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

Chong Wang [a,*], Cyrille Chazallon [a,b], Sandrine Braymand [a], Pierre Hornych [c]

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

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ABSTRACT

A key question concerning the application of recycled concrete aggregates (RCA) into pavement is the assessment of self-cementing properties of RCA, which increase the strength and stiffness of unbound base and subbase layers. In this paper, the assessment of self-cementing properties of RCA, the hydration of unhydrated binder and their influence on the microstructure and mechanical behaviour were studied by subjecting two different RCA (NRCA and ORCA, showing significantly different self-cementing properties), after curing for 0, 360 and 720 days, to the thermogravimetric analysis (TGA), scanning electron microscopic analysis (SEM) and monotonic triaxial tests. The results show that the unhydrated binder content of NRCA is low (between 6.2% and 7.9% in fines), and most of the unhydrated binder was hydrated after curing for 360 days. Besides, the sulfate attack products, ettringite, were also observed from both TGA and SEM, which could also lead to the self-cementing properties. The hydration products of unhydrated cement and sulfate attack products not only form bonds between particles, but also fill the small pores (width less than 3 μm), turning the open type of an unbound structure to a rigid dense skeleton structure.

1. Introduction

The economic and human activities produce a lot of construction and demolition wastes (CDW) each year. In Europe, over 800 million tonnes of CDW were produced in 2018 [1]. Concrete wastes are the main components and represent up to 75% of total CDW by weight [2]. Traditionally, those CDW will be disposed in landfills, occupying a large land space and imposing huge pressures on environment. To overcome these problems, recycling and reuse of concrete wastes in concrete [3] and pavement, as unbound granular materials in base and subbase layers, has become a topic of global concerns and has been widely reported in recent years [4–6].

Recently, it is found that, sometimes, the strength and stiffness of the unbound pavement base and subbase layers, built with recycled concrete aggregates (RCA), increase with time, known as self-cementing properties of RCA [7–9]. This is believed to be caused by the hydration of unhydrated cement in RCA, which is released by the crushing process to produce RCA [10]. After pavement construction, these unhydrated cement could hydrate with moisture and create bonds between particles when RCA are used in unbound pavement base and subbase layers, increasing the strength and stiffness of the pavement.

The effect of self-cementing properties on the long-term performance of RCA, used in unbound pavement base and subbase layers, has been reported by some researchers in recent years [7–11]. Arm [7] found that the increase of strength and stiffness in pavement unbound base and subbase layers is highest in the first few months. Poon et al. [9] 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. [11] observed that the hydration of unhydrated cement turns the unbound RCA specimen to the bound specimen after 360 days of curing, as indicated by the microstructure analyses (SEM). Those studies reveal that self-cementing properties have a significant impact on the long-term performance of pavement layers built with RCA. To date, however, the assessment and mechanism of self-cementing properties has not been thoroughly studied, which can help to better predict the long-term performance of pavement built with RCA.

At present, there are few studies investigated the self-cementing properties of RCA by different approaches, such as the semi-adiabatic calorimeter test, thermogravimetric analysis (TGA), X-ray diffraction (XRD) [8-10,12,13]. Among these methods, TGA is frequently adopted

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* Corresponding author: Chong WANG Tel.: +33768787850
E-mail address: chong.wang@insa-strasbourg.fr (C. Wang).

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by some researchers for the evaluation of unhydrated cement content, and for the study of cement hydration [14,15], because it allows the quantitative analysis to evaluate the hydrated compounds, such as calcium silicate hydrate (C–S–H) gel, portlandite ($Ca(OH)_2$), calcite ($CaCO_3$) and non-evaporable water. Oksri-Nelfia et al. [12] and Wang et al. [8] determined the unhydrated cement content in concrete waste based on the $Ca(OH)_2$ content of RCA, measured by TGA. However, $Ca(OH)_2$ content is easily influenced by the type of cement, carbonation and the use of supplementary cementing materials [16], which limits the application of this approach. Bordy et al. [13] quantified the unhydrated cement content based on the non-evaporable water content, for cement paste with a known composition, which is not suitable for RCA. Until now, there is still no standard method to evaluate unhydrated cement content in RCA.

As a result, this study aims to assess the self-cementing properties of RCA. An improved approach, based on the non-evaporable water content obtained from TGA, was proposed to quantify the unhydrated cement content of RCA. Then, the hydration of unhydrated cement, and its influence on the improvement of long-term performance (microstructure and mechanical behaviour) of two different RCA (NRCA and ORCA, showing significantly different self-cementing properties), were studied by submitting these RCA, after 0, 360 and 720 days of curing, to TGA analysis, SEM and monotonic triaxial tests. Furthermore, the mechanism of self-cementing properties was also analyzed based on these observations. The investigation not only leads to a better understanding of self-cementing properties, but also encourages the application of RCA as an unbound granular material in pavement base and subbase layers.

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 a known component, which is more realistic. The studied RCA were crushed 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, at a recycling plant in Strasbourg, France. 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. According to the crushing time, two RCA are designated by NRCA (new RCA, crushed in 2020) and ORCA (old RCA, crushed in 2012), respectively.

Some physical properties of NRCA and ORCA are summarized in Table 1. It shows that the water absorptions of NRCA and ORCA, between 4.3% to 10.86%, are higher than that of natural aggregates, typically lower than 3%, due to the attached mortar. Los Angeles coefficients (LA) and Micro-Deval coefficients (MDE) of NRCA and ORCA reveal that the resistance to fragmentation and wear fulfill the requirements for pavement base and subbase layers (LA$\leq$40 and MDE$\leq$35). The optimum moisture contents (OMC) are 12.93% (NRCA) and 11.51% (ORCA), higher than the most of natural aggregates (4%-6%) due to the higher water absorption of RCA. The maximum dry densities (MDD) are 1.98 g/cm^3 (NRCA) and 2.0 g/cm^3 (ORCA).

Table 1
Physical properties of NRCA and ORCA.

Properties		NRCA	ORCA	Test method
Water absorption (%)	coarse (10-20 mm)	4.64	4.30	NF EN 1097-6
	sand (4-10 mm)	5.81	5.19	
	fine (1-4 mm)	10.86	8.65	
Los Angeles coefficient (LA)		30.8	32.2	NF EN 1097-2
Micro-Deval coefficient (MDE)		21.6	21.3	NF EN 1097-1
Optimum moisture content (OMC) (%)		12.93	11.51	NF EN 13286-2
Maximum dry density (MDD) (g/cm^3)		1.98	2	NF EN 13286-2

2.2. Test methods

Thermogravimetric analysis (TGA), conducted by Setaram thermal analyzer (Setaram company, Caluire, France), was used to determine the unhydrated cement content of RCA (without curing). Since fine aggregates, containing less original natural aggregates, are the principal cause of self-cementing properties [9], only fine aggregates (0-2 mm) were used for the TGA and measurements of chemical compositions. 50-100 mg air-dried fine aggregates (0-2 mm) were subjected to TGA at a constant heating rate of 10 K/min from 25 °C to 1000 °C under nitrogen (N_2) atmosphere.

Chemical compositions of RCA can help to better understand the self-cementing properties. Thus, the pH value, water soluble sulfate content and calcite content of RCA fine aggregates (0-2 mm) were measured to characterize the chemical compositions and carbonation in University of Lorraine in Nancy, France. For pH value measurement, 30 g of oven-dried RCA fines aggregates (0-2 mm) and 75 g of distilled water were mixed and stirred for 2 minutes. 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. 1 kg of previously heated (60 °C) distilled water was added to 25 g of oven-dried fine aggregates (0-2 mm), 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 of RCA was measured by the calcimeter method (NF ISO 10693) to assess the degree of carbonation of the RCA, before use, especially for the ORCA after long-term storage. 0.5-2 g of powder from ground fine aggregates (0-2 mm) 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.

0-20 mm NRCA and ORCA were used to study the hydration of unhydrated cement, and the improvement of microstructure and mechanical behaviour due to the self-cementing properties. All the NRCA and ORCA specimens with 150 mm diameter and 285 mm height were compacted with a vibrating hammer to the optimum dry density (1.97 g/cm^3 and 1.99 g/cm^3 for NRCA and ORCA, respectively), 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 Table 1. Then, they were wrapped in plastic foils and stored indoors at a temperature of 18±5 °C, curing for 0 (without curing), 360 and 720 days. Afterwards, monotonic triaxial tests were performed with Wykeham Farrance triaxial apparatus (Controls group, Milan, Italy), under different confining pressures (20, 40 and 70 kPa) at a shear rate of 0.3 mm/min until failure, to study the effect of self-cementing properties on the mechanical behaviour.

SEM and TGA were performed to study the improvement of microstructure and the hydration of unhydrated cement in RCA. SEM and TGA samples were collected from the specimens curing for different times (0, 360 and 720 days) after monotonic triaxial test. Small SEM samples (length*width*height=15*15*5 mm^3) were dried using the freeze-drying method and coated with gold prior to SEM analysis by Tescan VEGA3 machine (Tescan group, Brno, Czech Republic). For TGA analysis, similarly, fine aggregates (0-2 mm) collected from the cured samples were used.

2.3. Methods to determine the unhydrated cement content by TGA

TGA is frequently adopted for the study of cement hydration [14] by evaluating the hydrated compounds of cement. According to the cement hydration process, unhydrated cement content can be quantified by the hydrated compounds of cement, such as $Ca(OH)_2$ content and non-evaporable water content (C_{water}). However, $Ca(OH)_2$ is easily influenced by the type of cement, carbonation that occurred, and the supplementary cementing materials [16]. In comparison, non-evaporable water, defined as the water retained on the specimen at the boiling temperature (105 °C), is much less sensitive to these factors [17,18]. That increases the accuracy and reliability of the proposed approach. Thus, C_{water} was used to estimate the unhydrated cement content of RCA in this study, instead of $Ca(OH)_2$ content, method used by Oksri-Nelfia et al. [12] and Wang et al. [8].

According to the TGA analysis, some hydrated compounds of cement can be determined. For example, the mass loss between the boiling temperature (105 °C) and 550 °C is due to loss of non-evaporable water, and the mass loss between 550 and 850 °C can be attributed to the decomposition of $CaCO_3$. Then, non-evaporable water content C_{water} and calcite content C_{CaCO3} can be calculated by:

$$C_{water} = M_{105^{\circ}C} - M_{550^{\circ}C} \tag{1}$$

$$C_{CaCO_3} = \frac{100.09}{44.01}\left(M_{550^{\circ}C} - M_{850^{\circ}C}\right) \tag{2}$$

where the ratio 100.09/44.01 corresponds to the molar mass ratio of $CaCO_3/CO_2$, $M_{T\,^{\circ}C}$ (T=105, 550 and 850, respectively) is the sample mass (%) obtained from TG curve at temperature T °C.

After determining C_{water} from the TG curve, the initial cement content (C_{cement}) of RCA can be calculated according to the hydration process of cement. For Portland cement, a complete hydration of per gram of cement, without any supplementary cementing materials (SCMs), such as fly ash, silica fume, etc., will release around 0.23-0.25 grams of non-evaporable water (taken as 0.24 in this study) [15,17,19].

For blended cement, the use of SCMs makes it difficult to estimate the amount of ultimate non-evaporable water content (0.24) due to the unknown stoichiometry and the type of SCMs [20]. To implement this methodology for blended cements, the SCMs are considered by their equivalent in Portland cement, using the k-value concept [20,21]. The equivalent binder content (C_{binder}) can be expressed as:

$$C_{binder} = C_{cement} + k * C_{SCMs} \tag{3}$$

where C_{binder} is the equivalent binder content, C_{cement} is the Portland cement content, C_{SCMs} is the SCMs content (C_{SCMs}=0 for Portland cement) and coefficient k is the equivalent coefficient of SCMs to Portland cement. Table 2 summarizes the k values for different types of SCMs. By this way, the unknown ultimate non-evaporable water for blended cement can be considered as the same as the Portland cement (0.24), and the effect of SCMs on the self-cementing properties of RCA can be considered.

Then, for RCA made by Portland cement or blended cement, the relationship between C_{water} and C_{binder} can be expressed as:

$$C_{water} = 0.24 * \alpha * C_{binder} \tag{4}$$

where α is the degree of cement hydration in RCA. For concrete after a long service life, the ultimate degree of cement hydration α is mainly influenced by the initial water cement ratio (w/c), and can be calculated by the following equation developed by Mills [22] which is frequently used to model cement hydration [12,23]:

$$\alpha = \frac{1.031 * \frac{w}{c}}{0.194 + \frac{w}{c}} \tag{5}$$

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

$$C_{unhydrated} = (1 - \alpha) * C_{binder} \tag{6}$$

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) suggests that carbonation of NRCA is negligible.

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 of RCA fine aggregates

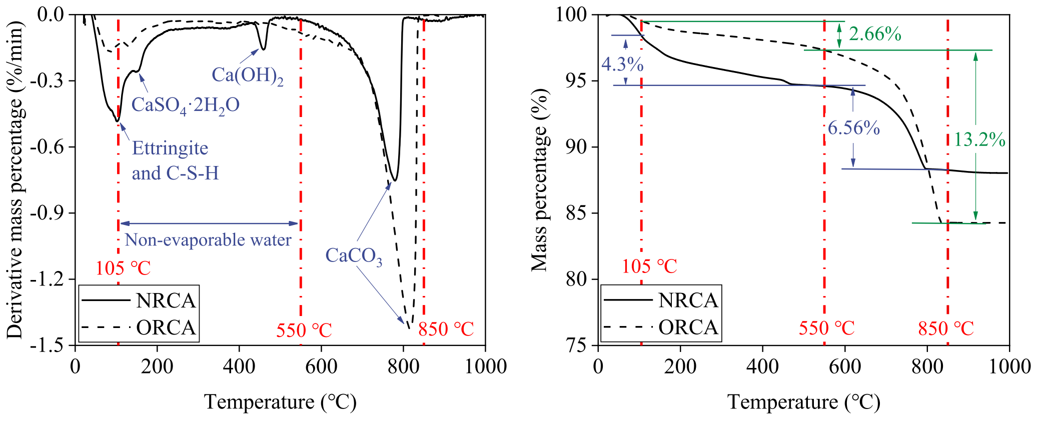
Fig. 1 shows the TGA results of NRCA and ORCA fine aggregates (0-2 mm) without curing (curing for 0 day), presented as the derivative thermogravimetry (DTG) curves and thermogravimetry (TG) curves. DTG curve indicates the rate of mass change, which can be used to identify the decomposition of RCA components. 4 main peaks can be observed in DTG curve of NRCA. The first peak, around 100 °C, is due to the decomposition of ettringite and C-S-H [24]. In fact, they cannot be clearly identified in TGA since their peaks are partially overlapped [24,25]. The peak of gypsum ($CaSO_4{\cdot}2H_2O$) is around 150 °C. $Ca(OH)_2$ can be found in the third peak, between 430 and 490 °C [24]. The decompositions of ettringite, C-S-H, gypsum and $Ca(OH)_2$ lead to the loss of non-evaporable water (between 105 to 550 °C). The last peak, between 550 to 850 °C, is caused by the decomposition of $CaCO_3$.

The mass loss of NRCA and ORCA, due to the loss of non-evaporable water (between 105 °C and 550 °C) and the decomposition of $CaCO_3$ (between 550 °C and 850 °C), are presented in TG curves (Fig. 1 (b)) and Table 3, as well as non-evaporable water content C_{water} and calcite content C_{CaCO3} calculated by Equations (1) and (2). It can be observed that NRCA has a much higher C_{water} and a much lower C_{CaCO3} than those of ORCA, caused by the high degree of carbonation of ORCA due to the long-term storage. In fact, these C_{CaCO3} values (Table 3) were also compared with the values obtained with the calcimeter method (Table 4). It indicates that the two calculation methods lead to the same results, showing the reliability of the TGA analysis results.

The other measurement results, such as pH value, water soluble sulfate content and calcite content are summarized in Table 4. The pH value is another widely used parameter to evaluate self-cementing properties of RCA by other researchers as it can be measured easily and quickly [9,26,27]. The results show that the pH value of NRCA (13.07) is much higher than that of ORCA (10.53). Paige-Green [26] 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. The high pH value implies more soluble alkaline hydration products, suggesting that the RCA were not completely carbonated and may contain some unhydrated cement.

Sulfate attack is a nonignorable disease for hydraulically bound materials, which leads to an expansion in solid volume by forming gypsum or ettringite [28]. According to the European standard NF EN 13285 [29] and the French national and regional technical guides [30,31], 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 contents of both NRCA and ORCA are under this limit.

Both calcimeter method (Table 4) and TGA analysis results (Table 3) show that the calcite content of NRCA (14.7% and 14.92% respectively) is only half that of ORCA (29.97% and 30.09% respectively). 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 calcite could also come from the original natural aggregates (NA) [32], although an effort was made to eliminate the influence of original NA by



(a) DTG curves (b) TG curves

Fig. 1. DTG and TG curves of NRCA and ORCA without curing: (a) DTG curves and (b) TG curves.

Table 3
Mass loss of NRCA and ORCA in different temperature ranges.

Materials	Mass loss (%)		Non-evaporable water C_{water} (%)	CaCO$_3$ content C_{CaCO3}(%)
	105-550 °C	550-850 °C		
NRCA	4.30	6.56	4.30	14.92
ORCA	2.66	13.23	2.66	30.09

Table 4
The chemical composition of NRCA and ORCA.

Properties	NRCA	ORCA	Test method
pH value	13.07	10.53	BS 1377-3
Water soluble sulfate content (%)	0.23	0.13	NF EN 1744-1
Calcite content (%)	14.7	29.97	NF ISO 10693

limiting the maximum particle size (2 mm).

3.2. *Potential unhydrated binder content in RCA fine aggregates*

Subsequently, the C_{binder} and $C_{unhydrated}$ of NRCA can be calculated based on the C_{water}, by Equations (4) and (6). Since ORCA were stored for a long period before use, the partial unhydrated binder has already hydrated, resulting in a much higher α, which cannot be calculated by Equation (5). Thus, only C_{binder} and $C_{unhydrated}$ of NRCA could be calculated in this study.

Fig. 2 presents the C_{binder} and $C_{unhydrated}$ of NRCA calculated by Equations (4) and (6), for varying initial water-cement ratios w/c, since the initial w/c and original composition of the concrete are not known. Generally, the typical w/c ratio for conventional concrete ranges from 0.4 to 0.5 [33], and the typical C_{binder} 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 [34]. It appears that within the typical w/c ratio (0.4-0.5), C_{binder} of NRCA is between 24.1% and 25.8%, as shown in Fig. 2, which is slightly higher than that of typical conventional concrete (15.5%-21.3%). This is due to the fact that the tested fine aggregates (0-2 mm) have a higher paste content than the global concrete [35], resulting in a higher C_{binder} of NRCA than that of typical concrete. Thus, within the typical w/c ratio (0.4-0.5), the potential $C_{unhydrated}$ of NRCA (0-2 mm) can be calculated by Equation (6), which is between 6.2% and 7.9%.

Recall that the Ca(OH)$_2$ content, obtained also from TGA, which is easily influenced by the type of cement, carbonation and the use of supplementary cementing materials [16], was also used as an indicator to quantify C_{binder} and $C_{unhydrated}$ by other researchers [8,12]. Previous study [8] indicated that C_{binder} of NRCA calculated by Ca(OH)$_2$ content (between 11.7% and 14.2%) is much lower than the value calculated by non-evaporable water content (between 24.1% and 25.8%), and also lower than that of typical concrete (between 15.5% and 21.3%). It indicates that non-evaporable water content was more suitable to calculate the unhydrated cement content of RCA, instead of Ca(OH)$_2$.

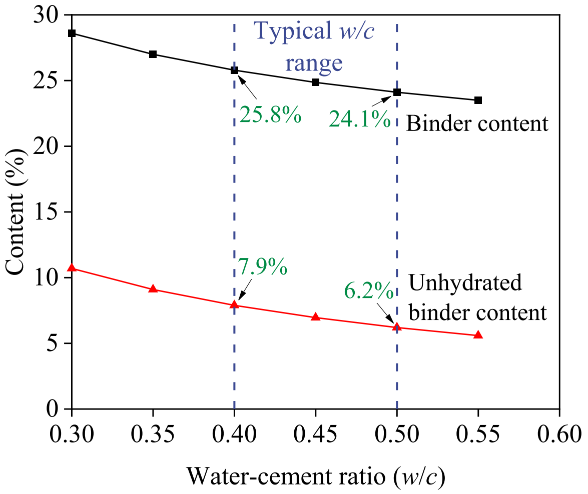


Fig. 2. Equivalent binder content C_{binder} and unhydrated binder content $C_{unhydrated}$ of NRCA for varying w/c.

3.3. *Hydration of unhydrated binder in RCA*

To study the hydration of unhydrated binder in RCA during curing phase, the comparison of the TG-DTG curves of NRCA and ORCA, after curing for different times (0, 360 and 720 days), are presented in Figs. 3 and 4. In the DTG curve of NRCA after curing for 720 days, the intensity of ettringite peak (around 100 °C) is increased, while the peak of gypsum CaSO$_4$·2H$_2$O (around 150 °C) is disappeared, and the intensity of Ca(OH)$_2$ peak (around 450 °C) is reduced, than those after curing for 0 and 360 days. On the contrary, for ORCA (Fig. 4), the DTG and TG curves are almost the same after curing for 0 and 360 days, in agreement with the negligible self-cementing properties of ORCA indicated by the low pH value. Note that ORCA curing for 720 days was not subjected to TGA due to the negligible self-cementing properties.

Afterwards, the mass loss of NRCA and ORCA after curing for different times (0, 360 and 720 days), in different temperature ranges,

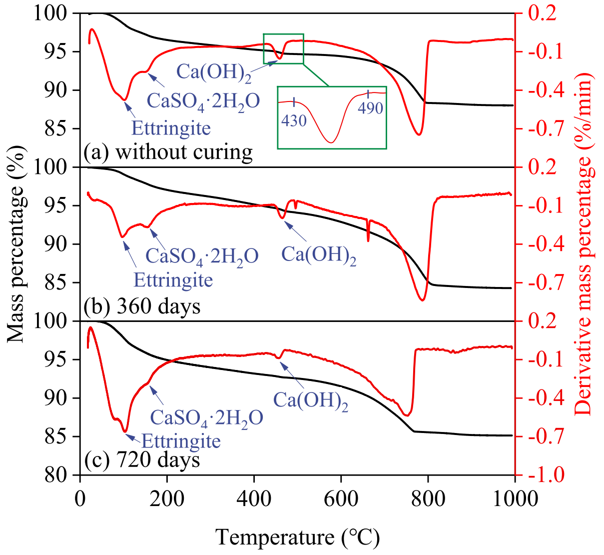


Fig. 3. Comparison of TG-DTG curves of NRCA curing for different times: (a) without curing; (b) 360 days and (c) 720 days.

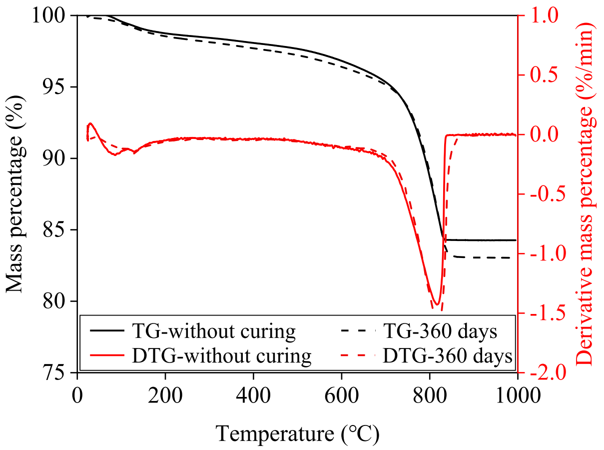


Fig. 4. Comparison of TG-DTG curves of ORCA without curing and curing for 360 days.

due to the loss of non-evaporable water content (between 105 and 550 °C) and the decomposition of ettringite (between 70/90 and 120 °C), $CaSO_4 \cdot 2H_2O$ (between 140 and 170 °C) and $Ca(OH)_2$ (between 430 and 490 °C), were calculated from their TG curves (Fig. 3), as summarized in Table 5. As the DTG curve indicates the rate of mass change due to the decomposition of RCA, it was suggested by European standard EN ISO 11358-1 [36] to facilitate the identification of the starting and ending decomposition temperatures. The peak of DTG curve corresponds to the maximum rate of mass loss, which is the inflection point of TG curve. The two points around this peak, where the gradient of DTG curve starts to change, correspond to the starting and ending decomposition points. For example, the starting and ending decomposition temperatures of $Ca(OH)_2$ is 430 and 490 °C, respectively, as presented in Fig. 3 (a). All these corresponding decomposition temperatures were chosen carefully according to the change of gradient of the DTG curves, to improve the accuracy of quantification [37].

Table 5
Mass losses of NRCA and ORCA in different temperature ranges.

Mass loss (%)	Temperature range (°C)	NRCA			ORCA	
		0	360	720	0	360
Non-evaporable water	105-550	4.30	5.34	5.37	2.66	2.54
Ettringite	70/90-120	1.20	1.12	1.58		
$CaSO_4 \cdot 2H_2O$	140-170	0.66	0.66	None		
$Ca(OH)_2$	430-490	0.50	0.71	0.39		
$CaCO_3$	550-850	6.56	9.06	6.76	13.23	13.75

Fig. 5 presents the mass losses of NRCA after curing for different times, in those different temperature ranges. Since ORCA shows negligible self-cementing properties from TGA analysis, only the results of NRCA in different temperature ranges are presented. It can be observed that during the 360 days of curing, a significant increase of non-evaporable water content of NRCA can be observed, from 4.3% to 5.34%, increasing 1.04%, which is believed to be related to the hydration of unhydrated binder in NRCA. Thus, $Ca(OH)_2$ content also increases slightly, as a result of the hydration of unhydrated binder.

Between curing for 360 days and 720 days, it shows that non-evaporable water content of NRCA reaches a constant value (5.37%), indicating that the hydration of unhydrated binder almost stops after curing for 360 days. Besides, both $CaSO_4 \cdot 2H_2O$ and $Ca(OH)_2$ contents decrease while ettringite content increases after curing for 720 days. Note that the ettringite, formed by the reactions between $CaSO_4 \cdot 2H_2O$, $Ca(OH)_2$ and cement hydration products [38], can fill the pores, improving the microstructure and mechanical behaviour of RCA specimen, which could also lead to the self-cementing properties of RCA.

According to the increased non-evaporable water content (1.04%) of NRCA, the amount of hydrated binder during the curing phase can be calculated by Equation (4) (α equal to 1), which is 4.3%. In comparison to the total unhydrated binder content (between 6.2% and 7.9%) as mentioned above, it appears that most of unhydrated binder (between 55% to 70%) were hydrated during the first 360 days curing, and this hydration stops after curing for 360 days. This is in agreement with other researchers [7], who indicated that the strength and stiffness of RCA base and subbase layers increase faster in the first few months, and then a continuous increase at a lower rate can be observed, even up to 10 years after construction.

3.4. Microstructural observations of RCA specimen

The microstructures of compacted NRCA specimens without curing and after 360 days of curing, observed by SEM under different magnification (2400 × and 4000 ×), are presented in Figs. 6 and 7. Note that these figures were taken randomly at different positions to better represent the microstructure of RCA specimen. Owing to the fact that the

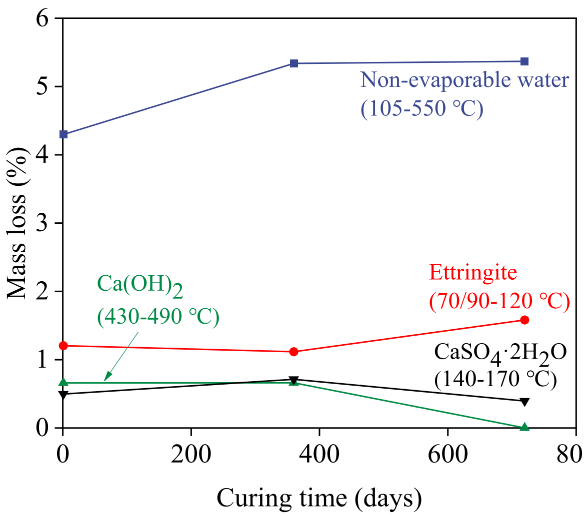


Fig. 5. The evolution of mass loss for NRCA in different temperature ranges, due to the decomposition of non-evaporable water, ettringite, $CaSO_4 \cdot 2H_2O$ and $Ca(OH)_2$.

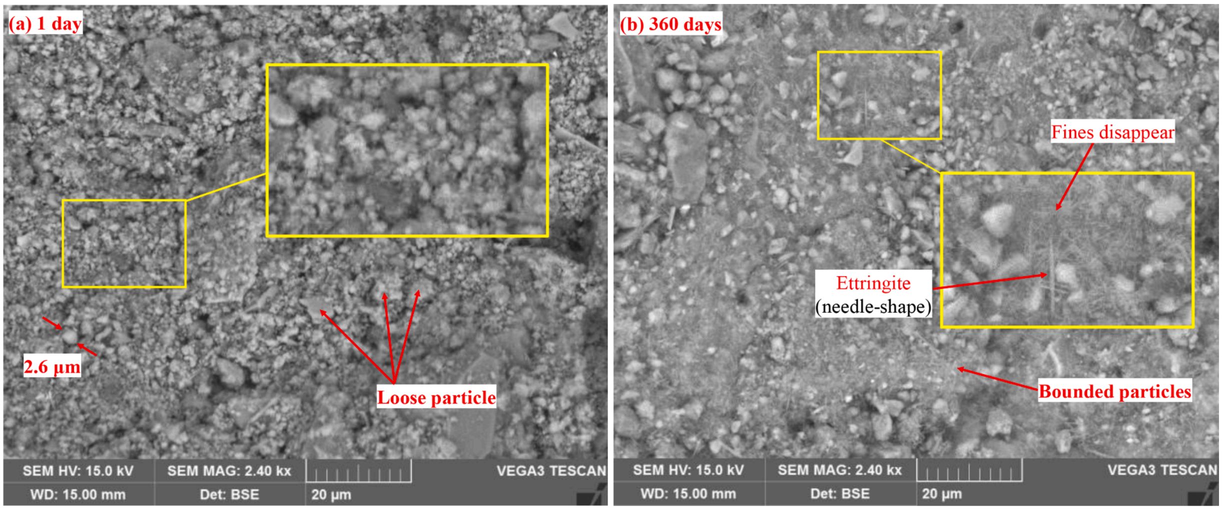


Fig. 6. SEM images of NRCA without curing and after curing for 360 days (2400 ×): (a) without curing; (b) 360 days.

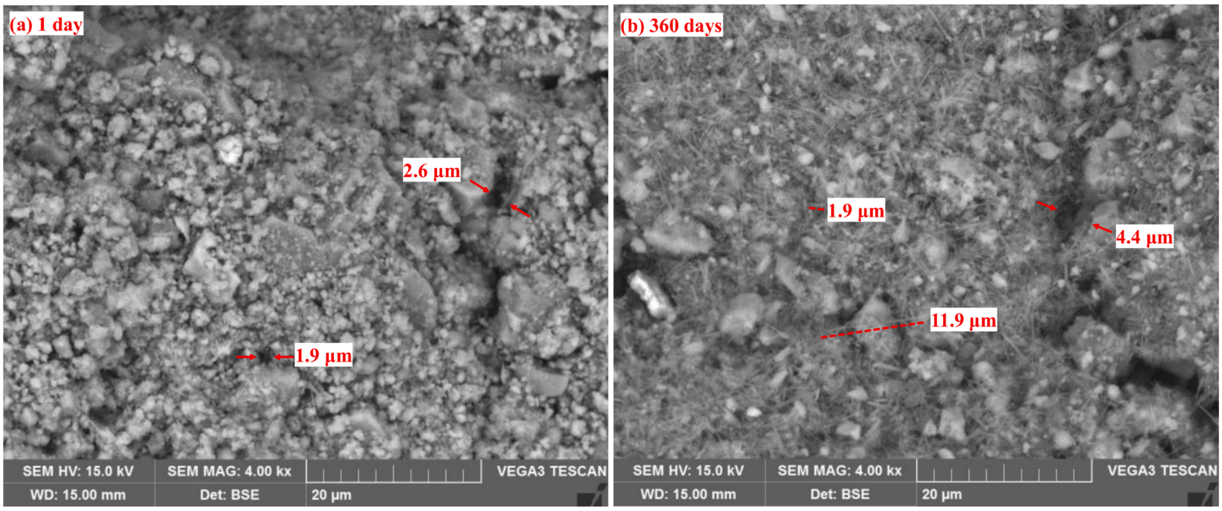


Fig. 7. SEM images of NRCA without curing and after curing for 360 days (4000 ×): (a) without curing; (b) 360 days.

self-cementing properties of ORCA are negligible, and that no new hydration products were formed as indicated by TGA, only the microstructure of NRCA was studied. As shown in Fig. 6 (a) and Fig. 7 (a), compacted NRCA specimens without curing (1 day) exhibits a relatively open type microstructure, with numerous fine particles assembled between coarse aggregates, exhibiting many different sizes of pores.

Fig. 6 (b) and Fig. 7 (b) show the influence of self-cementing properties on the microstructures of NRCA specimens. It appears that the microstructure of NRCA after curing for 360 days is much denser, with a visible decrease of number and size of small pores (width less than 3 μm), as the hydration of unhydrated cement form bonds between particles. For the larger pores (width larger than 3 μm), the influence of the self-cementing properties on the microstructures appears limited, since the unhydrated cement content is low. 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 a rigid dense skeleton structure (curing for 360 days), increasing the strength and stiffness of RCA and changing unbound pavement layers to bound layers.

Fig. 6 (b) and Fig. 7 (b) also show that the amount of fine aggregates decreases after curing for 360 days, which could be attributed to the hydration of unhydrated cement in fine aggregates. It also indicates that the unhydrated cement in fine aggregates are responsible for the self-cementing properties of RCA, in good agreement with Poon et al. [9].

Among these hydration products, it is possible to observe that numerous needle-shape hydration products (Fig. 7 (b)), ettringite, are formed after curing for 360 days, which was observed also by Jitsangiam et al. [11]. This is also in good agreement with the observation from TGA. The ettringite, formed by the reactions between $CaSO_4{\cdot}2H_2O$, $Ca(OH)_2$ and cement hydration products [38] as mentioned above, can absorb a large amount of water and has a large volume, filling the small pores (width less than 3 μm). Despite that the water soluble sulfate content of NRCA (0.23%) is much lower than the limitation (0.7%), as mentioned above, many ettringite were still formed. It should be mentioned that once the voids are fully filled by the hydration products and ettringite, the continuous formation of ettringite can lead to the swelling and cracking of the structure, known as sulfate attack of concrete [39], 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.

3.5. *Hypothesis for mechanism of self-cementing properties*

Fig. 8 presents the results of the monotonic triaxial tests performed on the NRCA and ORCA specimens after curing for 0 day and 360 days, in terms of maximum shear strength and secant modulus E_{50}, defined as

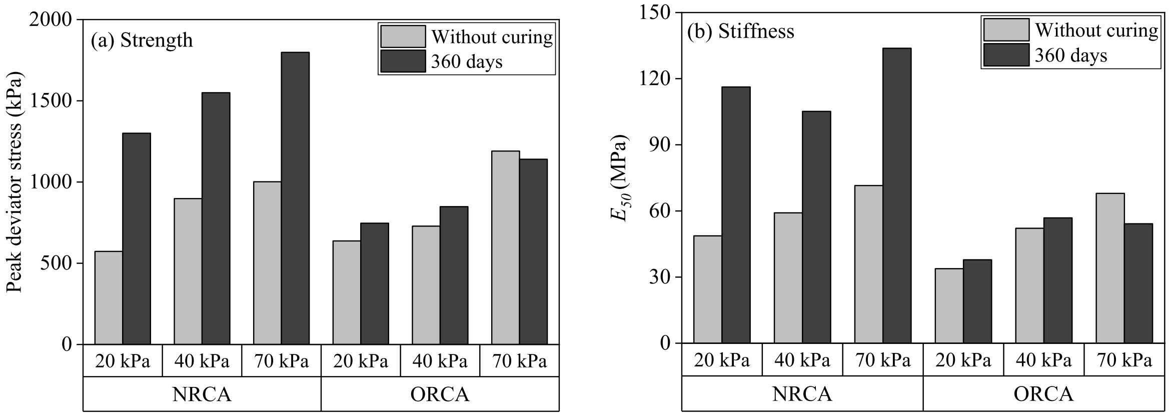


Fig. 8. Development of strength and stiffness of RCA for different confining pressures (20/40/70 kPa), after curing for 0 and 360 days: (a) shear strength; (b) stiffness.

the ratio of deviator stress q to the axial strain at stress level equal to 50% of peak deviator stress. For NRCA, the shear strength and stiffness increase significantly after curing for 360 days (approximately by a factor of two), under both confining pressures, confirming its strong self-cementing properties, as observed also by Jitsangiam et al. [11]. On the contrary, the strength and stiffness of ORCA remain almost constant due to the negligible self-cementing properties. These results are in good agreement with the TGA analysis and SEM observation results.

Recall that between 360 days and 720 days, the non-evaporable water content of NRCA stops increasing, while a continuous formation of ettringite can be observed from both TGA and SEM results. It indicates that the increase of mechanical behaviour of RCA can be divided into two phases. The first phase (before 360 days in this study) is primarily due to the hydration of unhydrated cement, where the strength and stiffness increase very fast. In the second phase (after 360 days in this study), the continuous formation of ettringite can fill the small pores (width less than 3 μm) and densify the microstructure, increasing the load-bearing capacity by increasing the particle contact area and decreasing the average stress in each particle. As a result, the strength and stiffness of RCA specimen increase continuously even when the hydration of unhydrated binder stops. This was supported by both laboratory tests [8,40] and field tests [7], from which a fast increase of strength and stiffness of RCA specimen can be observed in the first months, and then increase continually even after curing for 360 days. Besides, the hydration of unhydrated cement and the formation of ettringite also consume free water, around 1% indicated by the increased non-evaporable water content. The decreased free water content and the improved dense microstructure can lead to the increase of matric suction, which can also improve the mechanical properties of RCA specimens [41].

4. Conclusions

This study investigated the self-cementing properties of RCA, used as unbound granular materials in pavement, and their influence on the improvement of microstructure and mechanical behaviour, by subjecting two different RCA, NRCA crushed recently (New RCA) and ORCA crushed long time ago (ORCA), after curing for 0, 360 and 720 days, to TGA, SEM analysis and monotonic triaxial tests. The chemical properties, including the pH value, water soluble sulfate content and calcite content, were also studied. Based on these results, the self-cementing mechanisms were discussed. The following conclusions can be drawn from this research:

1. Both TGA analysis, pH value and $CaCO_3$ content show that ORCA was carbonated due to the long-term storage after crushing, decreasing self-cementing properties of ORCA.
2. 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 6.2% and 7.9%.
3. During the 720 days of curing, the non-evaporable water content of NRCA increases from 4.3% (without curing) to 5.34% (360 days), and then reaches a constant value, indicating that the effective unhydrated cement of NRCA is almost totally hydrated in the first 360 days. While for ORCA, showing negligible self-cementing properties, the non-evaporable water content remained almost constant.
4. Although the water-soluble sulfate contents of both NRCA (0.23%) and ORCA (0.13%) are under the limit standard (0.7%), many sulfate attack products, ettringite, were observed in NRCA from both TGA analysis and SEM observations.
5. SEM observations have shown that the initial open granular structure (curing 1 day) becomes stiffer and denser skeleton structure after curing for 360 days, with the small pores (width less than 3 μm) filled by hydration products and ettringite.
6. The increase of mechanical behaviour of RCA can be divided into two phases, a fast increasing phase primarily due to the hydration of unhydrated cement and a slower increasing phase due to the formation of ettringite. In addition, the decrease of free water and the increase of matric suction can also improve the performance of RCA.

CRediT authorship contribution statement

Chong Wang: Writing – review & editing, Writing – original draft, Investigation. **Cyrille Chazallon:** Writing – review & editing, Project administration, Methodology. **Sandrine Braymand:** Writing – review & editing, Methodology, Formal analysis. **Pierre Hornych:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

[1] Eurostat, Energy, transport and environment statistics. 2018.

[2] C.M. Nwakaire, S.P. Yap, C.C. Onn, C.W. Yuen, H.A. Ibrahim, Utilisation of recycled concrete aggregates for sustainable highway pavement applications; a review, Constr. Build. Mater. 235 (2020), https://doi.org/10.1016/j.conbuildmat.2019.117444.

[3] F. Althoey, O. Zaid, J. de-Prado-Gil, C. Palencia, E. Ali, I. Hakeem, R. Martínez-García, Impact of sulfate activation of rice husk ash on the performance of high strength steel fiber reinforced recycled aggregate concrete, J. Build. Eng. 54 (2022) 104610, https://doi.org/10.1016/j.jobe.2022.104610.

[4] E. Yaghoubi, M.M. Disfani, A. Arulrajah, J. Kodikara, Impact of compaction method on mechanical characteristics of unbound granular recycled materials, Road Mater. Pavement Des. 19 (4) (2018) 912–934, https://doi.org/10.1080/14680629.2017.1283354.

[5] J.O. Bestgen, M. Hatipoglu, B. Cetin, A.H. Aydilek, Mechanical and Environmental Suitability of Recycled Concrete Aggregate as a Highway Base Material, J. Mater. Civ. Eng. 28 (9) (2016), https://doi.org/10.1061/(asce)mt.1943-5533.0001564.

[6] C. Wang, C. Chazallon, P. Hornych, S. Braymand, Permanent and resilient deformation behaviour of recycled concrete aggregates from different sources, in pavement base and subbase, Road Mater. Pavement Des., (2022), https://doi.org/10.1080/14680629.2022.2134048.

[7] Arm, M., Self-cementing properties of crushed demolished concrete in unbound layers: results from triaxial tests and field tests. Waste Manage., 2001. 21(3): p. 235-239. https://doi.org/10.1016/s0956-053x(00)00095-7.

[8] C. Wang, C. Chazallon, S. Braymand, P. Hornych, Influence of self-cementing properties on the mechanical behaviour of recycled concrete aggregates under monotonic loading, Constr. Build. Mater. 367 (2023) 130259, https://doi.org/10.1016/j.conbuildmat.2022.130259.

[9] Poon, C.S., X.C. Qiao, and D.X. Chan, The cause and influence of self-cementing properties of fine recycled concrete aggregates on the properties of unbound sub-base. Waste Manage., 2006. 26(10): p. 1166-1172. https://doi.org/10.1016/j.wasman.2005.12.013.

[10] A. Amin, A. Hasnat, A.H. Khan, M. Ashiquzzaman, Residual Cementing Property in Recycled Fines and Coarse Aggregates: Occurrence and Quantification, J. Mater. Civ. Eng. 28 (4) (2016), https://doi.org/10.1061/(asce)mt.1943-5533.0001472.

[11] P. Jitsangiam, K. Boonserm, T. Phenrat, S. Chummuneerat, P. Chindaprasirt, H. Nikraz, Recycled Concrete Aggregates in Roadways: Laboratory Examination of Self-Cementing Characteristics, J. Mater. Civ. Eng. 27 (10) (2015), https://doi.org/10.1061/(asce)mt.1943-5533.0001245.

[12] L. Oksri-Nelfia, P.Y. Mahieux, O. Amiri, P. Turcry, J. Lux, Reuse of recycled crushed concrete fines as mineral addition in cementitious materials, Mater. Struct. 49 (8) (2016) 3239–3251, https://doi.org/10.1617/s11527-015-0716-1.

[13] A. Bordy, A. Younsi, S. Aggoun, B. Fiorio, Cement substitution by a recycled cement paste fine: Role of the residual anhydrous clinker, Constr. Build. Mater. 132 (2017) 1–8, https://doi.org/10.1016/j.conbuildmat.2016.11.080.

[14] S.M. Monteagudo, A. Moragues, J.C. Gavez, M.J. Casati, E. Reyes, The degree of hydration assessment of blended cement pastes by differential thermal and thermogravimetric analysis. Morphological evolution of the solid phases, Thermochim. Acta 592 (2014) 37–51, https://doi.org/10.1016/j.tca.2014.08.008.

[15] H. Zhang, S. Mu, J.S. Cai, J.Z. Liu, J.X. Hong, The role of iron in cement hydration process: From perspective of chemical admixture, Thermochim. Acta 722 (2023), https://doi.org/10.1016/j.tca.2023.179457.

[16] V.G. Papadakis, Experimental investigation and theoretical modeling of silica fume activity in concrete, Cem. Concr. Res. 29 (1) (1999) 79–86, https://doi.org/10.1016/s0008-8846(98)00171-9.

[17] I. Pane, W. Hansen, Investigation of blended cement hydration by isothermal calorimetry and thermal analysis, Cem. Concr. Res. 35 (6) (2005) 1155–1164, https://doi.org/10.1016/j.cemconres.2004.10.027.

[18] S.E. Chidiac, M. Shafikhani, Cement degree of hydration in mortar and concrete, J. Therm. Anal. Calorim. 138 (3) (2019) 2305–2313, https://doi.org/10.1007/s10973-019-08800-w.

[19] J.I. Bhatty, Hydration versus strength in a portland cement developed from domestic mineral wastes—A comparative study, Thermochim. Acta 106 (1986) 93–103, https://doi.org/10.1016/0040-6031(86)85120-6.

[20] W. Deboucha, N. Leklou, A. Khelidj, Combination effect of limestone filler and slag on hydration reactions in ternary cements, Eur. J. Environ. Civ. Eng. (2020), https://doi.org/10.1080/19648189.2020.1825233.

[21] V.G. Papadakis, S. Antiohos, S. Tsimas, Supplementary cementing materials in concrete - Part II: A fundamental estimation of the efficiency factor, Cem. Concr. Res. 32 (10) (2002) 1533–1538, https://doi.org/10.1016/s0008-8846(02)00829-3.

[22] R.H. Mills, Factors influencing cessation of hydration in water cured cement pastes, Highway Research Board (90) (1966).

[23] F. Lin, C. Meyer, Hydration kinetics modeling of Portland cement considering the effects of curing temperature and applied pressure, Cem. Concr. Res. 39 (4) (2009) 255–265, https://doi.org/10.1016/j.cemconres.2009.01.014.

[24] Z.L. Zhang, J. Du, M.L. Shi, Quantitative Analysis of the Calcium Hydroxide Content of EVA-Modified Cement Paste Based on TG-DSC in a Dual Atmosphere, Mater 15 (7) (2022), https://doi.org/10.3390/ma15072660.

[25] E. Qoku, T.A. Bier, T. Westphal, Phase assemblage in ettringite-forming cement pastes: A X-ray diffraction and thermal analysis characterization, J. Build. Eng. 12 (2017) 37–50, https://doi.org/10.1016/j.jobe.2017.05.005.

[26] P. Paige-Green, Preliminary evaluation of the reuse of cementitious materials, in 29th Annual Southern African Transport Conference (2010) 520–529. Pretoria, South Africa.

[27] J. Kim, B. Nam, Z. Behring, B. Al Muhit, Evaluation of Recementation Reactivity of Recycled Concrete Aggregate Fines, Transp. Res. Rec. 2401 (2014) 44–51, https://doi.org/10.3141/2401-05.

[28] Kampala, A., P. Jitsangiam, K. Pimraksa, and P. Chindaprasirt, An investigation of sulfate effects on compaction characteristics and strength development of cement-treated sulfate bearing clay subgrade. Road Mater. Pavement Des., 2021. 22(10): p. 2396-2409. https://doi.org/10.1080/14680629.2020.1753564.

[29] NF EN 13285, Unbound mixtures - Specifications. 2018.

[30] UNICEM IDF, Guide technique pour l'utilisation des materiaux regionaux d'Île-de-France. 2003.

[31] CETE de l'Est, Guides d'utilisation des matériaux lorrains en technique routière - Guide matériaux de démolition. 2009.

[32] D. Dollimore, J.D. Gupta, S. Lerdkanchanaporn, S. Nippani, A thermal analysis study of recycled portland cement concrete (RPCC) aggregates, Thermochim. Acta 357 (2000) 31–40, https://doi.org/10.1016/s0040-6031(00)00361-0.

[33] C.J. Shi, Z.M. Wu, J.F. Xiao, D.H. Wang, Z.Y. Huang, Z. Fang, A review on ultra high performance concrete: Part I. Raw materials and mixture design, Constr. Build. Mater. 101 (2015) 741–751, https://doi.org/10.1016/j.conbuildmat.2015.10.088.

[34] A. Ahmad, F. Farooq, P. Niewiadomski, K. Ostrowski, A. Akbar, F. Aslam, R. Alyousef, Prediction of Compressive Strength of Fly Ash Based Concrete Using Individual and Ensemble Algorithm, Mater 14 (4) (2021), https://doi.org/10.3390/ma14040794.

[35] Z. Zhao, S. Remond, D. Damidot, W. Xu, Influence of hardened cement paste content on the water absorption of fine recycled concrete aggregates, J. Sustainable Cem.-Based Mater. 2 (3-4) (2013) 186–203.

[36] EN ISO 11358-1, Plastics - Thermogravimetry (TG) of polymers - Part 1: General principles. 2022.

[37] X.J. Lyu, G. Yao, Z.M. Wang, Q. Wang, L. Li, Hydration kinetics and properties of cement blended with mechanically activated gold mine tailings, Thermochim. Acta 683 (2020), https://doi.org/10.1016/j.tca.2019.178457.

[38] G. Rajasekaran, Sulphate attack and ettringite formation in the lime and cement stabilized marine clays, Ocean Eng 32 (8-9) (2005) 1133–1159, https://doi.org/10.1016/j.oceaneng.2004.08.012.

[39] P.K. Mehta, Mechanism of sulfate attack on portland cement concrete—Another look, Cem. Concr. Res. 13 (3) (1983) 401–406, https://doi.org/10.1016/0008-8846(83)90040-6.

[40] C. Wang, C. Chazallon, P. Jing, P. Hornych, B. Latour, Effect of self-cementing properties on the mechanical behaviour of recycled concrete aggregates in unbound pavement layers, Transp. Geotech. 42 (2023), https://doi.org/10.1016/j.trgeo.2023.101054.

[41] P. Jing, H. Nowamooz, C. Chazallon, Unsaturated mechanical behaviour of a granular material, Road Mater. Pavement Des. 20 (6) (2019) 1429–1451, https://doi.org/10.1080/14680629.2018.1447506.

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