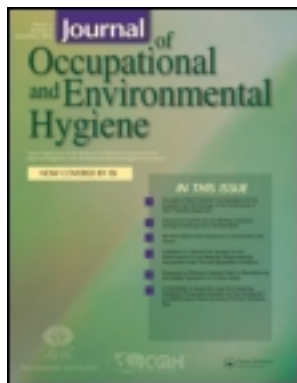


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Performance Evaluation of 26 Combinations of Chemical Protective Clothing Materials and Chemicals After Repeated Exposures and Decontaminations

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Effective decontamination of chemical protective clothing (CPC) is essential for reducing occupational skin diseases and disorders during a reuse scenario. To protect the workforce, the efficacy of decontamination methods and the reusability of CPC need to be evaluated. In this study, performance of 14 CPC materials against 12 liquid chemicals was evaluated based on standardized breakthrough time (BT) and steady-state permeation rate (SSPR). Thermal and water-detergent decontamination methods were used. Exposure/decontamination was repeated up to 11 cycles, or until the material failed, so that further testing became impossible. Changes in BT and SSPRs were determined for each material and chemical combination. There were 20 and 13 combinations that were able to complete 11 cycles with thermal and detergent methods, respectively. By comparing the beginning and ending cycles, mean BT increased 9% with the thermal method but slightly decreased (3.3%) with the detergent method, while mean SSPR decreased 2% with the thermal method, but slightly increased (1.4%) with the detergent method. Less than half of the changes were found statistically different ($p < 0.05$). Generally, the thermal method had higher decontamination efficacy than the detergent method.

Keywords breakthrough time, chemical protective clothing, decontamination, permeation testing, reusability, steady-state permeation rate

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The findings and conclusions of this report are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

INTRODUCTION

Skin disorders including diseases and injuries such as chemical burns and various types of dermatitis are common,

and often severely disabling for workers across a range of industry sectors. Chemical protective clothing (CPC), viewed by many as the most economical method of protecting workers' skin from chemical agents in vapor, liquid, and particulate forms is widely used. The number of workers in the United States who rely on CPC for skin protection is estimated to be approximately 15 million. A report from Specialists in Business Information⁽¹⁾ estimates the U.S. market for personal protective equipment (PPE) reached \$6.4 billion in 2007, rising 7% over 2006. The report forecasts the U.S. PPE market will hit \$7.2 billion by 2012.

The primary purpose of CPC is to protect the worker against chemical exposure by skin route. CPC has been marketed in three categories based on reusability: disposable, limited-reusable, or reusable.⁽²⁾ The category, however, can be changed when it is exposed to different chemicals. Disposable CPC is intended for one-time use and then discarded. Limited-reusable CPC is intended to be used several times prior to disposal, and reusable CPC is intended to be used, decontaminated, and repaired multiple times prior to disposal. Reusable CPC must be properly decontaminated and inspected for physical damage before it is put back into service. Prior to disposal, surface contamination should be removed from CPC to facilitate safe handling in preparation for disposal. Improper decontamination and handling of contaminated CPC can create serious health and/or environmental consequences.

Generally, there are two types of contamination: surface contamination and matrix contamination. Surface contamination is relatively easy to remove, while matrix contamination is much more difficult to eliminate when the contaminant dissolves in the outermost portion of the CPC material and then diffuses within the material. Because all polymer materials are permeable to some degree, it is likely the matrix will become contaminated following chemical contact. The potential risk to users following subsequent use of the CPC increases as it becomes more difficult to remove the matrix contamination.

The various methods for decontaminating CPC fall into two basic categories: physical methods and chemical methods. In the AIHA[®] *Guideline for the Decontamination of Chemical Protective Clothing and Equipment*,⁽²⁾ the thermal method (physical) and the detergent method (chemical) were recommended with several other methods for decontaminating CPC. To adequately protect the work force against dermal exposure to chemical hazards, decontamination efficacy of CPC should be carefully evaluated with appropriate methodologies.

It was previously established that changes in the permeation parameters and physical properties could be used to define the limits of reusability of selected CPC and glove materials.^(3,4) The present study extends the work to broader classes of materials and chemicals by 14 commonly used CPC materials and their abilities to protect against 12 of the 15 liquid chemicals addressed in *ASTM F1001-99a, Standard Guide for Selection of Chemicals to Evaluate Protective Clothing Materials*,⁽⁵⁾ comprising 26 material-chemical combinations. The ASTM standard provides a guide for selection of chemicals to evaluate protective clothing materials.

Two different decontamination methods were used: thermal decontamination and water-detergent (referred to as “detergent”) decontamination. This study investigated the effect of multiple decontaminations on the chemical resistance of the CPC and compared the efficacy of two different decontamination methods based on the changes in breakthrough time and steady-state permeation rate.

MATERIALS AND METHODS

Clothing Materials and Liquid Chemicals

Fourteen commonly used CPC products that contain seven different materials (i.e., natural rubber, nitrile, polyvinyl chloride, neoprene, Tychem, butyl, and Viton) were selected (Table I). The selection covers a majority of the materials that have been commonly used in the construction of CPC gloves, boots, and suits. Materials for assessment were inventoried, numbered, and logged upon receipt. Glove samples were randomly selected from the quantity purchased.

The 12 liquid chemicals were acetone, acetonitrile, dichloro methane, diethylamine, dimethylformamide, ethyl acetate, n-hexane, methanol, nitrobenzene, sulfuric acid, tetrachloroethylene, and toluene. The chemicals covered a broad range of representative chemical classes and properties.

The selection of the material-chemical combinations was based on the breakthrough time only. Material degradation during testing was not a consideration. In this study, 26 combinations were selected that had standardized breakthrough times (BTs) between 30 and 300 min. The BTs were based on the permeation data provided by the specific manufacturers for new CPC materials protecting against the selected chemicals.⁽⁶⁾ The basis for the criteria was that a combination with a BT less than 30 min may not provide adequate protection, and a combination with a BT longer than 300 min would be difficult to evaluate within a working day due to instrument warm-up, calibration of the instrument, preparation of the samples before

TABLE I. Chemical Protective Clothing Materials Tested

ID	Chemical Protective Clothing Material	Manufacturer
1	Butyl 874R glove	Best Manufacturing Company
2	Butyl 878 glove	Ansell Healthcare
3	Classic L-210 natural rubber glove	MAPA Professional
4	Neoprene 29-865 glove	Ansell Healthcare
5	Stanzoil Chemply N-440 neoprene glove	MAPA Professional
6	Solvex 37-155 Nitrile glove	Ansell Healthcare
7	Hustler 725R PVC/nitrile glove	MAPA Professional
8	Snorkel PVC glove	Ansell Healthcare
9	Tychem CPE suit material	DuPont
10	Tychem CPE2 suit material	DuPont
11	Tychem F suit material	DuPont
12	Viton 890 glove	Best Manufacturing Company
13	Viton glove	North Safety Products
14	Viton 892 glove	Best Manufacturing Company

the permeation test, and decontamination of the samples after the test. Table II lists the 26 material-chemical combinations. Chemical abstracts service (CAS) registry numbers of the chemicals are also shown in the table.

Thermal Stability Test

In this study, the conditions of the thermal decontamination, 100°C for 16 hr, were selected based on a study by Vahdat and Delaney⁽⁷⁾ and previous studies.^(3,4) To set a common benchmark for screening, all testing was conducted at these conditions. In practice, users may wish to perform the decontamination at higher or lower temperatures based on the characteristics of the contaminant (e.g., boiling point). To determine if the conditions were suitable for CPC, glove and suit materials, a thermal stability test was conducted first.

For the thermal stability test, a 3-in.-diameter circular swatch was cut from the palm side of each material. Samples were conditioned in a desiccator for at least 16 hr prior to the test and then were removed from the desiccator, weighed, and transferred to an explosion-proof oven. The oven was maintained at 100°C ± 2°C, which was verified by a calibrated scanning thermometer. After 16 hr in the oven, the samples were returned to the desiccator for approximately 16 hr then reweighed. The pre-weight, post-weight, and change in weight due to the temperature treatment were recorded. The samples were also visually examined for physical degradation.

TABLE II. Material-Chemical Combinations

Combination	Chemical Protective Clothing Material	Chemical	CAS Registry Number
1	Butyl 874R glove	Acetone	67-64-1
2	Butyl 878	Ethyl Acetate	141-78-6
3	Classic L-210 natural rubber glove	Dimethylformamide	68-12-2
4	Classic L-210 natural rubber glove	Methanol	67-56-1
5	Neoprene 29-865 Glove	Methanol	67-56-1
6	Neoprene 29-865 Glove	Sulfuric Acid, 95%	7664-93-9
7	Stanzoil Chemply N-440 neoprene glove	Acetonitrile	75-05-8
8	Stanzoil Chemply N-440 neoprene glove	Dimethylformamide	68-12-2
9	Stanzoil Chemply N-440 neoprene glove	n-Hexane	110-54-3
10	Stanzoil Chemply N-440 neoprene glove	Methanol	67-56-1
11	Solvex 37-155 nitrile glove	Methanol	67-56-1
12	Solvex 37-155 nitrile glove	Tetrachloroethylene	127-18-4
13	Hustler 725R PVC/nitrile glove	Diethylamine	109-89-7
14	Snorkel PVC glove	Sulfuric Acid, 95%	7664-93-9
15	Tychem CPE suit material	Acetone	67-64-1
16	Tychem CPE suit material	Diethylamine	109-89-7
17	Tychem CPE suit material	n-Hexane	110-54-3
18	Tychem CPE suit material	Nitrobenzene	98-95-3
19	Tychem CPE suit Material	Tetrachloroethylene	127-18-4
20	Tychem CPE2 suit material	Dimethylformamide	68-12-2
21	Tychem CPE2 suit material	Nitrobenzene	98-95-3
22	Tychem F suit material	Acetonitrile	75-05-8
23	Tychem F suit material	Methanol	67-56-1
24	Viton 890 glove	Dichloromethane	75-09-2
25	Viton glove	Dichloromethane	75-09-2
26	Viton 892 glove	Toluene	108-88-3

Permeation Test and Chemical Exposures

Similar to the thermal stability test, circular swatches were cut from the palm side of each material then conditioned for a minimum of 24 hr at standard laboratory temperature ($21 \pm 5^\circ\text{C}$) and humidity (30 to 80% RH) prior to permeation testing.

The permeation test was carried out in triplicate at room temperature based on *ASTM F739-07 Standard Test Method for Permeation of Liquids and Gases through Protective Clothing Materials under Conditions of Continuous Contact*.⁽⁸⁾ Two-inch ASTM permeation cells were used. The concentration for the permeant was determined using a gas chromatograph with a flame ionization detector (Model 8610C; SRI Instruments, Torrance, Calif.) in an open loop system. Measurement of the time of chemical exposure to the material began once the chemical was added to the permeation cell.

Decontamination of the Clothing Materials

After the permeation test, the permeation cell was disassembled and the swatch was air dried. The two different decontamination methods used were thermal decontamination and detergent decontamination. Based on previous studies,^(3,4,7) thermal

decontamination consisted of heating the test samples in an oven maintained at $100 \pm 1^\circ\text{C}$ for 16 hr. The detergent-water decontamination was carried out in a Labconco FlaskScrubber dishwasher. The wash program consisted of two 5-min wash cycles at 45°C with Alcojet detergent, and two 10-min rinse cycles at 45°C , followed by 25 min of drying at 90°C . The samples were allowed to re-equilibrate to $21 \pm 5^\circ\text{C}$ and 30 to 80% RH prior to the start of the next exposure/decontamination cycle.

Repeated Exposure and Decontamination Cycles

To fully investigate permeation behaviors after repeated exposure/decontamination cycles, two sets of tests were performed for each material-chemical combination. Each set comprised 11 exposure/decontamination cycles or until the material failed (did not allow a further permeation test due to significant degradation). A swatch of as-received material that had been removed from a glove or suit was used for the first cycle, and this same swatch was used for each of the remaining cycles. Approximately 1500 permeation tests were conducted to evaluate the 26 material-chemical combinations.

TABLE III. Thermal Stability of the Clothing Materials

ID	Material	Visual Appearance (new)	Pre-Weight g	Post-Weight g	Weight Change		Change in Visual Appearance
					g	%	
1	Butyl 874R glove (Best)	Black, textured, no liner	1.62337	1.58997	-0.0334	-2.0%	No change
2	Butyl 878 glove (Ansell)	Black, no texture, no liner	3.65016	3.60040	-0.04976	-1.4%	No change
3	Classic L-210 natural rubber glove	Yellow, textured palm, light yellow liner	2.27525	2.47651	0.20126	8.8%	Discolored, outer surface became dark yellow
4	Neoprene 29-865 glove	Olive green, textured palm, green-gray lining	2.50222	2.49705	-0.00517	-0.21%	Discolored, outer surface became dark brown
5	Stanzoil Chemply N-440 neoprene glove	Black, textured palm, red liner	4.56400	5.45847	0.89447	19%	Discolored, dark blotches on red liner
6	Solvex 37-155 Nitrile glove	Green, slight texture, no liner	1.82285	1.82097	-0.00188	-0.10%	No change
7	Hustler 725R PVC/Nitrile glove	Red, textured, cloth liner	6.40603	6.34818	-0.05785	-0.90%	No change
8	Snorkel PVC glove	Dark green, textured, cloth liner	5.48081	4.53697	-0.94384	-17%	No change
9	Tychem CPE suit material	Orange CP suit	3.33633	3.32412	-0.01221	-0.37%	No change
10	Tychem CPE2 suit material	Gray material (flat), textured, white liner	0.56510	0.56663	0.00153	0.27%	Discolored, brown splotches, outer surface glossy, physically curled
11	Tychem F suit material	Gray material (flat), textured, white liner	0.52590	0.52771	0.00181	0.34%	Discolored, outer surface glossy
12	Viton 890 glove (Best)	Black, no texture, no liner	4.71566	4.68253	-0.03313	-0.70%	No change
13	Viton glove (North)	Black, no texture, no liner	3.43041	3.43128	0.00087	0.030%	No change
14	Viton 892 glove (Best)	Black, no texture, no liner	2.50930	2.47651	-0.03279	-1.3%	No change

Note: Values in bold indicate that clothing materials had weight gains after being heated.

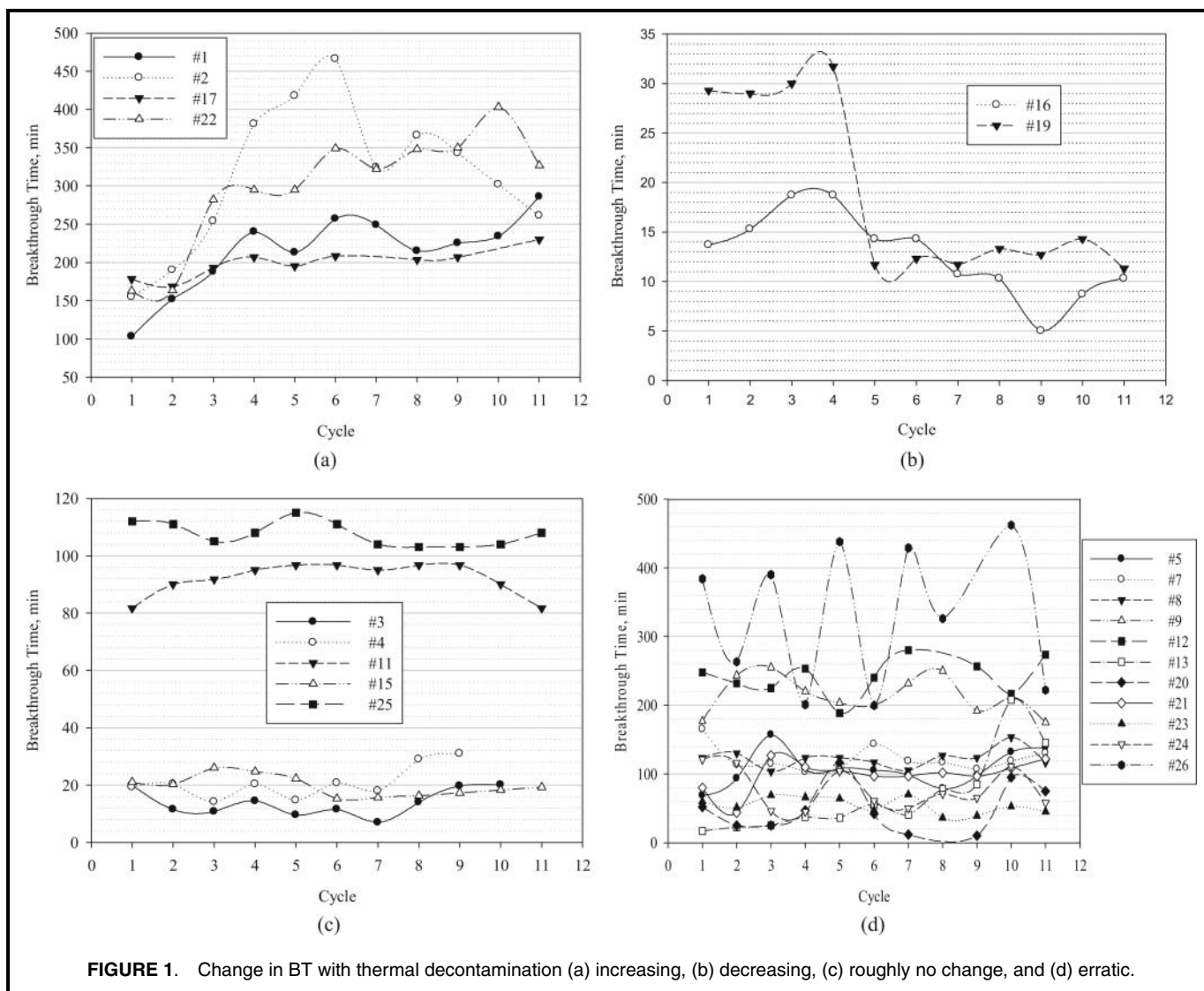
Data Analyses

BTs and SSPRs were calculated after each exposure/decontamination cycle using the Permeation Calculator (version 2.4.1) computer program.^(9,10) A significant decrease in the BT and/or an increase in the SSPR may be an indicator of a decline in the chemical resistance. A paired t-test was performed to assess the significance of the change in BT or SSPR of Cycle 1 vs. that of the last cycle for each individual combination within a decontamination method. A t-test—for the significance of the change in BT or SSPR of the last cycle for the same combination ID—was performed to assess the significance between the two decontamination methods.

RESULTS AND DISCUSSION

Thermal Stability of the Clothing Materials

Thermal stability of the clothing materials, including weight changes and changes in visual appearance, are shown in Table III. Overall, 9 of the 14 clothing materials had weight losses (0.1% to 17.2%), and the rest had weight gains (0.03% to 19.6%) after being heated to 100°C for 16 hr. Five of the materials, neoprene glove materials (IDs #4 and #5), Tychem suit materials (IDs #10 and #11), and natural rubber glove material (ID #3), changed color to varying degrees. For the materials with color changes, four had weight gains (0.27% to 19.6%) and only one had a weight loss (0.21%).



CPC degradation usually involves the chemical modification of the polymer by its environment. Since they are manufactured from polymers, all CPC materials are potentially degraded by heat via certain routes, such as depolymerization, side group elimination, cyclization, and carbonization. The most weight loss—observed for the Snoekel PVC glove (ID #8)—is believed to be caused by a side-group elimination process, which first loses HCl to form a conjugated polymer backbone.^(11,12) In contrast, the weight gains probably involved reactions such as carbonyl formation and thermo-oxidative crosslinking.⁽¹³⁾ Surfaces exposed to air promoted weight-gaining reactions that resulted in the polymer possessing a higher thermo-oxidative stability as a whole.⁽¹⁴⁾

Changes in BTs and SSPR of the CPC Materials Thermal Decontamination

For thermal decontamination, 20 of the 26 combinations were able to complete all 11 cycles. The materials that failed prior to 11 cycles included Combinations #3 (10 cycles), #4 (9

cycles), #6 (1 cycle), #10 (2 cycles), #14 (2 cycles), and #18 (7 cycles). Of these, CPC materials used for Combinations #3 and #4 (classic L-210 natural rubber glove) and #6 (Neoprene 29-865 glove) were most likely degraded by heat, which is consistent with the results shown in Table III. For Combinations #6 and #14, the concentrated sulfuric acid seemed to further degrade and damage the materials.

The change in BT values associated with the exposure/decontamination cycle for the 22 material-chemical combinations that completed at least nine cycles is shown in Figure 1. The four different types of behavior were simply grouped based on their graphical appearances. Four of the combinations (#1, #2, #17, and #22) exhibited a trend showing an increase in BT values with increasing cycle, and there were another two (#16 and #19) that exhibited the opposite tendency. BT values of five combinations were approximately constant over the cycles. Erratic BT values over the cycles were observed for the rest of the combinations.

The change in the SSPR values is shown in Figures 2a–d. The SSPRs of five combinations (#7, #9, #12, #17, and #26)

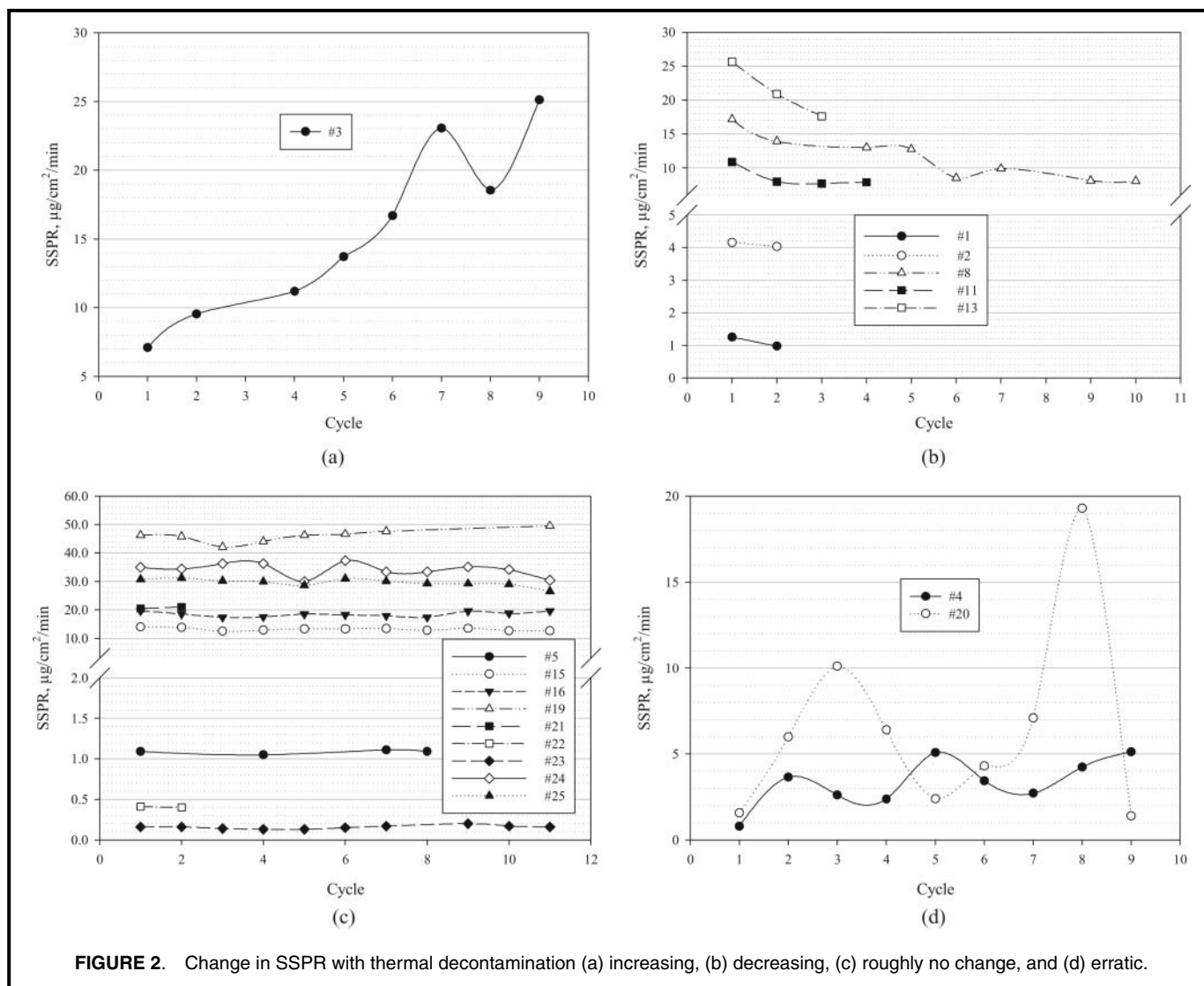


FIGURE 2. Change in SSPR with thermal decontamination (a) increasing, (b) decreasing, (c) roughly no change, and (d) erratic.

are not included, as the values were below the minimum detection rates between 0.03 and 0.08 $\mu\text{g}/\text{cm}^2/\text{min}$, depending on analytical sensitivities of the different chemicals. Some correlations of the behaviors between BT and SSPR were observed when comparing Figures 1 and 2. For instance, Combination #1 had an increase of BT with a decrease of SSPR (consistent to an increased chemical resistance), #25 had approximately constant BT and SSPR over the cycles, and #20 had erratic BT and SSPR. However, there were four combinations (#5, #21, #23, and #24) that exhibited erratic BT values but had approximately constant SSPRs over the cycles.

Table IV lists the means for BT and SSPR with the standard deviations just for the beginning and ending cycles, while ignoring the changes in between. Percentages in **bold** indicate that the changes were statistically significant (paired t-test, $p < 0.05$). Information in parentheses below a specific combination ID number represents the ending cycle number if the material failed prior to 11 cycles. For instance, (T2, D3) means that the material failed after completing two cycles for the thermal decontamination method and three cycles for the detergent

decontamination method, respectively. As can be seen from the table, 11 of the combinations showed increases in the BT, but only 45% of these combinations (#1, #2, #5, #17, and #22) showed a statistically significant increase. There were 12 combinations that exhibited decreases in the BT, but only 7 of them had decreases greater than 20%, and only 33% of these combinations (#7, #18, #19, and #24) showed a statistically significant decrease. Overall, the available mean BTs increased 9% when comparing the beginning and ending cycles. For the SSPRs, five of them showed increased values (two of them had increases greater than 20%) but none of the differences was statistically significant. Ten of the SSPRs showed decreased values, but only 40% of these combinations (#1, #8, #11, and #13) showed a statistically significant decrease. In general, SSPRs decreased with increasing cycles, with an average decrease of 2%.

Detergent Decontamination

Thirteen of the 26 combinations with detergent decontamination were able to undergo all 11 cycles. More material

TABLE IV. BT and SSPR Means at the Beginning and Ending Cycles

Combination	Thermal Decontamination						Detergent Decontamination					
	BT, min			SSPR, $\mu\text{g}/\text{cm}^2/\text{min}$			BT, min			SSPR, $\mu\text{g}/\text{cm}^2/\text{min}$		
	Begin	End	Change %	Begin	End	Change %	Begin	End	Change %	Begin	End	Change %
1	103.0 (13.1)	285.7 (63.2)	177.4	1.25 (0.12)	0.98 (0.11)	-21.6	170.0 (18.0)	354.3 (2.9)	108.4	0.78 (0.06)	0.70 (0.08)	-10.3
2	155.0 (21.8)	260.7 (30.5)	68.2	4.16 (0.39)	4.03 (0.40)	-3.1	131.7 (16.1)	260.3 (44.2)	97.6	5.53 (0.36)	2.10 (0.35)	-62.0
3 (T10) ^A	19.3 (1.9)	20.1 (*,*) ^B	4.1	7.09 (0.31)	25.1 (*,*) ^B	254.0	16.8 (1.3)	15.0 (0.0)	-10.7	7.82 (0.60)	6.82 (0.11)	-12.8
4 (T9) ^A	20.0 (4.1)	29.7 (*,*) ^B	48.5	0.80 (0.05)	5.13 (*,*) ^B	541.3	21.3 (1.2)	12.9 (1.7)	-39.4	1.07 (0.03)	1.54 (0.14)	43.9
5	68.3 (10.4)	138.3 (25.2)	102.5	1.09 (0.31)	1.09 (0.56)	0.0	65.0 (5.0)	46.7 (7.6)	-28.2	0.66 (0.05)	0.86 (0.03)	30.3
6 (T1, D1) ^A	72.0 (2.6)	NAC		ND ^D	NAC		114.7 (9.6)	ND ^D		NAC	NAC	
7 (D1) ^A	165.0 (18.0)	130.0 (15.0)	-21.2	BMD ^E	BMD ^E		178.3 (18.9)	78.3 (37.5)	-56.1	BMD ^E	BMD ^E	
8 (D8) ^A	123.3 (2.9)	116.7 (2.9)	-5.4	17.16 (1.54)	8.06 (0.09)	-53.0	103.3 (10.4)	90.0 (18.0)	-12.9	15.83 (0.34)	9.61 (0.17)	-39.3
9 (D10) ^A	176.7 (20.8)	175.0 (5.0)	-1.0	7.39 (0.38)	BMD ^E		186.7 (7.6)	153.3 (7.6)	-17.9	7.32 (0.32)	5.83 (0.16)	-20.4
10 (T2, D3) ^A	437.5 (38.9)	443.3 (37.5)	1.3	ND ^D	ND ^D		391.7 (27.5)	460.0 (0.00)	17.4	ND ^D	ND ^D	
11	81.7 (2.9)	81.7 (2.9)	0.0	10.83 (0.42)	7.83 (1.68)	-27.7	53.3 (5.8)	43.3 (2.9)	-18.8	12.7 (0.87)	8.63 (0.25)	-32.0
12 (D1) ^A	246.7 (36.9)	273.3 (20.2)	10.8	BMD ^E	BMD ^E		236.7 (24.7)	NAC		BMD ^E	NAC	
13	16.7 (1.5)	14.5 (2.1)	-13.2	25.63 (0.21)	17.60 (0.30)	-31.3	16.7 (1.5)	33.3 (10.4)	99.4	25.50 (1.11)	14.90 (0.10)	-41.6
14 (T2, D2) ^A	84.7 (2.1)	NAC		ND ^D	NAC		66.3 (3.8)	NAC		ND ^D	NAC	
15	21.0 (1.7)	19.3 (14.2)	-8.1	14.00 (0.36)	12.67 (0.42)	-9.5	16.0 (7.8)	19.7 (1.5)	23.1	13.77 (0.40)	12.70 (0.40)	-7.8
16	13.7 (0.6)	10.3 (7.2)	-24.8	19.63 (0.55)	19.63 (0.67)	0.0	14.0 (1.8)	8.3 (7.2)	-40.7	19.00 (0.35)	18.13 (0.86)	-4.6
17 (D10)	178.3 (2.9)	230.0 (5.0)	29.0	BMD ^E	BMD ^E		221.7 (5.8)	75.0 (113.0)	-66.2	0.15 (0.02)	BMD ^E	
18 (T7, D1) ^A	120.0 (0.0)	12.3 (2.5)	-89.8	6.43 (0.12)	6.60 (0.14)	2.6	113.3 (2.9)	NAC		6.60 (0.30)	NAC	
19 (D9) ^A	29.3 (0.6)	11.3 (6.5)	-61.4	46.20 (0.82)	49.47 (3.61)	7.1	30.0 (1.0)	20.3 (12.4)	-32.3	44.50 (1.18)	40.5 (2.10)	-9.0
20	51.7 (55.8)	75.0 (*,*) ^B	45.1	1.57 (2.02)	1.40 (*,*) ^B	-10.8	85.0 (31.2)	65.0 (5.0)	-12.5	0.90 (0.70)	5.00 (7.02)	455.6
21	80.0 (8.7)	121.7 (32.1)	52.1	20.50 (0.79)	21.00 (0.67)	2.4	55.0 (8.7)	48.3 (2.9)	-12.2	21.1 (4.33)	34.4 (2.62)	63.0
22	163.0 (1.7)	327.0 (60.2)	100.6	0.41 (0.03)	0.40 (0.00)	-2.4	140.0 (6.2)	91.0 (4.6)	-35.0	0.26 (0.02)	0.25 (0.04)	-3.8
23	60.0 (99.0)	45.0 (4.2)	-25.0	0.16 (0.02)	0.16 (0.01)	0.0	60.0 (5.2)	51.0 (0.0)	-15.0	0.19 (0.02)	0.16 (0.00)	-15.8
24 (D9) ^A	121.0 (6.2)	58.0 (3.5)	-52.1	34.90 (0.00)	30.40 (0.72)	-12.9	60.0 (32.4)	25.0 (7.5)	-58.3	22.53 (19.12)	35.23 (0.68)	56.4
25 (D9) ^A	112.0 (18.1)	108.0 (62.6)	-3.6	30.77 (1.42)	26.50 (0.40)	-13.9	80.0 (20.8)	76.0 (20.0)	-5.0	30.50 (1.93)	35.73 (2.93)	17.1
26 (D1) ^A	384.0 (24.6)	222.0 (229.9)	-42.2	BMD ^E	BMD ^E		452.0 (38.6)	NAC		BMD ^E	NAC	

Note: Numbers in parentheses represent the standard deviations. Percentages in **bold** indicate that the changes were statistically significantly different ($p < 0.05$).

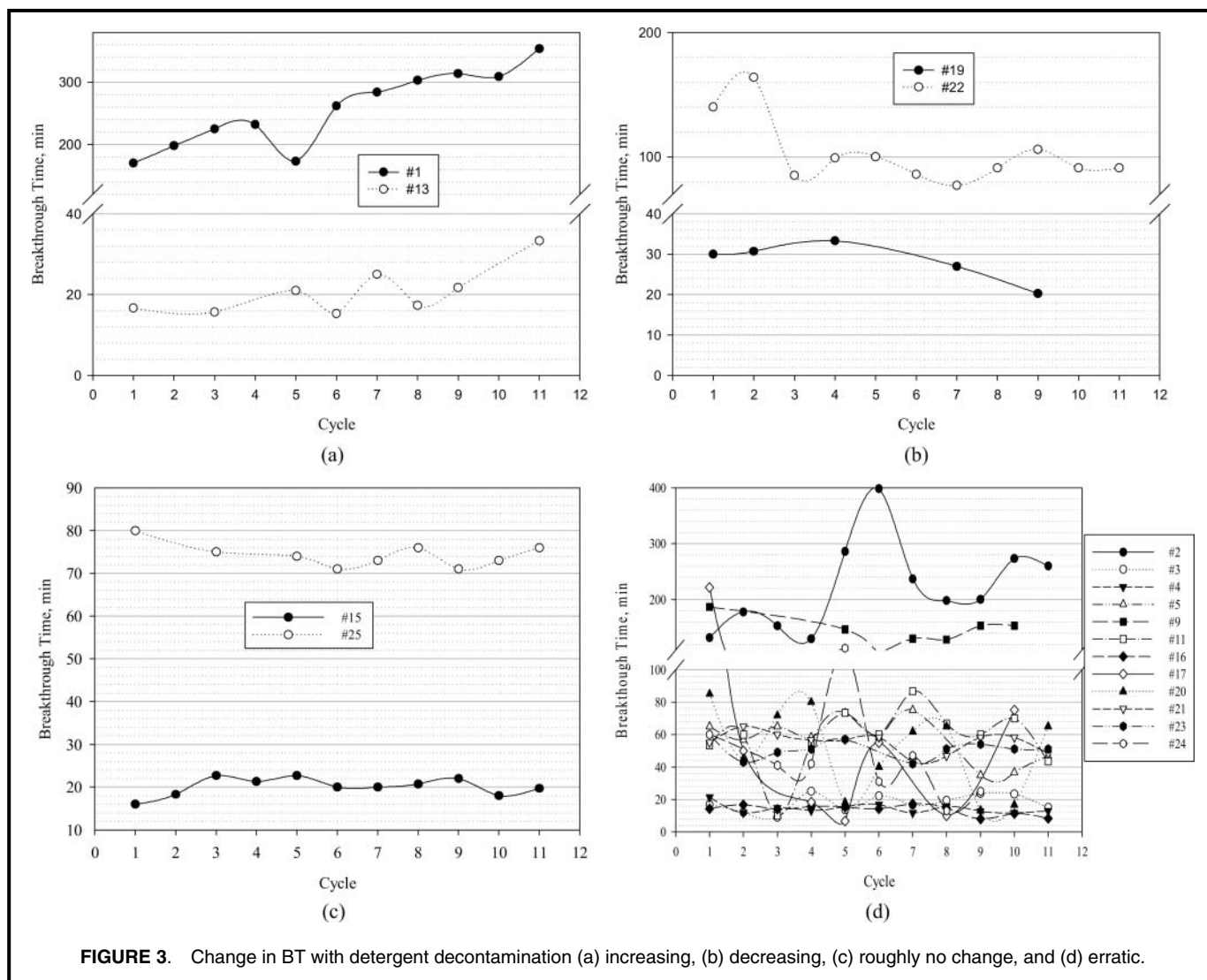
^AInformation in parentheses below a specific combination ID number represents the ending cycle number if the material failed prior to 11 cycles. For instance, (T2, D3) means that the material failed after completing two cycles for the thermal decontamination method and 3 cycles for the detergent decontamination method. Those without parentheses were able to complete 11 cycles.

^BStandard deviation not calculated as only one sample left at the ending cycle.

^CNAC = Not available due to material failures caused by the exposed chemicals or decontamination methods.

^DND = Not determined because required condition not achieved to allow calculation.

^EBMD = Below minimum detection of the SSPR between 0.03 and 0.08 $\mu\text{g}/\text{cm}^2/\text{min}$.

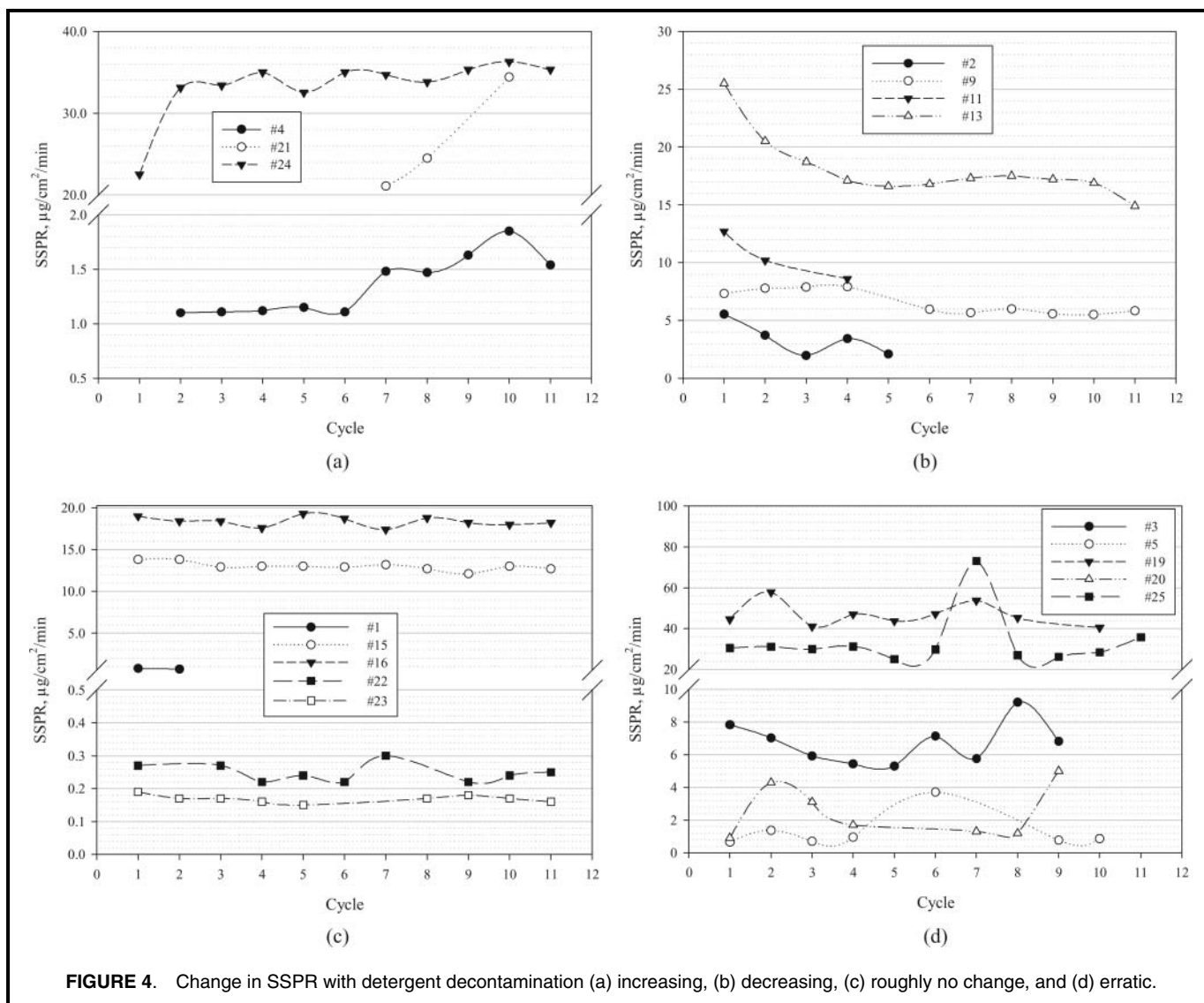


failures prior to Cycle 11 were found with the detergent decontamination than with the thermal decontamination (Table IV). As stated above, the material degradation for Combinations #6 and #14 is believed to be caused by the chemical exposure to concentrated sulfuric acid. As for Combination #10, the fact that the material (Stanzoil chemply N-440 neoprene glove) failed quickly for both the thermal and detergent methods (after 2 or 3 cycles) may be due to the methanol challenge chemical. Material failures for the rest of the combinations were probably due to either incomplete decontamination or the synergistic effect of the chemicals and the detergent, plus the heating at 90° for 25 min at the end of the detergent decontamination.

Figure 3a–d shows the change in the BTs against exposure/decontamination cycle for the combinations that underwent at least nine cycles with four different types of behavior, respectively. Two of them showed a trend of increasing BT values with increasing cycle, and another two exhibited the opposite tendency. The BT values of two other combinations were approximately constant over the cycles. Erratic BT values

over the cycles were observed for the rest of the combinations. It was observed that the BTs for Combination #1 increased, Combination #19 decreased, and Combination #25 consistently remained fairly constant for both decontamination methods. Furthermore, the BTs for combinations #5, #9, #20, #21, #23, and #24 were erratic for both decontamination methods.

The change in the SSPR values is shown in Figure 4a–d. The SSPRs for a few combinations are not included, as the values were below the minimum detection rates. The behaviors for Combinations #15, #16 (roughly no change), and Combination #20 (erratic) were consistent with the two different decontamination methods, while the remaining combinations were not. Some correlations of the behaviors between BT and SSPR were observed when comparing Figures 3 and 4. For instance, Combination #13 had an increase in BT with a decrease in SSPR, Combination #15 had approximately constant BT and SSPR over the cycles, and Combinations #3, #5, and #20 had both erratic BT and SSPR. For the remaining combinations, behaviors between BT and SSPR did not correlate. There were two combinations (#16 and #23)



that exhibited erratic BT values but had approximately constant SSPRs over the cycles. Similar to the thermal decontamination, there were more combinations that had erratic BT than erratic SSPR.

The beginning and the ending mean BT and SSPR values for the combinations with detergent decontamination can be found in Table IV. Sixteen out of the 21 combinations (76%) showed a decrease in the BTs, while 8 of them had decreases greater than 20%, but only 19% of the 16 combinations (#4, #5, and #22) showed a statistically significant decrease (paired t-test, $p < 0.05$). The other combinations exhibited increases in the BT, of which two combinations (#1 and #2) showed a statistically significant increase. Overall, the mean BT of the 21 combinations decreased 3.3%. For the SSPRs, six of the combinations (29%) showed increased values (five of them had increases greater than 20%) but only three of the changes (Combinations #5, #21, and #25) were statistically different. Twelve of the SSPRs (57%) showed decreased values, seven of which showed the decreases were statistically significant.

In general, SSPRs increased with increasing cycles, with an average increase of 1.4%.

Comparison of the Two Decontamination Methods

The BTs and SSPRs of the last cycles of the two decontamination methods were compared using 18 combinations that had BTs available and 14 combinations that had SSPRs available in both thermal and detergent methods (Table IV). The t-test was used to compare the BTs or SSPRs, of the last cycle, between the two decontamination methods on the same combination ID. Results indicated that the differences in the BTs were statistically significant for 33% of the combinations (#5, #9, #11, #21, #22, and #24), and the differences in the SSPRs, between the two decontamination methods, were statistically significant for 64% of the combinations. The combinations for which the SSPR was not significantly different were #11, #15, #16, #23, and #24. The mean BT of the last cycle for the thermal method was 31.8% higher than those with the

detergent method, while the mean SSPR of the last cycle for the thermal method was 6.3% lower than those for the detergent method. Because of the missing data points and the detection limit of the analytical method, the comparisons used 18 and 14 combinations for BT and SSPR, respectively.

The fact that the mean BT increased and SSPR decreased with increasing exposure/decontamination cycles, when using the thermal method, may indicate that some new CPC materials might not be cured correctly. Additional heat may cause more curing and crosslinking of the materials; thus, the material becomes more resistant to permeation. In contrast, the fact that the mean BT decreased and SSPR slightly increased with increasing exposure/decontamination cycles, when using the detergent method, could be associated with the plasticizers that were added to the polymer being dissolved by the detergent used. Since the plasticizers may not be covalently bonded with the polymer, dissolution or evaporation of the plasticizers happens mainly during the first exposure/decontamination cycle; thus, a greater loss of the permeation resistance was observed.

Although CPC has been marketed in three categories as stated earlier, the category could change depending on the challenge chemical. For instance, Neoprene was single-use when exposed to 95% sulfuric acid (Combination #6), but could undergo up to 11 cycles when exposed to methanol (Combination #5). Overall, there were 10 combinations that were able to complete up to 11 cycles by using either decontamination method (Table IV). Of them, four combinations (#1, #2, #5, and #22) showed statistically significant differences in BTs between the 1st and the 11th cycles. On the other hand, there were six combinations (#11, #13, #15, #16, #21, and #23) that did not show statistically significant differences in BTs between the 1st and the 11th cycles, indicating good multiple-use potential. Note that this was simply based on the changes in the BTs. To further evaluate the reusability, changes in physical properties of CPC materials should be assessed.⁽²⁾

The limitations of this study include relatively high variations obtained for some replicate measurements that could affect the statistical analyses. In addition, there were a few missing data points due to material damages as a result of severe degradation. Selection of the material-chemical combinations should have been based not only on the BTs but also material degradation data. In fact, both decontamination methods appeared to damage certain CPC materials. For thermal decontamination, a recent study showed that heating at either 70° or 100° for 10 hr appeared to be appropriate for neoprene gloves.⁽¹⁵⁾

SUMMARY AND CONCLUSIONS

This study evaluated the performance of 14 CPC materials against 12 liquid chemicals, based on changes in BT and SSPR. Two decontamination methods, thermal and detergent, were used. Exposure/decontamination was repeated

up to 11 cycles or until the material failed. Changes in the BT and SSPR were determined and then compared. There were more materials that could complete up to 11 cycles using the thermal method than those using the detergent method (20 vs. 13). Eleven combinations were able to undergo 11 cycles using either decontamination method. After repeated exposure/decontamination cycles, the thermal method resulted in a longer mean BT value with a slightly smaller mean SSPR, while the detergent method exhibited the opposite tendency. Thermal decontamination seems to remove the contaminated chemicals more effectively for most of the combinations. Multiple reuse of some CPC could be safe if effective decontamination methods are used to ensure that CPC still functions correctly and the materials do not fail after decontamination.

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