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# A hybrid catalytic membrane reactor for destruction of a chemical warfare simulant

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## ABSTRACT

The possibility of use of chemical weapons has increased in recent years, both as a result of potential terrorist attacks as well as of ongoing international conflicts. The successful application of a flow-through catalytic membrane reactor (FTCMR) as an individual protection system for the destruction of dimethyl methylphosphonate (DMMP), which is known as a chemical precursor (and used to simulate its characteristics) for Sarin (GB), a toxic chemical warfare agent (CWA) was previously investigated and reported by this group. As part of the study, the effect of the DMMP concentration in the feed on its complete combustion in the FTCMR was investigated. The studies indicate that the protection (complete conversion) time is a function of the DMMP concentration, with longer times observed for the lower concentrations, and shorter protection times associated with the higher concentrations. In this study a novel hybrid system is being developed that combines the FTCMR with a surface-flow membrane system (SFMS). Preliminary experimental results presented here manifest the main advantage of this hybrid system, combining the SFMS, capable of the physical removal of a large fraction of the CWA from contaminated air streams, and the FTCMR which completely oxidizes the remaining amount, which is the continuous CWA destruction for extended time periods which are appropriate for both individual and collective protection applications. The study investigates the impact on performance of the membrane characteristics, the transmembrane pressure gradient and the sweep ratio. Hybrid system performance is also compared with that of a sole FTCMR showing the superiority of the hybrid system in terms of offering higher destruction rates for DMMP and prolonged protection times.

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## 1. Introduction

Due to increased concerns regarding the risk of terrorist attacks involving the use of chemical warfare agents (CWAs), development of more efficient individual protection and collective protection systems has gained ample attention in recent years. The current technology for CWA removal is based on the use of adsorption with activated carbon (AC) beds. There are a number of technical challenges associated with the use of adsorption for CWA removal, however. They include (i) the fact that the removal of CWA on the AC adsorbents is via physisorption that is highly concentration-dependent, and desorption can occur during operation in the presence of concentration spikes or the presence of other volatile organic compounds (VOCs) in the air stream; (ii) the operation is discontinuous

with spent-bed disposal required because the CWAs are not destroyed but get accumulated in the bed; and (iii) the spent adsorbent bed is hazardous to handle after use, with exposure to high CWA concentrations being a very real likelihood during disposal. As a result, the use of membranes is attracting attention for this application.

Both conventional [1] and reactive [2,3] membrane-based separation systems have been investigated. The former make use of polymeric or mixed-matrix membranes which are tailor-made to be selective and to block the toxic CWA from going through while allowing the air and water vapor to permeate through the membrane. Membrane-based reactive separations, recently introduced by this group [2,3], on the other hand, make use of reactive inorganic membranes. Operating as flow-through catalytic membrane reactors (FTCMR), these systems have the ability to completely oxidize the toxic CWA. In a recent study on the use of such FTCMR, Motamedhashemi et al. [2] utilized a single asymmetric mesoporous alumina membrane to investigate the destruction of dimethyl methylphosphonate (DMMP), a nerve

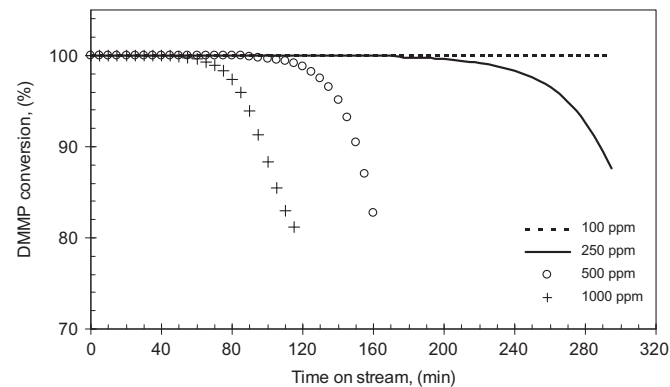
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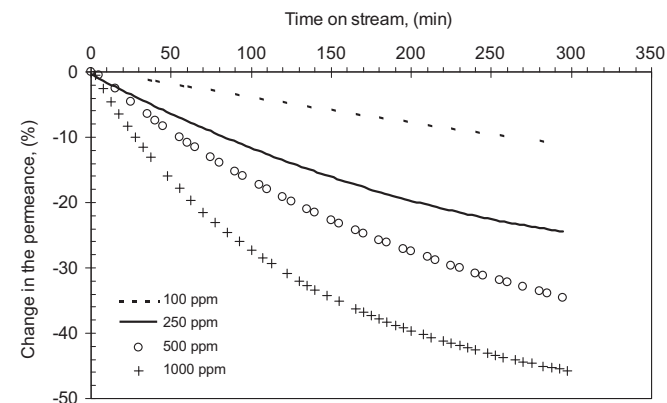
agent simulant, in air. The experimental results were quite promising indicating that complete DMMP conversion could be obtained with this reactive separation system. An experimentally validated model for the FTCMR was also developed [2,3], which was utilized to compare its performance, on an equitable basis, with other competitive reactor configurations (e.g., monolith reactors). A multi-tubular FTCMR is currently under development [4] and is slated for field-testing in the near future.

One of the key advantages of the use of FTCMR for DMMP destruction over other reactive systems is that the membrane completely traps the phosphorus-containing mineral acid by-products of catalytic oxidation, thus not allowing them to permeate through the device and to act as potential breathing irritants. As advantageous as this may be, there is a downside to it as well in that phosphorus accumulation eventually results in coating of the active sites resulting in diminished reactivity; more importantly, such deposits tend also to block the membrane pore structure thus decreasing its permeance and correspondingly the device's air throughput. As expected, experimental conditions leading to higher CWA destruction rates (mol/h), for example, higher CWA challenge concentrations also result in higher mineral acid deposition rates, and thus in a more significant impact on FTCMR activity and membrane throughput.

Such conclusions have been verified both experimentally and theoretically [2,3]. Figs. 1 and 2, for example, show the performance of a FTCMR simulated using the aforementioned experimentally-validated model [2,3] that accounts for a decrease in reactivity via active site coverage and decline in membrane throughput via pore blockage as a result of by-product deposition. The FTCMR in Figs. 1 and



**Fig. 1.** Effect of the DMMP feed concentration on the protection time, as predicted by the mathematical model [3] for a FTCMR (500 Å membrane, temperature = 573 K, shell-side to tube-side pressure ratio = 0.85).



**Fig. 2.** Effect of the DMMP feed concentration on the permeance, as predicted by the mathematical model [3] for a FTCMR (500 Å membrane, temperature = 573 K, shell-side to tube-side pressure ratio = 0.85).

2 contains a single, dual-layer tubular alumina membrane with a top layer with an average pore size  $\sim 500$  Å lying on the top of a macroporous alumina membrane support. Fig. 1 shows the conversion in the FTCMR when treating four different DMMP-air mixtures with feed concentrations of 100, 250, 500, and 1000 ppm<sub>v</sub>, respectively (further details about the model are discussed elsewhere [2,3]). The simulation results shown in Fig. 1, confirmed also by experimental observations [2,3], indicate that the protection time provided by the FTCMR is a function of the DMMP concentration in the feed. In addition, the correlation between protection time and the feed concentration is not linear. Fig. 2 shows the simulation results for the fractional change in the membrane permeance with respect to the time on stream; clearly, the rate of membrane permeance decline due to pore blockage by phosphorous-containing deposits is also a function of DMMP concentration in the feed-stream, with the lower decrease of the permeance corresponding to the lower feed concentrations.

Methods for removing the phosphorous-containing deposits and for recovering the properties of the membranes used in the FTCMR were investigated by this team, and further details are discussed elsewhere [3]. The most effective method involves washing the membranes after use with a dilute acid solution. The key challenge with this technique, as effective as it may be for recovery of the activity and the permeance of the membrane, is that the FTCMR module needs to be put "off-line" for the wash step. This may be feasible for collective protection operations, whereby one may be able to operate similarly to a pressure-swing adsorption (PSA) system for which some parts are being regenerated while others are in operation. For individual protection applications, however, the recovery step is likely to be a cumbersome task for the user, and definitely entails the risk of damaging the membrane and the FTCMR itself.

These experimental and modeling observations point out the fact that a more appropriate role for the FTCMR to play may be as a second stage in a dual-stage (hybrid) system, following a bulk-toxin removal unit serving as the first stage. Therefore, in this study a new concept is investigated which aims to prolong the effective catalytic membrane life during FTCMR operation. It involves the use of such a hybrid system, which combines a physical separation step, which removes the bulk of DMMP via the use of a surface-flow membrane system (SFMS), followed by the FTCMR as a second-stage and serving, potentially, as a polishing step. The main advantage of the proposed hybrid system is that it completely destructs the CWA amount that remains in the feed, after it passes through the SFMS, with a lower rate of pore blockage and catalytic activity decline, thus resulting in the continuous CWA destruction for extended time periods, which are appropriate for both individual and collective protection applications.

## 2. Molecular sieving vs. surface flow membrane systems

When contemplating using a first stage as part of a combined system for the continuous removal of DMMP from contaminated air streams, there are two choices to one's disposal. The first choice involves the use of membranes with molecular sieving characteristics. There are conflicting reports, in the technical literature, on the molecular size of DMMP. Kanan et al. [5], for example, reported a value of 0.57 nm for the kinetic diameter of DMMP using a space-filling model, a value which Lu et al. [6] disputed as being too low based on their experimental studies of DMMP vapor transport through a Q-1 phase butyl rubber membrane. Mäkie [7], indeed, calculated a Van Der Waals diameter for the DMMP molecule of 0.70 nm, with an even larger molecular diameter of 0.842 nm calculated by Lee et al. [8] using Monte Carlo simulations. Much better agreement exists among the estimates of the kinetic diameters of O<sub>2</sub> and N<sub>2</sub>, which for O<sub>2</sub> range from 0.343 to 0.356 nm and for N<sub>2</sub> from 0.364 to 0.368 nm [9–11].

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