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**ASSESSMENT OF CARBON SEQUESTRATION POTENTIAL OF CONCRETE BLOCKS  
WITH AN ACCELERATED ENVIRONMENTAL EXPOSURE CHAMBER**

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**ABSTRACT**

Portland cement based materials have the capacity to capture atmospheric CO<sub>2</sub> through carbonation reactions, yielding fixed calcium carbonate phases. In most cases carbonation reactions slowly progress over a timescale of decades before achieving complete carbonation. The ability to rapidly assess the potential CO<sub>2</sub> uptake of concrete blocks over their service life would allow for the refinement and selection of manufacturing methods that could optimize CO<sub>2</sub> recovery. Industrially produced concrete blocks manufactured under different curing conditions were exposed to a 30 °C, 3% CO<sub>2</sub>, 55% relative humidity chamber for 2, 4, 8, 16, and 30 days and the degree of carbonation of the cement paste assessed by phenolphthalein staining and petrographic microscope. Carbonation rates were found to be similar for both the CO<sub>2</sub>-injected and non CO<sub>2</sub>-injected blocks.

**KEYWORDS:** *concrete blocks, carbonation*

**INTRODUCTION**

Carbonation injection technology is being adopted by the concrete block manufacturing industry as part of an effort to help sequester CO<sub>2</sub> [1-9]. Before the blocks have hardened, CO<sub>2</sub> is introduced and precipitates within the blocks as nanometer to micrometer scale crystalline CaCO<sub>3</sub> [7,10,11]. Concrete also naturally carbonates over time in the presence of atmospheric CO<sub>2</sub>, but over a period of years or decades [12]. So, the question arises: over the life cycle of a concrete block, does early-

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age CO<sub>2</sub> injection impede, enhance, or have a negligible influence on the long-term natural carbonation process? To help answer this question, concrete blocks were retrieved from an industrial block manufacturer for an accelerated carbonation experiment. Half of the blocks were produced using CO<sub>2</sub> injection, and the other half were produced without CO<sub>2</sub> injection. As received, the CO<sub>2</sub> injected blocks were painted with a red stripe (red blocks), and the control blocks (without CO<sub>2</sub> injection) were painted with a yellow stripe (yellow blocks). The blocks were produced in successive production runs during the week of December 21, 2015. No other information with regard to composition was provided.

For accelerated simulations of the natural carbonation process, CO<sub>2</sub> concentrations in the range of 4-5% over one week have been reported as equivalent to one year of natural exposure [13,14]. However, concentrations >3% have also been reported to induce mineralogical changes that deviate from natural atmospheric carbonation [15]. Relative humidity (RH) is another important parameter for accelerated carbonation testing, and an RH of 65 % has been reported as optimal for the promotion of carbonation reactions [16].

Although a variety of methods for the assessment of the extent of carbonation have been explored [5,16-21] there is no established standardized method. Furthermore, in real-world situations, it also becomes necessary to distinguish between carbonate minerals attributed to carbonation, and carbonate minerals already present within carbonate aggregate, or within portland cement interground with limestone.

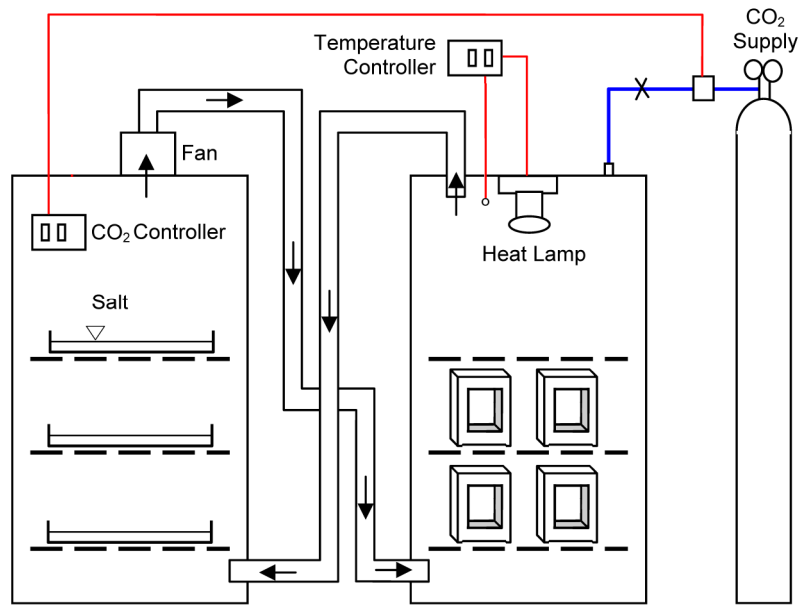
## **EXPERIMENTAL**

### ***Carbonation Chamber***

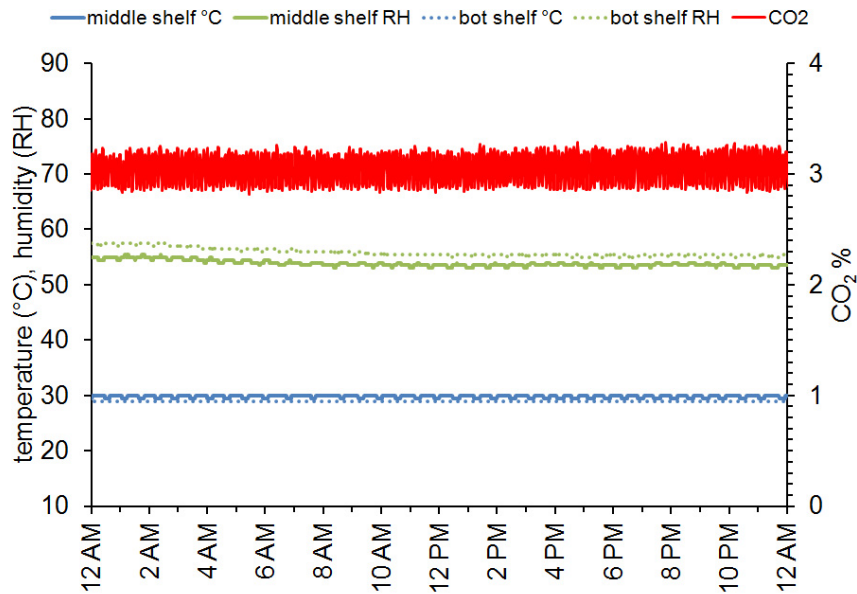
To accelerate the carbonation process, the blocks were placed in a chamber maintained at 30 °C, 55 % RH, and 3% CO<sub>2</sub> (Figure 1) [22]. The testing was commenced two weeks post-production. A saturated salt solution of a commercial de-icer blend of NaCl, KCl, and Ca<sub>2</sub>Cl was used to control humidity [23]. In order to fit inside the chamber, the blocks were cut in half. To demonstrate chamber performance, Figure 2 shows a typical day's worth of temperature, humidity, and CO<sub>2</sub> concentration data.

### ***Monitoring Carbonation Depth by Phenolphthalein Indicator Solution***

At the beginning of the experiment, a pair of yellow blocks and a pair of red blocks were set aside as controls. A 50 mm thick slice was cut from each block using a water-cooled diamond saw, and the fresh cut face sprayed with a phenolphthalein solution. When the solution comes in contact with calcium hydroxide present in the hydrated paste, the surface turns pink. Calcium hydroxide converts to CaCO<sub>3</sub> when exposed to CO<sub>2</sub>, so areas that do not turn pink after phenolphthalein application are considered to be carbonated [16]. Additional pairs of yellow and red blocks were placed in the carbonation chamber, and pulled at exposure intervals of two, four, eight, and sixteen days.



**Figure 1: Schematic of test chamber, adapted from McGrath [22].**



**Figure 2: Twenty four hours of temperature, humidity, and CO<sub>2</sub> concentration data.**

### *Monitoring Carbonation by Petrographic Microscope*

Epoxy impregnated polished thin sections were prepared from blocks after zero, two, and thirty days exposure. To minimize carbonation of the samples during preparation, the thin sections were prepared anhydrously, using mineral oil and kerosene as coolant. Furthermore, to avoid subsequent carbonation after preparation, glass coverslips were fixed to the thin section surface using mineral oil.

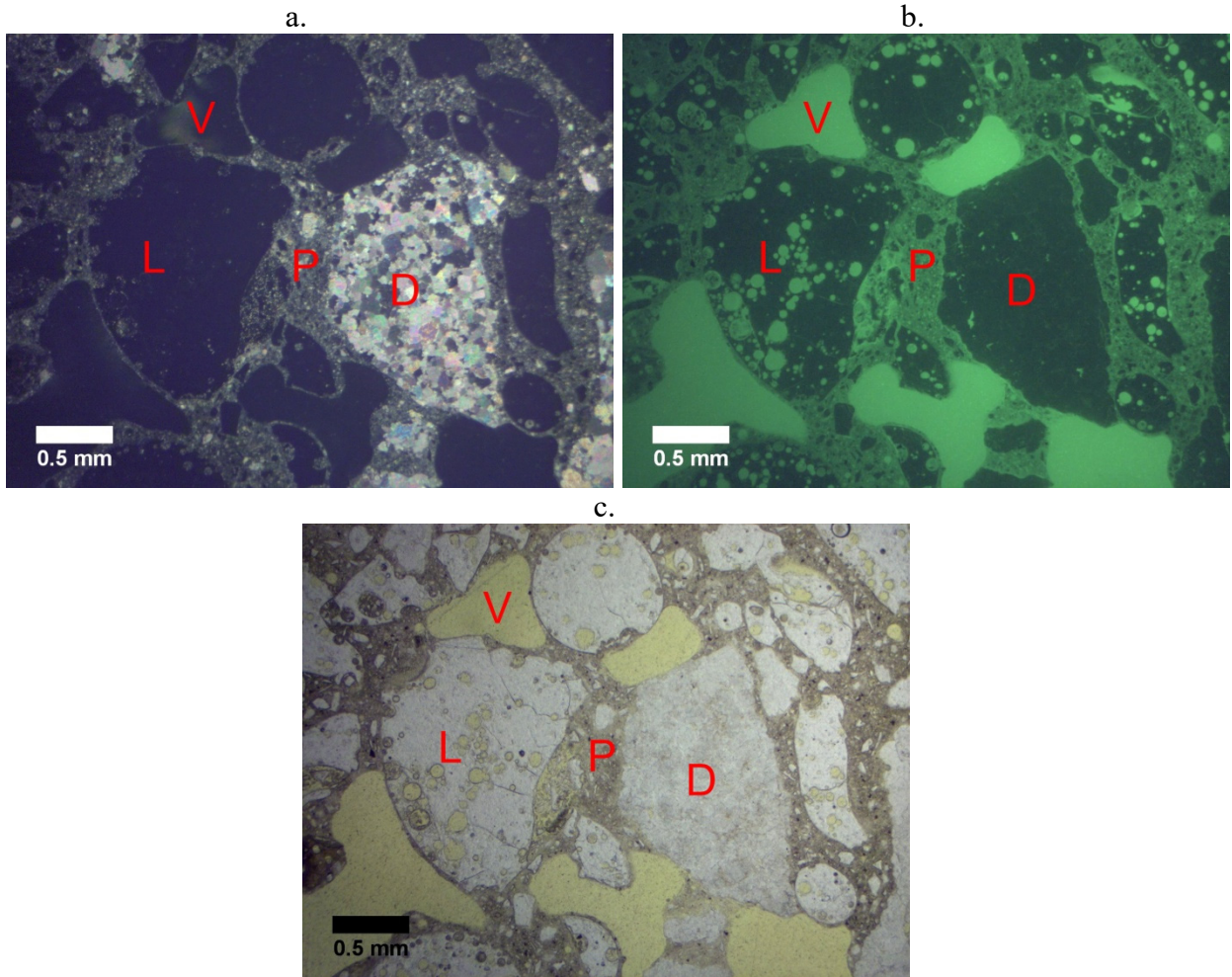
Under a petrographic microscope, some translucent minerals, when placed between two polarized filters (where the orientations of the filters are set 90° to each other) will exhibit interference colors as the minerals are revolved in different directions. Such minerals are termed anisotropic. Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) and quartz ( $\text{SiO}_2$ ) are two common examples of anisotropic minerals. The interference colors arise due to the fact that when light enters an anisotropic mineral, it is split into two orthogonal waves that travel with different velocities. After leaving the mineral, the waves return to their original velocities, but with an associated shift in phase. In a petrographic microscope, polarized light entering an anisotropic mineral from below is split into the two orthogonal waves, and the components of these waves that are parallel to the upper polarizing filter, when combined, can yield characteristic interference colors. The interference colors and their intensities are a function of the mineral's thickness, orientation, and the difference in wave velocity. Other translucent minerals or materials, when placed between crossed polarized filters will appear black, regardless of their orientation. Such materials are termed isotropic. Halite (rock salt) and glass are two common examples of isotropic materials. For those less familiar with petrographic methods, an excellent introduction is provided by Raith, Raase, and Reinhardt [24].

As hardened cement paste carbonates, microscopic crystals of calcite, aragonite, and vaterite (different varieties of  $\text{CaCO}_3$ ) are formed. These are all anisotropic minerals, so when carbonated paste is observed under crossed polarized light, they impart a distinctive bright appearance as compared to non-carbonated paste. Cement paste with a bright appearance under crossed polarized light is diagnostic of carbonation [25,26]. Of course, the utility of a petrographic microscope as applied to concrete is not limited to the detection of carbonated paste. In the case of the concrete blocks examined in this research, the petrographic microscope was also used to identify the aggregates used, and to directly observe porosity (Figure 3). Manufactured (crushed) dolostone aggregate particles were identified due to their bright appearance under crossed polarized light, and the typical rhombic shape of the individual dolomite crystals that make up the particles. Lightweight expanded glass aggregate particles were easily identified due to their dark appearance under crossed polars, as well as their many internal spherical voids. A fluorescent yellow dye was added to the epoxy to assist with the observation of pore space. The epoxy fills not only the larger  $\mu\text{m}$  to mm scale void spaces, but also the capillary pore spaces within the cement paste. A blue filter is used to excite the dye, which fluoresces green, and a yellow blocking filter is used to remove the blue wavelengths, so that only the fluoresced green wavelengths from pore spaces can be seen [25].

## RESULTS

### *Phenolphthalein Stain*

Figure 4 shows the slices cut from the blocks after application of the phenolphthalein solution. For the control blocks, the entire surface is stained pink, indicating that carbonation was negligible. After eight days exposure, the pink coloration is not as strong, and the pink coloration is absent within the first 1-2 cm of the block exterior. After sixteen days exposure, the pink coloration is almost completely absent, with only traces remaining in the yellow blocks.

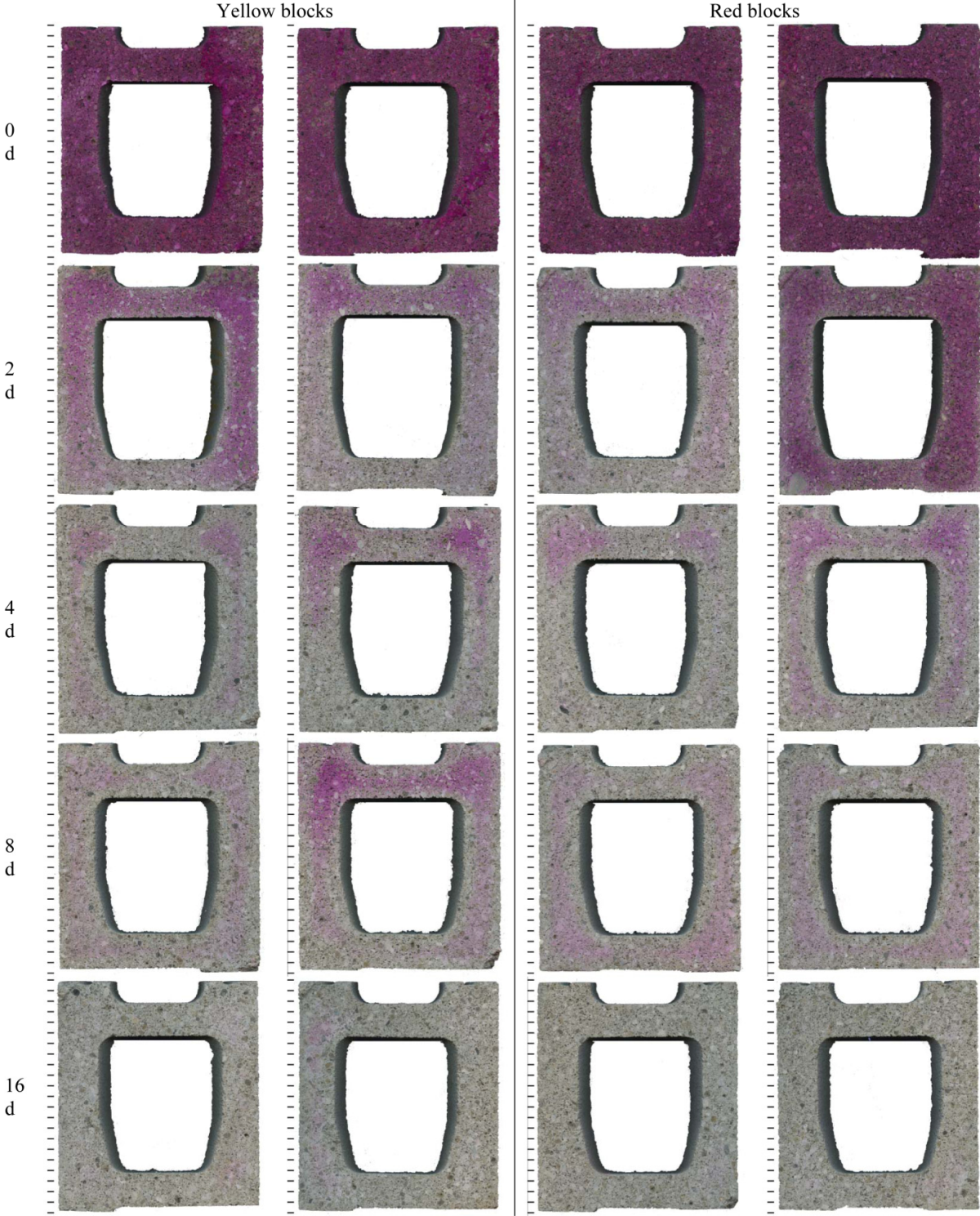


**Figure 3: Crossed polars (a), fluorescent (b), and plane polarized (c) images with example entrapped air void labeled “V”, light weight expanded glass aggregate particle “L”, cement paste “P”, and dolostone aggregate particle “D”.**

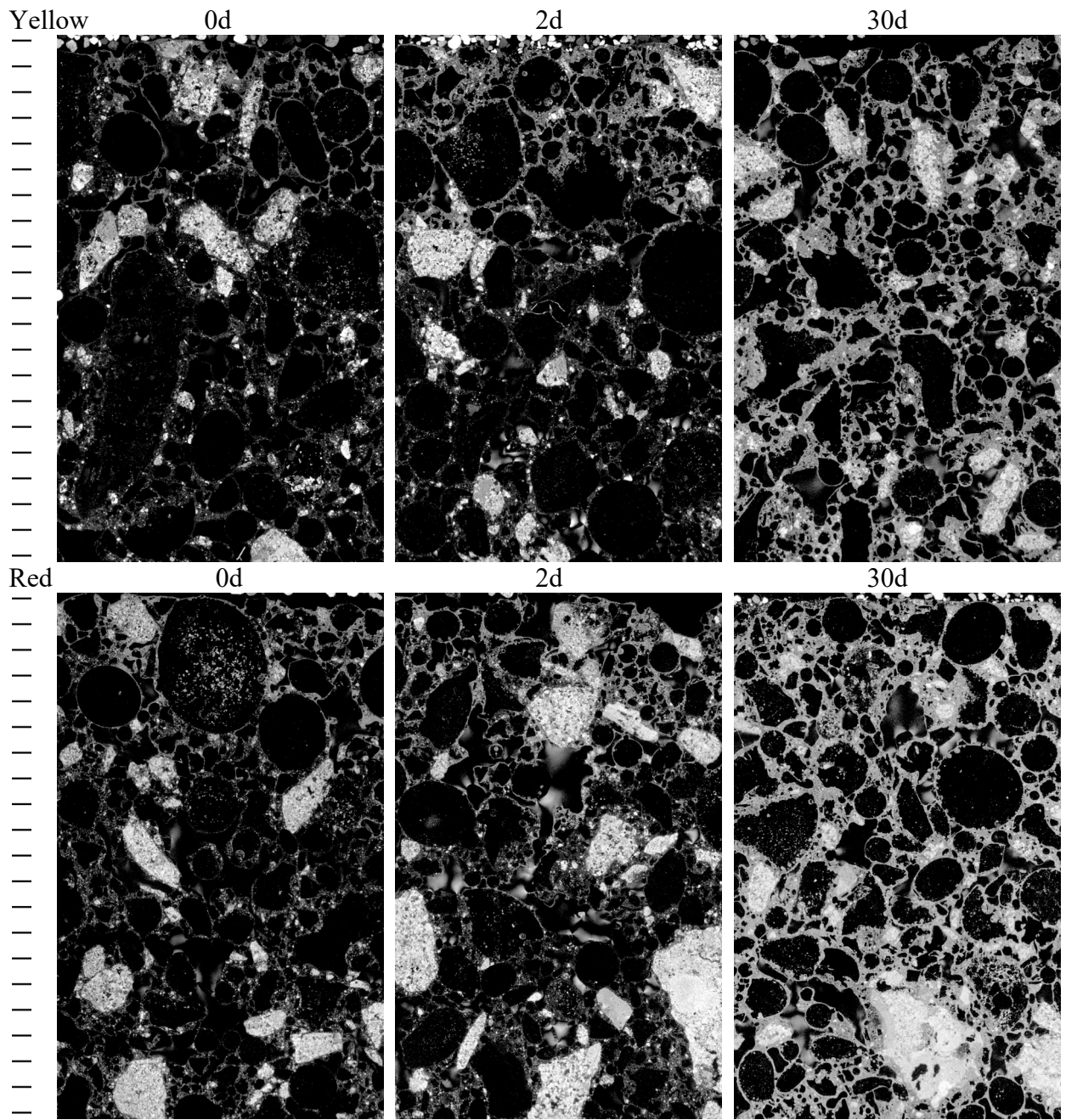
### ***Petrographic Microscope***

Figures 5 through 7 consist of optical images of the polished thin sections. Under cross-polarized light (Figure 5) the anisotropic dolostone aggregate particles are bright, while the isotropic LWA particles are completely dark. Also under cross-polarized light, the carbonated paste exhibits an intermediate brightness, while non-carbonated paste remains dark. Since both the dolostone aggregate and the carbonated cement paste appear bright, it is difficult to use cross-polarized light alone to quantify the degree of carbonation. To help isolate and quantify the relative amounts of carbonated paste, crossed polarized, fluorescent, and plane polarized light images were combined in 24-bit (0–255 intensity channels per band) red green blue (RGB) color space (Figure 6). In this false-color scheme, dolostone aggregate particles appear yellow/orange, porosity appears light blue, non-carbonated paste appears dark blue, carbonated paste appears pink, and LWA particles are for the most part green. At the very top of some of the images, rounded quartz sand grains

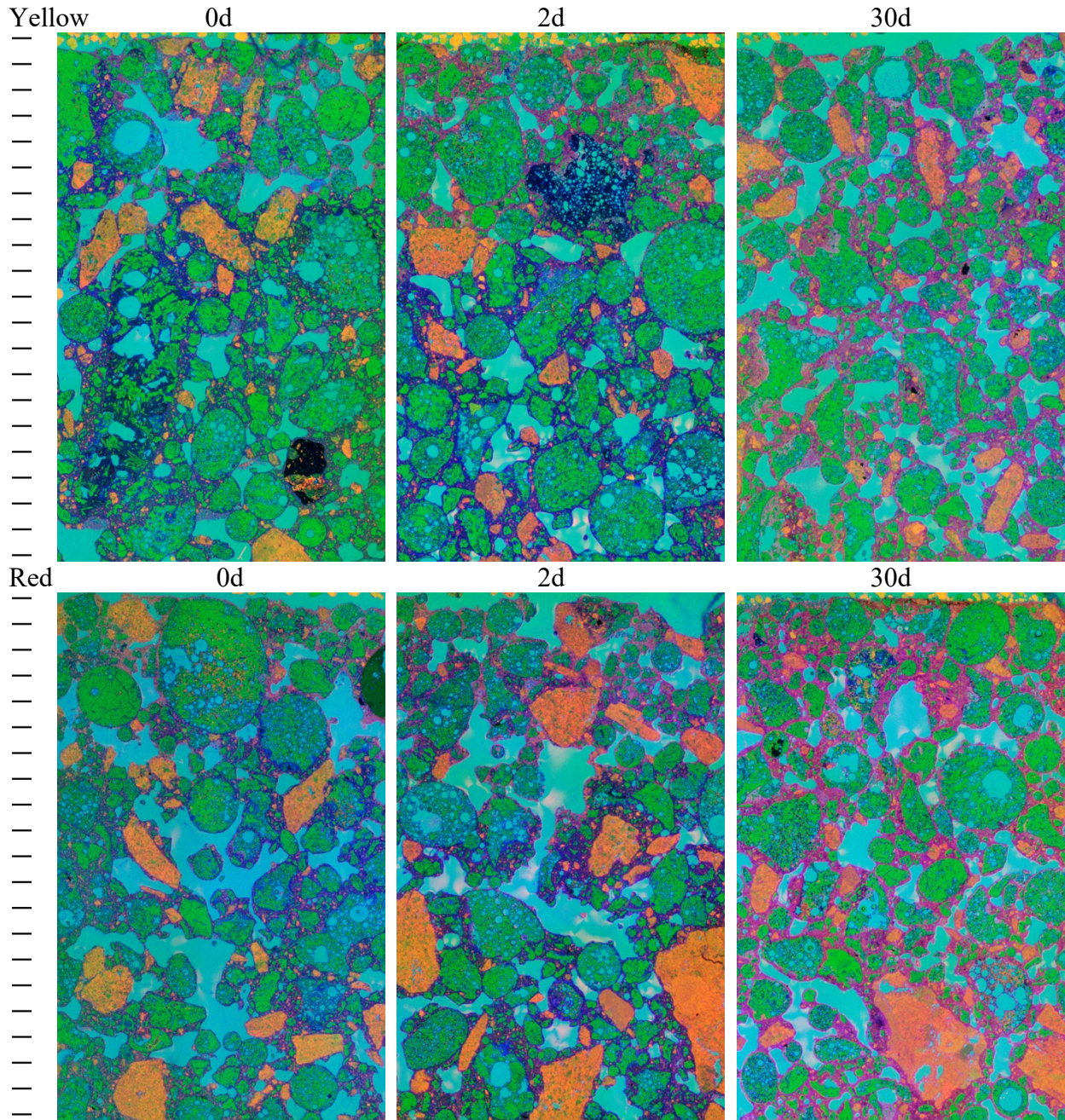
(yellow) are present, external to the blocks; the quartz sand was added during the epoxy impregnation step to help conserve epoxy.



**Figure 4: Phenolphthalein staining of saw cut surfaces through blocks versus duration (days) in the accelerated carbonation chamber (tic marks every cm)**



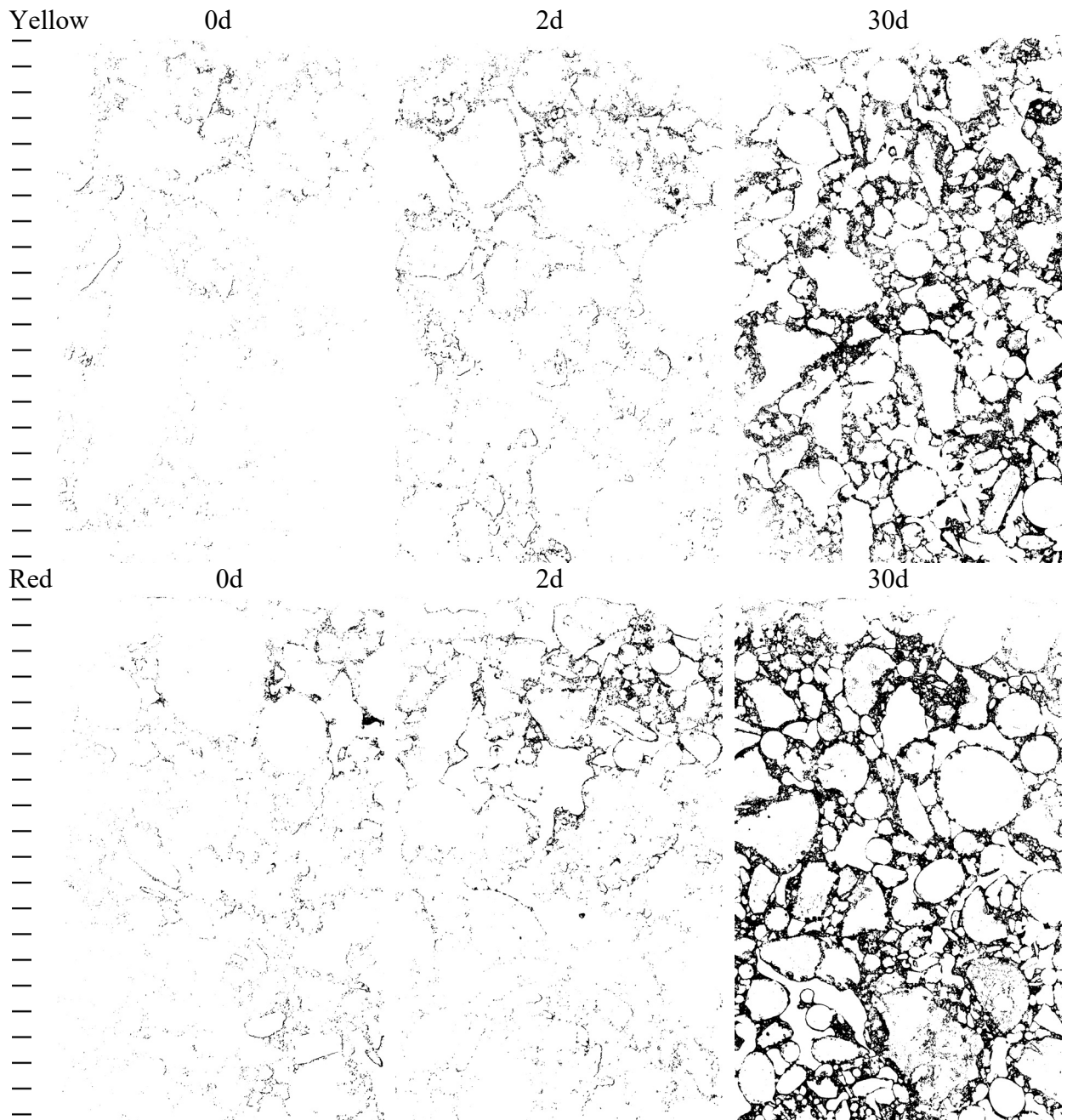
**Figure 5: Crossed polarized illumination; block exterior surface oriented at top, tic marks every mm.**



**Figure 6: Combined cross-polarized, fluorescent, and plane polarized light images in RGB color space; block exterior surface oriented at top, tic marks every mm.**

The pink (or magenta) hue of the carbonated paste is the result of brighter intensities in the red (cross polarized light) and blue (plane polarized light) bands, with less intensity in the green (fluorescent) band. A color threshold ( $R \geq 120$ ,  $G \leq 120$ ,  $B \geq 120$ ) was applied to extract the carbonated (magenta/pink) paste pixels, with the result shown in Figure 7. Figure 8 tabulates the carbonated pixel populations versus depth.

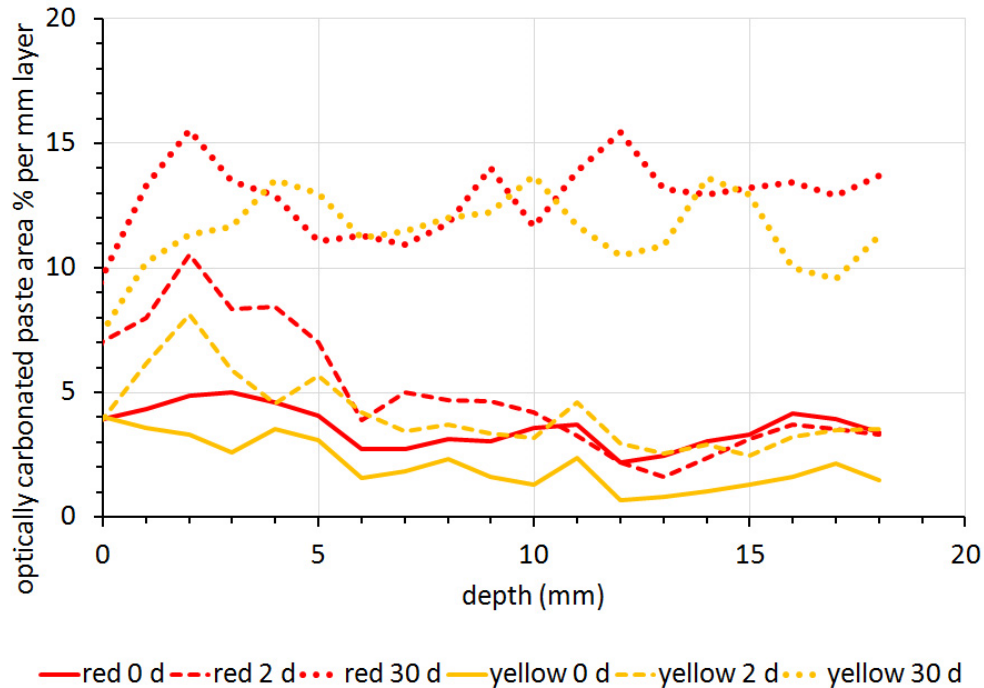




**Figure 7: Binary image of carbonated paste pixels (black); block exterior surface oriented at top, tic marks every mm.**

## CONCLUSIONS

Two methods of determining the extent of carbonation were explored to determine the influence of CO<sub>2</sub> injection on environmental carbonation rates in industrially-produced concrete blocks. From a qualitative perspective, the traditional phenolphthalein stain approach showed equivalent carbonation rates for CO<sub>2</sub>-injected and non CO<sub>2</sub>-injected blocks. The optical microscope method allowed for the distinction between carbonate aggregate and carbonated paste, and showed equivalent carbonation rates in profile for the CO<sub>2</sub>-injected and non CO<sub>2</sub>-injected blocks.



**Figure 8: Optically carbonated paste versus depth from polished thin sections.**

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