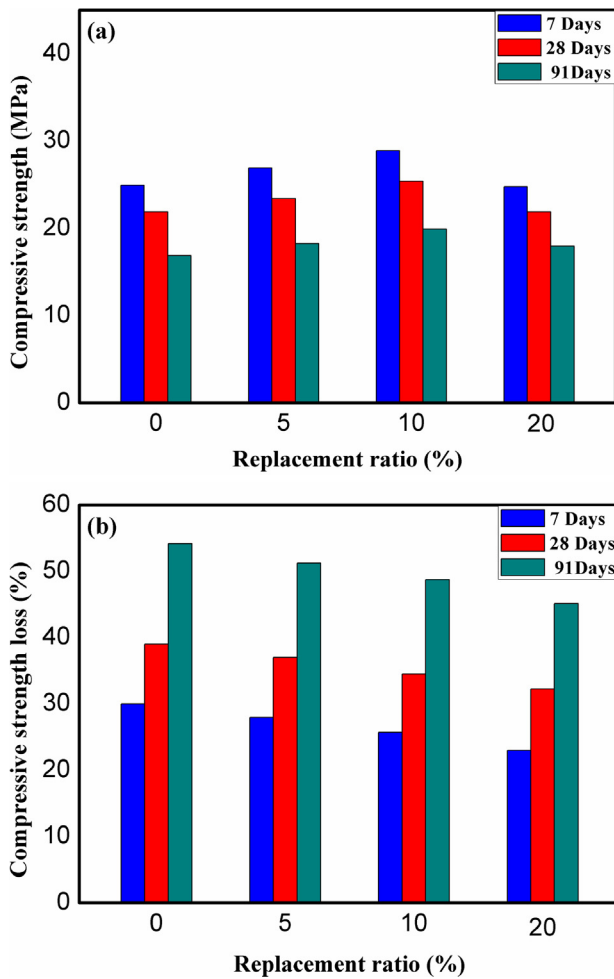


Fig. 3. Absolute value (a) and percentage change (b) in compressive strength of concrete mixes with GWD as partial cement replacement after 7, 28 and 91 days of exposure to a 5% by weight H_2SO_4 solution.

of Figs. 2 and 3, concrete specimens with 10% GWD displayed the highest compressive strength of all mixes at all testing days and increased the compressive strength by about 10%, 10.5% and 12% after 7, 28 and 91 days of exposure to a 5% by weight NaCl solution, respectively, relative to the control mix. On the other hand, similarly to Figs. 2 and 3, the concrete mix with 20% GWD displayed the lowest compressive strength at all testing days.

3.2. Effect of GWD on splitting tensile strength

The splitting tensile strength of concrete mixes with GWD after 7, 14 and 28 days of curing in lime-saturated water is shown in Fig. 5. The splitting tensile strength of all specimens with 10% GWD at all ages was higher than that of the other specimens, while the specimens with 20% GWD displayed the lowest splitting tensile strength at all ages. This agrees with the compressive strength test results and previous studies [22,26]. Specimens with 10% GWD displayed improvements in splitting tensile strength of about 13.5%, 15.5% and 8% after 7, 14 and 28 days of curing, respectively, relative to the control mix. It is concluded that the use of GWD as cement replacement up to 10% can improve the splitting tensile strength of concrete.

3.3. Effect of GWD on sulphuric acid resistance

The percentage change in the mass of the concrete mixes with GWD as partial cement replacement exposed to a 5% by weight

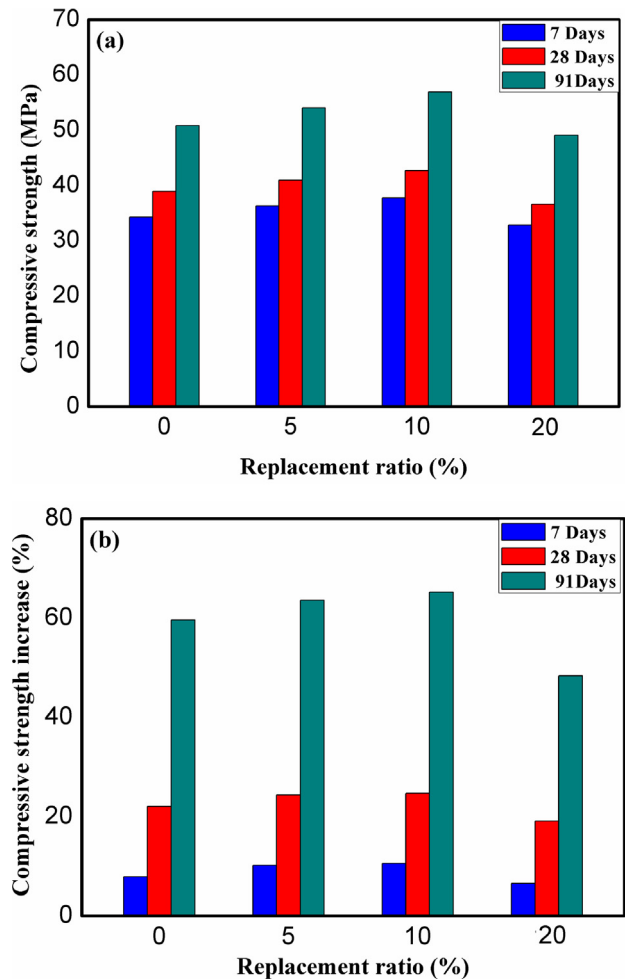


Fig. 4. Absolute value (a) and percentage change (b) in compressive strength of concrete mixes with GWD as partial cement replacement after 7, 28 and 91 days of exposure to a 5% by weight NaCl solution.

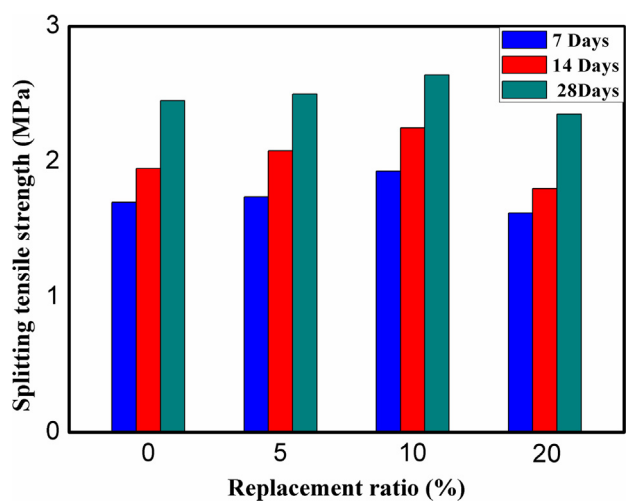


Fig. 5. Splitting tensile strength of concrete mixes GWD after 7, 14 and 28 days of curing in lime-saturated water.

H_2SO_4 solution with pH 1.0 versus immersion time is shown in Fig. 6. Concrete mixes with different ratios of GWD displayed a higher resistance to acid attack compared to the control mix. This means that using GWD as partial replacement of cement can be

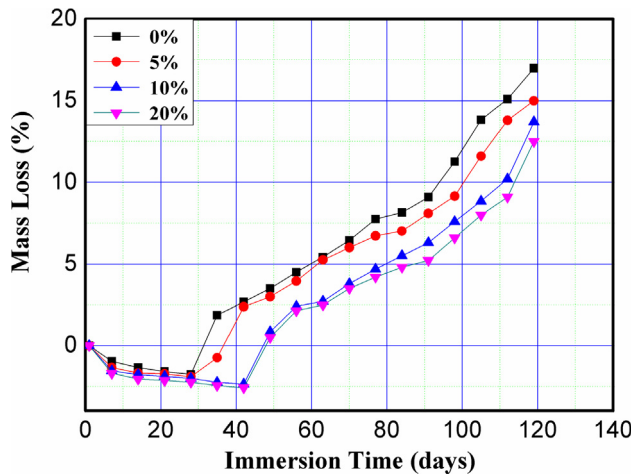


Fig. 6. Percentage change in the mass of concrete mixes with GWD as partial cement replacement exposed to a 5% by weight H_2SO_4 solution with pH 1.0 versus immersion time.

considered as an effective way to improve the resistance of concrete mixes to acid attack. These results are in good agreement with previous studies [4,38,41]. When sulphuric acid reacts with the hydration products, dissolution of the hydrated composites and hydrogen ions occurs [52]. It was reported that sulphuric acid attack is more dangerous than sulphate attack due to the attack of sulphate ions besides the dissolution of hydrogen [4]. The speed of this action depends on several factors, such as the pore structure, porosity of the concrete structure, sulphuric acid concentration and pH value of the solution [53]. Therefore, the higher resistance of the concrete mixes with GWD may be attributed to the improved microstructure of the concrete matrix, which affects the structure of concrete.

Consequently, using GWD as partial cement replacement decreases the amount of pores in the concrete structure and its porosity. As seen in Fig. 6, the maximum loss of all concrete mixes exposed to H_2SO_4 solution was observed after 91 days exposure to the H_2SO_4 solution. Fig. 6 also shows that the control mix had a mass loss of 17% after 91 days of exposure, the worst result of all. For mixes with GWD, as the replacement ratio of GWD increases, the mass loss gradually declines. This result is in good agreement with a previous study conducted by Aarthi and Arunachalam [38]. Therefore, specimens with 20% GWD displayed the best performance of all mixes and had a reduction of mass loss of 26.5% relative to the control mix.

3.4. Water absorption

The water absorption of concrete mixes with GWD as partial cement replacement after 7, 14 and 28 days of curing in lime-saturated water and after 7, 28 and 91 days of exposure to H_2SO_4 and NaCl solutions is shown in Fig. 7. As seen in Fig. 7a, the concrete mix with 5% GWD revealed the lowest water absorption of all mixes at all ages, while the mix with 20% GWD displayed the highest water absorption at all ages. These results are in good agreement with a previous study [38]. The water absorption of the mixes with 5% and 10% GWD is 4% and 2%, respectively, lower than that of the control mix, after 28 days of curing in lime-saturated water. Therefore, it can be concluded that using GWD up to 10% as partial cement replacement can slightly decrease the water absorption of concrete mix. These results are in good agreement with a previous study conducted by Aarthi and Arunachalam [38]. As seen in Fig. 7b and c, the water absorption of all mixes with GWD is lower than that of the control mix. This

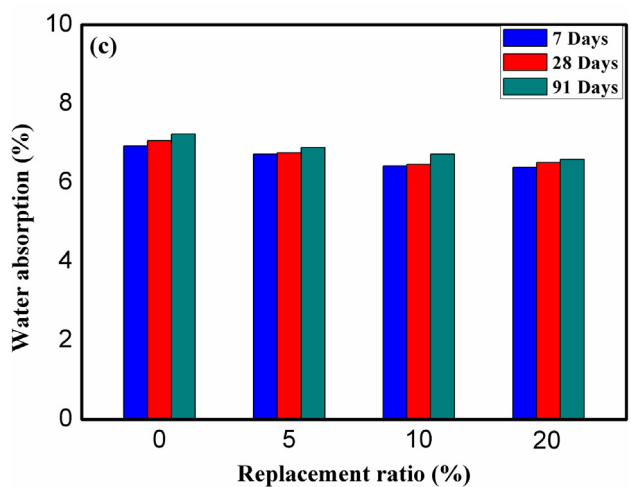
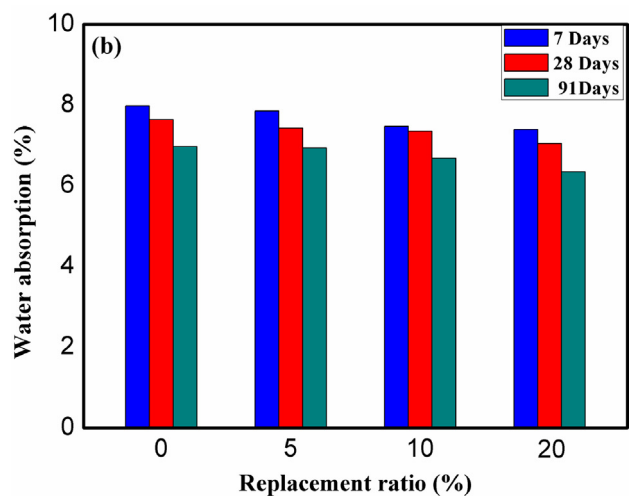
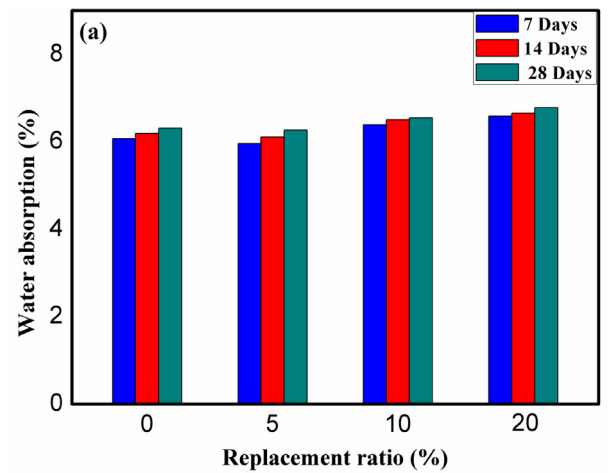


Fig. 7. Water absorption of concrete mixes with GWD as partial cement replacement after 7, 14 and 28 days of (a) water curing in saturated lime water and after 7, 28 and 91 days of exposure to 5% by weight H_2SO_4 (b) and NaCl solutions (c).

means that using GWD as partial cement replacement in concrete production can decrease the concrete water absorption after exposure to adverse environments (H_2SO_4 and NaCl solutions). In fact, the water absorption at all testing days decreases as the GWD content increases. As shown in Fig. 7b, the water absorption of all concrete mixes decreases as the time of exposure to the H_2SO_4 solution increases. On the other hand, as seen in Fig. 7c,

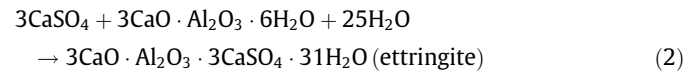
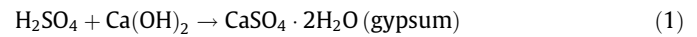
the water absorption of all concrete mixes increases as the time of exposure to the NaCl solution increases. This means that the NaCl solution has more negative impact on the water absorption of concrete mixes than the H₂SO₄ solution. It can also be concluded from Fig. 7 that GWD had no significant effect on the water absorption of concrete mixes compared to other mechanical and durability properties.

3.5. Variation of open circuit potential (OCP)

Fig. 8 shows the variation of average OCP values of the steel rebars embedded in concrete after 119 days of immersion (28 days in lime saturated water and 91 days in 5% by weight NaCl and H₂SO₄ solutions). The vertical red arrow in Fig. 8 separates 28 days of lime-saturated curing from the 91 days of immersion in NaCl or H₂SO₄ solutions. Fig. 8a represents the OCP data relating to the NaCl solution and Fig. 8b the results for concrete specimens exposed to the H₂SO₄ solution. Dashed lines in Fig. 8a and b separate the different zones of potential regarding corrosion risk. According to ASTM C876-91, three regions of above -200 mV/CCS (copper copper-sulfate), between -200 and -350 mV/SCE and lower than -350 mV/CCS can be distinguished when corrosion risk is considered. In this regard, OCP values under -350 mV/CCS denote strong corrosion probability.

As seen in Fig. 8, due to rising of pH next to the steel rebar, the OCP value increases during the curing process. On the other hand, exposing the specimens to chloride or sulfate solutions resulted in decreasing the OCP values. Such decrease can be originated by aggressive anions to the concrete itself or the passive layer formed on the steel rebar surface. In the case of NaCl solution, the main aggressive anion is Cl⁻. Chloride is supposed to activate the steel rebar surface and deteriorate the hydroxide passive layer formed in alkaline environment near the steel rebar [54]. To achieve this, the chloride ions need to penetrate into the concrete structure and reach the steel rebar surface. So, the more porous the concrete structure, the more chloride anions can reach the steel rebar surface and the more corrosion can be expected. The addition of GWD to the concrete mix could have beneficial effects by filling the pores of the concrete structure [22] and can therefore hinder the penetration of chlorides into the concrete pores. As seen in Fig. 8a, the OCP value of concrete specimens No. 1 and 2 with 0% and 5% GWD as cement replacement falls rapidly into the corrosion area, while for concrete specimens No. 3 and 4 with 10% and 20% GWD as cement replacement stay much longer in the safe or

uncertain regions. Sulfuric acid media is likely to be more dangerous for the concrete structure. Sulfuric acid can react with the calcium hydroxide or calcium aluminate hydrates and form calcium sulfate dehydrate-gypsum and ettringite through the following reactions [55]:



Formation of gypsum and ettringite can lead to an expansive deterioration of the concrete structure. This could increase the porosity of the concrete structure and therefore the water and anions could easily reach the steel rebar surface. The deterioration of the concrete structure in sulphuric acid solution can be seen in Fig. 9a, compared to the similar specimens exposed to NaCl solution Fig. 9b. The formation of new crystals, as well as the deterioration and porous appearance of the concrete surface in the specimen immersed in H₂SO₄, is obvious in Fig. 9.

As mentioned above, the main influence of sulphuric acid is to weaken the concrete structure, while NaCl has a direct effect on the steel rebar itself. So it is rational to expect that the OCP of steel rebar in concrete represents lower values in the NaCl solution relative to the H₂SO₄ solution. Fig. 8 shows this phenomenon clearly. After 119 days (28 days in lime saturated water and 91 days in 5% by weight NaCl and H₂SO₄ solutions), the OCP values of all concrete specimens exposed to H₂SO₄ were lower than that of those in the NaCl solution. Furthermore, the specimens with 10% and 20% GWD showed a higher value of OCP compared to the mixes with 0% and 5% GWD in the H₂SO₄ solution as well.

3.6. Effect of GWD on the corrosion resistance of steel rebars

To better understand the corrosion status of the steel rebars embedded in concrete, the corrosion resistance of all concrete specimens was evaluated using the EIS method after 91 days of immersion in 5% by weight H₂SO₄ and NaCl solutions. The resulting Nyquist spectrums are shown in Fig. 10. It can be inferred that the system shows two capacitive loops and therefore the equivalent circuit might consist of two chains of a resistor parallel to a capacitor, as is conventional in these systems [44]. The first one reflects the concrete behaviour and the second one is related to the electrochemical response of the steel rebar surface. These two chains are

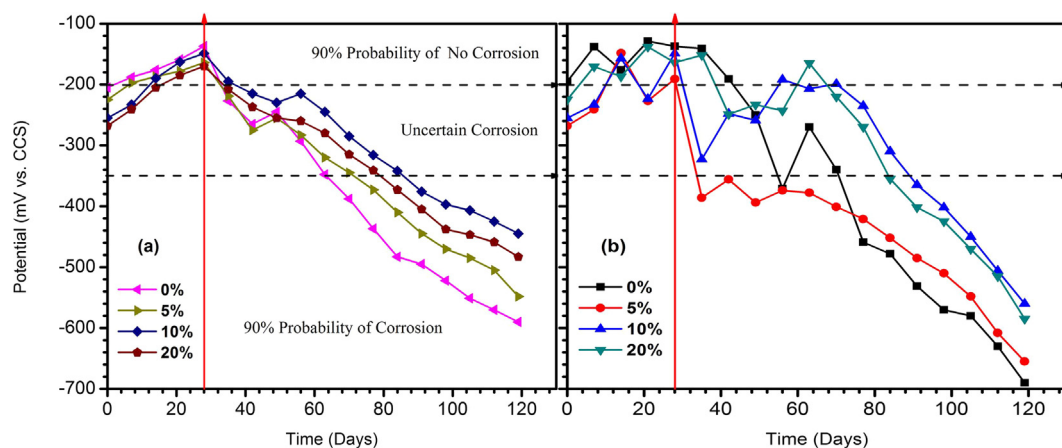


Fig. 8. OCP results of concrete mixes with GWD as partial cement replacement during 28 days of curing in lime-saturated water and 91 days immersion in (a) 5% NaCl and (b) 5% H₂SO₄ solutions. The potentials are relative to copper copper-sulphate reference electrode according to ASTM C876-91. Regions of corrosion status are shown with dashed lines.

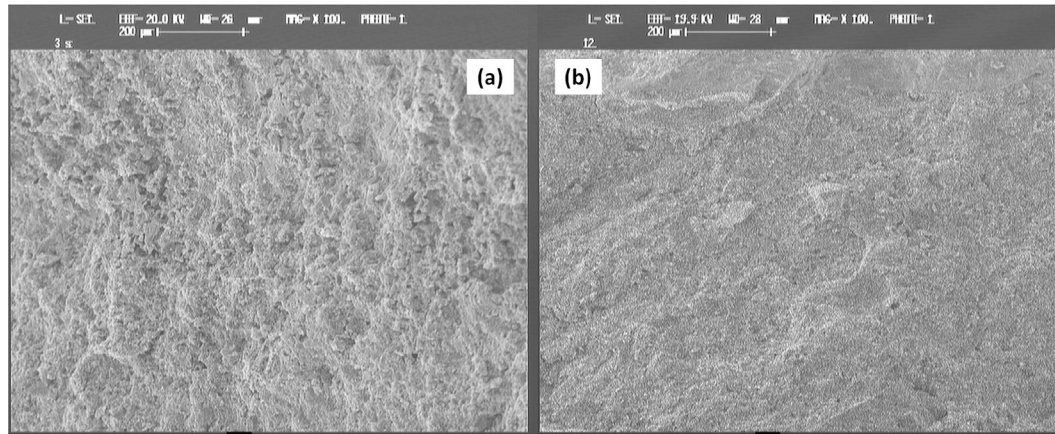


Fig. 9. Microstructure of concrete mixes with 10% GWD as partial cement replacement after 91 days of immersion in (a) 5% H₂SO₄ and (b) 5% NaCl solutions, obtained by SEM analysis.

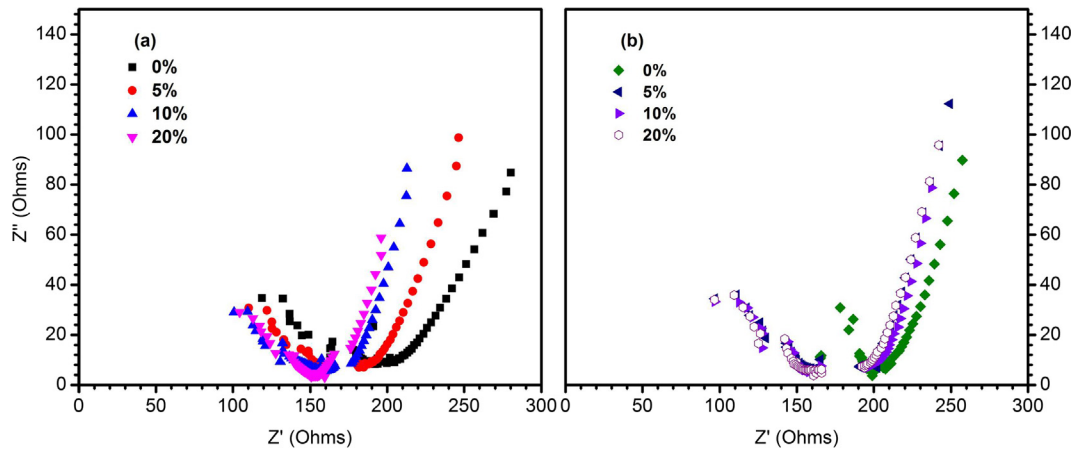


Fig. 10. Nyquist plots of concrete mixes with GWD as partial cement replacement during 28 days of curing in lime-saturated water and 91 days immersion in (a) 5% NaCl and (b) 5% H₂SO₄ solutions.

Table 5

Fitted values of EIS results obtained after 91 days of immersion in 5% by weight NaCl and H₂SO₄ solutions.

Solution	Mix No.	R_c (Ω)	$P_c(F/S^{1-n})$	n_c	R_{ct} (Ω)	$P_{dl}(F/S^{1-n})$	n_{dl}
NaCl	1	190	1.2×10^{-6}	0.60	20000	0.0097	0.44
	2	180	3.6×10^{-6}	0.51	50000	0.0099	0.60
	3	170	2.6×10^{-4}	0.20	60000	0.0143	0.67
	4	155	4.3×10^{-5}	0.29	65000	0.0179	0.55
H ₂ SO ₄	1	200	1.2×10^{-6}	0.60	40000	0.0097	0.59
	2	175	3.5×10^{-6}	0.51	50000	0.0099	0.62
	3	170	7.2×10^{-6}	0.45	65000	0.0125	0.61
	4	165	1.0×10^{-5}	0.40	65000	0.0098	0.61

connected to the resistor, which is denoted by the solution resistance between the reference electrode and the concrete surface. The latter resistor has a negligible value in comparison with other resistors associated in an equivalent circuit. The EIS results were fitted with the mentioned circuit and the obtained amounts are reported in Table 5. According to this table, the charge transfer resistance (R_{ct}) can suitably show the corrosion status of concrete specimens. It is obvious that using GWD especially at replacement ratios of 10% and 20% improves the R_{ct} significantly. In addition, comparing the resulting values from the two solutions, the R_{ct} for the H₂SO₄ solution is a bit higher than that of the NaCl one. So it

can be said that the 5% H₂SO₄ solution was less destructive than the 5% NaCl, at least until 91 days of immersion.

4. Conclusion

In this research, the influence of GWD as partial replacement of cement after 91 days of exposure to 5% by weight H₂SO₄ and NaCl solutions was investigated. For this purpose, compressive and splitting tensile strengths, resistance to acid attack, water absorption, OCP and EIS tests and SEM analysis were conducted and the following conclusions were drawn:

- Concrete specimens with 10% GWD displayed higher compressive strength during the curing process in lime-saturated water and after exposure to H₂SO₄ and NaCl solutions than the other concrete mixes.
- Chloride attack, unlike acid attack, is not aggressive and does not deteriorate the concrete structure or decrease its compressive strength.
- Mass lost results revealed that using GWD as partial replacement of cement can be considered an effective way of improving the resistance of concrete mixes to acid attack. Specimens with 20% GWD displayed the most positive effect of all mixes and had a 26.5% lower mass loss relative to the control mix.
- The NaCl solution has less effect on the water absorption of concrete mixes than the H₂SO₄ solution. The effect of GWD on the water absorption of concrete mixes was lower than that of the mechanical and durability properties.
- Mixes with GWD replacement ratios of 10% and 20% showed higher potentials. However, the OCP values of all specimens were located in the corrosion risk zone after 28 days immersion in lime saturated water and 91 days in 5% by weight NaCl and H₂SO₄ solutions. In addition, the OCP values of specimens exposed to 5% by weight H₂SO₄ solution were higher than that of those in the NaCl solution.
- The R_{ct} obtained from EIS data in 91th day of immersion in H₂SO₄ and NaCl solutions show that, by increasing the GWD content, the charge transfer resistance increases, especially for GWD replacement ratios of 10% and 20%. Furthermore, it can be inferred that the H₂SO₄ solution is less aggressive than the NaCl solution as long as the corrosion behaviour is considered.

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Data availability

All raw data required to reproduce these findings are available in the paper itself.

Conflict of interest

The authors have no conflict of interest whatsoever.

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