Design Rules for Chemostrictive Materials as Selective Molecular Barriers

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As materials become more advanced, there are opportunities to incorporate multiple engineering functions into them, including chemical sensing coupled to actuation for the control of permeability. Recent interest in chemically responsive materials motivates the question of how to design and optimize such systems to address a specific molecular target. This work formulates an engineering analysis of “chemostrictive materials” that respond to a chemical stimulus by reducing their permeability through constriction of their void volume. The extent to which the material can constrict to reduce chemical diffusivity and the sensitivity of the material to constrict in the presence of a target chemical are explored as parameters which affect the barrier properties of the materials. Further examined are materials that are augmented to also degrade the chemical target by an assumed first-order decomposition reaction in addition. As a case study, the minimum material specifications for chemostrictive personal protective equipment (PPE) designed to reduce exposure to a variety of chemical hazards are presented. Chemostrictive materials possess potential as ideal components for advanced PPE that is highly permeable under safe conditions to allow for comfort and temperature regulation but constricts in the presence of contaminants to protect the wearer.

1. Introduction

A material that is incapable of responding chemically or mechan-ically to its environment must be engineered to meet performance specifications under worst-case scenario conditions, often sacrificing performance at other conditions. Materials capable of responding to their environment may achieve optimal performance under a much wider set of conditions, such as thermally responsive building insulation to increase energy efficiency,[1] responsive food packaging to increase quality and shelf-life,[2] and water purification and filtration systems used to obtain enhanced control of contaminant removal.[3] To further the design and adoption of reversibly chemically responsive systems, we introduce the concept of a chemically responsive material, where exposure to a particular chemical or biological agent induces constriction—a process referred to as chemostriction.

This chemostriction would impede chemical diffusivity through the material and reduce or eliminate flux of the target species. We envision using chemostrictive materials as adaptive molecular barriers to limit or eliminate the permeation of select chemical contaminants. Such a material would be characterized, in its most simple form, by its ability to sense contaminant presence and subsequently constrict and reduce chemical permeability.

Current constricting and actuating material systems are broad in scope and function. Electroactive polymers capable of shape, size, and configurational actuation when stimulated by an electrical field[4] or their electrochemical[5] and biological environments,[6] thermally responsive fibers and yarns which transition between tight and loose states,[7,8] photoresponsive fibers which configure and bend toward a light source,[9] and magnetically responsive soft materials[10] are four such examples. Further, material systems capable of direct chemical sensing such as organic polymer-based chemiresistive gas sensors,[11] inorganic metal oxide-based chemical sensors,[12] and a host of 2D material-based gas sensors,[13] as well as other nanomaterial-based sensors including carbon nanotubes,[14] nanowires,[15] and quantum dots[16] have all been reported.

A direct coupling of chemical sensing with actuation and/or con-traction has been shown in hydrogels that selectively gel, reversibly constrict, and change shape in the presence of specific biological components,[17,18] as well as polymers that swell[19] or collapse[20] to block pores in membrane materials to reduce permeability. More generally, systems which are driven by electrical stimuli to change permeability may be coupled with a chemiresistive sensor to provide chemically responsive constricted. Porous polymer membranes which are able to expand and contract to control permeability,[21] as well as those that allow selective opening and closing of nanochannels,[22] are two such systems that when combined with a given chemiresistive sensor would yield chemostrictive systems.

In this work we present a framework based on the diffusive transport of a contaminant to analyze the performance of any chemostrictive material. We numerically evaluate chemostrictive materials characterized by the extent the material can constrict and reduce chemical diffusivity and the sensitivity of the material to constrict in the presence of a given chemical, an example schematic of which is shown in Figure 1. We analyze the steady-state and time-dependent response of a chemostrictive material...
barrier upon exposure and removal of a contaminant. Further, we explore the effects of incorporating catalytic degradation of a contaminant species within the material. Finally, we present a case study for the use of chemostrictive materials as personal protective equipment (PPE) to protect against various chemical hazards including the organophosphorus nerve agent VX.\[23\]

2. Problem Statement

Fickian diffusion represents an idealization of diffusive transport of a chemical within a medium. Incorporation of selective adsorption, reaction, or interaction between a chemical and the medium through which it is diffusing introduces concentration-dependent molecular transport within the medium. Well summarized by Crank,\[24\] the study of concentration-dependent diffusion goes back over a century\[25\] and covers both augmented (e.g., the enhanced diffusion of a solvent through a polymer\[26\]) and diminished (e.g., the impeded diffusion of ionic species through a medium to which they can adsorb\[25\]) diffusion due to increased concentration of the diffusing species.

Here we examine the concentration-dependent diffusive transport of a contaminant species through a generic material of thickness \(\delta\), as shown in Figure 2. The material represents a protective layer separating the contaminant on the exposed outer side \((x = 0)\) at a concentration \(C_0\) with the unexposed inner side \((x = \delta)\) where contaminant concentration is approximated as zero. We model contaminant diffusion within the material as governed by a concentration-dependent diffusivity, where this diffusivity ranges from some maximum value, \(D_{\text{max}}\) in the limit of no contaminant and some minimum value \(D_{\text{min}}\) at or above some saturating concentration. The transition between these two limits is proportional to the fraction of occupied adsorption sites \(\theta\) such that local diffusivity.

\[
D(C) = \theta D_{\text{min}} + (1 - \theta) D_{\text{max}}
\]  

Figure 2. Model system for chemostrictive material modeling. Contaminant diffuses through a chemostrictive textile with a diffusivity governed by its local concentration within the textile. For a nonchemostrictive textile, a general steady-state concentration profile is shown in blue.

We approximate \(\theta\) with a Langmuir isotherm, where for some given number of adsorption sites the fraction occupied is taken as

\[
\theta = \frac{KC}{1 + KC}
\]  

(2)

where \(K\) is an association constant describing the contaminant’s ability to adsorb to the material. We treat the adsorptive capacity of the material as negligibly small compared with the concentration of contaminant and do not account for any changes in concentration due to this adsorption. Note that a number of concentration-dependent diffusivities based on well-established adsorption isotherms could be incorporated.\[25\] Regardless of the physical or chemical mechanism by which the material recognizes a contaminant and subsequently constricts, our use of a Langmuir isotherm introduces behavior we envision to be

Figure 1. Schematic of an example chemostrictive material. The presence of contaminants induces a reversible constriction of the material, reducing its molecular permeability.
inherent to chemostrictive materials, namely, saturation in contaminant recognition and the resulting constriction.

The time-dependent governing equation for contaminant transport within the material is then

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[ D(C) \frac{\partial C}{\partial x} \right] - \frac{\partial}{\partial x} \left[ D_{\text{max}} + D_{\text{min}} KC \frac{\partial C}{\partial x} \right]$$

This equation can be written in a dimensionless form.

$$\frac{\partial \tilde{C}}{\partial \tilde{t}} = \frac{\partial}{\partial \tilde{x}} \left[ \tilde{D}(\tilde{C}) \frac{\partial \tilde{C}}{\partial \tilde{x}} \right] - \frac{\partial}{\partial \tilde{x}} \left[ \tilde{D}_{\text{max}} + \tilde{D}_{\text{min}} \frac{\partial \tilde{C}}{\partial \tilde{x}} \right]$$

with parameters

$$\gamma = \frac{C}{C_0}$$
$$\varepsilon = \frac{x}{\delta}$$
$$\tau = \frac{D_{\text{max}} t}{\delta^2}$$
$$\alpha = \frac{D_{\text{min}}}{D_{\text{max}}}$$
$$\beta = \frac{1}{KC_0}$$

corresponding to a dimensionless concentration, spatial variable, time, diffusivity, and dissociation constant, respectively. For the time-dependent problem, we begin with a completely uncontaminated system and impose a constant external contaminant concentration—the corresponding nondimensional boundary conditions are: $$\gamma(\varepsilon, \tau = 0) = 0, \gamma(\varepsilon = 0, \tau) = 1, \gamma(\varepsilon = 1, \tau) = 0$$, as shown in Figure 2.

3. Results and Discussion

3.1. Steady-State Behavior of Chemostrictive Material

The performance of a chemostrictive material acting as a molecular barrier is characterized by the diffusive flux of the contaminant through the material. To begin, we analyze the steady-state concentration profile within the material—achieved in the limit of a long exposure time. For the system described in Figure 2, a nonconstricting material ($D_{\text{min}} = D_{\text{max}}$) has the following diffusive flux $J$.

$$J = -D_{\text{max}} \frac{C_0}{\delta}$$

For a constricting material

$$J = -D_{\text{max}} \frac{\partial C}{\partial x(x=0)} = -D(C_0) \frac{\partial C}{\partial x(x=0)}$$

An analytical solution exists for the steady-state concentration gradient on the inside edge.

$$\frac{\partial \tilde{C}}{\partial \tilde{x}(x=\tilde{d})} = -\left[ \frac{D_{\text{min}}}{D_{\text{max}}} + 1 \right] \frac{\partial \tilde{C}}{\partial \tilde{x}} - \frac{\partial}{\partial \tilde{x}} \left[ \frac{D_{\text{max}} + D_{\text{min}} KC \frac{\partial \tilde{C}}{\partial \tilde{x}}}{KC + 1} \right]$$

In dimensional form

$$\frac{\partial C}{\partial x(x=0)} = -\left[ \frac{D_{\text{min}}}{D_{\text{max}}} + 1 \right] \frac{\partial C}{\partial x} - \frac{\partial}{\partial x} \left[ \frac{D_{\text{max}} + D_{\text{min}} KC \frac{\partial C}{\partial x}}{KC + 1} \right]$$

Analogously in dimensionless form

$$\frac{\partial \tilde{C}}{\partial \tilde{t}(\varepsilon=0)} = \beta(1 - \alpha) \ln \left( \frac{\beta}{\beta + 1} \right) - \alpha$$

We refer to the value of this nondimensional concentration gradient as the “dimensionless flux” through the material. The value of Equation (13) is equivalent to the relative reduction in flux through the chemostrictive material (in the direction from $x = 0$ to $x = 1$) compared with a nonconstricting material with diffusivity $D_{\text{max}}$. To show this

$$J_{\text{chemostrictive}} = \frac{C_0}{\delta} \frac{\partial C}{\partial x(x=0)} = -\frac{\partial C}{\partial x(x=0)}$$

Bound between one and zero, the value of the steady-state dimensionless flux is shown for a range of $\alpha$ and $\beta$ values in Figure 3. Material performance increases with decreasing $\alpha$ and $\beta$. However, this performance is divided into two limiting regimes. When $\alpha > \beta$, the external concentration or the sensitivity of the material is so large that the material is effectively saturated, resulting in complete constriction throughout. No improvement in the material’s sensitivity ($K$) or the external concentration ($C_0$) has any effect on the material’s performance. In this limit, the material needs to be able to contract further to have any improved performance. The contaminant is at its minimum diffusivity throughout and the dimensionless flux approaches $\alpha$. In contrast, when $\beta \gg \alpha$, the contaminant exposure level, $C_0$, or the sensitivity, $K$, are by themselves or together so low that the material cannot completely constrict to reach an effective diffusivity of $D_{\text{min}}$. That is, the material is unable to constrict as far as possible due to the inability to sense or bind the contaminate. In this regime, material performance is independent of its minimum diffusivity $\alpha$ and the degree to which the material could potentially constrict.

3.2. Completely Constrictive Material

For a material which can reversibly transition between a permeable and a completely impermeable state ($\alpha \to 0$), performance at steady state is uniquely a function of sensitivity and external contaminant concentration. In this case, the steady-state dimensionless flux through the material is given as

$$\frac{\partial \tilde{C}}{\partial \tilde{t}(\varepsilon=1)} = \beta \ln \left( \frac{\beta + 1}{\beta} \right)$$

In dimensional form, this concentration gradient is

$$\frac{dC}{dx(\varepsilon=0)} = \frac{1}{\delta K} \ln(1 + KC_\alpha)$$

The dimensionless flux for a completely constrictive material is shown in Figure 4 over a range of sensitivity values, $K$, and contaminant concentrations, $C_\alpha$. 

3.3. Adding Reactive Degradation of the Contaminant

Some researchers have attempted to create molecular barriers by embedding catalysts that degrade the target molecule as it permeates through the material.\[27–31\] In this section, we consider the case where such catalysts are added to a chemostrictive material to enhance its overall function.

To model contaminant degradation within a chemostrictive material, we introduce a first-order homogeneous degradation rate with rate constant $k$. This is incorporated into the dimensional and nondimensional governing equations as

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[ \frac{D_{\text{max}} + D_{\text{min}}KC}{\delta + 1} \frac{\partial C}{\partial x} \right] - kC \tag{17}$$

$$\frac{\partial \gamma}{\partial \tau} = \frac{\partial}{\partial e} \left[ \frac{\beta + \alpha \gamma}{\beta + \gamma} \frac{\partial \gamma}{\partial e} \right] - \gamma Da \tag{18}$$

where $Da$ is the Damköhler number for the system.

$$Da = \frac{k \delta^2}{D_{\text{max}}} \tag{19}$$

which describes the ratio of reaction rate to the maximum rate of diffusive mass transfer. The steady-state dimensionless flux for a chemostrictive material where $\alpha = \beta$ that degrades contaminant at a rate defined by the Damköhler number is shown in Figure 5. Note that because of the homogeneous degradation, the flux through any cross section of the material is not constant. For these cases, the flux reported is that which exits the material on the edge which is not exposed to the contaminant ($x = \delta$, $e = 1$). All solutions for the system incorporating reactive degradation were found numerically with COMSOL Multiphysics 5.5.

Reactive degradation of a contaminant causes a nonlinear impact on the flux through the material (Figure 5B). For larger...
values of $\alpha$ and $\beta$ (when the dimensionless flux is larger), introducing reactive degradation has a larger net effect on lowering the flux (Figure 5C). However, as the material becomes intrinsically more constrictive (at lower $\alpha$ and $\beta$ values), improvements to reaction rate show increasing proportional effect, even for more modest reaction rates, due to the increased residence time of contaminants in the material (Figure 5D).

### 3.4. Dynamics of Chemostriiction

Beginning with an uncontaminated system, upon chemical exposure, the flux monotonically increases until it reaches its steady-state value (Figure 6A). As the value of the steady-state flux decreases, the time for the system to reach this flux increases (Figure 6A). This is intuitively explained by the inverse relationship between average contaminant diffusivity $D_{\text{ave}}$ and the time-scale of diffusion through the material $t_{\text{diff}}$.

\[
t_{\text{diff}} \sim \frac{\delta^2}{D_{\text{ave}}} \tag{20}
\]

Once the contaminant source is removed, the transition of the material from a constricted to an unconstricted state results in an asymmetric unloading of the contaminant from the material. A minority of the contaminant will inevitably diffuse through the

Figure 5. A) Steady-state concentration profile within chemosstrictive material with reactive degradation. Introducing component degradation within the chemosstrictive material reduces the diffusive flux through the material as well as lowers the total concentration of species within the material any given time. B) Steady-state dimensionless flux through a chemosstrictive material with reactive degradation. Incorporation of catalytic degradation of contaminant within a chemosstrictive material reduces total species flux. C) Net change in dimensionless flux with added reactive degradation. Materials show higher overall reduction of contaminant flux when $\alpha$ and $\beta$ are large. D) Relative change in dimensionless flux with added reactive degradation. Materials show higher relative reduction of contaminant flux when $\alpha$ and $\beta$ are small.
material—however this amount is parameter dependent and does not uniquely correlate to the steady-state flux of the system.

This asymmetric unloading of the material is shown in Figure 7 and is characterized by the following ratio.

\[
\phi_u = \frac{\int_{\tau_u}^{\infty} \frac{d\tau}{\gamma(\varepsilon=\tau)} \, d\tau}{\int_{\tau_u}^{\infty} \frac{d\tau}{\gamma(\varepsilon=0)} \, d\tau}
\]  

(21)

where \( \tau_u \) represents the time at which the contaminant is removed, and the boundary value on the outside of the material is taken to be \( \gamma(\varepsilon=0, \tau=\tau_u) = 0 \). The time-dependent flux of unloading in this case, as well as the aforementioned ratio, can serve as a key parameter to characterize chemostrictive materials. While monitoring, the steady-state flux provides the measure of overall performance, but it does not explicitly provide values for \( \alpha \) or \( \beta \). For example, when \( \alpha = \beta = 0.1 \), the steady-state dimensionless flux is nearly 0.32. The same flux is achieved in the situation where \( \alpha = 0.3 \) and \( \beta = 0.0055 \) or when \( \alpha = 0.001 \) and \( \beta = 0.16 \) (Table 1). However, each condition approaches steady-state operation at different rates, as shown in Figure 6. Further, incorporation of reactive degradation has the strongest effect when the material is limited in \( \alpha \) (i.e., \( \alpha \gg \beta \)) (Table 1).

### 3.5. Potential Characterization of a Chemostrictive Textile

Characterizing a textile as limited in \( \alpha \) or limited in \( \beta \) requires more than measuring the steady-state flux at a constant external contaminant concentration. By exposing the textile to an ever-increasing concentration of contaminant, the steady-state dimensionless flux will eventually reach a constant value as \( \alpha \gg \beta \) (Figure 7). In this regime, the performance of the textile approaches the value of \( \alpha \). Then, knowing the value of this first parameter, Equation (13) may be used to determine the value of \( \beta \) and \( K \) from the measurement of steady-state flux at any known external concentration.

To demonstrate this point, we take the three textiles with the given parameters in Table 1 with no reactive degradation.
Table 1. Summary of steady-state chemostrictive material performance for materials with the same steady-state flux but varying ability to constrict (\(\alpha\)), sensitivity to contaminate (\(\beta\)), and varying rates of reactive degradation (\(Da\)).

| \(\alpha\) | \(\beta\) | \(\phi_0\) | \(-\frac{\partial}{\partial \epsilon}(Da = 0)\) | \(-\frac{\partial}{\partial \epsilon}(Da = 1)\) | \(-\frac{\partial}{\partial \epsilon}(Da = 10)\) |
|-----------|-----------|------------|----------------|----------------|----------------|
| 0.3       | 5.5 \times 10^{-3} | 7.3 \times 10^{-2} | 0.32            | 0.21            | 3.0 \times 10^{-2} |
| 0.1       | 0.1       | 8.5 \times 10^{-2} | 0.32            | 0.23            | 5.9 \times 10^{-2} |
| 3.5 \times 10^{-3} | 0.16     | 10.3 \times 10^{-2} | 0.32            | 0.25            | 6.4 \times 10^{-2} |

(Da = 0). Assuming these values of \(\beta\) are for a given exposure of \(C_0 = 4.0 \times 10^{-5}\) mol L\(^{-1}\) (\(\approx\)1,000 ppm for a gas at ambient temperature and pressure) gives the following values of \(1/K\) for each of the three materials as 2.2 \times 10^{-7}, 4.0 \times 10^{-6}, and 6.4 \times 10^{-6} mol L\(^{-1}\) for the values of \(\beta\) equal to 0.0055, 0.1, and 0.16, respectively. Measuring performance at increasing concentration leads to the concentration-dependent results (Figure 7) and allows for unambiguous characterization of each material’s performance and unique parameters \(\alpha\) and \(K\).

4. Case Study: Engineering Chemostrictive PPE

One increasingly important set of materials that would gain from the incorporation of chemostrictive barriers is PPE. For those fighting infectious disease, remediating chemically or biologically contaminated areas, or responding to chemical weapons attacks, PPE is necessary for humans to combat biological, chemical, or nuclear hazards. However, the plastics, rubbers, or fibers used to produce protective equipment such as hazmat suits reduce dexterity and comfort when worn. Importantly, these suits are thermally insulating and do not allow the wearer to regulate body temperature through sweat for evaporative cooling.[32] The suit’s impermeability prevents water vapor from escaping in the same manner as contaminants are prevented from entering. As a result, overheating may begin as early as an hour into use, depending on activity level.[33–35] Heat stress can result in decreased mechanical and cognitive function and if no measures are taken may progress to fatal heat stroke.[36] To combat this overheating, time of use may be limited, or periodic breaks from activity may be necessary.[37]

An optimal solution would be the use of a chemostrictive material that would actuate to protect the wearer from contaminant species in the environment but only when required. Such a system would need to be physically robust enough to wear and provide adequate protection to an array of chemical and biological contaminants. Here, we walk through the design of a chemostrictive material, based on a given contaminant level and time of exposure. Specifically, we carry out the calculations necessary to determine the performance necessary to design PPE to protect against exposure to the organophosphorus nerve agent VX.[23]

We assume a constant textile thickness, \(\delta\), of 1 mm and a total textile surface area of 2 m\(^2\) (an estimate for the surface area of an average adult)[38]. For an exposure time of 1 h, we find the reduction in flux necessary across the chemostrictive textile to stay below a dose equal to the dermal LD50 of VX. This limit is taken as 11.2 mg, from an LD50 of 0.14 mg of VX per kg of body weight,[23] assuming a body weight of 80 kg. We take an exposure level, \(C_0\), equal to a VX-saturated atmosphere at 25 °C, which gives a VX concentration in the gas phase of 10.5 mg m\(^{-3}\) (0.0393 mol m\(^{-3}\)).[23] For this exposure level and length, the critical steady-state flux of VX through the chemostrictive textile to fall below the specified threshold must fall below 1.56 \times 10^{-3} mg m\(^{-2}\) s\(^{-1}\), calculated as follows.

\[
J_{\text{crit}} = \frac{11.2 \text{ mg}}{(2 \text{ m}^2)(3600 \text{ s})} = 1.56 \times 10^{-3} \text{ mg m}^{-2} \text{ s}^{-1}
\]  
(22)

To determine the degree to which the chemostrictive material will need to restrict VX transport, we must first calculate what the flux would be through an unconstricted textile. This flux of VX through an unconstricted textile requires the aforementioned physical parameters for the textile, as well as some species diffusivity within the textile. This diffusivity, \(D_{\text{max}}\), is approximated as a characteristic value of vapor diffusivity in air, 10^{-5} m\(^2\) s\(^{-1}\) (0.1 cm\(^2\) s\(^{-1}\)). The steady-state flux \(J_{\text{unstrict}}\) of VX through an unconstricted textile would then be

\[
J_{\text{unstrict}} = \frac{(10.5 \text{ mg m}^{-3})(10^{-5} \text{ m}^2 \text{ s}^{-1})}{(10^{-3} \text{ m})} = 0.105 \text{ mg m}^{-2} \text{ s}^{-1}
\]

(23)

Using Equation (14), we find

\[
-\frac{\partial}{\partial \epsilon}(\epsilon = 1) = J_{\text{unstrict}} = \frac{1.56 \times 10^{-3} \text{ mg m}^{-2} \text{ s}^{-1}}{0.105 \text{ mg m}^{-2} \text{ s}^{-1}} = 1.49 \times 10^{-2}
\]

(24)

Having calculated the flux reduction necessary to protect the user from VX for an exposure time of 1 h, the minimum requirements for \(\alpha\) and \(\beta\) can be derived from a steady-state approximation. Knowing both \(C_0\) and \(D_{\text{max}}\), the required minimum diffusivity \(D_{\text{min}}\) and association constant \(K\) can be found easily: \(K = \frac{\beta}{\alpha D_{\text{max}}}\) and \(D_{\text{min}} = \alpha D_{\text{max}}\).

The necessary flux reduction to 1.56 \times 10^{-3} mg m\(^{-2}\) s\(^{-1}\) can be achieved by reducing \(D_{\text{min}}\) to below 10^{-7} m\(^2\) s\(^{-1}\) (\(\alpha = 0.01\)) at association constant \(K\) values of 0.1 \mu m (\(\beta = 0.025\)) or lower (Figure 8A). For reference, the necessary \(D_{\text{min}}\) value is on the order of liquid–liquid diffusion, and the binding constant is two orders of magnitude weaker than what is achieved by many modern small-molecule drugs at 1 nM.[19]

These constrained values of diffusivity and sensitivity are relaxed by incorporating contaminant degradation into the textile. We can use the dimensional model to examine the required reaction rate \(k\) needed to relax constraints on \(D_{\text{min}}\) and \(K\). For simplicity, we again use the case where \(\alpha = \beta\) (Figure 5B). To achieve the necessary flux reduction for VX with
The rate of the first-order reaction must reach nearly 0.5 s⁻¹, nearly two orders of magnitude larger than what has been achieved experimentally in metal-organic framework (MOF) systems,[40] which have achieved degradation rates on the order of 0.01 s⁻¹. In general, for the range of diffusivities shown in Figure 5B, k must exceed roughly 0.1 s⁻¹ before the rate of decomposition of the chemical agent meaningfully contributes to textile efficacy. These results are for the same exposure and geometric values as presented in subfigure (A). Material performance where the parameter \( \alpha = \beta \) is presented to represent a chemosensitive material which is neither strongly limited by its ability to constrict or its sensitivity to and concentration of the external contaminant.

Table 2. Necessary flux reduction for protection against chemical hazards. Exposure length is taken as 1 h, material thickness is set at 1 mm, and the required flux reduction is that necessary to prevent the permeation of an amount of chemical hazard equal to LD50, as specified for a person of body weight 80 kg.

| Chemical          | VX[23] | Tabun[23] | Sarin[23] | Methylene chloride | Hydrogen cyanide | Ammonia | Sulfur mustard |
|-------------------|--------|-----------|-----------|--------------------|------------------|---------|---------------|
| Dermal LD50       | 0.14   | 14        | 24        | >2,000[41]         | 100[42]          | 200[43] | 20[44,45]     |
| Exposure level[4] | 10.5   | 610       | 22,000    | 170,000[46]        | 500[47]          | 2,100[48]| 940[49]       |
| Dimensionless flux reduction | 1.48 × 10⁻² | 2.54 × 10⁻² | 1.21 × 10⁻¹ | 1.30 × 10⁻² | 0.22 | 7.40 × 10⁻² | 2.36 × 10⁻³ |
| Critical flux     | 1.56 × 10⁻¹ | 0.15      | 0.26      | 22.1               | 1.1               | 1.55    | 2.22 × 10⁻²   |

Exposure is taken as the concentration of the chemical agent at its saturated vapor pressure at 25 °C for the high-boiling agents Tabun, Sarin, VX, and sulfur mustard and ten times the concentration deemed Immediately Dangerous to Life or Health for the highly volatile or gaseous chemicals dichloromethane, hydrogen cyanide, and ammonia.

Dermal LD50 as reported for a dog, in agreement with a dermal lethal dose of 4–5 g as reported by the World Health Organization.

5. Conclusion

We have presented the concept for chemically actuated material systems deemed a chemosensitive material. Such a material would be able to reversibly transition between a permeable and impermeable state, where this change is actuated by the presence of a specific chemical entity. Upon constriction, transport of the chemical through the material is reduced or excluded. In the absence of chemical exposure, the material returns to its unconstricted state, allowing unimpeded transport throughout. We find that the performance of any such material system to serve as a barrier for molecular transport is reliant on two parameters, defined as the maximum reduction in diffusivity achieved...
upon constriction and the sensitivity of the material to constrict in the presence of contaminant. We have modeled the performance of the material, including the dynamics of constriction and unconstric ting, as well as textile performance incorporating reactive degradation of contaminant. We have determined the necessary performance of chemorestrictive material-based PPE for a range of chemical hazards. Overall, the present model can guide the development of chemorestrictive molecular barriers, including for use as responsive PPE.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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