Appendix D
Additional Details on Water-Reactive Materials

Appendix D provides detailed information on the water-reactive materials listed in the Table of Initial Isolation and Protective Action Distances. Supplementary information on all water-reactive materials in the toxic by inhalation by water reactivity (TIHWR) list is provided in Table D.1. In addition, for the 37 new materials added to the TIHWR list, a brief summary of reasons supporting their inclusion is provided.

Table D.1 Supplementary Information on Water-Reactive Materials in the *2000 Emergency Response Guidebook*[a]

UN No.	TIH	Exp	Name	Prod.	St	Dens	S.Y.	ε	C
1162		X	Dimethyldichlorosilane	HCl	L	1.10	0.565	0.41	0.96
1242			Methyldichlorosilane	HCl	L	1.11	0.634	0.1	0.33
1250		X	Methyltrichlorosilane	HCl	L	1.27	0.732	0.33	1.31
1295			Trichlorosilane	HCl	L	1.34	0.808	0.33	1.5
1298		X	Trimethylchlorosilane	HCl	L	0.85	0.336	0.37	1.45
1340			Phosphorus pentasulfide	H_2S	S	2.09	0.766	0.6	0.2
1360		X	Calcium phosphide	PH_3	S	2.51	0.373	0.29	0.36
1397			Aluminum phosphide	PH_3	S	2.40	0.587	0.3	0.1
1412			Lithium amide	NH_3	S	1.18	0.740	0.1	5
1419			Magnesium aluminum phosphide	PH_3	S	2.20	0.529	0.3	0.1
1432			Sodium phosphide	PH_3	S	1.74	0.283	0.3	0.1
1433			Stannic phosphide	PH_3	S	5.18	0.239	0.3	0.1
1541			Acetone cyanohydrin	HCN	L	0.93	0.317	0.2	0.2
1680			Potassium cyanide	HCN	S	1.52	0.415	0.2	0.1
1689			Sodium cyanide	HCN	S	1.52	0.552	0.2	0.1
1714			Zinc phosphide	PH_3	S	4.55	0.263	0.3	0.2
1716			Acetyl bromide	HBr	L	1.66	0.658	0.4	5
1717			Acetyl chloride	HCl	L	1.11	0.464	0.4	5
1724			Allyl trichlorosilane, stabilized	HCl	L	1.21	0.623	0.33	1.5
1725			Aluminum bromide, anhydrous	HBr	S	2.54	0.910	0.6	0.1
1726			Aluminum chloride, anhydrous	HCl	S	2.44	0.820	0.1	0.2
1728			Amyltrichlorosilane	HCl	L	1.16	0.532	0.1	0.7
1732			Antimony pentafluoride	HF	L	2.99	0.461	0.4	5
1736			Benzoyl chloride	HCl	L	1.21	0.259	0.1	0.33
1745	X		Bromine pentafluoride	Br_2	L	2.47	0.456	0.04	0.2
1745	X		Bromine pentafluoride	HF	L	2.47	0.572	0.4	5
1746	X		Bromine trifluoride	Br_2	L	2.80	0.591	0.02	0.2
1746	X		Bromine trifluoride	HF	L	2.80	0.438	0.6	5
1747			Butyltrichlorosilane	HCl	L	1.16	0.571	0.1	0.7
1749	X		Chlorine trifluoride	Cl_2	G	1.77	0.383	0.05	1
1749	X		Chlorine trifluoride	HF	L	1.77	0.649	0.6	5
1752		X	Chloroacetyl chloride	HCl	L	1.50	0.323	0.1	0.33
1754			Chlorosulfonic acid	HCl	L	1.76	0.313	0.2	0.1
1758			Chromium oxychloride	HCl	L	1.91	0.471	0.1	0.1
1777			Fluorosulfonic acid	HF	L	1.73	0.200	0.1	5
1801			Octyltrichlorosilane	HCl	L	1.33	0.442	0.33	1.5
1806			Phosphorus pentachloride	HCl	S	1.60	0.875	0.2	5

Continued

Table D.1 Supplementary Information on Water-Reactive Materials in the *2000 Emergency Response Guidebook*[a] (Cont.)

UN No.	TIH	Exp	Name	Prod.	St	Dens	S.Y.	ε	C
1807			Phosphorus pentoxide	H_2PO_4	S	1.50	1.410	0.05	0.2
1809		X	Phosphorus trichloride	HCl	L	1.57	0.796	0.33	3
1810		X	Phosphorus oxychloride	HCl	L	1.67	0.713	0.21	10
1816		X	Silicon tetrachloride	HCl	L	1.48	0.858	0.34	0.83
1828	X		Sulfur chlorides	SO_2	L	1.62	0.252	0.12	0.2
1828	X		Sulfur chlorides	HCl	L	1.62	0.540	0.08	0.6
1828	X		Sulfur chlorides	H_2S	L	1.62	0.474	0.1	0.6
1829	X		Sulfur trioxide	H_2SO_4	S	1.92	1.230	0.2	0.2
1831	X	X	Oleum	H_2SO_4	L	1.80	1.500	0.07	10
1834	X	X	Sulfuryl chloride	HCl	L	1.66	0.540	0.2	0.92
1834	X		Sulfuryl chloride	H_2SO_4	L	1.66	0.726	0.05	0.2
1836		X	Thionyl chloride	SO_2	L	1.63	0.538	1	2.71
1836	X	X	Thionyl chloride	HCl	L	1.63	0.613	0.08	0.59
1838	X	X	Titanium tetrachloride	HCl	L	1.73	0.769	0.27	0.89
1898			Acetyl iodide	HI	L	2.07	0.753	0.4	0.2
1939		X	Phosphorus oxybromide, molten2	HBr	L	2.82	0.847	0.21	20
2004			Magnesium diamide	NH_3	S	1.39	0.604	0.1	0.1
2011			Magnesium phosphide	PH_3	S	2.06	0.504	0.3	0.15
2012			Potassium phosphide	PH_3	S	2.50	0.229	0.3	0.1
2013			Strontium phosphide	PH_3	S	2.68	0.209	0.3	0.1
2442			Trichloroacetyl chloride	HCl	L	1.63	0.314	0.1	0.33
2495			Iodine pentafluoride	HF	L	3.75	0.450	0.2	5
2691		X	Phosphorus pentabromide	HBr	S	2.00	0.940	0.31	3
2692	X		Boron tribromide	HBr	L	2.65	0.971	0.1	0.8
2806			Lithium nitride	NH_3	S	1.27	0.489	0.2	1
2977			Uranium hexafluoride, fissile	HF	S	4.68	0.341	0.2	5
2978			Uranium hexafluoride, non-fissile	HF	S	4.68	0.341	0.2	5
2985		X	Chlorosilanes, n.o.s.	HCl	L	1.10	0.565	0.41	0.96
2986		X	Chlorosilanes, flam., corr, n.o.s.	HCl	L	1.10	0.565	0.41	0.96
2987			Chlorosilanes, corrosive, n.o.s.	HCl	L	1.10	0.565	0.41	0.96
2988			Chlorosilanes, wtr-rctv, flam., corr.,n.o.s.	HCl	L	1.10	0.565	0.41	0.96
3048			Aluminum phosphide pesticide	PH_3	S	2.40	0.587	0.3	0.05
3049			Metal alkyl halides n.o.s.	HCl		1.60	0.500	0.05	5
3052			Aluminum alkyl halides	HCl		1.60	0.500	0.05	5
9191			Chlorine dioxide, hydrate, frozen	Cl_2	S	1.40	0.084	0.05	5
N/A			Sodium methylcarbamodithioate)	H_2S	L	1.00	0.000	0	0
N/A			Sodium methylcarbamodithioate	CH_5N	L	1.00	0.000	0	0

[a] Exp = experiment performed, St = normal state during shipment (solid, liquid, gas), Dens = density (g/cm^3), S.Y. = stoichiometric yield of TIH (kg TIH/kg spilled parent), ε = efficiency factor (average fraction of S.Y. produced), and C = primary rate constant at 20°C.

Reasons to Support Why Materials Were Added to the TIHWR List

UN#1162 dimethyldichlorosilane: Experiment established a substantial rate of evolution of HCl when the chemical was mixed with water.

UN#1340 phosphorus pentasulfide: The material "Readily liberates toxic hydrogen sulfide and phosphorus pentaoxide and evolves heat on contact with moisture" (Lewis 1966).

UN#1384 sodium hydrosulfite: The compound is soluble in water and would dissolve smoothly with no evolution of gases in most spills. However, large spills into restricted amounts of water cause heating with subsequent decomposition and evolution of SO_2 and possibly H_2S.

UN#1541 acetone cyanohydrin: This compound readily decomposes to HCN and acetone. The protective action distance is greater when spilled into water because of likely evolution of HCN.

UN#1724 allyl trichlorosilane, stabilized: This compound generates HCl when mixed with water. Experimental results on the related compound methyltrichlorosilane suggested a higher rate of evolution than previously considered.

UN#1728 amyltrichlorosilane: It generates HCl when mixed with water. Experimental results on the related compound methyltrichlorosilane suggested a higher rate of evolution than previously considered.

UN#1736 benzoyl chloride: The compound generates HCl when spilled into water. Large spills, especially into restricted amounts of water, could cause a medium to large hazard.

UN#1745 bromine pentafluoride: It explodes or ignites on contact with many hydrogen-containing materials (including water). Products of reaction include HF and possibly Br_2. This material was recommended for inclusion on the 1996 North American ERG list.

UN#1746 bromine trifluoride: It reacts explosively or violently with water to generate HF and possibly Br_2. It was recommended for inclusion in the NAERG96 list.

UN#1747 butyltrichlorosilane: This chemical generates HCl when mixed with water. Experimental results on the related compound methyltrichlorosilane suggested a higher rate of evolution than previously considered.

UN#1749 chlorine trifluoride: The compound reacts explosively with water to generate HF and possibly Cl_2. It was recommended for inclusion on the NAERG96 list.

UN#1752 chloroacetyl chloride: Experiment established a substantial rate of evolution of HCl when the material was mixed with water. The chemical was recommended for inclusion on the NAERG96 list.

UN#1754 chlorosulfonic acid: This acid is a source of very toxic fumes. It decomposes explosively on contact with water to generate HCl. This product is a less serious TIH than chlorosulfonic acid itself.

UN#1801 octyltrichlorosilane: This compound generates HCl when mixed with water. Experimental results on the related compound methyltrichlorosilane suggested a higher rate of evolution than previously considered.

UN#1807 phosphorus pentoxide: The chemical reacts violently with water, generating much heat. It is capable of raising an acidic mist of phosphoric acid.

UN#1809 phosphorus trichloride: Experiment established a substantial rate of evolution of HCl when the material was mixed with water.

UN#1810 phosphorus oxychloride: Experiment established a substantial rate of evolution of HCl when the material was mixed with water.

UN#1828 sulfur chloride: The compound was included on the basis of descriptions of its reactivity in standard references.

UN#1829 sulfur trioxide: This compound reacts exothermically with water to generate sulfuric acid. Local heating is known to raise a persistent acidic mist.

UN#1831 oleum: No gaseous emission was observed in the millimole experiment. However, the reaction of this chemical with water is very exothermic, and it is known to raise a mist of droplets of sulfuric acid, which gave rise to its alternate name, “fuming sulfuric acid.”

UN#1834 sulfuryl chloride: Experiment established a substantial rate of evolution of HCl when the compound was mixed with water.

UN#1838 titanium tetrachloride: Experiment established a substantial rate of evolution of HCl when the chemical was mixed with water.

UN#1923 calcium hydrosulfite: The compound dissolves smoothly in water under many conditions. In an industrial accident, the reaction of the related compound sodium hydrosulfite with a restricted amount of water at a larger scale generated enough heat to start decomposition in the undissolved portion and evolution of toxic gases.

UN#1939 phosphorus oxybromide, solid: Experiment with the related compound phosphorus oxychloride established a substantial rate of evolution of a hydrogen halide.

UN#2308 nitrosylsulfuric acid: Experiment established a substantial rate of evolution of NO_2 when the material was mixed with water.

UN#2442 trichloroacetyl chloride: Experiment established with the related compound chloroacetyl chloride a substantial rate of evolution of HCl.

UN#2495 iodine pentafluoride: The literature reports "Violent reaction with water" (Sax 1992).

UN#2576 phosphorus oxybromide, molten: Experiment established a substantial rate of evolution of a hydrogen halide in the case of the related compound phosphorus oxychloride.

UN#2691 phosphorus pentabromide: Experiment established a substantial rate of evolution of HBr when the material was mixed with water.

UN#2692 boron tribromide: The chemical literature suggested that water reaction would cause evolution of toxic gases at rates comparable to those of the related compound BCl_3.

UN#2985 chlorosilanes n.o.s.: Most chlorosilanes generate HCl at some rate if spilled into water.

UN#2986 chlorosilanes, flammable, corrosive n.o.s.: Most chlorosilanes generate HCl at some rate if spilled into water.

UN#2987 chlorosilanes, corrosive n.o.s.: Most chlorosilanes generate HCl at some rate if spilled into water.

UN#2988 chlorosilanes, water reactive, flammable, corrosive, n.o.s.: Most chlorosilanes generate HCl at some rate if spilled into water.

UN#3049 metal alkyl halides n.o.s.: Most metal alkyl halides generate hydrogen halides at some rate if spilled into water.

UN#3052 aluminum alkyl halides: Most aluminum alkyl halides generate hydrogen halides at some rate if spilled into water.

UN#N/A metam sodium (sodium methylcarbamodithioate): This pesticide is known to have generated TIH gases at a toxic level when spilled into a river.