Case Studies in Construction Materials 8 (2018) 87–96

Contents lists available at ScienceDirect

Case Studies in Construction Materials

journal homepage: www.elsevier.com/locate/cscm

Case study

Microstructures and physical properties of waste garnets as a promising construction materials

Habeeb Lateef Muttashar[a,*], Nazri Bin Ali[b], Mohd Azreen Mohd Ariffin[b], Mohd Warid Hussin[b]

[a] Department of Structure and Materials, Faculty of Civil Engineering & UTM Construction Research Centre University Technology Malaysia, 81310, UTM, Johor Bahru, Johor, Malaysia
[b] Forensic Engineering Centre, Faculty of Civil Engineering, University Technology Malaysia, 81310, UTM, Johor Bahru, Johor, Malaysia

ARTICLE INFO

Keywords:
Spent garnet
Sand
Micro-structures
Recycling
Concrete

ABSTRACT

Rapid industrial growth has witnessed the ever-increasing utilization of sand from rivers for various construction purposes, which caused an over-exploitation of rivers' beds and disturbed the eco-system. strong engineering properties of waste garnets offer a recycling alternative to create efficient construction materials. Recycling of garnets provides a cost-effective and environmentally responsible solution rather than dumping it as industrial waste. In this spirit, this article presents an investigation into the capacity of spent garnets as sand replacement. The main parameters studied were the evolution of leaching performance, microstructure of the raw spent garnet and sand specimens. The microstructures, boning vibrations and thermal properties of the raw materials were determined using X-ray diffraction (XRD), field emission scanning microscopy (FESEM), Fourier transform infrared (FTIR) spectroscopy, and thermo gravimetric analysis (TGA). Admirable features of the results suggest that the spent garnet is proven to be suitable replacement of sand. It is established that proper exploitation of spent garnet as an alternative to sand could save the earth from depleting the natural resources which is essential for sustainable development.

1. Introduction

Fast industrial expansion has witnessed the ever-increasing utilization of sand from rivers for several construction purposes [1], which led to an over-utilization of rivers' beds and disturbed the ecosystem [2]. Numerous problems have emerged including the increase of river bed depth, lowering of the water table, increase of salinity and destruction of river embankments [3]. Recently, intensive researches have established that modified concretes obtained by incorporating waste materials can lead to sustainable product development. Such concrete structures not only allow for greener and environmentally sound construction but also protect the excessive consumption of natural fine aggregates that are non-renewable [4]. Thus, proper use of fine aggregates in the concretes as alternative materials became an absolute necessity for the replacement of river sand. In this regard, utilization of waste garnets emerged as a promising alternative in its own right. So far, no details literature review has been performed on this new waste material that shows its potential towards concrete applications. In the context of Malaysia, the topic spent garnet is becoming a significant issue in terms of recycling this new waste material and further reuse as useful sand replacement in concrete. Statistics revealed that the amount of garnet imported from Australia to Malaysia in the year 2013 was 2000 t. This amount was imported by MMHE

* Corresponding author.
E-mail address: lmhabeeb2@live.utm.my (H.L. Muttashar).

https://doi.org/10.1016/j.cscm.2017.12.001
Received 28 August 2017; Accepted 8 December 2017

(Malaysian Marine and Heavy Engineering Sdn. Bhd.). However, heavy mineral sands are the class of ore deposit that is a significant resource of rare earth elements and industrial minerals including diamond, garnet, sapphire, and other valuable gemstones or metals. The so called "garnet" is a generic word that refers to an assemblage of multifaceted minerals of silicate compounds containing Calcium (Ca), Magnesium (Mg), Ferrous iron (Fe) or Manganese (Mn), Aluminium (Al), Chromium (Cr), Ferric iron (Fe) or even Titanium (Ti) having analogous crystal lattice structures and varied chemical formulas Castel, 2010. Interestingly, the angular fractures and hardness properties of garnets together with their ability to be recycled make them advantageous for numerous abrasive applications. The common chemical composition of garnet is $A_3B_2(SiO_4)_3$ wherein the element "A" may be Ca, Mg, ferrous iron, or Mn, Al, Cr, ferric iron or Ti [5]. Garnets have major industrial uses such as water jet cutting, abrasive blast medium and powder, granule for water filtration, etc. [6]. In 2002, the total estimated global production of industrial garnet was 440,000 T, wherein China, Australia, India, and the USA were the major producers. The USA alone produced about 9% of the totally produced industrial garnet worldwide [7,8].

Production in both Australia and India was more than the USA. Currently, Russia and Turkey are mining garnet to meet mainly their domestic market demand. Besides, some garnet resources with tiny mining facilities are situated in Chile, Canada, Czech Republic, South Africa, Pakistan, Spain, Ukraine, and Thailand to meet their domestic demand. Industries in Australia have been steadily enhancing their garnet manufacturing and export. Meanwhile, China and India have augmented the garnet production and became vital supplier of garnet sources for other nations. Thus, use of spent garnet to make concrete in place of fine aggregates will avoid the over-usage of natural sand and gravels. This research effort is expected to bring modernization in the Malaysian construction industries, encourage builders and engineers to use eco-friendly spent garnet based GPCs than the conventional one made of natural river sand, create more jobs and save environment from further pollution.

2. Materials and methods

2.1. Materials

In this study, the spent garnet was acquired from southern Johor (Malaysia). Subsequently, various characterizations and tests were made. These include: visual inspection, physical properties, chemical composition and leaching behaviour. The morphology, mineral composition and thermal analysis were determined. Fig. 1 illustrates the physical appearance of spent garnet and sand used as fine aggregates.

The chemical composition of the spent garnet was determined using S4 Pioneer X-ray fluorescence spectroscopy (XRF) as displayed in Fig. 2. This spectrometer works by irradiating the samples in an intense X-ray beam from a radioisotope source. The primary source of the rays excites the sample by detaching the tightly bound inner shell electrons from their orbits in the excited atoms of the samples. When the excited atoms are relaxed to the original state, fluorescent X-rays are emitted. The energies of the detected emitted rays using an energy dispersive detector are used for the identification of elementsdioisotope source. The primary source of the rays excites the sample by detaching the tightly bound inner shell electrons from their orbits in the excited atoms of the samples. When the excited atoms are relaxed to the original state, fluorescent X-rays are emitted. The energies of the detected emitted rays using an energy dispersive detector are used for the identification of elements in the sample while the intensity of the X-rays is employed to determine the quantity of the elements. The crystalline and amorphous phase of the constituent materials was verified using X-ray diffraction (XRD) analysis. A Rigaku XRD machine (Fig. 3) was used.

The structural properties of the spent garnet in terms of bonding vibrations were determinedusing Fourier transform infrared (FTIR) spectroscopy. The room temperature absorption/transmission infrared spectra were recorded in the wavenumber range of 400–4000 cm^{-1}. Fig. 4 displays the Perking Elmer FTIR instrument that was used to identify the chemical functionality and molecular bonding. Using potassium bromide (KBr) pellet technique a transparent disk-shaped material was prepared and tested. The

Fig. 1. Appearance of fine aggregates (sand and garnet) used in the concrete production.

Fig. 2. Bruker S4 Pioneer XRF spectrometer.

Fig. 3. Rigaku X-ray diffractometer.

pellet was made by mixing with 100 mg of KBr in agate spent garnet material and then pressed using a pellet die hydraulic press. Nitrogen gas was used to purge the spectrometer.

Thermal properties of the spent garnet was also characterized using thermogravimetric and differential thermal analyser (TGA/DTA) up to a temperature of 1000 °C with heating rate of 10 °C/min as presented in Fig. 5. The thermal stability of the materials due to decomposition was determined. Generally, TGA is employed to evaluate the selected properties of materials that display mass alteration (loss or gain) arise from oxidation or moisture loss and decompositions.

The presence of heavy metals contents in the spent garnet including Arsenic (As), Barium (Ba), Cadmium (Cd), Cromium (Cr), Lead (Pb), Selenium (Se), Silver (Ag), Zinc (Zn) and Copper (Cu) were tested using toxicity characteristic leaching procedure (TCLP) developed by the United States Environmental Protection Agency (US EPA). The Test Method 1311 (1999) from EPA was used, wherein spent garnet materials of size below 2.00 mm were mixed with deionized water in the liquid to solid ratio of 20:1. Two test samples were agitated with the revolution of 30 rpm for 24 h (Fig. 6). The samples were filtered to remove particulates and larger colloids using 0.45 μm membrane filter. After extracting and filtering the leachates, the inductively coupled plasma mass spectrometry (ICP–MS) was performed to determine the heavy metals ion contents. The leaching test was performed at the Institute of Bioproduct Development laboratory, UTM – Johor Bahru, Malaysia.

The fine aggregates in the form of naturally occurring river sand was tested via specific gravity on saturated surface-dry basis, oven-dry basis bulk density, water absorption and sieve analysis.

Fig. 4. FTIR spectrophotometer.

Fig. 5. TGA/DTA instrument.

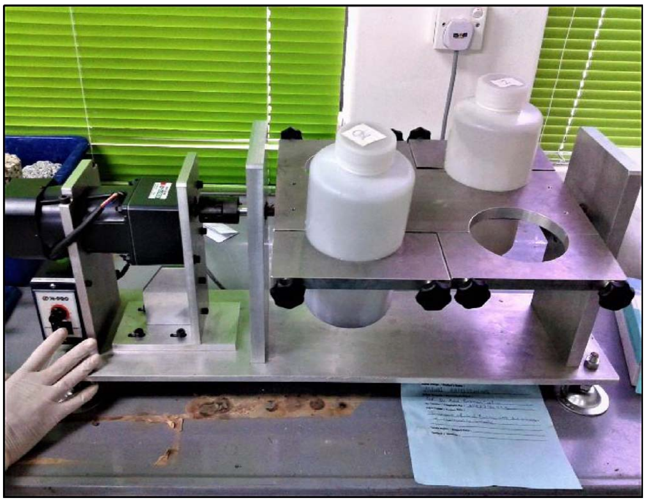

Fig. 6. leaching test.

Table 1
Physical properties of spent garnet.

Properties	Spent garnet	River sand	Permissible limits	Relevant standards or reference
Specific gravity	3.0	2.6	2.6–2.7	Neville [9]
Fineness modulus	2.05	2.66	2.3–3.2	[22]
Hardness	7.5	6	1–10	Mohs scale
Bulk density	1922 kg/m^3	1640 kg/m^3	1300–1750	Mehta and Monteiro [10]
Water absorption	6%	3%	2%–3%	BS EN 1097-6 [11]

3. Results and discussion

3.1. Physical properties

The test results on the physical characteristics of spent garnet are presented in Table 1. The spent garnet showed the value of specific gravity of 3.0, which is higher than that of natural sand (usually varies from 2.6 and 2.7) [9]. The high specific gravity of spent garnet was ascribed to the elevated contents of iron oxide (Fe_2O_3) in it. The water absorption value of 6% was higher than the maximum limit of 3% recommended by BS EN 1097-6 [11] for fine aggregate. The bulk density was 1922 kg/m^3, which is higher than the limits of 1300 to 1750 kg/m^3 required for normal weight concrete as specified by Mehta and Monteiro [10] and Neville and Brooks [12]. The bulk density of spent garnet is higher when compared to that of river sand and this might be due to reduced void content. The finer particles of spent garnet might have filled pore and optimized the pore structure, however, it lead to higher water demand [7,8].

3.2. Grading of spent garnet

Fig. 7 shows the result of the grading of spent garnet and river sand as derived from sieve analysis. The coefficient of grading was 1.02 and 1.02 for spent garnet and river sand, which were greater than 1. Therefore, the spent garnet material was also considered as well graded. The particle size distribution of the spent garnet material falls within the upper and lower limits of medium grading limits (M) for fine aggregate specified by BS 882 [13] which is equivalent to zone II classification of BS 812-103.1 [14]. For river sand this occurred into coarse grading limits (C) of BS 882 [13], which fall into zone I classification of BS 812-103.1 [14]. The fine aggregate for concrete are generally required to conform to any one of the three grading limits of BS 882 [13]. The coarse, medium or fine indicated by the grading limits in which the grading falls were designated as C, M and F, respectively. The percentage retained on 5 mm sieve size was 0% for spent garnet and 2% for sand, which were within the recommended limits of 0–5% of BS 882 [13] grading requirements for fine aggregates. This affirmed that the grading of spent garnet was conformed to the recommended grading for fine aggregates suitable for concrete production.

3.3. Chemical composition of spent garnet

The chemical compositions of the spent garnet and the river sand were evaluated using XRF spectroscopy as enlisted in Table 2. The major component of spent garnet was iron oxide (Fe_2O_3). The mass content of iron oxide for spent garnet and river sand were 43.06% and 0.7%, respectively. The alumina (Al_2O_3) content for spent garnet is 13.88% and Silicon oxide (SiO_2) content was 33.76%

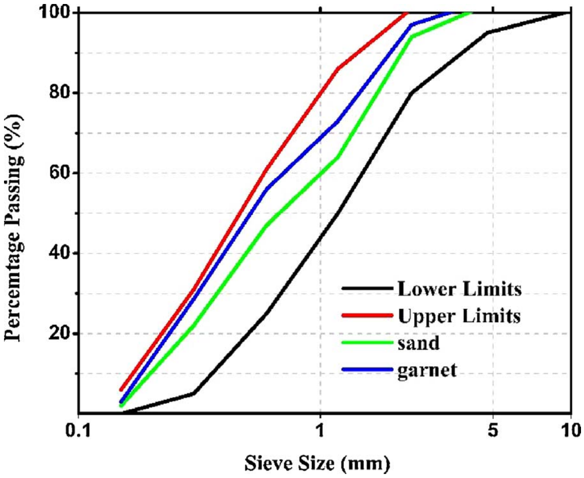

Fig. 7. Sieve size dependent percentage passing of the spent garnet.

Table 2
Chemical composition of spent garnet obtained from XRF analysis.

Chemical Compounds	Weight% of spent garnet	Weight% of sand
Fe_2O_3	43.06	0.7
SiO_2	33.76	96.4
Al_2O_3	13.88	–
CaO	4.15	0.14
MgO	2.91	–
MnO	1.08	–
TiO_2	0.78	1.1
K_2O	0.14	–
P_2O_5	0.21	–
ZnO	0.06	–
Cr_2O_3	0.05	–
(LOI)	–	1.1

while sand has SiO_2 of 96.4%. Iron oxide, Fe_2O_3 is the main colorant in spent garnet, being responsible for the reddish colour. The calcium oxide (CaO) content for spent garnet is 4.15% and river sand, 0.14%. However, the presences of Cu, Zn and Pb in the chemical composition will possibly affect the hydration process of SCGPC [15]. Interestingly, no trace of sulphur trioxide was found in the chemical composition.

3.4. Leaching test

The contents of weighty metals such as As, Cd, Ba, Cr, Se, Pb, Ag, Cu and Zn in the raw garnet are tested to guarantee the materials safety. The TCLP established by the US EPA was employed to determine the contents of heavy metals present in the garnet as summarized in Table 3. The heavy metals contents were discerned to be lower than the control limits. The contents of As, Ba, Cr, Cd, Zn and Pb in the leachate were below the allowable regulatory limit for waters (ground water, surface water and tap water) and farmland soil based on the requirement of U. S EPA (2000) standards.Thus, the spent garnet used in this study can be considered as safe material with the following specifications.

3.5. XRD analysis

Fig. 8 displays the XRD patterns of spent garnet, which revealed several sharp crystalline peaks in the angular range of 25° and 100°. The observed sharp crystalline peaks were assigned to the crystalline phases of quartz (SiO_2), Magnesium (Mg) and Aluminium Cobalt (Alco). Quartz is the major phase and is generally known to be nonreactive [16], but usually increase the packing density and long-term strength development [17].

Fig. 9 depicts the XRD patterns for river sand, where the appearance of crystalline peaks indicated the presence of quartz (SiO_2) as major crystalline mineral. The crystalline silicate phases could be beneficial for generating calcium silicate hydrate (CSH) gel or calcium aluminium silicate hydrate (CASH) in the concrete.

3.6. Thermogravimetric and differential thermal analysis (TGA/DTA)

Figs. 10 and 11 illustrates the TGA/DTA curves of spent garnet and river sand, respectively. The endothermic dip in the spent garnet was observed between 350 °C to 500 °C. This dip is usually related to the loss of surface water and dihydroxylation of the material [18]. The exothermic peak (heat release) was appeared between 550 °C and 750 °C due to the oxidation reaction of organic

Table 3
Presence of heavy metals in spent garnet determined using TCLP analysis.

Detected metals	Results (mg/l)	
	Spent garnet	Regulatory limits
Arsenic (As)	0.000103	5.0
Cadmium (Cd)	0.000445	1.0
Chromium (Cr)	0.006195	5.0
Cuprum (Cu)	0.00462	25
Nickel (Ni)	0.000159	2
Barium (Ba)	1.145093	100
Plumbed (Pb)	Not Detected	0.05
Selenium (Se)	0.000757	1.0
Cobalt (Co)	0.00017	8
Zinc (Zn)	0.127609	250

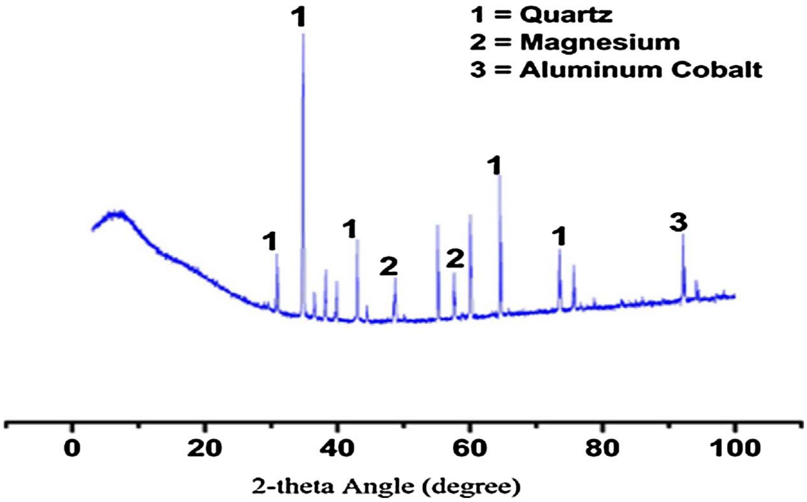

Fig. 8. XRD pattern of spent garnet.

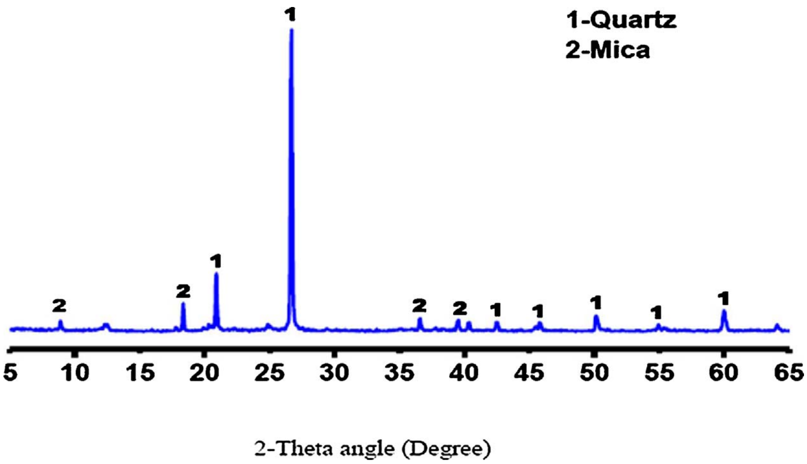

Fig. 9. XRD pattern of river sand.

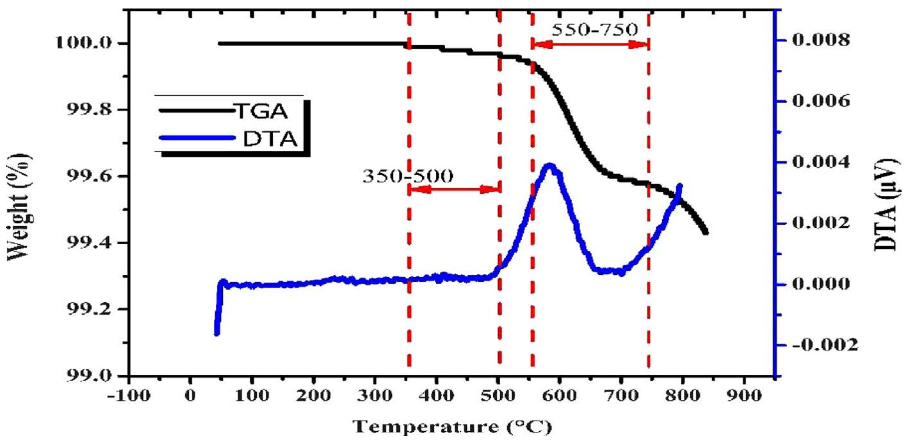

Fig. 10. TGA/DTA curve of spent garnet.

matter in spent garnet with a weight loss of 0.4% in this period. Meanwhile, the oxidation of hematite was also occurred in this temperature range, but the heat and weight variation were concealed by the stronger oxidation reaction of organic matter in spent garnet. The observed weight loss of about 0.2% for the sample in between 700 and 900 °C was ascribed to the decomposition of

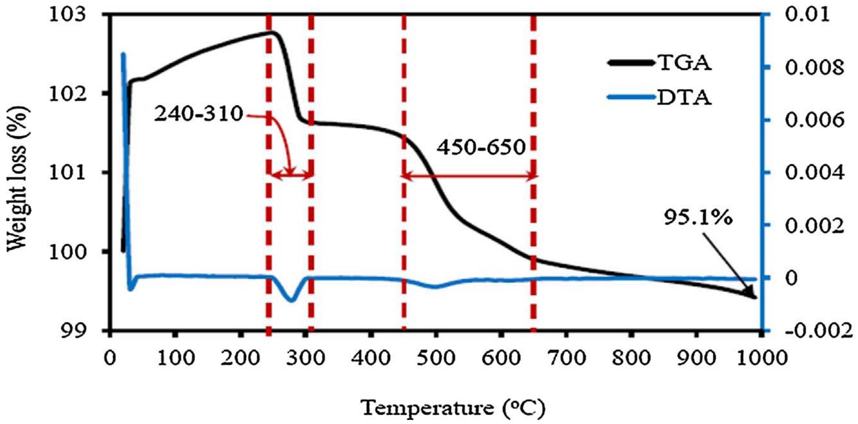

Fig. 11. TGA/DTA curve of river sand.

calcite into CaO at 768.5 °C [19] and dehydroxylation of quartz in the range of 850–900 °C.

The endothermic peaks of river sand at 40 °C and 130 °C were also attributed to the loss of surface water and dihydroxylation. The difference between the DTA temperatures due to endothermic reaction of the sand and that of the spent garnet was significant. GA curve further showed that the sample decomposed from 100% to 99. 4% for spent garnet, which correspond to the mass loss of 0.4% and 0.6% due to the decomposition of adsorbed water between 450 and 550 °C and 700–850 °C, respectively, making loss of about 1%. However, river sand decomposed from 100 to 95.1% with a loss of about 4.9%. Comparing the values, spent garnet decomposed less than river sand when exposed to temperature and this could be due loose nature of the particles.

3.7. Fourier transform infrared (FTIR) spectra

Figs. 12 and 13 present the FTIR spectra for spent garnet and river sand, respectively. The spectra of spent garnet (Fig. 12) were comprised of two groups of absorptions such as the outer hydroxyl groups and the inner hydroxyl group. The external groups were located in the upper unshared plane, whereas the inner groups were situated in the lower shared plane of the octahedral sheet. The spectrum of the minerals was arranged in the sheets as per the occupation of octahedral and tetrahedral sites in the lattice. The inner hydroxyl groups were positioned amid the tetrahedral and octahedral sheets, which revealed the IR absorption $\approx 3733\ cm^{-1}$. The observed strong absorption band at about $3847\ cm^{-1}$ was assigned to the in-phase symmetric stretching. Conversely, the occurrence of an weak band at $3445\ cm^{-1}$ was allocated to the out-of-plane stretching vibration [23]. The absorption bands at 1018 and $964\ cm^{-1}$ were approved to Si—O symmetric and asymmetric stretching vibrations, respectively [20]. The IR absorption bands at 569 and $452\ cm^{-1}$ were allocated to the Si—O—Al and Si—O—Si bending vibrations, respectively. The band at $1431\ cm^{-1}$ exhibited the stretching vibration of Fe_2OH [20], a characteristic compound of spent garnet minerals as also revealed in the XRF spectra. The IR spectra spent garnet further displayed that the absorption bands were due to bonding vibrations of OH and Si—O groups. Presence of these groups often plays a significant role in the water absorption rate and differentiation of mineral composition.

The FTIR spectra of river sand (Fig. 13) revealed significant IR peaks at $778\ cm^{-1}$ and $1032\ cm^{-1}$, which were allocated to the

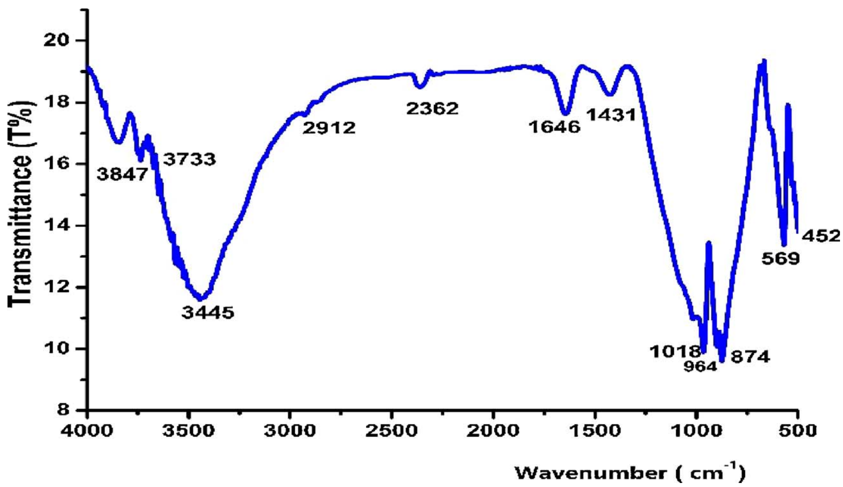

Fig. 12. FTIR spectra of spent garnet.

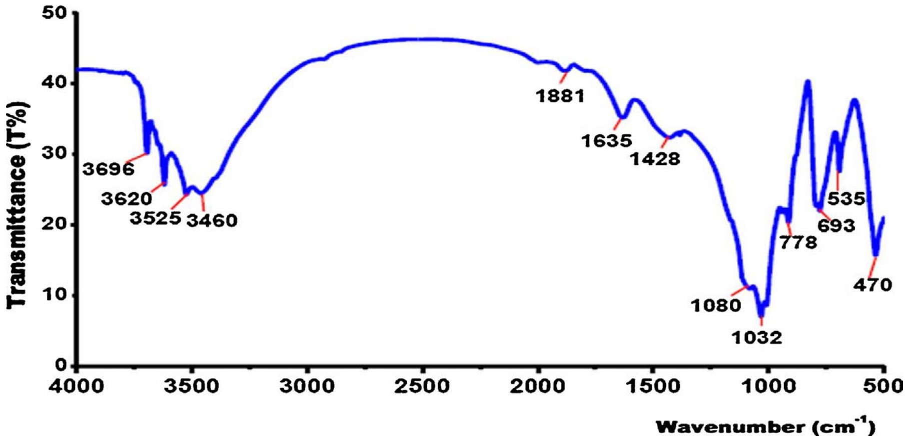

Fig. 13. FTIR spectra of river sand.

symmetric and asymmetric stretching vibration of Si—O bond, respectively. Yet again, the appearance of an IR band at 694 cm^{-1} was approved to the asymmetric and symmetric bending vibration of Si—O bond. The bands at 3620 cm^{-1} and 3697 cm^{-1} were allocated to the symmetric and asymmetric stretching of calcium hydrate (CH) group [21]. The bands associated with the stretching vibration of OH group of interlayer water molecule during surface absorption were also evidenced. It was affirmed that pure silica was the main component of the river sand. The FTIR results were supported by the XRF data, both of which revealed high amount of silica content in the river sand.

4. Conclusion

The spent garnet material was found to be well graded as its grading fall to zone II within the specified limits of BS 812-103.1 [14]. Spent garnet has a large proportion of reactive and inert materials in the crystalline form as revealed by the XRD patterns. The chemical composition of spent garnet revealed iron content, alumina and high silica. The spent garnet showed the value of specific gravity of 3.0, which is higher than that of natural sand (usually varies from 2.6 and 2.7) [9]. The high specific gravity of spent garnet was ascribed to the elevated contents of iron oxide (Fe_2O_3) in it. The water absorption value of 6% was higher than the maximum limit of 3% recommended by BS EN 1097-6 [11] for fine aggregate. The leaching behaviour of spent garnet and safety properties is within the acceptable limits. The endothermic dip in the spent garnet was observed between 350 °C–500 °C. This dip is usually related to the loss of surface water and dihydroxylation of the material. The exothermic peak (heat release) was appeared between 550 °C and 750 °C due to the oxidation reaction of organic matter in spent garnet with a weight loss of 0.4% in this period. The result obtained from this study demonstrated that it is possible to apply spent garnet in concrete.

References

[1] K. Kankam Charles, et al., Stress-strain characteristics of concrete containing quarry rock dust as partial replacement of sand, Case Stud. Constr. Mater. 7 (2017) 66–72.
[2] F. Lollini, M. Carsana, L. Bertolini, A study on the cement-based decorative materials in the San Fedele Church in Milan, Case Stud. Constr. Mater. (2017).
[3] J.J. Gourley, C.M. Calvert, Automated detection of the bright band using WSR-88D data, Weather Forecast. 18 (4) (2003) 585–599.
[4] J. Temuujin, A. van Riessen, K.J.D. MacKenzie, Preparation and characterisation of fly ash based geopolymer mortars, Constr. Build. Mater. 24 (10) (2010) 1906–1910.
[5] H.L. Muttashar, M.A.M. Ariffin, M.N. Hussein, M.W. Hussin, S.B. Ishaq, Self-compacting geopolymer concrete with spend garnet as sand replacement, J. Build. Eng. 15 (2018) 85–94.
[6] S. Lindtner, G.D. Hertz, P. Dourish, Emerging sites of HCI innovation: hackerspaces, hardware startups & incubators, Proceedings of the SIGCHI Conference on Human Factors in Computing Systems, ACM, 2014, pp. 439–448.
[7] H.L. Muttashar, M.W. Hussin, M.A.M. Ariffin, J. Mirza, N. Hasanah, A.U. Shettima, Mechanical properties of self-compacting geopolymer concrete containing spent garnet as replacement for fine aggregate, Jurnal Teknologi 79 (3) (2017) 23–29.
[8] H.L. Muttashar, M.A. Mohd Ariffin, M.W. Hussin, S.B. Ishaq, Realisation of enhanced self-compacting geopolymer concrete using spent garnet as sand replacement, Mag. Concr. Res. (2017) 1–12.
[9] A.M. Neville, Properties of Concrete, Pearson Education Limited, London, 2011.
[10] P.K. Mehta, P.J.M. Monteiro, Concrete: Microstructure, Properties, and Materials, McGraw-Hill Education, 2013.
[11] BS EN 1097-6, Determination of Particle Density and Water Absorption, BSI Standards Publication, London, 2013.
[12] A.M. Neville, J.J. Brooks, Concrete Technology, Pearson Education Limited, Essex, England, UK, 2010.
[13] BS 882, Specification for Aggregate from Natural Sources for Concrete 14 BSI Standards Publication, 1992.
[14] BS 8110-2, Structural Use of Concrete: Code of Practice for Special Circumstances, BSI Standards Publication, 1985.
[15] Z. Giergiczny, A. Krol, Immobilization of heavy metals (Pb, Cu, Cr, Zn, Cd, Mn) in the mineral additions containing concrete composites, J. Hazard. Mater. 160 (2–3) (2008) 247–255.
[16] X. Yao, Z. Zhang, H. Zhu, Y. Chen, Geopolymerization process of alkali–metakaolinite characterized by isothermal calorimetry, Thermochim. Acta 493 (1–2) (2009) 49–54.
[17] H.L.M. Alzuabidi, Engineering Properties of Mortar Containing High Volume Biomass from Palm Oil Mills, Universiti Teknologi, Malaysia, 2013 Doctoral dissertation.
[18] B. Maifala, N.M.S. Tabbiruka, Chemical and thermal characterization of a clayey material found near gaborone dam, Appl. Sci. Environ. Manag. 11 (4) (2007)

77–80.
[19] L. Cai, B. Ma, X. Li, Y. Lv, Z. Liu, S. Jian, Mechanical and hydration characteristics of autoclaved aerated concrete (Aac) containing iron-tailings: effect of content and fineness, Constr. Build. Mater. 128 (2016) 361–372.
[20] S. Kaufhold, M. Hein, R. Dohrmann, K. Ufer, Quantification of the mineralogical composition of clays using ftir spectroscopy, Vib. Spectrosc. 59 (2012) 29–39.
[21] X. Huang, R. Ranade, V.C. Li, Feasibility study of developing green Ecc using iron ore tailings powder as cement replacement, J. Mater. Civil Eng. 25 (7) (2013) 923–931.
[22] ASTM C33 (2003), American standard testing of materials - specification for concrete aggregates, American society of testing and materials Publication, 2003, p. 11.
[23] J. Kristof, R.L. Frost, A. Felinger, J. Mink, Ftir spectroscopic study of intercalated kaolinite, J. Mol. Struct. 410–411 (1997) 119–122.