

## Article

# Studying the C–H Crystals and Mechanical Properties of Sustainable Concrete Containing Recycled Coarse Aggregate with Used Nano-Silica

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**Abstract:** The present study aims to replace 30%, 40%, and 50% of the natural coarse aggregate (NCA) of concrete with recycled coarse aggregate containing used nano-silica (RCA-UNS) to produce a new sustainable concrete. Three groups of concrete are made and their mechanical properties and microstructure are studied. In the first group, which was the control group, normal concrete was used. In the second group, 30%, 40%, and 50% of the NCA were replaced with coarse aggregate obtained from crushed concrete of the control samples and with 0.5% nano-silica as filler. In the third group, 30%, 40%, and 50% of the concrete samples' NCA were replaced with aggregates obtained from 90-day crushed samples of the second group. Water absorption, fresh concrete slump, and compressive strength of the three groups were investigated and compared through scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) tests. The results show that the third group's compressive strengths increased by 12.8%, 10.9%, and 10% with replacing 30%, 40%, and 50% of NAC with RCA-NS at 28 days compared to the control samples, respectively. This could be due to the secondary production of calcium silicate hydrate due to the presence of new cement paste. The third group's microstructure was also improved due to the change in the C–H and the production of extra C–S–H. Therefore, the hydration of cement with water produces C–H crystals while reactions are induced by recycled aggregate containing used nano-silica.

**Keywords:** sustainable concrete; sustainable materials; recycled coarse aggregate; concrete; used nano-silica; compressive strength; sustainable construction materials; recycled concrete; materials design; composite materials



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## 1. Introduction

An average of 40 billion tons of natural aggregates (NA) is used to make concrete in fine and coarse form worldwide [1,2] leading to scarcity of these resources. In addition, the production and processing of NA play an essential role in the generation of dust, noise and greenhouse gases which have a serious negative impact on the environment. Therefore, the need to create an alternative source of NA is of concern to the engineering community today. Furthermore, because of industrial waste in the current century, the need to use recycled materials has become of vital importance, particularly in the construction industry [3,4]. A significant amount of construction and demolition waste is generated annually from the construction industry in all countries of the world. The most influential producers of this waste are China, India and the United States, producing approximately

three billion tons of waste [1,5]. Therefore, recycling and re-use of this degraded waste as recycled aggregates are considered sufficient to reduce natural resource scarcity and better manage waste and environmental resources. Some research has shown that the use of recycled aggregate in concrete not only has social benefits but also creates a sustainable concrete structure. Sustainability factors include conserving energy and natural resources, reducing adverse effects on the environment, saving construction costs, reducing waste storage space [6–8]. Recycled aggregates are produced by separating degraded concrete parts from other unwanted materials and crushing them with appropriate grading [9,10]. Despite the many environmental and economic benefits, the usage of recycled aggregates in construction engineering is generally not accepted and is limited to non-structural uses such as embankments, sub-base of roads and mortar. The main reason for the limited use of recycled aggregates is the low quality of these materials due to micro-cracks and voids compared to natural aggregates [11]. The voids cause low density and high water absorption [1]. It has been reported that various factors such as the amount and moisture of recycled coarse aggregates (RCA), water to cement ratio, source concrete strength, number of crushing steps, age of primary concrete, and the amount of adhesive mortar have an important effect on regulating the properties of these aggregates [12–15]. Furthermore, the use of small amounts of recycled fine aggregates, between 6% to 10%, was recommended [16]. Moreover, there are interphases between cement and natural aggregates called the interfacial transition zone (ITZ) in the normal concrete. Cracks may pass through the ITZ and cause the concrete to fail, if the concrete is subjected to load. Therefore, this zone is a weak bond in the concrete. In concrete containing recycled coarse aggregate, there are more types and numbers of these ITZs compared with normal concrete [17]. The percentage of RCA used in structural concrete varies in different studies [18]. Due to the high water absorption tendency of RCA, the presence of cracks in the RCA, the decrease of workability, reduction in interfacial transition zone bonding, and the increased porosity of concrete, the use of RCA was limited [12,16]. However, the recommended amount of RCA usage in structural concretes as replacement of natural coarse aggregates (NCA) is 30% to 50% [16].

On the other hand, hydration of cement is a chemical reaction between water, tricalcium silicate and dicalcium silicate. During the reaction of cement with water, calcium hydroxide (C–H) crystal and calcium silica hydrate (C–S–H) are produced. However, the C–H crystals are less important than C–S–H in terms of increasing compressive strength. The C–H crystals are beneficial in that case to keep the concrete pH high, maintain a passive layer, and postpone the corrosion. The C–S–H is the main source for the strength of cement based materials. One way to decrease the C–H crystals in the cement matrix is by adding pozzolanic materials such as nano-silica to react with C–H crystals present in the matrix. As a result of this pozzolanic reaction, additional C–S–H is produced and the amount of C–H crystals inside the matrix is decreased, this led to the improvement of the micro structure of cement based materials [6].

Today, the use of nanotechnology in concrete structures has increased due to its high impacts on stability [19,20], and the durability and strength of concrete materials. Furthermore, adding nano-materials such as nano-silica to the mix design of concrete provides sustainable concrete [21,22]. Nano-materials, which range between 1 to 100 nanometers in size, can have different positive chemical and physical effects on concrete [15,23,24]. For instance, the addition of nano-silica increases the possibility of reaction with C–H crystal and the production of C–S–H which enhances the strength of the cement structure and fills the pores in the concrete [25]. Suitable silica cementitious materials such as nano-silica are added to the concrete, react with the C–H crystal, and then produce secondary C–S–H, reducing pores and permeability and increasing the compressive strength of concrete [26]. Nano-silica is a material that accelerates the hydration reaction and reacts fast [26]. Nano-silica consists of very fine particles of approximately 10 to 100 nanometers, which are ball-shaped with a small diameter and are used as an additive in concrete water [27,28]. Researchers have shown that nano-silica materials react rapidly with calcium hydroxide and

very small amounts of these materials have the same pozzolanic effect [29,30]. Nano-silica produces higher compressive strength, is more widely used and more environmentally friendly than other nano-materials such as nano-clay [31]. In cement paste, by adding nanosilica, the hydration acceleration of cement increases and in the first moments, calcium hydroxide is formed due to the increase in the contact surface of nano-silica with water [19].

A great deal of research has been carried out on the application of nano-silica in ordinary concrete [25,28,32]. Furthermore, several research studies have been conducted on the application of Nano-silica with RCA in concrete demonstrating a reduction in the slump of concrete [17,33,34]. Also, currently nano-silica gained a huge interest from the construction industry to improve the concrete properties and produce a high performance sustainable concrete [20]. In the near future, the amount of demolished concrete which includes nano-silica will also be increased. However, there is a lack of knowledge of the reuse of recycled concrete aggregates containing used nano-silica (RCA-UNS). This means that a concrete structure made from recycled coarse aggregates with nano-silica might be recycled again. No research has been carried out on these massive amounts of recycled coarse aggregates containing used nano-silica in concrete. Thus, no data on the properties of these recycled coarse aggregates containing used nano-silica exists. Accordingly, reuse of recycled coarse aggregates containing used nano-silica is important.

To do so, ordinary concrete samples were made as the control for the first group at the ages of 7, 28 and 90 days. In the second group, 30%, 40%, and 50% of the NCA of concrete samples were replaced with coarse aggregate obtained from crushing concrete of control samples and followed by the addition of nano-silica. In the third group, 30%, 40%, and 50% of the NCA of concrete samples were replaced with the aggregates obtained from 90-day crushing of the samples of the second group. Water absorption, fresh concrete slump, compressive strength, scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and X-ray diffraction (XRD) of the three groups were compared.

## 2. Materials and Methods

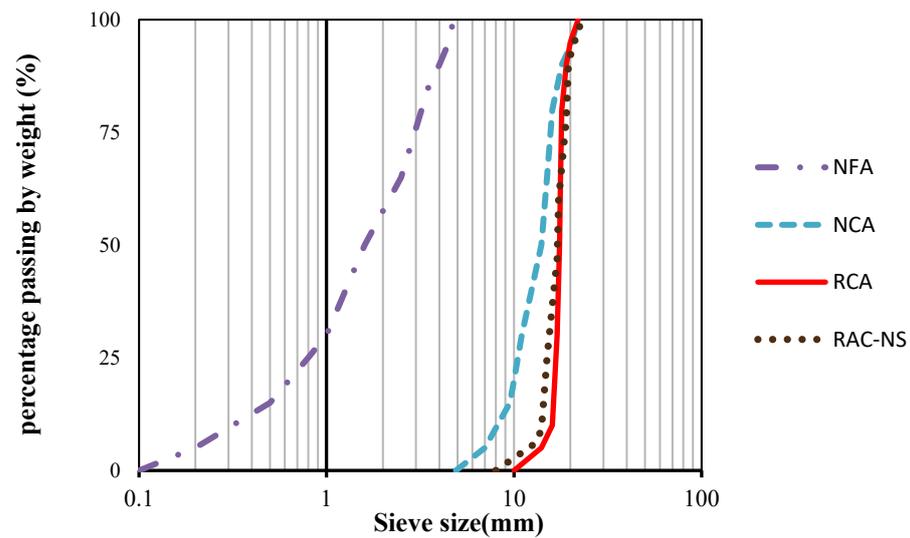
### 2.1. Cement, Water, Natural Aggregates and Superplasticizer

Type-I of Portland cement (Kurdistan Cement Co., Bijar, Iran) with a density of  $3.20 \text{ g/cm}^3$  based on ASTM C 150A [35] was used in this research. For mixing water, regular drinking water with  $\text{pH} = 7$  was utilized. The natural aggregates of all three groups in the concrete mixing design were based on ASTM C128 [36]. The natural coarse aggregates with water absorption of 0.71% had irregular and crushed shape with a maximum size of 13 mm and density of 2.45 according to ASTM C 127 [37]. The natural fine aggregate (NFA) used was river sand with water absorption of 0.60%, 4.75 mm maximum sizes and the density of 2.6. The natural fine aggregates were the same for all groups. The grading curve for NA for the three groups is shown in Figure 1. The black dashed line in Figure 1 represents the control sample aggregates (natural aggregates). A liquid superplasticizer additive based on naphthalene sulfonate was used to increase workability. Its density was  $1.33 \text{ g/cm}^3$ , and 0.5% of the weight of cement was used in concrete according to the superplasticizer catalogue. A constant amount of superplasticizer was used in all concrete mixes.

### 2.2. Recycled Coarse Aggregates (RCA and RCA Containing Used Nano-Silica (RCA-NS))

The second group of concrete specimens, recycled coarse aggregates containing nano-silica, was named RCA-NS. This group of recycled coarse aggregates (RCA) was obtained by crushing 90-day control samples using impact crusher because at the age of 90 days the control concrete has almost reached its final strength. To increase workability, the fine aggregates were separated by sieving and the old cement with air pressure. The largest and the smallest sizes of RCA aggregate were approximately 22.5 mm and 10 mm, respectively. The water absorption and the specific gravity of RCA were, in the order mentioned, approximately 2.2% and 2.45. The grading curve of RCA, is illustrated with a red solid line in Figure 1.

The third group of concrete samples was named RCA-UNS. By crushing the 90-day samples of the second group (RCA-NS), RCA-NS were obtained for use in the third group. The specific gravity and water absorption of RCA-NS were 2.35 and almost 2.9%, respectively. The largest and smallest sizes of RCA-NS aggregates were approximately 23 mm and 8 mm, respectively. The cement coat from the aggregates was removed by using ultrasonic cleaning method to improve the bonding between the new cement paste and RCA [38]. Its grading curve is represented by black dots in Figure 1.



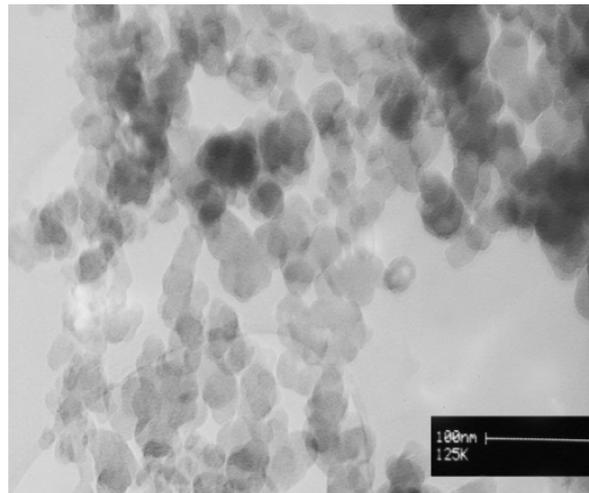
**Figure 1.** Grading curve of natural aggregates (NA) for the three groups, recycled coarse aggregates (RCA) of group two, recycled coarse aggregates containing nano-silica (RCA-NS) of group three.

### 2.3. Nano-Silica

Nano-silica (obtained from the EVONIK company, Germany) was available as powder with 99.9% SiO<sub>2</sub> and 10–14 nm particle size. The color was white (Figure 2), pore size was 1.2 mL/g pore volume with 50 m<sup>2</sup>/g surface area, and density of 2.50. Figure 3 shows an image of the Nano-silica used in group two which was provided by the Iranian Nanomaterials Pioneers Company. The percentage of Nano silica used in concrete varies between 0.4 to 1.5 wt% of the cement as mentioned in previous research [15,21]. In the second group of this study, Nano-silica was used and added as 0.5% of the weight of cement [20]. Table 1 shows the chemical composition and physical properties of the cement and nano-silica.



**Figure 2.** The nano-silica powder.



**Figure 3.** The scanning electron microscope (SEM) image of Nano-silica (provided by Iranian Nanomaterials Pioneers Company).

**Table 1.** Chemical and physical composition of cement and nano-silica.

Chemical Composition (%)	Cement	Nano-Silica
SiO <sub>2</sub>	21.20	99.9
Al <sub>2</sub> O <sub>3</sub>	3.41	-
Fe <sub>2</sub> O <sub>3</sub>	2.78	-
CaO	62.32	-
MgO	1.91	-
K <sub>2</sub> O	0.23	-
Other	8.15	0.1
Physical properties		
density	3.1	2.87
Average size	13.9 micron	10–14 Nm

#### 2.4. Concrete Preparation and Mix Design

In order to achieve the objectives of the research, the amount of cement, the ratio of water to cement, and natural fine aggregates were considered constant in all mix designs. In this regard, an attempt was made to maintain constant conditions and only the amount of aggregate replacement differed. The water to cement ratio of concrete was 0.45 in all concrete mixtures. This ratio of water to cement was high because water might be absorbed in recycled concrete and concrete slump could be very low. In addition, a dark brown liquid superplasticizer (based on naphthalene sulfate) was added to increase workability. For the experiments, a concrete mix was made according to Table 2 to make a cubic sample for ages 7, 28 and 90 days (three samples for each age). RCA-NS standard cubic specimens (second group) were made using natural aggregates with 30%, 40% and 50% RCA and 0.5% Wt. of cement of added Nano-silica. These samples were tested at different ages and the 90-day coarse aggregates of these samples were used as recycled coarse aggregate containing used Nano-silica in the third group. In addition, RCA-UNS cubic samples (third group) were prepared using natural aggregates with 30%, 40% and 50% RCA-NS according to Table 2.

The steps for mixing the materials were as follows: before adding water, all aggregates were loaded and mixed in the mixer up to 2 min. Then, the amount of water needed for water absorption of aggregates was added and mixed with a high-speed mixer for up to 2 min. In the case of the second group, nano-silica was first added with half of the remaining water and added to the mixture. The cement was then added to the mixture and mixed for 3 min. Finally, the superplasticizer was mixed with the other half of the mixing

water and added to the concrete within 2 min. Concrete mixing was stopped for one minute until the superplasticizer began to react. During this time, the mixer was covered so that the concrete water did not evaporate. The concrete was mixed at high speed for another 3 min until it reached the desired performance. This was followed by placing the concrete in standard cubic ( $10 \times 10 \times 10$  cm) molds. To avoid water evaporation, a plastic sheet was used on cubic molds. The molds were opened after one day. After demolding, all samples were cured in a water tank at  $20^\circ\text{C}$  according to ASTM C 511 [39]. For greater accuracy, 3 samples were made from each mold and the statistical average was calculated [39].

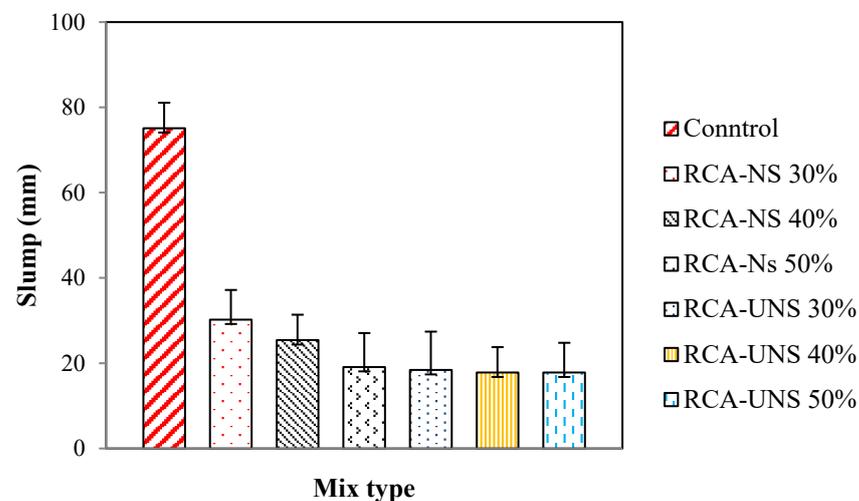
**Table 2.** Mix design of all samples.

Mix Design	w/c	Cement Kg/m <sup>3</sup>	Nano-Silica (%Wt of Cement)	RCA and RCA-NS Kg/m <sup>3</sup>	NCA Kg/m <sup>3</sup>	Natural Fine Aggregates Kg/m <sup>3</sup>
Control	0.45	400	0	0	1150	700
RCA-NS 30%	0.45	400	0.5	345	805	700
RCA-NS 40%	0.45	400	0.5	460	609	700
RCA-NS 50%	0.45	400	0.5	575	575	700
RCA-UNS 30%	0.45	400	0	345	805	700
RCA-UNS 40%	0.45	400	0	460	690	700
RCA-UNS 50%	0.45	400	0	575	575	700

### 3. Results and Discussion

#### 3.1. Slump of Fresh Concrete

The slump of fresh concrete test of recycled concrete is one of the most important tests due to the adsorption of mixing water by recycled aggregates and old cement. One of the disadvantages of recycled concrete is slump loss [40]. The results of fresh concrete slump based on ASTM C143 [41] are presented in Figure 4. The slump of the control concrete was 79 mm. However, the slump of RCA-NS samples decreased with 30%, 40% and 50% of RCA by 30, 25 and 19 mm, respectively, this phenomenon was also observed in previous research [1,20,26]. The slump of RCA-UNS samples with 30%, 40% and 50% RCA-NS were reduced to 18.5, 18 and 18 mm, respectively. This was because the used nano-silica absorbed excess amounts of mixing water and reduced workability. Moreover, mortar attached to aggregates from the first and second groups was the cause of the low reduction of slump in the third group.



**Figure 4.** Slump of fresh concrete for all samples.

### 3.2. Water Absorption of Concrete Samples

Water absorption of all concrete samples in this study was performed following the method described in ASTM C642-13 standard test [42]. In the samples of this test, broken parts of the internal (core) of the concrete were used to measure water absorption. Figure 5 shows the water absorption of concrete samples at 28 days. The results show that the sample of 30% RCA-NS had greater water absorption than the control mixture. This could be as a result of recycled coarse aggregates which increase bleeding, segregation, and air voids [43]. The water absorption percentage of the control sample was 3.8%, while this amount for the RCA-NS sample with 30%, 40% and 50% of RCA were 4.3, 4.4 and 4.7, respectively. This increase in water absorption with rising percentage of RCA has also been reported by Younes et al. [19]. Furthermore, the high-water absorption of RCA-NS samples can be attributed to the inherent nature of the pores of recycled coarse particles and adsorption by the old mortar in them. The water penetrated into the cement matrix due to the ability of aggregate to absorb water, the presence of fine pores and capillary phenomena. The water absorption percentages of RCA-UNS samples with 30%, 40% and 50% recycled coarse aggregates containing used nano-silica were 3.7%, 3.6% and 3.6%, respectively. As can be observed in Figure 5, contrary to expectations, the water absorption of RCA-UNS samples decreased compared to control and RCA-NS samples. This phenomenon might be due to hydration of old cements and the formation of additional C-S-H which could play a positive role in filling pores and cracks of the samples.

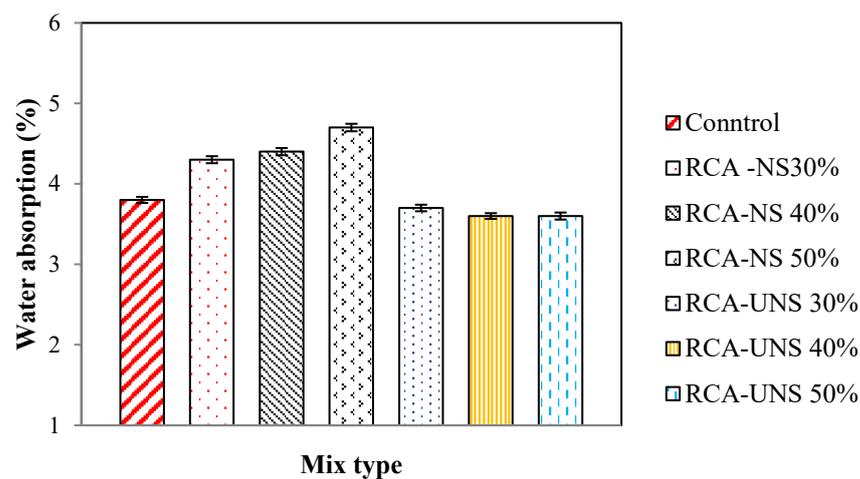


Figure 5. Water absorption of concrete samples at 28 days.

### 3.3. Compressive Strength of Samples

The compressive strength test using standard cubic specimens at 7, 28, and 90 days was in accordance with BS 1881 [44]. One way to make sustainable concrete is to increase its mechanical properties such as compressive strength. The results of the compressive strength tests for the ages mentioned are shown in Figure 6. By looking at the error bars, there are overlaps for different percentages of RCA. By considering a 95% confidence interval, it can be concluded that compressive strengths of all of the RCA samples are almost the same and a different percentage of RCA has no significant impact on the compressive strength regardless of being compared to the control sample. For all of the RCA samples, it is obvious that compressive strength has been dropped compared to the control sample. As illustrated in Figure 6, in the third group (RCA-UNS), there was a 5.7%, 4.6% and 4.4% increase in compressive strength at 7 days compared to the sample, respectively [45,46].

The compressive strength of the second group (RCA-NS) with the replacement of 30%, 40% and 50% of RCA aggregates were respectively 30.1, 29.3 and 28.7 MPa at 28 days of age, while the compressive strength of the control sample was 32 MPa. The decrease in compressive strength in the second group was due to the weak bond between recycled

coarse aggregates and also the characteristics of these aggregates such as old mortar, the presence of impurities, cracks, and porosity (which in previous research decreased to a greater extent [17,22,40]); however, nano-silica partially compensated for this weakness. Furthermore, as shown in Figure 6, compressive strength was recorded as 36.1, 35.5, and 35.2 MPa at 28 days by replacing with 30%, 40%, and 50% of RCA-NS aggregates, respectively. This increase in compressive strength in the third group may be due to the presence of sufficient water to complete the hydration of the third amount of cement paste. This amount can act as filler and improve the ITZ of concrete. In addition, the replacement of 30% of natural coarse aggregate of concrete with recycled coarse aggregate containing used nano-silica (RCA-UNS 30%) increased the compressive strength by 15.7% compared to the control samples at 90 days. This increase in compressive strength at older ages (90 days) is also observed in this bar chart. This increase in compressive strength is consistent with the water absorption test of the samples. Therefore, the addition of 30% recycled coarse aggregate containing used nano-silica increased the compressive strength by approximately 12%.

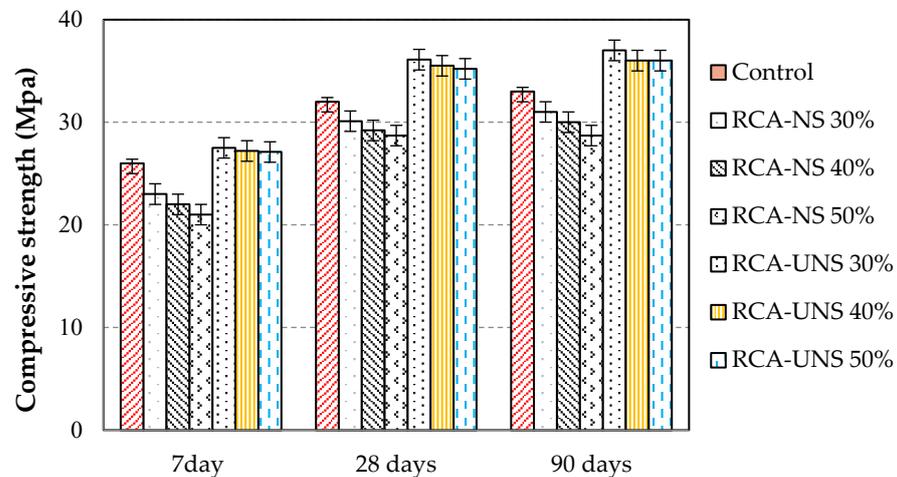


Figure 6. Compressive strength test of samples.

Figure 7 shows the failure modes of the samples. As can be observed in a, the desired failure of the control concrete sample occurred in such a way that with increasing pressure, the 4 sides evenly cracked and after failure, the remaining piece was stacked in two inverted pyramids or the two pyramids were separated. However, in the RCA-NS sample, fragmentation failure occurred only at the surfaces of the sample, which could be a plastic failure mode in the sample (Figure 7b). In the RCA-UNS example, the plastic failure mode is also shown in Figure 7c.

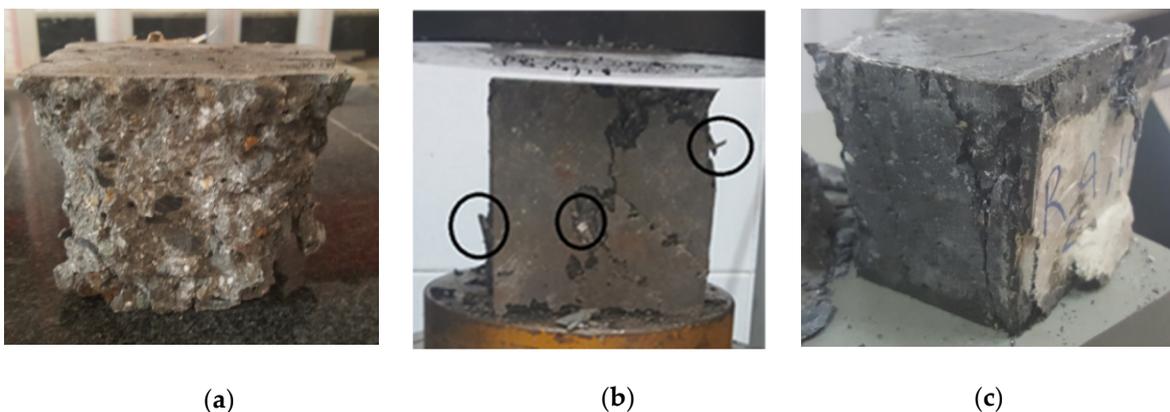


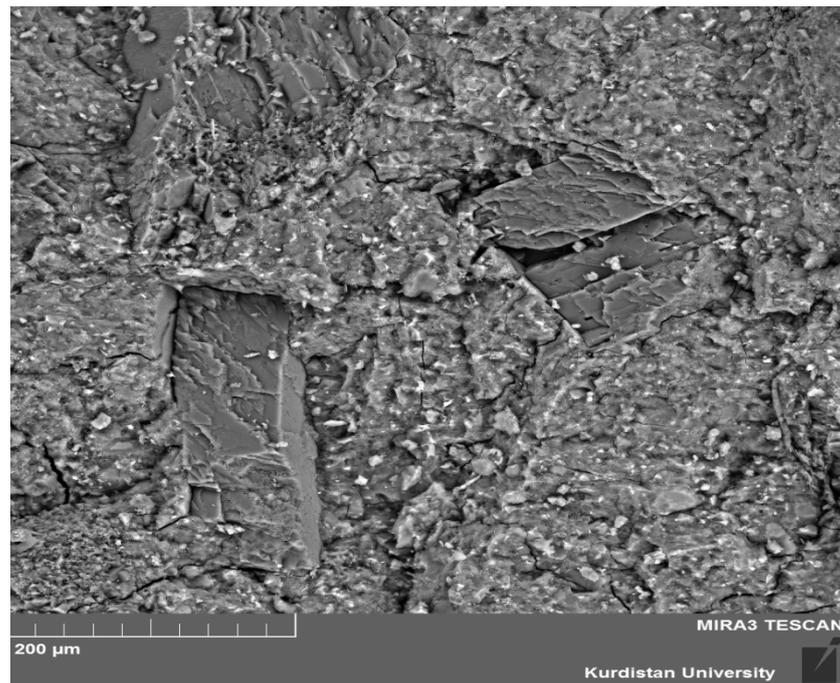
Figure 7. The failure modes of the (a) control, (b) RCA-NS, and (c) RCA-UNS samples.

### 3.4. Scanning Electron Microscopy (SEM) of Samples

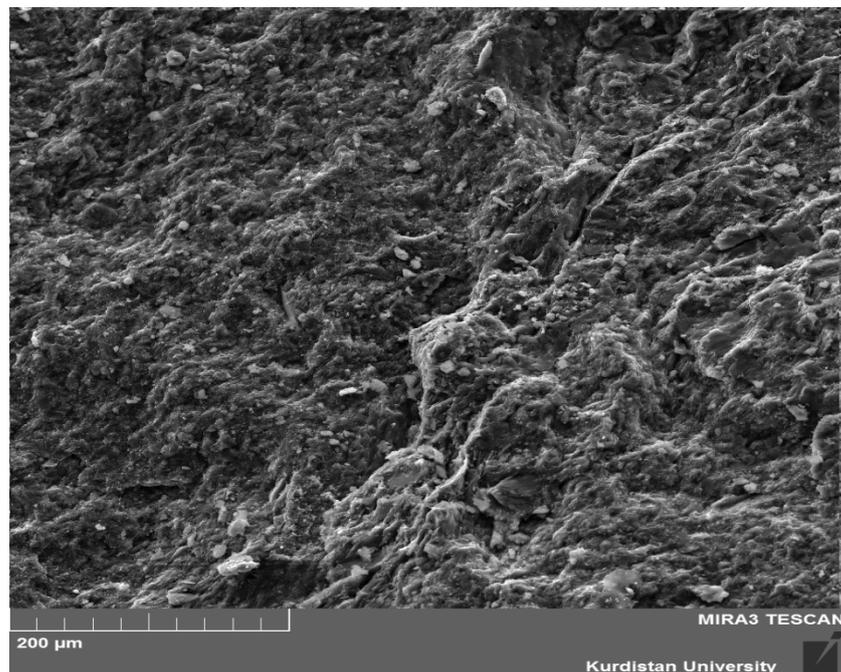
Images of small-sized structures with SEM (TSCAN test machine made in Czech Republic) at 28 days are shown in Figures 8–10. Figures 8–10 show the microscopic structure images of the control sample, the RCA-NS 30%, and the RCA-UNS 30% sample, respectively. Figure 8 illustrates the significant amount of porosity, micro cracks, C–H, C–S–H, and most of the unreacted material. The unreacted material was due to the excessive amount of cement and some remaining cementitious materials [38]. Figure 9 demonstrates that RCA aggregates increased porosity and small cracks, and prevented secondary C–S–H formation. The C–S–H is a compound which is the main product of Portland cement hydration and a major factor in the strength of cement and all cement-based products. Approximately 50% to 60% of the volume of fully hydrated cement paste solids is C–S–H [47]. Figure 10 shows more C–S–H formation than Figures 8 and 9. The SEM results confirm previous research findings on water absorption and compressive strength and show that in the RCA-UNS 30% sample, C–S–H was produced in comparison to the control and RCA-NS 30% samples. The SEM images illustrate that used Nano-silica or new cement reduced porosity and micro cracks in the RCA-UNS 30% sample. Therefore, the size of the pores and C–H crystals are reduced creating a microstructure that is extra compressed when coarse aggregate containing used nano-silica was used. Also, Figure 10 showed that RCA-UNS 30% samples have larger ITZ compared to the RCA-NS 30% in Figure 9.



Figure 8. SEM of control sample at 28 days.



**Figure 9.** SEM of RCA-NS 30% sample at 28 days.

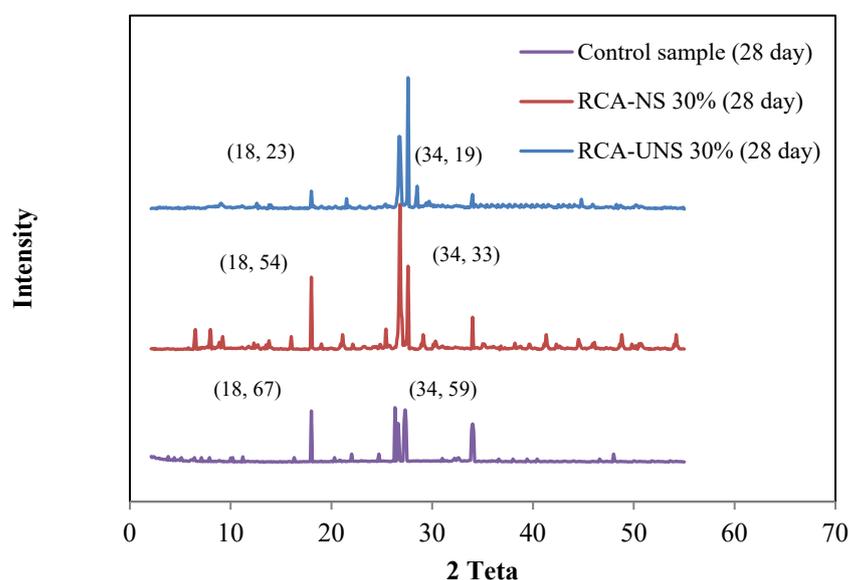


**Figure 10.** SEM of RCA-UNS 30% sample at 28 days.

### 3.5. X-ray Diffraction (XRD) Patterns of Samples

Figure 11 shows the XRD pattern (obtained from SAXess Co., Niederösterreich, Austria) for control samples, RCA-NS 30%, and RCA-UNS 30% at University of Kurdistan at 28 days. At  $18^\circ$  and  $34^\circ$  (2 Theta) from XRD patterns, intensity peaks of C–H crystal were traced [23,45]. To prepare the samples of this test, a powder form (300 microns) obtained from a combination of aggregate and mortar from broken parts of the compressive strength test was used. Intensity peaks of C–H crystal in the control sample were 67 and 59 at  $18^\circ$  and  $34^\circ$  (2Theta), respectively. In the RCA-NS 30%, intensity peaks of C–H crystal were 54

and 33 at 18° and 34° (2Theta), respectively. As shown in Figure 11, the intensity peaks of C–H crystal in the RCN-NS 30% samples were slightly reduced compared to the control sample due to low C–H crystal consumption and C–S–H formation. The reason may be that the specific gravity of recycled coarse aggregates (resulted from demolishing RCA-NS mixtures) is lower than that of natural coarse aggregates and the natural coarse aggregate was substituted based on weight and, considering the fact that the mixture design was not based on volumetric ratios, this would result in lowering the cement content by replacing natural coarse aggregate with RCA in the unit volume of concrete. Furthermore, it can be observed that the intensity peaks of C–H crystal in RCA-UNS 30% samples decreased by 65% and 67% at 18° and 34° (2Theta), respectively compared to the control sample. This decrease in intensity peaks of C–H crystal related to quartz (SiO<sub>2</sub>) was due to the production of secondary C–S–H, which has also been reported by other researchers [32,38,48]. Reaction and effect of coarse aggregate containing used nano-silica on C–H crystallization is more remarkable. Findings from the XRD test were consistent with the compressive strength, SEM test.

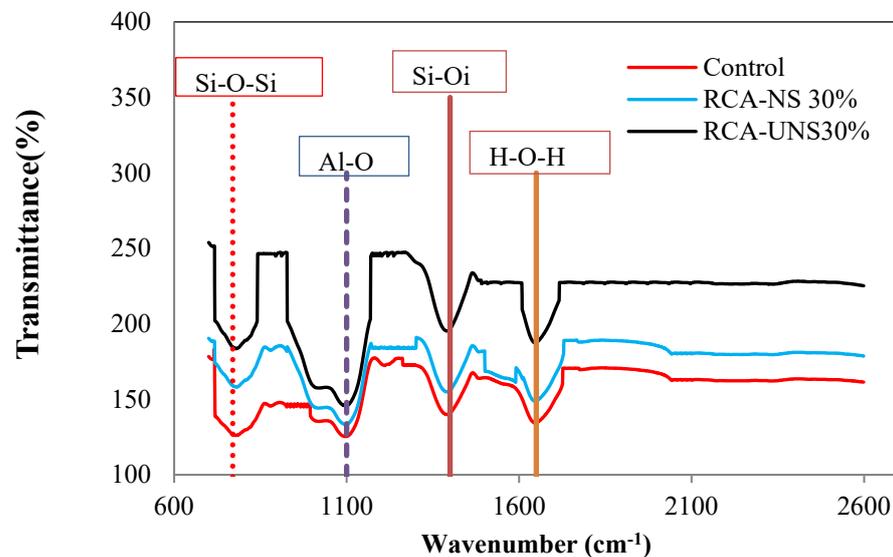


**Figure 11.** X-ray diffraction (XRD) of Control, RCA-NS 30%, and RCA-UNS 30% samples at 28 days.

### 3.6. Fourier Transform Infrared (FT-IR) Graphs of Samples

To discover the variations in the C–S–H chains related to Si–O–Si, Si–H, O–C–O and O–H bands, FT-IR graph tests were conducted. FT-IR test samples were in powder form. These powders were obtained by grinding the broken part of the compressive strength test, which includes cement and aggregates. After grinding, the powder was sieved with a 300 micron sieve. The FT-IR graphs (Bruker machine, made in the Netherlands, tested at University of Kurdistan) of the control, RCA-NS 30%, and RCA-UNS 30% samples at 28 days, between 600–2600  $\text{cm}^{-1}$ , are shown in Figure 12. The stretching vibration of O–H at 1600–1640  $\text{cm}^{-1}$  was due to the increased molecule of water in the samples [49]. The 30% of natural coarse aggregates replacement with recycled coarse aggregate (RCA-NS 30%) increased the O–H stretching vibrations which were further augmented if replacement with recycled coarse aggregate contained used nano-silica (RCA-UNS 30%). Another strong band was the stretching vibration of O–C–O at 1300–1400  $\text{cm}^{-1}$  which was due to atmospheric carbonation. The strongest band was Si–H at 1350–1450  $\text{cm}^{-1}$  due to depolymerization. The Si–H bands increased in RCA-UNS 30% samples likely [49,50]. The changes in Si–O–Si transmittance band at 750–800  $\text{cm}^{-1}$  indicate that a secondary C–S–H was formed, which has also been reported in other research [23,51]. The replacement of 30% natural coarse aggregates with recycled coarse aggregate containing used Nano-silica

(RCA-UNS 30%) increased the Si–O–Si transmittance bands. The results of FT-IR graphs of samples were in agreement with compressive strength, SEM, and XRD results.



**Figure 12.** Fourier transform infrared (FT-IR) spectra of the control, RCA-NS 30%, and RCA-UNS 30% samples at 28 days.

#### 4. Conclusions

In this study, for the first time, 30%, 40% and 50% of recycled coarse aggregates containing used Nano-silica (RCA-UNS) were reused in concrete. For this purpose, ordinary concrete samples were made and tested for the control group, also named the first group. In the second group (for comparison and use in third group samples), 30%, 40% and 50% of natural coarse aggregates were replaced by recycled coarse aggregates of the concrete obtained from the control samples. In the samples of the second group, nano-silica was added to the mixture at the rate of 0.5% by weight of cement (RCA-NS). Furthermore, in the samples of the third group, 30%, 40% and 50% of the natural coarse aggregates were replaced by recycled concrete from recycled coarse aggregates containing used nano-silica, obtained from the samples of the second group at 90 days. Water absorption, fresh concrete slump, compressive strength, SEM, FT-IR, and XRD tests of these three groups were compared.

- The findings demonstrate that the water absorption of RCA-UNS samples decreased compared to the control sample.
- Moreover, the findings of the compressive strength test illustrated that compressive strength in the third group increased 12.8%, 10.9%, and 10% by replacing 30%, 40%, and 50% of NAC with RCA-NS at 28 days compared to control samples.
- The SEM results confirm previous results such as water absorption and compressive strength and show that the RCA-UNS 30% sample produced extra C–S–H.
- In addition, the XRD and FT-IR graphs illustrate that in the RCA-UNS samples, more C–H crystal was consumed and converted to C–S–H.
- For the production of sustainable concrete, 30% of natural coarse aggregates can be replaced with recycled coarse aggregate containing used nano-silica. Therefore, the hydration of cement with water produces C–H crystals while reactions induced by coarse aggregate containing used nano-silica consume the C–H crystals.

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## References

1. Muduli, R.; Mukharjee, B.B. Performance assessment of concrete incorporating recycled coarse aggregates and metakaolin: A systematic approach. *Constr. Build. Mater.* **2020**, *233*, 117223. [[CrossRef](#)]
2. Li, Q.; Hu, J. Mechanical and Durability Properties of Cement-Stabilized Recycled Concrete Aggregate. *Sustainability* **2020**, *12*, 7380. [[CrossRef](#)]
3. Danraka, M.N.; Aziz, F.N.A.A.; Jaafar, M.S.; Nasir, N.M.; Abdurashid, S. Application of Wood Waste Ash in Concrete Making: Revisited. *Lect. Notes Civ. Eng.* **2019**, 69–78. [[CrossRef](#)]
4. Bostanci, S.C. Use of waste marble dust and recycled glass for sustainable concrete production. *J. Clean. Prod.* **2020**, *251*, 119785. [[CrossRef](#)]
5. Nguyen, T.T.H.; Mai, H.H.; Phan, D.H.; Nguyen, D.L. Responses of Concrete Using Steel Slag as Coarse Aggregate Replacement under Splitting and Flexure. *Sustainability* **2020**, *12*, 4913. [[CrossRef](#)]
6. Thomas, B.S.; Hasan, S.K.; Arel, S. Sustainable concrete containing palm oil fuel ash as a supplementary cementitious material—A review. *Renew. Sustain. Energy Rev.* **2017**, *80*, 550–561. [[CrossRef](#)]
7. Memon, S.A.; Khan, M.K. Ash blended cement composites: Eco-friendly and sustainable option for utilization of corncob ash. *J. Clean. Prod.* **2018**, *175*, 442–455. [[CrossRef](#)]
8. Collivignarelli, M.C.; Cillari, G.; Ricciardi, P.; Miino, M.C.; Torretta, V.; Rada, E.C.; Abbà, A. The Production of Sustainable Concrete with the Use of Alternative Aggregates: A Review. *Sustainability* **2020**, *12*, 7903. [[CrossRef](#)]
9. Golewski, G.L. Generalized Fracture Toughness and Compressive Strength of Sustainable Concrete Including Low Calcium Fly Ash. *Materials* **2017**, *10*, 1393. [[CrossRef](#)]
10. Zhang, M.H.; Islam, J. Use of nano-silica to reduce setting time and increase early strength of concretes with high volumes of fly ash or slag. *Constr. Build. Mater.* **2012**, *29*, 573–580. [[CrossRef](#)]
11. Tam, V.W.; Soomro, Y.; Evangelista, A.C.J. A review of recycled aggregate in concrete applications (2000–2017). *Constr. Build. Mater.* **2018**, *172*, 272–292. [[CrossRef](#)]
12. Majhi, R.; Nayak, A.N.; Mukharjee, B.B. Development of sustainable concrete using recycled coarse aggregate and ground granulated blast furnace slag. *Constr. Build. Mater.* **2018**, *159*, 417–430. [[CrossRef](#)]
13. Katare, V.D.; Madurwar, M.V. Design and investigation of sustainable pozzolanic material. *J. Clean. Prod.* **2020**, *24*, 14–25. [[CrossRef](#)]
14. Nicoara, A.I.; Stoica, A.E.; Vrabec, M.; Rogan, N.S.; Sturm, S.; Ow-Yang, C.; Gulgun, M.A.; Bundur, Z.B.; Ciuca, I.; Vasile, B.S. End-of-Life Materials Used as Supplementary Cementitious Materials in the Concrete Industry. *Materials* **2020**, *13*, 1954. [[CrossRef](#)] [[PubMed](#)]
15. Golewski, G.L. Green concrete composite incorporating fly ash with high strength and fracture toughness. *J. Clean. Prod.* **2018**, *172*, 218–226. [[CrossRef](#)]
16. Zhang, L.W.; Sojobi, A.O.; Kodur, V.K.R.; Liew, K.M. Effective utilization and recycling of mixed recycled aggregates for a green environment. *J. Clean. Prod.* **2019**, *236*, 117600. [[CrossRef](#)]
17. Mukharjee, B.B.; Barai, S.V. Influence of nano-silica on the properties of recycled aggregate concrete. *Constr. Build. Mater.* **2014**, *55*, 29–37. [[CrossRef](#)]
18. Omrane, M.; Kenai, S.; Kadri, E.; Ait-Mokhtar, A. Performance and durability of self compacting concrete using recycled concrete aggregates and natural pozzolan. *J. Clean. Prod.* **2017**, *165*, 415–430. [[CrossRef](#)]
19. Ling, T.C.; Poon, S.V. Use of recycled CRT funnel glass as fine aggregate in dry mix concrete paving blocks. *J. Cleaner Prod.* **2014**, *68*, 209–215. [[CrossRef](#)]

20. Wang, X.; Cheng, F.; Wang, Y.; Zhang, X.; Niu, H. Impact properties of recycled aggregate concrete with nanosilica modification. *Adv. Civ. Eng.* **2020**, 1–10. [[CrossRef](#)]
21. Prasada Rao, D.V.; Navaneethamma, V. Influence of nano-silica on strength properties of concrete containing rice husk ash. *Int. J. Adv. Res.* **2016**, 3, 39–43.
22. Younis, K.H.; Mustafa, S. Feasibility of Using Nanoparticles of SiO<sub>2</sub> to Improve the Performance of Recycled Aggregate Concrete. *Adv. Mater. Sci. Eng.* **2018**, 2018, 1–11. [[CrossRef](#)]
23. Farzadnia, N.; Noorvand, H.; Yasin, A.M.; Aziz, F.N.A. The effect of nano silica on short term drying shrinkage of POFA cement mortars. *Constr. Build. Mater.* **2015**, 95, 636–646. [[CrossRef](#)]
24. Zhao, S.; Zhang, Q. Effect of Silica Fume in Concrete on Mechanical Properties and Dynamic Behaviors under Impact Loading. *Materials* **2019**, 12, 3263. [[CrossRef](#)] [[PubMed](#)]
25. Sikora, P.; Horszczaruk, E.; Skoczylas, K.; Rucins, T. Thermal properties of cement mortars containing waste glass aggregate and nanosilica. *Procedia Eng.* **2017**, 196, 159–166. [[CrossRef](#)]
26. Hosseini, P.; Booshehrian, A.; Madari, A. Developing Concrete Recycling Strategies by Utilization of Nano-SiO<sub>2</sub> Particles. *Waste Biomass Valorization* **2011**, 2, 347–355. [[CrossRef](#)]
27. Li, W.; Long, C.; Tam, V.W.Y.; Poon, C.S.; Duan, H. Effects of nano-particles on failure process and microstructural properties of recycled aggregate concrete. *Constr. Build. Mater.* **2017**, 142, 42–50. [[CrossRef](#)]
28. Varghese, J.; Gopinath, A.; Bahurudeen, A.; Senthilkumar, R. Influence of nano-silica on characteristics of cement mortar and concrete. *Sustain. Constr. Build. Mater.* **2018**, 25, 839–851.
29. Roychand, R.; Silva, S.D.; Setunge, S.; Law, D. A quantitative study on the effect of nano SiO<sub>2</sub>, nano Al<sub>2</sub>O<sub>3</sub> and nano CaCO<sub>3</sub> on the physicochemical properties of very high volume fly ash cement composite. *Eur. J. Environ. Civ. Eng.* **2017**, 2, 1–16. [[CrossRef](#)]
30. Vishwakarma, V.; Ramachandran, D. Green Concrete mix using solid waste and nanoparticles as alternatives—A review. *Constr. Build. Mater.* **2018**, 162, 96–103. [[CrossRef](#)]
31. Kawashima, S.; Hou, P.; Wang, K.; Corr, D.J.; Shah, S.P. Activation of fly ash through nanomodification. *Adv. Green Bind. Syst.* **2013**, 294, 1–11.
32. Adak, D.; Sarkar, M.; Mandal, S. Structural performance of nano-silica modified fly-ash based geopolymer concrete. *Constr. Build. Mater.* **2017**, 135, 430–439. [[CrossRef](#)]
33. Mukharjee, B.B.; Barai, S.V. Characteristics of sustainable concrete incorporating recycled coarse aggregates and colloidal nano-silica. *Adv. Concr. Constr.* **2015**, 3, 187–202. [[CrossRef](#)]
34. Ying, J.; Zhou, B.; Xiao, J. Pore structure and chloride diffusivity of recycled aggregate concrete with nano-SiO<sub>2</sub> and nano-TiO<sub>2</sub>. *Constr. Build. Mater.* **2017**, 150, 49–55. [[CrossRef](#)]
35. ASTM C150A. Standard Specification for Portland Cement. In *Annual book of Standards*; ASTM International: West Conshohocken, PA, USA, 1999.
36. ASTM C128. *Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Fine Aggregate*; ASTM International: West Conshohocken, PA, USA, 2004.
37. ASTM C127. *Standard Test Method for Specific Gravity and Absorption of Coarse Aggregate*; ASTM International: West Conshohocken, PA, USA, 1993.
38. Ibrahim, M.; Johari, M.A.M.; Rahman, M.K.; Maslehuddin, M. Effect of alkaline activators and binder content on the properties of natural pozzolan-based alkali activated concrete. *Constr. Build. Mater.* **2017**, 147, 648–660. [[CrossRef](#)]
39. ASTM C511. *Standard Specification for Mixing Rooms, Moist Cabinets, Moist Rooms, and Water Storage Tanks Used in the Testing of Hydraulic Cements and Concretes*; ASTM International: Washington, DC, USA, 2013.
40. Mukharjee, B.B.; Barai, S.V. Influence of incorporation of nano-silica and recycled aggregates on compressive strength and microstructure of concrete. *Constr. Build. Mater.* **2014**, 71, 570–578. [[CrossRef](#)]
41. ASTM C143. *Slump of Hydraulic Cement Concrete*; ASTM International: West Conshohocken, PA, USA, 1998.
42. ASTM C642-13. *Standard Test Method for Density, Absorption, and Voids in Hardened Concrete*; ASTM International: West Conshohocken, PA, USA, 2013.
43. Poon, C.S.; Kou, S.C.; Lam, L. Influence of recycled aggregate on slump and bleeding of fresh concrete. *Mater. Struct.* **2007**, 40, 981–988. [[CrossRef](#)]
44. BS 1881. *Testing Concrete. Methods for Analysis of Hardened Concrete*; BSI: London, UK, 2014.
45. Farzadnia, N.; Ali, A.; Demirboga, R.; Anwar, M.P. Effect of halloysite nanoclay on mechanical properties, thermal behavior and microstructure of cement mortars. *Cem. Concr. Res.* **2013**, 48, 97–104. [[CrossRef](#)]
46. Huang, Y.; He, X.; Wang, Q.; Sun, Y. Mechanical properties of sea sand recycled aggregate concrete under axial compression. *Constr. Build. Mater.* **2018**, 175, 55–63. [[CrossRef](#)]
47. Tamanna, K.; Raman, S.N.; Jamil, M.; Hamid, R. Utilization of wood waste ash in construction technology: A review. *Constr. Build. Mater.* **2020**, 237, 117654. [[CrossRef](#)]
48. Aghabaglou, A.M.; Tuyan, M.; Ramyar, K. Mechanical and durability performance of concrete incorporating fine recycled concrete and glass aggregates. *Mater. Struct.* **2015**, 48, 2629–2640. [[CrossRef](#)]
49. Lei, B.; Li, W.; Tang, Z.; Tam, V.W.; Sun, Z. Durability of recycled aggregate concrete under coupling mechanical loading and freeze-thaw cycle in salt solution. *Constr. Build. Mater.* **2018**, 163, 840–849. [[CrossRef](#)]

- 
50. Rudić, O.; Ducman, V.; Malešev, M.; Radonjanin, V.; Draganić, S.; Šupić, S.; Radeka, M. Aggregates Obtained by Alkali Activation of Fly Ash: The Effect of Granulation, Pelletization Methods and Curing Regimes. *Materials* **2019**, *12*, 776. [[CrossRef](#)] [[PubMed](#)]
  51. Pan, X.; Shi, C.; Farzadnia, N.; Hu, X.; Zheng, J. Properties and microstructure of CO<sub>2</sub> surface treated cement mortars with subsequent lime-saturated water curing. *Cem. Concr. Compos.* **2019**, *99*, 89–99. [[CrossRef](#)]