# Evolution of the microstructure and shrinkage of recycled aggregates during accelerated carbonation

*Farah Kaddah[a], Harifidy Ranaivomanana[b], Ouali Amiri[c], Emmanuel Rozière[a, *]*

*Civil engineering and Mechanics Research Institute (GeM), UMR CNRS 6183,*

*[a] Ecole Centrale de Nantes, 1 rue de la Noe, 44321 Nantes, France*

*[b] IUT de Saint-Nazaire, 58 rue Michel Ange, 44606 Saint-Nazaire, France*

*[c] Polytech'Nantes, Campus Gavy, Boulevard de l'Université, 44603 Saint-Nazaire, France*

*[*] Corresponding author, Emmanuel.Roziere@ec-nantes.fr*

**RESUME** La carbonatation accélérée des granulats recyclés (RCA) est envisagée pour améliorer leurs propriétés. Plusieurs phénomènes physico-chimiques et mécaniques se produisent durant la carbonatation d'un mortier de ciment. Pour les étudier, des échantillons de mortier sont soumis à la carbonatation accélérée afin de suivre l'évolution de leur retrait en fonction du degré de carbonatation. Dans un premier temps, la carbonatation de la portlandite et la précipitation de la calcite dominent et sont accompagnés d'un léger retrait de carbonatation. Par la suite, la carbonatation des C-S-H devient prépondérante conduisant à la formation de vatérite et d'aragonite ainsi qu'au développement un fort retrait de carbonatation favorisant l'apparition de microfissures.

**Keywords** Carbonation, Recycled Concrete Aggregates, Shrinkage.

## I.  INTRODUCTION

While there is a critical shortage of natural aggregates for the production of new concretes, the huge production of cement-based materials cause serious ecological and environmental problems. Therefore, the reuse of construction and demolition waste is imperative to achieve sustainable development in the construction industry. Compared to typical natural aggregate (NA), recycled concrete aggregate (RCA) has a lower quality. In recent years, accelerated carbonation technique has been suggested to improve the quality of RCA. In France, this topic has been addressed in the framework of the national FastCarb project and ANR CO₂NCRETE

The accelerated carbonation of RCAs requires significant $CO_2$ pressure. The carbonation shrinkage generated in these conditions and its effects remain neglected. This study aims to monitor the evolution of the carbonation shrinkage developed during accelerated carbonation of RCAs in order to assess its intensity and effects.

## II.  MATERIALS AND EXPERIMENTAL PROGRAM

### A.  *Materials and samples preparation*

Due to the great variability of RCAs and the inability to assess accurately their composition and to measure carbonation shrinkage at particle scale, the experimental program was carried out on

mortar representing the mortar bound to the natural aggregate in the recycled aggregate. Portland cement CEM I 52.5 and natural siliceous sand (0-2 mm) were used. Cylindrical mortar samples (Ø 20×160 mm) were prepared with mixture proportions of cement: sand: water of 1: 2.6: 0.6. All the samples were demolded after 24 h and then soaked in a tap water tank for 180 days at $23 \pm 1$ °C.

*B. Experimental program*

After the curing period, a preconditioning was carried out before carbonation. The samples were dried at 40°C for 10 days, and then stored for another 17 days in an air-conditioned room (T=20°C, relative humidity RH=55%) to homogenize the internal humidity. Before carbonation, the samples were protected transversely on their bases with a layer of resin. They are then subjected to two-dimensional carbonation in a climatic chamber connected to a $CO_2$ tank at 20°C, 65% relative humidity and 15% $CO_2$ (accelerated carbonation) and in an air-conditioned room at 20 °C, 55% relative humidity and 0.04% $CO_2$ ( natural carbonation). The thermogravimetric analysis was performed on carbonated samples (accelerated carbonation) at different carbonation times. The temperature ranged from 20 to 1000°C with a heating rate of 10°C per minute. The contents of portlandite, vaterite + aragonite, and calcite were then calculated using the differential thermogravimetric (DTG) analysis.

Some cylindrical samples were equipped with metal studs. These studs made it possible to place the cylinder in a vertical sensor to measure the longitudinal deformation. After the curing, the shrinkage was measured in the carbonation chamber and the air-conditioned room.

The parameter chosen to represent the progress of carbonation is the ratio between the actual quantity of $CO_2$ captured and the theoretical maximum quantity of $CO_2$ that can be captured.

Carbonation rate (CR) = $\frac{\text{Mass CO2 bound at time t}}{\text{Mass CO2max}} * 100$                    **Equation 1**

The actual amount of $CO_2$ captured is determined from the TGA results while the theoretical maximum amount of $CO_2$ is determined based on the composition of the cement according to the following equation (Zhan et al., 2013):

$CO_{2max}$ = 0.785(CaO-0.7SO$_3$)+1.091MgO+1.420Na$_2$O+0,935K$_2$O                    **Equation 2**

## II.    Results and discussion

*A. Carbonation products*

Based on the DTG curves obtained at different carbonation times and therefore at different carbonation rates, FIGURE 1 shows the evolution of the proportions of portlandite and calcium carbonate polymorphs during carbonation as a function of the carbonation rate. Prior to carbonation (CR = 0%), portlandite and calcite are present. As the carbonation progresses (CR increases), portlandite rapidly decreases and completely disappears when CR reaches 25% while the amount of calcite significantly increases. Then the amount of calcite remains almost constant as the carbonation progresses while the other two polymorphs of calcium carbonate (vaterite and aragonite) precipitate (Morandeau et al., 2014). The more advanced the carbonation, the greater the amounts of aragonite and vaterite become.
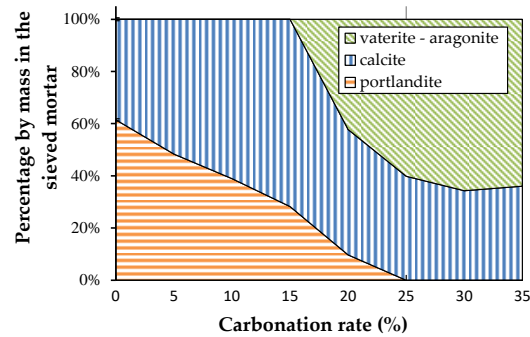
**FIGURE 1 : Evolution of the mass distribution of the four components (calcite, portlandite, vaterite and aragonite) with respect to the total mass = mass calcite + mass portlandite + mass aragonite + mass vaterite**

The type of calcium carbonate polymorph formed depends on the type of carbonated hydrates and therefore on the pH of the interstitial solution. The carbonation of portlandite initially dominates. As long as Portlandite is not completely dissolved, it maintains a basic pH of the pore solution due to its buffering effect. At this stage of carbonation, the precipitation of calcite – the stable polymorph of calcium carbonate – is dominant (Li et al., 2020). As carbonation progresses, the portlandite consumption becomes very slow compared to other hydrates, especially C-S-H. However, C-S-H having no buffering effect, the pH of interstitial solution drops to less than 9. The precipitation of other polymorphs (vaterite, aragonite) becomes predominant at this stage.
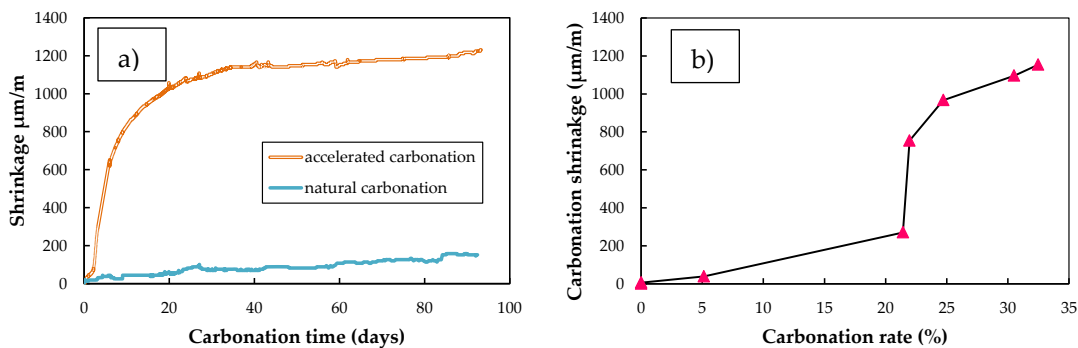
*B.   Carbonation shrinkage*



**FIGURE 2 : Shrinkage of mortar during carbonation as a function of a) carbonation time and b) carbonation rate**

Shrinkage was monitored during preconditioning and carbonation. At the end of the preconditioning, the shrinkage stabilizes and consequently the shrinkage measured during the natural and accelerated carbonation (FIGURE 2-a) corresponds exclusively to the carbonation shrinkage. The bottom curve of FIGURE 2-a corresponds to the shrinkage of the cylinder placed in the air-conditioned room and undergoing natural carbonation while the upper curve corresponds to the shrinkage of a sample undergoing accelerated carbonation in the carbonation chamber. In the air-conditioned room, a stabilization of shrinkage was observed while it increased significantly in the carbonation chamber. The difference between the two curves can therefore be attributed to the accelerated carbonation shrinkage. FIGURE 2-b shows the evolution of the carbonation shrinkage as a function of carbonation rate. The shrinkage increased slightly in the

first days of carbonation when the CR increased from 0 to 20%; a more significant increase was observed on the following days when the CR increased from 20 to 27%. Then the shrinkage begins to stabilize. As reported in the literature, carbonation shrinkage is mainly due to the decalcification and polymerization of C-S-H followed by the formation of amorphous silica gel (Auroy et al., 2018). Such mechanisms may explain the slight increase in shrinkage at the first days of carbonation given that portlandite carbonation is dominant compared to that of C-S-H. While the amount of portlandite sharply decreases (FIGURE 1) after the first days of carbonation, the carbonation of CSH becomes predominant and results in a significant carbonation shrinkage . Then, most of the hydration products (notably portlandite and C-S-H) carbonate and the shrinkage starts to stabilize. It should be noted that the shrinkage caused by carbonation (about 1000 μm/m) is significant. Moreover, it is slightly underestimated because the relative humidity of natural carbonation is slightly lower than that used for accelerated carbonation. This shrinkage can cause the development of microcracks in the carbonated zone (Cui et al., 2020) and therefore affect the transfer properties of RCA (Kaddah et al., 2022).

## CONCLUSION

Carbonation of portlandite initially dominates, leading to the precipitation of calcite (the stable polymorph of calcium carbonate) and accompanied by a slight increase of the carbonation shrinkage. As the carbonation progresses the portlandite is depleted. As consequence, the pH of the concrete decreases and the carbonation of C-S-H becomes predominant, which leads to the precipitation of aragonite and vaterite (unstable polymorphs of $CaCO_3$). The carbonation shrinkage becomes significant during this stage and it is likely to cause damage and cracking.

## REFERENCES

Auroy, M., Poyet, S., Le Bescop, P., Torrenti, J.-M., Charpentier, T., Moskura, M., Bourbon, X., 2018. Comparison between natural and accelerated carbonation (3% CO2): Impact on mineralogy, microstructure, water retention and cracking. Cem. Concr. Res. 109, 64–80. https://doi.org/10.1016/j.cemconres.2018.04.012

Cui, D., Zuo, X., Zheng, K., Talukdar, S., 2020. Tomography-Based Investigation on the Carbonation Behavior through the Surface-Opening Cracks of Sliced Paste Specimen 17.

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. J. CO2 Util. 57, 101885. https://doi.org/10.1016/j.jcou.2022.101885

Li, Y., Liu, W., Xing, F., Wang, S., Tang, L., Lin, S., Dong, Z., 2020. Carbonation of the synthetic calcium silicate hydrate (C-S-H) under different concentrations of CO2: Chemical phases analysis and kinetics. J. CO2 Util. 35, 303–313. https://doi.org/10.1016/j.jcou.2019.10.001

Morandeau, A., Thiéry, M., Dangla, P., 2014. Investigation of the carbonation mechanism of CH and C-S-H in terms of kinetics, microstructure changes and moisture properties. Cem. Concr. Res. 56, 153–170. https://doi.org/10.1016/j.cemconres.2013.11.015

Zhan, B., Poon, C., Shi, C., 2013. CO2 curing for improving the properties of concrete blocks containing recycled aggregates. Cem. Concr. Compos. 42, 1–8. https://doi.org/10.1016/j.cemconcomp.2013.04.013