CFD ANALYSIS OF CHEMICALLY REACTIVE POLLUTANTS IN 2D TEST ROOM

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ABSTRACT

Recently, theoretical analyses have begun to evaluate some free radicals and other products that are generated by chemical reactions. Especially, the products of ozone / terpene reactions cause greater airway irritation in mice than would be predicted based on the known response of mice to ozone or terpenes. This paper presents an analysis of chemically reactive pollutants in indoor air. We have used CFD technique to simulate bimolecular reactions occurring indoors. In this research, the Second Order Rate Constant model which is a simple and fundamental model reproducing bimolecular Reaction is adopted. In order to demonstrate the performance of the Rate Constant models, CFD simulations are carried out for a 2D test room. Three sets of chemical compounds, ozone / terpene, are used in this study. The quantity of production substance C_{prod} through the chemical reaction is proportional to the concentration of source substances (Ozone and terpene).

INDEX TERMS

CFD, VOCs, Diffusion, Deposition, Chemical Reaction

INTRODUCTION

The concentration distribution of the chemical pollutants (e.g. VOC) in a room was analyzed and reported by modeling the diffusion within the building material and within the room air; this included the sorption on the building material surface [Murakami et al., 2001]. The results of a numerical prediction of the concentration distribution and time history of the emission rates were reported [Murakami et al., 2000]. These results were sufficiently consistent with the results from experiments in a chamber. However, in actual measurements of VOC concentrations in a room, the measured concentration and the values estimated from the emission flux from each material in the room and the ventilation rate are not necessarily consistent with each other, and the existence of a phenomenon known as "lost TVOC" has been confirmed [Wolkoff, 1995]. One of the causes of this is believed to be the generation and decomposition of VOC due to chemical reactions in the air. In particular, it has been confirmed that ozone [O_3] in the room air actively generates various free radicals by reacting with the organic and inorganic compounds existing in the air. The free radicals and other products of reactions are often more irritating than their precursors. Regarding this background, simplified equations for the chemical reactions were modeled in this research, with the aim of establishing a method of estimating the concentration in the room that incorporates these phenomena.

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MODELING THE EQUATIONS FOR THE CHEMICAL REACTION

Various chemical reactions are assumed to take place in room air. In particular, various free radicals exist as intermediate products from these chemical reactions; however, these free radicals are in unstable states, posing great difficulties in both qualitative and quantitative estimation. In addition, it imposes a considerable additional burden on the computational process to accurately compute the behavior of these free radicals. Therefore, the purpose of the modeling was to estimate the total concentrations of the final products. In this research, the Second Order Rate Constant model which is a simple model reproducing bimolecular Reaction is adopted [Charles et al., 2000].

Bi-molecular Reaction and Reaction Modeling using the Rate Constant

A bi-molecular reaction is a chemical reaction involving multiple substances, and in order to numerically analyze this, it is necessary to solve multiple scalar equations corresponding to the number of reaction substances and products. The generation of unstable substances in a room during a bi-molecular reaction with highly reactive ozone and terpenes has been drawing attention.

The simplest chemical reaction modeling uses the rate constant [Nazaroff et al., 1986]. Assuming the concentration of the reaction substance "A" and "B" at a point in space to be C_1 (i,j,k) [ppb] and C_2 (i,j,k) [ppb] respectively, the transportation of the reaction substances are expressed by equation (1)and (2), and the bi-molecular reaction by equation (3).

$$\frac{\partial C_1}{\partial t} + \frac{\partial U_j C_1}{\partial x_j} = \frac{\partial}{\partial x_j} D \frac{\partial C_1}{\partial x_j} + S_A \tag{1}$$

$$\frac{\partial C_2}{\partial t} + \frac{\partial U_j C_2}{\partial x_j} = \frac{\partial}{\partial x_j} D \frac{\partial C_2}{\partial x_j} + S_B \tag{2}$$

$$S_A = S_B = -k_b \cdot C_1 \cdot C_2 \tag{3}$$

Here, S is the source term; k_b is the second order rate constant [1/ppb h]. From equation (3), changes over time in the concentration of substance "A" and "B" due to the bi-molecular reaction are computed. In addition, assuming the concentration of the hypothetical products (all products) by reaction to be C_{prod} [ppb], the amount of change over time is expressed by equation (4) and (5).

$$\frac{\partial C_{prod}}{\partial t} + \frac{\partial U_j C_{prod}}{\partial x_j} = \frac{\partial}{\partial x_j} D \frac{\partial C_{prod}}{\partial x_j} + S_{prod} \tag{4}$$

$$S_{prod} = k_{prod} \cdot C_{prod} = k_b \cdot C_1 \cdot C_2 \tag{5}$$

Here, k_{prod} is the first order rate constant [1/h] of the hypothetical reaction product C_{prod}.

EXISTING RESEARCH ON RATE CONSTANTS

A lot of second order rate constants have been measured in research by Atkinson et al. [Atkinson et al., 1990]. Data on the second order rate constants for ozone at 296K (23°C) and terpenes have been collected for reactions that are believed to exist in the room air. Some of the results of measurements made by Atkinson et al., are shown in Table 1. In this research, the data shown in Table 1 were used to estimate the chemical reactions and concentration distribution in the room air.

WALL SURFACE DEPOSITION FLUX MODELING OF OZONE

This research accounted for ozone as one of the reaction substances in the room. In accounting for the phenomena of the transportation of ozone in a room, it is necessary to consider not only its transporta-

Table 1 Cases Analyzed and Rate constant

	C_1	C_2	k_b [[1/ppb·h]	v_d [m/s]
Case0	Ozone	d-Limonene	-	-
Case1		d-Limonene	0.0184	-
Case2		α -terpinene	0.756	-
Case3		α -pinene	0.00756	-
Case4		d-Limonene	0.0184	4.0×10^{-4}
Case5		α -terpinene	0.756	
Case6		α -pinene	0.00756	

Table 2 Numerical Conditions

Turbulence model	Low Re type k- ε model (MKC model)
Mesh	68(x) × 64(z)
Scheme	Convection Term : Up wind (first order)
Inflow condition	U_{in}= 3.0m/s, $k_{in}=3/2\cdot(U_{in}\times0.015)^2$, $\varepsilon_{in}=C_\mu k_{in}^{3/2}/l_{in}$, C_μ=0.09, $l_{in}=L_0/7$,
Outflow condition	U_{out} , k_{out}, ε_{out} = free slip
Re number	U_0L_0/ν = 4200
Wall treatment	no slip

tion with ventilation, and chemical reaction, but also the phenomena of sorption by the solid walls. We proposed simple adsorption/desorption models for a sorptive material surface using the adsorption isotherms described in the previous report [Murakami et al., 2001]. In this report, a model of deposition using the deposition velocity v_d [m/s] was adopted, taking into account the deposition of ozone on the solid wall surfaces [Seinfeld, 1985]. The deposition flux against a solid surface using the deposition velocity v_d is expressed by the following equation:

$$Js = v_d\left(Cs - 0\right) \qquad (6)$$

Here, Js is the deposition flux. Cs is a reference concentration. The deposition velocity v_d correspond to the convective mass transfer coefficient there the surface concentration assumed to be zero. According to Nazaroff et al., ozone deposition rates in general building materials are estimated to be from 2.5×10^{-4} to 7.5×10^{-4} [m/s] [Nazaroff et al., 1986].

OUTLINE OF THE NUMERICAL ANALYSIS

Flow fields and diffusion fields were analyzed, targeting the room models used in the precise room model experiments [Ito et al., 2000]. An outline of the space to be analyzed is shown in Figure 1. When the air supply slot width is the representative length (L_0=20mm), the space is a 2-dimensional room of 75 L_0 (x)×50L_0 (z) (=1500mm×1000mm). Flow fields were analyzed using the low Reynolds type k-ε model [Murakami et al., 1996]. Numerical conditions are shown in Table 2. The bi-molecular reactions in the room were analyzed, assuming that stable and equal amounts of contaminant 1 (concentration C_1), here assumed as ozone, and contaminant 2 (concentration C_2) were generated from source 1 and source 2. Also, both the left and right walls were assumed to be contaminant 1, ozone, and deposition surfaces. The deposition velocity v_d [m/s] was taken as the value for general building materials, which is 4.0×10^{-4} [m/s]. The room temperature was assumed to be a constant 25℃. Analysis cases are shown in Table 1. The amount of chemical pollutants generated from the contamination sources and the amount of supply opening velocity were assumed to be representative scales, and the results of the analyses were all

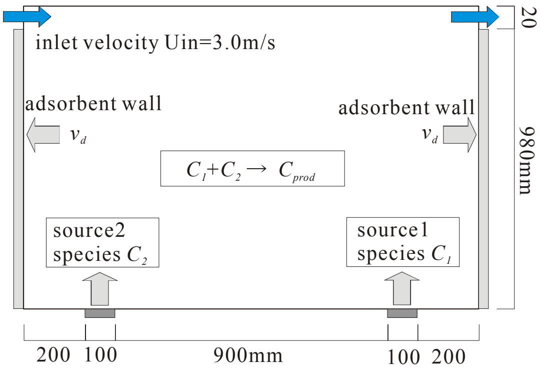


Figure 1 Room Model Analyzed

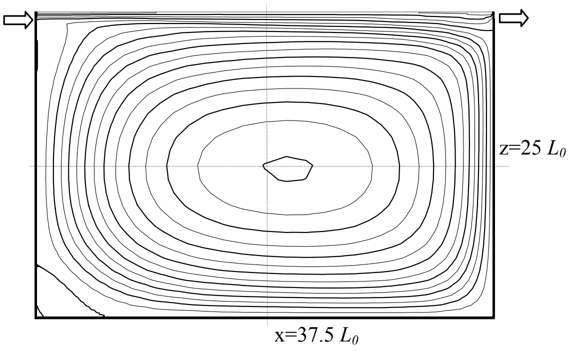
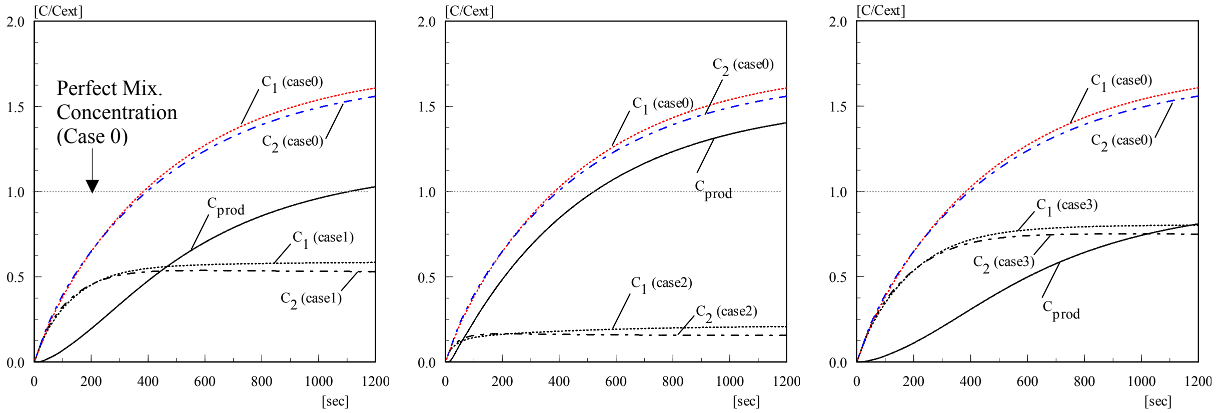
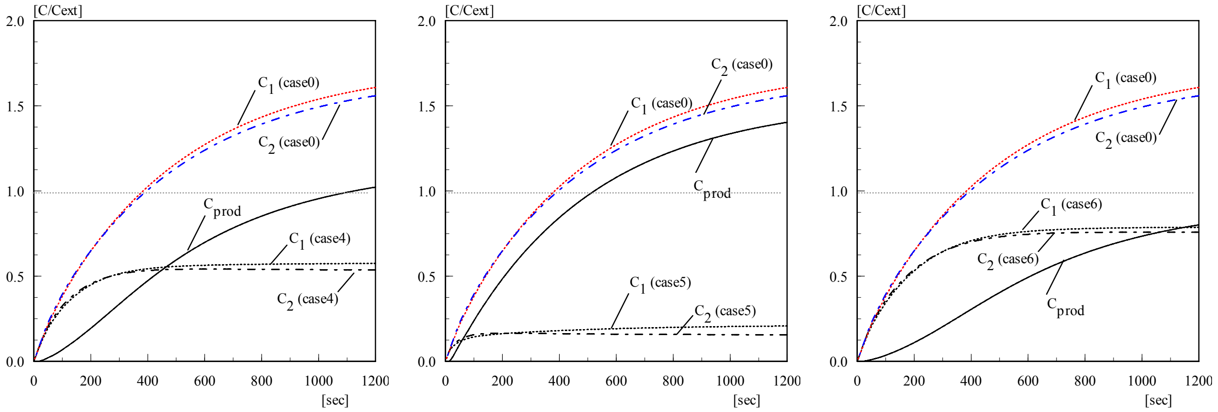


Figure 2 Stream line estimated by CFD



(1) Case1 (k_b=0.0184) (2) Case2 (k_b=0.756) (3) Case3 (k_b=0.00756)



(4) Case4 (k_b=0.0184, v_d=4.0×10^{-4}) (5) Case5 (k_b=0.756, v_d=4.0×10^{-4}) (6) Case6 (k_b=0.00756, v_d=4.0×10^{-4})

Figure 3 Time History of Room Averaged Concentration

(non-dimensional at perfect mixing concentration on Case0)

non-dimensional.

RESULTS OF THE NUMERICAL ANALYSIS

Stream lines predicted by CFD are shown in Figure 2. A large circulating flow was formed along the wall surface in the room, and a secondary vortex against the major flow was observed in the floor corner. Though omitted in this report, as a result of conducting precise room model experiments using LDV (Laser Doppler Velocimetory) system under the same conditions as the analysis cases in this research, the results were very consistent with the results for the low Reynolds number-type k-ε model, and it was confirmed that they analyze the flow fields with sufficient accuracy [Ito et al., 2000].

Time History of the Average Concentration in the Room

Results of the time history of the average concentration in the room in each case are shown in Figure 3. Results for case 0, in which only contaminants source were present, and disregarding chemical reactions and wall deposition effects, are shown together in the figure for comparison. C_1 and C_2 indicate the chemical substances shown in Table 1; C_{prod} indicates the reaction products.

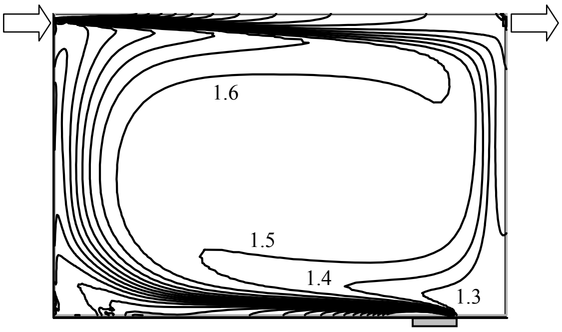
When equations (3) and (4) were assumed to apply in each case, both chemical substances (C_1 and C_2) always decreased when chemical reactions were generated in the room. Also, since C_{prod} was proportional to the second order rate constant k_b [1/ppb h], C_{prod} was the largest in case 2. In case 2 in particular, approximately 7 times as much reaction product C_{prod} existed compared to the steady concentration values of C_1 and C_2existing in the room, and the chemical reactions were an important factor in constituting the room VOC concentration. In cases 4 to 6, which considered the effects of ozone deposition on the solid walls (C_1 in these analyses), the effects of the reduction in the room ozone (C_1) concentration were approximately 1% compared to the results for cases 1 to 3, which were relatively small.

VOC concentration distribution in the room

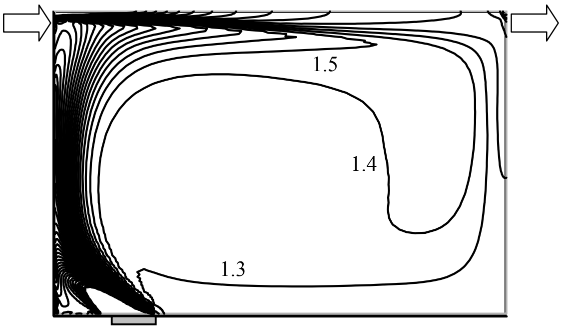
The VOC concentration distributions in the room are shown in Figure 4. This report shows case 2, in which reductions in concentration C_1 and C_2 were the greatest, as well as case 0, in which only contaminants were present, but omits the remaining cases. The concentration distributions were plotted up to 1200 seconds after computations began. Since a large clockwise circulating flow was formed in the room, contaminants generated from the contamination sources 1 (Figure 4 (1)) and 2 (Figure 4 (2)) transported along the floor and left wall forming a concentration distribution in the room. In case 2, which incorporated chemical reactions, the room concentration of contaminants C_1 and C_2 significantly decreased. Also, the reaction product C_{prod} became highly concentrated near contaminant 2 on the floor where both contaminants C_1 and C_2 became highly concentrated. Since the effects of the reduction in the ozone (C_1) concentration in the room were approximately 1% in cases which considered the effects of ozone deposition on the solid walls, there was almost no change in the room concentration distribution compared to cases which did not consider the effects of deposition.

CONSIDERATIONS

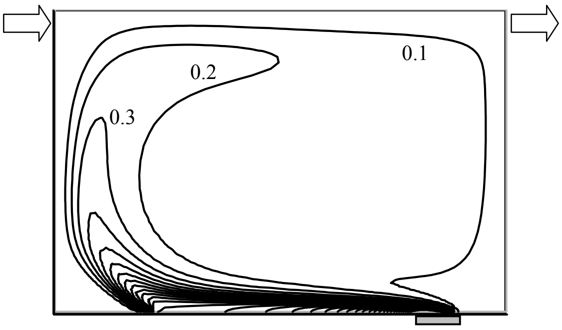
The chemical reaction models used in the analyses were based on the rate constants. In these models, the concentration of the reaction product C_{prod} was simply proportional to the second order constant k_b and also to



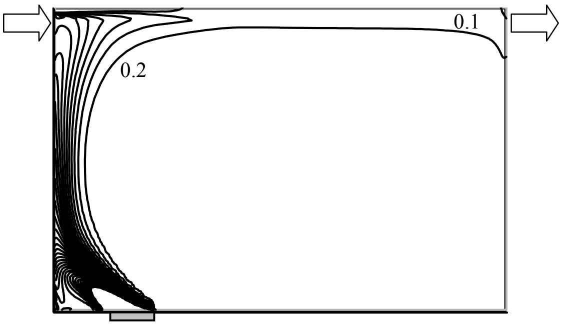
(1) C_1 Concentration Distribution (case0, k_b =0)



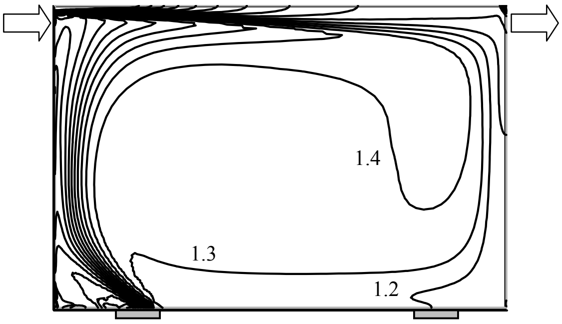
(2) C_2 Concentration Distribution (case0, k_b =0)



(3) C_1 Concentration Distribution (case2, k_b =0.756)



(4) C_2 Concentration Distribution (case2, k_b =0.756)



(5) C_{prod} Concentration Distribution (case2, k_b =0.756)

Figure 4 Concentration Distribution

(non-dimensional at perfect mixing concentration on Case0) the concentration of contaminants C_1 and C_2. In other words, these analyses were targeted exclusively under conditions where rate constants apply, and the range of application of the model needs further consideration. Also, it is difficult to measure experimentally reaction products containing free radicals in a room; however, it is possible to measure ozone and terpenes. Verification of the analyses results of experiment is a problem in future.

CONCLUDING REMARKS

(1) Chemical reaction equations were modeled in a simple manner by using rate constants, and were coupled with CFD analysis.

(2) As a result of estimating the amount of chemical reaction and VOC concentration distribution in room, using ozone and terpenes, under conditions in which rate constants apply, it was estimated that there would be reaction products that would exceed the room concentration from the VOC generated from the contaminant sources.

(3) As a result of conducting analyses coupled with models for ozone deposition onto solid wall surfaces using the deposition velocity, it became clear that the effects of reductions in the room concentration were relatively small compared to the amount of chemical reaction and elimination by ventilation.

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