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PERSONAL PROTECTIVE EQUIPMENT FOR HAZARDOUS MATERIAL SPILL SITUATIONS

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Introduction

The use of personal protective equipment is extremely important in spill situations because response personnel face exposure to chemicals that could cause serious injury or illness and even death. The unknown physical environment of a spill site and its multiple hazards distinguish such incidents from either spills in the laboratory or exposure to chemicals in the workplace. Spill responders entering a site cannot always predict what chemicals or concentrations they will encounter and what other hazards may be present.

Preventing exposure to toxic chemicals is a primary concern at spill sites. Substances can enter the unprotected body by inhalation,

ingestion, and permeation. Ingestion can occur when contaminants are absorbed during eating or smoking or by other forms of contact with the mouth. Some chemicals readily pass through the skin in a process known as permeation.

Clothing and respirators are the most common types of protective equipment required for spill response. Totally encapsulated

chemical protection suits (TECPS) or gas-tight suits are used when the contaminant is unknown or when skin-permeating or skin-attacking chemicals are present. The self-contained breathing apparatus (SCBA) provides the highest protection against the inhalation of chemical contaminants and is the most commonly used form of respiratory protection in the initial phases of a spill.

A NOTE TO OUR READERS

As you will probably have noticed, production of the Spill newsletter has been suspended for two years. We are preparing to post the newsletter on our website and will stop producing a paper copy. In the meantime, we're mailing out a few more issues in the "old fashioned" way. This is the first of these catch-up issues.

Merv Fingas

There are few standards and guidelines for selecting and using personal protective equipment for chemical spill cleanups. Most standards are written for use in the workplace and may require modification for emergency situations. This article is an updated review of the types of personal protective equipment required by those who respond to accidental chemical spills that occur away from the workplace. It looks at the different levels of response for chemical spills, the chemicals most often spilled, the type of protective clothing and respirators available, factors to consider in selecting protective equipment, and the basic components of a chemical spill response program.



A response team assesses a burned-out chemical warehouse using Level A.

Response Levels

The response levels used in North America are commonly accepted among spill response organizations including Environment Canada, the U.S. Environmental Protection Agency, and the U.S. Coast Guard. Gloves and boots are used throughout the first three protection levels.

Level A is the first-response or entry level. Totally encapsulated suits and self-contained breathing apparatus are used to protect against high or unknown levels of chemicals such as acids that may permeate or otherwise attack the skin.

Level B response involves the use of SCBAs with liquid-tight chemical-protection clothing or "splash" gear as it is sometimes known. Level B gear is used to enter a site where it is known that no skin-permeating or skin-attacking chemicals are present, or where high levels of

contaminant may be present that a standard air-purifying device would not protect against. There is a variety of acceptable options, but the clothing usually consists of a special water-tight suit or water-tight rain gear.

Level C response includes respirators and standard protective clothing, which typically consists of liquid-repellant coveralls made of polypropylene or treated cellulose fabrics, which are proving more comfortable than Tyvek. Cleanup crews often use this level of response when the situation has stabilized and chemical concentrations are known and are not likely to rise above the capability of the respirator. No skin-permeating or skin-attacking materials are present.

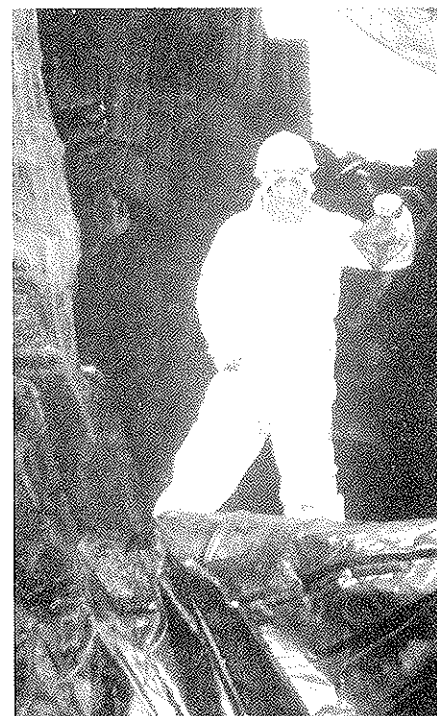
Level D response applies to spill sites where there are no airborne contaminants of concern and there is a minimal likelihood of harm by contact with the spilled material.

This would be the response level at many contaminated sites. Many organizations provide treated cotton coveralls or similar garb for working in such frequently occurring situations.

Frequently Spilled Compounds

When selecting protective equipment, the most important consideration is the target chemical. While it is not possible to be prepared for all types of chemical spills, it is possible to be prepared for the most frequently spilled chemicals.

Some common chemicals spilled from 1990 to 1999 and the frequency and volume of spills are listed in Table 1 (Fingas et al., 2002).



A worker using Level C response retrieves a label from a chemical drum.

Table 1 Frequently Spilled Substances (from 1990 to 1999)

Chemical	Number of Spills	Spill Volume (t)
Sulphuric acid	506	5310
Hydrochloric acid	377	770
PCBs	367	21
Ethylene glycol	349	200
Sodium hydroxide	339	4000
Ammonia	225	180
Nitric acid	134	24
Chlorine	124	31
Ammonium hydroxide	123	690
Sulphur	114	6600
Ammonium nitrate	98	1500
Methanol	80	1300
Sodium hypochlorite	78	50
Freon	73	14
Phosphoric acid	66	64
Mercury	65	103
Ethylbenzene	58	150
Toluene	58	100
Calcium chloride	52	500
Aluminum sulphate	52	223
Sodium chlorate	52	134
2,4-D	51	14
Benzene	50	88
Phenol	47	287
Naphtha	47	33
Ferric chloride	47	23
Ethanol	45	350
Chromic acid	45	39
Vinyl chloride	42	84
Xylenes	42	82
Formaldehyde	41	47
Hydrogen peroxide	40	96
Styrene monomer	36	75
Sodium chloride	35	4060
Calcium oxide	34	536
Nitrogen	32	214
Calcium carbonate	27	268
Maleic anhydride	27	6
Trichloroethane	27	1
Isopropanol	26	12
Halon	26	1
Urea	25	138
Potassium hydroxide	25	14
Sulphur dioxide	24	6
Glyphosate	24	3
Ammonium sulphate	23	22
Potassium chloride	22	9190
Sodium dichromate	21	21
Calcium hypochlorite	21	19
Hydrofluorosilicic acid	20	101

Canada has a national database which has been maintained for a number of years (Beach, 1982; Fingas, 1996). Such a database is useful in assessing priorities. Looking at total spills, only about 40 materials have been spilled more than 10 times and about 150 materials have been spilled more than 3 times. The data show that about 5% of the spills are single or one-time incidents with a low probability of repeat. About 90% of the incidents are spills of common industrial chemicals. Fifty substances account for about 80% of the spills and 100 substances for about 90% of the spills. Most spills are of high-volume production industrial chemicals while less common chemicals account for only a small number of spills.

A priority list of spill substances has been prepared using spill and toxicity data. A summary of the protection requirements necessary for the highest priority materials is provided in Table 2. The assessments are given in terms of whether self-contained breathing apparatus (SCBA) or encapsulated suits are required.

It is important to stress that the protection levels listed in the table are for typical spill situations. When chemicals and/or their concentrations are unknown or when working in enclosed or confined spaces, SCBAs and totally encapsulated suits must always be worn. Once chemical concentrations are known and the situation is under control, then lower levels of protection might be appropriate.

Overview of Equipment

A wide variety of respirators is available on the market. The two basic types of respirators are air-

Table 2 Specific Safety Concerns and Equipment Recommendations

Name	Health Exposure Limits					Maximum Use Capacity for Respirators ¹ (PPM)					Gas Mask	SCBA	Need TECPs under Normal Conditions? ²
	Significant Vapour at Normal Temperature	TLV (ppm)	TLV (mg/m ³)	STEL (ppm)	STEL (mg/m ³)	IDLH (ppm)	IDLH (mg/m ³)	Concern with Skin Contact	Canister half face	Regular Canister			
2,4-D		1	10			10	100		2	5	10	unlimited	
2-ethylhexanol									poss	poss	poss	unlimited	
Acetic acid	✓	10		15		50		corrosive	10	25	50	unlimited	c
Acetic anhydride	✓	5				200		corrosive	50	125	200	unlimited	c
Acetaldehyde	✓	100		150		2000			400	1000	2000	unlimited	
Acetone	✓	500		750		2500			500	1000	2500	unlimited	
Acetonitrile	✓	40		60		500			40	100	200	unlimited	
Acrylamide		0.01	0.03					permeation		escape only		unlimited	✓
Acrylonitrile	✓	2		10		85			20	50	85	unlimited	
Aldrin		0.02	0.25	0.05	0.75	2	25	absorbed	0.5	1	2	unlimited	
Aluminum chloride		2 (as aluminum salts or dust)							poss	poss	poss	unlimited	
Aluminum sulfate		2 (as aluminum salts or dust)							poss	poss	poss	unlimited	
Aminocarb									poss	poss	poss	unlimited	
Ammonia	✓	25		35		300			50	150	300	unlimited	
Ammonium chloride	as fume	5	10	9	20				10	25	50	unlimited	
Ammonium hydroxide	as ammonia								50	150	300	unlimited	
Ammonium nitrate									poss	poss	poss	poss	
Ammonium phosphates									poss	poss	poss	poss	
Ammonium sulfate									poss	poss	poss	poss	
Arsenic		0.003	0.01			1.5	5			escape only		unlimited	
Arsenic trioxide	as arsenic	0.003	0.01			1.5	5			escape only		unlimited	
Asbestos	fibre	0.1	fibres/cc						poss	poss	poss	poss	
Aniline		2				100		permeation	20	50	100	unlimited	
Atrazine		0.6	5						2	5	10	unlimited	
Avenge									poss	poss	poss	poss	
Azinphosmethyl		0.02	0.2			0.8	10	absorbed	0.2	0.4	0.8	unlimited	
Barium sulphate		1	10						poss	poss	poss	poss	
Benzene	✓	0.5		2.5		500		permeation	10	50	200	unlimited	c
Benzene hexachloride (Lindane)	0.04	0.5	0.1	1.5	4	50	absorbed	0.4	2	4	unlimited		
Benzoic acid									poss	poss	poss	poss	
Benzoyl chloride			ceiling	0.5		10			2	5	10	unlimited	
Biphenyl		0.2		0.6		16			2	8	16	unlimited	
2-Butanol		100		150		2000			200	1000	2000	unlimited	
Butyl acetate		150		200		1700			200	1000	1700	unlimited	
Butyl alcohol				25		1400			150	750	1400	unlimited	
Busan (2-bromo-4'-hydroxyacetophenone)								poss	poss	poss	poss	poss	
Calcium carbonate	dust		10						poss	poss	poss	poss	
Calcium chloride									poss	poss	poss	poss	
Calcium cyanide									poss	poss	poss	poss	
Calcium hydroxide		1.6	5						dust only	dust only	11	unlimited	
Calcium hypochlorite									poss	poss	poss	poss	
Calcium oxide		0.9	2	2	5	11	25		dust only	dust only	11	unlimited	
Calcium phosphate									poss	poss	poss	poss	
Caprolactam		5 vapour	1 (dust)	10 (vp)	3 (dust)				10	25	50	unlimited	
Carbaryl		0.6	5			12	100		2	6	12	unlimited	
Carbofuran		0.01	0.1						poss	poss	poss	poss	
Carbon black		7	3.5			3500	1750		700	1700	3500	unlimited	
Carbon dioxide	✓	5000		30000		40000			asphyxiant			unlimited	
Carbon disulphide	✓	10				500		permeation	10	25	50	500	✓
Carbon monoxide	✓	25		200		1200			100	500	1200	unlimited	
Carbon tetrachloride	✓	5		10		200		permeation	20	100	200	unlimited	
Carboxin									poss	poss	poss	poss	✓
Chlordane		0.03	0.5	0.1	2	6	100	absorbed	1	3	6	unlimited	
Chloroform		10				500				escape only		unlimited	
Chlorine	✓	0.5		1		10		corrosive	5	5	10	unlimited	✓
Chlorodifluoromethane	✓	1000		1250		2500			500	1500	2500	unlimited	
Chlorine dioxide		0.1		0.3			5		1	2.5	5	unlimited	
Chlorpyrifos		0.015	0.2					permeation			poss	poss	c
Chromic acid	as chromium		0.05					corrosive			poss	poss	c
Cobaltous nitrate	as cobalt		0.02								poss	poss	
Copper sulfate											poss	poss	
Creosote											poss	poss	
Cresol		5		10		250			25	125	250	unlimited	
Cyanides	✓	200		400		1300			250	700	1300	unlimited	
Demeton		0.1		0.3		0.9		absorbed	0.5	0.5	0.9	unlimited	
Diazinon		0.01	0.1	0.02	0.3			absorbed	0.2	0.5	1	unlimited	
Dicamba											poss	poss	
Diclofop-methyl											poss	poss	
1,2-dichlorobenzene		25		50		200			50	100	200	unlimited	
1,2-dichlorotetrafluoroethane	✓	1000		1250		15000		asphyxiant			unlimited		
Dichlorvos		0.10	0.9	0.3		11	100	absorbed	2	5	10	unlimited	
Dieldrin		0.016	0.25	0.05	0.75	3.16	50	absorbed	1	2	3	unlimited	
Diethanolamine		0.5	2					permeation	poss	poss	poss	poss	c
Diethylamine	✓	5		15		200		irritation	50	100	200	unlimited	c
Dimethoate											poss	poss	
Dimethylamine	✓	5		15		500			100	250	500	unlimited	c
Dinoseb									poss	poss	poss	poss	
Diethyl phthalate		0.3	5	0.6	10				poss	poss	poss	poss	
Diquat		0.03	0.5					absorbed	poss	poss	poss	poss	
Ethyl alcohol	✓	1000		5000		3300			400	2000	3300	unlimited	
Ethyl acetate	✓	400		1000		2000			1000	1500	2000	unlimited	
Ethyl acrylate	✓	5		15		300			50	150	300	unlimited	
Ethylamine	✓	5		15		600			100	250	500	unlimited	
Ethylbenzene	✓	100		125		800			150	400	800	unlimited	
Ethylene	✓	10000							asphyxiant only			unlimited	
Ethylene dichloride	✓	10		20		50			5	25	50	unlimited	
Ethylene glycol	✓	10		<16	<100	12	75		5	25	50	unlimited	
Ethylene oxide	✓	1				800				escape only		unlimited	
Fenitrothion									poss	poss	poss	poss	
Ferric (ous) chloride									poss	poss	poss	poss	
Ferric nitrate									poss	poss	poss	poss	
Ferric oxide									poss	poss	poss	poss	
Fluorescein									poss	poss	poss	poss	
Fluorine	✓	1		2		25				escape only		unlimited	✓
Formaldehyde	✓			<0.3		20			2	3	20	unlimited	
Formic acid	✓	5		10		30			5	15	30	unlimited	c
Freons	✓	~100				~2000				escape only		unlimited	
Glyphosate									poss	poss	poss	poss	
Halons	✓	~100				~2000				escape only		unlimited	
Hexane	✓	50		100		1100			not effective			unlimited	
Hydrazine	✓	0.01				50		limited usefulness			2.5	unlimited	c

	Health Exposure Limits					Maximum Use Capacity for Respirators ¹ (PPM)					NeedTECPS under Normal Conditions? ²		
	Significant Vapour at Normal Temperature	TLV (ppm)	TLV (mg/m³)	STEL (ppm)	STEL (mg/m³)	IDLH (ppm)	IDLH (mg/m³)	Concern with Skin Contact	Canister half face	Regular Canister			
Hydrochloric acid	✓	5				50		corrosive	10	25	50	unlimited	✓
Hydrofluoric acid	✓	3				30		corrosive	5	15	30	unlimited	✓
Hydrofluorosilicic acid								corrosive	poss	poss	poss	poss	✓
Hydrogen	✓												
Hydrogen chloride	✓	5				50		corrosive	10	25	50	unlimited	✓
Hydrogen peroxide	✓	1				75		corrosive	limited usefulness		75	unlimited	c
Hydrogen sulphide	✓	10		15		100			25	50	100	unlimited	
Isocyanates (eg. Toluene-2,4-diisocyanate)	✓	0.005		0.02		2.5		sensitizer	0.5	1	2.5	unlimited	
Isophthalic acid									poss	poss	poss	poss	
Isopropyl alcohol		400		500		2000			500	1000	2000	unlimited	
Lead sulphate			0.05 mg (as lead)						poss	poss	poss	poss	
Magnesium chloride									poss	poss	poss	poss	
Magnesium sulphate									poss	poss	poss	poss	
Malathion		0.7	10			18	250	absorbed	5	10	18	unlimited	
Maleic anhydride		0.1				2.5	10		limited usefulness		2.5	unlimited	
MCPA									poss	poss	poss	poss	
MDI		0.006	0.05	0.06	0.5	1.2	10	absorbed	0.2	0.5	1.2	unlimited	
Mercury		0.003	0.025			0.02	2	absorbed	0.005	0.01	0.02	unlimited	c
Methoxychlor		0.70	10	1.4	20	350	5000		70	200	350	unlimited	
Methyl alcohol	✓	200		250		6000		permeation	not effective			unlimited	
Methyl chloride	✓	50		100		2000		permeation	not effective			unlimited	
Methyl ethyl ketone	✓	200		300		3000		de-fatting	600	1500	3000	unlimited	
Methyl methacrylate	✓	50		100		1000			200	500	1000	unlimited	
Methyl parathion		0.2	0.2					absorbed	2	5	10	unlimited	
Methylene chloride		50				2300		de-fatting	limited usefulness			unlimited	
Metolachlor									poss	poss	poss	poss	
Naphtha		100				1000			200	600	1000	unlimited	
Naphthalene		10		15		250			50	150	250	unlimited	
Nickel sulphate			1.5 mg (as Ni)						poss	poss	poss	poss	
Nitric acid	✓	2		4		25		corrosive	limited	15	25	unlimited	c
Nitrogen (liquefied)	✓							freezing	asphyxiant only			unlimited	
Nonylphenol	✓							not necessary in most circumstances					
Oleum	✓		1 mg (as sulphuric acid)	3	2.5	15		corrosive	0.5	1	2.5	unlimited	
Oxygen (liquefied)	✓							freezing				unlimited	
Paraquat		0.05	0.5			0.09	1	absorbed	0.09	0.09	0.09	unlimited	
Parathion		0.01	0.1			0.8	10	absorbed	0.2	0.4	0.8	unlimited	
PCBs		0.01	0.1 (60 % chorine is half this)					absorbed	2	5	10	unlimited	
Pentachlorophenol		0.05	0.5	0.14	1.5	0.2	2.5	absorbed	0.2	0.2	0.2	unlimited	
Perchloroethylene	✓	25		100		150		defatting	limited usefulness		150	unlimited	
Phenol	✓	5				250		absorbed	50	125	250	unlimited	
Phenolsulphonic acid								corrosive	poss	poss	poss	poss	c
Phosphamidon									poss	poss	poss	poss	
Phosphoric acid		0.25	1	0.7	3	245	1000	corrosive	50	125	245	unlimited	c
Phosphorus		0.02	0.1			1	5		not effective			unlimited	
Phthalic anhydride		1		4		10	60	sensitizer	2	5	10	unlimited	
Picloram		1	10						20	50	100	unlimited	
Potassium chloride								not necessary in most circumstances					
Potassium cyanide		5 as CN-				11	25	moisture produces toxic CN-			11	unlimited	
Potassium hydroxide		0.9	2					corrosive	20	40	80	unlimited	
Potassium permanganate								not necessary in most circumstances					
Propylene glycol								not necessary in most circumstances	poss	poss		poss	poss
Propylene oxide	✓	5		10		400		irritation	not effective		400	unlimited	
Pyridine	✓	5		10		1000		irritation	50	250	1000	unlimited	
Sodium bisulphite								not necessary in most circumstances					
Sodium carbonate								not necessary in most circumstances					
Sodium chlorate								not necessary in most circumstances					
Sodium chloride								not necessary in most circumstances					
Sodium chlorite								not necessary in most circumstances					
Sodium chromate			0.05 mg as Chromium					not necessary in most circumstances					
Sodium cyanide (as CN-)		5 as CN-				11	25	moisture produces toxic CN-			11	unlimited	
Sodium dichromate			0.05 mg as Chromium										
Sodium hydrosulphite								not necessary in most circumstances					
Sodium hydroxide		1.2	2	2.4	4	6	10	corrosive	6	6	6	unlimited	
Sodium hypochlorite								corrosive					
sodium nitrite								not necessary in most circumstances					
sodium pentachlorophenate								not necessary in most circumstances					
Sodium silicate								not necessary in most circumstances					
Sodium sulphate								not necessary in most circumstances					
Sodium sulphide								not necessary in most circumstances					
Sodium sulphite								not necessary in most circumstances					
sodium thiocyanate								not necessary in most circumstances					
Styrene	✓	20		40		700		irritation	100	200	700	unlimited	
Sulfur								not necessary in most circumstances					
Sulfur dioxide	✓	2		5		100			20	50	100	unlimited	
Sulfuric acid	✓	0.2	1	0.7	3	4	15	corrosive	2	2	4	unlimited	
Tetraethyl lead		0.007	0.1			3	40	absorbed			3	unlimited	
Thallium sulfate			0.1 mg (as thallium)						poss	poss	poss	poss	
Titanium dioxide								not necessary in most circumstances					
Toluene	✓	50		150		500		permeation	100	250	500	unlimited	
Toluene-2,4-diisocyanate	✓	0.005		0.02		2.5		sensitization	escape only		2.5	unlimited	
Trichloroethane	✓	10				100		permeation	escape only		100	unlimited	
Trichloroethylene	✓	50		100		1000		de-fatting	escape only		1000	unlimited	
Trichlorfon									poss	poss	poss	poss	
Trifluralin									poss	poss	poss	poss	
Trinitrotoluene		0.01	0.1	0.02		53	500	permeation	escape only		50	unlimited	
Urea									poss	poss	poss	poss	
Urea formaldehyde								not necessary in most circumstances					
Urea nitrate									poss	poss	poss	poss	
Vinyl acetate		10		15					20	50	100	unlimited	
Vinyl chloride	✓	1						hazardous	escape only		25	unlimited	
Viscose (cellulose xanthate)								not necessary in most circumstances					
Xylenes	✓	100		150		900			200	450	900	unlimited	
Zinc chloride (fumes)		0.2	1	0.4	2	9	50		2	5	9	unlimited	
Zinc cyanide		5 as CN-				11	25	moisture produces toxic CN-			11	unlimited	
Zinc oxide (dust/fumes)		1.5	5	2.955	10	150	500		50	75	150	unlimited	
Zinc sulfate								not necessary in most circumstances					

¹ - Maximum Use Concentration is taken from commercial literature or it is generally taken that MUC for a gas mask is equal to IDLH, for a full facepiece respirator is half of IDLH and for a half facepiece air purifying respirator is 1/5 IDLH. It is important to note that MUC may vary with manufacturer and model. It is important to consult the manufacturer for specific data.

poss = possible, no MUC established, but respirator useable
unlimited = no limit set, but should not exceed 5000 X TLV

c = conditional
on potentially
high vapour
concentrations

² - A Totally-encapsulated Chemical Protective Suit (TECPS) should always be worn when entering spill sites where the substance and its concentrations are not known.

supplied and air-purifying. **Air-supplied respirators** are used when oxygen levels are in question as well as when contaminant levels are unknown or expected to be high. **Air-purifying respirators** are used when contaminant levels are relatively known and are below the maximum capacity of the respirator.

Protective clothing is quite diverse, but the most common items used for spill response are boots, gloves, totally encapsulated suits, splash gear or firefighters' bunker suits, and coveralls. The selection of totally encapsulated suits available is more limited than for respirators. Hearing protection and hard hats are used where necessary.

Selecting Respirators

Selecting respiratory protective equipment for use in the workplace has been the topic of several well-known guidelines (NIOSH, 1985; OE, 1991; CSA, 1993). Some publications have dealt with selecting respirators for spill situations (EPA, 1992; Fingas, 1996).

The difference between selecting a respirator for the workplace and one for use in spill situations hinges on the certainty with which both the substances present and their concentrations are known. In spill situations, maximum protection must often be used to deal with the possible presence of high concentrations of chemicals.

Respirators provide protection from three dangers: chemical contaminants, particulate matter, and oxygen deficiency. Chemical contaminants include a wide variety of materials such as those listed in Table 2. Particulate matter consists of small matter that can be inhaled. 'Respirable' particulate

matter has particulate sizes less than 10 μm in size, which lodge in the lungs and can cause permanent damage. Particulates are also important in view of chemical spill response because many chemicals can be absorbed by or adsorbed to particulate matter.

Many air-purifying devices are equipped with special types of filters, known as HEPA or High Efficiency Particulate filters, which remove the small particulates. Oxygen deficiency is a common danger associated with chemical contamination, particularly in confined spaces where the air is displaced by the chemical. Oxygen deficiency can only be protected against using air-supplied respirators.

Respiratory protective devices consist of a facepiece connected to either an air source or an air-purifying device. Facepieces for respirators are available in two basic configurations, half facepieces and full facepieces. Half

facepieces fit around the nose and do not have an integrated eye-shield.

Many devices are available on the market, some of which are listed in Table 3. This table also lists a protection factor which is the ratio of the concentration of the contaminant outside the facepiece to the concentration of the contaminant inside the facepiece. These protection factors represent an average value for a large number of individuals. Such values can be much lower, however, if the facepiece does not fit properly. For example, beards can cause leakage around a facepiece and reduce the protection factor by as much as 10 times.

Protection factors are important criteria for selecting respiratory protective equipment. The protection factor must be high enough to reduce the contaminant inside the facepiece to an acceptable level, usually taken as



A half facepiece mask with chemical cartridges.

Table 3 Respiratory Protection Equipment and Associated Protection Factors

Respirator	Protection Factor ¹
Air-Purifying Respirators - Dust Masks	
Single-use dust mask	5
Quarter mask	5
Half mask	10
Full-facepiece dust mask	100
Powered dust mask	1,000
Air-Purifying Respirators - Chemical Cartridge	
Half-facepiece mask	10
Full-facepiece mask	100
Supplied-air Respirators	
Demand half-facepiece mask	10
Demand full-facepiece mask	100
Pressure-demand half-facepiece mask	1,000
Pressure-demand full-facepiece mask	2,000
Continuous-flow helmet or suit	2,000
SCBAs (Self-Contained Breathing Apparatus)	
Open-circuit demand	100
Open-circuit pressure demand	10,000
Closed-circuit, oxygen cylinder type (all are full facepiece)	100

¹ Protection factor is the ratio of the contaminant concentration outside the facepiece versus the concentration inside

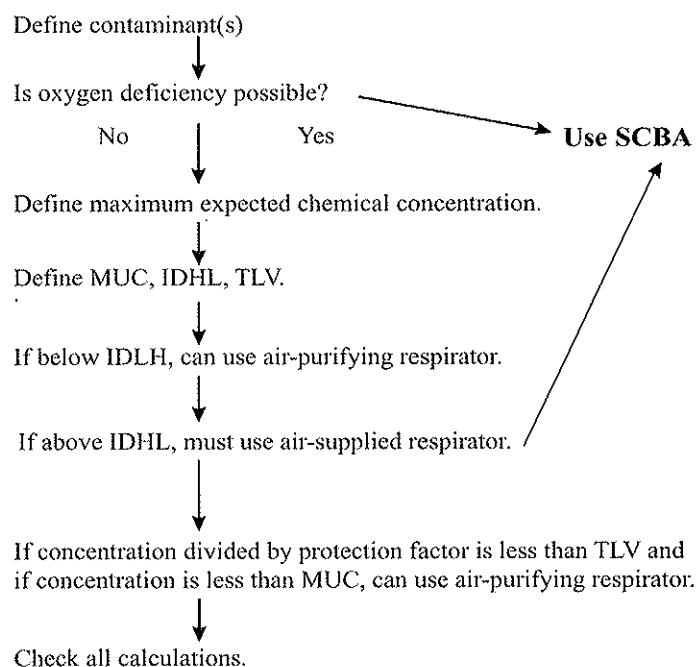


Figure 1 Respirator Selection Process

the TLV or Threshold Limit Value. The TLV values for commonly spilled materials are listed in Table 2.

These data are used in the following manner (ACGIH, 2002; NIOSH, 1997). A spill of a substance with a TLV of 5 ppm, which according to calculations could rise as high as 5,000 ppm, would require a respirator with a protection factor of at least 1,000. For a safety factor of 2, a protection factor of 2,000 would be required.

Pressure-demand SCBAs, which have a protection factor of about 10,000, represent the ultimate in safety and are generally used at spill scenes because the exact substance and level of the contaminants are not known until measurements have been made.

Air-purifying respirators are limited in the concentrations that they can handle or absorb. The top level at which an air-purifying respirator is useful is referred to as the "Immediately Dangerous to Life and Health" (IDLH) level. This is also the level at which a chemical can cause severe damage. The IDLH level represents the point at which one must either switch from an air-purifying respirator to an air-supplying respirator or escape from the environment. The IDLH values for commonly spilled chemicals are listed in Table 2.

Another requirement for air-purifying respirators is that they be used at contaminant concentrations less than the specified Maximum Use Concentration (MUC). The MUC is based on the capability of the sorbent in air-purifying respirators to deal with high concentrations of materials.

The selection process for a respirator is shown in Figure 1. The following guidelines can simplify

the selection process for respiratory protective devices for use at a spill scene.

1. The SCBA should be used in the following situations:
entry into an unknown situation; unknown or high levels of a toxic chemical are present; or there is any possibility of an oxygen shortage.
2. The air-purifying respirator can be used when the situation is stable and when the levels of chemicals are below the IDLH with very little possibility of them rising.

Regardless of the type of respirator used, the selection should be verified by taking measurements and calculating concentrations inside the facepiece. In the past, a number of qualitative measures using indicators such as banana oil and smoke were used which provided a rough indication of mask fit.

The protection factor can now be measured for a given mask and a given person. This is called 'fit

testing'. In the past 10 years, many quantitative fit-testing apparatuses have come onto the market. These directly measure the protection factor for a given mask by measuring the concentration of ambient particulate inside and outside a mask or by measuring the ingress of air using sensitive pressure transducers. The measurement devices now include computers or built-in computing devices to directly calculate protection factors and the percentage of facepiece leakage.

Fit testing should be done for new users as well as on an ongoing basis to ensure adequate protection. Sometimes, certain facial features, such as a scar or facial hair or a very thin face, result in a lack of proper protection. Such individuals should not be put in a position that requires respiratory protection.

Problems can arise when respirators are used in extreme hot or cold weather. The use of respirators in very hot conditions does not cause life-threatening events, but the user can tire

quickly and excessive sweating can cause face-seal problems with the mask.

In cold weather, icing of the regulator and fogging of the facepiece window are concerns. Icing of the regulator becomes serious because the decompression of the air can cause the moisture to precipitate and then freeze. The amount of water in the starting air is usually measured by the dew point, which is the temperature at which condensation occurs and moisture begins to form droplets of water. The dew point and water content of air are shown in Table 4. The CSA standard requires extensive filtration to remove the moisture (CSA, 1985).

When using supplied-air respirators in cold weather, a number of precautions are taken, including leaving tanks in heated vehicles before use. The fogging of lenses by exhaled moisture is readily prevented by using a device known as a 'nose cup' which directs moist air to the exhalation valve and away from the lens.

Table 4 Approximate Moisture Content in Compressed Breathing Air*

Atmospheric Dew Point (°C) 30- or 60-minute apparatus	Water content at atmospheric pressure (ppm)	Pressure Dew Point (°C) 30-minute apparatus at 2216 psig	60-minute apparatus at 4500 psig
-45.5	68	7	18
-48.5	48	2	12
-51	34	-2	8
-53 (CSA standard)	27	-5	4
-54	24	-6	3
-56.5	17	-10	-2
-59.5	11.5	-14	-6
-62	8	-18	-10
-65	5.5	-22	-15
-68	3.5	-27	-20
-70.5	2.3	-31	-24
-73	1.5	-34	-27

*data adapted from CSA, 1985

Another issue when using respirators is the need for prescription glasses in the facepiece. Regular glasses cannot be worn because anything that interferes with the seal of the facepiece is dangerous and illegal. Special lens holders are available that fit into the facepiece. Contact lenses, once not recommended for use in a respirator, can now be used, as new contact lenses allow for gas exchange and thus do not dry out and stick to the eyeball.

For air-supplied respirators, the quality of the air is also an issue. There are standards for the minimum air purity (CSA, 1985). The moisture content in the air is also an issue, especially when operating in cold climates, as this can cause the respirator to freeze.

Protective Clothing

Clothing, gloves, goggles, boots, and other such items are required to prevent the chemical from contacting the skin or eyes. In the case of vapours that can permeate the skin, gas-tight or totally encapsulated protection suits are required. In the case of chemicals that are corrosive or absorbed as liquids through the skin, protection is required to prevent contact with the substance itself. Some chemicals pose both dangers.

Chemicals gain access to the wearer or affect clothing material through three processes.

Permeation - This is the process by which molecules of liquid or gaseous chemicals move through clothing material. It is the most important indicator of the usefulness of a particular clothing material. Some chemicals can permeate through clothing material in only a few seconds. If these

chemicals are toxic, then the clothing material is not useful for chemical protection.

Penetration - This occurs when liquid or gaseous chemicals flow through closures, seams, pin holes, or other openings in the clothing. Penetration can occur regardless of the type of material selected, although some types of materials are more or less resistant to puncture mechanisms, such as abrasion or pin-holing, depending on the conditions the clothing is subjected to.

Degradation - This is the deterioration of clothing material caused by the action of the chemical. Degradation may change bulk properties such as tensile strength or cause small areas of the material to dissolve. In the past, most data on a material's resistance to chemicals related to degradation as there were no standards for measuring other types of chemical intrusion. Many different measurements were lumped together and termed "chemical compatibility". As will be shown later, degradation data, although important, are not usually as crucial as permeation data.

Permeation is the most important of the entry mechanisms in terms of spill response. It is chemical-dependent and changes with material thickness, temperature, and the presence of other solvents. It has been found that mixtures of different chemicals can sometimes permeate the clothing material much faster than any of the chemicals alone.

Existing data on permeation are primarily measured using the ASTM (American Society for Testing and Materials) procedure or the ISO (International Standards Organization) procedure. These prescribe the use of a standard test cell which consists of two spherical

halves. The clothing material to be tested is placed as a divider between these two halves. The challenge liquid is placed on one side, with air on the other side. The air is then monitored and breakthrough is said to occur when the chemical can be measured in the air space. As the clothing material is completely immersed in the challenge liquid, the test provides a conservative measure.

The time it takes for some chemicals to permeate some typical clothing materials is given in Table 5. Data are compiled from Forsberg and Keith, 1995. The clothing materials presented here are those commonly used in totally encapsulated suits or protective gloves. Permeation data is very important when selecting both of these items. Permeation times of less than 30 minutes imply that the material has little application to spills as this is the time usually spent in an encapsulated suit. In some cases, however, there is no material with a long enough permeation time and the material with the best permeation time must be used.

Specific permeation data on the clothing material actually used in the manufacture of the clothing item should be obtained whenever possible. As already noted, permeation data vary greatly, even with similar materials. Some of this variance may be due to the thickness of the material. The thicker the material, the longer the permeation time. In fact, thickness is so important that materials, such as those used in light clothing, that show significant permeation in thin sheets of typically 0.05 cm, can have no or little permeability at thicknesses of about 0.5 cm thick. Permeation through very thick synthetic materials, such as those in SCBA facepieces, may therefore not be a serious concern.

Table 5 Permeation Times for Clothing Materials (in minutes)
(Forsberg and Keith, 1995)

Chemical	BETEX*	Butyl	Rubber**	Neoprene	Nitrile	PVC***	Teflon	Viton
Acetic acid	>360	180	120	360	360	180	>480	120
Acetic anhydride	>360	>240	60	210	180	90	>180	60
Ammonia, anhydrous	>360	>480	2 (V)	>180	250 (V)	15 (V)	>300	
Ammonium hydroxide	>360	>480	120	360	360	180		>60
Benzene	15	30 (V)	3 (V)	12 (V)	15 (V)	1 (V)	>200	9 (V)
Chlorine	>360	>480	>480	>480	>480	30	>300	>480
Ethylene glycol	>360	>480	360	360	360	360	>480	
Formaldehyde	>360	>480	60	120	>360	70 (V)	>180	>480
Hexane	5	15 (V)	5	50 (V)	360	30	>300	>480
Hydrogen peroxide	>360		>360	6	>360	>360		
Hydrochloric acid	300	>480	360	>360	360	360	>480	>480
Hydrofluoric acid	>480	>480	150 (V)	360	120 (V)	360	>480	>480
Methanol	100	>480	15	10 (V)	180 (V)	2 (V)	>480	60
Nitric acid	>360	>480	360	150	100 (V)	240		60
Pentachlorophenol			150	6-360 (V)	>360	180		>480
Perchloroethylene	20	4 (V)	0	15 (V)	40 (V)	15 (V)	>180	>480
Phenol	>480	>480	60 (V)	180	60	20 (V)	>180	>480
PCBs		>480	60	>480	150 (V)		>480	>480
Sodium hydroxide	>360	>480	360	360	360	>360	>480	>480
Sodium hypochlorite	>360	>360	360	360	360	360		
Styrene	10	30 (V)	1 (V)	12	30	30	>240	>180
Sulphuric acid	>360	>480	80	>360	10 (V)	10 (V)		>240
Toluene	<10	10 (V)	5 (V)	10 (V)	20 (V)	10 (V)	>180	>180
Toluene diisocyanate		>480	7 (V)	0-240 (V)	240	480	>480	>480
Vinyl chloride					300			260
Xylenes	10	30 (V)	2 (V)	4 (V)	60 (V)	1 (V)	>180	>60

Legend

* BETEX = Butyl on neoprene

** Rubber = natural rubber

*** PVC = Polyvinyl chloride

0 indicates that the material should not be used, usually because material degrades

Blank indicates no testing performed

V Indicates highly variable data

Permeation times also vary with material fabrication and other differences may be due to erroneous data. It is important to verify the permeation data for a given material with more than one source.

Boots and gloves are the most important pieces of protective clothing because they most often come into contact with contaminated materials. The technology for manufacturing

gloves has improved in the past few years and many companies have good selection charts based on permeation data for their specific materials. The manufacture of boots has not progressed much, however, and very few specific permeation data are available for them.

Totally encapsulated chemical protection suits - Another important piece of clothing for chemical spills is the totally encapsulated chemical

protection suit (TECPS). This is used if the materials encountered are unknown or known to be skin-permeating. A few cautions should be noted in selecting totally encapsulated suits.

1. There are few standards governing the design and manufacture of these suits. Existing standards are applicable primarily to suits for firefighters. The buyer must therefore ensure

that the suit purchased is appropriate for use in a chemical spill response.

2. Any permeation data provided by the manufacturer must have been measured for the actual suit material and be generated by a standard method, preferably the ASTM method.

3. Suits that interfere with the seal of the facepiece of the Self-Contained Breathing Apparatus (SCBA) should not be purchased. Such practice is dangerous and contravenes most occupational health laws.

4. As gas-tight suits are sometimes made of several materials, permeation of the weakest material is the limiting factor. The permeation time of each material in the suit should be measured, as well as the joint between each type of material. It may be wise to avoid suits made of more than one type of material.

5. The suit should allow access to the controls of the SCBA, whether the SCBA is worn inside or outside the suit. Many responders prefer that the SCBA be worn outside the suit so that they have unrestricted access to the controls.

6. The question of whether the SCBA should (or can be) worn inside or outside the suit is still controversial. Sales staff may indicate that suits with built-in face masks are not safe or legal, but this is not correct.

7. Caution should be observed when dealing with sales people for totally encapsulated suits. Sales staff are often not familiar with the intricacies of spill response, the respiratory protection required, safety requirements at spill scenes, and permeation data for the clothing needed.

8. Any prospective suits should be tested for use in different weather conditions. Many suits cannot be used in cold weather because they are too stiff and some suits do not allow enough movement to perform many tasks.

9. Other users of the suit should be surveyed to ensure that the suit has performed well in actual chemical spill situations.

The use of totally encapsulated chemical protection suits is an extensive topic. Wearing TECPS is often physically and mentally stressful. In hot weather, a person wearing such a suit can lose as much as 2 kg of water through perspiration. Organizations such as the U.S. EPA have recommended that TECPS should not be worn for more than one hour a day and that this be done in two half-hour sessions. Two workers wearing chemically protected suits are shown in the photo.

Other clothing - The selection of other clothing material is less critical. Coveralls and other such clothing are not worn when there is a skin-penetrating material spilled. Disposable coveralls are now frequently worn at spill scenes and are useful for minimizing contact with chemicals. Treated cellulose fabrics are now more popular than Tyvek because of their greater comfort.

Goggles are used occasionally at the spill scene if there is a danger of material getting into eyes and if respirators with full facepiece masks are not worn. Splash guards are also occasionally used, but are not recommended as they were originally designed to protect construction workers from sparks and projectiles projected directly at the guard. In the case of liquid spills, the materials are often at ground level and the open area at

the bottom of the device can actually direct liquids to the face.

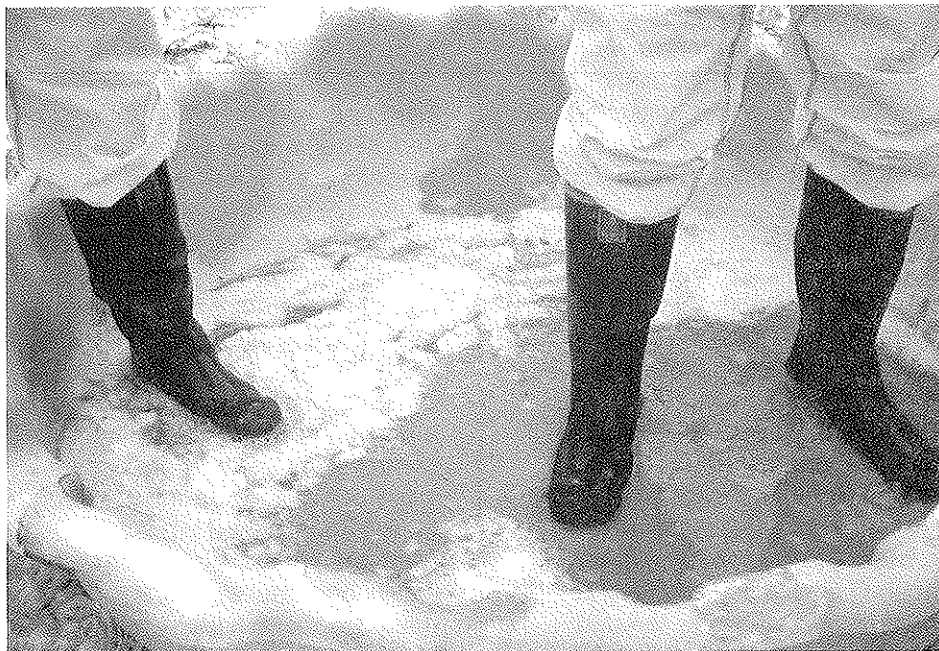
Hard hats and ear protectors should be used as required in any hazardous situation. Some types of protective clothing, such as totally encapsulated suits, do not readily allow for the use of hard hats, but most responders would not require both forms of protection at once.

Decontamination of clothing and breathing apparatus has been a controversial issue. There has been too much fixation on this task and far too complicated procedures have been proposed in the past. Totally encapsulated suits rarely need decontamination unless they have come in contact with a material. If this is the case, decontamination procedures for specific chemicals should be followed.

Generally, if the contaminant is a gas, the suit should be hung in a well ventilated area, away from the sun and people, for about two weeks. If the material is a liquid



A team working in Level A gear. It is important to work in 'buddy' groups of two or three.



Protective clothing, especially boots, must often be decontaminated after use.

that permeates, the suit may have to be destroyed or special procedures followed in consultation with the manufacturer.

Non-permeating liquids or solids can be washed from the suit by placing the person in the suit under a specially designed shower or other water spray. If the material is oily or can be removed easier with a detergent, this can be used. Only dish-washing detergents are mild enough to not affect the suit material. The suit can be more damaged by a harsh decontaminating mixture than if it is simply washed with water. While special detergents are available for decontaminating for bacteria and viruses, mild chlorine and peroxide solutions have also been used.

Boots must almost always be decontaminated after use at a chemical spill incident. A child's wading pool with a mild detergent is suitable for many situations as shown in the photo. The water

from the pool must often be treated as contaminated waste in the same way as the water from decontaminating suits must be treated. Gloves should be washed separately in a bucket in a similar manner to boots.

If it is suspected that equipment is contaminated, it is far better to dispose of it or put it into secure containers for further assessment than to try to reuse it without knowing that it is in good condition. Management will certainly be sympathetic and replace any equipment. In many organizations, this occurs so rarely that the occasional loss is not a serious economic problem.

Confined Spaces

Confined spaces are those areas with poor air circulation where gas concentrations can rise far beyond danger levels. There is a high potential for oxygen deficiency in

such areas as well as the danger of entrapment and fire. Confined spaces include sewers, closed rooms, and silos. Special occupational health and safety rules govern entry and work in confined spaces because they pose a high hazard. In many jurisdictions, the entry into confined spaces and details of activities and safety procedures followed must be recorded.

Chemical Spill Response Program

Response to chemical spills requires a complete program that includes medical testing, training, retraining, and practice. Purchasing, maintaining, upgrading, and replacing equipment are also part of the program. One or more persons in the organization should be responsible for supervising, coordinating, and developing such a program.

Publications are available to help in establishing a recognized and systematic program (EPA, 1992, OE, 1991). The program should be based on a carefully developed policy concerning spill-site entry procedures and minimum requirements for training and equipment.

There are many requirements for a thorough chemical spill response program. These include keeping records and developing check lists for equipment testing, donning and doffing of equipment, and site entry procedures. Detailed site safety plans and standard operating procedures must be developed. A specification should be in place to ensure that persons required to respond are fit to do so and this should include regular medical checkups.

Regular training, practice programs and technical refresher programs are essential. In the United States, 40 hours of training are required before an individual can enter a spill site. Annual refresher courses are also required.

Organizations such as Environment Canada and the U.S. Environmental Protection Agency have had such programs and policies in place for many years. Employees who are required to enter a spill site must have at least one week of training in using the assigned equipment and a refresher course of at least two days must be taken every year. Other response organizations should put similar requirements into place.

Environment Canada has issued its spill responders with self-contained breathing apparatus and totally encapsulated suits with all the accessories. This equipment is signed out by employees and kept until they leave the program. The equipment is repaired and replaced on a regular basis.

Conclusion

It is important to recognize that first-responders are generally like first-aiders. They perform limited emergency duties at the site but refer to specialists for further advice and follow-up action. Just as the first-aiders do not perform surgery at the site, those who respond to chemical spills should not be required to perform tasks beyond their training and capability. Response organizations should build up a network of information sources and consult professionals in the fields of chemistry and site remediation when required.

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The Spill Technology

Newsletter was started with modest intentions in 1976 to provide a forum for the exchange of information on spill countermeasures and other related matters. We now have more than 2,500 subscribers in over 40 countries. Readers are encouraged to submit articles on their work and views in this area to Dr. Merv Fingas.

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