



HAL
open science

Thermogravimetric analysis (TGA) for characterization of self-cementation of recycled concrete aggregates in pavement

Chong Wang, Cyrille Chazallon, Sandrine Braymand, Pierre Hornyh

► **To cite this version:**

Chong Wang, Cyrille Chazallon, Sandrine Braymand, Pierre Hornyh. Thermogravimetric analysis (TGA) for characterization of self-cementation of recycled concrete aggregates in pavement. *Thermochimica Acta*, 2024, 733, pp.179680. 10.1016/j.tca.2024.179680 . hal-04408957

HAL Id: hal-04408957

<https://hal.science/hal-04408957v1>

Submitted on 22 Jan 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

Thermogravimetric analysis (TGA) for characterization of self-cementation of recycled concrete aggregates in pavement

Chong Wang^a, Cyrille Chazallon^{a, b, *}, Sandrine Braymand^c, Pierre Hornych^d

^a ICUBE, UMR 7357, CNRS, Université de Strasbourg, INSA de Strasbourg, Strasbourg, France; ^b Laboratory of Rd. and Traffic Engineering, Shandong Jianzhu University, Jinan, People's Republic of China; ^c ICUBE, UMR 7357, CNRS, Université de Strasbourg, INSA de Strasbourg, Illkirch Cedex, France; ^d MAST-LAMES, Gustave Eiffel University, Nantes Campus, Bouguenais, France

ABSTRACT: A key question concerning the reuse of recycled concrete aggregates (RCA) in unbound pavement base and subbase layers is the assessment of self-cementing properties, which can improve significantly their performance. In this paper, the self-cementing properties and their influence on the long-term performance, microstructure and mechanical behavior, were studied by subjecting two different RCA (NRCA and ORCA) specimens, after different curing times (1 and 360 days), to thermogravimetric analysis (TGA), scanning electron microscopic analysis (SEM) and monotonic triaxial tests ($\sigma_3=20, 40$ and 70 kPa). The chemical properties, such as pH value, sulfate content and calcite content, were also investigated. The results show that the unhydrated cement content, responsible for the self-cementing properties of RCA, is low (6.0-7.6% in fine NRCA). However, after curing for 360 days, around half of the unhydrated cement (36% to 45%) was hydrated. The hydration products not only form bonds and fill the macro-pores (width less than $3 \mu\text{m}$) between particles, but also consume and decrease the free water content of RCA specimens, turning the open type of soil structure to a rigid tight skeleton structure, increasing both the strength and stiffness of RCA specimens.

KEY WORDS: Recycled concrete aggregate; Self-cementing properties; Thermogravimetric analysis; Microstructure; Road base

1 INTRODUCTION

Economic and human activities produce a lot of construction and demolition wastes (CDW) each year, occupying a large land space and imposing huge pressures on environment when depositing CDW in landfills. In Europe, over one third of the total waste produced is CDW (over 800 million tons in 2018) (Eurostat, 2018). In terms of CDW, concrete wastes are the main components and represent up to 75% of total CDW by weight (Nwakaire et al., 2020). To overcome these problems, recycling and reuse of concrete wastes in pavement base and subbase layers has become a topic of global concerns in recent years (Lu et al., 2021; Saberian et al., 2018; Sobhan et al., 2016; Yaghoubi et al., 2018).

It is well known that concrete structures contain partially unhydrated cement even after long term service (Lin & Meyer, 2009; Mills, 1966). However, the crushing process to produce recycled concrete aggregates (RCA) can expose these unhydrated cement particles (Amin et al.,

2016). Subsequently, when RCA are used in unbound base and subbase layers, instead of a cementitious matrix, this unhydrated cement could hydrate with moisture and create bonds between particles, increasing the strength and stiffness of the pavement layers, which is believed to be the principal reason of self-cementing properties of RCA (Bestgen et al., 2016; Bordy et al., 2017; Oksri-Nelfia et al., 2016; Poon et al., 2006).

Several approaches can be used to assess the self-cementing properties of RCA, such as the semi-adiabatic calorimeter test, thermogravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electron microscope (SEM) observations (Bordy et al., 2017; Kalinowska-Wichrowska et al., 2020; Oksri-Nelfia et al., 2016; J. J. Wang et al., 2018). Among these methods, TGA is favored by some researchers because it allows quantitative analysis (Bordy et al., 2017; Oksri-Nelfia et al., 2016). Oksri-Nelfia et al. (2016) proposed a model to quantify the unhydrated cement content in RCA, prepared with Portland cement, based on the portlandite (Ca(OH)_2) content obtained by TGA. The result revealed that the unhydrated cement content was very low in the studied RCA (2.3%). However, the Ca(OH)_2 content is easily influenced by the type of cement, carbonation and the use of supplementary cementing materials (Papadakis, 1999a, 1999b), which limits the application of this model.

Some researchers have studied the influence of self-cementing properties on the long-term performance of RCA (Amin et al., 2016; Kim et al., 2014; Poon et al., 2006). Arm (2001) found that the increase of strength and stiffness in unbound base and subbase layers caused by self-cementing properties is highest in the first few months. Poon et al. (2006) pointed out that the unhydrated cement content in fine aggregates (0-0.6 mm) is the principal cause of self-cementing properties. Jitsangiam et al. (2015) observed that the unbound RCA specimens evolved into bound specimens after 360 days of curing, as indicated by the microstructure analyses (SEM). To date, however, the mechanisms, and effect on the long-term performance, of self-cementing has not been thoroughly studied.

As a result, this study aims to assess these self-cementing properties and their influence on the improvement of long-term performance (microstructure and mechanical behavior). The chemical properties of two different RCA (NRCA and ORCA), such as pH value, sulfate content and calcite content, were firstly investigated. An improved model based on TGA was then proposed to quantify the unhydrated cement content of RCA. Then, the hydration of unhydrated cement and the influence of self-cementing properties on the microstructure and mechanical behavior of the two RCA (NRCA and ORCA), after 1 day and 360 days of curing, were studied by TGA, SEM and monotonic triaxial tests ($\sigma_3=20, 40$ and 70 kPa). Furthermore, the mechanisms leading to long-term performance improvement of RCA were also analyzed.

2 MATERIALS AND METHODS

2.1 Materials

The two RCA materials used in this study were sourced from different demolished buildings with unknown compositions, instead of casting and curing in the laboratory, using known component, which is more realistic. The two studied RCA were crushed by impact crushers in two recycling plants in France with a 20 mm maximum particle size:

— One RCA was crushed in 2020 at the beginning of the study (New RCA) at a recycling plant in Strasbourg, France, and is designated by NRCA.

— The other RCA was crushed in 2012 at a recycling plant in Gonesse, France, and stored outdoor in plastic bags to prevent further humidity and carbonation, and is designated by ORCA (for Old RCA). The long-term storage was expected to largely reduce the self-cementing properties of ORCA (Kim et al., 2014), so the two materials were expected to present different self-cementing properties.

Figure 1 and Figure 2 show the particle size distributions and modified Proctor curves of NRCA and ORCA. More physical properties of the studied materials can be found in C. Wang et al. (2022).

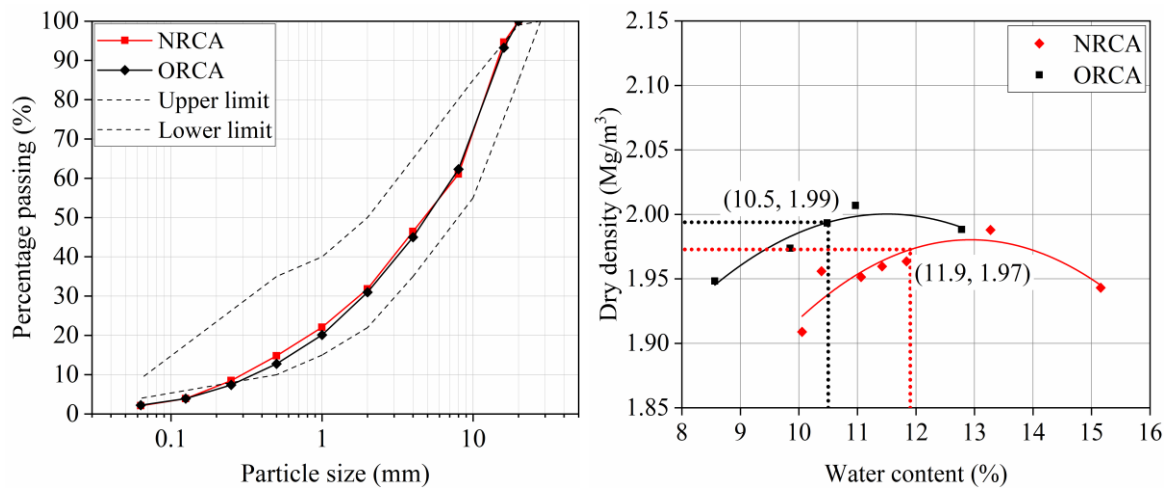


Figure 1. Particle size distributions of NRCA and ORCA.

Figure 2. Modified Proctor curves of NRCA and ORCA.

2.2 Test methods

The pH value, water soluble sulfate content and calcite content of RCA were measured to characterize the chemical composition and carbonation of RCA. To avoid the influence of original natural aggregates in RCA on the results, only fine aggregates (0-2 mm), previously dried in the oven at 60 °C (in order to avoid damaging RCA) to a constant mass, were used, since the small particles contain less original natural aggregates (Juan & Gutierrez, 2009) and govern the self-cementing properties of RCA (Poon et al., 2006).

For pH value measurement, 30 g of RCA fine aggregates and 75 g of distilled water were mixed and stirred for 2 minutes (BS 1377-3, 2018). Then, the pH value of each suspension, stored for 24 h, was measured by a pH meter.

Water soluble sulfate content of RCA was measured in accordance with the European standard NF EN 1744-1 (2014). 1 kg of previously heated (60 °C) distilled water was added to 25 g of fine aggregates, and the mixture was stirred for 15 minutes, while maintaining the temperature of 60 °C. Then, the solution was extracted using a filter and the water soluble sulfate content was measured by a photometer.

Calcite content was measured by the calcimeter method (NF ISO 10693, 1995) to assess the degree of carbonation of the two RCA, before use, especially for the ORCA after long-term storage. 0.5-2 g of powder from ground fine aggregates were first added to 10 ml of chlorhydric

acid and the volume of released carbon dioxide was measured. Then, the calcite content was calculated according to the measured volume of carbon dioxide.

Thermogravimetric analysis (TGA) was conducted to quantify the phases content of RCA, which were used to quantify unhydrated cement content in this study. In addition, to study the hydration of unhydrated cement during the curing stage, fine aggregates, extracted from the samples cured during 360 days, after monotonic triaxial tests, were also subjected to TGA. 50-100 mg of air-dried specimen, without curing and cured for 360 days, were heated at a constant heating rate of 10 °C/min from 25 °C to 1000 °C under N₂ atmosphere.

Scanning electron microscopic analysis (SEM) was conducted to inspect the microstructures of RCA without curing and cured for 360 days. SEM samples were collected from the specimens after monotonic triaxial tests and coated with gold prior to SEM analysis.

The monotonic triaxial tests were performed under different confining pressures (20, 40 and 70 kPa), and after 1 day and 360 days of curing. The tests were performed at a shear rate of 0.3 mm/min until failure. All the samples were compacted with a vibrating hammer, to the maximum dry density at the specific water content (optimum moisture content minus 1%), corresponding to 11.9% and 10.5% for NRCA and ORCA, respectively, as shown in Figure 2. Then, the specimens were wrapped in plastic foils and stored indoors at a temperature of 18 ± 5 °C, during 1 or 360 days.

2.3 Methods to determine the unhydrated cement content by TGA

Non-evaporable water content (C_{water}) and portlandite ($\text{Ca}(\text{OH})_2$) content, corresponding to the hydration of cement, are usually considered as suitable indicators of cement hydration (Taylor, 1997). In comparison to $\text{Ca}(\text{OH})_2$ which is easily influenced by the type of cement, carbonation and the supplementary cementing materials as mentioned above (Papadakis, 1999a, 1999b), non-evaporable water is much less sensitive to these factors (Chidiac & Shafikhani, 2019; Pane & Hansen, 2005), which increases the accuracy and reliability of the proposed model. Thus, C_{water} was used to calculate the unhydrated cement content of RCA in this study, instead of portlandite ($\text{Ca}(\text{OH})_2$) content used by Oksri-Nelfia et al. (2016). Note that the non-evaporable water, retained after freeze-drying, has often been wrongly identified with chemically bound water, present in interlayer spaces, which determination is complicated (Taylor, 1997). Figure 3 and Figure 4 show the derivative thermogravimetry (DTG) and thermogravimetry (TG) curves of NRCA and ORCA before curing. According to the endothermic peaks on the DTG curve (Figure 3), the decomposition of hydration products of NRCA can be divided into four major phases (Monteagudo et al., 2014; Ramachandran et al., 2002). The first phase between 0 and 105 °C represents the evaporation of free water. The second phase, between 105 and 430 °C, and third phase, between 430 and 490 °C (T_1), correspond to the decomposition of hydration products, such as calcium silicate hydrates (C-S-H), ettringite, gypsum and calcium hydroxide, which are used to calculate non-evaporable water C_{water} . The last phase, with the DTG peak between 490 to 850 °C (T_2), caused by the decomposition of calcite, was also used to determine the calcite content (C_{CaCO_3}) and compared with the calcimeter method. It should be mentioned that different materials may have a slightly different decomposition temperature instead of a fixed temperature range. To improve the accuracy of quantification, the corresponding decomposition temperatures (T_1 and T_2) are chosen carefully according to the slope of the DTG

curves, as summarized in Table 1. Then, C_{water} and C_{CaCO_3} can be determined from the TG curves (Figure 4) by:

$$C_{water} = M_{105^\circ C} - M_{T_1^\circ C} \quad (1)$$

$$C_{CaCO_3} = \frac{100.09}{44.01} (M_{T_1^\circ C} - M_{T_2^\circ C}) \quad (2)$$

where the ratio 100.09/44.01 corresponds to the molar mass ratio of $CaCO_3/CO_2$, while $M_{T^\circ C}$ is the sample weight (%) obtained from the TG curve at temperature $T^\circ C$. C_{water} and C_{CaCO_3} are the non-evaporable water content and calcite content.

After determining C_{water} from the TG curve, the cement content (C_{cement}) of RCA can be calculated according to the hydration process of cement. For that, it is assumed that a complete hydration of Portland cement, without any supplementary cementing materials (SCMs), such as fly ash, silica fume, etc., will release around 0.23-0.25 gram of non-evaporable water (taken as 0.24 in this study), per gram of cement (Bhatty, 1986; Mounanga et al., 2004; Pane & Hansen, 2005). Then, the relationship between C_{water} and cement content (C_{cement}) of RCA made with Portland cement can be expressed as:

$$C_{water} = 0.24 \times \alpha \times C_{cement} \quad (3)$$

where C_{water} and C_{cement} are the non-evaporable water content and Portland cement content in RCA, respectively. α is the degree of cement hydration. For concrete, after a long service life, the ultimate degree of cement hydration is mainly influenced by the initial water cement ratio (w/c), and can be calculated by the following equation developed by Mills (1966) which is frequently used to model cement hydration (Lin & Meyer, 2009; Oksri-Nelfia et al., 2016):

$$\alpha = \frac{1.031 * \frac{w}{c}}{0.194 + \frac{w}{c}} \quad (4)$$

As mentioned before, 0.23-0.25 gram of non-evaporable water is released per gram of fully hydrated Portland cement (CEM I type). Whereas for blended cement, the use of SCMs makes it difficult to estimate such values due to the unknown stoichiometry and type of SCMs (Deboucha et al., 2020). To implement this methodology for blended cements, the SCMs are considered by their equivalent in Portland cement, using the k -value concept (Deboucha et al., 2020; NF EN 206-1, 2004; Papadakis et al., 2002). With this approach, the unknown released non-evaporable water for blended cement can be considered as the same as the Portland cement (0.23-0.25 gram). In fact, this concept makes it possible to simply quantify the contributions of SCMs on the hydration of blended cements. Table 2 summarizes the k values for different types of SCMs. The equivalent binder content (C_{binder}) can be expressed as:

$$C_{binder} = C_{cement} + k * C_{SCMs} \quad (5)$$

Then, Equation (3) can be substituted by:

$$C_{water} = 0.24 \times \alpha \times C_{binder} \quad (6)$$

Finally, the unhydrated binder content ($C_{unhydrated}$) of NRCA can be determined as follows:

$$C_{unhydrated} = (1 - \alpha) \times C_{binder} \quad (7)$$

It should be mentioned that the carbonation of concrete can decrease the calculated C_{binder} and $C_{unhydrated}$ values, by decreasing the non-evaporable water content. However, the influence of

carbonation was not considered in this study as the high pH value of NRCA (13.07) suggested that carbonation of NRCA is negligible, which will be illustrated hereafter.

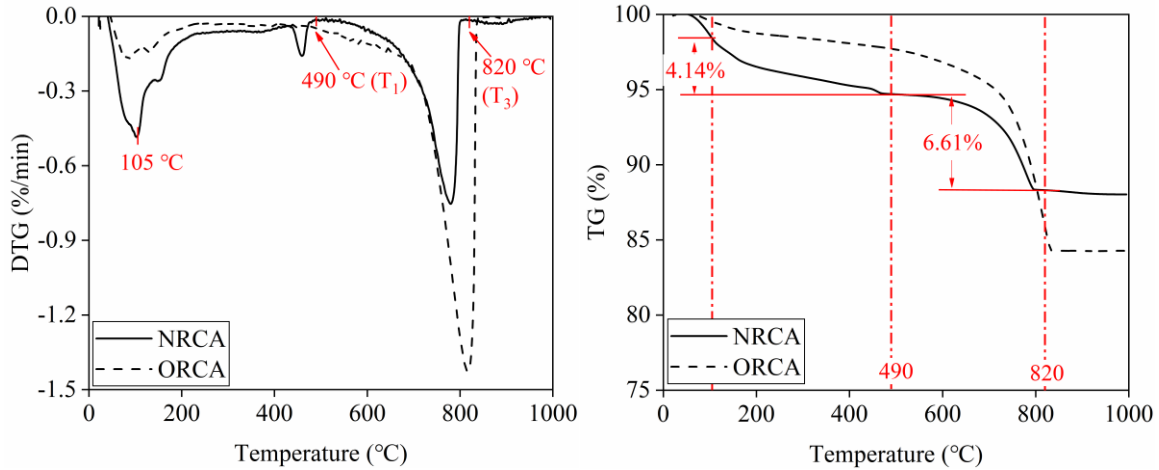


Figure 3. DTG curves of NRCA and ORCA without curing.

Figure 4. TG curves of NRCA and ORCA without curing.

Table 1. Decomposition temperatures of different phases for NRCA and ORCA.

Temperature/°C	NRCA (no curing)	NRCA (curing 360 days)	ORCA (no curing)	ORCA (curing 360 days)
T_1	490	490	470	470
T_2	820	830	840	860

Table 2. k values for different types of supplementary cementing materials.

Additive	Limestone filler	Blast furnace slag	Silica fume	Fly ash	
				CEM I 32.5	≥ CEM I 42.5
k value	0.25	0.9	2	0.2	0.4

3 RESULTS AND DISCUSSION

3.1 Chemical compositions

Table 3 shows the pH values, water soluble sulfate contents and calcite contents of NRCA and ORCA. Although the pH value cannot be related to the self-cementing properties of RCA directly, many scholars still use it to evaluate the self-cementing properties as it can be measured easily and quickly (Bestgen et al., 2016; Paige-Green, 2010; Poon et al., 2006). In fact, a high pH value implies more soluble alkaline hydration products, suggesting that the RCA were not completely carbonated and may contain some unhydrated cement. The results show that the pH value of NRCA (13.07) is much higher than that of ORCA (10.53). Paige-Green (2010) observed that RCA with a pH value higher than 11 exhibits self-cementing properties, indicating that NRCA should present self-cementing properties while those of ORCA should be negligible. This is consistent with the observations of Kim et al. (2014) who concluded that the self-cementing properties of RCA fines, stored in open stockpiles at high temperature and humidity, are negligible. Besides, Chang and Chen (2006) indicated that the concrete is not carbonated when the pH value (solid/water=1:10) is higher than 11.5, suggesting that

carbonation of NRCA is negligible while ORCA is highly carbonated due to the long-term storage.

Sulfate attack is a frequent deterioration mechanism of hydraulically bound materials, which leads to an expansion in solid volume by forming gypsum or ettringite (Hewlett & Liska, 2019; Kampala et al., 2021). According to the European standard NF EN 13285 (2018) and the French national and regional technical guides (CETE de l'Est, 2009; UNICEM IDF, 2003), the water soluble sulfate content of RCA, used in pavement base and subbase layers, should be less than 0.7%. Test results indicate that the water soluble sulfate content of both NRCA and ORCA are under this limit, although the water soluble sulfate content of NRCA (0.23%) is higher than that of ORCA (0.13%).

Table 3 also shows that the calcite content of NRCA (14.7%), measured by the calcimeter method, is only half that of ORCA (29.97%). This can be attributed to the long-term storage of ORCA and a large specific surface area after crushing, increasing the degree of carbonation while decreasing the pH value of ORCA, although ORCA was stored in plastic bags to prevent humidity and carbonation. However, part of the CaCO_3 could also come from the original natural aggregates (NA), although an effort was made to eliminate the influence of original NA by limiting the maximum particle size (2mm).

Table 3. Chemical compositions of NRCA and ORCA.

Properties	NRCA	ORCA	Limitation
pH value	13.07	10.53	No
Water soluble sulfate content/%	0.23	0.13	0.7
Calcite content/%	14.7	29.97	No

3.2 Unhydrated binder content

Since ORCA were stored for a long period before use (without curing), the partial unhydrated cement has already hydrated, resulting in a much higher α , which cannot be calculated by Equation (4). Besides, the high degree of carbonation of ORCA, as mentioned above, also decreases the accuracy of the proposed method. Thus, only C_{cement} of NRCA could be calculated in this study. To calculate the unhydrated binder content of NRCA, **Erreur ! Référence non valide pour un signet.** summaries the weight loss (%) of the studied materials before use (without curing) under different temperature ranges, as well as C_{water} and C_{CaCO_3} calculated on the basis of TG curves (see Figure 4). It can be observed that C_{water} of NRCA is much higher than that of ORCA, caused by the high degree of carbonation of ORCA after long-term storage. Besides, C_{CaCO_3} calculated by TGA (Table 4) were also compared with the values obtained with the calcimeter method (Table 3). It indicates that the two calculation method lead almost to the same results, showing the reliability of the TGA results.

Subsequently, the equivalent binder content (C_{binder}) and unhydrated binder content ($C_{unhydrated}$) of NRCA can be calculated based on C_{water} . Figure 5 presents the C_{binder} and $C_{unhydrated}$ of NRCA, for varying initial water-cement ratios w/c , because the initial w/c and original composition of the concrete structure are not known. Generally, the typical w/c ratio for conventional concrete ranges from 0.4 to 0.5 (Shi et al., 2015). The typical equivalent binder content is between 15.5% and 21.3% at this specified w/c ratio (0.4-0.5), according to hundreds

of concrete mixture compositions collected from the literature (Ahmad et al., 2021). It appears that within the typical w/c ratio (0.4-0.5), the C_{binder} of NRCA (23.3%-24.9%), calculated using C_{water} , is slightly higher than the typical equivalent binder content (15.5%-21.3%). This could be due to the fact that the tested fine aggregates (0-2 mm) have a higher mortar content than the global concrete (Juan & Gutierrez, 2009), resulting in a higher C_{binder} of NRCA than for a standard concrete. Thus, within the typical w/c ratio (0.4-0.5), the potential unhydrated binder content of NRCA (0-2 mm) can be estimated between 6.0% and 7.6%.

Table 4. Selected components of NRCA and ORCA without curing and after 360 days of curing.

Materials	Curing time /day	Weight loss/%		Non- evaporable water C_{water} /%	CaCO ₃ content C_{CaCO_3} /%
		105- T_1 °C (C_{water})	T_1 - T_2 °C (CaCO ₃)		
NRCA	0	4.14	6.61	4.14	15.04
	360	4.79	9.46	4.79	21.52
ORCA	0	2.10	13.78	2.10	31.34
	360	2.02	14.28	2.02	32.47

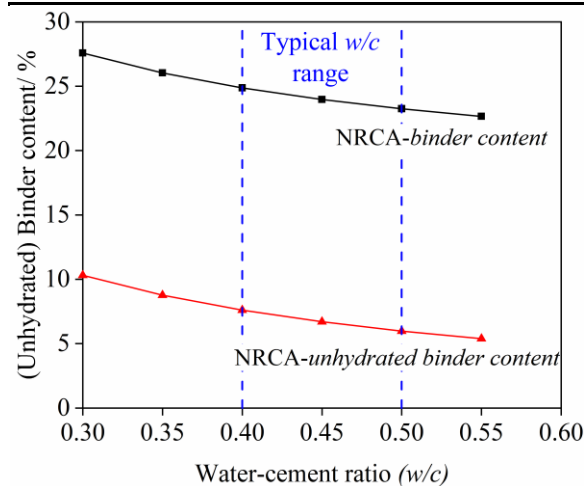


Figure 5. Binder content and unhydrated binder content of NRCA calculated by C_{water} and C_{CH} for varying w/c .

3.3 Hydration of unhydrated cement

To study the hydration of unhydrated cement during the curing phase, the fine aggregates of NRCA and ORCA (0-2mm), extracted from the cured samples (360 days) after monotonic triaxial tests, were also subjected to TGA. The comparison of the TG-DTG curves of NRCA and ORCA without curing and after curing for 360 days are presented in Figure 6. A significant increase of mass loss (TG/%) of NRCA after curing for 360 days can be observed, which is believed to be related to the hydration of unhydrated cement, increasing the non-evaporable water content. On the contrary, for ORCA, this increase of mass loss is negligible, in agreement with the negligible self-cementing properties of ORCA, indicated by the low pH value. Table 4 also summarizes the mass loss for different temperature ranges and the corresponding components (non-evaporable water and CaCO₃) of NRCA and ORCA after curing for 360 days.

Afterwards, the variation of non-evaporable water and CaCO₃ contents of NRCA and ORCA before and after curing for 360 days can be obtained, as presented in Table 5. The amount of

initially unhydrated binder, that was hydrated during the 360 days curing phase, named hydrated binder content, can be calculated by Equation (6) according to the variation of non-evaporable water content (α equal to 1), also summarized in Table 5. It appears that a slight increase of non-evaporable water (0.65%) can be observed for NRCA after 360 days of curing, indicating that some initially unhydrated binder (2.7%) was hydrated during the curing phase, leading to self-cementing properties. While for ORCA, no obvious variation of non-evaporable water is observed. These behaviors are in good agreement with the observed self-cementing properties of NRCA and ORCA.

Table 5 also reveals that the CaCO_3 content of both NRCA and ORCA increases after curing for 360 days, but that this increase is much higher for NRCA, which could be attributed to the carbonation. Note that the undried NRCA, after monotonic triaxial test, was not subjected to TGA immediately, but that it was stored in a plastic bag without good seal for another month. Under humid environment, especially for RCA which specific surface area is large, the CO_2 present in air dissolves quickly and the carbonation rate is maximum (Kurdowski, 2014). Thus, the carbonation could have occurred during the long-term curing or during the storage phase after the monotonic triaxial test. It should be pointed out that the carbonation during the curing stage can increase the strength and stiffness of RCA specimens (Terzis & Laloui, 2019; Zadeh et al., 2021), which could also lead to the observed self-cementing properties of RCA. However, this hypothesis needs to be confirmed by further studies.

In comparison with the total unhydrated binder content of NRCA (0-2 mm) without curing (6-7.6%), between 36% to 45% of the total unhydrated binder (2.7%) were hydrated after curing for 360 days. In other words, it can be estimated that about half of the unhydrated binder could hydrate during the first year after the construction of the pavement, and that the rest will continue to hydrate in the following years, which is in good agreement with Arm (2001). This phenomenon was also observed in several field tests (Korkiala-Tanttu et al., 2014; Lancieri et al., 2006; Y. H. Wang et al., 2016), which indicated that the strength and stiffness of RCA base and subbase layers increases faster in the first few years, and then continue to increase at a lower rate even up to 10 years after construction. Actually, the carbonation of NRCA observed above underestimates the hydration of unhydrated cement (2.7%), by decreasing the amount of non-evaporable water.

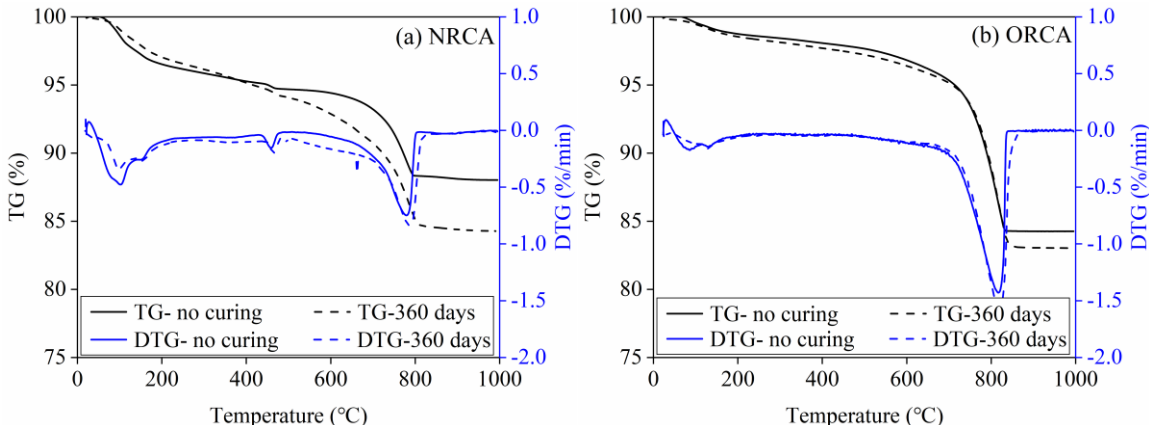


Figure 6. Comparison of TG-DTG curves of RCA without curing and after curing for 360 days: (a) NRCA; (b) ORCA.

Table 5. Variation of selected components and hydrated binder content of NRCA and ORCA .

Materials	ΔC_{water} /%	ΔC_{CaCO_3} /%	Hydrated binder content /%
NRCA	0.65	6.48	2.70
ORCA	-0.08	1.13	-0.34

3.4 Microstructural characteristics

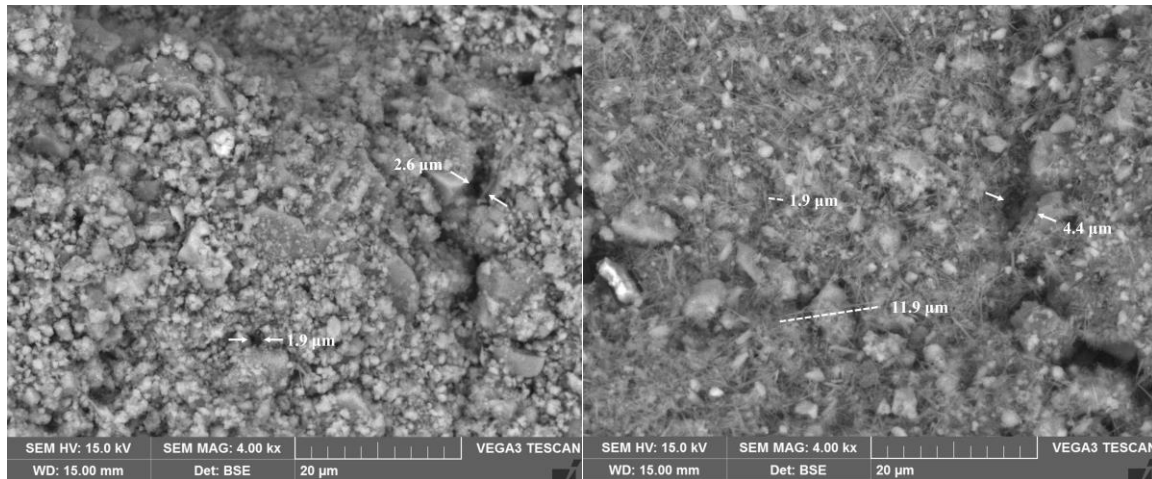
The microstructures of NRCA after 1 and 360 days of curing are presented in Figure 7. Owing to the fact that the self-cementing properties of ORCA are negligible, and that no new hydration products were formed, only the microstructure of NRCA was studied. As shown in Figure 7 (a), NRCA cured for 1 day exhibits a relatively open type of microstructure, with numerous fine particles assembled between coarse aggregates, leaving many different void sizes.

The SEM image of NRCA cured for 360 days (Figure 7 (b)) shows the influence of self-cementing properties on the microstructures of RCA specimens. It appears that the microstructure of NRCA after 360 days of curing is much denser, with a visible decrease of the number and size of small voids (width less than 3 μm). For the larger voids (width larger than 3 μm), the influence of the self-cementing properties on the microstructures appears limited. A compacted soil presents two different types of pores: micro-pores (within aggregates) and macro-pores (between aggregates), with a delimiting diameter around 0.65 μm for micro- and macro-pores (Su et al., 2022). The hydration products of unhydrated cement not only act as bonds between particles, but also fill the voids between particles (macro-pores), as seen in Figure 7 (b), confirmed by the observation made in this study. However, for large pores (large than 3 μm), the low amount of hydration production limits the bonding and filling effects. As a result, the small pores (width less than 3 μm) were filled and the open type of structure (curing 1 day) gradually turns to rigid tight skeleton structure (curing 360 days), increasing the strength and stiffness of RCA and turning unbound pavement layers to the bound layers.

Among the hydration products, it is possible to observe on figure 7 that numerous needle-shaped hydration products, ettringite, between few and ten μm long, are formed after 360 days of curing, associated with a decrease of the amount of fine particles. This ettringite ($\text{Ca}_6\text{Al}_2(\text{OH})_{12} \cdot (\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$) absorbs a large amount of water and has a large volume, filling the voids between particles. Furthermore, it can be observed that most of these ettringite needles are small (less than 10 μm long), and that only a few large ettringite needles are visible (Figure 7 (b)). In general, there are two types of ettringite: large ettringite (10-100 μm long) and small ettringite (typically 1-2 μm long) (Mehta, 1983). One explanation is that these small needle-shaped ettringite particles are formed by the reactions between sulfate and cement hydration products (Hewlett & Liska, 2019; Kampala et al., 2021), such as hydrated calcium aluminates. The low water soluble sulfate content of NRCA (0.23%) limits the growth and the size of the ettringite. In addition, the hydration of unhydrated cement can also lead to formation of ettringite.

Despite the water soluble sulfate content of NRCA (0.23%), which is much lower than the limit of the European standard (0.7%), as mentioned above, many small ettringite needles were

still formed. It should be mentioned that once the voids are fully filled by the hydration products of unhydrated cement and ettringite, the continuous formation of ettringite can lead to swelling and cracking of the structure, known as sulfate attack of concrete (Mehta, 1983), decreasing the strength and stiffness of RCA base and subbase layers. Although this phenomenon has not been observed yet in this study, the sulfate content of RCA should be strictly limited when RCA are used in unbound or bound pavement layers.



(a) 1 day (b) 360 days

Figure 7. SEM images of NRCA after 1day and 360 days of curing: (a) 1 day; (b) 360 days.

3.5 Mechanism of strength and stiffness development

Figure 8 presents the results of the monotonic triaxial tests performed on the two recycled concretes, in terms of maximum shear strength, and secant modulus E_{50} . The test were performed with 3 different confining pressures (20, 40 and 70 kPa), and after 1 day and 360 days of curing. For NRCA, the shear strength and stiffness increase significantly (approximately by a factor of two) after 360 days of curing, confirming its strong self-cementing properties. On the contrary, the strength and stiffness of ORCA remain almost constant, despite the sulfate content (0.13%) and carbonation (Table 5) observed in ORCA. It indicates that the hydration of unhydrated cement is the predominant cause of self-cementing properties.

These results indicate that the self-cementing mechanism is complex. On the one hand, the unhydrated cement, especially in fine aggregates, hydrates with moisture, as indicated by TGA (Table 5). The hydration products not only form bonds between particles, but also fill the small voids (width less than 3 μm), modifying the unbound, open structure into a stiffer, dense skeleton structure (Figure 7). In addition, the consumption of moisture due to the hydration process decreases the free water content (Table 5), which can also improve the mechanical properties of RCA specimens (Gaillard et al., 2019; Jing et al., 2019; Su et al., 2020). Furthermore, the sulfate present in the RCA, which leads to the formation of ettringite and the carbonation of RCA during the curing phase, can also contribute to the self-cementing properties of RCA. However, the effects of sulfate and carbonation on self-cementing appear limited, compared with the hydration of unhydrated cement, which needs to be confirmed by further studies.

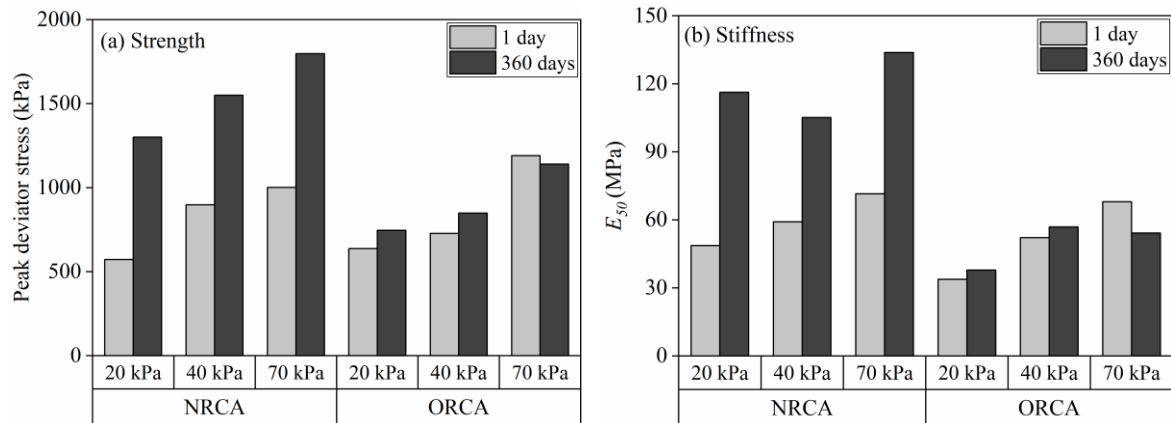


Figure 8. Development of strength and stiffness of RCA for different confining pressures (20/40/70 kPa), after 1 day and 360 days of curing : (a) Shear strength; (b) Stiffness.

4 CONCLUSIONS

This study investigated the self-cementing properties of RCA, used as unbound granular materials, and their influence on the improvement of long-term performance, in terms of microstructure and mechanical behavior. The chemical properties of two different RCA (NRCA and ORCA), including the pH value, sulfate content and calcite content, were firstly studied. Then, a model based on the non-evaporable water was proposed to quantify the unhydrated cement content. To study the hydration process of unhydrated cement, and its effect on the microstructure and on the mechanical behaviour, fresh RCA specimen (cured for 1 day), and specimen cured for 360 days were tested, using different methods : TGA, SEM and monotonic triaxial tests. Based on these results, the self-cementing mechanisms were discussed . The following conclusions can be drawn from this research:

1. The first material, NRCA, was recently crushed, and presented self-cementing properties. This was in agreement with its high pH value (13.07).
2. The second material, ORCA, crushed in 2012 and submitted to long term storage, presented only negligible cementation. It was found to be highly carbonated, resulting in a low pH value (10.53) and high calcite content (29.97%).
3. Although the water soluble sulfate contents of both NRCA (0.23%) and ORCA (0.13%) were lower than the permitted level (0.7%), sulfate attack products (ettringite) were observed in NRCA.
4. The non-evaporable water content is a good indicator to quantify unhydrated cement content. The potential unhydrated cement content of NRCA fine aggregates (0-2 mm) was estimated between 5.9% and 7.6%.
5. After 360 days of curing, the non-evaporable water content of NRCA increased, while for ORCA, it remained almost constant. For NRCA, almost half of the unhydrated cement (36% to 45%) was hydrated after curing for 360 days, confirming that the self-cementing effect is particularly important during the first year.
6. SEM observations have shown that the hydration products form bonds and fill the small voids between particles (width less than 3 μm), while for big voids (width larger than 3 μm), the filling effect is limited. The initial open granular structure becomes more rigid and more compact after curing 360 days.

7. The shear strength and stiffness of NRCA were multiplied by a factor of about 2 after 360 days of curing for all confining pressures. Conversely, the strength and stiffness of ORCA remained almost constant.
8. The hydration of unhydrated cement is responsible for the self-cementing properties of RCA. In addition, sulfate attack products (ettringite) and the decrease of free water also improve the mechanical behavior of RCA.

5 ACKNOWLEDGMENTS

The authors are grateful to several colleagues from Lorraine university for the laboratory tests, especially to Cecile Dilberto who conducted TGA test, Jean Michel Mechnling who measured soluble sulfate content and Sebastien Roux who measured calcite content by calcimeter method. This work is supported by the China Scholarship Council.

6 REFERENCES

- Ahmad, A., Farooq, F., Niewiadomski, P., Ostrowski, K., Akbar, A., Aslam, F., & Alyousef, R. (2021). Prediction of Compressive Strength of Fly Ash Based Concrete Using Individual and Ensemble Algorithm. *Materials*, 14(4), Article 794. <https://doi.org/10.3390/ma14040794>
- Amin, A., Hasnat, A., Khan, A. H., & Ashiquzzaman, M. (2016). Residual Cementing Property in Recycled Fines and Coarse Aggregates: Occurrence and Quantification. *Journal of Materials in Civil Engineering*, 28(4), Article 04015174. [https://doi.org/10.1061/\(asce\)mt.1943-5533.0001472](https://doi.org/10.1061/(asce)mt.1943-5533.0001472)
- Arm, M. (2001). Self-cementing properties of crushed demolished concrete in unbound layers: results from triaxial tests and field tests. *Waste Management*, 21(3), 235-239. [https://doi.org/10.1016/s0956-053x\(00\)00095-7](https://doi.org/10.1016/s0956-053x(00)00095-7)
- Bestgen, J. O., Hatipoglu, M., Cetin, B., & Aydilek, A. H. (2016). Mechanical and Environmental Suitability of Recycled Concrete Aggregate as a Highway Base Material. *Journal of Materials in Civil Engineering*, 28(9), Article 04016067. [https://doi.org/10.1061/\(asce\)mt.1943-5533.0001564](https://doi.org/10.1061/(asce)mt.1943-5533.0001564)
- Bhatty, J. I. (1986). HYDRATION VERSUS STRENGTH IN A PORTLAND-CEMENT DEVELOPED FROM DOMESTIC MINERAL WASTES - A COMPARATIVE-STUDY. *Thermochimica Acta*, 106, 93-103. [https://doi.org/10.1016/0040-6031\(86\)85120-6](https://doi.org/10.1016/0040-6031(86)85120-6)
- Bordy, A., Younsi, A., Aggoun, S., & Fiorio, B. (2017). Cement substitution by a recycled cement paste fine: Role of the residual anhydrous clinker. *Construction and Building Materials*, 132, 1-8. <https://doi.org/10.1016/j.conbuildmat.2016.11.080>
- BS 1377-3. (2018). Methods of test for soils for civil engineering purposes. Part 3: chemical and electro-chemical testing.
- CETE de l'Est. (2009). *Guides d'utilisation des matériaux lorrains en technique routière - Guide matériaux de démolition*. http://materrio.construction/mediatheque/media/35-guide_materiaux_de_demolition.pdf. http://materrio.construction/mediatheque/media/35-guide_materiaux_de_demolition.pdf
- Chang, C. F., & Chen, J. W. (2006). The experimental investigation of concrete carbonation depth. *Cement and Concrete Research*, 36(9), 1760-1767. <https://doi.org/10.1016/j.cemconres.2004.07.025>

- Chidiac, S. E., & Shafikhani, M. (2019). Cement degree of hydration in mortar and concrete. *Journal of Thermal Analysis and Calorimetry*, 138(3), 2305-2313. <https://doi.org/10.1007/s10973-019-08800-w>
- Deboucha, W., Leklou, N., & Khelidj, A. (2020). Combination effect of limestone filler and slag on hydration reactions in ternary cements. *European Journal of Environmental and Civil Engineering*. <https://doi.org/10.1080/19648189.2020.1825233>
- Eurostat. (2018). *Energy, transport and environment statistics*. <https://ec.europa.eu/eurostat/>
- Gaillard, L., Chazallon, C., Hornych, P., Quezada, J. C., & Raab, C. (2019). Thermo-hydro-mechanical behaviour of cold reclaimed asphalt aggregates without binder addition. *Road Materials and Pavement Design*, 20, S49-S63. <https://doi.org/10.1080/14680629.2019.1587490>
- Hewlett, P., & Liska, M. (2019). *Lea's chemistry of cement and concrete*. Butterworth-Heinemann.
- Jing, P., Nowamooz, H., & Chazallon, C. (2019). Unsaturated mechanical behaviour of a granular material. *Road Materials and Pavement Design*, 20(6), 1429-1451. <https://doi.org/10.1080/14680629.2018.1447506>
- Jitsangiam, P., Boonserm, K., Phenrat, T., Chummuneerat, S., Chindaprasirt, P., & Nikraz, H. (2015). Recycled Concrete Aggregates in Roadways: Laboratory Examination of Self-Cementing Characteristics. *Journal of Materials in Civil Engineering*, 27(10), Article 04014270. [https://doi.org/10.1061/\(asce\)mt.1943-5533.0001245](https://doi.org/10.1061/(asce)mt.1943-5533.0001245)
- Juan, M. S. D., & Gutierrez, P. A. (2009). Study on the influence of attached mortar content on the properties of recycled concrete aggregate. *Construction and Building Materials*, 23(2), 872-877. <https://doi.org/10.1016/j.conbuildmat.2008.04.012>
- Kalinowska-Wichrowska, K., Kosior-Kazberuk, M., & Pawluczuk, E. (2020). The Properties of Composites with Recycled Cement Mortar Used as a Supplementary Cementitious Material. *Materials*, 13(1), Article 64. <https://doi.org/10.3390/ma13010064>
- Kampala, A., Jitsangiam, P., Pimraksa, K., & Chindaprasirt, P. (2021). An investigation of sulfate effects on compaction characteristics and strength development of cement-treated sulfate bearing clay subgrade. *Road Materials and Pavement Design*, 22(10), 2396-2409. <https://doi.org/10.1080/14680629.2020.1753564>
- Kim, J., Nam, B., Behring, Z., & Al Muhit, B. (2014). Evaluation of Recementation Reactivity of Recycled Concrete Aggregate Fines. *Transportation Research Record*(2401), 44-51. <https://doi.org/10.3141/2401-05>
- Korkiala-Tanttu, L., Dettenborn, T., & Forsman, J. (2014). Long-term behavior of crushed concrete in road structure. (Ed.),^(Eds.). 23rd European Young Geotechnical Engineers Conference, August 2014.
- Kurdowski, W. (2014). *Cement and concrete chemistry*. Springer Science & Business.
- Lancieri, F., Marradi, A., & Mannucci, S. (2006, Jun). C&D waste for road construction: long time performance of roads constructed using recycled aggregate for unbound pavement layers. (Ed.),^(Eds.), *WIT Transactions on Ecology and the Environment*. 3rd International Conference on Waste Management and the Environment, Malta.
- Lin, F., & Meyer, C. (2009). Hydration kinetics modeling of Portland cement considering the effects of curing temperature and applied pressure. *Cement and Concrete Research*, 39(4), 255-265. <https://doi.org/10.1016/j.cemconres.2009.01.014>
- Lu, C., Chen, J. Y., Gu, C., Wang, J., Cai, Y. Q., Zhang, T. T., & Lin, G. (2021). Resilient and permanent deformation behaviors of construction and demolition wastes in unbound pavement base and subbase applications. *Transportation Geotechnics*, 28, Article 100541. <https://doi.org/10.1016/j.trgeo.2021.100541>

- Mehta, P. K. (1983). MECHANISM OF SULFATE ATTACK ON PORTLAND-CEMENT CONCRETE - ANOTHER LOOK. *Cement and Concrete Research*, 13(3), 401-406. [https://doi.org/10.1016/0008-8846\(83\)90040-6](https://doi.org/10.1016/0008-8846(83)90040-6)
- Mills, R. H. (1966). Factors influencing cessation of hydration in water cured cement pastes. *Highway Research Board*(90).
- Monteagudo, S. M., Moragues, A., Gavez, J. C., Casati, M. J., & Reyes, E. (2014). The degree of hydration assessment of blended cement pastes by differential thermal and thermogravimetric analysis. Morphological evolution of the solid phases. *Thermochimica Acta*, 592, 37-51. <https://doi.org/10.1016/j.tca.2014.08.008>
- Mounanga, P., Khelidj, A., Loukili, A., & Baroghel-Bouny, W. (2004). Predicting Ca(OH)₂ content and chemical shrinkage of hydrating cement pastes using analytical approach. *Cement and Concrete Research*, 34(2), 255-265. <https://doi.org/10.1016/j.cemconres.2003.07.006>
- NF EN 206-1. (2004). Concrete — Part 1: Specification, performance, production and conformity
- NF EN 1744-1. (2014). Tests for chemical properties of aggregates — Part 1: Chemical analysis
- NF EN 13285. (2018). Unbound mixtures - Specifications.
- NF ISO 10693. (1995). Soil quality---determination of carbonate content---volumetric method. Association Française de Normalisation ed Paris.
- Nwakaire, C. M., Yap, S. P., Onn, C. C., Yuen, C. W., & Ibrahim, H. A. (2020). Utilisation of recycled concrete aggregates for sustainable highway pavement applications; a review. *Construction and Building Materials*, 235, Article 117444. <https://doi.org/10.1016/j.conbuildmat.2019.117444>
- Oksri-Nelfia, L., Mahieux, P. Y., Amiri, O., Turcry, P., & Lux, J. (2016). Reuse of recycled crushed concrete fines as mineral addition in cementitious materials. *Materials and Structures*, 49(8), 3239-3251. <https://doi.org/10.1617/s11527-015-0716-1>
- Paige-Green, P. (2010, 16 - 19 August 2010). *Preliminary evaluation of the reuse of cementitious materials*. 29th Annual Southern African Transport Conference, Pretoria, South Africa.
- Pane, I., & Hansen, W. (2005). Investigation of blended cement hydration by isothermal calorimetry and thermal analysis. *Cement and Concrete Research*, 35(6), 1155-1164. <https://doi.org/10.1016/j.cemconres.2004.10.027>
- Papadakis, V. G. (1999a). Effect of fly ash on Portland cement systems Part I. Low-calcium fly ash. *Cement and Concrete Research*, 29(11), 1727-1736. [https://doi.org/10.1016/s0008-8846\(99\)00153-2](https://doi.org/10.1016/s0008-8846(99)00153-2)
- Papadakis, V. G. (1999b). Experimental investigation and theoretical modeling of silica fume activity in concrete. *Cement and Concrete Research*, 29(1), 79-86. [https://doi.org/10.1016/s0008-8846\(98\)00171-9](https://doi.org/10.1016/s0008-8846(98)00171-9)
- Papadakis, V. G., Antiohos, S., & Tsimas, S. (2002). Supplementary cementing materials in concrete - Part II: A fundamental estimation of the efficiency factor. *Cement and Concrete Research*, 32(10), 1533-1538, Article Pii s0008-8846(02)00829-3. [https://doi.org/10.1016/s0008-8846\(02\)00829-3](https://doi.org/10.1016/s0008-8846(02)00829-3)
- Poon, C. S., Qiao, X. C., & Chan, D. X. (2006). The cause and influence of self-cementing properties of fine recycled concrete aggregates on the properties of unbound sub-base. *Waste Management*, 26(10), 1166-1172. <https://doi.org/10.1016/j.wasman.2005.12.013>
- Ramachandran, V. S., Paroli, R. M., Beaudoin, J. J., & Delgado, A. H. (2002). *Handbook of thermal analysis of construction materials*. William Andrew.
- Saberian, M., Li, J., Nguyen, B., & Wang, G. (2018). Permanent deformation behaviour of pavement base and subbase containing recycle concrete aggregate, coarse and fine

- crumb rubber. *Construction and Building Materials*, 178, 51-58. <https://doi.org/10.1016/j.conbuildmat.2018.05.107>
- Shi, C. J., Wu, Z. M., Xiao, J. F., Wang, D. H., Huang, Z. Y., & Fang, Z. (2015). A review on ultra high performance concrete: Part I. Raw materials and mixture design. *Construction and Building Materials*, 101, 741-751. <https://doi.org/10.1016/j.conbuildmat.2015.10.088>
- Sobhan, K., Gonzalez, L., & Reddy, D. V. (2016). Durability of a pavement foundation made from recycled aggregate concrete subjected to cyclic wet-dry exposure and fatigue loading. *Materials and Structures*, 49(6), 2271-2284. <https://doi.org/10.1617/s11527-015-0648-9>
- Su, Y., Cui, Y. J., Dupla, J. C., & Canou, J. (2020). Investigation of the effect of water content on the mechanical behavior of track-bed materials under various coarse grain contents. *Construction and Building Materials*, 263, Article 120206. <https://doi.org/10.1016/j.conbuildmat.2020.120206>
- Su, Y., Cui, Y. J., Dupla, J. C., & Canou, J. (2022). Soil-water retention behaviour of fine/coarse soil mixture with varying coarse grain contents and fine soil dry densities. *Canadian Geotechnical Journal*, 59(2), 291-299. <https://doi.org/10.1139/cgj-2021-0054>
- Taylor, H. F. (1997). *Cement chemistry* (Vol. 2). Thomas Telford London.
- Terzis, D., & Laloui, L. (2019). A decade of progress and turning points in the understanding of bio-improved soils: A review. *Geomechanics for Energy and the Environment*, 19. <https://doi.org/10.1016/j.gete.2019.03.001>
- UNICEM IDF. (2003). *Guide technique pour l'utilisation des materiaux regionaux d'Île-de-France*. [http://materrio.construction/mediatheque/media/22-IDF_Betons_produits_demol\(2\).pdf](http://materrio.construction/mediatheque/media/22-IDF_Betons_produits_demol(2).pdf). [http://materrio.construction/mediatheque/media/22-IDF_Betons_produits_demol\(2\).pdf](http://materrio.construction/mediatheque/media/22-IDF_Betons_produits_demol(2).pdf)
- Wang, C., Chazallon, C., Hornych, P., & Braymand, S. (2022). Permanent and resilient deformation behaviour of recycled concrete aggregates from different sources, in pavement base and subbase. *Road Materials and Pavement Design*. <https://doi.org/10.1080/14680629.2022.2134048>
- Wang, J. J., Mu, M. L., & Liu, Y. L. (2018). Recycled cement. *Construction and Building Materials*, 190, 1124-1132. <https://doi.org/10.1016/j.conbuildmat.2018.09.181>
- Wang, Y. H., Hung, T., Zhao, K. C., & Sheng, Y. (2016, Jul 16-18). Re-cementation of Recycled Concrete Aggregate in Pavement Base or Sub-base. (Ed.),^(Eds.). 1st International Conference on Transportation Infrastructure and Materials (ICTIM), Xian, PEOPLES R CHINA.
- Yaghoubi, E., Disfani, M. M., Arulrajah, A., & Kodikara, J. (2018). Impact of compaction method on mechanical characteristics of unbound granular recycled materials. *Road Materials and Pavement Design*, 19(4), 912-934. <https://doi.org/10.1080/14680629.2017.1283354>
- Zadeh, A. H., Mamirov, M., Kim, S., & Hu, J. (2021). CO2-treatment of recycled concrete aggregates to improve mechanical and environmental properties for unbound applications. *Construction and Building Materials*, 275, Article 122180. <https://doi.org/10.1016/j.conbuildmat.2020.122180>