

# Influence of desorption on the indoor concentration of toxic gases

Edvard Karlsson<sup>a,\*</sup>, Ueli Huber<sup>b</sup>

<sup>a</sup> National Defence Research Establishment, Department of NBC Defence, S-901 82 Umeå, Sweden

<sup>b</sup> AC-Laboratorium, CH-3700 Spiez, Switzerland

Received 18 February 1995; accepted 20 November 1995

---

## Abstract

A theoretical model is developed which considers the influence of both deposition and desorption processes on the indoor concentration of toxic gases. The model is based on a simplification of the Langmuir theory. Model parameters for  $\text{NH}_3$ ,  $\text{Cl}_2$ , the nerve agent sarin, and a simulant for the nerve agent VX are calculated from available experiments with common indoor materials. The adaptation of parameters seems to work well for low to moderate exposure. The model is then used to study concentrations of the nerve agent sarin in ordinary buildings after a hypothetical attack. Desorption results in a residual indoor concentration over an extended period, and, in contrast to a non-desorbing gas, the indoor exposure  $\int_0^T c_i dt$  of a desorbing gas can therefore approach the outdoor exposure given sufficient time. For several indoor materials this approach is slow, especially under conditions of low ventilation. A very high deposition and a low desorption of sarin to/from unpainted concrete is found, thus demonstrating that rooms of unpainted concrete offers good protection against sarin.

*Keywords:* Desorption; Indoor gas concentration; Sarin; Theoretical model; Toxic gas

---

## 1. Introduction

In dispersion models from the 1960s, and also in subsequent models from the 1970s and the 1980s, indoor gas concentrations within ordinary buildings were often assumed to depend only on the outdoor concentration and the outdoor/indoor air exchange [1–3]. Despite giving lower maximum indoor than outdoor concentrations, these earlier models implied that the total indoor exposure  $\int_0^\infty c_i dt$  equals the total outdoor exposure  $\int_0^\infty c_o dt$

---

\* Corresponding author.

if the air exchange is constant with time [8]. During the second part of the 1970s, and during the 1980s, indoor deposition was introduced in dispersion models for  $\text{SO}_2$ ,  $\text{O}_3$ , and  $\text{NO}_2$  pollutants in urban air [4,5]. Indoor deposition has also been introduced in some models for accidental releases of toxic chemicals and attacks with chemical warfare agents [6–8]. The effect of deposition is to reduce both the concentration and the exposure, especially when decreasing the ventilation. However, Miyazaki [9] found in laboratory experiments that the deposition velocity of  $\text{NO}_2$  decreased for repeated exposure, thus indicating that the amount of agent on the surface will influence the deposition process. Van Leeuwen [6] and van der Weide [7] have also reported a decreasing gas deposition velocity with time for the nerve agent sarin. When calculating the deposition velocity from experiments, Karlsson [8] found a decreasing deposition velocity with time for  $\text{NH}_3$  and for trialkylphosphonoacetate (a simulant of the nerve agent VX). Laboratory experiments designed to study the deposition of the nerve agent sarin upon different indoor materials in a test box of glass showed decreasing sarin concentrations, often followed by an equilibrium state with a nearly constant concentration (Berglund [10], Berglund et al. [16]). The level of the equilibrium sarin concentration varied depending on the type of material in the box. Bingeli [11] reported the observation of deposition and desorption when determining air-lock flushing times for shelters by using a simulated warfare agent. These studies and observations point to a need to investigate how the amount of agent on the surface and the desorption processes of toxic gases reduce the protective effect of surface deposition. The purpose of the present work is to formulate a model for indoor toxic gas concentration taking into account both deposition and desorption, and to study the effect of both processes on the protective effect of seeking shelter within ordinary buildings. In this report, available data on deposition/desorption parameters are also reviewed.

## 2. Equations

The present treatment of deposition and desorption processes is an extension of the formulation given earlier by Karlsson [8]. The building or the room in question is represented by a chamber in which the air is considered to be well mixed. It is assumed that there is no other available indoor release mechanism for toxic gases except that caused by desorption. The change in time  $t$  of the indoor toxic gas concentration  $c_i$  can be formulated as

$$\frac{dc_i}{dt} = kc_o(1 - f_o) - kc_i - \sum_j^N (A_j/V) \frac{dm_j}{dt} - (V_{ei}/V) f_i c_i \quad (1)$$

where  $c_o$  is the outdoor toxic gas concentration,  $f_o$  is the external filter factor,  $k$  is the air exchange,  $A_j$  is the total indoor area of material  $j$ ,  $N$  is the number of different materials,  $V$  is the room volume and  $m_j$  is the amount of toxic gas deposited per unit area on the surface of material  $j$ ,  $V_{ei}$  is the flow of internal filtration, and  $f_i$  is the internal filter factor, which is the fraction of toxic gas removed by mask filters, lungs or other internal filtration equipment. The treatment of  $c_o$ ,  $f_o$ ,  $k$ ,  $V_{ei}$  and  $f_i$  is discussed by

Karlsson [8]. The flux of gas  $dm_j/dt$  to/from the indoor surfaces of material  $j$  is assumed to be proportional to the difference between the toxic gas concentration in the air  $c_i$  and the concentration  $c_j^*$  in equilibrium with the deposited toxic gas on the surface of material  $j$ . This assumption is similar to a formulation proposed by Horst and Slinn [12] for modelling the evaporation of chemicals

$$\frac{dm_j}{dt} = a_j(c_i - c_j^*), j = 1 \dots N \quad (2)$$

where  $a_j$  is the transfer velocity ( $m\ s^{-1}$ ). Eq. (2) is an extension of the usual formulation of deposition to non-desorbing surfaces, where  $c_j^*$  is zero and  $a_j$  is then equal to the deposition velocity. As for the latter, the transfer velocity  $a_j$  depends on turbulent diffusion in the room air, molecular diffusion in the viscous sub-layer and characteristics of the surface [8]. According to the Langmuir theory [13], deposition onto the surface is a physical process, and at low vapour pressure  $m_j$  is proportional to  $c_j^*$  for a given temperature. This means that the adsorption isotherm, defining the relationship between the equilibrium concentration  $c_j^*$  and the deposited amount  $m_j$ , is a linear function of  $m_j$ . For higher vapour pressures the Langmuir theory [13] postulates that  $m_j$  approaches a limiting value. However, there are several shortcomings in the Langmuir theory [13], especially at higher concentrations. As indoor concentration is normally low it seems reasonable to use the Langmuir theory [13] here and to assume  $c_j^*$  to be proportional to  $m_j$

$$c_j^* = b_j m_j, j = 1 \dots N \quad (3)$$

where  $b_j$  ( $m^{-1}$ ) is an equilibrium parameter depending on the identity of the gas, the adsorbing material, the ambient temperature, and perhaps also on humidity. Eq. (2) implies that deposition occurs when the indoor toxic gas concentration  $c_i$  is higher than the equilibrium value  $c_j^*$ , but when  $c_i$  becomes lower than  $c_j^*$  the deposition changes to desorption.

### 3. Calculation of model parameters $a_j$ , $b_j$

Measurements of the decrease of gas concentration in test rooms and in a laboratory test box (Karlsson et al., [14,15], Berglund and co-workers [10,16]) have been used to determine the parameters  $a_j$  and  $b_j$  for various common indoor materials. In these experiments a fan was mixing the air and thus giving high levels of turbulence, which means that observed transfer velocities depended mainly on the surface characteristics [8]. The studied agents were  $Cl_2$ ,  $NH_3$ , trialkylphosphonoacetate (a simulant of the nerve agent VX), and the nerve agent sarin. In these experiments the agents were released or gasified from the liquid phase during a period of  $\leq \approx 10$  min, during which significant deposition could occur. To take this initial deposition into account in the calculations of model parameters, the releases of agents were assumed to be instantaneous, thus giving an initial concentration  $c_i(0)$  equal to the released amount of agent divided by the room volume. For the test box experiments Eq. (1) was then integrated from  $t=0$  to  $t=T$ , for two materials (the glass walls of the test box and one test

material,  $N = 2$ ), with the assumption that  $m_1(0)$  and  $m_2(0)$ ,  $c_o$  and  $V_{ei}$  are zero. Then  $m_2(T)$  of the test material can be solved as follows

$$m_2(T) = \frac{V}{A_2} \left[ c_i(0) - c_i(T) - \int_0^T kc_i dt - \frac{A_1}{V} m_1(T) \right] \quad (4)$$

From Eq. (2) and Eq. (3)

$$\frac{dm_1}{dt} = a_1(c_i - b_1 m_1) \quad (5)$$

By using measured values of  $c_i$  and previously determined values of  $a_1$  and  $b_1$ , Eq. (5) was solved numerically to give  $m_1(T)$ , which was put into Eq. (4) to give  $m_2(T)$ . Eqs. (1)–(3) were then combined to give

$$\frac{dc_i}{dt} = -kc_i - (A_1/V)a_1(c_i - b_1 m_1) - (A_2/V)a_2(c_i - b_2 m_2) \quad (6)$$

For the test room experiments Eq. (6) can also be used, but now  $a_2$  and  $b_2$  represent the mean effect of deposition and desorption to/from all surfaces of the room, and  $A_1$  is zero (no glass walls). To solve  $a_2$  and  $b_2$  simultaneously, two equations at different values of the time  $T$  have to be formulated from Eq. (6). However, normally there is a possibility to formulate more than the minimum two equations, and different results can thus be achieved. The main procedure used here was to use  $c_i$  and  $dc_i(T)/dt$  from the beginning and the end of each trial, as those data best represent the often fast decrease of the toxic gas concentration in the beginning and the equilibrium state at the end. However, some problems in calculating  $a$  and  $b$  can be encountered, namely:

1. when  $dc_i/dt$  is approximated by finite differences  $\Delta c_i/\Delta t$  from the measurements, short  $\Delta t$  can be problematic because of small measurement errors, and because the exact time was not known when the gasifying was finished. Large  $\Delta t$  can be problematic because  $c_i$  decreases exponentially from time zero.
2. when there was a significant decrease of  $c_i$ , larger than that caused by the small ventilation, when the experimental trial was stopped.

In order to avoid problems related to (1),  $a$  and  $b$  were first calculated with the smallest possible  $\Delta t$ . Then a comparison was made between the measured concentration values of the trial, and a model solution of Eqs. (1)–(3) for  $c_i$  by using the calculated values of  $a$  and  $b$ . If there was poor agreement between the model and the measurements,  $\Delta t$  was increased, and a new comparison with the measurements was made, until the best values of  $a$  and  $b$  were found. Problem (2) may yield negative values of  $b$ , which is physically meaningless and could thus lead to negative model concentrations at long times. The appearance of the negative  $b$  values may be an indication of model shortcomings, inaccurate concentration measurements (often near the instrument detection limit), or may simply signify that the experimental trial in question was stopped too early. However, in order to avoid negative  $b$  values, and not to underestimate model toxic gas concentrations,  $dc_i/dt$  was assumed to be zero at the end of those trials giving negative  $b$ . It was further assumed that the final value of  $c_i$  was the mean of the two last measured values. Calculated values of  $a$  and  $b$  are summarized in Table 1.

Table 1  
Model parameters *a* and *b* calculated from experiments or from values of deposition velocities

Agent	Test box/ room	Vol (m <sup>3</sup> )	Material	Area (m <sup>2</sup> )	Temp. (°C)	Rel. humidity (%)	Initial concn. (mg m <sup>-3</sup> )	<i>k</i> (s <sup>-1</sup> )	<i>a</i> (m s <sup>-1</sup> ) mean ± σ	<i>b</i> (m <sup>-1</sup> ) mean ± σ	No. of trials	Based on ref.
Sarin	box	0.5	Glass silanized with Si (the empty test box)	3.8	≈ 20	0-60	5.3	6.5 × 10 <sup>-6</sup>	4.4 × 10 <sup>-5</sup> ± 0.83 × 10 <sup>-5</sup>	22.1 ± 5.8	3	[16]
Sarin	box	0.5	Plastic coated wallpaper on plasterboard	2.9	≈ 20	≈ 60	5.5-11.0	6.5 × 10 <sup>-6</sup>	1.7 × 10 <sup>-4</sup> ± 1.3 × 10 <sup>-4</sup>	0.45 ± 0.28	5	[10,16]
Sarin	box	0.5	Rough spruce	3.2	≈ 20	50-60	5.5-10.9	6.5 × 10 <sup>-6</sup>	1.3 × 10 <sup>-4</sup> ± 2.0 × 10 <sup>-4</sup>	0.73 ± 0.76	3	[10,16]
Sarin	box	0.5	Unpainted concrete	0.27-1.1	20-22	8-64	5.8-10.9	1.7 × 10 <sup>-7</sup>	7.2 × 10 <sup>-4</sup> ± 3.1 × 10 <sup>-4</sup>	0.026 ± 0.016	3	[10,16]
Sarin	large room	922	Old chalking paint on concrete	1700	15-17	40	3.5	5 × 10 <sup>-5</sup>	1.8 × 10 <sup>-4</sup>	0.009	1	Internal report
Sarin	large room	760	Alkyd or plastic paint on walls/roof, flat plastic carpet	≈ 1500	15-17	35	≈ 0.06	1.8 × 10 <sup>-5</sup>	≈ 0	-	1	Internal report
VX simulant	room	17	Painted walls, roof, and flat plastic carpet	54-60	15-20	< 30	0.049-0.244	1.1 × 10 <sup>-4</sup>	2.5 × 10 <sup>-4</sup> ± 1.2 × 10 <sup>-4</sup>	0.07 ± 0.03	3	[15]
NH <sub>3</sub>	room	17	Painted walls, roof, and flat plastic carpet	54	15-20	< 50	46-59	5 × 10 <sup>-5</sup>	1.1 × 10 <sup>-4</sup> ± 0.4 × 10 <sup>-4</sup>	0.05 ± 0.01	2	[14]
Cl <sub>2</sub>	room	38	Painted walls, roof, and flat plastic carpet	79	15-20	< 50	37-51	(4-7) × 10 <sup>-5</sup>	1.4 × 10 <sup>-4</sup> ± 0.6 × 10 <sup>-4</sup>	0.033 ± 0.012	2	[14]
Sarin <sup>a</sup>			Glass						4.3 × 10 <sup>-5</sup>	4.0		[7]
Sarin <sup>a</sup>			Textile						2.4 × 10 <sup>-4</sup>	0.094		[7]
Sarin <sup>a</sup>			Wall hanging						1.4 × 10 <sup>-4</sup>	0.16		[7]

<sup>a</sup> Values of deposition velocities (decreasing with time) are used to calculate *a* and *b*.

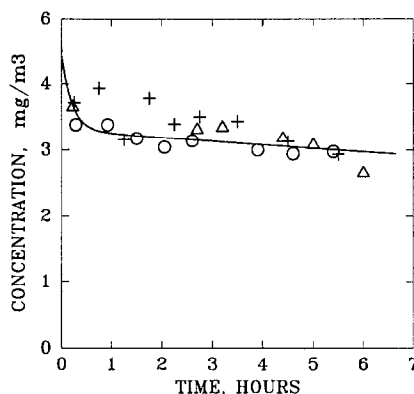


Fig. 1. Calculated and measured concentrations of nerve agent sarin in the empty test box (Berglund [10,16]).  
 —, calculated; +, O, Δ three series of measurements.

The table shows that  $a$  is low and  $b$  is high for sarin in the empty test box, pointing to a low deposition rate and a high equilibrium concentration  $c^*$ , which further reduces the deposition and gives an early change to desorption from the walls of the test box. This is favourable when determining  $a$  and  $b$  for different materials. Despite the relatively large spread of the data, unpainted concrete has significantly the highest value of  $a$  and among the lowest values of  $b$  for the nerve agent sarin. This shows a high deposition rate and a low equilibrium concentration, which means that desorption does not occur until the indoor concentration is very low. Thus, rooms of unpainted concrete are expected to give the best protection against sarin. Spruce has the largest variation between the trials, indicating a less satisfactory agreement between the model and the experimental data. The nerve agent sarin seems not to deposit on alkyd or acrylate paints or on a flat plastic carpet. By using Eqs. (1)–(3) and values of  $a$  and  $b$  from Table 1, solutions of  $c_i$  for the empty test box are shown in Fig. 1, and for the test box with pieces of unpainted concrete in Fig. 2. Measured concentrations are also shown for comparison. The adaptation of model parameters seems to be reasonable.

From laboratory experiments, Van der Weide [7] calculated deposition velocities of sarin for some indoor materials, assuming that the amount of agent on the surface does not influence the deposition process. However, these deposition velocities decrease with time, thus showing that the amount of agent on the surface does influence the process. By using these results  $a_j$  and  $b_j$  were determined in a similar way as above (Table 1). For glass, the value of  $a$  based on the work of Van der Weide [7] is very similar to the value based on Berglund et al. [16], but  $b$  is lower, probably because of the silicon-coated surface used by Berglund et al. [16]. For textiles and wall hangings,  $a$  is similar to that for plastic coated wallpaper and rough spruce based on Berglund et al. [16] and Berglund [10], but  $b$  is lower, thus giving a lower desorption, probably because textiles and wall hangings are more porous than wallpaper or spruce (see Section 5 below).

Huber [17] has studied the desorption of the nerve agent sarin from small pieces of unpainted concrete during 7 h, after first exposing the concrete to a stream of dry air with a sarin concentration of 9–40  $\text{mg m}^{-3}$  during 30–60 min. The transfer velocity  $a_j$

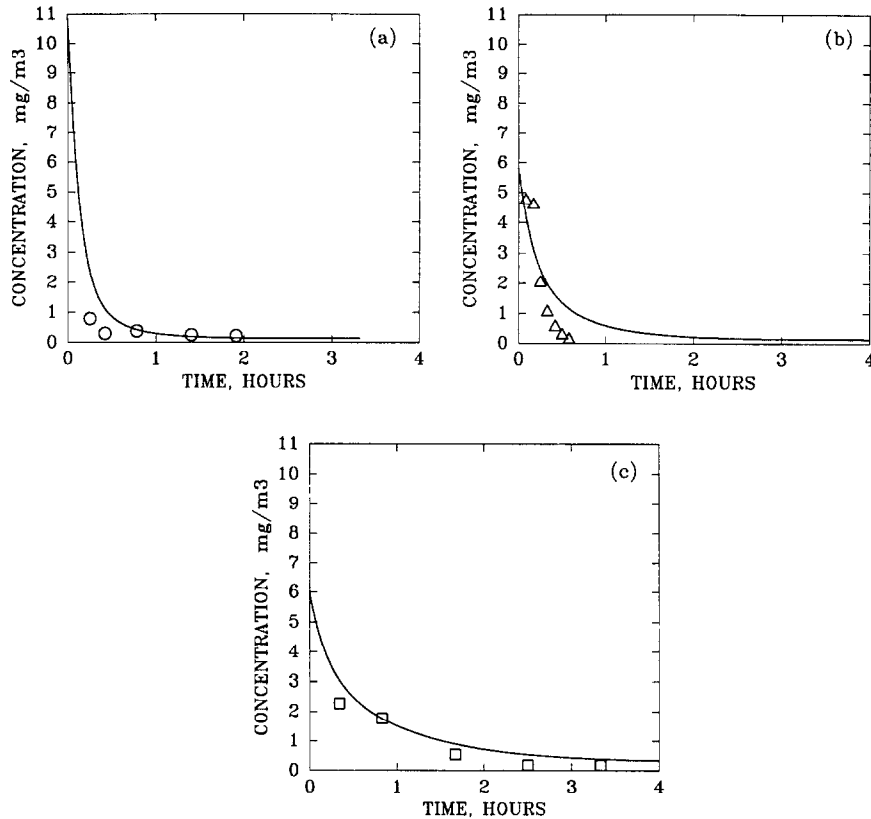


Fig. 2. Calculated and measured concentrations of nerve agent sarin in the test box with pieces of unpainted concrete (Berglund [10,16]). —, calculated;  $\circ$ ,  $\Delta$ ,  $\square$  three series of measurements. (a) Area of concrete =  $1.06 \text{ m}^2$  and initial concentration =  $10.9 \text{ mg m}^{-3}$ ; (b) area of concrete =  $0.53 \text{ m}^2$  and initial concentration =  $5.8 \text{ mg m}^{-3}$  (c) area of concrete =  $0.27 \text{ m}^2$  and initial concentration =  $6.0 \text{ mg m}^{-3}$ .

cannot be calculated from these experiments, but some information on  $b_j$  at high exposure can be achieved by assuming that (1) the total amount deposited is equal to the amount observed to desorb, (2) the value of  $a$  is equal to  $7 \times 10^{-4} \text{ m s}^{-1}$ , which is the value calculated from the data by Berglund et al. [10,16]; see Table 1. These assumptions gave  $b$  equal to  $0.5\text{--}1.7 \text{ m}^{-1}$ , which is much larger than the value ( $0.026 \text{ m}^{-1}$ ) based on the data by Berglund et al. [10,16] and will give a much higher equilibrium concentration  $c^*$ , and thus desorption will occur more easily. The difference indicates that sarin and unpainted concrete do not obey Eq. (3) at both low and high exposure. Neither did the full form of the Langmuir theory [13], where an additional constant  $d_j$  is introduced in Eq. (3) and

$$c_j^* = \frac{b_j m_j}{1 - b_j d_j m_j}$$

satisfactorily explain the data. Possibly the dry air used by Huber may influence the value of  $b$ . By assuming that  $b = 0.026 \text{ m}^{-1}$  for  $m < 11.5 \text{ mg m}^{-2}$ , and  $b = 1.5 \text{ m}^{-1}$

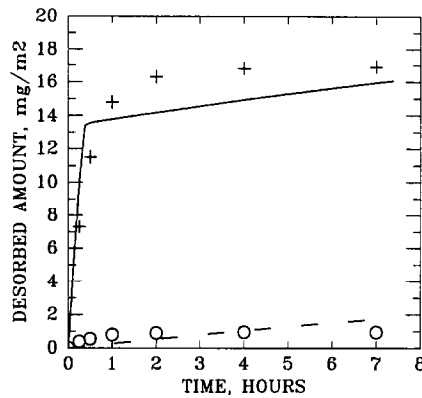


Fig. 3. Calculated and measured desorption of nerve agent sarin from unpainted concrete for two trials in the experiments by Huber [17]. Calculations are made with Eqs. (1)–(3) and assumptions that  $a = 7 \times 10^{-4} \text{ m s}^{-1}$ ,  $b = 0.026 \text{ m}^{-1}$  for  $m < 11.5 \text{ mg m}^{-2}$ , and  $b = 1.5 \text{ m}^{-1}$  for  $m \geq 11.5 \text{ mg m}^{-2}$ . —, calculated with a preceding exposure of  $40 \text{ mg m}^{-3}$  during 1 h; +, measurements from a trial with a preceding exposure of  $40 \text{ mg m}^{-3}$  during 1 h; ---, calculated with a preceding exposure of  $9 \text{ mg m}^{-3}$  during 0.5 h; O, measurements from a trial with a preceding exposure of  $9 \text{ mg m}^{-3}$  during 0.5 h.

for  $m \geq 11.5 \text{ mg m}^{-2}$ , the desorption measurements could be reproduced reasonably by Eqs. (1)–(3) for six of seven trials; see Fig. 3.

Huber [17] also studied the desorption of sarin from painted concrete, and the results showed much smaller desorption than from the unpainted concrete. The most probable explanation for this seems to be low deposition during the exposure period, because that

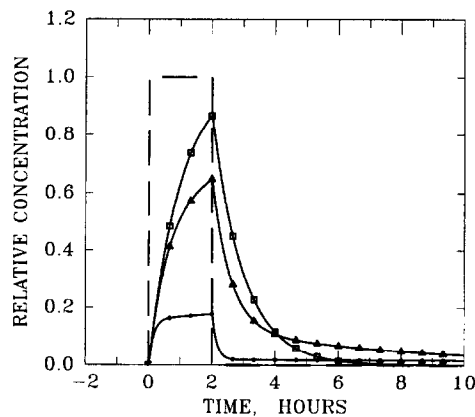


Fig. 4. Calculated indoor concentration for an inert gas (no desorption), and for the nerve agent sarin. The air exchange  $k$  is  $1.0 \text{ h}^{-1}$ ,  $f_o$  and  $V_{ei}$  are zero. The outdoor concentration  $c_o = 1.0$  during the time period 0–2 h but otherwise  $c_o$  is zero. —, outdoor; —□—, inert gas indoor; —△—, nerve agent sarin in room with plastic coated wallpaper ( $A/V = 1 \text{ m}^{-1}$ ), ceiling of acrylate paint and plastic carpet ( $A/V = 1 \text{ m}^{-1}$ ); —•—, nerve agent sarin in room with all surfaces of unpainted concrete ( $A/V = 2 \text{ m}^{-1}$ ).



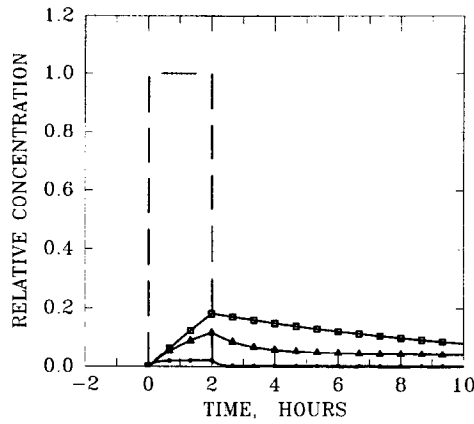


Fig. 5. Same as Fig. 4 but the air exchange  $k$  is  $0.1 \text{ h}^{-1}$ .

interpretation is supported by one trial with acryl and alkyd paints (Table 1) in which no deposition was observed.

#### 4. Indoor concentration and exposure

Numerical solutions of Eqs. (1)–(3) with  $a$  and  $b$  from Table 1 are shown in Fig. 4 for the nerve agent sarin in an ordinary room with the air exchange  $k$  equal to  $1 \text{ h}^{-1}$ ,

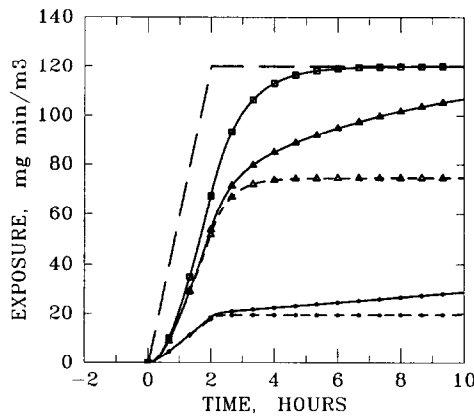


Fig. 6. Calculated exposure  $\int_0^T c dt$  for an inert gas (no desorption), and for the nerve agent sarin for the same case as shown in Fig. 4. The air exchange  $k$  is  $1.0 \text{ h}^{-1}$ ,  $f_o$  and  $V_{ei}$  are zero. The outdoor concentration  $c_o = 1.0 \text{ mg m}^{-3}$  during the time period 0–2 h. Otherwise  $c_o$  is zero. — — —, outdoor; —□—, inert gas indoor; —△—, nerve agent sarin in a room with plastic coated wallpaper ( $A/V = 1 \text{ m}^{-1}$ ), ceiling of acrylate paint and plastic carpet ( $A/V = 1 \text{ m}^{-1}$ ); --△--, gas with  $a$  equal to that of nerve agent sarin but  $b = 0$  (no desorption) in a room with plastic coated wallpaper, ceiling of acrylate paint and plastic carpet; —•—, nerve agent sarin in a room with all surfaces of unpainted concrete ( $A/V = 2 \text{ m}^{-1}$ ), --••--, gas with  $a$  equal to that of nerve agent sarin but  $b = 0$  (no desorption) in a room with all surfaces of unpainted concrete.

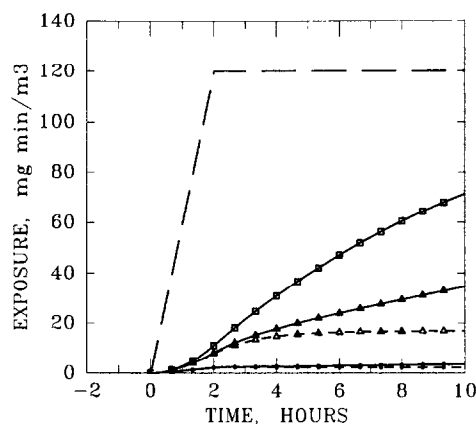


Fig. 7. Calculated exposure  $\int_0^\tau c dt$  for an inert gas (no desorption), and for the nerve agent sarin for the same case as shown in Fig. 5. Legends and conditions as in Fig. 6 but the air exchange  $k$  is  $0.1 \text{ h}^{-1}$ .

and in Fig. 5 for a sealed room with the air exchange  $k$  equal to  $0.1 \text{ h}^{-1}$ . Solutions for an inert gas ( $a$  and  $b = 0$ ) are also shown for comparison. The figures show that high  $a$  and low  $b$  result in a low sarin concentration, especially under conditions of low ventilation. The figures also show that, because of desorption, there is a low residual sarin concentration even after a long time.

The human health effects of breathing a given toxic gas depend on its concentration and the exposure time. The exposure  $\int_0^\tau c dt$ , where  $\tau$  is the exposure time, is often used to quantify toxic effects. The exposures for the cases shown in Figs. 4 and 5 are presented in Figs. 6 and 7. Because of gas desorption, the indoor exposure will increase slowly with time, and will eventually reach the outdoor value. In Figs. 6 and 7 the exposure of a gas with no desorption ( $b = 0$ ), but with the same transfer velocity  $a$  as the nerve agent sarin, is also shown. In contrast to a desorbing gas, the exposure of the non-desorbing gas reaches a maximum value which is less than that of the outdoor exposure. Thus the effect of desorption is to give an indoor exposure approaching the outdoor exposure. However, for low values of  $b$  this approach is very slow. Reduced ventilation also contributes to a slow increase of the indoor exposure.

## 5. Discussion

According to the Langmuir theory [13], the assumption in Eq. (3) that  $c_j^*$  is proportional to  $m_j$  holds only for low vapour pressures, and the desorption experiments of Huber [17] show that Eq. (3) does not hold for both low and high exposures of the nerve agent sarin. Thus the adsorption isotherm is not a linear function of vapour pressure. Neither did the full form of the Langmuir theory [13] satisfactorily explain the experiments by Huber and, despite higher desorption,  $m_j$  seems not to approach the upper limiting value  $1/b_j d_j$  postulated by the Langmuir theory. Similar shortcomings of

the Langmuir theory are also reported by Daniels and Albert [13]. The method of using two values of  $b_j$  (Fig. 3) is not a satisfactory solution, because the Langmuir theory means that  $b_j$  is a constant. Thus other theories which can explain the behaviour of the gas at both low and high exposure should be sought, e.g. the theories of micropores [20]. Additional deposition experiments at the higher gas concentrations that can be expected near sources of release are also needed. The equilibrium parameter  $b_j$  in Eq. (3) is expected to increase with temperature in a way similar to the vapour pressure of a liquid, and the heats of adsorption and desorption may be determined by using the Clausius–Clapeyron equation [13,22].

Possible diffusion into porous materials of walls, floors and ceilings, which may give a substantially larger total adsorbing surface, is not included in Eqs. (1)–(3). In some of the experiments [16] the concentration decreased continuously but at reduced rate, which may be an indication of diffusion into the material, chemisorption or destruction of the gas at the surface. Diffusion into the material could be treated in a similar manner to the treatment of outdoor dry deposition of gas into porous snow by Bales et al. [18] and by Karlsson [19]. Alternatively, diffusion into porous materials could be treated by using different transfer velocities  $a$  to and from the surface, or in a way similar to the treatment of adsorption in micropores of filters [20]. For reactive gases some chemisorption at the surface is expected, which may be the reason for the relatively low values of  $b$  for  $\text{Cl}_2$  and  $\text{NH}_3$ . The standard deviations of  $a$  and  $b$  in Table 1 are relatively large, which may be an indication of processes excluded from the model.

Experiments with the nerve agent sarin [10,16] could not be performed at high air humidity because the glass surfaces of the test box were adversely affected, possibly from decomposition of sarin on the surface. As high humidity may increase the deposition of gases which are soluble in water, or cause destruction of the gas, there is a need to improve the present experimental methods in this respect.

The effect of desorption is to cause a residual indoor toxic gas concentration over an extended time, causing the indoor exposure to approach the outdoor exposure. However, this approach is slow for low values of the parameter  $b$  and/or low ventilation. Thus the protective effect of deposition is reduced to some extent by desorption processes, but it is not eliminated. In particular, the protective effect of deposition is not lost for gases for which the concentration must exceed a threshold value in order to cause injury, or if  $\int c^n dt$  determines the effects and  $n > 1$  [21]. Increased ventilation when the gas cloud has passed outdoors will also reduce the adverse effects of desorption.

Table 1 indicates that there is no deposition of the nerve agent sarin on alkyd or acrylate paints or on plastic carpet. However, only one trial is available, and thus more experiments are needed to study deposition/desorption to and from painted surfaces. The experiments by Huber [17] on a painted surface also point to low deposition. One reason for this effect may be the low porosity of the paint and the flat plastic carpet.

The largest transfer velocity  $a$  according to Table 1 is  $7.2 \times 10^{-4} \text{ m s}^{-1}$  (sarin on unpainted concrete), which is near the theoretically estimated maximum transfer velocity ( $\approx 7 \times 10^{-4} \text{ m s}^{-1}$ ) which can be caused by turbulent and molecular transfer in rooms containing people or heat sources [8,5]. Thus all the values in Table 1 can be applied to such conditions. However, the assumption of well mixed conditions in a room may not be perfectly satisfied for  $a$  equal to  $7.2 \times 10^{-4} \text{ m s}^{-1}$ . In rooms with low turbulence

(e.g. no people or no heat sources) the maximum transfer velocity should be limited to  $\approx 4 \times 10^{-4} \text{ m s}^{-1}$  [8].

Nerve agents adsorbed onto indoor surfaces may be a contact risk. Thus repeated or prolonged contact between unprotected skin and the contaminated surfaces should be avoided.

## 6. Conclusions

An extension of the model of Karlsson [8] is used to study the influence of desorption processes on the indoor concentration of toxic gases. Deposition and desorption at the surface are based on a simplification of the Langmuir theory [13]. The adaptation of the model parameters from available data seems to work well at low to moderate exposure. However, when the deposited amount of agent increases, the slope of the adsorption isotherm defining the relationship between the equilibrium concentration  $c_j^*$  and the deposited amount  $m_j$  seems also to increase and the model does not work well. The model shows that desorption causes a residual indoor toxic gas concentration during an extended time. In contrast to a non-desorbing gas, the indoor exposure  $\int_0^T c_i dt$  will therefore approach the outdoor exposure. However, for low values of the equilibrium parameter  $b$  this approach is very slow. Reduced ventilation also attenuates the increase of the indoor exposure, and counteracts the amount deposited on indoor surfaces reaching the unfavourable range of the adsorption isotherm, where faster desorption can occur.

Calculated model parameters from available experiments show large variations for different gases and materials (Table 1). The nerve agent sarin has a large transfer velocity  $a$  and a low equilibrium parameter  $b$  for unpainted concrete, showing that rooms of that material give the best protection against sarin. The deposition of sarin onto glass is low and the desorption from glass is high. Sarin seems not to deposit on alkyd or acrylate paint or on plastic carpet. However, as only a few experimental trials are available for those materials, more experiments with painted surfaces are needed.

## Acknowledgements

We are grateful to Dr Stellan Winter and Dr Sven-Erik Gryning for critical review of the manuscript, to Mr. Tage Berglund, Mr. Hans-Åke Lakso and Mrs. Margaretha Lundquist for supplying experimental data, and to Dr. Marius van Zelm for supplying results from deposition experiments at TNO.

## References

- [1] T.S. Glickman and A.M. Ujihara, *J. Hazard. Mater.*, 23 (1990) 57.
- [2] P.C. Davies and G. Purdy, *Toxic Gas Assessments—The Effect of being Indoors*, Health and Safety Executive, Major Hazards Assessment Unit, Merseyside, 1986.

- [3] D.J. Wilson, *Emerg. Preparedn. Dig.*, 14 (1987) 19.
- [4] F.H. Shair and K.L. Heitner, *Environ. Sci. Technol.*, 8 (1974) 444.
- [5] W.W. Nazaroff and G.R. Cass, *Environ. Sci. Technol.*, 20 (1986) 924.
- [6] D.v. Leeuwen, Protection against toxic substances by remaining indoors, in *Methods for the determination of possible damage to people and objects resulting from releases of hazardous materials*, Directorate-GE, Voorburg, 1989 (CPR; 16E), Chapter 6.
- [7] H.C. van der Weide, Voortzetting onderzoek van de penetratie van gaswolken in huizen en de bescherming van personen in huizen (C-opdracht), PLM 1978-38, Prins Maurits Laboratorium, TNO, The Netherlands, 1978.
- [8] E. Karlsson, *J. Hazard. Mater.*, 38 (1994) 313.
- [9] T. Miyazaki, Adsorption characteristics of NO<sub>x</sub> by several kinds of interior materials, in T. Berglund, Lindvall and Sundell (Eds.), *Indoor Air*, Vol. 4, Chemical Characterization and Personal Exposure, Swedish Council for Building Research, Stockholm, 1984, pp. 103–110.
- [10] T. Berglund, Comparative results from deposition trials with sarin in a box, presented at Scientific Conference on Chemical Defense Research at U.S. Army ERDEC, 1993.
- [11] P. Binggeli, Shelter entry and exit procedures: Measurements with a simulation agent, *Proceedings of the Fourth International Symposium on Protection against Chemical Warfare Agents*, National Defence Research Establishment, Department of NBC Defence, Sweden, 1992, p. 97.
- [12] T.W. Horst and W.G.N. Slinn, *Atmos. Environ.*, 18 (1984) 1339.
- [13] F. Daniels and R.A. Albery, *Physical Chemistry*, 3rd edn., John Wiley & Sons, New York and London, 1966, pp. 287–289.
- [14] E. Karlsson, T. Berglund and L. Rittfeldt, Leakage of vapor clouds into ordinary buildings and sealed rooms, and their protective capacity, in K. Nieminen and E. Pääkkönen (Eds.), *Chemical Protection '92*, Symposium Proceedings. Research Center of the Defence Forces, Lakiala, Finland, 1992.
- [15] E. Karlsson, T. Berglund and L. Rittfeldt, On the protective capacity of sealed rooms against vapour clouds, *Proc. 4th Int. Symp. Protection Against Chemical Warfare Agents*, Stockholm, 8–12 June 1992, National Defence Research Establishment, Department of NBC Defence, S-901 82 Umeå, 1992, p. 152.
- [16] T. Berglund, E. Karlsson, H.-Å. Lakso, M. Lundqvist and M. Nordstrand, Deposition av gas på olika material i glasbox. FOA ArbetsPM D 40323-4.6, 1994.
- [17] U. Huber, Versuche über Ad- und Desorption von Sarin an Betonoberflächen, Internal Report, AC-Laboratorium Spiez, Switzerland, 1993.
- [18] R.C. Bales, M.P. Valdez and G.A. Dawson, *J. Geophys. Res.*, 92 (1987) 9789.
- [19] E. Karlsson, Theoretical model for dry deposition of nerve agents to snow and water surfaces, presented at Scientific Conference on Chemical Defense Research, U.S. Army Edgewood Research, Development and Engineering Center, 16–19 Nov 1993.
- [20] M.M. Dubinin, *Prog. Surf. Membr. Sci.*, 9 (1975) 1.
- [21] P.G. de Weger and J. Reuzel Damage caused by acute intoxication, in *Methods for the Determination of Possible Damage to People and Objects Resulting from Releases of Hazardous Materials*, Directorate-GE, Voorburg, 1989, (CPR; 16E), Chapter 5.
- [22] P.W. Atkins, *Physical Chemistry*, 4th edn., Oxford University Press, Oxford, 1990, pp. 884–894.