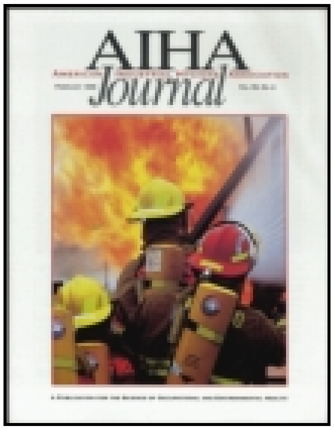

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Using Immersion Test Data to Screen Chemical Protective Clothing*

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A test to screen chemical protective materials in order to select potential candidates for further testing has been examined. The method involved determining the weight and volume changes in materials caused by immersion in the challenge chemical. Simple regression analysis showed that relatively short breakthrough times based on weight change and final thickness could be predicted with 90% confidence. Better results were obtained when discriminant analysis was used to classify breakthrough times greater than either 4 or 8 hr as a function of the weight change and final thickness. In 6% or less of the cases, actual breakthrough times were less than 4 or 8 hr when the predicted times were greater than these values. Discriminant analysis also was used to classify permeation rates as less than either 90 or 400 mg/m^2-min based on weight change and initial thickness. In this case, actual permeation rates less than these were predicted to be greater in 4% and 7% of the cases, respectively.

Introduction

Clothing protects a wearer from dermal and systemic toxins by interposing a barrier between the challenge and the individual. This barrier can fail by penetration of the chemical through openings—such as closures, seams, valves, pinholes, or tears—or by permeation of the chemical through the material itself. The first process, penetration, is a property primarily of the mechanical design, fabrication, and physical properties of the garment material. The second process, and the one of interest here, permeation, is primarily a function of the chemical properties of the challenge chemical and the garment material; that is, solution of the challenge, diffusion through the material, and then desorption.

In both the industrial and military environments there are a large number of hazardous chemicals, and solutions of these chemicals, from which protection may be needed. For each chemical or chemical mixture used in workplaces, there may be a number of specific chemical protective clothing (CPC) materials which would provide worker protection and a number which would not. Experimentally determining which would protect workers best is impractical without some method of screening the products to select a small group of candidates which feasibly might be tested. Currently, published permeation data for generic material classifications typically are used to determine possible candidates for further testing. Recent research, however, has suggested that chemical resistance characteristics of CPC materials bearing the same generic name may vary widely among individual manufacturers.(1) Perhaps this also may be true between lots from the same manufacturing facility. Further, most existing permeation data were obtained for materials challenged by pure chemicals and would be inappropriate for use in selecting candidate materials for use against chemical mixtures. Therefore, a screening method which reasonably could predict the chemical resistance of the actual material against the actual challenge chemical or mixture, based on existing information if possible, would be a superior method. Actual selection of CPC products from the group of candidate materials should be based on testing the specific manufacturer's products against the specific challenge chemical or mixture under use conditions.(2,3) Both laboratory(4,5) and field(6,7) methods for permeation testing have been presented elsewhere.

Methods

It is most often assumed that permeation is a three step process: (1) the challenge dissolves in the upstream side of the membrane, (2) diffuses through the membrane, and (3) is lost from the downstream side of membrane. From diffusion theory:

$$J = -D\frac{\partial c}{\partial x} \quad \textbf{(1)}$$

where J = flux through the material;
D = diffusion coefficient; and
$\partial c/\partial x$ = linear concentration gradient of challenge in the material.

A common assumption is that the upstream side is saturated with challenge while the concentration in the downstream side is zero. The concentration gradient through the membrane, $\partial c/\partial x$, then can be approximated by C_s/ℓ, where C_s is the saturation concentration and ℓ is the material thickness.

Based on this dependence of permeant flux on concentration gradient, a screening test (based on a measurement of the solubility of the challenge in the material and a material thickness) was tested. For a truly quantitative test, as indicated by Equation 1, the diffusion coefficient should be known also. The authors' goal, however, is a simple screening test, and currently, no simple way to estimate the diffusion

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coefficient is known. Further, the test need not predict breakthrough time or permeation rate exactly. It would be sufficient to indicate those materials which probably are not adequate for the job or those which should be considered further.

The approach was to use actual solubilities (determined from measured changes in weight, volume, or both) of the material when it was soaked in the challenge to predict permeation rate and breakthrough time. Breakthrough time is the time at which challenge first appears on the downstream side of the membrane.

To examine this approach, data were used that had been compiled by Arthur D. Little, Inc., in developing the *Guidelines for the Selection of Chemical Protective Clothing.*[8] These were for nonlaminated and noncomposite materials. In this database, usable data for 13 materials and 75 challenge compounds were found. The number of data points available for any one correlation depended upon the existence of values for the required variables for that specific correlation.

Results and Discussion

1. Regression Analyses

A linear regression analysis model was used to investigate correlations using the experimentally measured values as reported in the Guidelines.[8] The dependent variables investigated were the breakthrough time and permeation rate and the logs of these quantities. The independent variables were the volume and weight changes, number of moles absorbed calculated from the weight change and molecular weight, initial and final thickness, and the logs of all of these values. Final thickness was calculated from the reported initial thickness and percent volume change according to the equation:

$$\ell_f = \ell_I (1 + \Delta V/100)^{1/3}$$

where ℓ_f = final thickness;

ℓ_I = initial thickness; and

ΔV = percent volume change.

The best breakthrough time correlations are obtained when logarithmic functions are used with the final thickness and either the weight change or number of moles absorbed. This latter quantity is calculated from the weight change. A correlation using a quadratic function of these two variables also was tried but did not improve the fit to any useful extent. The results of the linear regression, shown as the final thickness and weight change corresponding to four different breakthrough times, are shown in Figure 1 for the 90% confidence level. This figure can be used to determine, at the 90% confidence level, the minimum final thickness and maximum weight change a material may exhibit, after an immersion test, to give a breakthrough at least as long as shown. For example, in a given situation, it is determined protection must be afforded for 30 min. If, after an immersion test, the final thickness is 0.050 cm, the corresponding weight change may be no greater than 25%. While the data from which these relationships were developed do not allow a time for the immersion test to be specified, 8 hr is probably the minimum.

The best correlation of permeation rate was with weight change and initial thickness. There is little utility to be gained, however, in using this regression, as the minimum rate which can be predicted with 90% confidence is approximately 500 mg/m^2-min.

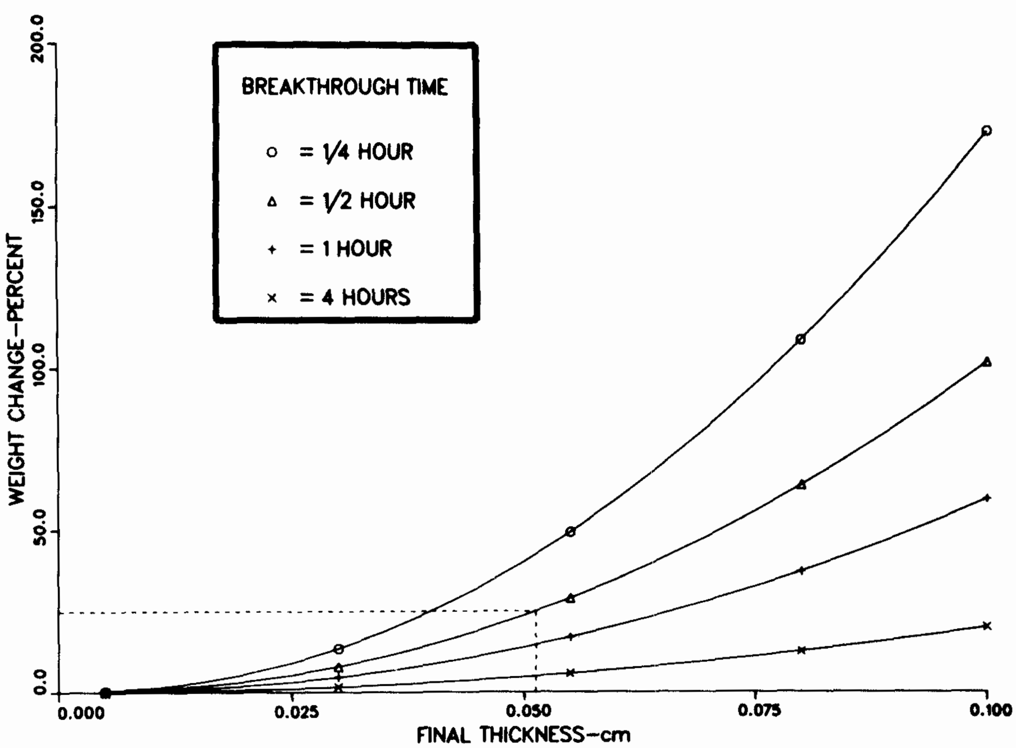

Figure 1—Breakthrough time as a function of weight change and final thickness

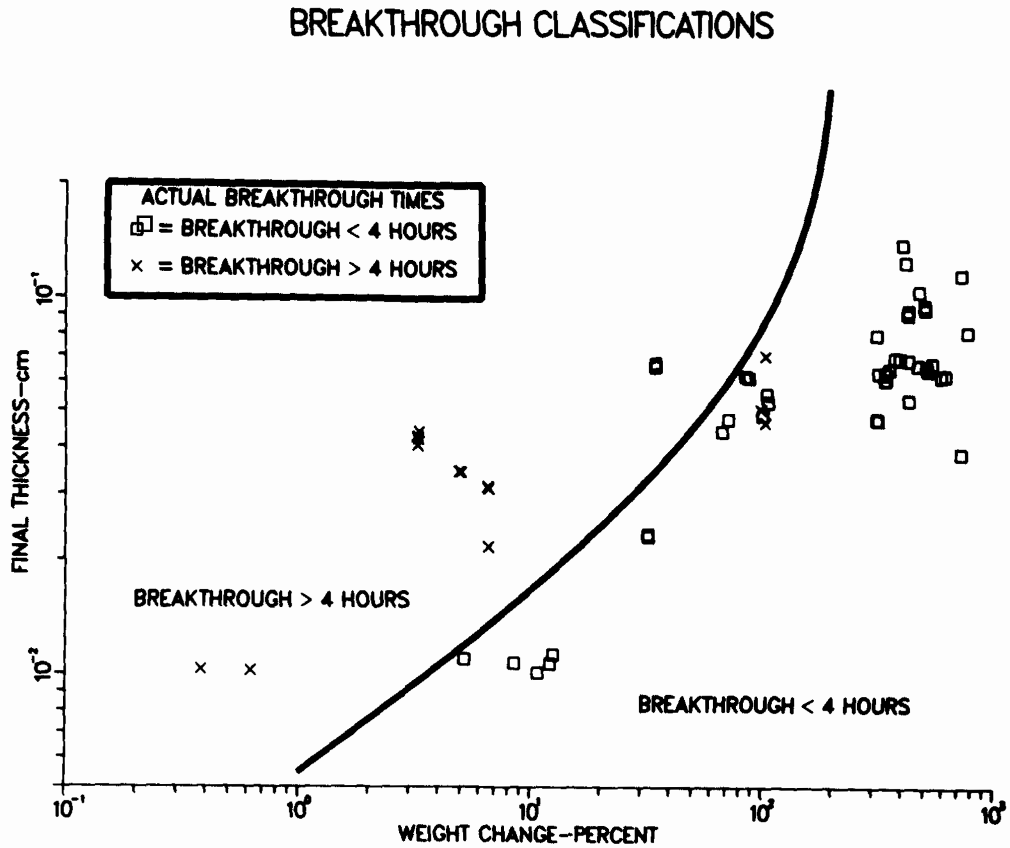

Figure 2—Breakthrough time classifications

2. Discriminant Analysis

Another screening test using discriminant analysis can be developed where observations based on independent variables are classified as being either greater or less than a preselected discriminant value. For example, suppose interest centers on the classification of breakthrough times as greater or less than 4 hr as a function of two independent variables. Figure 2 shows such a scheme where data from two independent variables, the final thickness and the weight change, are plotted with two symbols denoting the two classifications of breakthrough times. The crosses are for breakthrough times which were measured to be greater than 4 hr and the squares are for times less than this. Discriminant analysis is a procedure which splits this plot into regions. (For full details on this procedure see Morrison,[9] p. 130, or Cooley and Lohnes,[10] p. 134. In addition many commercial computer packages, such as SAS,[11] are available to do the computations.) One region corresponds to breakthrough times classified as less than 4 hr while the other is for breakthrough times greater than 4 hr. The curve in Figure 2 separates the plot into these two regions. To discover on which side of this line an observation resides, one evaluates a quadratic in the two variables. If the result of this calculation is negative, the breakthrough time is classified as less than 4 hr. If positive, the breakthrough time is classified as greater than 4 hr.

For 4-hr breakthrough times, corresponding to Figure 2, the quadratic function (DF) of log final thickness (LFT) and log % weight change (LWTCH) is given by the following:

$$\mathrm{DF} = 4.4767(\mathrm{LWTCH})^2 - 9.3866(\mathrm{LWTCH})(\mathrm{LFT}) - 40.0844(\mathrm{LWTCH}) - 4.8550(\mathrm{LFT})^2 + 19.1704(\mathrm{LFT}) + 68.2381.$$

The constants used in this calculation are shown in Table I, Section (1).

As an example of the use of the above equations as a screening test, suppose a material immersed in a challenge solution demonstrated a weight change of 100% (LWTCH = 2) and a final thickness of .02 (LFT = −1.7). DF would be calculated to be −8.7, and hence, the predicted breakthrough time would be classified as less than 4 hr. If the weight change were 1% (LWTCH = 0) with the same final thickness, DF would be 21.6. This observation would be classified as a breakthrough time greater than 4 hr since DF is positive.

From Figure 2 it is apparent that some of the observations are misclassified by this approach. Based on the final thickness and weight change, 5% of the observations whose actual breakthrough times were less than 4 hr were classified as being greater than 4 hr. Conversely, 6% of those classified as being greater than 4 hr were actually less than this.

Table II is a tabulation of the discriminant analyses results for breakthrough time. The top section is for the same data as that shown in Figure 2. The top row shows that of the breakthrough times measured to be less than 4 hr, 95% were classified correctly as less than 4 hr and only 5% were classified incorrectly. Of the breakthrough times which were actually greater than 4 hr, 79% were classified correctly and 21%

were classified incorrectly. In practice the longest possible breakthrough time is desired, so those data where the breakthrough time was classified as greater than 4 hr will be considered. The top right hand corner shows that only 5% of those with measured breakthrough times less than 4 hr were classified as having breakthrough times greater than this. Subjecting these materials to additional testing would have provided a high success ratio. The lower left corner, however, shows that of those with measured breakthrough times of greater than 4 hr, 21% were incorrectly classified and would have been discarded from further consideration.

The lower part of Table II gives the results when the discriminant value is increased to 8 hr. In this case 6% of those with measured breakthrough times less than 8 hr were classified wrongly.

The results for permeation rates with discriminant values of 90 or 400 mg/m^2-min, based on initial thickness (IT) and weight change (WTCH), are shown in Table III. In practice, the smallest possible rate is desired, so those values classified as less than 90 or 400 mg/m^3-min will be examined. For 90 mg/m^2-min, the upper left corner shows that 96% of those which actually exhibited rates less than 90 would have been candidates for further testing. Only 4% would have been discarded. As shown by the bottom left corner, however, about half of those with actual rates over 90 also would have been chosen for further testing. Thus, while most of the good materials would have been identified, a number of inadequate ones also would have been subjected to additional testing.

TABLE I
Discriminant Functions

(1) **Breakthrough time > 4 hr**

$$4.4767(LWTCH)^2 - 9.3866(LWTCH)(LFT) - 40.0844LWTCH - 4.8550(LFT)^2 + 19.1704LFT + 68.2381$$

If function is (−) then < 4 hr, if (+) > 4 hr

(2) **Breakthrough time > 8 hr**

$$2.0569(LWTCH)^2 - 5.0302(LWTCH)(LFT) - 29.9805LWTCH - 3.9828(LFT)^2 + 20.7375LFT + 65.9143$$

If function is (−) then < 8 hr, if (+) > 8 hr

(3) **Permeation rate < 90 mg/m^2-min**

$$898.3663(IT)^2 + .2348(IT)(WTCH) - 93.9226\,IT - 0.0003538(WTCH)^2 + 0.003318WTCH + 5.3178$$

If function is (−) then < 90 mg/m^2-min, if (+) > 90 mg/m^2-min

(4) **Permeation rate < 400 mg/m^2-min**

$$2443.8044(IT)^2 + 0.01547(IT)(WTCH) - 149.0806IT - 0.0002113(WTCH)^2 + 0.004932WTCH + 4.9126$$

If function is (−) then < 400 mg/m^2-min, if (+) > 400 mg/m^2-min

TABLE II
Discriminant Analyses
Breakthrough Time—Probabilities
(Percent)[A]

Measured	Classification[B]	
	Time < 4 hr	**Time > 4 hr**
Time < 4 hr	95	5
Time > 4 hr	21	79
	Time < 8 hr	**Time > 8 hr**
Time < 8 hr	94	6
Time > 8 hr	9	91

[A]58 data points
[B]Independent variables: logarithms of the weight change and final thickness

While discriminant analysis obviously does not allow one to pick materials with absolute certainty, it should markedly reduce the number of permeation tests needed to find materials which will afford protection against a given challenge. The quadratic functions for predicting breakthrough times and permeation rates are given in Table I. For each of these equations, the proper interpretation of the sign of DF (+ or −) is given.

Conclusions

Using the weight and volume changes which occur when a material is immersed in a challenge liquid, it is possible to predict breakthrough times less than about 1 hr with 90% confidence. Only permeation rates greater than about 500 μg/m^2-min could be predicted with this same confidence.

A useful screening test using discriminant analysis and these same weight and volume changes also is described. With discriminant analysis it is estimated that 6% or less of the time predicted breakthrough times would be greater than 4 or 8 hr when the measured time was less than 4 or 8 hr, respectively. Predicted permeation rates greater than 90 or 400 mg/m^2-min were measured to be less than these values 4% and 7% of the time, respectively. By measuring the initial thickness and then the weight change and final thickness of a sample of the material after immersing it in a challenge, and by using the discriminant functions in Table I, the probabilities of breakthrough times being greater than 4 or 8 hr and permeation rates being less than 90 or 400 mg/m^2-min can be estimated. On the basis of these probabilities and the actual level of protection required, a decision can be made about which materials should undergo additional testing.

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TABLE III
Discriminant Analyses
Permeation Rate—Probabilities (Percent)[A]

Measured[C]	Classification[B]	
	Rate < 90	**Rate > 90**
Rate < 90	96	4
Rate > 90	45	55
	Rate < 400	**Rate > 400**
Rate < 400	93	7
Rate > 400	27	73

[A]190 data points
[B]Independent variables: weight change and initial thickness
[C]mg/m^2-min

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