

Powder wastes from concrete recycling as a sustainable source of calcium carbonate mineral admixture

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ABSTRACT: Carbonation technology applied to cement-based materials from concrete recycling has been investigated as a promising approach to achieve carbon neutrality and to reintroduce these wastes into concrete's life cycle. In this research, carbon uptake potential of powder wastes from concrete recycling (PWCR) was evaluated. Samples were obtained from recycled concrete aggregate production – Recycled Concrete Aggregate Powder (RCAP), and from dewatered wash-out of returned fresh concrete – Concrete Slurry Waste (CSW). PWCR were used as mineral admixture replacing the sand, and it was observed that RCAP was naturally a fine powder with high CaCO_3 content, resulting in good mortar performance. In contrast, the coarse powder and with low CaCO_3 content CSW reduced mortar's performance. But with accelerated carbonation, carbonated CSW (CCSW) showed satisfactory performance when used in mortar. Therefore, there is high a potential to explore PWCR as a sustainable source of CaCO_3 to be reused as a mineral admixture.

1 INTRODUCTION

Concrete has been an essential material for the development of human society, and inevitably up to 10% of the ready-mix concrete returns to the industry (Xuan et al. 2018). Also, with the increasing deterioration of existing constructions, demolition and reconstruction sometimes is the most practical alternative, given the difficulties and costs of maintaining in use and safely recovering a deteriorated structure, and this generates large amounts of hardened concrete debris. Therefore, it is important to implement concrete recycling effectively to save the consumption of natural resources and to allow a circular and sustainable concrete industry economy (Lu et al. 2018, Ho et al. 2021).

Recycled concrete aggregates have already been reused, after being extracted from the demolished concrete, through a crushing process. A fine powder is produced as a final residue, which has been used as backfill and soil stabilization material, but it has not been incorporated into the life cycle of concrete. Also, from the returned fresh concrete, the aggregates can be separated from the fresh cement paste, through a washing process, and reused. But the solid agglomerated powder that remains, after decanting and filtering the slurry, usually is discarded.

These powder wastes from concrete recycling (PWCR) are composed of cement and aggregates particles, so usually they are not contaminated with other substances and are a high content calcium material. As cement-based materials can spontaneously uptake CO_2 from the air through the carbonation phenomenon, accelerated carbonation of PWCR may produce a material similar to ground limestone powder (calcium carbonate) to be reincorporated into the life cycle of concrete. That is the reason why combining carbonation and concrete recycling can be considered as a Carbon Capture, Utilization and Storage (CCUS) technology, and it has been investigated as one of the most feasible and valuable approaches to neutralize CO_2 emissions in the cement and concrete industry (WBCSD & IEA 2009). In this research, the viability of using PWCR as a source to obtain calcium carbonate mineral admixture was evaluated. Also, accelerated carbonation technology applied to PWCR was investigated as a technique to standardize these materials,

through analyses of the powder's chemical composition and the mechanical performance of mortars produced with non-carbonated and carbonated PWCR.

2 MATERIALS AND METHODS

2.1 Powder Wastes from Concrete Recycling (PWCR)

Two types of PWCR were evaluated: the by-product of recycled concrete aggregate production (Recycled Concrete Aggregate Powder – RCAP) and the dewatered slurry from returned fresh concrete (Concrete Slurry Waste – CSW). Material characterization was done by X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The XRD patterns were obtained using a Bruker AXS D2 PHASER equipped with the LYNXEYE detector. The measurement range was 5° to 60° 2θ with a step-size of approximately 0.025° per second. TGA (Netzsch) was conducted on approximately 50 mg of manually ground samples in open vessel heated continuously in temperature range from 25°C to 1000°C , at a heating rate of $20^{\circ}\text{C}/\text{min}$, in a nitrogen atmosphere, with a flow rate of 150 ml/min.

2.2 Accelerated carbonation methods applied to the PWCR

For solid-air carbonation, the water content of the samples, water-solid ratio (w/s), was varied in mass by adding distilled water. The samples were placed at an accelerated carbonation chamber of 5% CO_2 concentration, 60% of relative humidity (RH), 20°C temperature for 7 days.

For aqueous carbonation, solutions containing samples at a concentration of 25g/l were prepared with potable water containing CO_2 dissolved in it, using a commercial carbonated water maker (Aqueous A) and with distilled water and a gas flow CO_2 concentration of 100% (Aqueous B) and of 5% (Aqueous C), blown into the liquid using a gas washing bottle (scrubbing bottle) with glass filter. In all methods, the solution was stirred at atmospheric pressure using a magnetic stirrer. After the solutions' pH dropped from 12.5 to approximately 8.3, indicating the change in the alkalinity, each mixture was filtered using a paper filter, which retains $7\mu\text{m}$ size particles, and the solid material was dried at 40°C to remove the free water.

2.3 Mortar tests using PWCR

For mortar mix design, Ordinary Portland Cement (OPC) and OPC with 50% ground granulated blast furnace slag (GGBFS) replacement were used as binder. The water/cement ratio (W/C) was set at 0.55 and the sand/cement ratio (S/C) at 3:1. The PWCR types used were RCAP, CSW and the CSW carbonated using solid-air method with w/s >0.50 , identified as carbonated-CSW (CCSW). More powder information is presented in section 4. They were added as a sand replacement at 15% content. Also, pure limestone powder (LSP), with specific surface of $6,800\text{ cm}^2/\text{g}$ and average particle diameter of $3.26\mu\text{m}$ and D90 of $20\mu\text{m}$, was used as powder addition (Table 1).

Table 1. Mortar mix design.

Identification	Cement type	Powder addition	Slump flow
1 N	OPC	None	Control
2 B	OPC+GGBFS (50%)	None	Control
3 N-LSP	OPC	Limestone powder (LSP)	+ 39%
4 B-LSP	OPC+GGBFS (50%)	Limestone powder (LSP)	+ 38%
5 N-RCAP	OPC	Recycled concrete aggregate powder (RCAP)	+ 63%
6 B-RCAP	OPC+GGBFS (50%)	Recycled concrete aggregate powder (RCAP)	+ 63%
7 N-CSW	OPC	Concrete slurry waste (CSW)	+ 17%
8 B-CSW	OPC+GGBFS (50%)	Concrete slurry waste (CSW)	+ 9%
9 N-CCSW	OPC	Carbonated concrete slurry waste (CCSW)	+ 15%
10 B-CCSW	OPC+GGBFS (50%)	Carbonated concrete slurry waste (CCSW)	+ 25%

* Slump flow was controlled using polycarboxylic acid ether based high-range water reducer admixture.

2.3.1 Compressive strength test

The test was performed with cylindrical mortar specimens 50 mm diameter and 100 mm height cured in water.

2.3.2 Archimedes porosity test

Specimens were saturated with water in a vacuum chamber and the saturated and submerged masses were measured. After being kept in a chamber at 40°C and 40% RH until mass stabilization, the dry mass was obtained to calculate the porosity using the Archimedes principle.

2.3.3 Evaporation test

After finishing the 28 days curing period, mass variation due to the water evaporation was recorded continuously for mortar specimens 40x40x160 mm. Evaporation condition was 20°C temperature and RH of 60%.

2.3.4 Accelerated carbonation test

After 28 days of water curing, 40x40x160 mm specimens were dried at a 20°C and 60% RH environment for more 28 days and the 2 faces sealed specimens were carbonated in an accelerated carbonation chamber (20°C, 60% RH, CO₂ concentration of 5%). The carbonation depths were measured (in mm) using a phenolphthalein solution sprayed on a freshly split mortar surface. Average values were plotted as function of the square root of the exposure time *t* (in days) to determine the accelerated carbonation coefficient *K* (in mm/ $\sqrt{\text{days}}$).

3 RESULTS AND DISCUSSION

3.1 Material characterization

Figure 1 shows the XRD results of RCAP and CSW before and after being carbonated using solid-air and aqueous carbonation methods. For RCAP, there was a high peak of CaCO₃ and SiO₂, for both non-carbonated and carbonated samples, suggesting that previous natural carbonation occurred during concrete lifecycle and/or during the recycled concrete aggregate production. For CSW before carbonation, it was possible to find a high peak for Ca(OH)₂, but after the solid-air carbonation with w/s 0.50 and aqueous carbonation, the peak changed to CaCO₃. Especially for aqueous methods, the intensity peak for calcite was stronger, making clear the effectiveness of this method for CSW.

From TG-DTA, Ca(OH)₂ and CaCO₃ contents in the samples were quantified (Figure 2). RCAP showed no content of Ca(OH)₂, and high content of CaCO₃ even before carbonation (28%). And after 7 days of solid-air carbonation, changing w/s ratio from 0 to 1.00, or aqueous carbonation, in all samples there was a maximum increase of 4.6% in CaCO₃ content. Differently, for CSW as w/s ratio increased, solid-air carbonation progressed more than in lower water content samples and it was possible to verify complete change of Ca(OH)₂ to CaCO₃, specially for high water content samples.

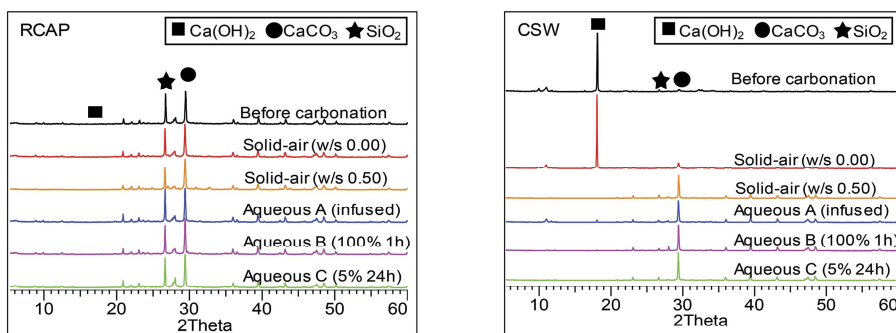


Figure 1. XRD pattern of RCAP and CSW carbonated using different methods.

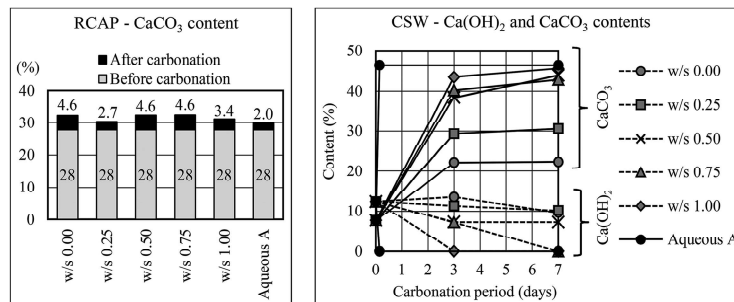


Figure 2. Ca(OH)₂ and CaCO₃ contents of RCAP and CSW carbonated using different methods.

3.2 CO₂ uptake determination

CO₂ uptake was determined as the amount of CO₂ absorbed by the powder during the accelerated carbonation and fixed in the solid phase as CaCO₃. This was calculated from the mass loss due to CaCO₃ decomposition of the carbonated and non-carbonated samples after TGA (Xuan et al. 2016, Kaliyavaradhan et al. 2020). As shown in Table 2, CO₂ uptake of CSW for the solid-air method increased as the w/s ratio increased. The maximum value was obtained for the aqueous method and was 22.14%, which means that 1 kilogram of the CSW analyzed can absorb approximately 221.4g of CO₂ in optimum conditions. For RCAP, CO₂ uptake varied between 1% to 2% and there was no correlation with the amount of water in the sample. Ho et al. (2021) reported that smaller particles size, less aggregate contamination, and thus a higher content of effective Ca ions, favored carbonation reaction under atmospheric pressure and low CO₂ concentration. Oppositely, the presence of fines from crushed aggregates, which are usually composed of silicate and limestone, decrease the percentage of effective Ca ions slightly and are essentially inert in relation to the carbonation process, reducing the CO₂ uptake. This explains RCAP low CO₂ uptake and CSW high CO₂ uptake, especially for samples with water availability.

Table 2. CO₂ uptake of PWCR samples carbonated using different methods.

Carbonation method		RCAP	CSW
Solid-air	w/s 0.00	1.47	7.23
	w/s 0.25	1.02	12.54
	w/s 0.50	1.49	20.27
	w/s 0.75	2.01	20.96
	w/s 1.00	1.09	21.74
Aqueous	A	1.36	22.14

3.3 Mortar performance

3.3.1 Compressive strength test results

The axial compressive strength test results are presented in Figure 3. It was estimated that the highest resistances were obtained for LSP mixes (with pure limestone powder), but the use of LSP resulted in only early age resistance gain compared to the control mixes N and B and did not affect the final mechanical resistance. About the PWCR addition, mortars with RCAP resulted in high axial compressive strength values. The use of CSW resulted in significantly different strengths for non-carbonated (CSW) and carbonated (CCSW) powder. Carbonation of the CSW improved the mechanical performance of the mortars with this mineral admixture. It was expected to have a slightly increase in early age with the use of non-carbonated CSW, attributed to the high content of hydration products and the seeding effect of C-S-H, which it is said to provide nucleation sites for the growth of hydration products, accelerating the early hydration period and increasing the early strength, but the current results showed a different pattern than observed in the literature (Lu et al. 2018).

3.3.2 Accelerated carbonation test results

The relationships between porosity and carbonation coefficient K and evaporation ratio and the coefficient K are shown in Figure 4 for OPC mortars and OPC+GGBFS mortars.

For OPC mortars, a good correlation could be established between porosity and coefficient K , but for OPC+GGBFS mortars, the differences in carbonation resistance for the mixes could not be explained only by the mortar's porosity. This is an indication that porosity of mortars with GGBFS replacement may have a complex porosity network, which cannot be evaluated considering only the total porosity amount. But when the evaporation ratio was correlated with the coefficient K , a good correlation could be found, both for OPC and OPC+GGBFS binders. For both binders, reduced water evaporation ratio resulted in improvement of the carbonation resistance. This shows that the water available inside the pores is a crucial factor that affects the progress of carbonation. About the effect of powders addition, RCAP addition improved carbonation resistance both for OPC and OPC+GGBFS mortars. On the other hand, the worst performance was obtained for CSW addition.

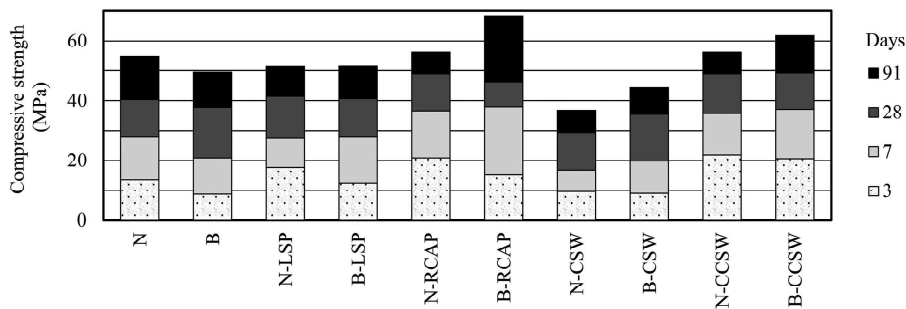


Figure 3. Mortar's compressive strength.

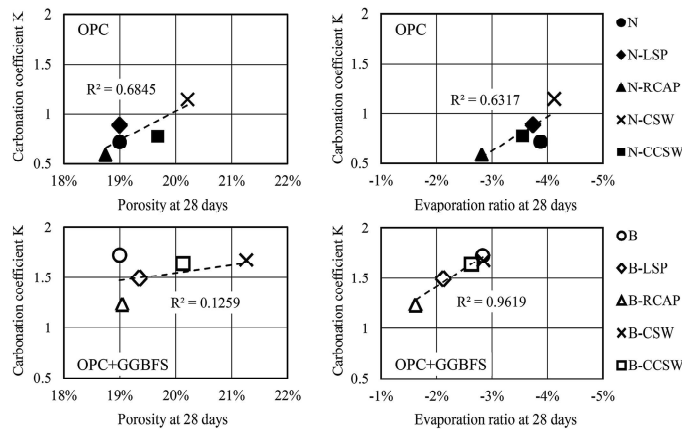


Figure 4. Relationship between porosity and carbonation coefficient K and evaporation ratio and carbonation coefficient K of mortars.

4 DISCUSSION

4.1 Effect of particle size and CaCO_3 content of PWCR

Limestone powder is a widely available and low-cost material. Its action combined with cement-based materials has been reported to be complex and dependent on several factors, such as particle size, dosage, polymorph of limestone, cement composition and supplementary cementitious materials (Wang et al. 2018). As shown in session 3.1, PWCR are composed of

hardened cement paste, which can be rich in calcium from $\text{Ca}(\text{OH})_2$ and C-S-H, and of fine aggregate particles, which may have CaCO_3 or SiO_2 in their composition. Therefore, they can be naturally or artificially a source to produce recycled limestone powder.

The effect of using PWCR in the mortar tests seems to be related to the particle size of the powders and the CaCO_3 content. As shown in Figure 5, RCAP is obtained after having undergone a crushing and grinding process, which naturally results in a fine powder. Oppositely, in CSW powder, hexagonal CH crystals and needle like ettringite are present from the ongoing hydration, which agglomerates the particles and results in a coarse powder without a proper treatment, such as drying and grinding. This difference in the particle size was not treated with the solid-air accelerated carbonation of CSW, showing to be one factor that influenced mortar's performance.

Another factor affecting mortar mixes performance was the CaCO_3 content. Cement producers add some percentage of calcium carbonate in industrialized cements, but many studies reported that there is an ideal amount of CaCO_3 to maximize performance of hardened cementitious materials, and that this can be higher than the tolerances regulated by current cement standards. Regarding the potential of reusing PWCR, it has been reported that precipitated CaCO_3 from carbonation of brines rich in Ca ions can potentially provide benefits to cement hydration (mineralogical changes), workability, strength and durability, when replacing cement at 10% mass content (McDonald et al. 2019). Also, carbonated hardened cement paste powder replacing 10% to 20% of cement increased strength up to 90 days in Lu et al. (2018) investigation. This is explained in literature, firstly, by the presence of calcite, that even in low weight percentages is sufficient to lead to formation of the calcium aluminates hemi-carbonate and monocarbonate, thus to a stabilization of ettringite. And these chemical reactions can result in lower porosity and higher compressive strength. In the experimental tests results, the positive results obtained for the mixes with CaCO_3 from PWCR, especially when combined with GGBFS seems to be related to the extra amount of alumina from this supplementary cementitious material, that affected reactivity of CaCO_3 . The second reason in literature explaining the positive influence of CaCO_3 from PWCR is the combination of additional nucleation and growth sites for hydration products lead to a chemical activation of the hydration of cement (Lothenbach et al. 2008). And finally, even with the use of high levels of calcite, most of them can still act as a filler, filling pores and micro-cracks, and this also explains the strength increase with the use of carbonated powders containing CaCO_3 (Liu et al. 2021). However, for a higher (30%) substitution of cement, there would be less hydration products, causing performance to decrease (Lu et al. 2018).

In this experimental study, PWCR replaced sand, so the filler effect was already expected. Coincidentally, the percentage of CaCO_3 in the powder wastes RCAP and CCSW, was similar and around 40% (Table 3), which resulted in the mortar mixes containing around 4.5% CaCO_3 solid material content, except for the percentage content inside the OPC (Figure 6). This content resulted in satisfactory performance for the mortars evaluated. But for LSP addition, which is a 99% CaCO_3 , there was no increase in performance, even it was the finest powder.

Additionally, there are reports about carbonation of cement-based materials producing not only CaCO_3 , but also (alumina-)silica gel and that it can quickly react with CH and result in the formation of more C-S-H (Zajac et al. 2020). Lawrence et al. (2003) also reported that short-term degree of hydration in mortar containing chemically inert quartz powders for a wide range of fineness (between 180 and 2000 m^2/kg) and cement replacement rates (up to 75%) was always higher than the reference mortar. This experimental study focused only on the CaCO_3 and did not focus on the influence of the supposed inert SiO_2 , nor the amorphous phase of the non-carbonated and carbonated powder wastes. Therefore, these components may also have a positive effect on the hardened cementitious material, especially if treated properly to an adequate particle size, maybe nanoscale particles (Li et al. 2015).

Table 3. $\text{Ca}(\text{OH})_2$ and CaCO_3 content in PWCR.

Content	LSP	RCAP	CSW	CCSW
$\text{Ca}(\text{OH})_2$	0%	2%	10%	2%
CaCO_3	99 %	36 %	7%	44%

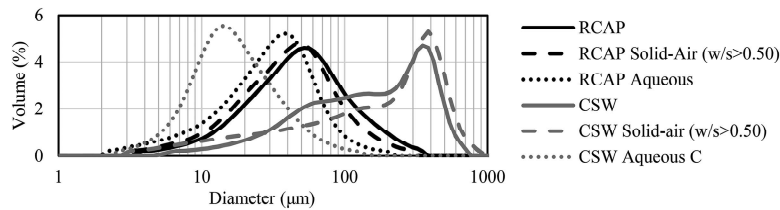


Figure 5. Particle size distribution of PWCR.

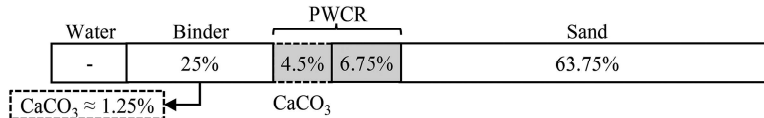


Figure 6. CaCO_3 content in mortars with RCAP and CCSW addition.

4.2 Carbonation applied to CSW for use as a value-added material

From session 3.3, the best mortar performance was obtained for B-RCAP mix, because of the combined filler effect for being a fine powder and hydration acceleration for containing CaCO_3 . However, setting other parameters for mortar mixes evaluation, as shown in Table 4, B-CCSW also showed a satisfactory mortar performance, adding the positive aspect of CO_2 uptake, compared to the mix B-RCAP. In this research, the carbonation technology applied to CSW, was the solid-air carbonation method, resulting in effective CaCO_3 formation, but without significant changes in the particle size distribution (PSD). As shown in Figure 5, the aqueous carbonation method can not only precipitate CaCO_3 , but finer CaCO_3 , not requiring grinding or other energy demanding processes. Therefore, it is expected to achieve even better performance for OPC+GGBFS mortars produced using CCSW carbonated with aqueous methods, transforming it into a value-added material and contributing holistically to the reduction in CO_2 emission, the CO_2 uptake and the concrete recycling.

Table 4. Evaluation of mixes' performance.

		Parameters			
Mix design		CO_2 emission reduction	CO_2 uptake	Concrete recycling	Mortar Performance
1	N	-	-	-	-
2	B	○	-	-	-
3	N-LSP	-	-	-	-
4	B-LSP	○	-	-	-
5	N-RCAP	-	-	○	○
6	B-RCAP	○	-	○	●
7	N-CSW	-	-	○	x
8	B-CSW	○	-	○	x
9	N-CCSW	-	○	○	○
10	B-CCSW	○	○	○	○

* Legend for the symbols:

● Extremely positive contribution

○ Positive contribution

- Neutral contribution

x Negative contribution

5 CONCLUSIONS

- Carbonation of PWCR: CSW showed high content of hydration products and it was a coarse powder. Both solid-air and aqueous carbonation changed the chemical

composition of CSW, transforming a still hydrating material to a chemically stable CaCO_3 . In the solid-air method, increasing the w/s improved the CO_2 uptake, but also stimulated the hydration of anhydrous cement from CSW, making it an even coarser powder. Therefore, it is necessary to have a grinding process (energy) to obtain fine powder material. But the aqueous method showed high efficiency for CO_2 uptake and also precipitated finer CaCO_3 , changing the particle size distribution. Differently, RCAP was naturally a fine powder, with high content of CaCO_3 and SiO_2 , from the crushing and grinding processes and/or previous natural carbonation, and its accelerated carbonation did not change the chemical composition nor the particle size distribution.

- Effect of PWCR in the mortar's performance: Compressive strength and carbonation resistance was improved with the addition of RCAP and CCSW, resulting in better performance than the control mixes. This indicates that there is an unexplored potential to reuse PWCR as a mineral admixture for mortar or concrete. This improvement showed to be related to the CaCO_3 content, which in RCAP and the carbonated CCSW samples was around 40%, resulting in approximately 5% CaCO_3 content of total solid material, and it was obtained regardless of the particle size of the powder, as RCAP was a fine and CCSW was a coarse powder. PWCR addition showed better performance combined with blended cement (OPC+GGBFS). This suggests that the mortar performance was influenced not only by an inert filler effect but also by a chemical effect (changes in hydration) caused by the CaCO_3 from the PWCR.

Therefore PWCR, both CSW and RCAP, can be a source of CaCO_3 . Also, the accelerated carbonation technology showed to be an adequate and valuable method to transform CSW to a value-added material and to promote its re-utilization, incorporating into the life cycle of concrete and leading to a circular and sustainable concrete industry economy.

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