**CEES 2023** 

# CEES 2023 | 2<sup>nd</sup> International Conference on Construction, Energy, Environment & Sustainability



27-30 June 2023, Funchal - Portugal

## CLAY-BASED PLASTERS FOR PASSIVE AIR POLLUTANT REMOVAL: THE CASE OF OZONE

Alessandra Ranesi <sup>1,2</sup> Elliott T. Gall <sup>3</sup> Rosário Veiga <sup>2</sup> Paulina Faria <sup>1</sup>

- <sup>1</sup> CERIS, NOVA School of Science and Technology, Universidade NOVA de Lisboa | Portugal
- <sup>2</sup> Buildings Department, National Laboratory of Civil Engineering | Portugal
- <sup>3</sup> Department of Mechanical and Materials Engineering, Portland State University, Portland, OR | USA Corresponding author: a.ranesi@campus.fct.unl.pt

#### **Keywords**

Sustainability; Passive Removal Materials; Ozone Deposition Velocities; IAQ; Earth plasters

#### **Abstract**

During the past decades many studies have explored the indoor air quality (IAQ) of residential and office buildings due to the large amount of time people spend indoors and potential for health impacts. For example, lack of control of indoor relative humidity can lead to adverse health outcomes like dry eye syndrome, asthma, and chronic skin and throat irritation. Indoor air quality is also affected by pollutants generated indoors, commonly by human activity, and pollutants coming from the outdoor, especially in absence of air cleaning systems. Indoor ozone is of important consideration in IAQ and has been studied and monitored during the last 20 years due to the effect on human health of the pollutant itself and its reaction products. While air cleaning, like carbon scrubbing, in building mechanical systems can solve or reduce indoor ozone concerns, it would not represent a "green choice". It would, in fact, increase the operational energy demand of the building. Instead, passive solutions for removing indoor ozone can be pursued. In many countries, plasters are applied on indoor walls and ceilings, commonly covering large surfaces. In this study two premixed clay-based plasters, produced by American Clay, were tested for ozone removal. The two premixed plastering mortars were applied on 95 mm diameter disks of drywall in a 5 mm-thick layer. The experiment was designed to evaluate the ozone reactivity of the two plasters and the drywall, quantifying their ozone deposition velocities. Results pointed to one of the clay-based premixed plaster as a good passive removal material. For instance, if applied on 9 m<sup>2</sup> partition drywall, it would increase 2.5 times the amount of ozone uptaken by the uncoated drywall. The other clay-based premixed plaster tested did not show the same good behavior probably because the addition of crushed seashells interferes with the removal mechanism.

### 1. INTRODUCTION

Ozone is a secondary pollutant, one of the principal constituents of photochemical gas, and its formation depends on meteorological factors combined with the presence of volatile organic compounds (VOCs) and nitrogen oxides, mainly related to the combustion of hydrocarbon fuels in urban areas. Weschler [1] expressed the indoor ozone concentration as a function of the ozone outdoor concentration and other indoor sources and sinks. Many studies have shown the dangerous effect of ozone exposure on human health. The exposure to ozone and its reaction products has been related to the occurrence of chronic respiratory diseases, such as asthma and sick building syndrome symptoms [2-5], and to an increased mortality risk [6-8].

Different measures can be adopted to ensure better IAQ and prevent occupants from exposure to high pollutant levels. The most common ones are energy demanding like mechanical filtration systems [9-11] but also some passive air pollution mitigation systems have been studied as plants [12-14] or building passive removal materials (PMR) [15, 16]. Some building materials, like drywall, carpet, tiles, plasters, etc., are commonly used indoors to cover big surfaces and for this reason their interaction with ozone has been of high interest in terms of ozone reaction and production of byproducts. Lamble et al., 2011 [17], for example, tested nineteen green building materials to ozone deposition velocities, reaction probability and carbonyl yields. Among the tested materials, the clay plaster and the clay-based paint showed the highest deposition velocities (ozone removal capacity). The clay response was related, by the authors, with the possible triggering effect the mineral content of clay (iron and aluminum) could have on the catalytic decomposition of the ozone. The paper also found high deposition velocities for drywall and linked it to a similar chemical reaction. Many other studies have been testing drywall and clay plaster as

promising building materials for ozone removal, although some variation can be found from study to study. Some authors [18,19] used a small chamber (about 10 L) like the experimental setup of Lamble et al. [17], while others used a bigger stainless-steel environmental chamber [20,21]. Another variation can be done on the exposure time as some authors did, studying the long-term performance of some building materials [22,23]. The clay-based plasters and paints showed a good ozone removal capacity and low byproduct emission rates even when tested at long exposure periods (up to 6 months).

According to the referred literature, among indoor coating materials, two clay plasters and one commercial drywall were selected for the present study. The two different formulations of clay plasters showed different behavior. It is well-known that the clay mineral composition influences the mechanical and physical properties of clay-based plasters [24-26] and it is possible that the clay specific mineralogy together with the different composition and manual application, results in different behaviors of the two clay plasters. Results of ozone deposition velocities and reaction rate are presented and analyzed below.

#### 2. MATERIALS AND METHODS

#### 2.1. MATERIALS

Two different powdered premixed clay-based plasters were selected for the study. Both plasters are produced by American Clay [27] to be applied as finishing thin layers (3 to 5 mm). The first plaster is a base product (Cl) made of clay and very fine sand. The second plaster, called maritime clay plaster (Cl\_M), presents the addition of crushed seashells. Both plasters present crème color and are applied on drywall with a final thickness of approx. 5 mm. According to the technical sheets [27], the plasters are applied in three coats, waiting 24 hours between each application to ensure low shrinkage and good adhesion to the support. The drywall (support) was previously painted with a water-based commercial primer (Zinsser) with sand addition. Five circular specimens with a diameter of about 95 mm (Figure 1) are prepared for both the clay (DW\_Cl) and the maritime clay (DW\_Cl\_M) plasters. Moreover, three samples of drywall, cut in square shape of about 65 cm size, were added to the study for comparison. All the samples are covered with aluminum foil on five sides, leaving only the top surface exposed for the study.





Figure 1. Specimens of clay and maritime clay plasters applied on drywall.

#### 2.2. THE EXPERIMENTAL SETUP

Two identical airtight glass chambers of 6.5 liters volume are set in parallel into a temperature-controlled environment. The relative humidity (RH) and temperature (T) inside the chambers are continuously monitored (10 seconds intervals) and the ozone concentration can be monitored either at the inlet  $(C_0)$  or the exhaust (C) if the flow is directed to the bypass or the chamber. The airflow is controlled by the Mass Flow Control (GFC, AALBORG), run through a particle filter (HEPA) and an activated carbon filter before passing through the ozone generator (UV lamp). The generator is set on a concentration of 85-100 ppb. The airflow is humidified to  $50\pm10\%$  RH and split between the two chambers. The setup is designed to keep the two chambers under the same conditions. One chamber, the control, is used to quantify the ozone deposition velocity of the glass  $(v_{d,g})$  for each experiment and the other chamber is used to place the samples (on the bottom, with the studied surface horizontally projected) and calculate the ozone deposition velocity and ozone reactivity for each studied material. The protocol consisted of three successive steps. The experiment starts with 1.5 hours flushing clean air in both the chambers. Then, the ozone generator would be switched on and for 45 minutes the ozonated air would be sent to the bypass for the inlet ozone

concentration reading. After, the stream would be directed from the bypass to the chamber for 1 hour to read the ozone concentration at the exhaust. During the experiment the airflow is 1.3 l/min in each chamber and between different materials the passivation of the chamber is ensuring flushing ozone at >300 ppb for 16 hours.

### 2.3. QUANTIFIED PARAMETERS - DEPOSITION VELOCITY, OZONE REACTIVITY AND REMOVAL EFFICIENCY

The deposition velocity of the material is calculated starting from the mass balance (eq. 1):

$$V\frac{dC_{O3}}{dt} = Q(C - C_0) - C(v_dA_s - v_{d,g}A_g)\varepsilon$$
(1)

with V (I) the volume of the chamber,  $C_{03}$  (ppb) the ozone concentration, Q (I/min) the airflow,  $C_0$  (ppb) the concentration inlet and C (ppb) the concentration at the exhaust,  $v_d$  and  $v_{d,g}$  (m·min<sup>-1</sup>) the deposition velocities of the sample's exposed surface  $A_s$  and the chamber's exposed surface  $A_g$  (m<sup>2</sup>). Once the system reaches steady-state, with  $\frac{dC_{03}}{dz_0}$ =0, it is possible to write the eq. (1)

as eq. 2:

$$v_d = \lambda \left(\frac{V}{A_s}\right) \times \left(\frac{C_0}{C} - 1\right) - v_{d,g} \left(\frac{A_g - A_s}{A_g} - 1\right)$$
 (2)

where  $\lambda$  (min<sup>-1</sup>) is the air exchange rate calculated as Q/V. The deposition velocity of the empty chamber,  $v_{d,g}$  is given by the control chamber and calculated by eq. 3:

$$v_{d,g} = \lambda \left(\frac{V}{A_g}\right) \times \left(\frac{C_0}{C} - 1\right)$$
 (3)

The ozone reaction rate R (µg·min<sup>-1</sup>) of the material exposed surface was quantified according to eq. 4:

$$R = v_d A_s C_{O3} \tag{4}$$

where  $v_d$  is the deposition velocity expressed in m·min<sup>-1</sup>,  $A_s$  the exposed material surface (m<sup>2</sup>),  $C_{O3}$  the ozone concentration (µg m<sup>-3</sup>).

#### 3. RESULTS

Figure 2 shows the deposition velocities calculated according to Eq.2, as the average on three specimens and respective standard deviations. The higher standard deviation shown by the plaster DW\_CL is probably due to the manual application of the plaster and the heterogeneity specific of the raw clay. The drywall deposition velocity of 0.16±0.017 cm·s<sup>-1</sup> is consistent with values found in literature. According to previous studies, also run in small chambers, the drywall deposition velocity was found 0.15 cm·s<sup>-1</sup> [18] and 0.18±0.056 cm·s<sup>-1</sup> [17]. The application of the clay plaster on the drywall improves its ozone removal capacity. Lamble et al. [17], when testing a clay-based plaster, found its deposition velocity to be 0.14±0.02 cm·s<sup>-1</sup> which agrees with the results of 0.22±0.053 and 0.15±0.005 cm·s<sup>-1</sup> here presented, considering the possible difference in clay mineralogy and surface roughness.

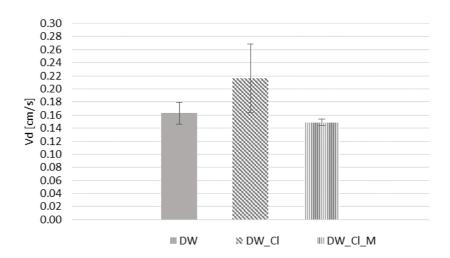


Figure 2. Ozone deposition velocities and standard deviations for the drywall (DW), the clay plaster (DW\_CI) and the maritime clay plaster (DW CI M) applied on the drywall.

The ozone reaction rate (R) for DW, DW\_Cl and DW\_Cl\_M specimens (average value out of 3), exposed to the same concentration of ozone (100 ppb) at the same temperature of 23 °C, is found 13.5, 62.2 and 21.3  $\mu$ g/h, respectively. Considering that the exposed surfaces are respectively 0.004, 0.007 and 0.007 m², one squared meter of each material would be able to remove 11.6, 31.7 and 10.6 g/h. Thus, a partition drywall of 3 m x 3 m will remove 104.4 g of ozone per hour and, if coated with 5 mm of clay plaster CL, will remove up to 258.3 g/h. The ozone removal efficiency, in agreement with results from deposition velocity and reaction rate, points out that the addition of seashells worsened the ozone reaction of the clay-based plaster. It is possible that the crushed seashells, known to improve the hygroscopic behavior of lime mortars [28], interfere (chemically or physically) with the ozone removal mechanism of the clay.

#### 4. CONCLUSIONS

Due to the harmful effect that ozone has on human health, the use of passive removal materials is recommended to mitigate occupant's ozone exposure. The ozone reaction of three building materials was investigated in the present study. The ozone deposition velocities, reactivity and removal efficiency were presented. The building materials here tested were a commercial drywall and two differently formulated clay plasters: one basic formulation (CI) and one basic formulation with crushed seashells addition (maritime plaster CI\_M). Results were consistent with the ones found in literature for similar tested materials and apparatus-procedures. It was found that coating a 9 m² partition drywall, for instance, with 5 mm of clay plaster, would increase about 2.5 times the passive ozone removal of the drywall itself. Nevertheless, the two clay plasters showed different reactivity to ozone, with the maritime plaster quite lower than the plaster without any addition. Future studies are warranted to deeper investigate the ozone uptaken mechanism considering the water vapor reactivity of each material.

#### **Acknowledgements**

This research was funded by Portuguese Foundation for Science and Technology: Alessandra Ranesi Doctoral Training Programme EcoCoRe grant number PD/BD/150399/2019 and Civil Engineering Research and Innovation for Sustainability (CERIS) project UIDB/04625/2020. Furthermore, the authors would like to acknowledge the support provided by the National Laboratory of Civil Engineering (LNEC), through the project REUSE - Wall coverings for Rehabilitation: Safety and Sustainability-and the support provided by the Healthy Buildings Research Laboratory (HRBL) of the Portland State University.

#### References

- [1] Weschler, C.J., 2000. "Ozone in indoor environments: concentration and chemistry", Indoor Air 10, 269-288. https://doi.org/10.1034/j.1600-0668.2000.010004269.x.
- [2] Apte, M.G., Buchanan, I.S.H., Mendell, M.J., 2008. "Outdoor ozone and building-related symptoms in the BASE study", Indoor Air 18, 156-170. https://doi.org/10.1111/j.1600-0668.2008.00521.x.
- [3] Weschler, C.J., 2006. "ozone's impact on public health: contributions from indoor exposures to ozone and products of ozone-initiated chemistry", Environmental Health Perspectives 114, 10. https://doi.org/10.1289/ehp.9256.

- [4] Kelly, F.J., Fussell, J.C., 2011. "Air pollution and airway disease", Clinical & Experimental Allergy 41, 1059-1071. https://doi.org/10.1111/j.1365-2222.2011.03776.x.
- [5] Trasande, L., Thurston, G.D., 2005. "The role of air pollution in asthma and other pediatric morbidities", Journal of Allergy and Clinical Immunology 115:4, 689-699. https://doi.org/10.1016/j.jaci.2005.01.056.
- [6] Bell, M.L., McDermott, A., Zeger, S.L., Samet, J.M., Dominici, F., 2004. "Ozone and short-term mortality in 95 US urban communities", JAMA 292:19, 2372–2378. https://doi.org/10.1001/jama.292.19.2372.
- [7] Bell, M.L., Peng, R.D., Dominici, F., 2006. "The exposure—response curve for ozone and risk of mortality and the adequacy of current ozone regulations", Environmental Health Perspectives 114:4. https://doi.org/10.1289/ehp.8816
- [8] Gryparis, A., Forsberg, B., Katsouyanni, K., Analitis, A., Touloumi, G., Schwartz, J., Samoli, E., Medina, S., Anderson, H.R., Niciu, E.M., Wichmann, H.-E., Kriz, B., Kosnik, M., Skorkovsky, J., Vonk, J.M., Dörtbudak. Z., 2004. "Acute effects of ozone on mortality from the "air pollution and health: a European approach" project", American Journal of Respiratory and Critical Care Medicine 170:10, 1080-1087. https://www.atsjournals.org/doi/abs/10.1164/rccm.200403-333OC.
- [9] Nazaroff, W.W., Weschler, C.J., 2022. "Indoor ozone: concentrations and influencing factors", Indoor Air 32, 1. https://doi.org/10.1111/ina.12942.
- [10] Hyttinen, M., Pasanen, P., Kalliokoski, P., 2006. "Removal of ozone on clean, dusty and sooty supply air filters", Atmospheric Environment 40:2, 315-325. https://doi.org/10.1016/j.atmosenv.2005.09.040.
- [11] Lee, P., Davidson, J., 1999. "Evaluation of activated carbon filters for removal of ozone at the PPB level", American Industrial Hygiene Association Journal 60:5, 589-600. https://doi.org/10.1080/00028899908984478.
- [12] Abbass, O.A., Sailor, D.J., Gall, E.T., 2017. "Effectiveness of indoor plants for passive removal of indoor ozone". Building and Environment 119, 62-70. https://doi.org/10.1016/j.buildenv.2017.04.007.
- [13] Berardi, U., GhaffarianHoseini, A.H., GhaffarianHoseini, A., 2014. "State-of-the-art analysis of the environmental benefits of green roofs", Applied Energy 115, 411-428. https://doi.org/10.1016/j.apenergy.2013.10.047.
- [14] Abbass, O.A., Sailor, D.J., Gall, E.T., 2018. "Ozone removal efficiency and surface analysis of green and white roof HVAC filters", Building and Environment 136, 118-127. https://doi.org/10.1016/j.buildenv.2018.03.042.
- [15] Jing, L., Wang, J., 2022. "Study on indoor ozone removal by PRM under the influence of typical factor". Proceedings of the 16th ROOMVENT Conference. September 16-19, Xi'an, China. A. Li, T. Olofsson and R. Kosonen (Eds.). https://doi.org/10.1051/e3sconf/202235.
- [16] Shen, J., Gao, Z., 2018. "Ozone removal on building material surface: a literature review", Building and Environment 134, 205-217. https://doi.org/10.1016/j.buildenv.2018.02.046.
- [17] Lamble, S.P., Corsi, R.L., Morrison, G.C., 2011. "Ozone deposition velocities, reaction probabilities and product yields for green building materials", Atmospheric Environment 45: 38, 6965-6972. https://doi.org/10.1016/j.atmosenv.2011.09.025.
- [18] Rim, D., Gall, E.T., Maddalena, R.L., Nazaroff, W.W., 2016. "Ozone reaction with interior building materials: influence of diurnal ozone variation, temperature and humidity", Atmospheric Environment 125: A, 15-23. https://doi.org/10.1016/j.atmosenv.2015.10.093.
- [19] Lin, C.-C., Hsu, S.-C., 2015. "Deposition velocities and impact of physical properties on ozone removal for building materials", Atmospheric Environment 101, 194-199. https://doi.org/10.1016/j.atmosenv.2014.11.029.
- [20] Gall, E.T., Darling, E., Siegel, J.A., Morrison, G.C., Corsi, R.L., 2013. "Evaluation of three common green building materials for ozone removal, and primary and secondary emissions of aldehydes", Atmospheric Environment 77, 910-918. https://doi.org/10.1016/j.atmosenv.2013.06.014.
- [21] Kunkel, D.A., Gall, E.T., Siegel, J.A., Novoselac, A., Morrison, G.C., Corsi, R.L., 2010. "Passive reduction of human exposure to indoor ozone", Building and Environment 45: 2, 445-452. https://doi.org/10.1016/j.buildenv.2009.06.024.

- [22] Cros, C.J., Morrison, G.C., Siegel, J.A., Corsi, R.L., 2012. "Long-term performance of passive materials for removal of ozone from indoor air", Indoor Air 22:1, 43-53. https://doi.org/10.1111/j.1600-0668.2011.00734.x
- [23] Darling, E., Corsi, R.L., 2017. "Field-to-laboratory analysis of clay wall coatings as passive removal materials for ozone in buildings", Indoor Air 27, 658-669. https://doi.org/10.1111/ina.12345.
- [24] Lima, J., Faria, P., Santos Silva, A., 2020. "Earth plasters: the influence of clay mineralogy in the plasters' properties", International Journal of Architectural Heritage 14:7, 948-963, https://doi.org/10.1080/15583058.2020.1727064.
- [25] Santos, T., Gomes, M.I., Santos Silva, A., Ferraz, E., Faria, P., 2020. "Comparison of mineralogical, mechanical and hygroscopic characteristic of earthen, gypsum and cement-based plasters". Construction and Building Materials 254, 119222. https://doi.org/10.1016/j.conbuildmat.2020.119222.
- [26] Carcione, J.M., Gei, D., Yu, T., Jing, B., 2019. "Effect of clay and mineralogy on permeability". Pure and Applied Geophysics 176, 2581–2594. https://doi.org/10.1007/s00024-019-02117-3.
- [27] https://www.americanclay.com/technical-documents.
- [28] Martínez-García, C., González-Fonteboa, B., Carro-López, D., Martínez-Abella, F., Faria, P., 2022. "Hygrothermal behaviour of air lime coatings with mussel shell sand", Construction Technologies and Architecture 1, 627-634. https://doi.org/10.4028/www.scientific.net/cta.1.627.