



Article Fresh and Hardened Properties of Self-Compacting Concrete Comprising a Copper Slag

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Abstract: Recycling trash and protecting natural resources are two of the many benefits of using copper slag as a fine aggregate in a concrete building. However, stakeholders need proven research output to build trust and initiate or enhance the use of such industrial waste in buildings. This study evaluated self-compacting concrete's fresh and hardened characteristics (SCC) comprising a copper slag aggregate (CSA). For this purpose, six mixes were prepared by substituting river sand with CSA up to 50%, with a 10% increment. The properties of fresh SCC were evaluated using slump flow, V-funnel, and L-box tests. Several parameters of SCC were examined, including water absorption, sorptivity, chloride ion penetration, sulphate attack, and acid attack tests. Energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) were used to investigate the concrete microstructure. The results indicated that the fresh characteristics of SCC were enhanced as the amount of CSA increased consistently. The durability properties showed a considerable enhancement in SCC mixes comprising up to 20% of CSA.

Keywords: concrete; copper slag; compressive strength; acid attack; microstructure

1. Introduction

Massive volumes of industrial by-products are produced and disposed of worldwide, posing severe issues. Heavy metals, including arsenic, cadmium, and lead, can be found in high amounts in copper slag, causing them to be classified as hazardous wastes [1]. These metals harm human health and lead to air and water pollution. Due to a lack of landfill space and, as a result, rising costs of natural river sand, efforts have been undertaken to recycle or reuse them. One method is to utilize industrial derivatives in concrete, which will be advantageous in ecological and financial terms.

Concrete's durability may be characterized by its resistance to chemical, biological, and physical disintegration [2–5]. Chemical attack can take several forms, including sulphate resistance [6], acid resistance [7], the effect of carbonation [8], chloride ion penetration [9–11], the alkali-silica aggregate effect, and depending on the concrete exposed to the environment. The excessive loading of concrete buildings, the impact of abrasion, frost attack, and natural disasters, such as earthquakes, floods, and fires, can all cause physical disintegration [12]. Bacteria, sponges, lichens, marine borers, mosses, and boring shells are part of the biological onslaught [13,14]. Chemical attack, on the other hand, is predominantly accountable for the disintegration of concrete structures [15,16], and researchers must focus on durability [17–20]. Apart from durability, the manufacturing cost of concrete mainly depends on the constituent materials being used from natural recourses. To develop durability and minimize manufacturing costs, industrial by-products can be one of the alternate solutions [21–26]. Various industrial subsidiary products, including steel slag, copper slag,



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). fly ash, metakaolin, and silica fume, were used as fine aggregate or cement substitutes in SCC, lowering costs and increasing durability.

According to the literature, CSA has been successfully used as a fine aggregate alternative in SCC. It is a type of industrial waste produced in large quantities by the copper industry that might be used to replace river sand in concrete manufacturing. Depending on the cooling of melted slag outflow from the smelter, CSA is formed as a supplementary from copper metal, whether as closely packed copper slag or pulverized copper slag. When molten slag is poured into water, it solidifies as granulated CSA, whereas air-cooled slag solidifies into dense CSA. The main ingredients of a copper admixture charge are sulphides and oxides of iron and copper; minor compounds include SiO₂, Al₂O₃, CaO, and MgO [27]. When silica is added to the smelting process, it combines with the oxides to generate tightly bound silicate anions. The inclusion of lime and alumina helps to stabilise the slag structure. According to Sterlite Industries India Ltd., for every tonne (t) of copper metal production, about 1.8 to 2.2 t of slag are produced [28]. Over 33 tonnes of slag are produced worldwide, whereas three copper companies in India, Sterlite, Birla Copper, and Hindustan Copper, create roughly 6 to 6.5 t of slag at various locations [28]. This vast CSA is often discarded as waste, causing environmental degradation. The increasing concrete industry has been hampered by the paucity of natural resources, such as sand. As a result, the utilization of CSA as an alternative to natural river sand in concrete will be a feasible technological, environmental, and economical option. CSA has previously been utilized in the building industry as an alternative to cement or a partial or whole substitute for sand. Moreover, this CSA is extremely firm and non-leachable.

According to the published research, the strength and durability attributes of typically vibrated concrete improved with the inclusion of CSA as a binder or fine aggregate substitution, according to the published research [29–41]. Al-Jabri et al. [34] suggested using supplementary sand containing up to 40–50% of CSA in conventionally vibrated concrete. A matrix with 100% of CSA as a fine aggregate substitution was regarded as a suitable solution by Prem et al. [42]. Afshoon and Sharifi [43] investigated the strength and toughness of SCC mixes with CSA as a cement replacement from up to 30% with a five percent increase. The utilization of CSA up to 15% in place of cement produced better or equivalent results. Many studies on SCC with CSA as a substitute for natural sand have been published [44–47]; SCC's fresh characteristics were enhanced by using CSA (0–100%). The concrete strength of the slag was experiential to grow until it replaced 60 percent of the CSA. When CSA and a mingled concrete model were subjected to a sulphate solution, Hwang and Laiw [48] found no significant impact. When compared to the shrinkage values of concrete manufactured using sand, Ayano and Sakata [49] established that concrete made with CSA had inferior drying shrinkage values. SCC mixtures improved in fresh and hardened properties when the sand was fully replaced with CSA, and fly ash was replaced with 10 percent metakaolin [50]. However, there is limited information on the hardened properties (long-term) according to the literature review of SCC containing CSA. So, the study focused on the hardened properties of CSA-based SCC that are conducted in the long-term features, not just in terms of strength but also in terms of durability.

The evaluation of the permeation characteristics of SCC integrating CSA from 0–50% as an alternative for natural sand was also explored in this investigation. Initially, the fresh and concrete strength properties of SCC were analyzed. The permeation qualities, such as water absorption, sorptivity, rapid chloride penetration test (RCPT), sulphate attack, and acid attack, were explored. Additionally, SCC blends were also subjected to microstructural examination. Only a few types of research have been carried out in the durability studies using CSA in SCC. This investigation focused on all major durability studies without mineral admixtures and mono binder ingredients. Most of the research focused on the binary or ternary binder and the mineral admixtures' utilization.

2. Experimental Programme

2.1. Materials

To meet the standards of IS 12269 and ASTM C 150M-17 [51,52], ordinary Portland cement (OPC) of grade 53, which is equivalent to ASTM Type I cement, was used in this investigation. This experimental study used locally available natural river sand that met IS 383 and ASTM C 33M-16 [53,54]. According to IS 383, the sand is classified as zone III. Granulated CSA was employed as a natural sand substitute from 0% to 50% with a 10% increment: 0, 10, 20, 30, 40, and 50%. CSA was obtained from Sterlite Copper, SIP-COT Industrial Complex, Thoothukudi, Tamilnadu, India. According to IS 383, CSA is of substantial size and is located in Zone I. The sieve analysis of CSA, the fine and coarse aggregates, are depicted in Figure 1. The manual sieving technique is adopted to find the sieve analysis of CSA; fine and coarse aggregates are as per IS 2386 Part 1 1963 [55]. Tables 1 and 2 show the essential components of cement, CSA, and fine and coarse aggregates. Aside from that, Master Glenium SKY 8233, a superplasticizer based on polycarboxylic ethers, was added with 1% by weight of the binder to generate fresh SCC properties. It met the standards of IS 9103 [56] with a relative density of 1.08, chloride content of less than 0.2, and a pH of 6 at 25 °C.



Figure 1. Sieve analysis of fine aggregate, CSA, and coarse aggregate.

Table 1. Chemical composition of cement and CSA.

Component (%)	Cement	CSA
CaO	66.67	3.31
SiO ₂	18.91	33.62
Fe ₂ O ₃	4.94	55.6
Al_2O_3	4.51	3.65
SO_3	2.5	1.12
MgO	0.87	1.51
K ₂ O	0.43	0.82
Na ₂ O	0.12	0.37
Loss of ignition	1.05	_

Description	Size	Specific Gravity	Water Absorption (%)	Fineness Modulus	Unit Weight (kg/m ³)	Specific Surface Area (cm²/g)
Cement	90 µ	3.15	_	_	1382	2250
Fine Aggregate	<4.75 mm	2.68	0.42	2.88	1238	-
Coarse Aggregate	20 mm-4.75 mm	2.7	0.92	7.08	1784	-
CSA	<4.75 mm	3.6	0.37	2.63	1926	-

Table 2. Physical properties of constituent materials.

2.2. Mixtures

Six distinct concrete blends were made, each with various CSAs ranging from 0% to 50% with a 10% increase. SCC-CSA0 was used as the control mix, with CSA0 standing for the 0% copper slag aggregate. Other blends were labeled similarly, with the amount of CSA changing. For all mixes comprising a fixed quantity of OPC and 196 kg/m³ correspondingly at an invariable w/b ratio of 0.4, the total cementitious content of 488 kg/m³ was maintained. Table 3 shows the mix of proportions for all of the concrete mixtures. The equivalent volume approach was used to vary the amounts of CSA and sand. The whole mix's coarse aggregate and water content were set at 772 kg/m³ and 196 kg/m³, respectively. Masahiro Ouchi et al. suggested the mixing procedure followed in this investigation [57], of which the flowchart is shown in Figure 2.

Table 3. Mix proportions of SCC mixtures.

Mix ID	Cement (kg/m ³)	Fine Aggregate (kg/m ³)	CSA (kg/m ³)	Coarse Aggregate (kg/m ³)	Water (kg/m ³)	SP (kg/m ³)	W/B Ratio
SCC-CSA0	488	884	0	772	196	4.9	0.4
SCC-CSA10	488	796	88	772	196	4.9	0.4
SCC-CSA20	488	708	176	772	196	4.9	0.4
SCC-CSA30	488	619	265	772	196	4.9	0.4
SCC-CSA40	488	531	353	772	196	4.9	0.4
SCC-CSA50	488	442	442	772	196	4.9	0.4



Figure 2. Mixing procedure of SCC.

2.3. Testing Procedure

The design combination was finalized after a significant number of tests according to the EFNARC [58] standards. Before casting the specimens, slump flow, T_{50} slump flow

time, V-funnel, and L-box experiments were used to measure the flowability, viscosity, and passing ability of SCC. For each hardened properties test, three samples of each combination were prepared. For example, 15 cubes were cast for 7, 28, 56, 90, and 120 days, respectively, to perform the compressive test for the conventional mix. Concrete's compressive strength was evaluated on 150 mm cubes after 7, 28, 56, 90, and 120 days of curing, according to IS 516-1959 [59]. To examine the permeation characteristics, 50 mm long and 100 mm diameter cylinder sample sizes were used. Water absorption, sorptivity, RCPT, sulphate attack, and acid attack tests were carried out according to ASTM C642 [60], ASTM C1585 [61], ASTM C1202 [62], ASTM C1012-04 [63], and ASTM C1898 [64], respectively. SEM and EDS were used to investigate the microstructure of SCC. A small piece of broken samples was acquired from the interior core composition of the matrix after the concrete strength test was completed. After that, it was layered with a gold coat and analyzed by SEM-EDS.

3. Results and Discussions

3.1. Fresh Properties

The EFNARC [58] criteria were used to assess the freshness of the SCC mixes. The SCC mixtures' flow, filling, and passing ability improved when CSA was added in various quantities. The fresh states of SCC during laboratory testing are shown in Figure 3. Figures 4 and 5 show the fresh properties of all SCC mixtures. The slump flow for the SCC mixtures containing 0–50% of CSA ranged from 624 mm to 758 mm. CSA is a glassy and smooth texture; as a result, it increases the flowability of the SCC mixtures. The findings were consistent with the research [31,37,46,65,66] and additionally tried to compare the present results with previous findings. With the inclusion of CSA, the T₅₀ and V-funnel time consumed by the SCC mixes decreased. The lack of consistency [65] and the less water absorption nature of CSA resulted in a decrease in the T_{50} slump flow value. It took 5 s for the conventional SCC mix to drain the V-funnel, but only 3 s for the SCC containing 50% of CSA. This scenario might be due to the lower viscidity of the SCC mixtures containing CSA. Based on the flowability values and viscosity class (VF2) based on the V-funnel's duration, the SCC mixes were classified as SF1 (the conventional mix) and SF2 (the copper slag aggregate mix). The CSA particles improved the L-box values of the SCC mixtures significantly. The L-box values satisfy the passing ability of the SCC mixes. All of the SCC mixes had a passing ability value between 0.88 and 1.00 [58]. The substantial particles (the slag and aggregates) in the SCC mix descended to the bottom of the L-box as the CSA percentage rose. The SCC mixtures with more than 20% of CSA have also been observed to exhibit evidence of bleeding and segregation. CSA has a high unit weight, a smooth glass texture, and poor water absorption characteristics. On the other hand, all of the SCC blends were well inside the [58] range. The SCC mixtures containing CSA were unwavering at all degrees of substitution up to 50%.



Figure 3. Fresh condition of SCC; (a) slump flow, (b) V-funnel, and (c) L-box.



Mix ID

Figure 4. Slump flow and T₅₀ results of the SCC mixes.



Figure 5. V-funnel & L-box ratio values of the SCC mixes.

3.2. Hardened Properties

3.2.1. Compressive Strength

Figure 6 shows the laboratory's casting, curing, and testing of the SCC specimens. Figure 7 depicts the SCC compressive strength after 7, 28, 56, 90, and 120 days of curing. The SCC mixtures containing up to 20% of CSA showed a considerable improvement in compressive strength at all ages. At 28 days, the compressive strength of the conventional SCC was enhanced from 32.25 MPa to 39.45 MPa when mixed with 20% CSA. The SCC mix with a 20% CSA strength enhanced from 35.87 MPa to 44.84 MPa, 41.11 MPa to 52.07, and 42.48 MPa to 53.86 MPa after 56, 90, and 120 days. It is due to the irregular sharp edges of CSA, which helped the SCC matrix to adhere firmly [31]. From 7 to 28 days, the rate of growth in compressive strength was highest. The 50% CSA SCC mix had the lowest compressive strength, albeit it did not degrade further than that of conventional concrete at any curing age. This may be due to CSA's ability to absorb less water and its smooth glass structure, resulting in surplus water in concrete, so the influence of the W/C ratio over 20% of CSA with an 80% fine aggregate combination has to be studied in detail. According to Hwang and Laiw [48], the contribution of the pozzolanic reaction

improved the compressive strength of the SCC mixtures, including up to 80% CSA. Ayano and Sakata [66] stated that concrete prepared with CSA took longer to cure but did not impact the strength or durability of the SCC mixes. For 20%CSA SCC blends, Sharma and Khan [45] showed maximum compressive strength enhancement.



Figure 6. SCC specimens; (a) casting, (b) curing and, (c) compressive testing.



Figure 7. Compressive strength at different curing ages.

3.2.2. Water Absorption

When hardened concrete is subjected to harsh conditions, the water absorption experiment measures the absorption value in addition to the presence of voids. At all of the curing ages, water absorption of the SCC mixtures was observed to be quite below 6.8% (Figure 8). The SCC mixtures with up to 20% of CSA were shown to have a considerable decrease in absorption. At 28, 56, 90, and 120 days, the absorption rate for SCC-CSA20 was lowered by 15.18, 16.32, 17.08, and 18.86%, respectively, when compared to SCC-CSA0. The lowering of the pores was due to the improvement in aggregate particle packing [47]. The water absorption value increased considerably with more CSA in the concrete mix. It was ascribed to increased free water content in the SCC mixes with increased CSA percentages [31], which resulted in the development of additional voids. When CSA quantities in SCC exceeded 20%, the volume of the permeable voids started to increase, which is not preferable since the presence of more voids ingress harmful ingredients into it. Figure 9 shows the proportion of the permeable voids found in the SCC mixtures. At 28, 56, 90, and 120 days of curing, the quantity of the permeability voids (in percent) in SCC decreased as the CSA percentage increased up to 20%. At 28, 56, 90, and 120 days after curing, the porous voids (in percent) in an SCC mix having 100 percent sand were 14.13, 14.08, 13.93, and 13.86%. At 28, 56, 90, and 120 days, this decreased to 13.76, 13.63, 13.52, and 13.39 percent for the 20% CSA SCC mixtures, respectively. These findings may be linked to the compressive strength of SCC. The findings of [19] agreed with the conclusions of this study. Al-Jabri et al. [31] observed a 40% decrease in water absorption when CSA was utilized as a fine aggregate in regularly vibrated concrete mixtures. The value became equivalent with the inclusion of more CSA until it was replaced entirely in the concrete mix. Even with a 100% CSA substitution, Prem et al. [42] reported that there was improved water absorption by increasing the W/C ratios to 0.37, 0.47, and 0.57. The water absorption value decreases in concrete mixtures, adding up to 15% of CSA as a cement substitute [43]. However, the value increased when the replacement was greater than 15%. According to Rajasekar et al. [67], CSA replacement reduced water absorption by up to 60 percent in UHSC (ultra-high-strength concrete).





Figure 8. Water absorption of the SCC mixes.

Figure 9. Volume of permeable voids of the SCC mixes.

3.2.3. Sorptivity

The change in the absorption depth was estimated using the ASTM C 1585-13 [61] procedure. The schematic and laboratory test setup images are shown in Figure 10. The initial absorption was determined by monitoring the mass change throughout the first 6 h. Sorptivity is primarily responsible for the vulnerability of the unsaturated concrete to water penetration [61]. It is primarily determined by the concrete mix proportions, admixture type, supplemental cementitious ingredients, aggregate physical qualities, and placement technique [68]. Figure 11 depicts the sorptivity coefficients (mm/ \sqrt{sec}) trend pertaining to the SCC blends. In SCC, adding CSA up to 20% resulted in a significant reduction in sorptivity. At 28 days of curing, a sorptivity rate of 0.018 mm/ $\sqrt{\text{sec}}$ for conventional concrete was lowered to 0.014 mm/ $\sqrt{\text{sec}}$ for a 20% CSA SCC mix. At 28, 56, 90, and 120 days, the 20% CSA SCC mix had the lowest sorptivity value. The other durability characteristics followed a similar pattern. Up to 120 days after curing, the SCC mixes' sorptivity, having exceeded the 20% slag, was nearly identical to the control concrete. The contribution of OPC and CSA to improving the pore composition of the SCC blends may cause lower sorptivity values. Large permeable capillaries were transformed into smaller and less permeable capillaries due to this [69]. The results are consistent with those findings of water absorption in the SCC mixtures, resulting in a considerable enhancement in the compressive strength of up to 20% of CSA. The additive absorption of water in the SCC blends with CSA was up to 20% lower than in the concrete mixture without CSA. At 120 days of curing, Sharma and Khan [46] found a reduction in sorptivity resulting in up to a 60 percent CSA substitution. Rajasekar et al. [67] reported a 60 percent reduction in sorptivity for UHPC containing CSA, making the concrete impermeable. The compressive strength results were consistent with the durability data.





Figure 10. Sorptivity of the SCC mixes; (a) schematic test setup and (b) laboratory test setup.

Figure 11. Sorptivity of the SCC mixes.

3.2.4. Rapid Chloride Penetration Test

Figure 12 illustrates a sample image under an RCPT in the laboratory. At 28, 56, 90, and 120 days, the SCC mixtures containing up to 20% of CSA showed a significant reduction in chloride ion penetration. Under the impact of CSA, the penetration of the matrix was lowered due to the narrowing of the pores [70]. This was shown by water absorption tests, which showed that adding slag lowered the absorption by up to 20%. At 28 days of curing, all of the SCC mixes were classified as having an extremely low to low chloride ion penetration. The results of the chloride ion penetration after 56, 90, and 120 days of curing were substantially more important than the findings at 28 days. At 56, 90, and 120 days of the curing period, Figure 13 demonstrates that the chloride ion penetration of the SCC mixes was in the extremely low range. At 56 and 90 days of cure, the results varied from 620 to 900 and 580 to 700 coulombs. At 120 days, however, the chloride ion penetration values had decreased much more and were determined to be in the variety of 390 to 440 coulombs. The slag had a substantially greater impact on chloride ion penetration at subsequent curing stages. The long-term stability of concrete constructions might be accomplished because of the minimal penetration of chloride ions in concrete, and the study's findings agreed with [69,71–75]. When compared to 28 days of curing, the impact of CSA in concrete as a cement substitute was greater after 90 days [76]. The RCPT values after 90 days of curing were reported by Brindha and Nagan [71]. CSA mingled concrete's chloride ion penetration value was classified as extremely low. With two different W/C ratios (0.4 and 0.5). Thomas et al. [70] found that the chloride ion penetration value of concrete containing CSA decreased by up to 30%. However, with a 0.45 W/C ratio, the drop in penetration lasted until a 40% CSA replacement. Because of the improved pore structure, the chloride ion penetration was reduced with an increased CSA, up to 15% of the binder replacement [73]. Rajasekar et al. [67] found an extremely low chloride ion penetration in UHSC containing up to 60% CSA. The CSA, on the other hand, did not appear to have a significant impact on the chloride ion penetration values of concrete mixtures in several studies [43]. According to ASTM C1202 [62], the chloride ion penetration values of concrete mixes including CSA were classified as low and very low.



Figure 12. SCC samples under the chloride ion penetration test.



Figure 13. Chloride ion penetration of the SCC mixes.

3.2.5. Sulphate Attack

The experimental test photos are shown in Figure 14. The change in the mass percentage in the SCC mixtures exposed to a sulphate attack is illustrated in Figure 15. It was experiential that the mass variation had two phases. The mass of the concrete specimens rose after 28, 56, and 90 days of the sulphate attack. This was because the solution countered the cement hydration products, filling the pores and increasing the mass of the material. The mass continued to reduce as hydration products (C-S-H and calcium hydroxide) progressively suspended from the surface, and the specimens became very loose and sanded in the end phase of the sulphate attack (at 120 days).



Figure 14. Laboratory observation of the SCC exposed to sulphate; (**a**) samples in the immersed solution, (**b**) samples taken out from the sulphate solution, and (**c**) and (**d**) samples after the dried condition.



Figure 15. Change in the mass after exposure to the sulphate solution.

At 28, 56, 90, and 120 days of the sulphate curing period, the strength of the SCC-CSA0 was 31.40, 33.51, 33.60, and 28.63 MPa. At 28, 56, 90, and 120 days after the sulphate curing, the strength of SCC-CSA20 was 38.34, 40.64, 40.67, and 37.00 MPa, respectively. From 28 to 90 days, marginal improvements in the strength of the SCC mixes were recognized when they were immersed in a sulphate solution with curing periods. As the sulphate immersion duration enlarged from 28 to 90 days, the compressive strength increased by around 7.92%, 7.39%, 5.89%, 8.00%, 9.10%, and 9.80% in the SCC blends including 0%, 10%, 20%, 30%, 40%, and 50% CSA. Due to the interaction among the sulphate ions and calcium hydroxide available in the sulphate solution, a slight reduction in strength was noticed after 90 days of immersion in sulphate [76]. At 120 days, the SCC mixes incorporating 0 percent-50 percent CSA had a strength loss of around 9.45 percent to 18.45 percent compared to at 90 days. On the other hand, the SCC strength at 120 days was nearly equal to that of the sulphate-exposed SCC mixtures at 28 days (Figure 16). Figure 16 indicates that 20% of CSA has superior strength attributes to conventional and all other CSA substitutes, even though the mass reduction is not minimal. This was due to the improved particle packing and enhanced bonding between the CSA and the binder that was achieved when CSA was replaced by 20%, resulting in increased compressive strength. SCC can be generated utilizing CSA in certain ratios, depending on the strength needs from a construction perspective, especially in places exposed to harsh conditions involving sulphate attacks.

3.2.6. Acid Attack

The picture (Figure 17) depicts the experimental test photos of an acid attack. Figure 18 shows the findings of a mass change for the specimens subjected to 5% hydrochloric acid solutions. The mass change varied from 7.48 to 10.47%, 9.21 to 13.67%, 11.34 to 17.94%, and 15.86 to 21.68% after 28, 56, 90, and 120 days of exposure to the HCL solution. It can be shown that combinations containing 20% and 30% of copper slag had the least amount of mass fluctuation. However, compared to conventional concrete, all of the CSA compositions have a lesser mass change. This is due to the material's porous nature and the lack of additional fillers.



Sulphate Imerssion (days)

Figure 16. Compressive strength after exposure to the sulphate solution.



Figure 17. Laboratory observation of the SCC exposed to acid; (**a**) samples in immersed solution, (**b**) samples taken out from acid solution, and (**c**) and (**d**) samples after removal of the unstable particles.



Figure 18. Change in mass after exposure to the acid solution.

The strength of conventional concrete was 25.00, 21.71, 19.21, and 17.92 MPa after 28, 56, 90, and 120 days of acid curing. Correspondingly, the strength of 20% of CSA was 36.90, 35.05, 34.15, and 31.39 MPa at 28, 56, 90, and 120 days after the acid curing. Figure 19 indicates that increasing the period of the curing specimens in the hydrochloric acid solution reduces the rate of compressive strength development. The compressive strength decreased by 32.95%, 15.71%, 15.05%, 19.61%, 28.48%, and 31.00% in the SCC blends containing 0%, 10%, 20%, 30%, 40%, and 50% of CSA as the acid concentration-time rose from 28 to 120 days. This decrease in the concrete strength is due to the OPC's ability to absorb more hydrochloric acid being enhanced by a high calcium carbonate (CaCO₃) concentration [75,77]. The fineness of the cement boosts the acid's aggressiveness, allowing it to quickly leach the paste, especially on the bare surface of the specimen. The occurrence of CSA in the SCC mixture, on the other hand, is unaffected (Figure 17d), indicating its acid resistance.

Overall, this study used a total of six distinct proportions. Among all of the ingredients, fine aggregate and CSA are varied in proportion, while all others remain constant. One of the important parameters that might define the qualities of concrete is the water-to-cement ratio, which is one of the invariable ingredients. Based on the physical observations and test results, it was determined that a 20% CSA with 80% fine aggregate combination has an appropriate W/C ratio, resulting in the improved homogeneity of the concrete mix and improved hardened concrete results. The scope of the influence of the W/C ratio over the 20% CSA with 80% fine aggregate combination was subjected to separate research by the authors.



Figure 19. Compressive strength after exposure to the acid solution.

3.3. Microstructure

3.3.1. Scanning Electron Microscopy Observations

Figure 20 illustrates the concrete microstructure after 120 days for the SCC-CSA0 and SCC-CSA20 at $1000 \times$ magnification. The images provided in this research are of the SCC mixtures that have had their minor visible alterations examined. The microstructural formations significantly impact the concrete mixtures' strength and rheological properties. An SEM examination is used to investigate the morphology of the concrete matrix. A comparison was made to comprehend the differences in the microstructure of the SCC matrix after the normal and chemical curing. At 120 days, an SCC mix consisting entirely of sand (SCC-CSA0) revealed the arrangement of irregular calcium silicate hydrate (C-S-H) layers. Portlandite with C-S-H layers was produced from an SCC mix enclosing 20% of CSA and was observed, and due to the effect of a better grain density, the strength was increased. Uneven C-S-H formations with a small number of voids and micro-cracks were seen in the SCC mix (SCC-CSA0) subjected to sulphate at 120 days for the sulphate exposed SCC mixes. SCC-CSA20 possessed a solid structure with homogeneous C-S-H formations, minimal voids, and no indications of microcracks. The micrographs of the SCC specimens subjected to hydrochloric acid for 120 days show that the concrete surface deteriorated significantly. The SEM studies of SCC-CSA0 and SCC-CSA20 reveal a greater gypsum crystal precipitation and microcracks, confirming the cement paste's severe leaching on the concrete's surface. The chemical reaction between the cement paste hydrates and hydrochloric acid causes gypsum crystals to form.



Figure 20. SEM analysis of the SCC-CSA0 (left) and SCC-CSA20 (right) mixes at 120 days.

3.3.2. Energy Dispersive Spectroscopy Observations

Furthermore, the fundamental composition of the concrete mixes and their spectrums at 120 days of curing age were investigated using EDS. The main peaks of Ca, O, Si, and Al in the SCC-CSA0 and SCC-CSA20 mixtures are seen in the EDS analysis. S, Fe, C, K, Mg, and Na are the other elements found. Figure 21 shows an EDS analysis of the SCC mixtures. The CSA-SCC mix with 20% of CSA had the most silica. The appearance of large Ca and Si peaks in the respective spectra verifies the creation of a C-S-H gel. The presence of Ca and Si are essential ingredients for the occurrence of C-S-H's formation. According

to the results of the EDS, the principal peaks are Ca and Si; as a result, when the ratio of Ca/Si decreases, the strength characteristics of concrete increase. It could be because of the change of calcium hydrate into C-S-H films, which increases the overall porosity and refines the concrete matrix [28–30].



Figure 21. Cont.



Figure 21. EDS spectrum of the SCC-CSA0 and SCC-CSA20 mixes at 120 days.

4. Conclusions

This study showed CSA as a sustainable resource that may be utilized as a fine aggregate without mineral admixtures and with a mono binder ingredient in SCC manufacturing. Including CSA, the durability qualities of SCC are water absorption, sorptivity, chloride ion penetration, sulphate resistance, and an acid resistance increase of up to a 20% replacement. The detailed findings are as follows:

- With the increase of CSA, the fresh characteristics of SCC have improved. The compressive strength of the SCC blends, including up to 50% of slag, was superior to that of conventional concrete. The strength development was optimum when 20% of the CSA was replaced.
- The SCC mixtures with a 20% slag substitution had the lowest absorption value. The absorption rate for SCC with 20% of CSA was reduced by 15.18, 16.32, 17.08, and 18.86% at the ages of 28, 56, 90, and 120 days.
- A CSA incorporation lowered the sorptivity of the SCC mixtures for up to 120 days. At a 20% slag replacement, a maximum decrease of about 25, 21, 18, and 16% compared to conventional concrete was calculated at 28, 56, 90, and 120 days.
- At the later age of curing, the impact of CSA on the chloride ion penetration was significantly more pronounced. At 90 and 120 days, the SCC mixtures were classified as having very low permeability. According to the test results, CSA successfully enhanced the overall sulphate resistance compared to a conventional SCC mix.
- For the HCL solution immersed in the SCC mixes, the compressive strength is reduced compared to normally cured concrete. However, the slag in the SCC mixes is not damaged by the HCL solution due to its extremely stable and non-leachable nature.
- The microstructure reported the existence of calcium silicate hydrate layers under SEM examination, resulting in a denser and more homogenous concrete matrix. The ratio of peaks of Ca/Si lowers by 20% CSA, increasing the strength qualities of concrete, according to the EDS measurements. Based on the findings of the research, it is recommended that natural river sand can be replaced with CSA at a rate of 20%.

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