

Time-Scale Analysis for Reactive Deposition of Ozone via Passive Reactive Materials

Elliott Gall¹, Clement Cros¹, Richard Corsi^{1,*}, and Jeffrey Siegel¹

¹University of Texas, Austin, TX

*Corresponding email: corsi@mail.utexas.edu

SUMMARY

Passive reactive materials (PRMs), materials that remove harmful and/or irritating pollutants with few or no byproducts, offer a novel approach to clean indoor air with minimal or no energy inputs. In this paper we present the results of a time-scale analysis for the removal of ozone in indoor environments via two promising PRMs, gypsum wallboard and activated carbon panels. An improved understanding of the factors that limit pollutant uptake at surfaces will allow for the design of better systems for removing indoor contaminants. Ozone removal time-scales for PRMs are on the order of 10^2 - 10^3 seconds, compared to 10^4 seconds for homogeneous reactions and 10^2 - 10^3 seconds for background reactions with indoor surfaces. This work illustrates that the installation of a PRM can result in significant reductions of indoor ozone by providing a complementary or preferential ozone removal pathway.

KEYWORDS

Indoor air pollution, energy, chemistry, control

INTRODUCTION

Building ventilation accounts for approximately 30% of building energy demand (Liddament and Orme, 1998). Green building protocols attempt to reduce this demand by weatherproofing to reduce infiltration and recirculating conditioned indoor air. These methods result in increased and prolonged occupant exposure to indoor air pollutants and reaction byproducts, e.g., oxidized reaction products formed from indoor ozone chemistry. As ventilation rates are reduced, it is necessary to develop technologies that address indoor air quality without energy expenditure. Furthermore, indoor atmospheres account for approximately 50% of overall population intake of ozone representing a significant human health hazard (Bell et al., 2005; Weschler, 2006). As such, we have begun exploring the use of PRMs to remove indoor ozone. Since achieving significant ozone removal may require an engineered solution to optimize the reactivity of the material and the mass transfer of a room, an understanding of time scales for both ozone transport and reaction are desirable.

METHODS

Two promising PRMs, unpainted gypsum board and activated carbon, were selected based on previous studies which illustrate their potential to react with ozone and produce no or few byproducts (Kleno et al., 2001). Important time-scale parameters were taken from the literature where possible (see Table 1).

This paper considers two aspects of ozone removal in buildings: 1) phenomena that compete with PRMs for ozone removal, and 2) phenomena that govern the transport to and reaction of ozone with a PRM. The former phenomena are further divided into: a) removal to a PRM, b) removal to background surfaces, and c) homogeneous reactions with indoor pollutants. The

latter set of phenomena is further divided into a) transport from bulk air to the edge of the PRM boundary layer, b) boundary layer transport and c) heterogeneous reaction with the PRM.

Table 1. Parameters for processes leading to ozone transport and removal to PRMs

<i>Parameter</i>	<i>Name</i>	<i>Value</i>	<i>Reference</i>
V_{d-PRM}	Desposition velocity to PRM	$10^{-3} - 10^{-2} \text{ m s}^{-1}$	2
A_{PRM}	PRM reactive surface area	10 m^2	2
V	Room volume	38 m^3	2
V_{d-BG}	Deposition velocity to background	$10^{-4} - 10^{-3} \text{ m s}^{-1}$	2
A_{BG}	Background reactive surface area	53 m^2	2
$R_{\text{pollutant-O}_3}$	Reaction rate constant	$2 \times 10^{-6} - 5 \times 10^{-6} \text{ ppb}^{-1} \text{ s}^{-1}$	4
[Pollutant]	Gas-phase pollutant concentration	10 ppb	Assumed
δ_{bulk}	Bulk air to boundary layer distance	1.6 m	2
$v_{\text{bulk air}}$	Bulk air veocity	$0.03-0.95 \text{ m s}^{-1}$	2
$A_{\text{characteristic}}$	Charactertistic area for diffusion	11 m^2	2
D	Diffusion coefficient	$1.2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$	4
δ_{turb}	Turbulent boundary layer thickness	10^{-4} m	3
k_g	Mass-transfer coefficient	$3 \times 10^{-4} - 2 \times 10^{-3} \text{ m s}^{-1}$	2
MFP	Mean free path, air	$6.5 \times 10^{-8} \text{ m}$	4
γ	PRM Reaction probability	$10^{-7} - 10^{-4}$	2
$\langle v \rangle$	Boltzmann velocity	362 m s^{-1}	4

1. Waring, M.S. and Siegel, J.A., 2009; 2. Kunkel et al., 2009; 3. Zhao et al., 2008; 4. Mallard et al., 2008.

RESULTS AND DISCUSSION

For a PRM to be an effective scavenger of ozone it must compete favorably with homogenous reactions between ozone and indoor gases as well as reactions with typical indoor surfaces. Resulting time scales and associated equations for various ozone removal processes are presented in Table 2. The reaction time-scale for ozone removal to background indoor surfaces is 10^2-10^3 s (1b in Table 2), a range similar to that for activated carbon and gypsum PRMs (1a in Table 2). This indicates that these PRMs can provide a preferred or complementary removal pathway over indoor surfaces, depending upon the reactivity of a PRM material with ozone, and the air motion and mass transfer conditions in both the core air and adjacent to the PRM. This is possible even with the relatively small PRM area, 10 m^2 , considered in this analysis.

There is substantial disparity in time-scales between heterogeneous reactions with PRMs and homogeneous chemistry. Ozone removal by reactions with d-limonene or α -pinene and ozone is characterized by a time scale of approximately 10^4 s , 1 to 2 orders of magnitude longer than for removal to the PRM. The homogeneous reaction time-scale assumes a well-mixed bulk room, as does the transport of ozone from bulk air to the boundary layer of a surface. Since d-limonene and α -pinene are relatively reactive compounds with ozone, it is reasonable to assume that the presence of a PRM will dominate over most homogenous reactions.

The time-scale analysis shows that transport from bulk air to the PRM boundary layer occurs over 10^0-10^1 seconds for advection versus 10^5 seconds for molecular diffusion. Transport

through the boundary layer is predicted to occur over 10^{-4} - 10^2 s, depending on the nature of the PRM. Therefore, depending upon the specific fluid dynamic conditions of the room, advective transport to, and diffusion through, a laminar boundary layer are the major contributing resistances to ozone removal on a PRM. When comparing transport time-scales to heterogeneous reactions, 10^0 - 10^2 s versus 10^{-6} s, it is obvious that reactions with PRMs contribute little resistance compared to transport. As such, ozone removal can be greatly increased by optimizing fluid mechanic conditions such that a high airflow reaches the PRM. This can be accomplished by placing a standing room fan pointed toward a PRM. Experimental work has shown that a higher perpendicular face velocity results in enhanced ozone removal (Kunkel et al., 2009).

Table 2. Time Scale Analysis for Indoor Ozone Transport and Removal.

Phenomena	Governing Equation	Range (seconds)	Reference
1) Indoor Ozone Removal Pathways:			
a) Removal to PRM	$t_{PRM} = \frac{1}{\frac{v_{d-PRM} A_{PRM}}{V}}$	$10^3 - 10^2$	1
b) Removal to Background Surfaces	$t_{BG} = \frac{1}{\frac{v_{d-BG} A_{BG}}{V}}$	$10^3 - 10^2$	1
c) Homogeneous Chemistry			
Limonene	$t_{homogeneous} = (R_{pollutant-O_3} * [O_3])^{-1}$	10^4	3
Pinene		10^4	3
2) Bulk Indoor Air to PRM Surface:			
a) Transport from bulk air to outer edge of boundary layer			
Advection	$t_{advection} = \frac{\delta_{bulk}}{v_{bulkair}}$	$10^1 - 10^0$	1
Molecular Diffusion	$t_{diffusion} = \frac{A_{characteristic}}{4D}$	10^5	3
b) Transport through boundary layer			
Through turbulent boundary layer	$t_{turbulent} = \frac{\delta_{turb}^2}{D}$	10^{-4}	2
Through laminar boundary layer	$t_{diffusion} = \frac{D}{k_g^2}$	$10^2 - 10^0$	3,4
c) Heterogeneous reaction with surfaces			
PRMs	$t_{heterogeneous} = \frac{2MFP}{3 \left(\frac{\gamma < v >}{4} \right)}$	$10^{-6} - 10^{-5}$	1,5

1: Kunkel et al., 2009; 2. Zhao et al., 2007; 3. Mallard, F. 2008; 4. Sparks et al., 1996; 5. Cano-Ruiz et al., 1993.

Many other opportunities for PRM implementation exist in indoor environments. Slot diffusers are a common HVAC component installed in many commercial buildings. Often, slot diffusers are installed in the ceiling adjacent to walls, such that conditioned air travels down the wall before mixing with bulk indoor air. Computational fluid dynamic modeling of these slot diffusers has shown that airspeeds similar to upper values used in this study are achievable. Placement of PRMs along these same walls would result in enhanced ozone removal without additional energy input. PRMs could also be hung from the ceiling beneath a square louvered diffuser, a more typical residential installation.

For true passive removal, enhanced airflow could be realized on a southern facing wall. Heated air along a southern facing wall will expand, becoming less dense and rising, setting up a convective flow. Future experimental work will characterize airspeeds and removal under such conditions. Furthering this concept, the installation of a false wall on the southern face of a building could result in additional surface area for PRM installation (on the inside of the false wall and the inside of the building structure wall). A vent from the room could allow transport of bulk air to the cavity, with clean air returned to the bulk room.

CONCLUSIONS

This analysis showed that PRM reaction time scales competed with existing indoor surfaces, and were one to two orders of magnitude faster than indoor homogenous chemistry. Building designers and air quality engineers could significantly improve indoor air quality and reduce ozone exposure by controlling concentrations of ozone in indoor environments. Passive reactive materials present a novel means for accomplishing this goal with little or no additional energy expenditure. Important considerations are presented herein for choosing a reactive material as well as optimizing room conditions such that the PRM can preferentially react and remove ozone over time-scales much shorter than those associated with homogeneous reactions and removal to existing indoor surfaces.

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