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DIFFUSION PROCESS OF CHEMICAL AGENTS IN BARRIER POLYMERS AS A KEY FACTOR OF DECONTAMINATION EFFICIENCY

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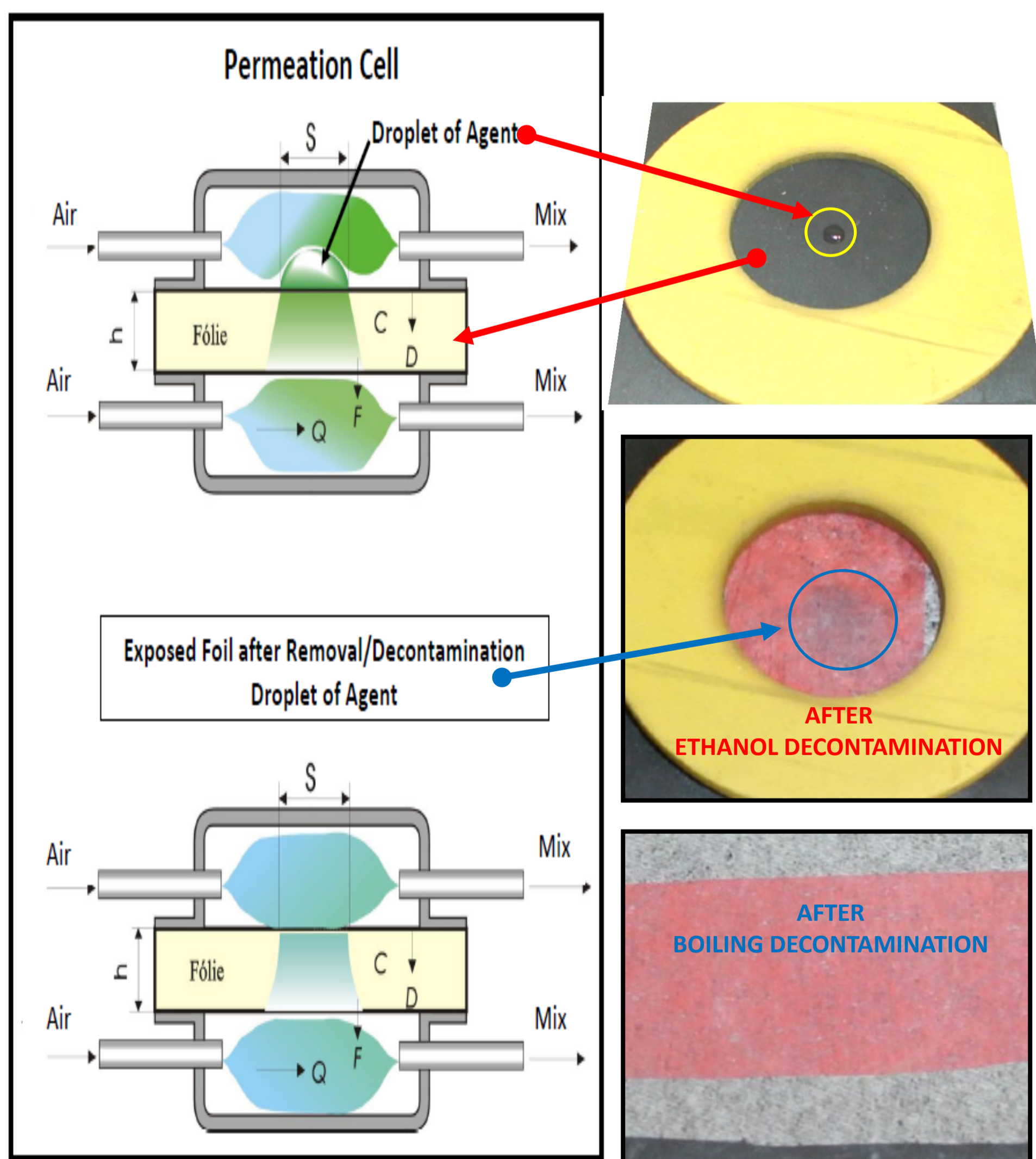
ABSTRACT

Chemical Warfare Agents (CWA) and/or Toxic Industrial Chemicals (TIC) can contaminate protective barrier materials made of polymer basis. Chemical molecules permeate and penetrate into the depth of majority barrier material through diffusion process. Despite the removal of liquid portion of a chemical from external surface of barrier material, diffusion process of a chemical continues also in reverse direction, back towards original surface. This reversible secondary contamination of the surface creates further delayed safe contact and representing off-gassing hazards. The objective of the research was to describe the mechanism and conditions of selected chemicals permeation through and out of polymer material after its surface decontamination. Outcomes of the research can be utilized also in advanced studies for CWA dermal permeation and skin effective decontamination.

MATERIAL AND METHODS

Polymer membranes of polyethylene (PE) and butyl rubber (IIR) used for manufacturing of PPE had been exposed with S-Mustard agent (HD 90% of purity), dichlorhexan (DCH), and the mixture of HD 90% and DCH 10% in permeation cell, under define temperature and time exposure. The access of chemical agents after define exposure of a membrane had been removed from its exposed surface by decontamination with ethanol or sodium hypochlorite (5% solution for 5 min. of exposure, drying with swab, washed with distilled water and drying with swab) or with powdered active charcoal and/or bentonite (thickness of layer 1 mm). Thorough decontamination of swatches was done in boiling solution of 2% bicarbonate for 2 hours.

Permeation and desorption of the chemicals with membranes was monitored through colorimetric contact detection and gas chromatography, in order to identify surface decontamination efficiency and desorption process afterwards.

Permeation Cell

Exposed Foil after Removal/Decontamination Droplet of Agent

AFTER ETHANOL DECONTAMINATION

AFTER BOILING DECONTAMINATION

RESULTS AND DISCUSSION

Study demonstrates reversible diffusion of chemical substances from exposed barrier protection materials even after thorough surface decontamination. The level of internal contamination of barrier material depends on their resistance characteristics (resistance/breakthrough time) and such as thickness of barrier material, diffusion coefficient, solid/polymer solubility, temperature, time of exposure and physical/chemical properties of challenging chemicals.

Permeation and diffusion process of liquid agent in polymer matrix is controlled according **Fick Law,** where:

F is velocity of sorption and desorption [g.cm⁻².s⁻¹]
D is diffusion coefficient [cm².s⁻¹]
C_1 is concentration of agent on surface of a barrier [g.cm⁻³]
C_2 is concentration inside of a barrier [g.cm⁻³]
h is thickness of a barrier in [cm]

$$F = D \cdot \frac{C_1 - C_2}{h}$$

Diffusion process is also controlled through ambient temperature according **Arrhenius formula,** where:
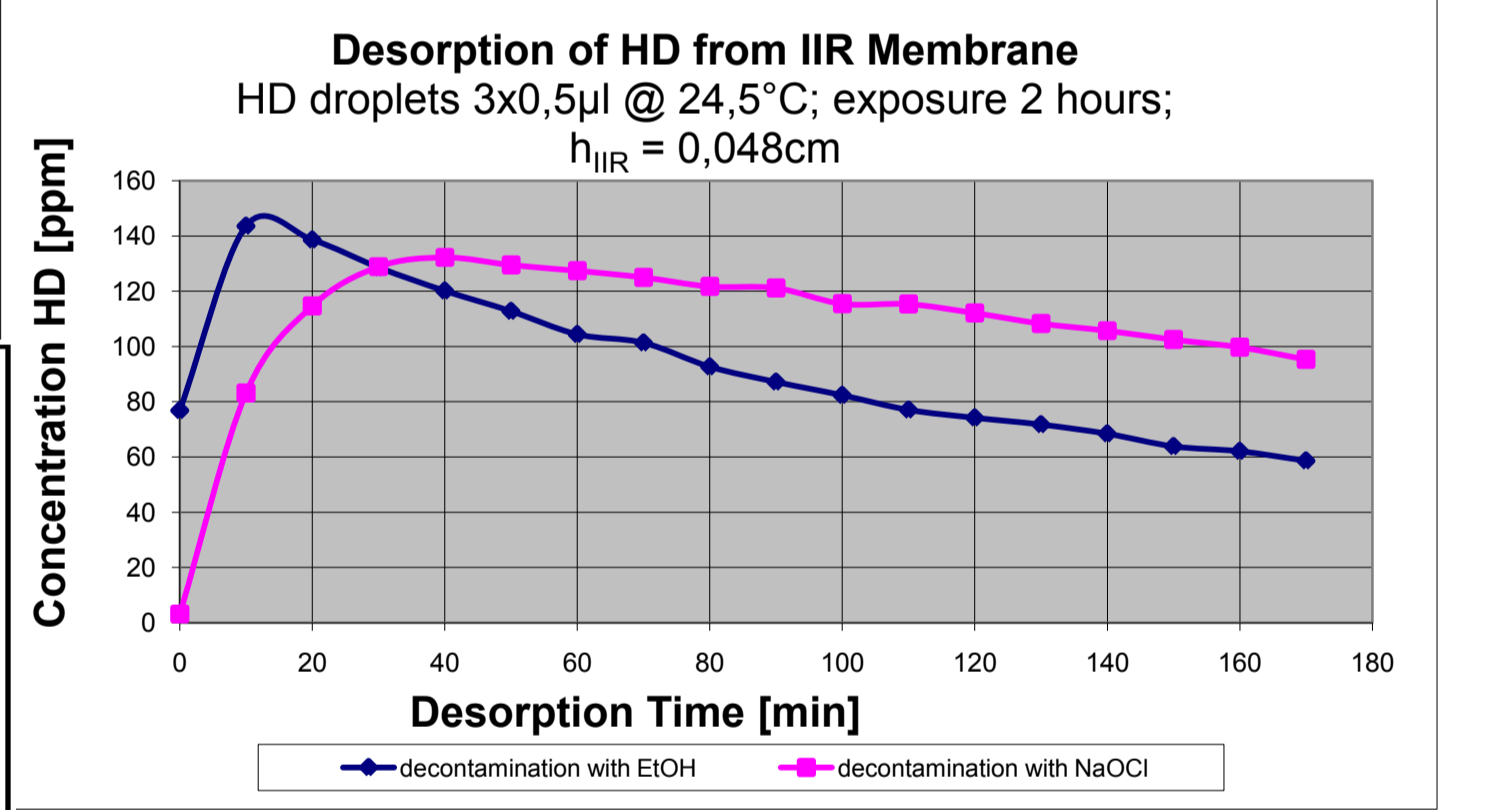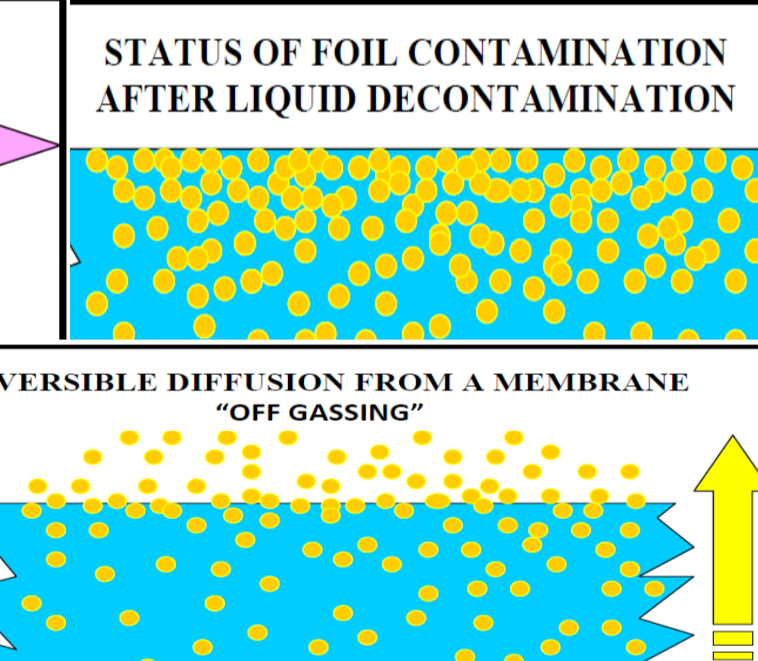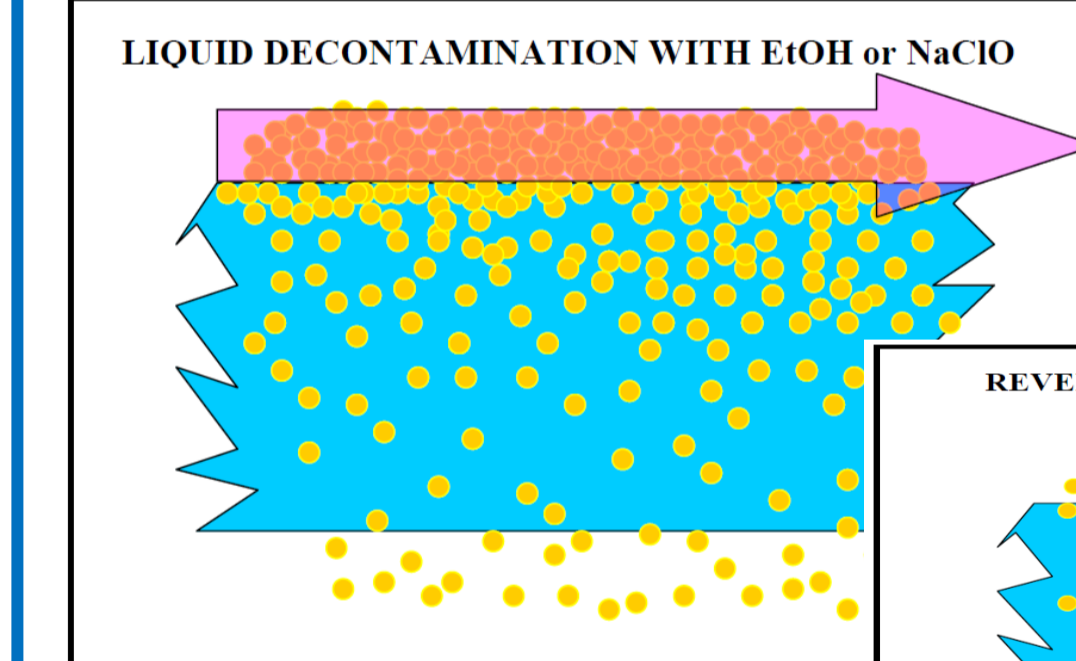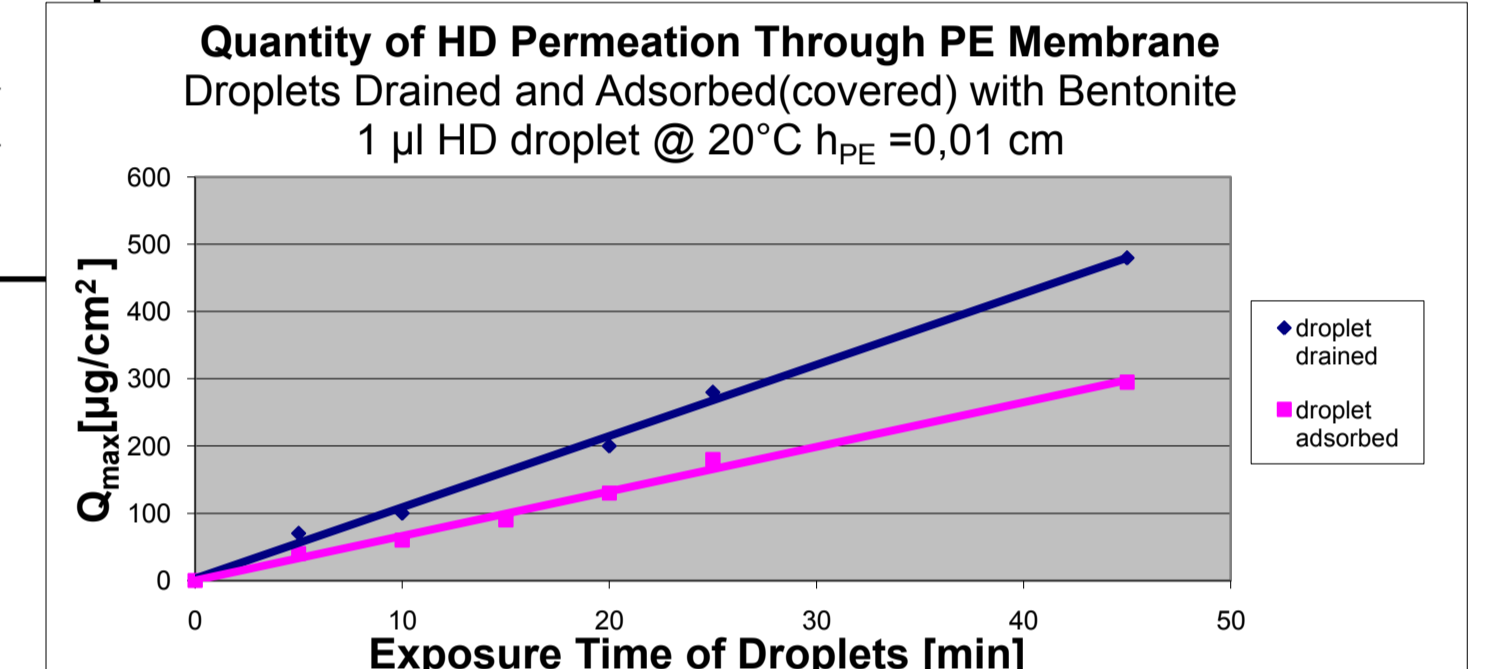
D_0 is frequency factor
E_D is diffusion activation energy
R is gas constant
T is absolute temperature

$$D = D_0 \cdot e^{-E_D/RT}$$

Water based decontamination mixtures and dry sorbents are enabling to remove liquid contamination only from the surface of polymer matrixes. Hydrophobic and non-porous polymer surface prevents interaction of chemically active water based solution with the chemical contaminant already permeated into the mass of polymer material. In both cases of polymer materi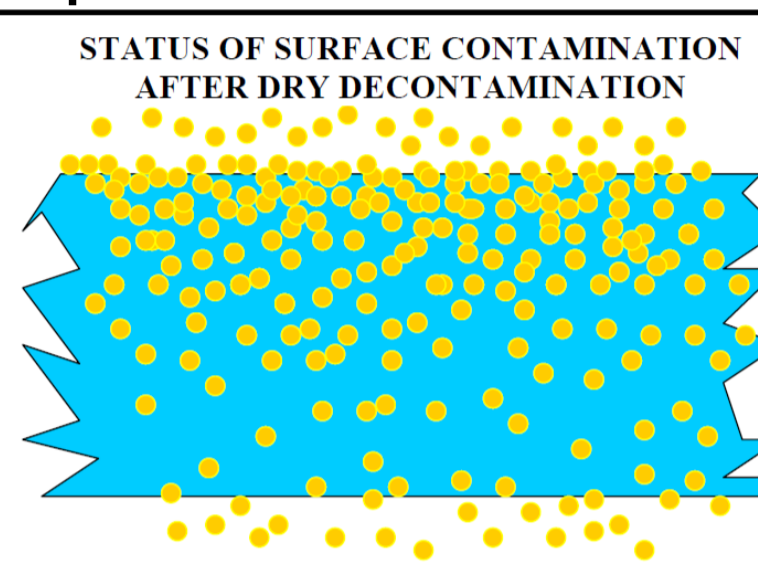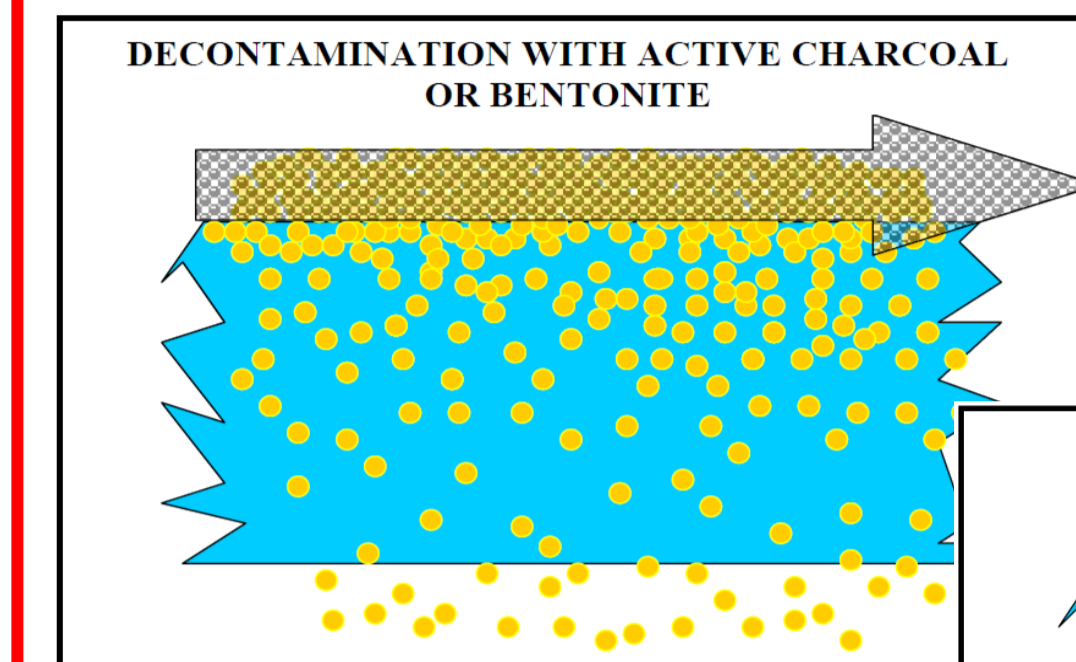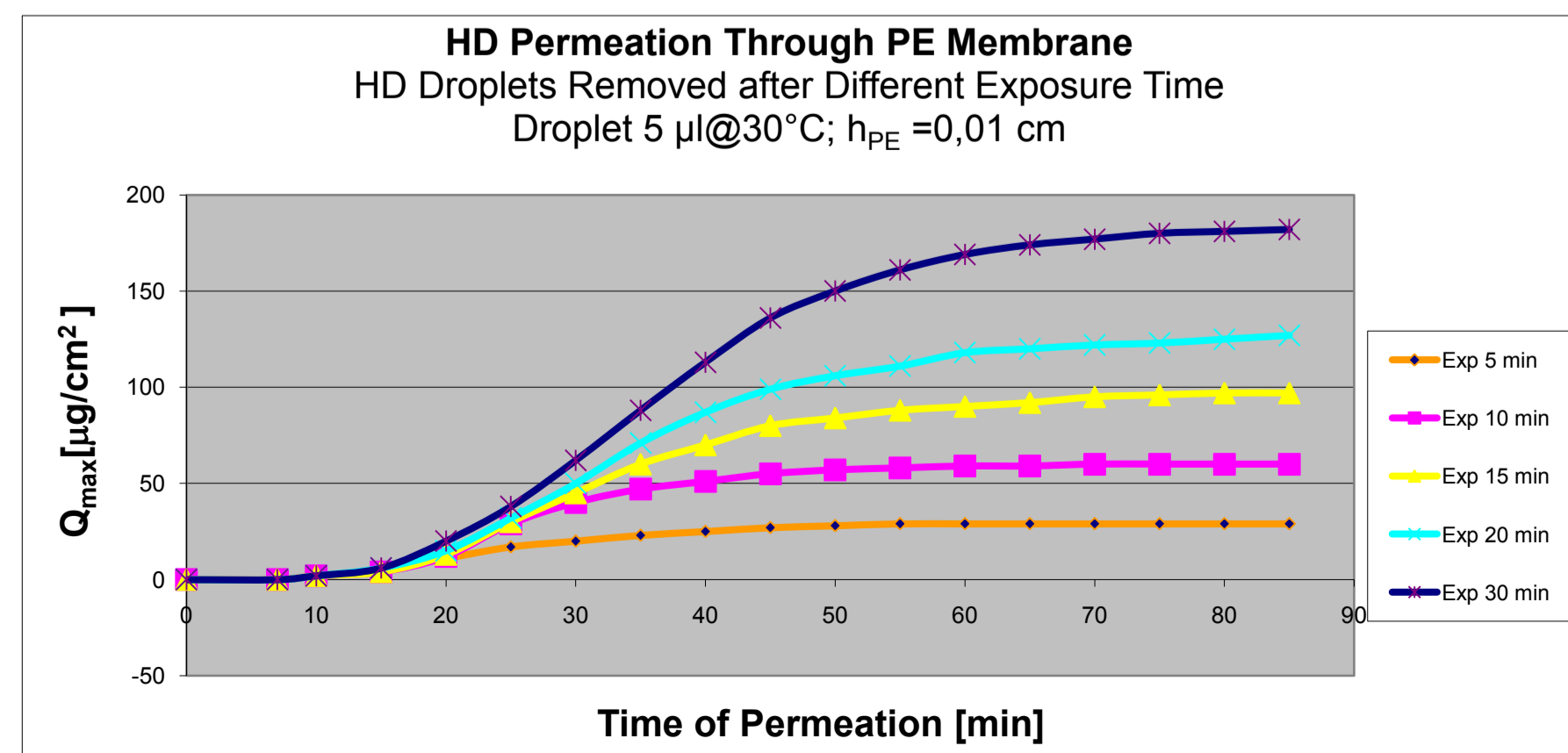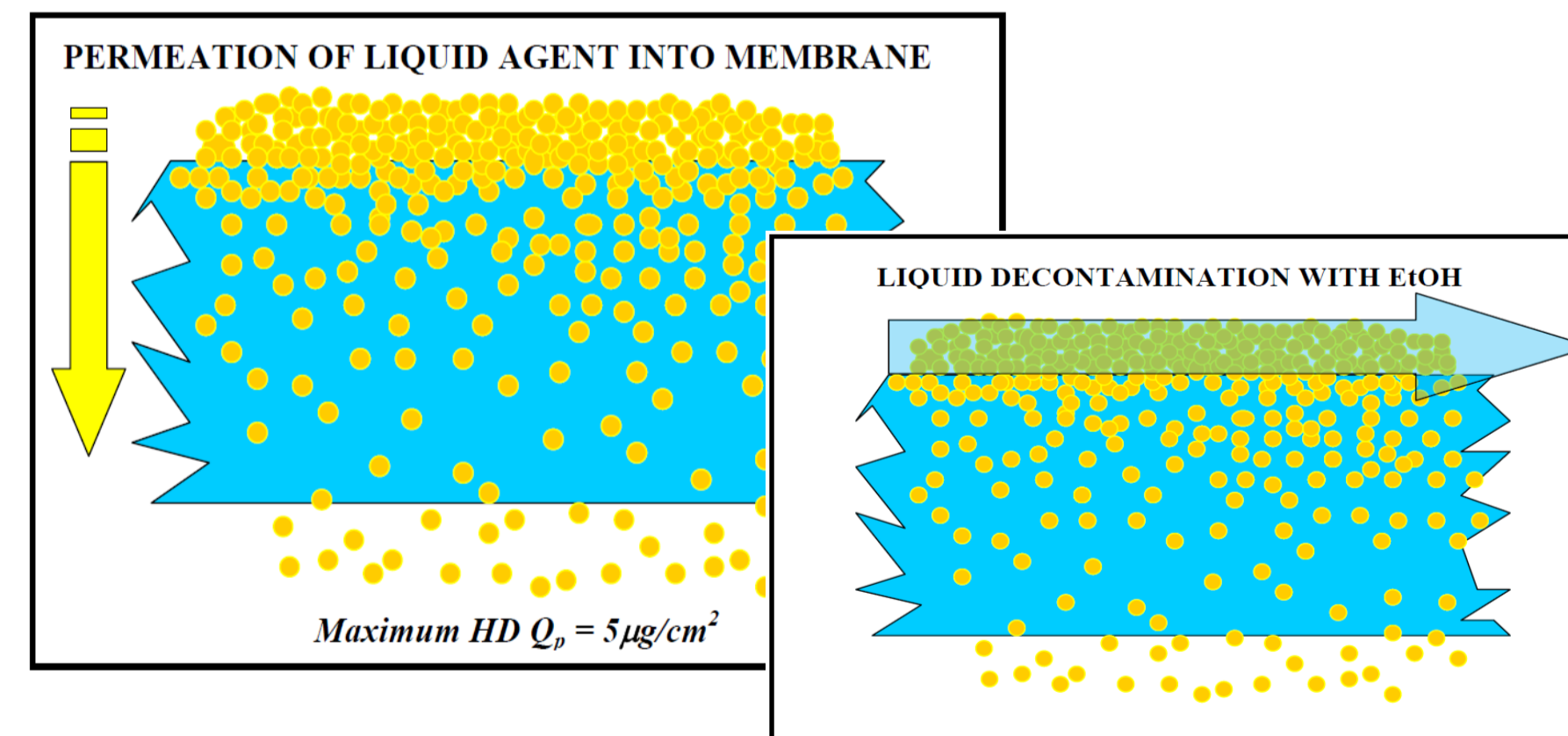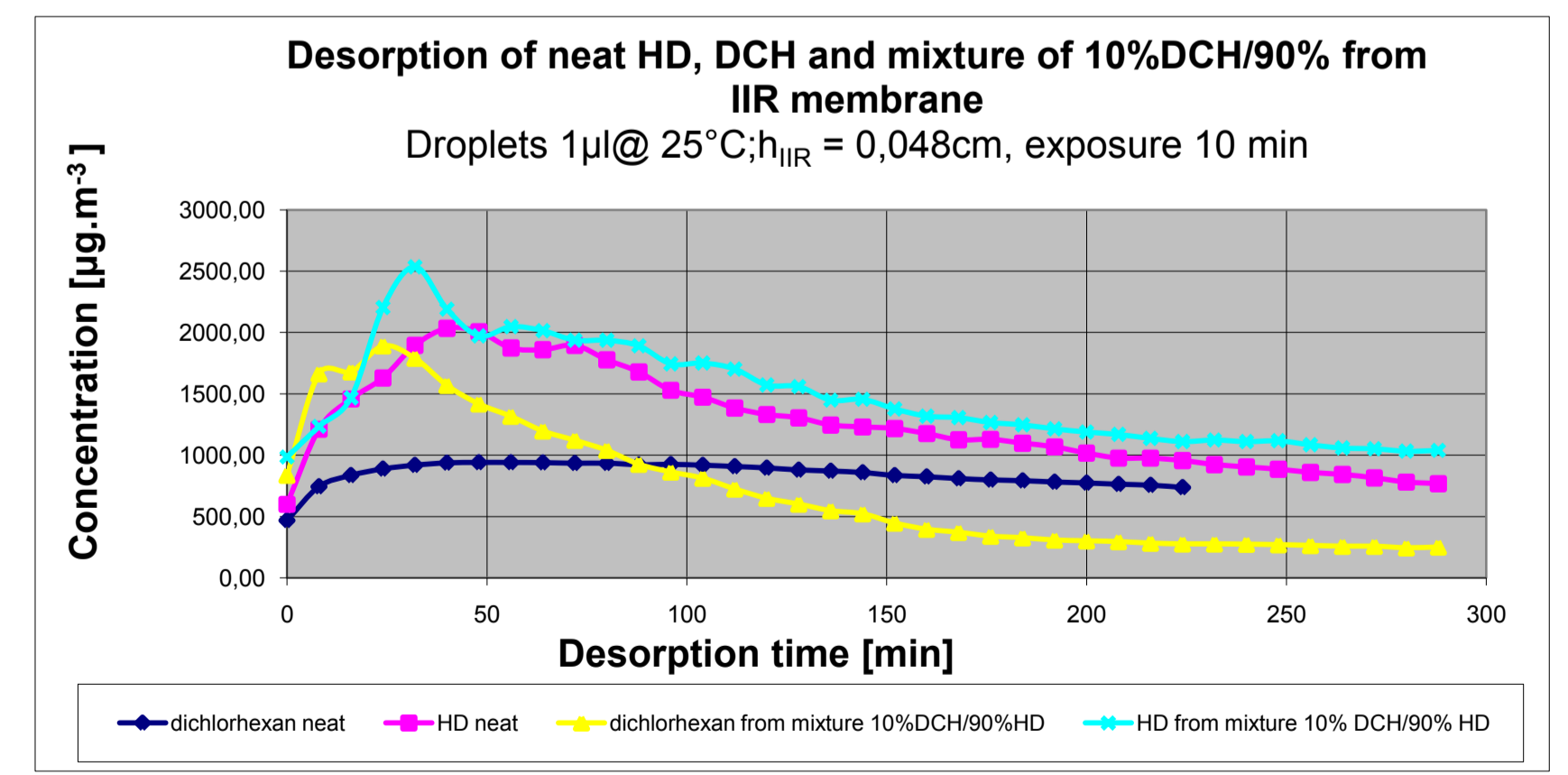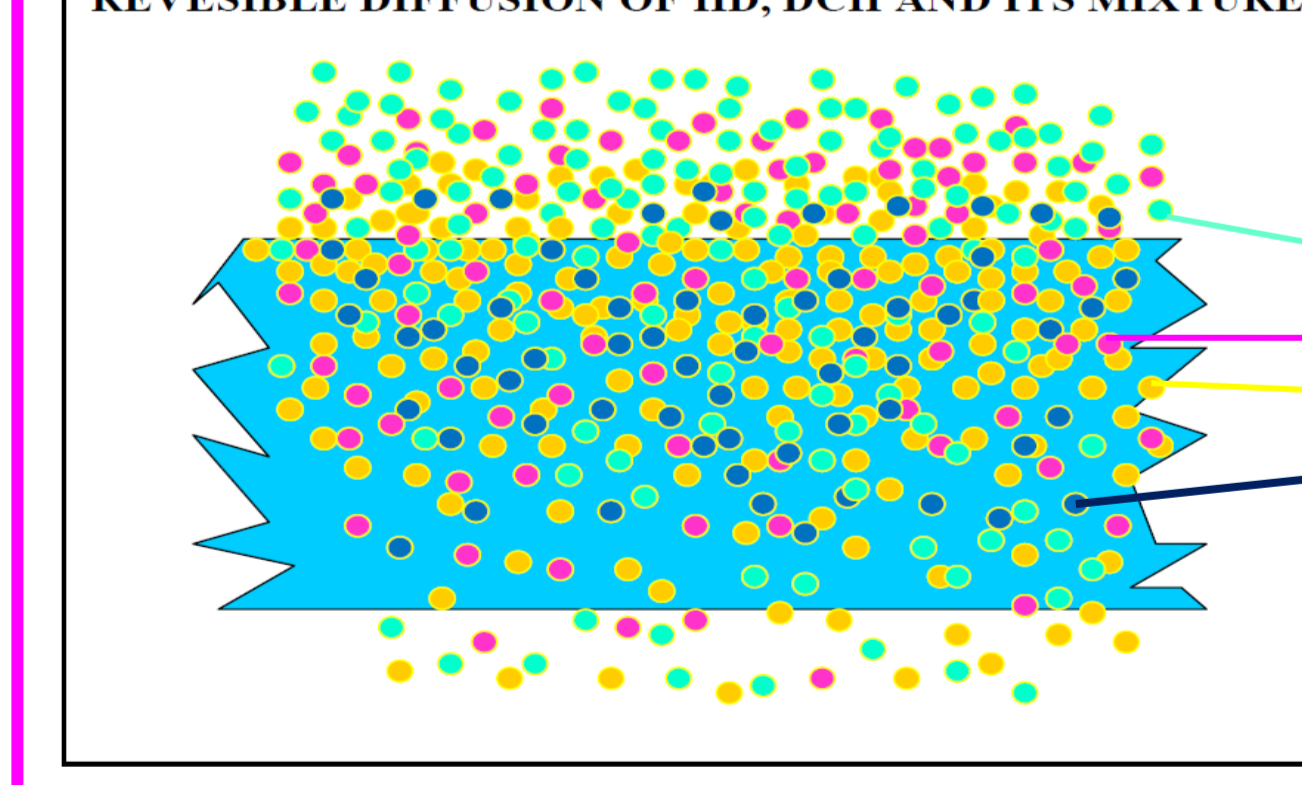al decontamination there is continuing reversible diffusion process, resulting in release of absorbed contaminant back onto decontaminated surface. Diluted HD with 10% of DCH causes faster desorption of HD from the IIR polymer matrix. Physical decontamination with EtOH remains threshold of the agent on the surface of polymer matrix and which is accompanied with sub sequential desorption of the agent. In the case of decontamination with chemically active mixture, such as solution of NaClO the efficiency of decontamination is significantly higher and reducing also following desorption of the agent. However, reaction products might slowdown and prolong desorption of the agent in comparison with only physical dilution and removal the agent with EtOH. Satisfactory decontamination of HD at the IIR type matrix can be achieved in hot chemically active decontamination solution, when temperature speed up the process of reverse diffusion and support also chemical reaction with a contaminant.

DECONTAMINATION WITH ACTIVE CHARCOAL OR BENTONITE

STATUS OF SURFACE CONTAMINATION AFTER DRY DECONTAMINATION

DECONTAMINATION WITH SORBENT

Breakthrough Time of HD through PE Membrane
HD droplet 1µl @ 20°C, h_{PE} = 0,010 cm; droplets decontaminated after exposure time with active charcoal and bentonite

Quantity of HD Permeation Through PE Membrane
Droplets Drained and Adsorbed(covered) with Bentonite
1 µl HD droplet @ 20°C h_{PE} =0,01 cm

LIQUID DECONTAMINATION WITH EtOH or NaClO

STATUS OF FOIL CONTAMINATION AFTER LIQUID DECONTAMINATION

REVERSIBLE DIFFUSION FROM A MEMBRANE "OFF GASSING"

Desorption of HD from IIR Membrane
HD droplets 3x0,5µl @ 24,5°C; exposure 2 hours; h_{IIR} = 0,048cm

PERMEATION OF LIQUID AGENT INTO MEMBRANE

LIQUID DECONTAMINATION WITH EtOH

Maximum HD Q_p = 5µg/cm²

HD Permeation Through PE Membrane
HD Droplets Removed after Different Exposure Time
Droplet 5 µl@30°C; h_{PE} =0,01 cm

Exp 5 min
Exp 10 min
Exp 15 min
Exp 20 min
Exp 30 min

REVESIBLE DIFFUSION OF HD, DCH AND ITS MIXTURE

Desorption of neat HD, DCH and mixture of 10%DCH/90% from IIR membrane
Droplets 1µl@ 25°C;h_{IIR} = 0,048cm, exposure 10 min

dichlorhexan neat
HD neat
dichlorhexan from mixture 10%DCH/90%HD
HD from mixture 10% DCH/90% HD

CONCLUSIONS

Diffusion of chemical liquid contaminants into barrier protection material represents potential hazards of secondary contamination after surface decontamination was performed. Serious concern has to be given to potential cases, when additional solvent(s) with CWA and/or TIC can be used to accelerate permeation, due to the process of reverse diffusion through barrier protective materials and thus challenging protective properties of personal protective ensemble. Currently used different barrier material for PPE should be evaluated against mixtures of CWAs with selected solvents as "vehiculum" of penetration to polymer matrixes and accelerating also desorption of agents. Mathematical apparatus describing diffusion and permeation processes through polymer membranes can be used for prediction purposes and comparative studies for modeling of dermal exposure and skin decontamination. Actual decontamination efficiency can be determined based on further experimental and modeling research results.