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S Roucan, Fionn McGregor, Antonin Fabbri, Céline Perlot-Bascoules, J-C Morel. Indoor CO₂ buffering potential of clay-based building materials. IOP Conference Series: Earth and Environmental Science, 2022, 1078 (1), pp.012135. 10.1088/1755-1315/1078/1/012135 . hal-04111665

HAL Id: hal-04111665

<https://univ-pau.hal.science/hal-04111665>

Submitted on 31 May 2023

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To cite this article: S Roucan *et al* 2022 *IOP Conf. Ser.: Earth Environ. Sci.* **1078** 012135

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Indoor CO₂ buffering potential of clay-based building materials

S Roucan¹, F McGregor¹, A Fabbri², C Perlot-Bascou¹ and J-C Morel²

¹ Université de Pau et des Pays de l'Adour, E2S UPPA, SIAME, Anglet, France

² LTDS, UMR 5513 CNRS, ENTPE, 2 rue Maurice Audin, Vaulx-en-Velin, France
sofia.roucan@univ-pau.fr

Abstract. To mitigate the anthropogenic greenhouse gas emissions from the operational energy consumption in buildings, increasingly high-performance envelopes are developed. A reduction in indoor air renewal is observed that leads to a higher pollutant concentration in the built environment. Particular attention was given to CO₂, an anthropogenic gas that has consequences on the Indoor Air Quality (IAQ) and the health of occupants. Developing a passive regulation system appears to be a promising solution for improving IAQ and reducing the energy consumption of ventilation systems. For that purpose, earth-based materials present interesting characteristics through the presence of clay minerals and their microstructure. In this context, this paper aims at presenting a novel experimental method to assess the CO₂ retention potential of natural earth plasters. The method uses a thermogravimetric device (TGA/DSC) associated with a gas mixer and humid air generator. The mass variation resulting from the interaction of the increasing CO₂ content could thereby be measured and analysed. Results show the important role of reversibility in the phenomenon: the majority of the captured CO₂ being released when the CO₂ concentration drops. It also highlights the role of the relative humidity on the retention capacity. As the retention of CO₂ is lower when the material is wet, the water molecules may occupy part of the adsorption sites and react themselves with the CO₂. This experiment provides the first values and thus evidence of the CO₂ retention capacity and passive regulation potential of this material.

Keywords: Earth plaster, Thermogravimetric method, Indoor air quality, adsorption/desorption, CO₂ retention.

1. Introduction

A great proportion, around a half, of the globally consumed energy can be attributed to the building and construction sector, which is also responsible for around a half of the waste produced in Europe [1]. Therefore considerably affecting climate change but also the related environmental consequences such as the loss of biodiversity and air and water pollution. The sector is therefore facing challenges to reduce its impact and as it is now well identified this means more energy efficient buildings, reducing the carbon footprint and a better waste management [2]. In this context, the aim to improve the energy efficiency of building had a negative impact on indoor air quality (IAQ), notably by reducing the air exchange rate. IAQ and comfort is gaining interest as the modern civilisation spends most of its time indoors [3]. A poor IAQ may increase respiratory irritation or worsen the global health condition, an example is the famous sick building syndrome [4]. It is therefore very important to recognize the interdependencies between IAQ, energy efficiency, environmental sustainability and human health. For example, a recent



study has investigated the IAQ in highly energy efficient buildings in France (RT2012 rule), just after construction, the concentrations of some pollutants exceeded by 50% the median values in France. They highlight the constant need of mechanical ventilation in those buildings to avoid severe increase of pollutant concentration and a risk to human health [5].

While energy efficiency and IAQ are sometimes viewed as incompatible, many strategies support both ends. Passive regulation of the internal climate appears to be a promising solution since it can be beneficial to reduce the energy consumption of Heating Ventilation Air-Conditioning (HVAC) systems and improve the IAQ. For that purpose, raw earth used as plasters presents ideal characteristic. Earthen materials are known for their hygroscopic properties on the regulation of indoor moisture humidity and their thermal inertia for heat storage [6] [7]. Through the presence of clay minerals and their microstructure they could regulate the concentration of indoor pollutants on the same principles as moisture humidity. In addition, they are fulfilling a truly circular economy approach without affecting natural resources [8], the earth being sourced from waste (mainly excavation works) from the construction sector and being reusable infinitely. Some relevant publications on indoor air pollutants retention had already concluded that one of the most promising passive removal materials for indoor ozone control are clay-based plasters and clay paints [9].

As a starting point for studies on the contribution of raw earth to IAQ, the interactions between CO₂ and the clay material will be described. This gas was chosen because the elevated concentrations that occur indoors are mainly due to human metabolism, i.e. related to the occupation of the room. High occupant densities in inadequately ventilated spaces can generate indoor CO₂ levels that exceed the threshold of 1 000 ppm [10], it has been measured in several European schools [11]. Furthermore, there is evidence that even at concentrations considered to be low, CO₂ can have a harmful impact on health, particularly on fragile populations (children, elderly, people with chronic illnesses). These effects can range from cognitive impairment to chronic disease depending on the concentration and time of exposure [12] [13]. However, the CO₂ buffering capacity of earthen materials has been little studied. To the best of our knowledge, there are only few studies focusing on Y-type zeolite impregnated amines [14], silica supported amine [15] and cement render [16]. There are few data available and no existing protocol to check whether raw earth is buffering indoor CO₂.

For that purpose, a first step is to identify the key parameters for CO₂ retention and study them independently and interdependently. These influencing parameters include: the nature of the clay, the CO₂ concentration, the water content of the materials, the exposure time and the cyclic effect of exposure. This paper aims to present an original experimental method based on the coupling between a thermogravimetric apparatus, a gas mixer, and a wet gas generator. This apparatus can measure the variations in mass induced by the interactions between the injected gas (mixture of dry air, water vapour and CO₂) and the clay material. Analysis focuses on the influence of the Relative Humidity (RH) and CO₂ concentration of the air as the key parameters which influence the CO₂ retention in the material.

2. Materials and method

2.1. Materials

For this preliminary study, a single soil is considered to limit the number of influencing parameters. The determining factors for the choice of the soil were its suitability for construction, in order to study a material representative of real construction systems, and a soil already amply characterized in order to know precisely its granulometric, mineralogical and micro-structural composition. The earth chosen was collected on a century-old pisé construction in the town of Dagneux in the south-east of France and referenced as DAG [17].

Following both the French standard NF EN ISO 17892-4 [18] and NF P 94-068 [19] we obtained the particle size distribution and the methylene blue value (MB) of the earth, given in table 1. It reveals that the clay fraction of the soil is not much active. Finally, powder X-ray diffraction (XRD) was used to identify the mineralogical composition of the soil. It was performed on oriented aggregates using two preparations: air dried or natural and after glycolation. The identified agents are mainly non-expanding clay minerals (kaolinite), which seems to be consistent to some extent with the MB value. The main characteristics of the studied soil are summarized in table 1.

Geotechnical properties	Sand and fine gravel (5-0.06mm)	27 %
	Silt (60-2 μ m)	55 %
	Clay (<2 μ m)	18 %
	Methylene Blue value (MB)	1.8
Mineral composition	Main clay minerals	Kaolinite/Smectite

Table 1. Main properties of the soil DAG.

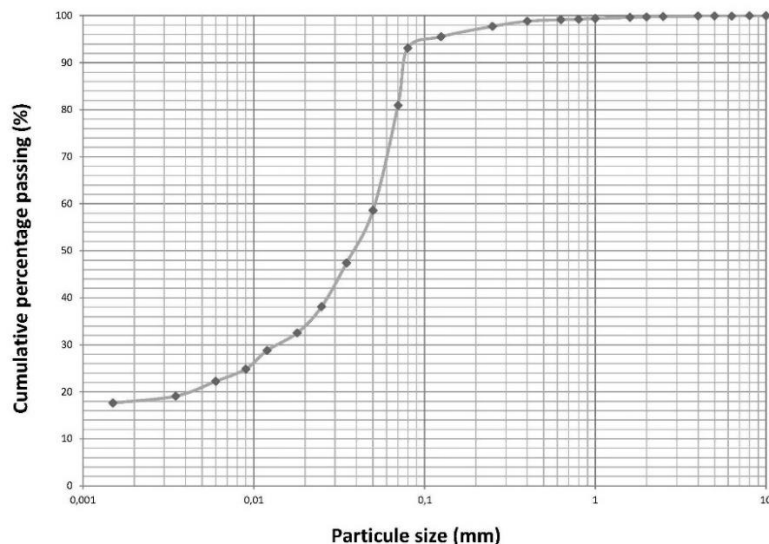


Figure 1. Particle size distribution of the soil DAG.

2.2. Sample preparation

In order to focus on the fine fraction of the soil which presents the highest surface area, the soil was sieved at 80 μ m with the help of water. It was then heated to a maximal temperature of 95 $^{\circ}$ C to avoid burning the clays, during 48 h until constant mass was reached. The residue was then grinded with a small mobile crusher to obtain a fine powder again. The geotechnical properties of this fraction below 80 μ m are deduced from table 1 and the particle size distribution (figure 1): 22% of sand and fine gravel, 59% of silt and 19% of clays.

The influence of the Relative Humidity (RH) of the indoor air is studied and consequently the water content of the material. We choose to run the experiments at two relative humidity: 0.5% RH and 50% RH to represent the situation of a near-dry material and a usual RH found indoor. To equilibrate the material before testing, we used hermetic boxes with saline solution (silica gel and potassium carbonate), stored in a climate chamber at a constant temperature of 20 $^{\circ}$ C \pm 2 $^{\circ}$ C. Once constant mass with a variation of less than 0.2% for at least 24 hours was reached, 100 mg of material was tested in the experimental device.

2.3. Experimental Set-up

The experimental set-up presented here was especially designed for the study of the retention of CO₂ by earthen materials under wet atmosphere. The general objective of the experiment is to follow the mass variations as a function of the atmosphere (CO₂ concentration, Relative Humidity, temperature) in which the sample is located in order to calculate the retention capacity and to study the reversibility of the phenomenon. The set-up is composed of: gas cylinders, gas mixer to select the desired CO₂ concentration, pressure regulator, wet gas generator, Setaram SENSYS-Evo-TG-DSC thermobalance, CO₂ sensors as shown in figure 2. The operation and role of each device is detailed below.

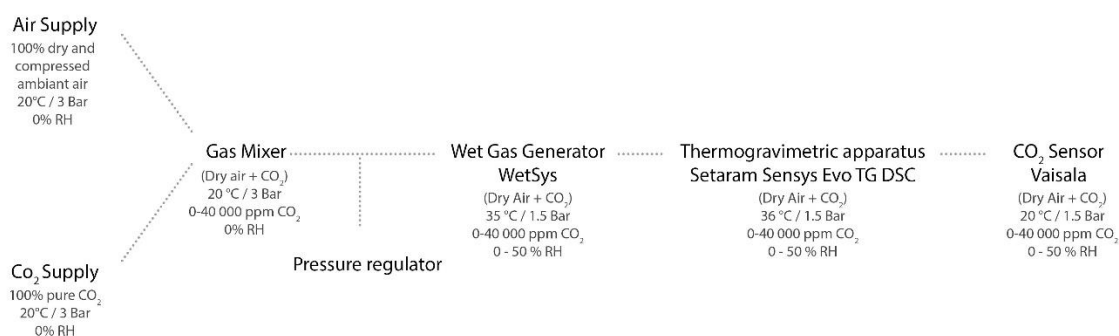


Figure 2. Principle of the experimental set-up.

The experimental set up starts with a gas mixer. It was designed using two Burkert Mass Flow Controllers (MFC), one for the CO₂ supply and one for the dry air. It allows the generation of a mixture of dry air and CO₂ by precisely controlling the two flow rates and thus the CO₂ concentration of the mixture. The flow range for the CO₂ MFC is 0 to 0.25 ml/min and for the dry air cylinder is 0 to 0.5 ml/min. These ranges were chosen to achieve the lowest possible CO₂ flow rate and the highest possible air flow rate to reach low CO₂ concentrations in the mixture, representative of that in indoor air. The desired CO₂ concentration is calculated from the respective flow rates of the two mass flow controllers, which are themselves controlled via the associated Communicator Burkert software. At the outlet of the mixer, a pressure regulator, allows to decrease the flow from 200 ml/min to 50 ml/min for the wet gas generator inlet.

Then, to obtain a humid air in the measuring cell a wet gas generator is connected. It allows to load a gas at a relative humidity between 0.5% and 90% with a stability of $\pm 0.3\%$ RH. The dry inlet gas is splitted in two lines, one remaining dry and the other one saturated with water. The two gas streams are mixed in a chamber. According to reach the desired relative humidity, the respective flow rates are adjusted for the gas mixture. The humid gas resulting from this operation is then transferred to the thermogravimetric device via a heated transfer line with a flow rate of 50 ml/min to eliminate any risk of condensation.

Next is the Setaram SENSYS-Evo-TG-DSC: a thermal analyser used for gravimetric (TG) and calorimetric (DSC) measurements shown in figure 3a.

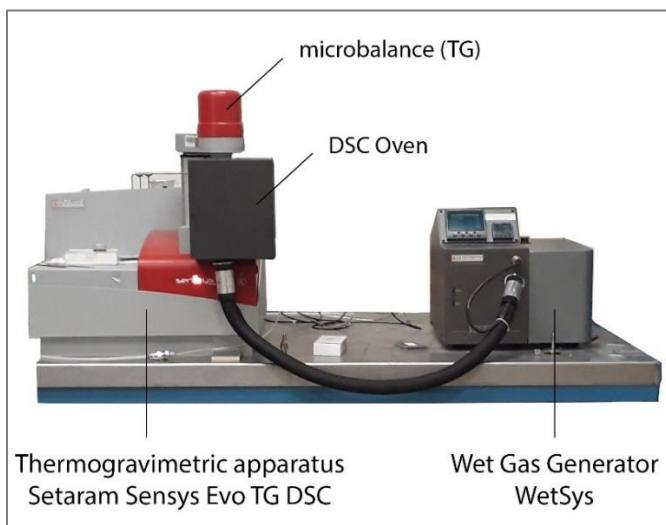


Figure 3a. Picture of the thermogravimetric apparatus connected to the wet gas generator.



Figure 3b. Introduction of the two crucibles in the columns.

The TG part (figure 3b.) is composed of a symmetrical beam balance connected to two columns, one for reference containing an inert material, the other for measurement containing the sample. The alumina crucibles containing the sample and the inert material are hung on each side and introduced in the columns. The symmetrical balance allows a compensation of the buoyancy effect resulting on a very high sensitive TG determination. In the measurement range of the device, the accuracy on the mass is announced to 0.02 μg to 0.002 μg . The calorimetry part consists of an oven and a thermocouples' network surrounding the measurement and reference cells. The DSC measurements will not be discussed in this paper. In addition, to avoid steam condensation, a programmable thermostat bath keeps the oven walls at a temperature above the dew point of the water vapor. At temperature close to ambient, it is this thermostat bath that regulates the temperature at 36°C for the experiment cells.

Finally, a Vaisala CO₂ sensor is used to measure the exact CO₂ concentration of the gas mixture. Here it is placed at the outlet of the SENSYS but it can be placed at other locations on the experimental line as needed.

2.4. Protocol

This paper presents and compares two experiments done two weeks apart. A first experiment with a quasi-dry sample (0.5% RH) named A and a second with a 50% RH equilibrated sample named B. Although the protocols are the same, the duration of the CO₂ concentration steps differs for the two experiments. The A experiment (0.5% RH) consisted of four steps of 24 hours meanwhile the B experiment (50% RH) consisted of three steps of 6 hours each.

The tests are carried out in three stages. The first stage consists of three days of stabilization, the sample being swept by an air flow without CO₂ at the desired humidity. It allows us to correct the effects of changes in RH that the material would have undergone between the humidity-controlled boxes and the SENSYS' measuring cell and to correct the difference between the humidity delivered by the wet gas generator and the one inside the boxes. Then several CO₂ concentration steps are applied and finally the last phase consists again of a pure air sweep at the desired humidity to observe if the material releases CO₂, release being as important as retention in a buffering effect. The tests are done in steady state, the

measuring cell is continuously swept/scanned by the humid gas mixture and the balance is itself swept by a protective gas.

The details for the two experiments are presented below:

	Experiment A	Experiment B
Relative Humidity %	0.5	50
Number of steps	4	3
CO ₂ concentration step 1 (ppm)	1 500	/
CO ₂ concentration step 2 (ppm)	17 000	17 000
CO ₂ concentration step 3 (ppm)	40 000	40 000
CO ₂ concentration step 4 (ppm)	0	0
Temperature (°C)	36	36

Table 2. Experimental characteristics of the two experiments.

3. Result and discussion

3.1. Results

As the duration of each concentration step was different between the experiments we decided to keep only the first 3 hours of each step and to concatenate the resulting curves. That is, the measurement points that were located 3h after the beginning of the step were eliminated from the graph. The restriction to three hours allows us to accurately model what would typically happen in a classroom with fluctuating occupancy, to use a fixed step time for A and B for comparison. Furthermore, during this duration equilibrium was reached for all steps of A and B experiments.

In figure 4, the results of the relative mass variation with time of the sample exposed to different CO₂ concentration are shown for a near-dry material (on the left, A) and a 50% RH equilibrated material (on the right, B).

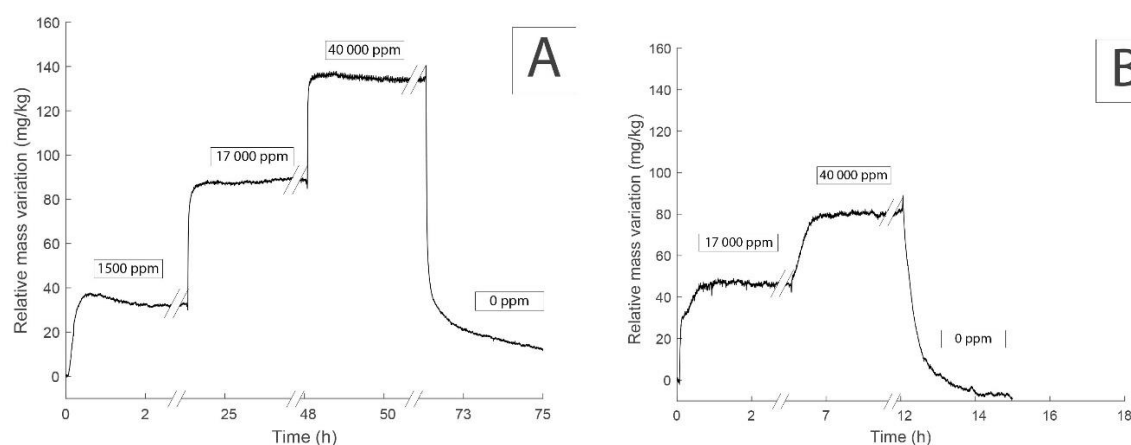


Figure 4. Relative mass variation with time of the sample exposed to different CO₂ concentration for A (0.5% RH) and B (50% RH).

The magnitude of this mass uptake can be quantified through the calculation of the CO₂ retention capacity, denoted by Q and equal to the mass of CO₂ captured within the material per kg of material. For a given CO₂ concentration, Q was found to increase when the air relative humidity decreased. Indeed, for 17 000 ppm, $Q = 89$ mg CO₂/kg for the sample at 0.5% RH and $Q = 46$ mg CO₂/kg for the sample at 50% RH. For 40 000 ppm, $Q = 132$ mg CO₂/kg for 0.5% RH and $Q = 82$ mg CO₂/kg for 50%

RH. One way to explain that might be the increasing competition, at the adsorption site, between water and CO_2 molecules as the water content increases. Another interesting point concerns CO_2 uptake kinetic. Whatever RH and CO_2 concentration conditions, a short period of time (lower than 1h) is necessary to reach a constant mass. It tends to suggest that CO_2 uptake within the material is rather driven by rapid physical adsorption processes than much longer chemical interactions between CO_2 and the solid matrix. But a closer look on the results underlines that while the adsorption time is almost instantaneous (less than 10min) for dry samples, when water content increases (i.e. for RH=50% condition) it is rather around to 30min. This effect might be a consequence of a modification in the water uptake processes: from adsorption for a dry sample to a mix between adsorption and dissolution for wet samples.

When the CO_2 concentration decreases from 40 000 ppm to 0, a rapid and important mass loss is observed. Overall, the majority of the captured CO_2 is released. This indicates the presence of a rather reversible phenomenon that could be physical adsorption, or physisorption, involving low-energy physical interactions that are easy to break. However, chemical adsorption, or chemisorption, may also take place, yet this has not been evidenced so far through the collected data.

3.2. Discussion

Figure 5 shows the CO_2 retention capacity of the material as a function of the CO_2 concentration in the air for both the wet (50% RH) and the nearly dry material (0.5% RH).

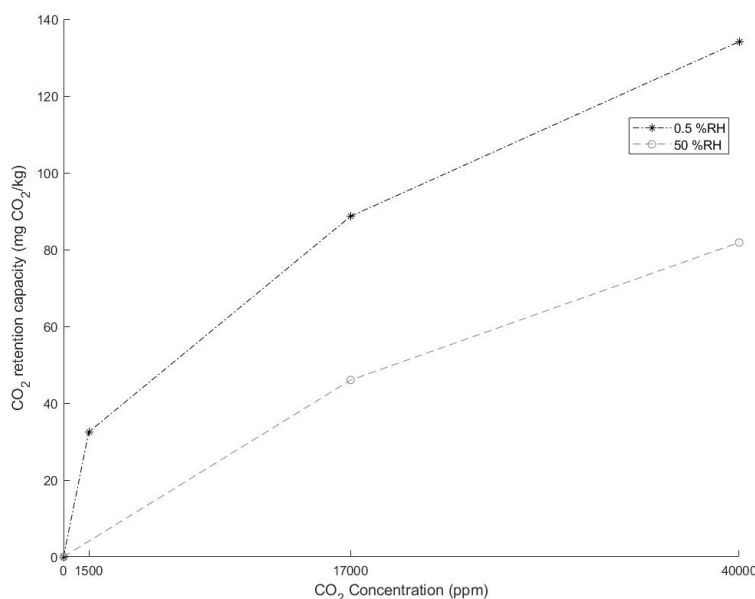


Figure 5. CO_2 retention capacity of the material as a function of the CO_2 concentration in the air for both the wet (50% RH) and the nearly dry material (0.5% RH).

As seen previously, the curve for the dry material is higher than that for the wet material because the dry material retains more CO_2 . From the shape of the curve it could be observed that the retention capacity of the material is not linear with the CO_2 concentration but that after a certain concentration its capacity becomes saturated. To determine this saturation, more CO_2 steps have to be performed and a wider range of concentrations explored. Comparing our results to the literature Lee et. al [14] found retention coefficients of zeolites modified with amines in the range of 70 000 mg CO_2 /kg to 160 000 mg CO_2 /kg for 1 500 ppm at 25°C. Similarly, Rajan et al. [15] found for silica impregnated with amines coefficients ranging from 8 000 mg CO_2 /kg to 90 000 mg CO_2 /kg for 3 000 ppm at 25°C. Although these values are

a thousand times higher, the materials presented in the literature have much lower desorption rates than our material and could not be coated over the entire surface of a wall. However, it shows that an optimisation of the process is possible, especially by maximising the amount of clay in the plaster.

4. Conclusion

To conclude, this paper has presented a new experimental method based on gravimetry to assess whether earth-based material could regulate the indoor CO₂ level. Results have shown the importance of the water content of the material related to the relative humidity of the air. At a given CO₂ concentration: the retention capacity of the material decreases from 89 mg CO₂/kg to 46 mg CO₂/kg with the RH rising from 0.5% to 50%, indicating that the water molecules could occupy part of the available adsorption sites and create new reactions with the CO₂ molecules such as dissolution. Moreover, the reversibility of the process has been studied and the majority of the CO₂ captured has been released in the two RH conditions (0.5% and 50%). This indicates the presence of a rather reversible phenomenon that could be physical adsorption.

This experiment provides the first values of CO₂ retention capacity for raw earth and thus provides evidence of the passive regulation capacity of this material. Further research is currently underway to correctly describe the retention mechanism and to understand the influence of experimental parameters, the nature of the clay and the microstructure of the material.

Acknowledgments

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 945416.

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