Study of carbonation kinetics of a recycled sand

Khaoula MEBREK[1,2], Rachid CHERIF[1], Abdelkarim AÏT-MOKHTAR[1], Mathieu LEMAIRE[1]

[1] *LaSIE UMR CNRS 7356, University of La Rochelle, Avenue Michel Crépeau, 17042 La Rochelle Cedex 1, France.*

[2] *Agence de La Transition Ecologique (ADEME), 20 Avenue du Grésillé B.P.90406, 49004 ANGERS CEDEX 01*

Abstract

Recycled sand from inert construction waste appears as a possible substitute for concrete production, not least because of the increased demand for sustainable building materials. This work explores the carbonation kinetics of a recycled sand. In addition to CO_2 fixation, the carbonation of recycled sand reduces its water absorption coefficient and increases its density, which could improve the properties of recycled sand based-concrete. For this purpose, recycled sands (0/4) were exposed to CO_2 in a controlled carbonation chamber with two main points of interest: (i) a comprehensive study of the carbonation process; (ii) a monitoring of the mass and pH evolution during carbonation and the carbonation products from thermogravimetric analysis (TGA). Firstly, we have noticed a quick mass increase of the sand within the first eight hours of exposure to CO_2, indicating a rapid carbonation of the cementitious matrix; secondly, there are extended pH changes and significant $CaCO_3$ generation, indicating an extensive and intensive initial carbonation phase. The results were used to deduce the carbonation kinetic of the recycled sand used, which is useful for recycled sands processing strategies prior to their incorporation into concrete.

Keyword. Carbonation kinetics, accelerated carbonation, recycled sand, pH monitoring, thermogravimetric analysis.

I.INTRODUCTION

The Waste Framework Directive 2008/98/EC mandates that each European Union member state must achieve a minimum recycling rate of 70% of construction and demolition wastes (CDW) since 2020 (Song and Ryou, 2014). To meet this target, recycling CDW into construction materials like aggregates, cement, concrete, and sands is imperative (Kou et al., 2012; Sormunen and Kärki, 2019). Otherwise, sand holds a primary position as the most utilized material in the construction industry with river sand being the most natural aggregate employed in the production of concrete materials throughout the entire construction sector (Kou et al., 2012).

Consequently, there is an increasing need for utilizing the inert component of CDW to manufacture recycled sands (de Larrad and Colina, 2018), addressing the pressing demand for alternative resources (Yazoghli-Marzouk et al., 2014). However, due to the presence of two extra elements (pre-existing adhered mortar and pre-existing interfacial transition zones (ITZ), Coarse Recycled Concrete Aggregates (CRCA) demonstrate poorer proprieties, such as reduced density, increased water absorption, and higher crush values compared to Natural Aggregates (NA), resulting in mechanical and durability issues within the concrete. Because of these factors, CRCA find predominant use in non-structural applications (Ke et al., 2020). Nevertheless, when employed

in structural contexts, there are stringent limits on the CRCA replacement ratio in Recycled Aggregate Concrete (RAC) (Limbachiya et al., 2007; Mahieux et al., 2017). For instance, the European standards NF EN 206+A2/CN (2022) set a maximum replacement ratio of 60% RCA in the environment classes X0, XC1 and XC2 and 30% recycled fine aggregates (RFA) in X0. RFA exhibits a greater quantities of residual cement paste, resulting in weaker properties compared to both natural sand and CRCA. This has a detrimental impact on workability and can negatively influence the mechanical and durability performances of the hardened concrete (Akhtar and Sarmah, 2018).

In order to encourage the adoption of RCA, various techniques have been introduced for pre-treatment to enhance their overall quality and, therefore, to increase the proportion of their substitution in the concrete mix. One notable method gaining substantial interest involves using accelerated carbonation. The accelerated carbonation not only efficiently enhances the proprieties of recycled aggregates (Kou et al., 2014; Torrenti et al., 2022; Zhan et al., 2014; Zhang et al., 2015a, 2015b), but also achieves sequestration of CO_2. In this context, it is theoretically postulated that one ton of cement incorporated in RCA could potentially absorb around 0.5 tons of CO_2 (Monkman and Shao, 2010). Studies have indicated that the utilization of Carbonated Recycled Aggregate (CRA) improves the adhesive strength between RCA and the new mortar. This enhancement is attributed to the presence of $CaCO_3$ on the CRA surface, which results in rearrangement and clogging effect of the microstructure of the attached mortar phase. However, investigations on the influence of incorporating Carbonated Recycled Sand (CRS) and Carbonated Recycled Powder (CRP) in concrete remain significantly limited. Carbonation processes in recycled sand are still poorly studied. That said, (Thiery et al., 2013) discussed the carbonation mechanism of a bed of Recycled sand. The study focuses on the rate of CO_2 absorption using model materials composed of sieved grains (1.5 mm to 2.5 mm.) of cement crushed paste from CEM I. They demonstrate that the carbonation rate can be influenced by both external and internal mass transfer within the particle. (Dos Reis et al., 2020) suggested to mix the grain to enhance the mass transfer around the particles and accelerate the over-all process. (Zhang et al., 2015b) and (Tang et al., 2023) focused on the effect of the incorporation of CRS in cementitious materials on their mechanical behavior. The studies discussed above have focused on developing new methods of treatment by accelerated carbonation of RS in order to improve the CO_2 storage and enhance the physical proprieties of RS. Also, some of them focused on parameters affecting the carbonation process. However, monitoring the process of carbonation assessing the rate, progression of carbonation and the potential CO_2 absorption of RS are needed in order to calculate the carbonation kinetic of RS and to highlight the optimum conditions to enhance/accelerate the RS carbonation.

The aim of this paper is to monitor the carbonation kinetic of a recycled sand with a particle size fraction of 0/4. The study was performed on a sand crushed from a mortar mixed in laboratory and based on standardized non-carbonated sand. 24 hours after mixing, the mortar was cured in water during 28 days in order to avoid carbonation. After that, the sand crushed was exposed to accelerated carbonation in laboratory during 7 days (until a maximum carbonation). A monitoring of the mass gain, pH evolution and carbonation products by TGA was carried out on the sand during carbonation.

II.TESTS AND PROCEDURES

A. Materials

The recycled sand (RS) employed in this research were produced in laboratory conditions from a standardized mortar. A purely siliceous standardized sand (0/4 mm) was used to ensure that the sand does not contain carbonates. Ordinary Portland cement CEM I 52.5 N according to the European Standard EN 197-1 was used. The mass fractions of the principal clinker phases provided by the manufacturer (Calcia, Bussac-France) and based on the Bogue calculation method are 65% C_3S, 13% C_2S, 7% C_3A, 13% C_4AF and 4.9% gypsum. The chemical composition and density of the cement used is given in Table 1.

Table 1. Chemical composition and density of the cement used.

Composition	Cao	SiO_2	Al_2O_3	Fe_2O_3	SO_3	K_2O	Na_2O	Density
CEM I (wt%)	64.20	20.50	5.00	3.90	2.50	0.29	0..05	3.80

The water-to-cement ratio (w/c) of the mortars used was 0.6, while the sand-to-cement ratio was 3. They were cast in cylindrical molds of Ø 11x22 cm². After 24 hours, the mortar specimens were demolded and stored in water at an ambient laboratory temperature until the age of 28 days. Next, the mortar specimens were cut into small pieces before being fed into the crusher. After crushing, various particle sizes less than 4 mm were obtained, since the crusher was set to 4 mm. This study required 5 kg of sand, which was crushed in about 1 hour. The desired RS particle distribution size (0/4mm) was obtained by sieving and then exposed to accelerated carbonation. Initial state of the recycled sand (RS) used was assessed through phenolphthalein spraying before carbonation. The pink color indicates that there is no initial natural carbonation of the RS (Figure 1). In addition, the initial water content of RS after crushing was 2.30 %.

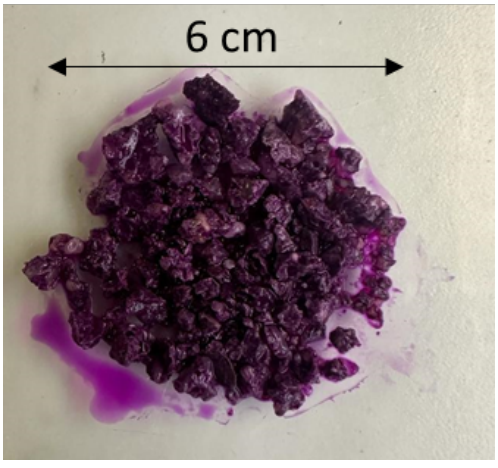

Figure 1. Phenolphthalein spraying on the recycled sand.

B. Accelerated carbonation

Plastic bins containing bed of recycled sand with a particle size fraction of 0/4 mm were placed in a carbonation chamber with a volume of 0.25 m^3 and a CO_2 concentration of 3% to 4% and relative humidity of 65%. A fan is positioned at the top of the chamber to ensure the homogenization of the ambient air. Relative humidity control is achieved using saturated saline solutions composed of magnesium nitrate. It should be noted that this relative humidity may vary within the chamber, depending on the evolution of the solid and liquid phases i the material. This is an aspect that has not been followed up in this work. In order to monitor carbonation of the recycled sand, colorimetric phenolphthalein test, mass monitoring, pH evolution and thermogravimetric analysis (TGA) were carried out on sand samples during the carbonation at the following exposure times: 0; 8; 24; 32; 48; 56; 72; 80; 96; 104; 120; 128; 144; and 152 hours. For pH measurements, the recycled sand (before or after carbonation) was immersed in distilled water with stirring and a pH probe accurate to 10^{-2}. The pH value was considered after stabilization. For TGA, a Setaram Setsys Evolution® device with a heating rate of 10°C/min from 20 to 1000°C was used. Powder samples of 100 ± 10 mg were used. Note that the water content of the recycled sand after carbonation (CRS) was 1.58 %.

CO_2 fixation by the CRS modifies a priori the mass of the specimen. The mass gain during carbonation was monitored using two cups containing the recycled sand studied, then were placed in the carbonation chamber. These cups were removed at each exposure time to measure mass, then replaced in the chamber. Thermogravimetric Analysis (TGA) and pH level measurement were also used for a comprehensive study. At these same intervals, some quantities were extracted from the chamber for pH readings and TGA testing.

III. Results

A. Phenolphthalein spraying test

A first qualitative phenolphthalein spraying method was used to asses the initial carbonation state of RS. Noted that, due to the small size of the sand particles, this method was used only to confirm the overall quality status of the carbonation of the RS. Figures 2 shows the colorimetric phenolphthalein test on RS during exposure to CO_2. Following six days of accelerated carbonation, recycled sands (0/4mm) seemed completely carbonated when the carbonation assessment using phenolphthalein spraying is conducted.

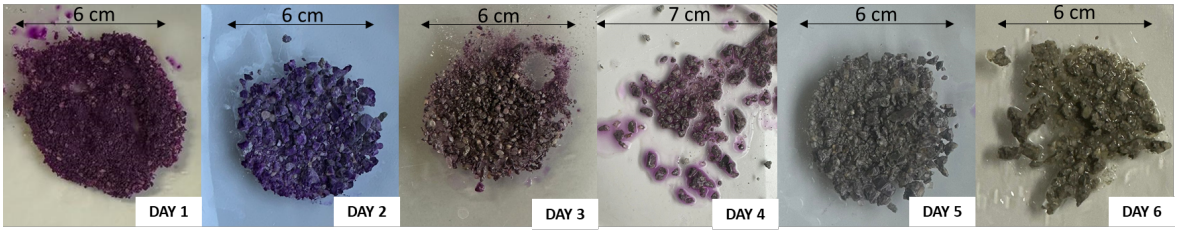

Figure 2. Result of Phenolphthalein spraying on carbonated recycled sand.

B. Mass gain monitoring

Mass gain is frequently cited in the literature as a sign of carbonation, that produces calcium carbonates ($CaCO_3$). Figure 3 displays the relative variations in recycled sand mass for the both cups used. The results showed an increase in mass overall as the carbonation process progressed, which may have resulted from CO_2 fixation (CO_2 uptake by adhered cement past) *(Zhang et al., 2016)*. In parallel, an hydraulic reaction with the cement paste particles present in the recycled sand or carbonation of the cement paste particles *(Hou, 2021)*. But one finding in particular has to be highlighted: during the first stage of carbonation (8 hours), there was a noticeable rise in mass and decreased later which was linked to the cementitious matrix's faster carbonation *(Hou, 2021, Kaddah et al., 2022)*. The mass increase may be associated with either a fast hydraulic response or the carbonation of leftover cement pastes particles that were adhered to the recycled sand's surface, it corresponds to the formation of initial carbonation products, which have a significant impact on mass *(Sereng, 2020)*. However, after this time a slighter increase is observed, suggesting a slowing down of the process. This is may be due to a saturation point or a transition to diffusion processes, which could act as a factor reducing the reaction. Beyond these results, the mass tracking has demonstrated that the samples are stabilized at a state of quasi-constant mass variation, which corresponds to a maximum carbonation of the RS used. Further information is given in "Discussions" section concerning the probable reason of the SR mass gain.

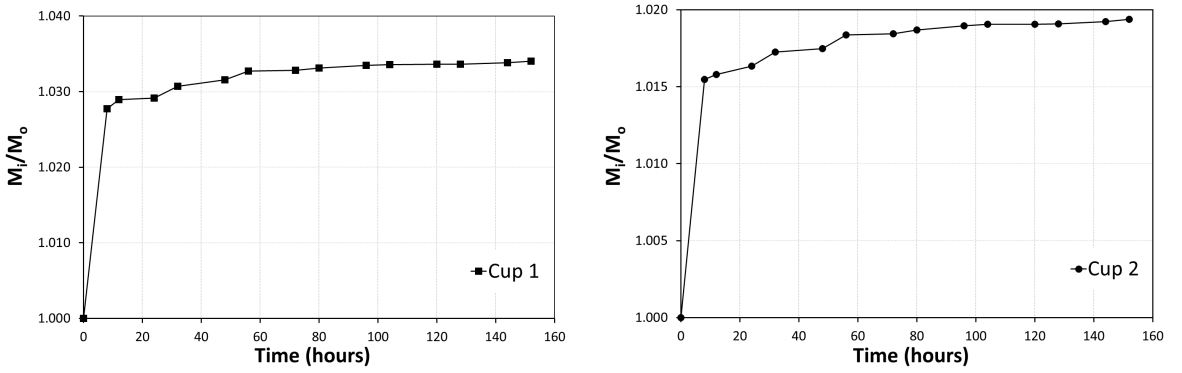

Figure 3. Mass gain of recycled sand during carbonation in the both cups used.

C. pH monitoring

Figure 4 shows the pH evolution of the recycled sand during carbonation. The results highlight a gradual decrease in pH over time. The quick pH decrease during the first eight hours of carbonation is in accordance with the mass gain discussed above. The decrease is likely the result of a quick hydrolysis reaction or an early reaction with the remains of the old cement paste adhered to the sand's grain surface *(Sereng, 2020)*. A second, weaker pH decrease kinetic was observed up to 6 days of carbonation (i.e., up to pH of 8.50). The results do not show stability in the pH of the carbonated recycled sand (CRS) at the end of the test, contrary to what was observed above for the monitoring of mass gain. We note that a more in-depth and longer-term monitoring of pH as a function of the carbonation of CRS is required. We recall that the pH decrease during carbonation of recycled sand is due to the carbonation of the old cement matrix (Portlandite dissolution and precipitation of calcium carbonates) *(Hou, 2021)*.

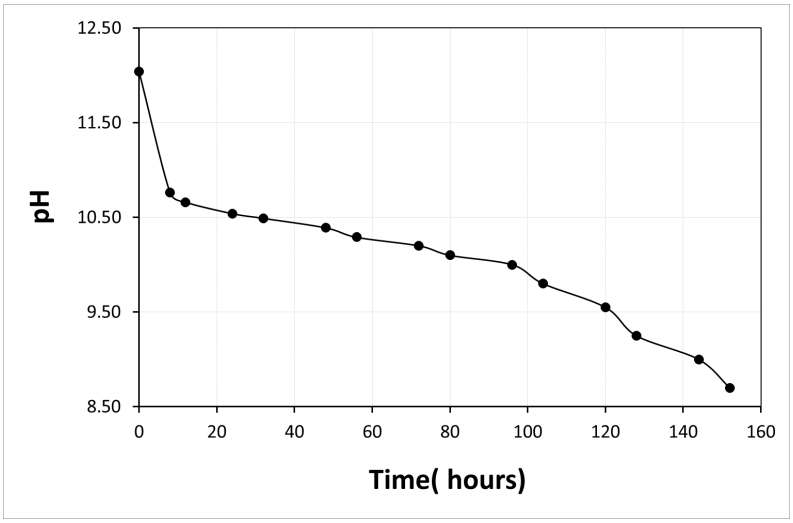

Figure 4. pH evolution of the recycled sand during carbonation.

D. Thermogravimetric Analysis (TGA)

Figure 5 shows TG curves and dTG ones of the recycled sand exposed to accelerated carbonation at 0; 8; 56 and 152 h. The amounts of the RS samples tested were 110 ± 6 mg. We recalled that the first peak at 120°C of the dTG curve is attributed to mass loss from free-vapor water evaporation and dehydration of gypsum. The second pick reveals a significant difference between the pre-carbonation and residual RS values between 430 and 500°C confirms the cement hydrates $Ca(OH)_2$ dissolution. Before carbonation, $Ca(OH)_2$ phase is seen between 400°C and 500°C; however, it decreases after carbonation, revealing the complete Portlandite decomposition. In the interval of 670 and 800°C, the $CaCO_3$ decomposition becomes more significant with CRS, showing a preferential development of metastable forms of calcium carbonate *(Lin et al., 2009)*.

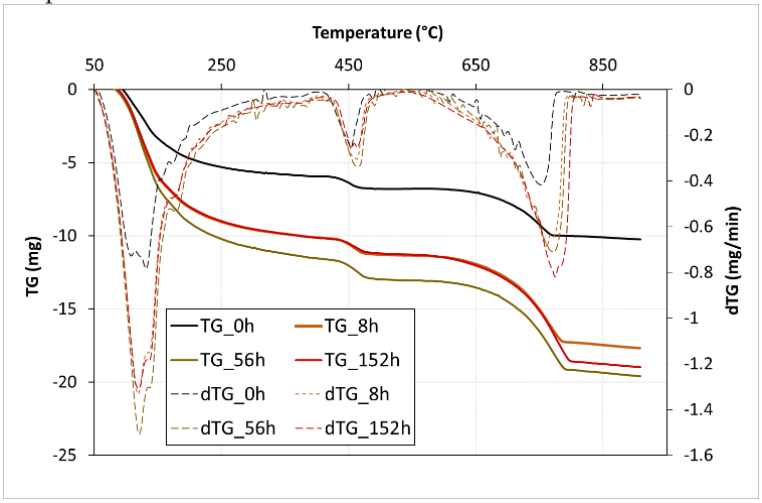

Figure 5. TG/dTG curves of recycled sand carbonation**.**

IV. Discussion

First, an increase in the mass of the recycled sand was observed as a function of the time of exposure to CO_2. The reasons of the mass gain could be: (1) humidity transport in the sand until

stabilization of water content of sand with the RH of the carbonation chamber.; (2) CO_2 capture which reacted mainly with portlandite dissolved in water to form $CaCO_3$; (3) H_2O produced by carbonation reaction. As a decrease in water content was observed in the SR before and after carbonation (2.30% and 1.58%, respectively), we can conclude that the mass gain in the carbonated SR (SRC) comes from CO_2 capture, which is in accordance with *(Zhang et al., 2016)*. Further measurements are required to confirm this result. The pH evolution of the recycled sand was monitored during CO_2 exposure by a pH meter (quantitatively) and by colorimetric phenolphthalein test (qualitatively). Quantitative monitoring showed a decrease in pH as a function of exposure time, due to the consumption of Portlandite. The colorimetric phenolphthalein test remained insensitive to this decrease (pink color) until day 5 of exposure, when the color becomes overall gray (Figure 2). This corresponds to a pH of around 9.70. Furthermore, we found that the pH of the recycled sand after 160 hours (about 7 days) of carbonation was not yet stable (i.e., carbonation not yet complete), yet the mass of the sand was relatively stable. This means that pH monitoring is more sensitive to carbonation than mass monitoring. The latter is not an accurate indicator of carbonation in view of phenomena acting in opposite directions during carbonation. CO2 fixation is accompanied by the release of water, which evaporates to maintain RH.

During eight hours of carbonation, a significant increase in $CaCO_3$ production is followed by a decrease in $Ca(OH)_2$. The latter was significantly decomposed, then after this duration, the amount of $CaCO_3$ continue to increase until about day 6. Long-term stabilization of the carbonation reaction may be revealed by identical fluctuations between 8 hours up to 6 days. These results suggest that the early carbonation phase is intensive, leading to a substantial production of $CaCO_3$, after that the CO_2 was more difficult to diffuse into the inner part of RCA, leading to an equilibrium in the process and exhibits rather stable changes over time *(Silva et al., 2019)*.

V. Conclusion

This article presents an experimental investigation of the carbonation kinetic of a laboratory-obtained recycled sable (0/4). The investigation covers the phenolphthalein test, mass gain, pH monitoring, and thermogravimetric analysis (TGA) on RS exposed to accelerated carbonation. The paper's preliminary findings include:

1. A significant rise in mass within the first hours of carbonation (eight for our study), which points out a quick response from the cementitious matrix. After 4-day carbonation, the mass evolution of the carbonated recycled sand was relatively stable. Based on SR water content monitoring before and after carbonation, the SR mass gain is due to CO_2 capture.

2. The gradual pH decrease of carbonated recycled sand over time is consistent with carbonation reactions, indicating a continuous precipitation of calcium carbonate. After 6-day carbonation, the pH of sand was not yet stable, contrary to mass gain, which could mean that the recycled sand carbonation was not yet maximum. pH monitoring is, a priori, more sensitive to carbonation than mass monitoring.

3. A substantial initial increase in $CaCO_3$ production during the first eight hours of carbonation, followed by a consistent rise in $CaCO_3$ content until 152 hours. This indicates a prolonged equilibrium phase in the carbonation process, suggesting difficulty in CO_2 diffusion into the inner part of RS beyond the initial intensive carbonation phase.

Acknowledgments

The authors would like to thank the Nouvelle Aquitaine Region and the Ecological Transition Agency (ADEME) for funding this work.

REFERENCES

Akhtar, A., Sarmah, A.K., 2018. Construction and demolition waste generation and properties of recycled aggregate concrete: A global perspective. Journal of Cleaner Production 186, 262–281. https://doi.org/10.1016/j.jclepro.2018.03.085

De Larrad, F., Colina, H., 2018. Le béton recyclé. Ouvrages Scientifiques, OSI4.

Dos Reis, G.S., Cazacliu, B.G., Artoni, R., Torrenti, J., 2020. Effect of the accelerated carbonation treatment on the recycled sand physicochemical characteristics through the rolling carbonation process. Journal of CO_2 Utilization 39, 101181. https://doi.org/10.1016/j.jcou.2020.101181

Hou, Y., 2021. Contribution au développement de la valorisation des déchets inertes du BTP : Étude de la carbonatation des granulats recyclés compactés, Thèse de doctorat, La Rochelle université, France.

Kaddah, F., Ranaivomanana, H., Amiri, O., Rozière, E., 2022. Accelerated carbonation of recycled concrete aggregates: Investigation on the microstructure and transport properties at cement paste and mortar scales. Journal of CO_2 Utilization 57, 101885. https://doi.org/10.1016/j.jcou.2022.101885

Ke, X., Xu, D., Cai, M., 2020. Experimental and numerical study on the eccentric compressive performance of RAC-encased RACFST composite columns. Engineering Structures 224, 111227. https://doi.org/10.1016/j.engstruct.2020.111227

Kou, S., Zhan, B., Poon, C., 2012. Feasibility study of using recycled fresh concrete waste as coarse aggregates in concrete. Construction and Building Materials 28, 549–556. https://doi.org/10.1016/j.conbuildmat.2011.08.027

Kou, S.-C., Zhan, B., Poon, C.-S., 2014. Use of a CO_2 curing step to improve the properties of concrete prepared with recycled aggregates. Cement and Concrete Composites 45, 22–28. https://doi.org/10.1016/j.cemconcomp.2013.09.008

Limbachiya, M.C., Marrocchino, E., Koulouris, A., 2007. Chemical–mineralogical characterisation of coarse recycled concrete aggregate. Waste Management 27, 201–208. https://doi.org/10.1016/j.wasman.2006.01.005

Lin, Y., Hu, Q., Chen, J., Ji, J., Teng, H.H., 2009. Formation of Metastable $CaCO_3$ Polymorphs in the Presence of Oxides and Silicates. Crystal Growth & Design 9, 4634–4641. https://doi.org/10.1021/cg900085

Mahieux, P.-Y., Turcry, P., Hamdoun, H., Amiri, O., Ferber, V., Chateau, L., 2017. Projet RECYMENT : Réactivité physico-chimique de graves recyclées utilisées en technique routière 35.

Monkman, S., Shao, Y., 2010. Integration of carbon sequestration into curing process of precast concrete. Can. J. Civ. Eng. 37, 302–310. https://doi.org/10.1139/L09-140

Sereng, M., 2020. Amélioration des propriétés des granulats recyclés par stockage de CO_2 : étude de la faisabilité pré-industrielle.

Silva, R.V., De Brito, J., Dhir, R.K., 2019. Use of recycled aggregates arising from construction and demolition waste in new construction applications. Journal of Cleaner Production 236, 117629. https://doi.org/10.1016/j.jclepro.2019.117629

Song, I.H., Ryou, J.S., 2014. Hybrid techniques for quality improvement of recycled fine aggregate. Construction and Building Materials 72, 56–64. https://doi.org/10.1016/j.conbuildmat.2014.08.041

Sormunen, P., Kärki, T., 2019. Recycled construction and demolition waste as a possible source of materials for composite manufacturing. Journal of Building Engineering 24, 100742. https://doi.org/10.1016/j.jobe.2019.100742

Tang, Y., Xiao, J., Wang, D., Zhang, M., 2023. Effect of carbonation treatment on fracture behavior of low-carbon mortar with recycled sand and recycled powder. Cement and Concrete Composites 142, 105178. https://doi.org/10.1016/j.cemconcomp.2023.105178

Thiery, M., Dangla, P., Belin, P., Habert, G., Roussel, N., 2013. Carbonation kinetics of a bed of recycled concrete aggregates: A laboratory study on model materials. Cement and Concrete Research 46, 50–65. https://doi.org/10.1016/j.cemconres.2013.01.005

Torrenti, J.M., Amiri, O., Barnes-Davin, L., Bougrain, F., Braymand, S., Cazacliu, B., Colin, J., Cudeville, A., Dangla, P., Djerbi, A., Doutreleau, M., Feraille, A., Gueguen, M., Guillot, X., Hou, Y., Izoret, L., Jacob, Y.-P., Jeong, J., Hiu Hoong, J.D.L., Mahieux, P.-Y., Mai-Nhu, J., Martinez, H., Meyer, V., Morin, V., Pernin, T., Potier, J.-M., Poulizac, L., Rougeau, P., Saadé, M., Schmitt, L., Sedran, T., Sereng, M., Soive, A., Dos Reys, G.S., Turcry, P., 2022. The FastCarb project: Taking advantage of the accelerated carbonation of recycled concrete aggregates. Case Studies in Construction Materials 17, e01349. https://doi.org/10.1016/j.cscm.2022.e01349.