PARTIAL REPLACEMENT OF SILICA NANOPARTICLES IN CEMENT PASTE FOR CO_2 REGENERATION CAPTURE APPLICATION

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ABSTRACT: A promising, supplementary material, highly reactive silica nanoparticles tend to react with calcium species (Ca^{2+}) in cement, which produces more hydrated phases. The high amount of calcium species and the potential of capturing carbon dioxide (CO_2) through carbonation implies the suitability of cement paste as a CO_2 sorbent material. However, limited studies could be found highlighting the effect of silica nanoparticle inclusion on the CO_2 capture property of hardened cement paste. Thus, this study investigates the effect of silica nanoparticle partial replacement on the CO_2 capture capacity and regeneration performance of hardened cement paste. XRD and SEM analysis proved the formation of more hydrated phases upon partially replacing silica nanoparticles in cement. Partial replacement of 3.00 % with silica nanoparticles significantly improved CO_2 regeneration capture at room temperature among the other cement paste samples. This study found that the presence of silica nanoparticles in cement paste triggered the formation of more hydrated phases, which served as active sites for CO_2 capture to occur and, thus, improved the CO_2 capture capacity and regeneration performance.

ABSTRAK: Sebagai salah satu bahan tambahan yang berpotensi, nanozarah silika sangat reaktif dan cenderung bertindak balas dengan spesies kalsium (Ca^{2+}) dalam simen di mana terhasilnya lebih banyak fasa terhidrat. Jumlah spesies kalsium yang tinggi dan berpotensi menangkap karbon dioksida (CO_2) melalui pengkarbonan menunjukkan kesesuaian pes simen digunakan sebagai bahan penyerap CO_2. Walau bagaimanapun, kajian adalah terhad terhadap kesan kemasukan nanozarah silika pada sifat tangkapan pes simen CO_2 yang dikeraskan. Oleh itu, kajian ini adalah berkenaan kesan penggantian separa nanopartikel silika ke atas kapasiti tangkapan CO_2 dan prestasi penjanaan semula pes simen yang dikeraskan. Analisis XRD dan SEM membuktikan pembentukan lebih banyak fasa terhidrat apabila penggantian separa nanopartikel silika pada simen. Penggantian separa nanopartikel silika 3% menunjukkan peningkatan ketara tangkapan penjanaan semula CO_2 pada suhu bilik di antara sampel pes simen lain. Kajian ini mendapati bahawa kehadiran nanozarah silika dalam pes simen mencetuskan pembentukan lebih banyak fasa terhidrat yang berfungsi sebagai tapak aktif bagi penangkapan CO_2 berlaku dan dengan ini, membawa kepada peningkatan kapasiti penangkapan CO_2 dan prestasi penjanaan semula.

KEYWORDS: *Silica nanoparticles, cement paste, hydrated phases and CO_2 regeneration capture.*

1. INTRODUCTION

Cement-based material could be one of the potential calcium-based materials for the CO_2 capture application since it contains a high amount of calcium species and possesses an ability to react with CO_2. A similar argument was made by Chai et al. [1]. This ability to react with carbon dioxide is known as carbonation [2-4]. CO_2 tends to react with the main hydration compounds in the cement-based materials matrix, calcium hydroxide ($Ca(OH)_2$) and calcium silicate hydrate (C-S-H), which leads to the formation of calcium carbonate ($CaCO_3$). Thus, carbonation proved that CO_2 capture was possible for cement-based materials. Since the CO_2 capture of cement-based materials would likely proceed even after demolition [1,3], the potential of cement-based materials to capture CO_2 could be an excellent advancement in CO_2 capture applications.

Production of more of these hydration products would likely improve the properties of cement-based materials, including the CO_2 capture property. Previously, it had been reported that the inclusion of silica nanoparticles had significantly improved the properties of the hardened cement-based materials due to the occurrence of an aggressive hydration reaction that led to the formation of more hydrated phases [5-11]. With the presence of water, the nano-sized silica tends to react with calcium species (Ca^{2+}) in cement and lead to the formation of C-S-H and secondary C-S-H. Thus, improvement in properties could be expected. However, limited studies could be found that highlight the effect of silica nanoparticle inclusion on the CO_2 capture property of the hardened cement paste. Thus, this study investigates the effect of silica nanoparticle partial replacement on the CO_2 capture capacity and regeneration performance of the hardened cement paste.

2. EXPERIMENTAL

2.1. Materials

Silica nanoparticle was produced from rice husk ash (RHA) using the precipitation method, according to a previous study [12]. The powder obtained contains high-purity (98.91%) amorphous silica nanoparticles, proven by XRF analysis. Fig. 1 shows the micrograph of silica particles in the synthesized powder that have a particle diameter of less than 50 nm. Meanwhile, the Ordinary Portland cement (OPC) used was brand YTL Cement and obtained from a local supplier.

2.2. Preparation of Cement Paste Samples

The percentage of silica nanoparticles was limited to a maximum of 3.00 % weight since the largest increment in compressive strength was achieved with partial replacement of 3.00 % silica nanoparticles, as stated in an earlier study by [13]. The water-to-cement (w/c) ratio was maintained at 0.4 to highlight the effect of partially replacing silica nanoparticles in cement paste. The samples were prepared based on Table 1. Initially, silica nanoparticles and OPC powders were mixed. Then, an appropriate amount of water was added to the mixture. Meanwhile, the procedure was to mix the OPC cement powder and water to prepare the reference sample. All the mixing procedures were conducted using a mortar mixer. Next, the paste was poured into the 50 mm x 50 mm x 50 mm cube-shaped mold. This steel mold was brushed with grease to ensure easy removal of cement cubes after they were hardened. After 24 hours, all the hardened cement/silica nanoparticle paste samples were unmoulded and proceeded to the curing process by submerging them entirely in water. At a standard curing duration of 28 days [14], each composition's hardened samples were taken out from the water, and the specified characterization proceeded.

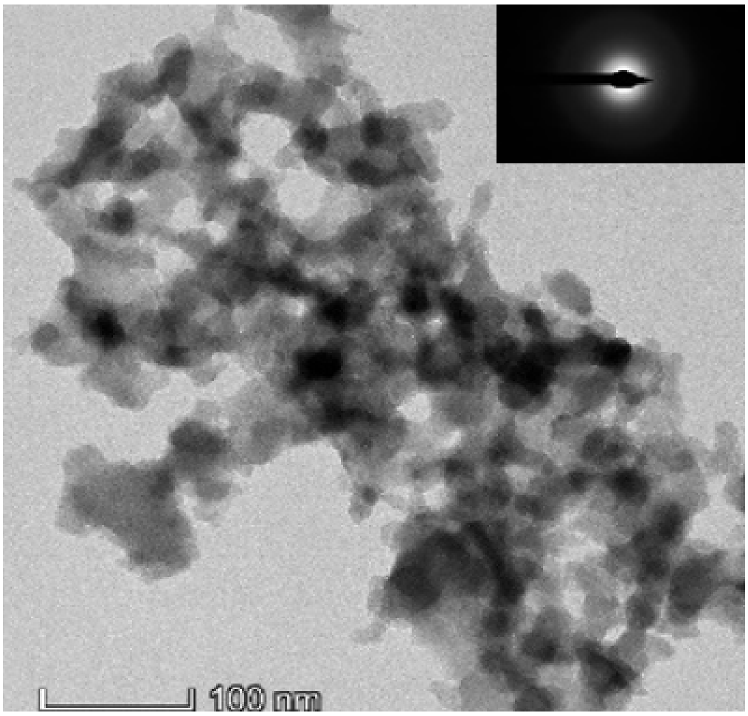

Figure 1. TEM micrograph of the synthesized silica nanoparticle powder [12].

Table 1. Composition of cement paste samples.

Sample	Cement (%)	Silica nanoparticle (%)
REF	100.00	0.00
NS0	99.25	0.75
NS1	98.50	1.50
NS2	97.75	2.25
NS3	97.00	3.00

2.2. Characterization

2.1.1. X-Ray Diffraction (XRD) Analysis

Diffraction (XRD) for phase structure analysis. This analysis uses the D2 Phaser machine by Bruker. The pattern was collected at 2θ range from 5° to 70°.

2.1.2. Scanning Electron Microscopy – Energy Dispersive X-Ray Spectroscopy (SEM-EDX) Analysis

The morphological characteristics observation and elemental mapping analysis were conducted through Scanning Electron Microscopy – Energy Dispersive X-Ray Spectroscopy (SEM-EDX) analysis using a JSM-IT100 machine by JEOL. The analysis was done by comparing the micrographs obtained with the ones from previous research [15,16]. The micrographs of the reference and cement paste samples with 3.00 % silica nanoparticle partial replacement were compared to highlight the hydration phase development. Before the analysis, the samples were oven-dried at 100°C overnight and coated with palladium using a mini sputter coater SC7620.

2.1.3. CO_2 Regeneration Capture Performance

This CO_2 regeneration capture experiment utilized the prepared cubic cement samples, a container with gas ports, and a pure CO_2 gas supply alongside a timer and weighing scale. Each cubic sample's initial weight was measured before being sealed in a container where CO_2 gas was introduced for 30 minutes. Afterward, the sample was removed, and its weight was measured again. This process was repeated for a total of 150 minutes (5 cycles), which was broken into 30 minutes per cycle with a 10-minute gap between cycles. The CO_2 capture capacity for each cycle was calculated as follows:

$$CO_2\ capture\ capacity_x = \frac{W_x(g) - W_i(g)}{W_i(g)} \times 1000 \tag{1}$$

According to Eq. (1), the CO_2 capture capacity was determined by subtracting the initial weight of the sample (W_i) from its weight after 30 minutes of exposure (W_x), with x representing the cycle number. The CO_2 capture capacity was then graphed against the percentage of nano-silica partial replacement to observe the material's performance over 150 minutes of CO_2 exposure at 28 days of curing, providing insights into the prepared sample's performance in capturing CO_2 at room temperature. The experimental setup is shown in Fig. 2.

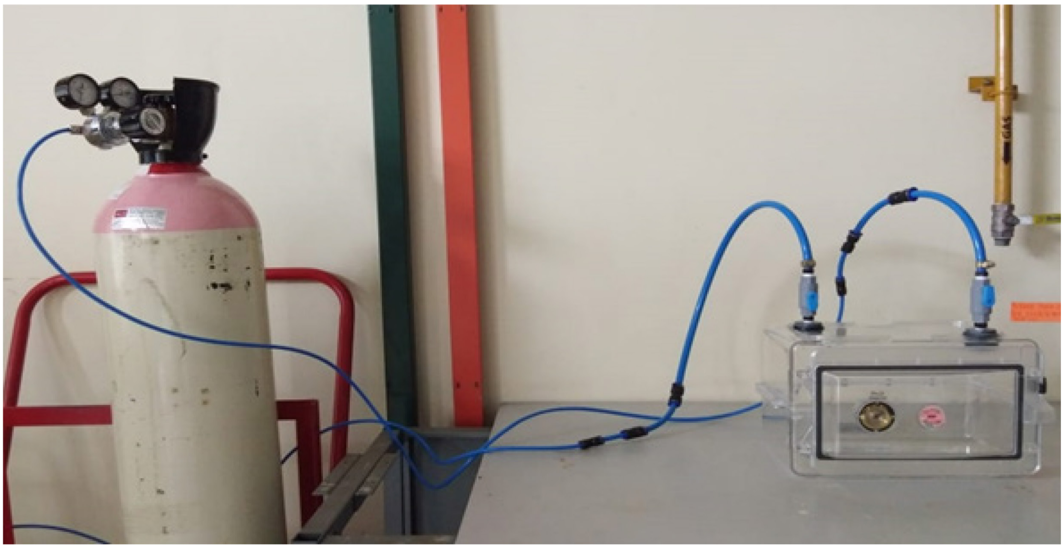

Figure 1. Customized experimental setup for CO_2 regeneration capture performance test.

3. RESULTS AND DISCUSSION

3.1. XRD Analysis: Development of Hydration Phases Upon Silica Nanoparticles Addition

Fig. 3 displays the XRD pattern of the samples containing different silica nanoparticle partial replacement percentages after 28 days of curing. For this analysis, the characteristic peaks of interest were $Ca(OH)_2$ and C-S-H phases. As can be observed, all samples exhibited a similar pattern, which consisted of similar characteristic peaks at 2θ similar locations, however, with different intensities. A similar trend was observed in previous studies [17-19], in which the peaks located at about 30.00° belonged to the C-S-H phase, while peaks at about 18.00° and 34.00° belonged to the $Ca(OH)_2$ phase. Previous research claimed that the peak intensity could reflect the content of the identified phase [19]. Thus, this finding could indicate the presence of similar phases in all samples, but in different proportions.

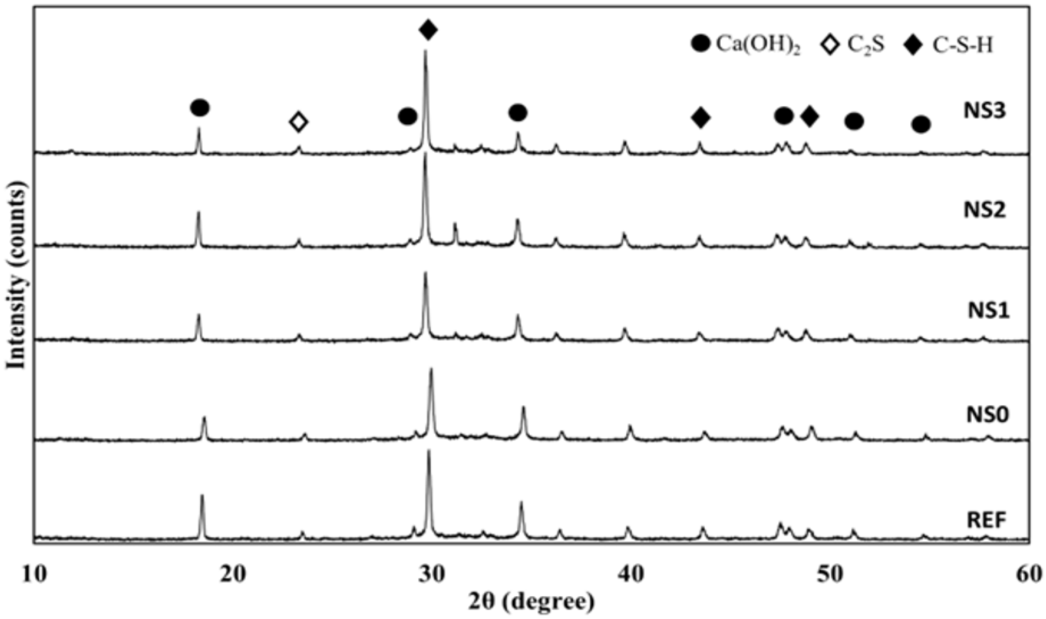

Figure 3. XRD patterns of the hardened cement paste samples at 28 days of curing.

Table 2 summarizes the peak intensity of the $Ca(OH)_2$ and C-S-H phases in samples at 28 days of curing upon different percentages of silica nanoparticle partial replacement. The result indicates that as the percentage of silica nanoparticles increases, there is a clear pattern of increasing and decreasing among these characteristic peaks. As can be observed, partial replacement of 3.00 % silica nanoparticle exhibited the highest increment in the intensity of the C-S-H peak, which was about 11%, and the highest decrement in intensity for both $Ca(OH)_2$ peaks as compared to the sample REF and other percentages of silica nanoparticle. According to this analysis, the presence of silica nanoparticles in cement paste may cause the $Ca(OH)_2$ phase to be consumed and an additional C-S-H phase to be produced.

Table 2. Intensities of the $Ca(OH)_2$ and C-S-H peaks in the XRD pattern.

Sample	**Silica nanoparticle (%)**	**Peak intensity (cps)**		
		~18°	**~29°**	**~34°**
REF	0.00	37.03	72.21	30.01
NS0	0.75	19.47	58.64	27.85
NS1	1.50	21.71	54.94	20.34
NS2	2.25	29.10	75.69	22.62
NS3	3.00	17.95	79.84	19.63

It has been reported that silica nanoparticles could promote hydration reactions in hardened cement paste materials [6,11,18,20,21]. This is a result of silica nanoparticles' tendency to react with calcium species (Ca^{2+}) in cement, which increases the production of an additional C-S-H phase, known as the secondary C-S-H phase. Hence, the availability of more C-S-H phases in the hardened cement paste structure could significantly improve the properties of the hardened cement paste samples.

3.2. Morphological Observation and Elemental Mapping Analysis

The development of these hydrated phases in the hardened cement paste samples was further investigated by SEM-EDX analysis. Fig. 4 shows the SEM micrographs of all samples at 28 days of curing at 1500X magnification. The micrographs displayed the formation of more fibrous and flocculated structure throughout the observed morphology upon increasing percentage of silica nanoparticles partial replacement. As compared with a previous study by [15], the micrographs of all samples displayed the common morphological traits of the hydration phases that were present in cement-based materials.

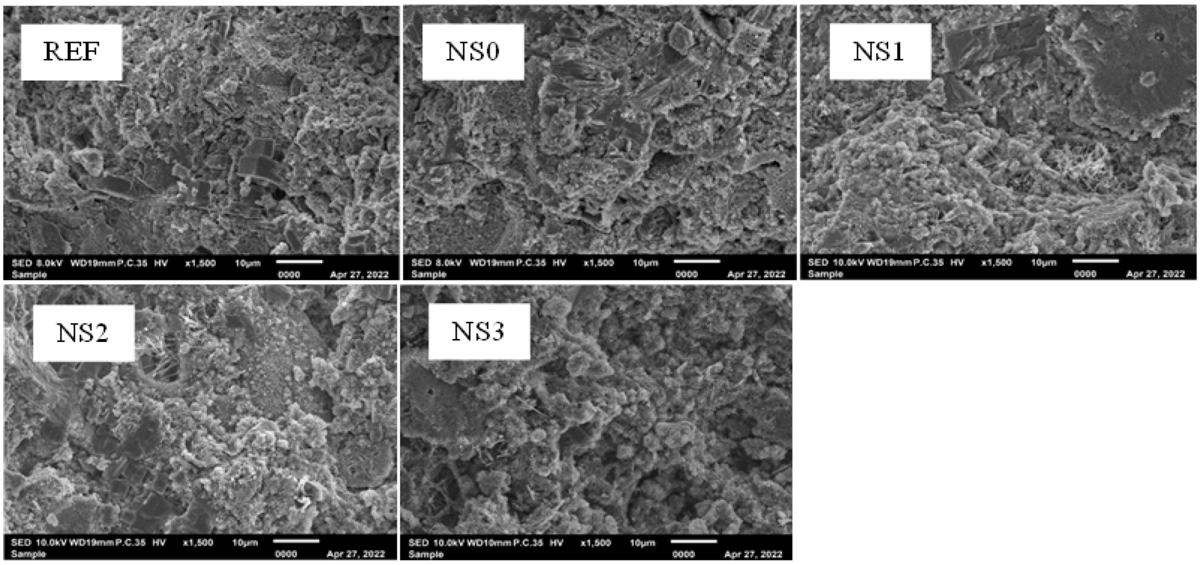

Figure 4. SEM micrographs of cement paste samples upon different percentages of silica nanoparticle partial replacement at 28 days of curing.

To better understand these morphological characteristics, the micrographs of the reference sample and cement paste sample with partial replacement of 3.00 % silica nanoparticle (sample NS3) were compared in Fig. 4 at 2500X magnification.

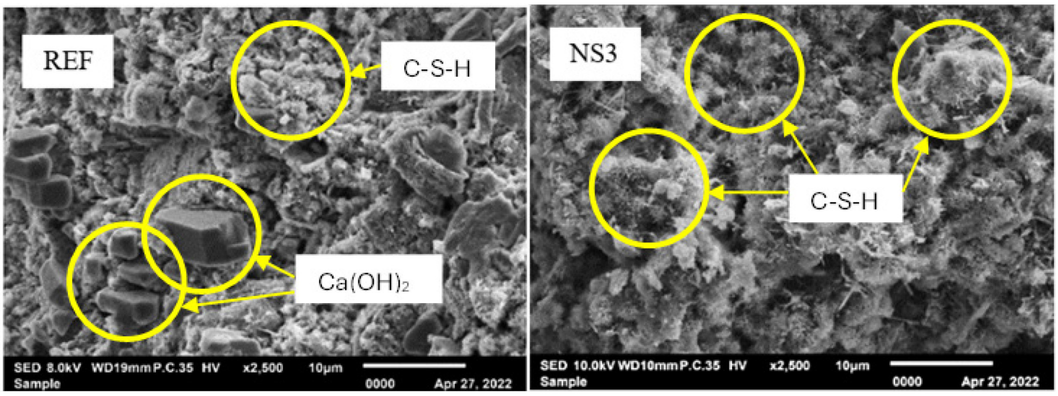

Figure 5. SEM micrographs of the sample REF and NS3 at 28 days of curing.

Previously, researchers have reported that the sheet-like structure indicates the presence of the $Ca(OH)_2$ phase; meanwhile, the C-S-H phase could be represented in different types of structures, such as fibrous and flock-like structures [15,16]. According to the micrographs obtained, sample NS3 has a morphology that is mostly covered with the C-S-H phase compared to sample REF. This observation suggests that more formation of the C-S-H phase could be expected upon increasing the percentage of silica nanoparticle partial replacement in cement.

Moreover, this finding is supported by Table 3 which summarizes the Ca/Si atomic ratio of the samples at 28 days of curing which was obtained from EDX analysis. Table 3 shows that the values of the Ca/Si ratio of the cement paste samples decreased upon the increasing percentage of silica nanoparticle partial replacement, in which the highest percentage of decrement of about 40 % was observed in sample NS3 compared to the sample REF. Previous researchers claimed that the decrement in Ca/Si ratio value indicates the presence of additional C-S-H phases in cement that led to the development of a densified and compact microstructure [10,17]. Thus, it could be concluded that more C-S-H phase was formed when a 3.00 % silica nanoparticle was partially replaced compared to the other samples, which agreed with the findings in XRD and SEM analyses.

Table 3. Ca/Si ratio of each cement paste sample.

Sample	Silica nanoparticle (%)	Ca/Si
REF	0.00	5.08
NS0	0.75	4.56
NS1	1.50	4.16
NS2	2.25	4.20
NS3	3.00	3.05

These phase analyses suggest that silica nanoparticles could modify the morphology of the cured cement paste by promoting a more intense hydration reaction. The properties could significantly improve as the additional hydration products formed in the hardened cement paste structure. Hence, better CO_2 regeneration capture of the hardened cement paste sample could be expected upon the partial replacement of silica nanoparticles.

3.3. CO_2 Regeneration Capture Performance

Fig. 6 shows the samples' CO_2 capture capacity and regeneration performance based on the percentage of silica nanoparticle partial replacement. Based on the result, the CO_2 capture capacity and the regeneration performance of the samples increased as the percentage of silica nanoparticle partial replacement increased throughout the 150 minutes of CO_2 exposure.

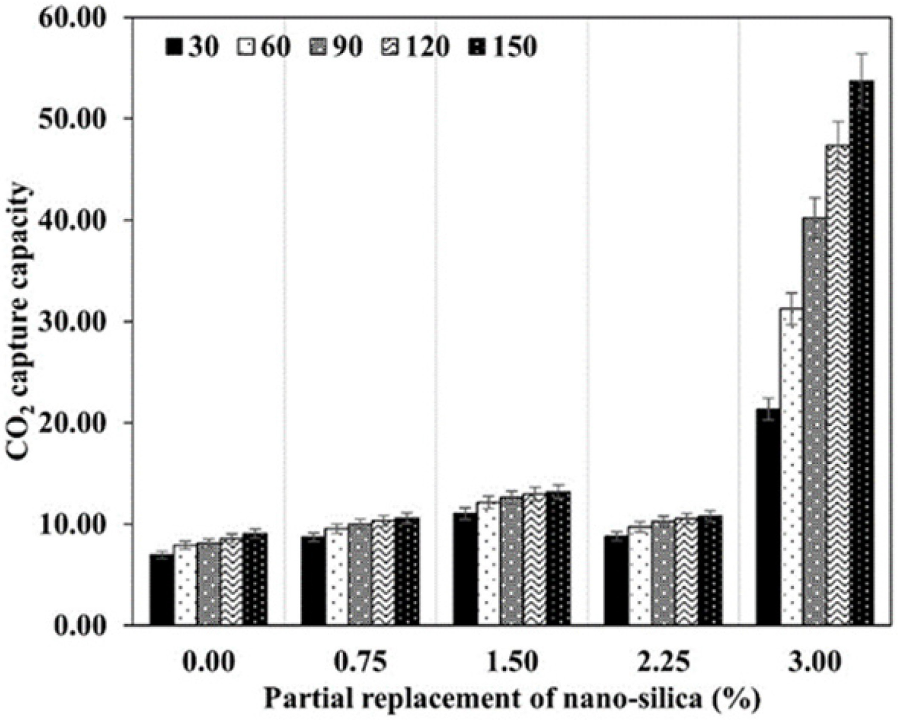

Figure 6. CO_2 regeneration captures the performance of all cement paste samples at 28 days of curing.

The partial replacement of 3.00 % silica nanoparticles yields a remarkable performance. For the initial CO_2 capture capacity (the first 30 minutes of CO_2 exposure), up to 208.25 % increment in CO_2 capture capacity was achieved upon the 3.00 % silica nanoparticle partial replacement (21.44 mg CO_2 captured/mg sample) compared to the reference sample (6.95 mg CO_2 captured/mg sample)

Based on the result, the CO_2 capture capacity and the regeneration performance of the samples increased as the percentage of silica nanoparticle partial replacement increased throughout the 150 minutes of CO_2 exposure. The partial replacement of 3.00 % silica nanoparticles yielded a remarkable performance. For the initial CO_2 capture capacity (the first 30 minutes of CO_2 exposure), up to 208.25 % increment in CO_2 capture capacity was achieved upon the 3.00 % silica nanoparticle partial replacement (21.44 mg CO_2 captured/mg sample) compared to the reference sample (6.95 mg CO_2 captured/mg sample).

During the 150 minutes of CO_2 exposure, cement samples with silica nanoparticles exhibited better CO_2 regeneration capture performance than the reference sample. The sample with 3.00 % silica nanoparticle partial replacement exhibited a total of 53.88 mg CO_2 captured/mg sample capture capacity, which indicates about a 493.76 % increment in CO_2 regeneration capture performance throughout the 5 cycles of CO_2 exposure compared to the sample REF, which only exhibited a total of 9.07 mg CO_2 captured/mg sample capture capacity. According to the result obtained, the CO_2 capture capacity could experience further increment if the experimental duration was prolonged, as the result still indicates an increasing pattern in the CO_2 capture capacity.

More C-S-H phases have formed upon the partial replacement of silica nanoparticles in cement. As explained in the carbonation reaction, these hydration products are responsible for the CO_2 capture property. So, the presence of more C-S-H phases allows more CO_2 to be captured. This led to a significant increment in the CO_2 capture capacity, and the development of cement paste with better regeneration capture performance could be expected. Similar findings were obtained from previous studies [2,22].

These findings indicate that the presence of silica nanoparticles in cement affects the CO_2 regeneration capture performance of the hardened cement paste samples. A significant improvement was achieved with a partial replacement of 3.00 % silica nanoparticles.

4. CONCLUSION

This research's findings indicate that silica nanoparticles altered the morphology of the hardened cement paste samples and affected its CO_2 capture property and regeneration performance. A significant improvement was exhibited by the hardened cement paste sample with partial replacement of 3.00 % silica nanoparticle, compared to the other samples. The inclusion of silica nanoparticles boosts cement hydration and increases C-S-H phase production. Production of more C-S-H phases had remarkably influenced the CO_2 regeneration capture ability of the hardened cement paste sample. Upon the presence of silica nanoparticles in cement, a higher capture capacity at each cycle of CO_2 exposure could be expected, which implies better regeneration performance.

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