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Evaluation of Acid Attack on Concrete Containing Spent Garnet as Partial Sand Replacement

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Abstract: This research studied the water absorption of concrete containing spent garnet and determine the durability of concrete containing spent garnet in acidic environment. The materials used along the experiment works were spent garnet, river sand, crushed stone, ordinary Portland cement and water. In this study, spent garnet were used as sand replacement with 0%, 10%, 20%, 30% and 40% in concrete mix designs. First and foremost, the water absorption test was conducted on three (3) set of water-curing cube specimens with dimension 100 mm cube for the plain concrete and for each percentage of spent garnet concrete mixes and was done in compliance with the BS 1881: Part122 (1983) specification. After that, the durability tests under 5% of hydrochloric acid attack and 5 % of sulphuric acid attack were conducted by preparing corresponding sets of concrete specimens which were three (3) set of 28 days water-curing specimens for each percentage of spent garnet in different acid immersion according to Standard ASTM C1898 – 20 while the compressive strength was under standard in BS EN:12390-3: 2019. In the end of the study, the physical appearances of the samples were observed and the weight loss for each sample was tested and recorded accordingly. From the results obtained, the highest percentage of water absorption of concrete was C20 which was 7.80%. However, the stronger average concrete strength of concretes from both acids with the achieved target compressive strength was concrete C20 but also with lowest weight loss. The concrete containing with 20% of spent garnet had better acid resistant in terms of visual assessment not only toward sulphuric acid attack but also toward hydrochloric acid attack. The application of 20% of spent garnet as sand replacement was hence can provide stronger acid resistant in maintaining the supporting strength of concrete. In conclusion, the durability of normal concrete should be investigated over a longer length of time to mimic the real-world circumstance in which a structure is erected.

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Keywords: Spent Garnet, Water Absorption, Durability of Concrete

1. Introduction

Spent garnet is the universal appellation for a cluster of composite silicate natural resources with comparable crystal-like assemblies and varied chemical configurations [1]. By referring to the data obtained, the chemical compositions for garnet are SiO_2 (33.7%), Al_2O_3 (13.9%), Fe_2O_3 (43.1%), TiO_2 (0.78%), CaO (4.15%) and MgO (2.91%) [2]. Garnet is metallic-free iron, making it ideal for all surface preparation fields, including stainless steel, anti-magnetic steel and all other alloys, and has many advantages such as recyclable, low health risk, low dusting, fast cutting, low-free content of silica and with no measurable heavy-metal concentrations. Garnet is well-matched to most fields of the surface preparation industry with and without following coatings, in particular shipyards, new construction, conversion and restoration, including anti-magnetic and other special steels, as well as aluminium superstructures and aluminium and fibre glass hulls. A proper management of scheduled wastes is essential implemented by all parties in Malaysia based on the specified guidelines with requirement for site selection and design criteria in packaging, labelling and storage of waste materials such as spent garnet.

There were a lot of researches completed by adjusting different sorts of recycled waste materials in substituting the material of concrete. Those researchers had proven that modified concrete can enhance the properties of concrete and reduce the landfills along with the environmental issues. Spent garnet is one of the studied materials that can replace fine aggregates in concrete-mix. Since the industrial waterjet cutting is mined for removal and thus the cast-off garnet sand is collected to be used sporadically as fine aggregates in construction and road infrastructure. The waste from waterjet cutting was studied to evaluate the likelihood of garnet sand in transforming as a concrete aggregate and trench backfill [3]. Besides, in order to minimize the cost of waterjet cutting, a process for restoring the abrasiveness of garnet sand was conducted at Tomsk Polytechnic University. Garnet waste substitutes quartz sand in both cases. The findings supported the likelihood that cast-off garnet sand could be used as aggregates in concrete, however, there is no confirmation yet for its application as trench backfill [3].

The utilization of concrete in construction sector has been a common scene and a main material to be used. Fine aggregate is one of the main materials required in forming a concrete which also composing cement, water, and aggregates. Therefore, sand replacement will be taken in preserving the availability of nature fine aggregates due to the high demand of construction sector. It was reported that there had plenty cases of environmental problems happened every year due to the disposal of million tons of spent garnet into the oceans, quarries, landfills and rivers [1]. Therefore, spent garnet is a great choice to be reused as sand replacement in construction industry. Implementation of sand replacement in the concrete production directly solve the destruction of river embankments, landfill problem and ecosystem of aquatic under the rivers. Other than that, the utilized spent garnets needed to proceed with several durability tests and to determine the quality of modified concrete containing spent garnets in fulfilling the requirements for the current construction industry. Therefore, spent garnets could be the most suitable alternative material to replace river sand as fine aggregate to become a more environmental-friendly material in the future construction sector. Evaluation of acid attack in normal strength concrete in this study was identified with the exposure of concrete toward acid environment which might happened daily. Different acid attack tests were prepared and data from the durability tests will be analyzed in this research.

2. Materials and methodology

This materials and methodology section had concluded the required materials and different experimental testing processes conducted throughout the whole study.

2.1 Materials and mix design

According to BS EN 197-1 standard, Portland cement with 95 to 100% of Portland cement clinker content is suitable for making concrete. Thus, the cement that capable to be obtained from laboratory was ordinary Portland cement [4]. The primary concrete ingredient used was ordinary Portland cement

(OPC) given to its availability and low price. In this study, river sand was used as fine aggregate for concrete mixing. The river sand that passed through a 5mm of sieve were determined as fine aggregates. Apart from that, sieve analysis test was carried out for each portion of river sand before used in mixture of concrete according to ASTM C136 / C136M – 19 with standard test method in sieving process for both fine and coarse aggregates. The serving coarse aggregates that retained at 5 mm but passes 10 mm through sieve analysis was used in compliance with BS EN 933 (2012). Crushed stones were used in concrete mixes as coarse aggregates with an angular and rough surface texture. Standard grade of concrete with M30 was selected as the targeted concrete mixes to be determined throughout the whole research. M30 grade of concrete was equaling to a compressive strength of 30 MPa (4350 psi). It was concluded that the production of M30 concrete equivalent to proportion of cement: fine aggregate: coarse aggregate: water with 510: 650: 980: 230 in standard ratio of 1: 1.27: 1.92: 0.45. Table 1 shows the mix proportions of materials for M30 concrete.

Table 1 : Mix proportions of materials for M30 concrete

SI unit	**Types of mixes**	**Cement (kg/m^3)**	**Water (kg/m^3)**	**Fine Aggregate (kg/m^3)**		**Coarse Aggregate (kg/m^3)**
				River Sand	**Spent Garnet**	
1	C0	510	230	650	-	980
2	C10	510	230	585	65	980
3	C20	510	230	520	130	980
4	C30	510	230	455	195	980
5	C40	510	230	390	260	980

2.2 Methods

The flowchart of the methodology in completing related laboratory work in more systematically was illustrated in Figure 1. The flowchart had included the preparation of materials, concrete mix design, determination of fresh concrete, durability tests and water absorption test.

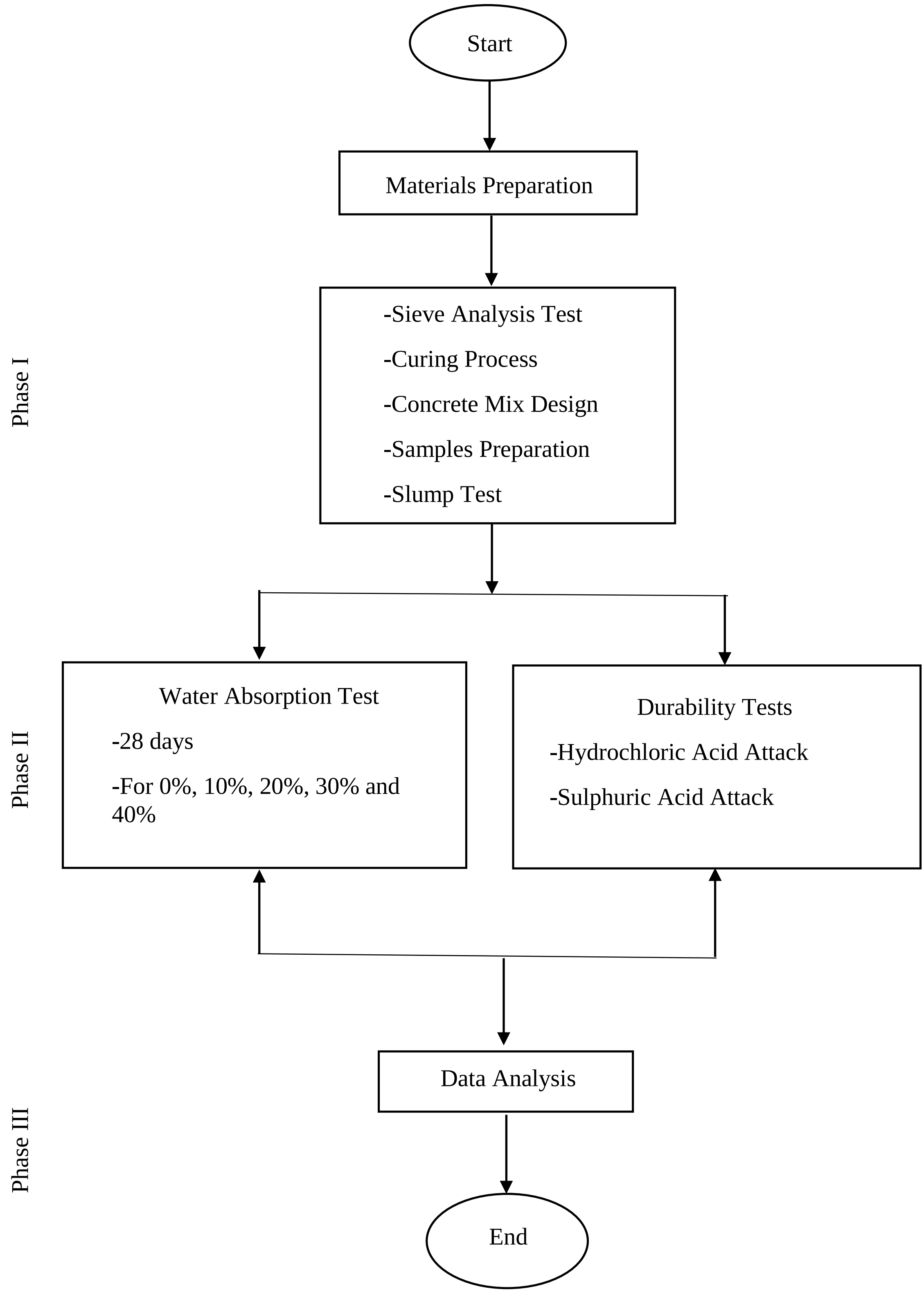

Figure 1: Flowchart of Methodology

2.2.1 Water absorption test

The water absorption test was done in compliance with the BS 1881: Part122 (1983) specification, which specified an immersion method used to assess the percentage of water absorbed by concrete. The apparatus that was required in this test were water tank, heating and drying oven. This test was conducted on three (3) set of water-curing cube specimens with dimension 100 mm × 100 mm × 100 mm for the plain concrete and also three (3) set for each percentage of spent garnet concrete mixes which were 0%, 10%, 20%, 30% and 40%. The water curing process or immersion of concretes in water were kept at (20±2) °C for 28 days. After that, separation for each sample and was shaken thoroughly, followed by wiping up with a cloth to remove free water. The weights of these wet specimens were subsequently measured and recorded. After the specimens were removed from the curing tank, the cured specimens were first oven dried at (105±5) °C for (72±2) h and subsequently cooled down to room temperature for (24±0.5) h before being weighed [5]. The weights of these dry specimens were subsequently measured and recorded. In addition, each specimen's absorption was calculated as an increase in the mass resulting from immersion and was expressed as a percentage differential between the wet and dry specimens' weights. Based on a specification in BS 1881: Part 122 (1983), the calculation was performed using the following equation 1.

$$\mathrm{W_a} = \frac{W_w - W_d}{W_d} \text{ x } 100\% \qquad Eq. 1$$

Where:

$\mathrm{W_a}$ = Percentage of water absorbed (%)

$\mathrm{W_w}$ = Weight of wet specimen (g)

$\mathrm{W_d}$ = Weight of dry specimen (g)

2.2.2 Hydrochloric acid attack

The chemical resistance of concrete to acid attack was determined according to Standard ASTM C1898 – 20. Initially, three (3) set of concrete cubes with dimension 100 mm x 100 mm x 100 mm were prepared respectively for each percentage of concretes that containing 0%, 10%, 20%, 30% and 40% of spent garnet. The cubes were weighted and immersed in water mixed with 5% hydrochloric acid for 28 days following 28 days of curing. The acid solvent was stirred every week in order to retain concentration. The cubes were analyzed physically after 28 days of immersion, and changes in size were observed. Finally, the weights of the specimens were identified after 28 days of immersion and the weight loss or change in mass were hence assessed. The compressive strengths of the specimens were established after 28 days of immersion and observed the deterioration phase for each concrete samples. Weight loss (%) was added as a measure for evaluating concrete deterioration. Therefore, equation 2 was used to compute both average weight loss ($\mathrm{W_l}$) for each cubic specimen (10 x 10 x 10) cm in each acid attack respectively. However, the average loss (%) of strength after immersion in 5% sulphuric acid were performed by using the equation 3.

$$W_l = \frac{W_u - W_p}{W_u} \text{ x}100\% \qquad Eq. 2$$

Where:
W_p = Weight (kg) of specimen after 28 days in acid solution
W_u = Initial weight (kg) of specimen before immersion in acid solution

$$f_1 = \frac{f_w - f_h}{f_w} \text{ x}100\% \qquad Eq. 3$$

Where:
f_1 = Average loss (%) of strength after immersion in 5% hydrochloric acid
f_w = Average compressive strength after 56 days of normal portable water curing (MPa)

f_h = Average compressive strength after 28 days of acid immersion in 5% hydrochloric acid (MPa)

2.2.3 Sulphuric acid attack

The chemical resistance of concrete to acid attack was determined according to Standard ASTM C1898 – 20. The acid resistance test was conducted over 100 mm size concrete cube specimens. In addition, three (3) set of concrete cubes with dimension 100 mm x 100 mm x 100 mm were prepared respectively for each percentage of concretes that containing 0%, 10%, 20%, 30% and 40% of spent garnet. Initially, the 28-day water-curing concrete cubes were weighted and immersed in an acid tank containing solution 5% sulphuric acid. The cubes were taken out of the tank shortly after the completion of the predetermined immersion period and the surfaces of concrete are thoroughly washed. The weight of the concrete cubes was calculated and the weight loss was measured at an average percentage. The compressive strength test on the acid attack specimens was also carried out and the percentage loss of the specimens' compressive strength was noticed. The acid resistance of concrete cubes was measured over a duration 28 days. The appearances of each concrete after the immersion in different acid solutions were observed and recorded. The average loss (%) of strength after immersion in 5% sulphuric acid were performed by using the equation 4.

$$f_2 = \frac{f_w - f_s}{f_w} \text{x}100\% \qquad Eq. 4$$

Where:

f_2 = Average loss (%) of strength after immersion in 5% sulphuric acid

f_w = Average compressive strength after 56 days of normal portable water curing (MPa)

f_s = Average compressive strength after 28 days of acid immersion in 5% sulphuric acid (MPa)

3. Results and discussion

3.1 Water absorption test

Table 2 shows that the percentage of water absorption by different spent garnet content of concrete mixes. Figure 2 shows the average percentage of water absorbed, W_a (%) after 28 days for each mix designation.

Table 2: Percentage of water absorption by different spent garnet content of concrete mixes

Mix designation	Spent Garnet Content (%)	Average Weight of Specimen (g)		Percentage of water absorbed, W_a (%)
		Wet Specimen, W_w (After 28 Days of Water Immersion)	Dry Specimen, W_d (After Oven-dried (105 ± 5) °C for (72 ± 2) h)	
C0	0	2239	2094	6.92
C10	10	2198	2027	8.44
C20	20	2243	2068	8.46
C30	30	2275	2119	7.36
C40	40	2316	2149	7.77

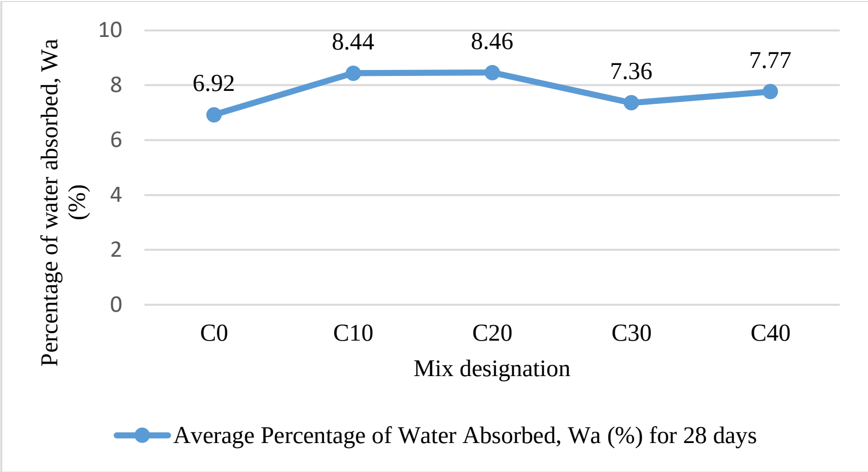

Figure 2: Average percentage of water absorbed, W_a (%) after 28 days for each mix designation.

Based on the Figure 2 , it can illustrate that the percentage of water absorbed, W_a (%) for each mix designation was ranging around 6 to 9%. The result was acceptable as the ability of absorption for all fine aggregate relatively sufficient in order to improve the compressive strength of concrete. This result showed that the absorptivity of spent garnet was significant high and can indirectly increase the concrete permeability. Figure 3 shows the heating and drying oven that used in this study.

Figure 3: Heating and Drying Oven

3.2 Hydrochloric acid attack

Table 3 shows the assumed scale of acid attack assessment for the concrete mixes as the physical appearance assessment. Concrete surface deterioration scale will be observed physically from various angle of observation. Table 4 shows the visual assessment of concrete.

Table 3: Visual assessment of concrete effected due to acid attack

Assumed Scale	Acid attack assessment
I.	No attack
II.	Very slight
III.	Slight
IV.	Moderate
V.	Severe
VI.	Very severe
VII.	Partial disintegration

Table 4: Visual assessment of concrete

Mix designation	5% hydrochloric acid
C0	Severe
C10	Severe
C20	Severe
C30	Severe
C40	Severe

Based on the observation upon the physical appearances of concrete cubes, there were similar assumed scale of acid attack assessment for different percentage of spent garnet in each type of acid solution respectively [6]. The control specimen C0 and the concrete with 10%, 20 %, 30% and 40% of spent garnet results in a severe degree of deterioration with formation of brown layer structure. Figure 4 shows that the immersion of concretes in 5% hydrochloric acid solution for duration of 28 days. Furthermore, there will be comparison of the average compressive between the specimens after immersion in 5% hydrochloric acid and the specimens with water immersion are hence recorded in Table 5 and so thus with the average loss (%) of every mix designation.

Figure 4 : Immersion of concretes in 5% hydrochloric acid solution for duration of 28 days.

Table 5: Compressive strength of concrete cubes containing spent garnet after immersion in 5% hydrochloric acid.

Mix designation	**Spent Garnet Content (%)**	**Average compressive strength (MPa)**		**Average loss (%) of strength after immersion in 5% hydrochloric acid, f_1**
		Strength after 56 days of normal portable water curing strength, f_w	Residual strength after 28 days of acid immersion in 5% hydrochloric acid, f_h	
C0	0	36.5	32.7	10.41
C10	10	32.9	29.5	10.33
C20	20	34.1	30.8	9.68
C30	30	30.5	26.4	13.44
C40	40	29.6	26.0	12.16

The average compressive strength for C0, C10, C20, C30 and C40 were 32.7MPa, 29.5MPa, 30.8MPa, 26.4MPa and 26.0MPa. The average loss (%) of strength after immersion in 5% hydrochloric acid for C0, C10, C20, C30 and C40 were 10.41%, 10.33%, 9.68%, 13.44%, and 12.16%. According to the data collected, showed that the C20 with lowest percentage of 9.68% for concrete strength loss while C30 with highest percentage of 13.44% for concrete strength loss. Therefore, the utilization of spent garnet in concrete mixture was considered had enough ability to provide a better acid resistant toward hydrochloric acid and the structures could withstand for longer period as the time of expose increase interaction of hydrochloric acid with Ca (OH) to create soluble calcium chloride, which is dissoluble in water, might account for the drop in C20 concrete compressive strength following immersion in hydrochloric acid solution. However, the average weight of concretes before and after immersion in 5% hydrochloric acid along with weight loss (%) for each percentage of mix designation are recorded in Table 6.

Table 6: Weight loss of concrete after immersion in 5% hydrochloric acid

Specimen	Weight Loss, W_l (%)
C0	0.043
C10	0.216
C20	0.043
C30	0.256
C40	0.465

Among all the mix designations, the highest weight loss (%) after immersion in 5% hydrochloric acid was C40 whereas the minimum in the concrete mix C20. By comparing it to zero content of spent garnet, the most suitable amount of spent garnet to control the weight loss is C20. Due to the acid absorption ability of spent garnet will increase with higher contents, hence concrete C20 with medium range of content can avoid the interaction of chemical composition with hydrochloric acid.

3.3 Sulphuric Acid Attack

Table 7 shows the visual assessment of concrete after the sulphuric acid attack. Concrete surface deterioration scale will be observed physically from various angle of observation and will be determined according to the acid attack assessment.

Table 7: Visual assessment of concrete

Mix designation	5% sulphuric acid
C0	Very severe
C10	Very severe
C20	Very severe
C30	Very severe
C40	Very severe

After 28 days of immersion, signs of degradation may be seen on the specimens. The physical degeneration of concrete subjected to acid attack has been seen similarly for C0, C10, C20, C30, and C40. The concretes formed degradation as the cement paste from the surface, edge and corner of concretes peeled off until the coarse aggregate can be clearly seemed. Figure 5 shows the immersion of concretes in 5% sulphuric acid solution for duration of 28 days. The comparison of the average compressive between the specimens after immersion in 5% sulphuric acid and the specimens with water immersion are hence recorded in Table 8 and the average loss (%) of every mix designation are measured.

Figure 5: Immersion of concretes in 5% sulphuric acid solution for duration of 28 days.

Table 8: Compressive strength of concrete cubes containing spent garnet after immersion in 5% sulphuric acid.

Mix designation	Spent Garnet Content (%)	Average compressive strength (MPa)		Average loss (%) of strength after immersion in 5% sulphuric acid, f_2
		Strength after 56 days of normal portable water curing strength, f_w	Residual strength after 28 days of acid immersion in 5% sulphuric acid, f_s	
C0	0	36.5	22.4	38.63
C10	10	32.9	18.0	45.29
C20	20	34.1	19.3	43.40
C30	30	30.5	18.1	40.66
C40	40	29.6	14.3	51.69

During the sulphuric acid attack, the average compressive strength for all mix designation concretes were drop drastically compared to immersion in normal portable water curing. C20 with 20% of spent garnet had the most ability to withstand sulphuric acid attack in which it had the highest strength value which is 19.3MPa and C40 with 40% of spent garnet unable to provide better acid resistant with lowest strength value of 14.3MPa. Statistics showed that the C30 with lowest percentage of 40.66% for concrete strength loss while C40 with highest percentage of 51.69% for concrete strength loss. Therefore, the utilization of spent garnet in concrete mixture could not able to provide a good sulphuric acid resistant and the structures will erode with the time of expose increase. The reaction of sulphuric acid with calcium hydroxide to generate dehydrate gypsum might explain the reduction in the 28-days cube compressive strength of spent garnet concrete following immersion in sulphuric acid solutions. Sulphuric acid interacts with calcium aluminate hydrate gel to produce calcium sulfo-aluminate, which was quite destructive [7]. The average weight of concretes before and after immersion in 5% sulphuric acid along with weight loss (%) for each percentage of mix designation were recorded in Table 9.

Table 9 : Weight loss of concrete after immersion in 5% sulphuric acid (%)

Specimen	Weight Loss, W_l (%)
C0	3.95
C10	0.216
C20	2.14
C30	0.256

C40	1.55

Based on the collected data, the weight loss (%) after immersion in 5% sulphuric acid for C0, C10, C20, C30 and C40 were 3.95%, 2.14%, 1.55%, 4.79%, and 5.61%. Among all the mix designations, the highest weight loss (%) after immersion in 5% sulphuric acid was C40 whereas the minimum in the concrete mix C20. Ettringite was formed when the sulphuric ion reacts with calcium hydroxide, causing fissures to appear in the concrete. As a result, fine aggregate particles began to fall away from their original location. In general, when more spent garnet is used, the weight loss of concrete increases [8].

3.4 Comparison of hydrochloric acid attack and sulphuric acid attack

For 5 % hydrochloric acid attack, there was no cementitious component leaching occur. However, the surface of the concretes was eroded severely by the chemical attack and turned brownish. The control specimen C0 and the concrete with 10%, 20 %, 30% and 40% of spent garnet resulted in a severe degree of deterioration with formation of brown layer structure. However, for 5 % sulphuric acid attack, the physical degeneration of concrete subjected to acid attack has been seen similarly for C0, C10, C20, C30, and C40. The concretes formed degradation as the cement paste from the surface, edge and corner of concretes peeled off until the coarse aggregate can be clearly seemed.

From Figure 6 showed that the compressive strength graph between water curing and acids immersion, it was clearly displayed that the compressive strength for concretes under hydrochloric acid having a higher strength value compared to sulphuric acid. This outcome proved that the acid resistance ability of concretes containing spent garnet in hydrochloric acid attack was better than in sulphuric acid attack. When compared to sulphuric acid attack, the weight loss (%) and decrease in compressive strength of concrete cube specimens is found to be less in the case of hydrochloric acid attack. The amount of cement pastes accessible to react chemically determines the severity of concrete degradation when exposed to sulphuric acid and hydrochloric acid solutions [9].

In addition, Figure 7 shows the overall weight loss of concrete mixes (%). According to the weight loss (%) after immersion in 5% sulphuric acid and 5% hydrochloric acid, the percentage values obtained between both acids was quite different. The weight loss (%) due to sulphuric acid attack was relatively higher than due to hydrochloric acid attack and the highest weight loss for mix designation of concretes was C40 which was 5.61% and 0.465% respectively in each type of acid attack. While the lowest weight loss for mix designation of concretes was both C20 which was 1.55% and 0.043% respectively in each type of acid attack. Sulphuric acid clearly caused more damage to the concrete of each combination than hydrochloric acid did. It was because calcium sulphate (in the event of sulphuric acid immersion) has a greater capacity to dissolve in water than calcium chloride (in case of hydrochloric acid immersion) [10].

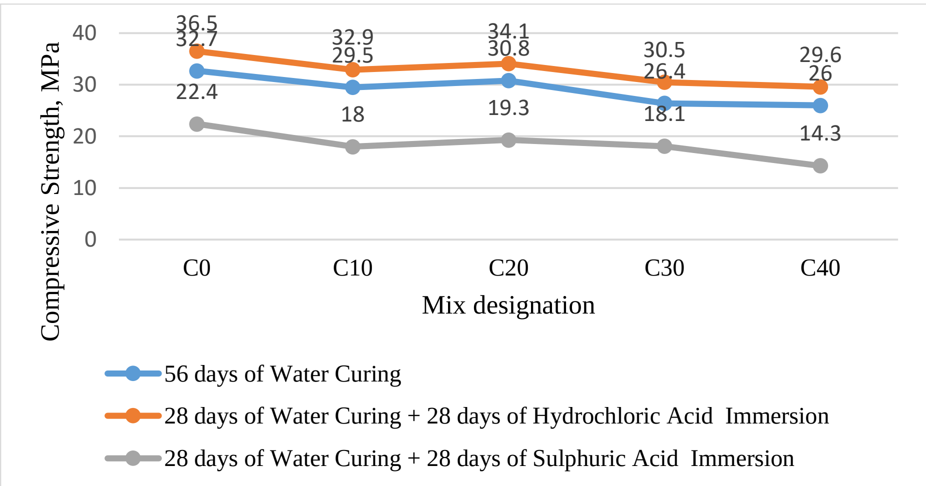

Figure 6 : Compressive strength of concrete mixes.

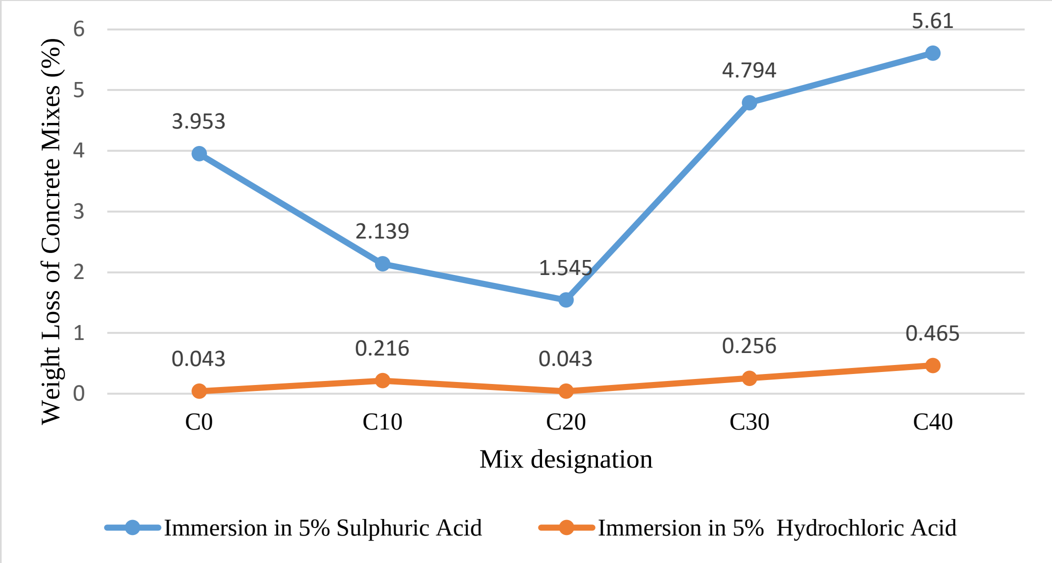

Figure 7: Weight loss of concrete mixes (%)

4. Conclusion

By referring to the objectives of the study, both the initiatives were successfully achieved. According to the experimental results, the highest percentage of water absorption of concrete was C20 which was 8.46 %. The average range of water absorption was around 6-9% and this was acceptable as the requirements for concretes material. The result was acceptable as the ability of absorption for all fine aggregate relatively sufficient in order to improve the compressive strength of concrete. Therefore, the first objective of the study that the water absorption of concrete containing spent garnet was hence studied and achieved. Besides, the chemical resistance of concrete specimens was successfully evaluated by determining the physical appearance, compressive strength and weight loss of concretes. Different chemical attack resulted that different performance of the concretes and it concluded that the utilization of spent garnet in the sand replacement in resisting the aggressive acid attack showed great outcomes by using 20 % of spent garnet. This is due to the stronger average concrete strength of concretes from both acids with the achieved target compressive strength was concrete C20 which having 30.8MPa and 19.3MPa for each acid respectively and also the lowest weight loss among all mix designation of concretes which was 1.55% and 0.043% respectively in each type of acid attack. However, the occurrence of inconsistency of compressive strength values for getting the average value in each mix designation during the experimental process could not be neglected. This occurrence might due to several factors in which one of the factors was the unequal distribution of acidic solution when mixing with tapped water inside the containers used. The surface of interaction of concrete cubes with the higher portion of strong acid would cause higher degradation of compressive strength towards the surrounding concrete cubes. Since C20 has a similar strength to plain concrete, spent garnet may be utilized up to 20% as a replacement. In conclusion, this study concluded that using spent garnet as a fine aggregate replacement in concrete mixture might potentially minimize the amount of natural river sand used in concrete, hence reducing landfill space, which may lead to additional environmental difficulties.

Based on this study, there are a few recommendations could be implemented in improving the quality of the study in the upcoming constructions. The recommendations are as follows:

1. The higher concentration of acid solutions can be applied in the future researches to provide clearer physical appearance differences among different spent garnet contents.
2. The relationship between the partial replacement of spent garnet and the normal concrete should be conducted more in the future.

3. The proportion of spent garnet should be researched in further detail. For example, 0%, 5%, 10%, 15%, 20%, 25%, 30%, 35% and 40%.
4. The durability of normal concrete should be investigated over a longer length of time in order to mimic the real-world circumstance in which a structure is erected.
5. The equal spaces of allocation for cube samples between one another should be located accordingly in order to experience same deterioration rate by acid attack in future similar researches.

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