

Article

Quantification of Residual Unhydrated Cement Content in Cement Pastes as a Potential for Recovery

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Abstract: All types of concrete contain residual unhydrated cement. For example, unhydrated cement is present in high-strength concrete due to low water/cement ratios, as well as in old concrete due to coarser cement used in the past, and in fresh concrete waste due to the lack of curing. These residues of unhydrated cement are a waste of resources with potential for recovery and reuse. In this work, X-ray diffraction, thermogravimetric analysis, and analytical modeling were used to quantify the residual cement and the hydration degree of various cement pastes to explore their recovery potential. The study included cement pastes with water/cement ratios of 0.2–0.6 and residual unhydrated cement was found to be in the range 6–36%, indicating great potential for recovery and further use in the manufacture of new concrete.

Keywords: recovery; residual unhydrated cement; degree of hydration; X-ray diffraction; thermogravimetric analysis; analytical modeling



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1. Introduction

The amount of construction and demolition waste (C&DW) generated globally has exceeded 3 billion tons per year, the major portion of which is, in many countries, concrete waste [1]. Recycling this waste can both prevent an increase in the area needed for waste disposal and avoid the extraction of non-renewable raw materials, reducing the environmental impact of extensive deforestation, top-soil loss, water pollution, air pollution, and CO₂ emissions [2].

Recycled C&DW is used mainly in road construction as base and sub-base and to a lesser degree in concrete fabrication as recycled aggregates [3]. Each recycling application of concrete waste requires a different quality and, therefore, a different treatment. Recycled aggregates may contain particles of natural aggregate that are fully or partially surrounded by a layer of cement paste/mortar or they may essentially be a lump of cement paste/mortar [4]. Mainly because of the attached cement paste/mortar, recycled aggregates are characterized by lower density, higher absorption, higher Los Angeles abrasion value, and higher sulfate content [5]. The use of recycled aggregate in new concrete, therefore, usually requires beneficiation to improve its quality by removing (or reducing) the attached cement paste and mortar. Various methods of beneficiation, which can partially or completely remove the mortar content of recycled aggregates exist, including thermal treatment (e.g., heating) [5,6], mechanical treatment (e.g., rubbing) [7], thermal-mechanical treatment [6,7], chemical-mechanical treatment (e.g., freeze-thaw cycles) [8], microwave-assisted treatment [7], ultrasonic cleaning [9], acid treatment [7,8,10], silica fume impregnation [9], and polymer treatment [11], to name a few.

All of the techniques cited above use the recovered natural aggregate as recycled aggregate, while the attached cement paste/mortar that is removed from it has currently no use. Most studies on concrete recycling focus only on the recycled aggregate, clean of any attached cement paste/mortar; only a few attempts have been made to recycle

the hydrated cement paste itself. Hydrated cement paste is usually ground to achieve fine particle size, and the fines are used as raw material in clinker production, as a cement replacement in blended cements, or as supplementary cementitious material in new paste/mortar/concrete [12]. Clinker production, however, requires a high temperature, causing decomposition of the hydrated cement paste [13–15]. Several studies investigated the possibility of rehydrating the decomposed hydrated cement paste fines after thermal treatment [14,16–18]. Another category of studies investigated the cementing contribution of hydrated cement paste fines through cement replacement, with no further treatment [19–22]. In these studies, new mortar/cement paste was produced, in which cement was replaced, at different replacement rates, by recycled fines from crushing and grinding of concrete/cement paste. For comparison, in [19], limestone filler was used to replace cement, while in [21], natural fine sand was used as an inert replacement. All studies found a progressive decrease in strength with the increase in the replacement rate of cement by said fine materials [19–21]. In [22], the same trend was found, except for the 20% replacement level sample, which achieved better results than the 10% replacement level sample, but still exhibited lower strength than the reference. The authors in [22] suggest that the optimal rate of replacement should be around 20–30% due to the filler effect and binder effect of the recycled fines. Several other negative effects were also evaluated at increasing replacement rates of cement by recycled fines, namely, lower hydration level, lower heat of hydration, higher porosity, and higher carbonation depth [20]. In [23], crushed concrete was considered an inert material, with a similar behavior to quartz filler.

Nevertheless, specimens containing recycled fines exhibited significantly higher strength than specimens in which cement was replaced by natural fine sand, at the same proportion and at the same age. This implies that recycled fines have some cementing properties, while natural fine sand is inert [21]. The same trend was reported in [19] regarding limestone filler: specimens containing recycled fines yielded equivalent or even higher values of compressive strength than specimens with limestone filler.

Since none of the recycled fines have cementing properties equivalent to that of new Portland cement, a decrease in compressive strength is expected with the increase in real water/cement (w/c) ratio. The paste is not composed entirely of unhydrated cement, which means that the contribution of cementing properties is proportional to the unhydrated cement content.

Quantification of residual unhydrated cement in hardened concrete/paste is essential to evaluate the recovery potential of old cement paste/mortar for further use in new concrete, not as inert aggregate but as an active supplementary cementitious material (SCM) with cementing properties.

An extensive study of residual unhydrated cement in old cement paste/mortar/concrete in quantitative terms is required to understand the feasibility and practicality of the possible recovery. Such a study is currently missing in the literature. This research aims to answer the following questions: How much unhydrated cement remains in old hydrated cement paste? Is the content of unhydrated cement significant for recovery? It also includes a comparison of different methods of quantification, as well as a comparison between different materials (w/c ratios).

2. Scientific Background

According to [24–26], an appreciable amount of unhydrated cement grains may be found in the microstructure of hydrated cement pastes even after a long hydration time, i.e., cement grains do not always achieve complete hydration. Cement hydration happens through the solution, with the interfacial dissolution reactions of anhydrous cement compounds and precipitation of hydrates [27–29].

Solubility has an important role, as well. To achieve the hydration of the anhydrous compounds, the solubility of the (future) hydrates must be lower than that of the anhydrous compounds [27]. For example, when calcium hydroxide concentrations are below 3.6×10^{-2} mol/L, alite (C_3S) (In this article, the cement chemistry notation is used for

clinker minerals and hydrated phases.) hydrates because it is more soluble than calcium silicate hydrate (C-S-H) [27].

At first, the dissolution of alite is faster than the diffusion leading to a concentration gradient near the surface and to oversaturation of the liquid phase [27]. As a result, first-stage hydrates precipitate at the surface of the grain [30]. After this initial reaction, hydration decreases during the induction period, followed by a second acceleration period, a deceleration period, and a slow continuous reaction [31]. During the acceleration period, second-stage hydrates are formed.

The unhydrated (anhydrous) cement grain dissolves and diminishes in diameter while the hydrates precipitate on the surface of the grain, surrounding it with several layers of growing C-S-H [27–29,32]. These layers of C-S-H are different depending on the precipitation order: the first layer around the unhydrated core (inner C-S-H) is more homogeneous, while the outer C-S-H is more diffuse [33]. Complete hydration is not achievable since the gel layers around the unhydrated core prevent further hydration [34]. The unhydrated core of the cement constitutes reserve of strength [35]. Several factors are associated with the remaining unhydrated cement, as follows:

Cement particle size: According to [36], particle size is one of the most important factors controlling hydration. Larger grains of cement may never achieve complete hydration and the internal part almost always remains in an unhydrated condition for a long time [37]. According to [34], in grains with a diameter greater than 20–25 µm, there is always a core of cement that does not undergo hydration. [24] refers to even higher values: cement particles larger than 45 µm are difficult to hydrate and those larger than 75 µm may never hydrate completely.

Water required for complete hydration: Water is present in hydrated cement systems in several forms: capillary (free) water that fills the capillary pores of the hardened paste, gel water that fills the gel space of the hardened paste (physically adsorbed water, interlayer water), and non-evaporable water that is part of the structure of the solid hydration product (water of constitution, chemically bound water) [38].

Cement hydration is determined by the reactions of each compound when mixed with water, based on the stoichiometry of the complete hydration [38,39]. The minimum water content required to chemically bound and complete hydration depends on the cement phase composition since each compound requires a different water content. Equation (1) presents the generic calculation for the mass of chemically bound water per mass of cement (w_{cb}/c).

$$w_{cb}/c = A \cdot p_{C3S} + B \cdot p_{C2S} + C \cdot p_{C3A} + D \cdot p_{C4AF} \quad (1)$$

where p_{C3S} , p_{C2S} , p_{C3A} , and p_{C4AF} are the mass ratios of major minerals in cement: alite, belite, tricalcium aluminate, and ferrite, respectively, A – D are coefficients [38–40].

Different coefficients (A – D) can be found in the literature for the reaction of alite (A): 0.187 [38], 0.197 [39], 0.23 [40]; belite (B): 0.158 [38], 0.157 [39], 0.196 [40]; tricalcium aluminate (C): 0.665 [38], 0.667 [39], 0.522 [40]; and ferrite (D): 0.213 [38], 0.26 [39], 0.109 [40]. The specific volume of non-evaporable water is defined as 0.72 cm³/g, which is lower than the specific volume of the capillary water (1 cm³/g) [38].

The literature usually gives the minimum content of chemically bound water for complete hydration as 0.23 for regular Type I Portland cement (23% of cement mass), which means that 1 g of anhydrous cement requires 0.23 g of water for full hydration [25,31,34,38]. Concrete/cement paste with a lower water content will present residual unhydrated cement, as is the case, for example, with high-strength concrete and high-performance concrete, which have low w/c ratios and, therefore, contain an insufficient amount of water for complete hydration.

Lack of space for hydration: Hydration products occupy a larger volume than the original cement grain—around 2.2 more [31,34,38]—and so there is a critical w/c ratio at which there is no capillary porosity and no space left for hydration products [31,41]. Researchers experimentally determined that the critical w/c ratio that provides enough space for all of the cement to react with no capillary porosity left (maximum degree of

hydration) is 0.38 [41]. The same value is later reported in [31,34]. Similar values (0.36–0.40) were reported in [25,42], and [26] reports that complete hydration can be achieved in the range of $0.38 < w/c < 0.75$. At lower w/c ratios, complete hydration cannot be achieved: the capillary porosity is reduced, and not enough space is available for hydration products. As a result, hydration will stop even if there is still unreacted cement present. According to [36], lack of water and lack of space are the two most important factors controlling hydration.

Curing duration and conditions: Curing conditions ensure that sufficient water is available to the cement grains in order to sustain the rate and degree of hydration necessary to achieve the desired concrete properties at the required time [43]. Hydration can end prematurely if curing conditions (duration, relative humidity, and temperature) are not appropriate, regardless of the w/c ratio. For hydration to proceed, relative humidity should be above 75% [44]. Lower relative humidity leads to a decrease in the amount of physically bound water in the paste, which reduces the amount of exposed unhydrated cement and the space available for hydration products [44].

The degree of hydration (α) expresses the extent of the hydration process relative to full hydration. This means that full hydration is represented by a hydration degree of 1 (or 100%) and all other hydration extents are denoted by degrees of hydration lower than 1. In such cases of incomplete hydration, some amount of anhydrous (unhydrated) cement remains in the hydrated cement paste, even after a long hydration time [24–26]. According to the definition, and as expressed in Equation (2), the degree of hydration at time t is calculated as the mass ratio between the reacted cement (m_c) at time t and the initial anhydrous cement (m_{ci}) at time $t = 0$ or 1 minus the mass ratio between the residual unhydrated cement (m_{cRU}) at time t and the initial cement content (m_{ci}) at time $t = 0$:

$$\alpha(t) = m_c / m_{ci} = 1 - (m_{cRU} / m_{ci}) \quad (2)$$

where:

$\alpha(t)$ is the degree of hydration at time t ,

m_c is the mass of the reacted cement,

m_{ci} is the mass of the initial cement content,

m_{cRU} is the mass of the residual unhydrated cement.

This equation can be rearranged to express the mass of residual unhydrated cement per mass of initial cement (m_{cRU} / m_{ci}) as $(1 - \alpha)$ or, alternatively, the mass of residual unhydrated cement per initial mass of cement paste (m_{cRU} / m_p) as $(1 - \alpha) / (1 + w/c)$, where m_p is the initial mass of cement paste.

There are several methods to quantify the degree of hydration of cementitious materials. Each method is guided by different approach and quantifies a different aspect of the system: the heat of hydration (calorimetry), bound water content (thermal analysis), amount of portlandite (thermal analysis, X-ray diffraction), amount of unhydrated cement (X-ray diffraction, electron microscopy, nuclear magnetic resonance), and so on.

The quantification of residual unhydrated cement is usually only one step in the quantification of the degree of hydration [33,45–47] and is rarely performed as a final goal, as is required in order to evaluate the recovery potential of old concrete. In this work, thermal analysis and X-ray diffraction were used as methods for the quantification of residual unhydrated cement, as discussed below in detail.

3. Materials and Methods

3.1. Materials

In this work, parent cement paste was produced in the laboratory in order to quantify the degree of hydration and the residual unhydrated cement content using different methods.

The cement used in this work was Portland cement CEM I 52.5 N from Nesher Israel Cement Enterprises Ltd. conforming to EN 197 [48]. The chemical composition of the cement was obtained by inductively coupled plasma. Table 1 presents the chemical analysis of the cement.

Table 1. Chemical analysis of CEM I 52.5 N *.

Parameter	Mass (%)	Parameter	Mass (%)
CaO	62.16	P ₂ O ₅	0.4
SiO ₂	19.02	Mn ₂ O ₃	0.05
Al ₂ O ₃	5.42	SO ₃	2.48
Fe ₂ O ₃	3.82	IR	0.76
MgO	1.31	FL	2.8
TiO ₂	0.53	LOI ₂₅₀	0.41
K ₂ O	0.37	LOI ₉₅₀	2.52
Na ₂ O ₅	0.22	LOI _{total}	2.93

* Data obtained from Nesher.

The specific surface area was 4679 cm²/g, as measured according to EN 196-6 2018 [49]. Cement density was 3.169 g/cm³, as obtained by helium pycnometer (Quantachrome Ultrapyc 1200e), with a resolution of 0.0001 g/cm³ and a pressure of 14 psig.

Based on the chemical composition presented in Table 1, a mineralogical analysis of the cement phases was performed both according to Bogue's calculation [50] as modified by Taylor [51] and by XRD (see Table 2).

Table 2. Mineralogical analysis of cement phases (%).

	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Bogue calculation modified by Taylor	62.61	6.58	4.48	13.71
XRD	60.93	12.93	5.85	12.4

The chemical admixture used in this work was Glenium 27, which is a liquid high range water reducing/superplasticizing admixture (SP) based on chains of modified polycarboxylic ether, with a specific gravity of 1.044 and active/solid content of 20% (by mass) according to EN 480-8 2012 [52].

3.2. Sample Preparation

3.2.1. Parent Cement Paste

The parent cement paste was produced with different w/c ratios. Some of the samples refer to normal strength concrete (with a w/c ratio of 0.6) and others to high-performance concrete with lower w/c ratios (0.3 and 0.2).

The materials used to produce the parent samples were cement, tap water, and SP, when needed, according to preliminary workability tests. Mechanical mixing was performed using a standard pan mixer as described in EN 196-1 2016 [53]. Table 3 presents the composition of the different mixes.

Table 3. Composition of cement paste mixes produced in the laboratory (kg/m³).

	CP0.2	CP0.3	CP0.6
Cement CEM I 52.5N	1779.6	1572.9	1056.3
Total water *	355.9	471.9	633.8
SP dosage (%) **	2.5	0.4	-
w/c ratio	0.20	0.30	0.60

* Total water includes the water contained in the liquid SP and the water added to the mixture. ** SP dosage is presented as a percentage of the active/solid content (by mass) relative to the mass of cement.

Curing was started one day after casting, when the specimens were removed from the molds and placed in water at 20 ± 1 °C for 28 days.

3.2.2. Cement Paste Fines

After the curing duration, the specimens were oven dried at 105 °C until reaching constant mass, and then transferred to a vacuum desiccator to dry. Subsequently, the specimens were tested for compressive strength, followed by crushing in a jaw crusher and milling in a vibratory ball mill. Milling was performed for 30 min with a material/grinding media ratio of 1/20. Grinding media was stainless steel cylpebs and no grinding aids were added.

3.3. Experimental Methods

The cement paste fines were tested for particle size distribution, thermal analysis, and X-ray diffraction. In addition, hydration was modeled using the CEMHYD3D model. Compressive strength was tested before crushing the specimens so as to relate cement paste strength to the results.

3.3.1. Compressive Strength

Compressive strength was tested following the procedure described in EN 12390-3 2019 [54]. In this work, 50 mm × 50 mm × 50 mm cubes specimens were used. For each w/c ratio, 6 specimens were tested.

3.3.2. Particle Size Distribution

Particle size distribution (PSD) was measured by laser diffraction using a Mastersizer 2000 (Malvern), with isopropanol as the dispersant liquid to avoid a reaction.

3.3.3. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed using a Linseis STA PT-1000. Air atmosphere and alumina crucibles (3 mL volume) were used and approximately 325 mg of crushed cement paste was tested for each sample. The heating program was the same for all samples: from 20 °C to 1000 °C at a heating rate of 5 °C/min.

The degree of hydration was calculated as the ratio between the measured non-evaporable water content (w_n) and the amount of chemically bound water required for full hydration (w_{cb}).

There is no consensus in the literature regarding the content of w_n . It is usually calculated as the mass loss from an initial to a final temperature ($WL_{T_i-T_f}$), with some correction factor (CF). Different initial temperatures (T_i) are considered in the literature, for example, 50 °C after solvent exchange [55], 105 °C [47,56–61], 110 °C [62] and 140 °C [63].

The final temperature (T_f) also varies in the literature from 950 °C [62] to 1000 °C [47,56,60], 1050 °C [57,58], and 1100 °C [59,63]. In [55], T_f is 550/600 °C to exclude the mass loss from decarbonation (above 600 °C). Similarly, [56] corrects the amount of non-evaporable water by subtracting 59% of the decarbonation mass loss (at 580–1000 °C), where the value 0.59 comes from $(1-0.41)$, and 0.41 is the ratio between the molar masses of water and CO₂ (18 and 44 g/mol, respectively). Other researchers correct the content of non-evaporable water by subtracting 59% of the difference between the mass loss relative to the decarbonation of the sample and the mass loss relative to the decarbonation of the anhydrous material (530–1100 °C) [59]. The same CF is used by [61], but with a narrower temperature range for the decarbonation (600–800 °C), whereas [60] use this same CF for samples with mineral additions, with three additional items: addition of the device's drift, subtraction of loss on ignition (LOI) of the cement (multiplied by the cement mass in the sample), and subtraction of the LOI of the addition (multiplied by the addition mass in the sample). In [63], the mass loss related to the decarbonation of the anhydrous material is subtracted, but no reduction coefficient is used. A common CF is subtracting the LOI of the cement [47,57,62].

In this work, w_n was calculated as the mass loss from an initial (105 °C) to a final temperature (550 °C), with two correction factors (CF): (1) addition of 41% of the difference between the decarbonation mass loss of the sample and the decarbonation mass loss of the anhydrous cement (600–800 °C); and (2) subtraction of the loss on ignition of cement. w_{cb} was calculated as the non-evaporable water in Equation (1), with the coefficients from [40]: ($p_{C3S} = 0.23$, $p_{C2S} = 0.196$, $p_{C3A} = 0.522$, and $p_{C4AF} = 0.109$). The content of residual cement was calculated using Equation (2).

3.3.4. X-ray Diffraction

X-ray diffraction (XRD) was performed using a Thermo Fisher Scientific ARL X'TRA powder diffractometer. The diffractometer geometry included a Bragg-Brentano θ – θ measurement setup and a goniometer radius of 260 mm. The X-ray source included $\text{CuK}\alpha_2$ radiation ($\lambda = 1.54 \text{ \AA}$) and generator operation of 45 kV and 40 mA. The diffractometer optics included a flexible incident/diffracted beam slit system, adjustable between 0 and 10 mm via micrometer, with Soller slits of 4.6° and 1.3° (no monochromator). The detector was solid-state silicon lithium Si(Li), with step scanning mode. The sample was $22 \times 22 \text{ mm}^2$ (powder), the spinning speed was constant, and sample loading was side loading. The scan parameters were an angular range of 8 – $52^\circ 2\theta$, step size of $0.02^\circ 2\theta$, and time per step of 1 s. The internal standard method was applied.

According to [64], the Rietveld quantitative phase analysis results must be normalized to the mass of initial anhydrous cement (per 100 g) or the mass of cement paste (per 100 g) and depending on the presence/absence of free water. For a dried sample, the calculation should take into account the bound water content based on TGA, as follows [64]:

$$W_{\text{paste}} = W_{\text{Rietveld}} / [(100 - WL_{950}) \cdot (1 + w/c)] \quad (3)$$

$$W_{\text{anhydrous cement}} = W_{\text{Rietveld}} / (100 - WL_{950}) \quad (4)$$

Residual unhydrated cement content was calculated using Equations (3) and (4) and the degree of hydration was calculated using Equation (2).

3.4. CEMHYD3D Modeling

Modeling was performed using the CEMHYD3D model, version 3.0. It is a three-dimensional cement hydration and microstructure development modeling package developed by the National Institute of Standards and Technology (NIST, USA). Version 3.0 of the model contains several computer programs written in C language that simulate cement-based materials' microstructural development and performance properties [65,66].

The hydration simulation was performed for 672 h (28 days), under initial saturated conditions, with an initial system temperature of 23 °C (ambient temperature constant at 23 °C, isothermal conditions).

The pre-factor for the nucleation probability of calcium hydroxide was 0.0001 (scale factor of 9000), the pre-factor for the nucleation probability of gypsum forming hemihydrate and anhydrite was 0.01 (scale factor of 9000), the pre-factor for the nucleation probability of hydrogarnet (C_3AH_6) was 0.00002 (scale factor of 10,000), and the pre-factor for the nucleation probability of iron (III) oxide-hydroxide ($\text{Fe}(\text{OH})_3$) was 0.002 (scale factor of 2500).

The activation energy for the cement hydration reactions was 40 KJ/mole.

4. Results

4.1. Compressive Strength

There is an expected tendency for higher compressive strength at lower w/c ratios. Indeed, both CP0.2 and CP0.3 present high compressive strength, achieving $117.1 \pm 7 \text{ MPa}$ and $78.8 \pm 6.2 \text{ MPa}$, respectively, at 28 days, while CP0.6 presents a significantly lower value ($25.9 \pm 2.3 \text{ MPa}$).

4.2. Particle Size Distribution

Figure 1 presents the PSD of ground cement paste. It is evident that the PSD is divided into two parts, which may designate different fractions of cement paste fines. Two visible peaks are present: the first is assumed to be associated with the residual unhydrated cement and the second is assumed to be associated with the hydrated paste. The PSD of the original Portland cement used to prepare the cement pastes is given in Figure 1 for reference.

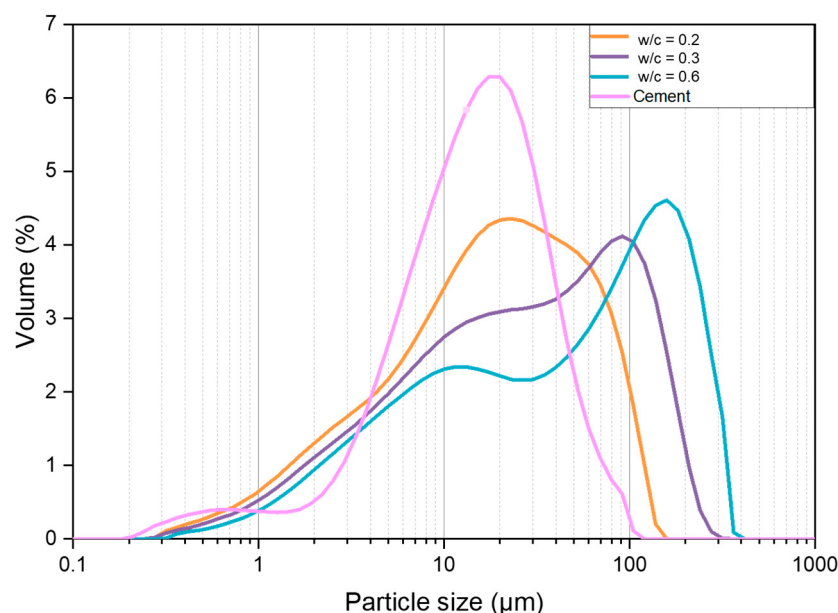


Figure 1. Particle size distribution of ground cement pastes and original Portland cement by volume fraction.

The left peak (located at the left side of the distribution, at the smaller particle size) in all samples is in the range of 12–22 μm and it coincides with the major peak of the original Portland cement. Considering this, an analysis of the residual cement in the cement paste fines samples can be performed assuming that the peak height indicates the amount of residual cement. Thus, the content of residual cement increases with decreasing w/c ratio.

The right peak (located at the right side of the distribution, at the coarser particle size) in all cement paste samples is assumed to represent the hydrated paste. The peak height indicates the amount of the hydrated paste, while the peak location indicates its fineness. The amount of hydrated cement decreases with decreasing w/c ratio, as does particle size. The position of the second peak ranges from approximately 69 μm to 91 μm (for CP0.2, CP0.3) and to 158 μm (for CP0.6). This tendency may imply that agglomeration has occurred since no grinding aids were used.

It is important to note that cement particles are usually considered spherical, with an equivalent diameter, while hydrated paste particles present a less circular shape. Since they are composed of different phases, hydrated paste particles are joint particles, and estimated as a rotating coordinate system or even approximately rectangular shaped [67]. For this reason, the peak associated with the hydrated phase appears at a coarser particle size.

Considering that the milling process effectively separated the unhydrated cement core from the hydrated shell (C-S-H), the higher left peak and the lower right peak of CP0.2 PSD indicate a lower reaction degree of the cement in this mix, resulting in a larger remaining core and higher content of residual cement. Similarly, the lower left peak and the higher right peak of CP0.6 PSD indicate a higher reaction degree of the cement in this mix, resulting in a smaller remaining core and lower content of residual cement.

4.3. Thermogravimetric Analysis

TGA was performed after 28 days of curing. Table 4 presents calculations of portlandite content (CH), degree of hydration (α), and residual cement (m_{cRU}). Portlandite content is expressed considering carbonation (values without considering carbonation are given in parentheses). The significant difference between portlandite values in CP0.2, considering and without considering carbonation, indicates the occurrence of high levels of carbonation, while the smaller difference between the portlandite values for both CP0.3 and CP0.6 indicates the occurrence of low levels of carbonation. Portlandite values are slightly higher than the values found in [62].

Table 4. TGA calculations.

	CP0.2		CP0.3		CP0.6	
	Per 100 g initial cement	Per 100 g paste	Per 100 g initial cement	Per 100 g paste	Per 100 g initial cement	Per 100 g paste
CH (g)	15.1 (8.1)	12.6 (6.7)	18.2 (16.0)	14.0 (12.3)	23.6 (21.8)	14.8 (13.6)
m_{cRU} (g)	43.7	36.4	29.1	22.4	9.9	6.2
α (%)	56.3		70.9		90.1	

As expected, samples with lower w/c ratios demonstrated lower degrees of hydration and, therefore, higher contents of residual cement. There is a good linear correlation between the degree of hydration, residual cement, and portlandite content as seen in Figure 2. The increasing content of portlandite indicates a higher degree of hydration and therefore a lower content of residual cement.

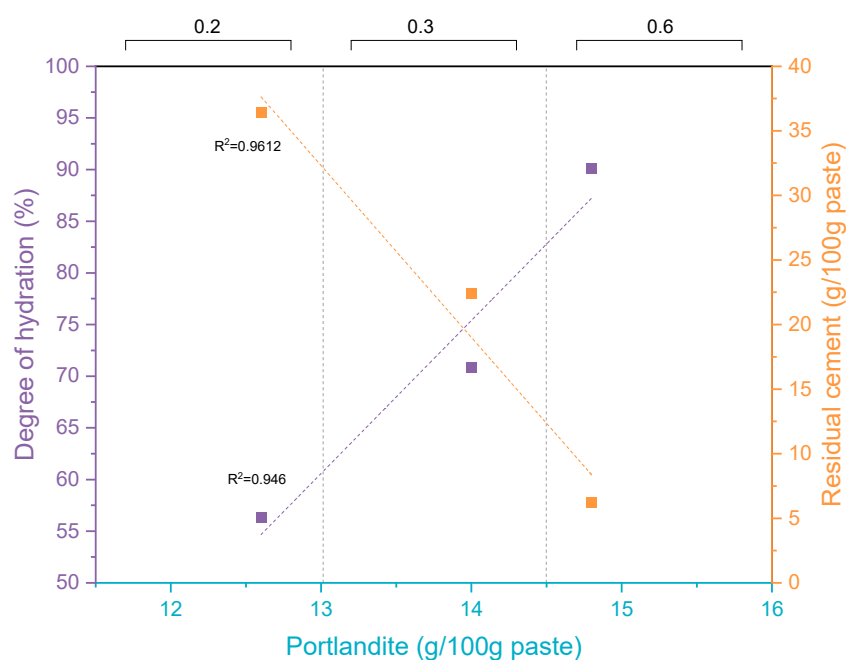


Figure 2. TGA—Correlation between parameters.

According to Equation (2), the content of hydrated cement per mass of initial cement can be extracted directly as the degree of hydration, while the content of hydrated cement per mass of paste depends on the w/c ratio. The mass of hydrated cement per 100 g of hydrated paste was calculated as 46.9, 54.5, and 56.3 g for CP0.2, CP0.3, and CP0.6, respectively. CP0.2 exhibits the lowest hydrated cement content and the highest residual cement content, while the increase in w/c ratio leads to an increase in hydrated cement content and a decrease in residual cement content. CP0.3 and CP0.6 exhibit similar hydrated

cement contents, while CP0.6 exhibits a significantly lower value of residual cement, indicating higher porosity. The porosity corresponds to the mass of remaining free water in the system. Since both CP0.3 and CP0.6 exhibit similar hydrated cement contents (54.5–56.3 g per 100 g of hydrated paste), the water content consumed for hydration of this cement is assumed to be similar for both CP0.3 and CP0.6. However, because of the higher w/c ratio, CP0.6 presents a higher initial amount of water, and therefore, a higher amount of remaining water in the system. This remaining water is translated to porosity.

4.4. X-ray Diffraction

Figure 3 presents XRD scans for samples after 28 days of curing and Table 5 presents calculations based on Rietveld refinement as well as portlandite content considering carbonation (values without considering carbonation are in parentheses). Portlandite values for the sample differ slightly, indicating low carbonation level in XRD samples. In agreement with TGA, the CP0.2 sample demonstrated stronger carbonation.

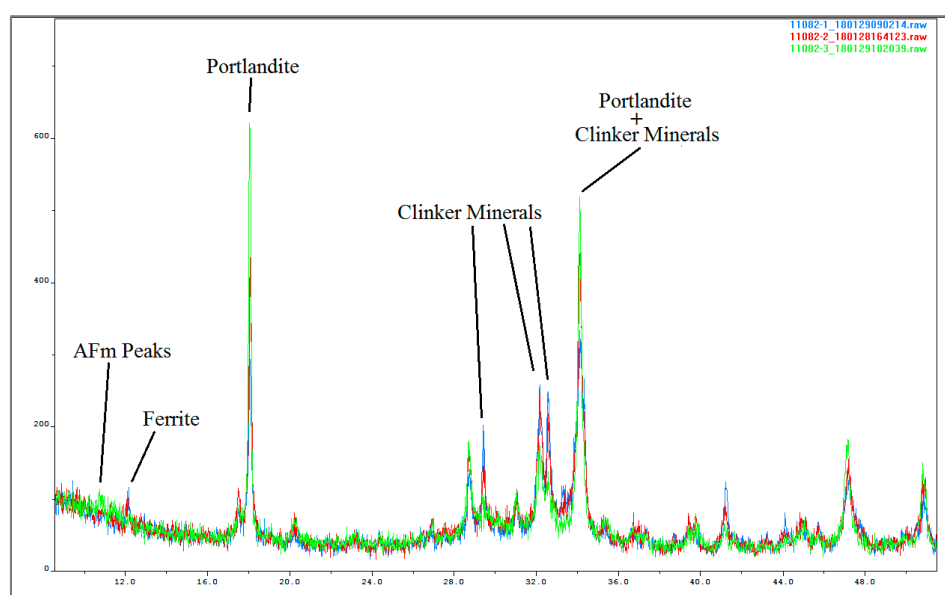


Figure 3. XRD results. Color code is blue—CP0.2, red—CP0.3, green—CP0.6.

Table 5. XRD calculations.

	CP0.2		CP0.3		CP0.6	
	Per 100 g initial cement	Per 100 g paste	Per 100 g initial cement	Per 100 g paste	Per 100 g initial cement	Per 100 g paste
C ₃ S (g)	9.6	8.0	4.1	3.2	2.0	1.2
C ₂ S (g)	13.5	11.2	13.4	10.3	13.2	8.2
C ₃ A (g)	1.9	1.5	1.6	1.2	0.7	0.5
C ₄ AF (g)	4.9	4.1	4.7	3.6	0.1	0.1
m _{CRU} (g)	29.9	24.8	23.8	18.3	16.0	10.0
CH (g)	13.2 (11.7)	11.0 (9.8)	16.6 (15.3)	12.8 (11.8)	23.9 (22.7)	14.9 (14.2)
CC (g)	2.0	1.6	1.8	1.4	1.6	1.0
Amorphous (g)	72.7	60.6	76.8	59.0	81.7	51.1
α (%)	68.3	-	74.8	-	83.0	-

Figure 4 presents the calculated degree of hydration, portlandite content, and residual cement content as a function of the w/c ratio. In agreement with TGA, the lower the w/c ratio, the lower the degree of hydration and, therefore, the higher the content of residual cement, and the lower the content of portlandite.

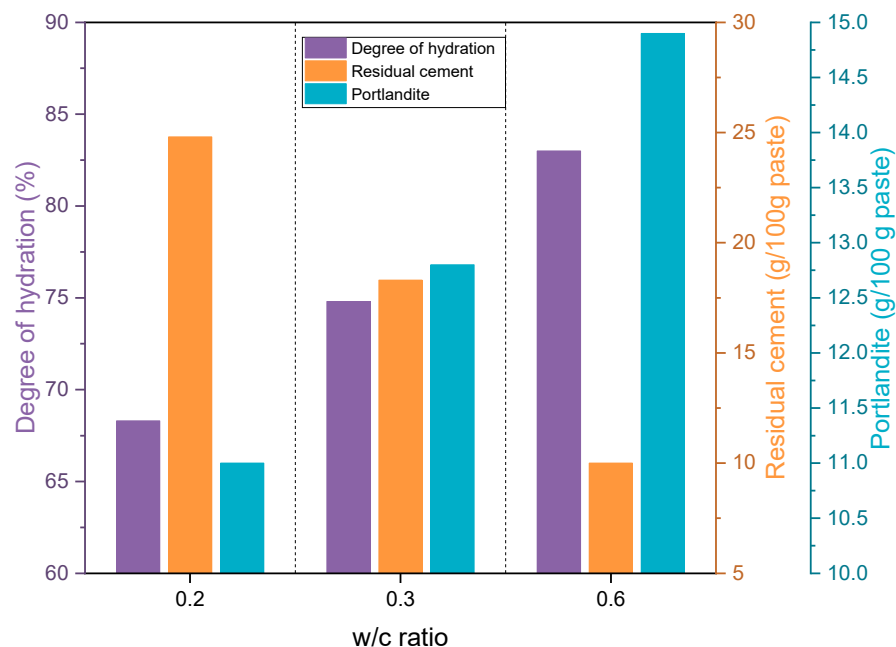


Figure 4. XRD—Portlandite content, residual cement content, and degree of hydration.

Figure 5 reveals a very strong linear correlation between the degree of hydration, the residual cement content and the portlandite content. Once again, the increase in portlandite content indicates a higher degree of hydration and, therefore, a lower residual cement content.

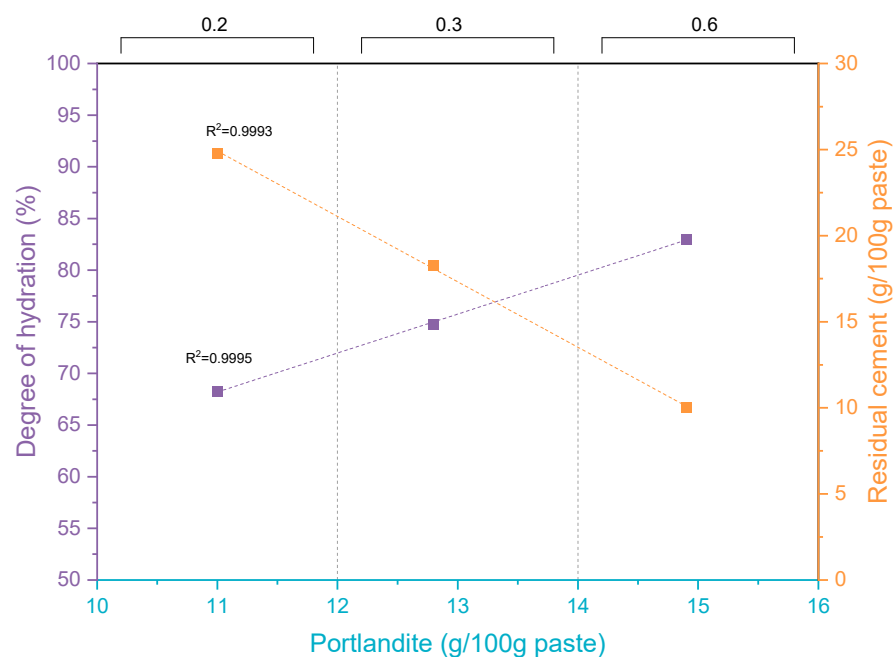


Figure 5. XRD—Correlation between parameters.

The mass of hydrated cement per 100 g of hydrated paste was calculated. CP0.2 and CP0.3 present similar contents of hydrated cement (56.9–57.5 g), while CP0.6 exhibits a

lower value (51.9 g). A lower content of hydrated cement was expected for CP0.2, but since the degree of hydration from XRD (68.3%) is significantly higher than the TGA value (56.3%), the content is also higher. Similarly, a higher content of hydrated cement was expected for CP0.6, but since the degree of hydration from XRD (83%) is significantly lower than the TGA value (90.1%), the content is also lower.

Figure 6 presents the mineral composition of the residual cement content. Most of the residual cement was present in the form of belite, which corresponds to 45, 56, and 82% of the residual cement for the CP0.2, CP0.3, and CP0.6 samples, respectively. When considering both silicate phases (belite and alite), they represented 77, 74, and 95% of the residual cement in the CP0.2, CP0.3, and CP0.6 samples, respectively. As expected, the content of tricalcium aluminate in all samples was very low.

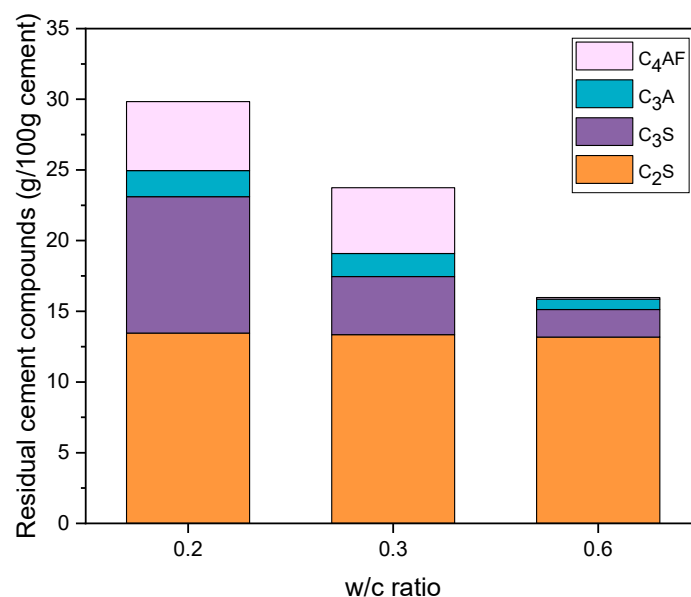


Figure 6. XRD—Residual cement composition.

Figure 7 presents the calculated degree of reaction for each cement compound. Alite exhibited significant reactions even at low w/c ratios. The degree of reaction for alite ranged from 85% in CP0.2 to 93 and 97% in CP0.3 and CP0.6, respectively. The degree of reaction of tricalcium aluminate and ferrite was 68, 72, and 88% and 60, 62, and 99% for CP0.2, CP0.3, and CP0.6, respectively. Belite exhibited a very low degree of reaction in all cement pastes, ranging from 5 to 7% and so all cement pastes exhibited high belite contents. This was expected since belite undergoes slower hydration and, as previously stated, most of the residual cement is in the form of belite.

CP0.2 presents the lowest degree of reaction for all compounds, which is in agreement with the high amount of residual cement, while CP0.6 presents the highest degree of reaction for all compounds, which is in agreement the low amount of residual cement.

It is interesting to note that, in addition to a high content of residual belite, CP0.2 has a high content of residual alite (the content of residual silicates represents approximately 23% of the initial cement mass; see Figure 6). This demonstrates that significantly low w/c ratios cannot achieve high hydration levels due to the lack of water and space for hydration products, thus achieving a low degree of reaction for all cement components.

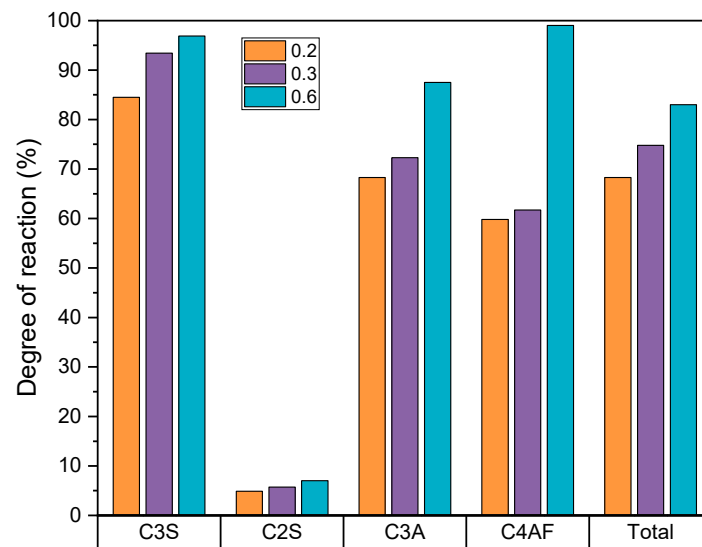


Figure 7. XRD—Degree of reaction of each cement component.

4.5. CEMHYD3D Modeling

Table 6 presents results of the hydration model at the age of 28 days.

Table 6. CEMHYD3D results.

	CP0.2		CP0.3		CP0.6	
	Per 100 g initial cement	Per 100 g paste	Per 100 g initial cement	Per 100 g paste	Per 100 g initial cement	Per 100 g paste
C ₃ S (g)	18.7	14.2	5.7	4.0	1.4	0.9
C ₂ S (g)	14.0	10.7	10.4	7.2	6.2	3.7
C ₃ A (g)	1.5	1.1	0.6	0.4	0.2	0.1
C ₄ AF (g)	9.2	7.0	8.1	5.7	6.9	4.1
<i>m</i> _{CRU} (g)	43.4	33.0	24.8	17.3	14.7	8.8
CSH ₂ , CSH _{0.5} CSH (g)	2.5	1.9	1.1	0.8	0.8	0.4
CH (g)	20.3	15.4	26.3	18.3	29.0	17.1
C-S-H (g)	50.7	38.4	68.1	47.3	78.0	46.0
C ₃ AH ₆ (g)	6.4	4.8	6.0	4.2	8.0	4.7
AFt (g)	6.6	5.1	6.9	4.8	9.6	5.6
AFm (g)	0.0	0.0	4.5	3.1	2.2	1.3
FH ₃ (g)	1.0	0.7	1.5	1.0	2.0	1.2
α (%)	56.6		75.2		85.3	
Porosity (volume %)		1.9		8.9		33.8
pH	13.09		13.47		13.28	
Chemical shrinkage (mm ³ /g cement)	41.5		53.8		61.2	

Figure 8 presents the calculated degree of hydration, the portlandite content, and residual cement content as a function of the w/c ratio. In agreement with TGA and XRD results, samples with lower w/c ratios present lower degrees of hydration and, therefore, higher residual cement contents.

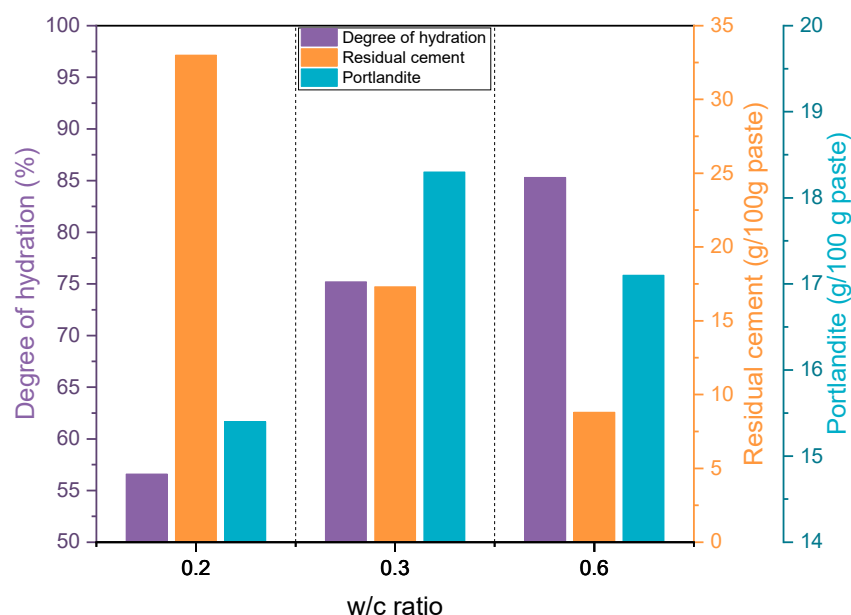


Figure 8. CEMHYD3D—Portlandite content, residual cement content, and degree of hydration.

On the other hand, the content of portlandite (per mass of paste) does not increase progressively with the increase in w/c ratio, as seen in the experimental methods, but increases with the increase in w/c ratio from 0.2 to 0.3, followed by a decrease with the increase in w/c ratio from 0.3 to 0.6. The same trend is seen in C-S-H content and hydrated cement content (per mass of paste).

The contents of the hydration products (portlandite and C-S-H) are not necessarily proportional to the content of residual cement, but rather are proportional to the hydrated cement content. Considering that the pastes were prepared with different w/c ratios and, therefore, with different initial amounts of cement, the content of hydrated cement per mass of paste does not necessarily increase with the increase in w/c ratio as could be expected. According to the CEMHYD3D model, the hydrated cement content follows the same trend as portlandite and C-S-H, confirming the linear relationship between the contents of both hydration products and the content of hydrated cement (see Figure 9). No linear relationship, however, is seen with the w/c ratio when analyzing per mass of paste.

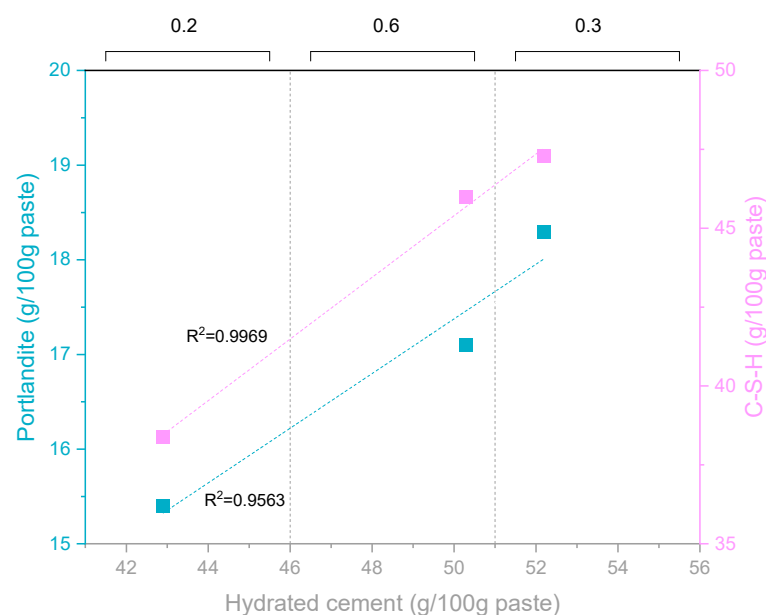


Figure 9. CEMHYD3D—Correlation between parameters.

As expected, when the hydration products (portlandite and C-S-H) are analyzed per mass of initial cement, an increase is observed in both contents with the increase in w/c ratio.

It is interesting to note that the degree of hydration depends, by definition, on the initial amount of cement and not on the amount of paste, and so the content of hydrated cement and of residual cement, per mass of initial cement, will always be proportional to the degree of hydration. If, however, the hydrated cement content and residual cement content are calculated per mass of paste, this relationship does not necessarily hold. When considering the w/c ratio and calculating the mass of the paste, cases with higher w/c ratios can be observed presenting lower contents of hydrated cement and hydration products (see Figures 8 and 9).

The content of hydrated cement in CP0.2 is very similar to the TGA value, since both methods yield very similar degrees of hydration, while hydrated cement content in CP0.3 is very similar to the XRD value, for the same reason. CP0.6 presents an intermediate value (53.3 g) between TGA and XRD values (56.3 and 51.9 g, respectively).

Figure 10 presents the content of the residual cement and its mineral composition. Cement paste CP0.2 has the highest residual cement content in the form of alite (43%) and belite (32%), while CP0.3 and CP0.6 have a lower content of alite (10–23% of the residual cement) and a higher amount of belite (42% of the residual cement). The content of tricalcium aluminate across all samples is very low, as expected, and the ferrite content is very similar: around 7–8 g per 100 g of initial cement.

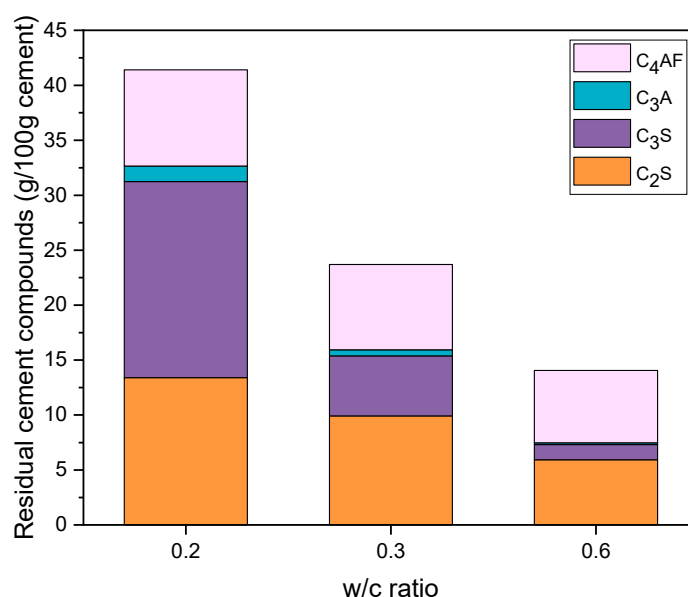


Figure 10. CEMHYD3D—Residual cement composition.

Figure 11 shows the calculated degree of reaction of each compound. In agreement with XRD, CP0.2 presents the lowest degree of reaction for all clinker minerals, which is in line with the high amount of residual cement, while CP0.6 presents the highest degree of reaction for all clinker minerals, which is in agreement with the low content of residual cement.

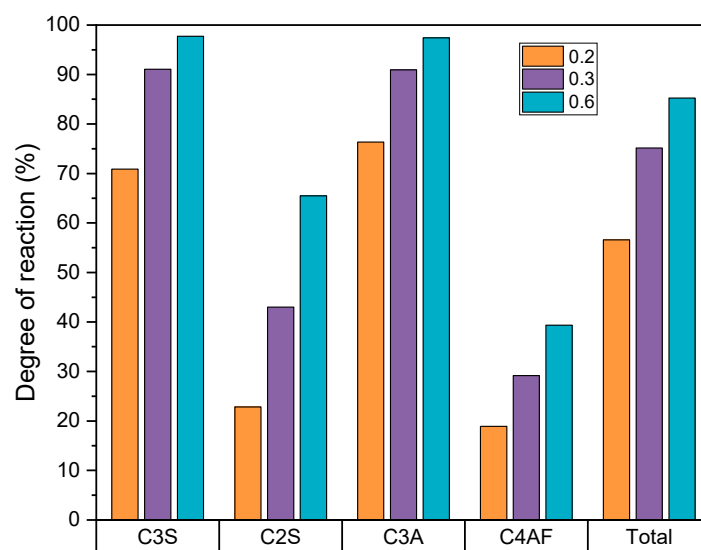


Figure 11. CEMHYD3D—Degree of reaction of each cement compound.

Alite and tricalcium aluminate have similar reaction degrees, ranging from 71–76% for CP0.2, 91% for CP0.3, and 97–98% for CP0.6. According to the model, belite exhibits an unexpectedly significant degree of reaction of 23, 43, and 65% for CP0.2, CP0.3, and CP0.6, respectively, while ferrite exhibits an unexpectedly low degree of reaction of 19, 29, and 39% for CP0.2, CP0.3, and CP0.6, respectively.

As evident in the XRD results, CP0.2 presents a high content of residual alite and belite (the residual silicate content represents approximately 31% of the initial cement mass).

Figure 12 presents images generated by the model. Residual alite (red), belite (cyan), and ferrite (yellow) are visually dominant in CP0.2 (Figure 12a), in agreement with Table 7 and Figure 10, while only small amounts of alite and ferrite are present in CP0.3 alongside a higher belite content (Figure 12b). In CP0.6, alite is almost nonexistent, while belite and ferrite are present in small amounts (Figure 12c). Tricalcium aluminate (green) is almost nonexistent in all samples, in agreement with the data shown in Figure 10. Hydration products—portlandite (blue) and C-S-H (orange)—are present across all samples and are more visually predominant in samples CP0.3 and CP0.6. Porosity (black) is almost nonexistent in CP0.2, while it is slightly visible in CP0.3, and significantly visible in CP0.6. Gypsum (gray) is not visible in any of the samples.

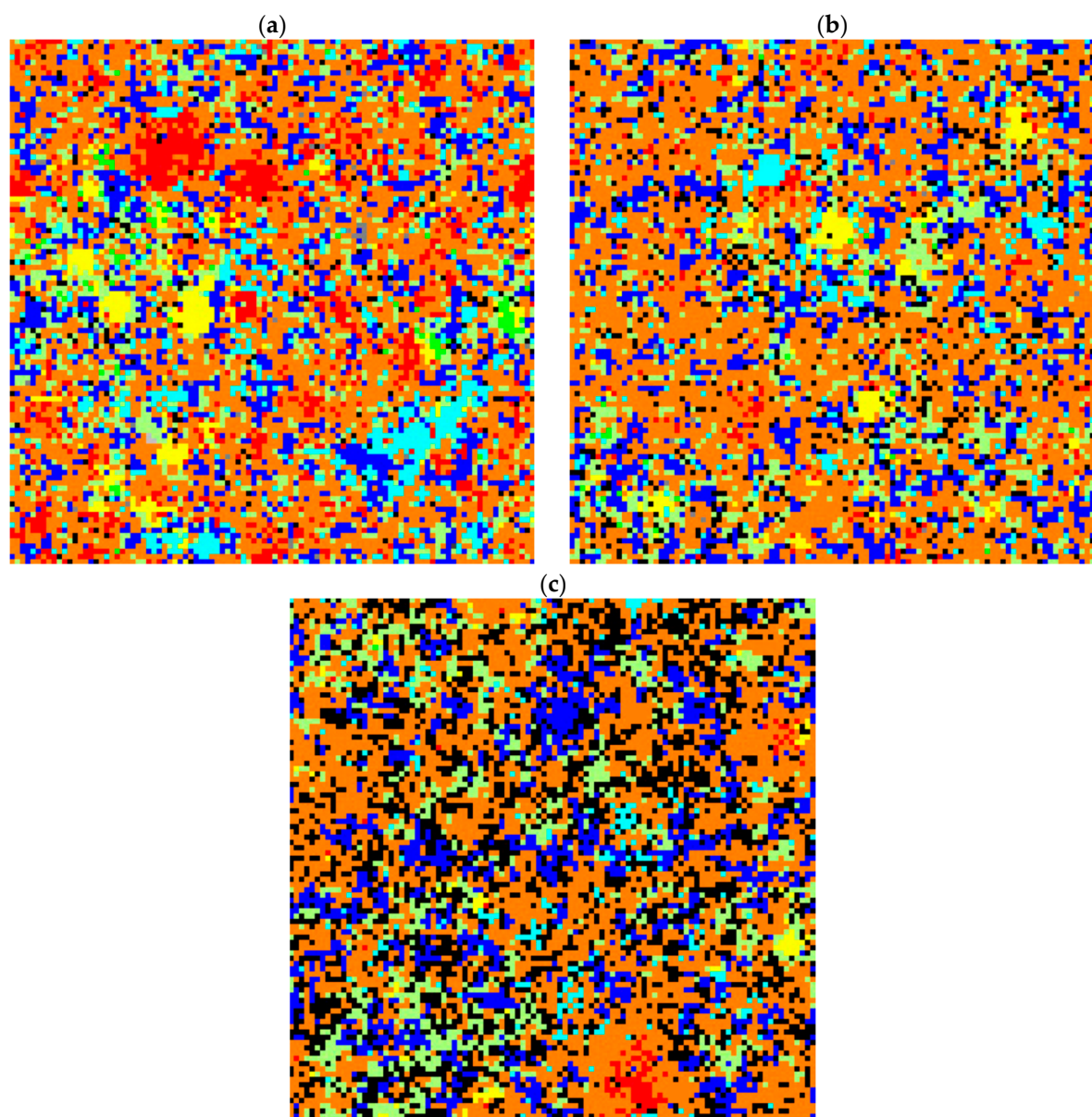


Figure 12. CEMHYD3D resulting images for CP0.2 (a), CP0.3 (b), and CP0.6 (c). Color code is red- C_3S , cyan- C_2S , green- C_3A , yellow- C_4AF , gray-gypsum, blue-CH, orange-C-S-H, black-porosity.

Table 7. Summary.

		CP0.2	CP0.3	CP0.6
Degree of hydration (%)	CEMHYD3D	56.6	75.2	85.3
	TGA	56.3	70.9	90.1
	XRD	68.3	74.8	83.0
Residual cement (g/100 g paste)	CEMHYD3D	33.0	17.3	8.8
	TGA	36.4	22.4	6.2
	XRD	24.8	18.3	10.0

5. Discussion

Both experimental methods still have unclosed issues that lack consensus, such as diverse temperature ranges for quantifying bound water, uncertain temperature ranges

for C-S-H decompositions, overlapping diffraction peaks, consideration of C-S-H phase in XRD, etc. In this work, thermal analysis and X-ray diffraction were performed, in addition to CEMHYD3D model, to quantify the residual unhydrated cement and the degree of hydration. The contribution of concrete/cement paste waste as an active cementitious material, in new concrete, depends on the quantity of unhydrated cement, and so quantification is essential for the recovery potential study.

Table 7 summarizes the results obtained for degree of hydration and amount of residual cement as obtained by the different methods—see Figures 13 and 14.

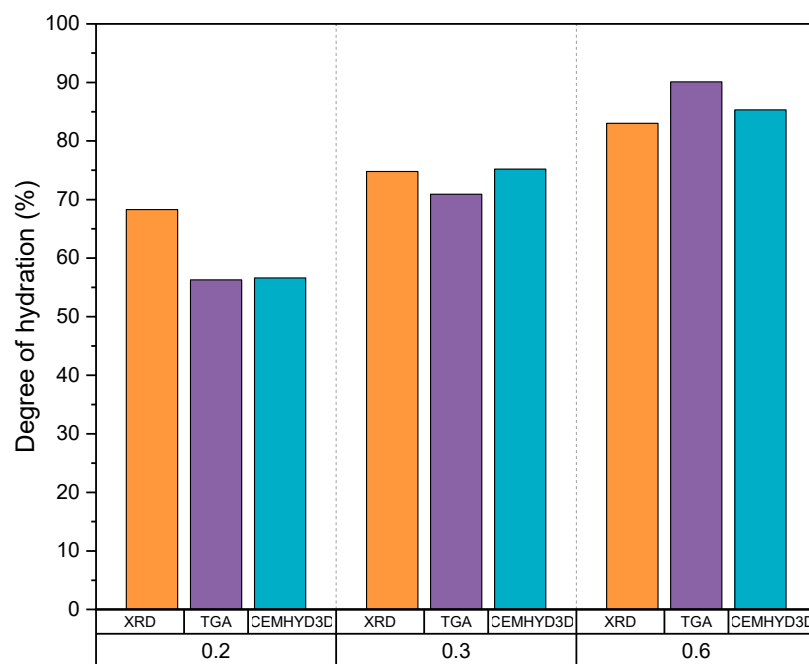


Figure 13. Comparison between methods: Degree of hydration.

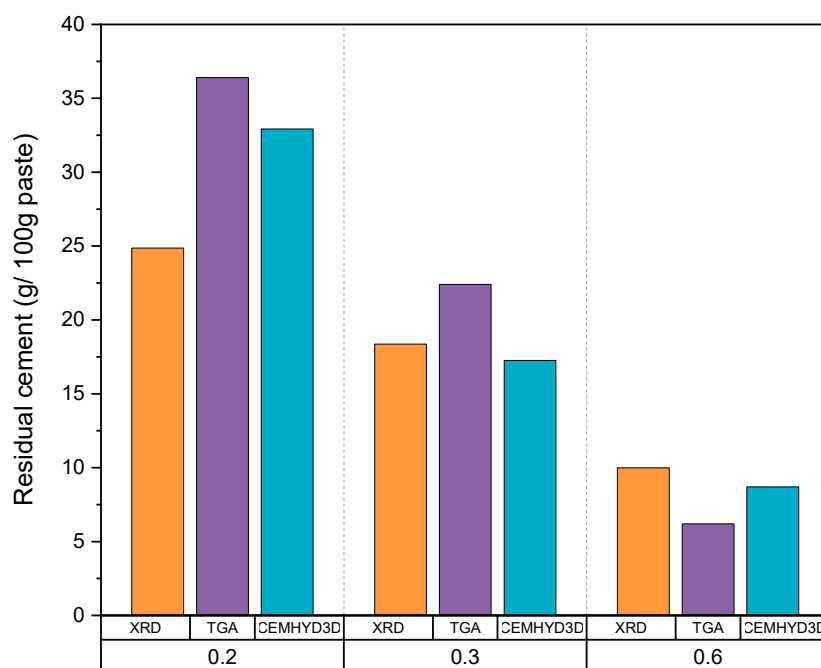


Figure 14. Comparison between methods: Residual cement.

For CP0.3 and CP0.6, the hydration values are in good agreement for all methods, with differences below 9%. For CP0.2, TGA and the CEMHYD3D model give the same values, while XRD gives a significantly higher degree of hydration (+21%).

According to the literature, low w/c ratios are associated with low degrees of hydration (Figure 15). For the lower w/c ratio (0.2), this present work presents values in agreement to the literature from TGA and the CEMHYD3D model, while XRD yielded a higher value. For a 0.3 w/c ratio, all methods in this present work presents higher values than the cited in the literature. For the higher w/c ratio (0.6), the values from XRD and the CEMHYD3D model are in agreement to the literature, while TGA yields a higher value.

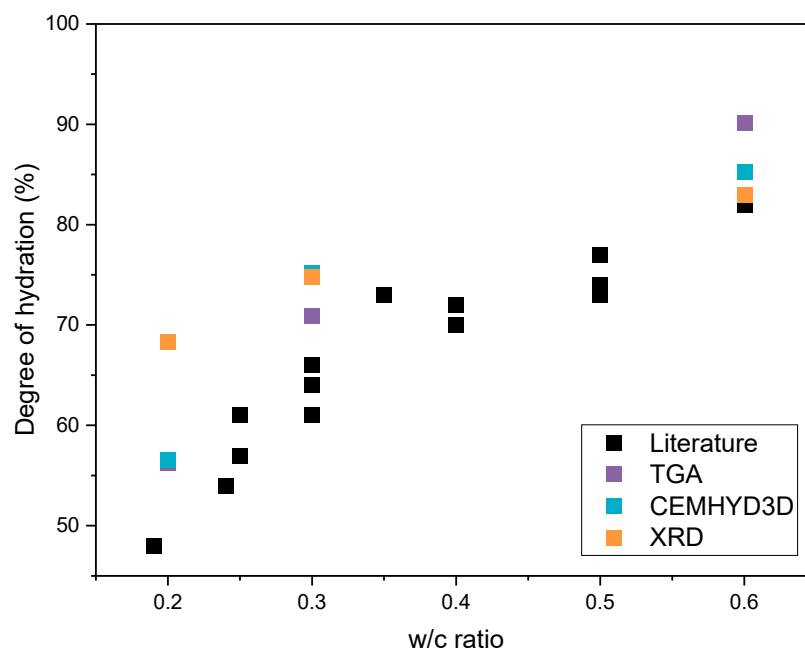


Figure 15. Correlation between degree of hydration and w/c ratio from this work results and literature [45,57,62,68,69].

It is interesting to note that the paste containing the lowest w/c ratio (CP0.2) presents the lowest degree of hydration and the highest compressive strength, across all methods. This suggests that compressive strength does not depend mainly on the hydrated cement. In this case, the porosity has a stronger effect on compressive strength. As a result, the sample with the lowest porosity achieves higher strength (CP0.2), while the one with the highest porosity achieves lower strength (CP0.6). The effect of porosity on compressive strength was studied by [70–72], among others. The porosity values resulting from CEMHYD3D model are correlated to compressive strength in Figure 16, where the tendency is consistent with the literature [34].

All methods present the same trend of decreasing content of residual cement with the increase in w/c ratio. Low w/c ratios (0.2 and 0.3) present a similar behavior: TGA presents the higher value, followed by the CEMHYD3D model and XRD. For CP0.3 and CP0.6, the residual cement values are in good agreement for XRD and the CEMHYD3D model, while for CP0.2, the CEMHYD3D model is higher (+25%).

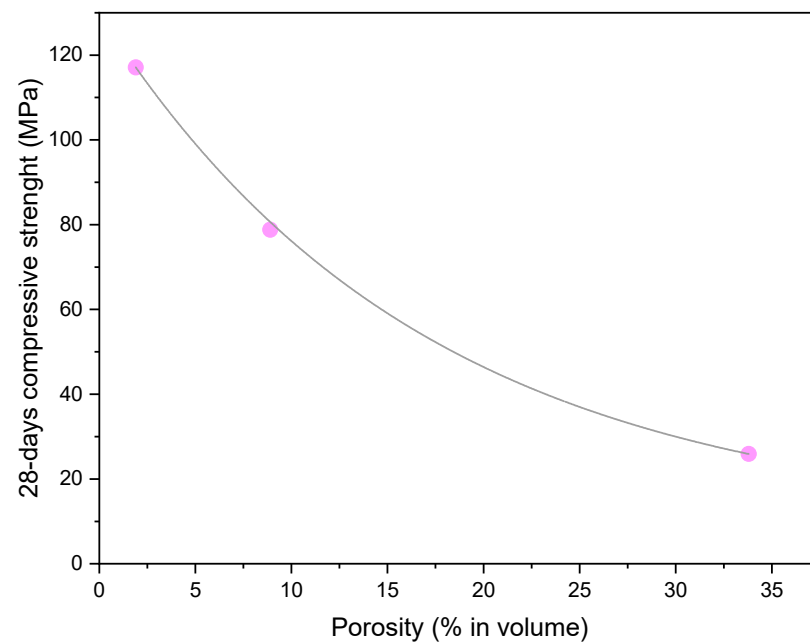


Figure 16. Correlation between compressive strength and porosity.

Figure 17 presents the relevant literature values and the results from this present work. For the lower w/c ratio (0.2), this present work presents values in agreement to the literature from TGA and the CEMHYD3D model, while XRD yielded a lower value. For a 0.3 w/c ratio, the value from TGA agrees to the literature, while XRD and the CEMHYD3D model yielded lower values. For the higher w/c ratio (0.6), the values from XRD and the CEMHYD3D model are in agreement to the literature, while TGA yields a lower value.

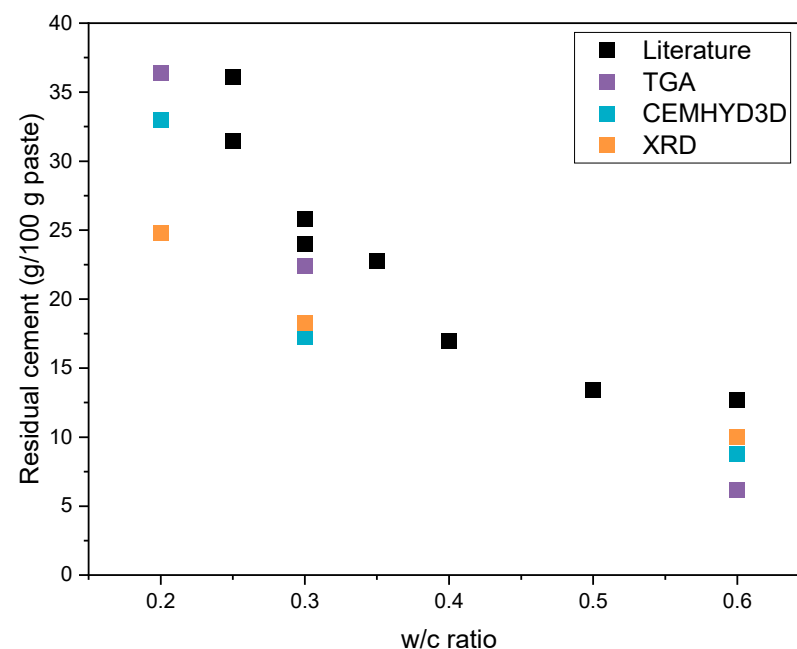


Figure 17. Correlation between residual cement and w/c ratio from this work results and literature [45,57,62,68,69].

It should be noted that the drying method used in the sample preparation of this work was oven drying at 105 °C, until reaching constant mass, which may have influenced the results of the thermal analysis. Oven drying can potentially remove some of the bound water (from C-S-H, ettringite, and monosulfate), in addition to removing the free water,

thus explaining the difference between the methods. The non-evaporable water content may be higher than the measured value, resulting in a higher degree of hydration and lower residual cement content. Indeed, the residual cement content obtained from TGA is higher than that obtained by the other methods for CP0.2 and CP0.3. In addition, normalization of the portlandite value to either paste or anhydrous mass uses the bound water content and, therefore, a higher value could have been obtained if a different drying method was used. We suggest that future studies implement a different hydration stoppage method.

In order to practically apply the research results in the construction industry, it is necessary to make some arrangements. First, an adaptation needs to be done, since the research results are based on cement paste, and they need to be expanded to concrete, with additional variables (aggregates, transition zone, etc.). Secondly, the research results are based on laboratory conditions, and they need to be expanded to real C&DW, with several additional variables and a large variability. Due to the difficult homogeneity of construction waste, in a real recycling facility, concrete waste must be properly separated, and each batch must be quantified. The amount of unhydrated cement will depend on many factors and must be estimated for each application.

6. Conclusions

The presented research investigated the potential of residual unhydrated cement present in C&DW with different w/c ratios. In this work, cement pastes with low w/c ratios revealed significant amounts of residual cement: 25–36% for w/c ratio of 0.2 and 17–22% for w/c ratio of 0.3. Even high w/c ratios exhibited residual cement (6–10%). This proves that the quality and strength of the parent concrete strongly affect the amount of residual unhydrated cement and its potential recovery. Since the application of high-strength concretes has been steadily increasing over the years, the content of residual cement in C&DW is also increasing. In addition, old concrete structures and fresh concrete waste from ready-mixed concrete plants also provide significant amounts of residual cement, due to larger cement particle sizes and lack of curing, respectively. As a result, the high potential for recovery of residual cement from C&DW has been proven/demonstrated.

Most of the residual cement was present in the form of alite and belite. When considering both silicate phases, they represented 74–95% of the residual cement. This means that the residual cement is not only found in significant amounts but also is composed mostly of silicates, which indicates that the residual cement is suitable for further use in new concrete.

It has been demonstrated that the ground material consists of two parts: the residual unhydrated cement and hydrated paste. Both parts are suitable for further use in new concrete. The first may play an active binder role when hydrated, while the latter can serve as a filler with no separation needed, and depending on the content of residual unhydrated cement, the material can be used as SCM.

Different experimental methods and modeling were evaluated as a tool for the assessment of residual unhydrated cement. XRD provided the most reliable results. The drying method used in the sample preparation may have influenced the results of the thermal analysis, and therefore a different hydration stoppage method is suggested for future studies.

The model (CEMHYD3D) provided good results though few problems have been observed. The particle size limitation of 1 voxel ($1 \mu\text{m}^3$) should be considered, and the lack of possibility to consider carbonation also poses some limitations. As a result of lack of carbonation, the content of portlandite was overestimated. All the other results obtained from the model were supported by the experimental results. This allows the use of the modeling for easy estimation of the content of residual unhydrated cement and its composition, and therefore, theoretical evaluation of the recovery potential.

The potential for recovery depends on quantitative and qualitative factors: content and composition of residual cement. In addition, the need to liberate the active cement core for further hydration must be taken into consideration. The methods to achieve optimum

liberation must be further investigated in future studies. Furthermore, the use of recovered residual cement as an SCM in new concrete must be investigated in future studies.

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References

1. Akhtar, A.; Sarmah, A.K. Construction and Demolition Waste Generation and Properties of Recycled Aggregate Concrete: A Global Perspective. *J. Clean. Prod.* **2018**, *186*, 262–281. [\[CrossRef\]](#)
2. Pacheco-Torgal, F. Introduction to the Recycling of Construction and Demolition Waste (CDW). In *Handbook of Recycled Concrete and Demolition Waste*; Pacheco-Torgal, F., Tam, V.W.Y., Labrincha, J.A., Ding, Y., de Brito, J., Eds.; Woodhead Publishing: Sawston, UK, 2013; pp. 1–8.
3. Coelho, A.; De Brito, J. Preparation of Concrete Aggregates from Construction and Demolition Waste (CDW). In *Handbook of Recycled Concrete and Demolition Waste*; Pacheco-Torgal, F., Tam, V.W.Y., Labrincha, J.A., Ding, Y., de Brito, J., Eds.; Woodhead Publishing: Sawston, UK, 2013; pp. 210–245. ISBN 9780857096906.
4. Akbarnezhad, A. Separation Processes to Improve the Quality of Recycled Concrete Aggregates (RCA). In *Handbook of Recycled Concrete and Demolition Waste*; Pacheco-Torgal, F., Tam, V.W.Y., Labrincha, J.A., Ding, Y., de Brito, J., Eds.; Woodhead Publishing: Sawston, UK, 2013; pp. 246–269.
5. De Juan, M.S.; Gutiérrez, P.A. Study on the Influence of Attached Mortar Content on the Properties of Recycled Concrete Aggregate. *Constr. Build. Mater.* **2009**, *23*, 872–877. [\[CrossRef\]](#)
6. Shima, H.; Tateyashiki, H.; Matsushashi, R.; Yoshida, Y. An Advanced Concrete Recycling Technology and Its Applicability Assessment through Input-Output Analysis. *J. Adv. Concr. Technol.* **2005**, *3*, 53–67. [\[CrossRef\]](#)
7. Akbarnezhad, A.; Ong, K.C.G.; Zhang, M.H.; Tam, C.T.; Foo, T.W.J. Microwave-Assisted Beneficiation of Recycled Concrete Aggregates. *Constr. Build. Mater.* **2011**, *25*, 3469–3479. [\[CrossRef\]](#)
8. Butler, L.; West, J.S.; Tighe, S.L. The Effect of Recycled Concrete Aggregate Properties on the Bond Strength between RCA Concrete and Steel Reinforcement. *Cem. Concr. Res.* **2011**, *41*, 1037–1049. [\[CrossRef\]](#)
9. Katz, A. Treatments for the Improvement of Recycled Aggregate. *J. Mater. Civ. Eng.* **2004**, *16*, 597–603. [\[CrossRef\]](#)
10. Tam, V.W.Y.; Tam, C.M.; Le, K.N. Removal of Cement Mortar Remains from Recycled Aggregate Using Pre-Soaking Approaches. *Resour. Conserv. Recycl.* **2007**, *50*, 82–101. [\[CrossRef\]](#)
11. Spaeth, V.; Djerbi Tegger, A. Improvement of Recycled Concrete Aggregate Properties by Polymer Treatments. *Int. J. Sustain. Built Environ.* **2013**, *2*, 143–152. [\[CrossRef\]](#)
12. Cyr, M.; Diliberto, C.; Lecomte, A.; Izoret, L. Recycled Concrete as Cement Main Constituent (CMC) or Supplementary Cementitious Materials (SCM). In *Concrete Recycling—Research and Practice*; de Larrard, F., Colina, H., Eds.; Taylor & Francis Group: Boca Raton, FL, USA, 2019; pp. 83–98.
13. Zhutovsky, S.; Karinski, Y.S.; Feldgun, V.R.; Yankelevsky, D.Z. Loading Branch of the Barotropic Equation of State for Cementitious Composites under Extremely High Pressures. *Int. J. Solids Struct.* **2020**, *188*, 181–188. [\[CrossRef\]](#)
14. Zhutovsky, S.; Shishkin, A. Recycling of Hydrated Portland Cement Paste into New Clinker. *Constr. Build. Mater.* **2021**, *280*, 122510. [\[CrossRef\]](#)
15. Zhutovsky, S.; Shishkin, A. Recycling of Hydrated Portland Cement Paste for Clinker Production. In Proceedings of the RILEM-SC2020 Ambitioning a Sustainable Future for Built Environment: Comprehensive Strategies for Unprecedented Challenges, Guimarães, Portugal, 9 March 2020. [\[CrossRef\]](#)
16. Gastaldi, D.; Canonico, F.; Capelli, L.; Buzzi, L.; Boccaleri, E.; Irico, S. An Investigation on the Recycling of Hydrated Cement from Concrete Demolition Waste. *Cem. Concr. Compos.* **2015**, *61*, 29–35. [\[CrossRef\]](#)
17. De Schepper, M.; Snellings, R.; De Buysser, K.; Van Driessche, I.; De Belie, N. The Hydration of Cement Regenerated from Completely Recyclable Concrete. *Constr. Build. Mater.* **2014**, *60*, 33–41. [\[CrossRef\]](#)
18. Snellings, R.; De Schepper, M.; De Buysser, K.; Van Driessche, I.; De Belie, N. Clinkering Reactions during Firing of Recyclable Concrete. *J. Am. Ceram. Soc.* **2012**, *95*, 1741–1749. [\[CrossRef\]](#)

19. Oksri-Nelfia, L.; Mahieux, P.-Y.; Amiri, O.; Turcry, P.; Lux, J. Reuse of Recycled Crushed Concrete Fines as Mineral Addition in Cementitious Materials. *Mater. Struct.* **2016**, *49*, 3239–3251. [\[CrossRef\]](#)
20. Bordy, A.; Younsi, A.; Aggoun, S.; Fiorio, B. Cement Substitution by a Recycled Cement Paste Fine: Role of the Residual Anhydrous Clinker. *Constr. Build. Mater.* **2017**, *132*, 1–8. [\[CrossRef\]](#)
21. Amin, A.F.M.S.; Hasnat, A.; Khan, A.H.; Ashiquzzaman, M. Residual Cementing Property in Recycled Fines and Coarse Aggregates: Occurrence and Quantification. *J. Mater. Civ. Eng.* **2015**, *28*, 4015174. [\[CrossRef\]](#)
22. Topič, J.; Prošek, Z.; Plachý, T. Influence of Increasing Amount of Recycled Concrete Powder on Mechanical Properties of Cement Paste. *IOP Conf. Ser. Mater. Sci. Eng.* **2017**, *236*, 012094. [\[CrossRef\]](#)
23. Grabois, T.M.; Cordeiro, G.C.; Toledo Filho, R.D. The Influence of Recycled Concrete and Clay Brick Particles on the Strength and Porosity of Cement-Based Pastes. In *Calcined Clays for Sustainable Concrete*; RILEM Bookseries; Martirena, F., Favier, A., Scrivener, K., Eds.; Springer: Dordrecht, The Netherlands, 2017; pp. 189–194. ISBN 978-94-024-1207-9.
24. Mehta, P.K. *Concrete: Structure, Properties, and Materials*; Prentice-Hall, Ed.: Hoboken, NJ, USA, 1986.
25. Neville, A.M. *Properties of Concrete*; Longman: London, UK, 2012; ISBN 9780889867178.
26. Mills, R.H. Factors Influencing Cessation of Hydration in Water-Cured Cement Pastes. *Highw. Res. Board Spec. Rep.* **1966**, *90*, 406–424.
27. Scrivener, K.L.; Nonat, A. Hydration of Cementitious Materials, Present and Future. *Cem. Concr. Res.* **2011**, *41*, 651–665. [\[CrossRef\]](#)
28. Pommersheim, J.M.; Clifton, J.R. Mathematical Modeling of Tricalcium Silicate Hydration. *Cem. Concr. Res.* **1979**, *9*, 765–770. [\[CrossRef\]](#)
29. Pommersheim, J.M.; Clifton, J.R.; Frohnsdorff, G. Conceptual and Mathematical Models for Tricalcium Silicate Hydration. In Proceedings of the 7th International Congress on Chemistry of Cement, Subtheme VII, Paris, France, 7 July 1980; pp. 195–200.
30. Beaudoin, J.; Odler, I. Hydration, Setting and Hardening of Portland Cement. In *Lea's Chemistry of Cement and Concrete*; Hewlett, P.C., Liska, M., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; pp. 157–250. ISBN 978-0-08-100773-0.
31. Taylor, H.F.W. *Cement Chemistry*, 2nd ed.; Thomas Telford Publishing: London, UK, 1997; ISBN 0-7277-3945-X.
32. Garrault, S.; Behr, T.; Nonat, A. Formation of the C–S–H Layer during Early Hydration of Tricalcium Silicate Grains with Different Sizes. *J. Phys. Chem. B* **2006**, *110*, 270–275. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Scrivener, K.L. Backscattered Electron Imaging of Cementitious Microstructures: Understanding and Quantification. *Cem. Concr. Compos.* **2004**, *26*, 935–945. [\[CrossRef\]](#)
34. Soroka, I. *Portland Cement Paste and Concrete*; The Macmillan Press Ltd.: London, UK, 1979; ISBN 978-1-349-03996-8. [\[CrossRef\]](#)
35. Gambhir, M.L. *Concrete Technology: Theory and Practice*, 5th ed.; MHE Rentals India Pvt. Ltd.: New Delhi, India, 2013.
36. Bullard, J.W.; Jennings, H.M.; Livingston, R.A.; Nonat, A.; Scherer, G.W.; Schweitzer, J.S.; Scrivener, K.L.; Thomas, J.J. Mechanisms of Cement Hydration. *Cem. Concr. Res.* **2011**, *41*, 1208–1223. [\[CrossRef\]](#)
37. Diamond, S. The Microstructure of Cement Paste and Concrete—A Visual Primer. *Cem. Concr. Compos.* **2004**, *26*, 919–933. [\[CrossRef\]](#)
38. Powers, T.C.; Brownnyard, T.L. Studies of the Physical Properties of Hardened Portland Cement Paste—Part 5. *J. Proc.* **1947**, *43*, 669–712.
39. Brouwers, H.J.H. *A Hydration Model of Portland Cement Using the Work of Powers and Brownnyard*; Eindhoven University of Technology: Skokie, IL, USA, 2011; ISBN 978-90-6814-184-9.
40. Copeland, L.E.; Kantro, D.L.; Verbeck, G. Chemistry of Hydration of Portland Cement. In Proceedings of the 4th International Symposium on Chemistry of Cement, Washington, DC, USA, 2–7 October 1960; Volume 1, pp. 429–468.
41. Powers, T.C. Physical Properties of Cement Paste. In Proceedings of the Fourth International Symposium on the Chemistry of Cement, Washington, DC, USA, 2–7 October 1960; Volume 5, pp. 577–613.
42. Mather, B.; Hime, W.G. Amount of Water Required for Complete Hydration of Portland Cement. *Concr. Int.* **2002**, *24*, 56–58.
43. American Concrete Institute. *ACI Committee 308 Guide to External Curing of Concrete*; American Concrete Institute: Farmington Hills, MI, USA, 2016; pp. 1–36.
44. Jensen, O.M. Thermodynamic Limitation of Self-Desiccation. *Cem. Concr. Res.* **1995**, *25*, 157–164. [\[CrossRef\]](#)
45. Igarashi, S.; Kawamura, M.; Watanabe, A. Analysis of Cement Pastes and Mortars by a Combination of Backscatter-Based SEM Image Analysis and Calculations Based on the Powers Model. *Cem. Concr. Compos.* **2004**, *26*, 977–985. [\[CrossRef\]](#)
46. Gaël, B.; Christelle, T.; Gilles, E.; Sandrine, G.; Tristan, S.F. Determination of the Proportion of Anhydrous Cement Using SEM Image Analysis. *Constr. Build. Mater.* **2016**, *126*, 157–164. [\[CrossRef\]](#)
47. Feng, X.; Garboczi, E.J.; Bentz, D.P.; Stutzman, P.E.; Mason, T.O. Estimation of the Degree of Hydration of Blended Cement Pastes by a Scanning Electron Microscope Point-Counting Procedure. *Cem. Concr. Res.* **2004**, *34*, 1787–1793. [\[CrossRef\]](#)
48. EN197-1; Cement. Part 1: Composition, Specifications and Conformity Criteria for Common Cements. CEN—European Committee for Standardisation: Brussels, Belgium, 2011.
49. EN196-6; Method of Testing Cement. Part 6: Determination of Fineness. CEN—European Committee for Standardisation: Brussels, Belgium, 2018.
50. Bogue, R.H. Calculation of the Compounds in Portland Cement. *Ind. Eng. Chem.* **1929**, *1*, 192–197. [\[CrossRef\]](#)
51. Taylor, H.F.W. Modification of the Bogue Calculation. *Adv. Cem. Res.* **1989**, *2*, 73–77. [\[CrossRef\]](#)
52. EN480-8; Admixtures for Concrete, Mortar and Grout—Test Methods. Part 8: Determination of the Conventional Dry Material Content. CEN—European Committee for Standardisation: Brussels, Belgium, 2012.

53. BS EN 196-1; Methods of Testing Cement Part 1: Determination of Strength. CEN—European Committee for Standardisation: Brussels, Belgium, 2016. [\[CrossRef\]](#)
54. EN12390-3; Testing Hardened Concrete. Part 3: Compressive Strength of Test Specimens. CEN—European Committee for Standardisation: Brussels, Belgium, 2019.
55. Lothenbach, B.; Durdziński, P.; De Weerd, K. Thermogravimetric Analysis. In *A Practical Guide to Microstructural Analysis of Cementitious Materials*; Scrivener, K., Snellings, R., Lothenbach, B., Eds.; Taylor & Francis Group: Boca Raton, FL, USA, 2016; pp. 177–211.
56. Bhatti, J.I. Hydration versus Strength in a Portland Cement Developed from Domestic Mineral Wastes—A Comparative Study. *Thermochim. Acta* **1986**, *106*, 93–103. [\[CrossRef\]](#)
57. Wong, H.S.; Buenfeld, N.R. Determining the Water-Cement Ratio, Cement Content, Water Content and Degree of Hydration of Hardened Cement Paste: Method Development and Validation on Paste Samples. *Cem. Concr. Res.* **2009**, *39*, 957–965. [\[CrossRef\]](#)
58. Shui, Z.; Xuan, D.; Chen, W.; Yu, R.; Zhang, R. Cementitious Characteristics of Hydrated Cement Paste Subjected to Various Dehydration Temperatures. *Constr. Build. Mater.* **2009**, *23*, 531–537. [\[CrossRef\]](#)
59. Monteagudo, S.M.; Moragues, A.; Gálvez, J.C.; Casati, M.J.; Reyes, E. The Degree of Hydration Assessment of Blended Cement Pastes by Differential Thermal and Thermogravimetric Analysis. Morphological Evolution of the Solid Phases. *Thermochim. Acta* **2014**, *592*, 37–51. [\[CrossRef\]](#)
60. Deboucha, W.; Leklou, N.; Khelidj, A.; Oudjit, M.N. Hydration Development of Mineral Additives Blended Cement Using Thermogravimetric Analysis (TGA): Methodology of Calculating the Degree of Hydration. *Constr. Build. Mater.* **2017**, *146*, 687–701. [\[CrossRef\]](#)
61. Meziani, M.; Chelouah, N.; Amiri, O.; Leklou, N. Blended Cement Hydration Assessment by Thermogravimetric Analysis and Isothermal Calorimetry. *MATEC Web Conf.* **2018**, *149*, 01062. [\[CrossRef\]](#)
62. Lam, L.; Wong, Y.L.; Poon, C.S. Degree of Hydration and Gel/Space Ratio of High-Volume Fly Ash/Cement Systems. *Cem. Concr. Res.* **2000**, *30*, 747–756. [\[CrossRef\]](#)
63. Pane, I.; Hansen, W. Investigation of Blended Cement Hydration by Isothermal Calorimetry and Thermal Analysis. *Cem. Concr. Res.* **2005**, *35*, 1155–1164. [\[CrossRef\]](#)
64. Snellings, R. X-ray Powder Diffraction Applied to Cement. In *A Practical Guide to Microstructural Analysis of Cementitious Materials*; Scrivener, K., Snellings, R., Lothenbach, B., Eds.; Taylor & Francis Group: Boca Raton, FL, USA, 2016; pp. 107–176.
65. Garboczi, E.J.; Bentz, D.P.; Snyder, K.A.; Martys, N.S.; Stutzman, P.E.; Ferraris, C.F.; Bullard, J.W. *Modeling and Measuring the Structure and Properties of Cement-Based Materials*; National Institute of Standards and Technology: Gaithersburg, MD, USA, 2014.
66. Bentz, D.P. NISTIR 7232. CEMHYD3D: A Three-Dimensional Cement Hydration and Microstructure Development Modeling Package, Version 3.0; NIST—National Institute of Standards and Technology: Gaithersburg, MD, USA, 2005.
67. Sun, J.; Huang, Y. Modeling the Simultaneous Effects of Particle Size and Porosity in Simulating Geo-Materials. *Materials* **2022**, *15*, 1576. [\[CrossRef\]](#)
68. Liao, W.; Sun, X.; Kumar, A.; Sun, H.; Ma, H. Hydration of Binary Portland Cement Blends Containing Silica Fume: A Decoupling Method to Estimate Degrees of Hydration and Pozzolanic Reaction. *Front. Mater.* **2019**, *6*, 78. [\[CrossRef\]](#)
69. Liu, Z.; Xu, D.; Zhang, Y. Experimental Investigation and Quantitative Calculation of the Degree of Hydration and Products in Fly Ash-Cement Mixtures. *Adv. Mater. Sci. Eng.* **2017**, *2017*, 2437270. [\[CrossRef\]](#)
70. Powers, T.C.C. Structure and Physical Properties of Hardened Portland Cement Paste. *J. Am. Ceram. Soc.* **1958**, *41*, 1–6. [\[CrossRef\]](#)
71. Schiller, K.K. Strength of Porous Materials. *Cem. Concr. Res.* **1971**, *1*, 419–422. [\[CrossRef\]](#)
72. Odler, I.; Röfler, M. Investigations on the Relationship between Porosity, Structure and Strength of Hydrated Portland Cement Pastes. II. Effect of Pore Structure and of Degree of Hydration. *Cem. Concr. Res.* **1985**, *15*, 401–410. [\[CrossRef\]](#)

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