Technically Speaking

Chemicals Which React With Water

by John Nordin, PhD

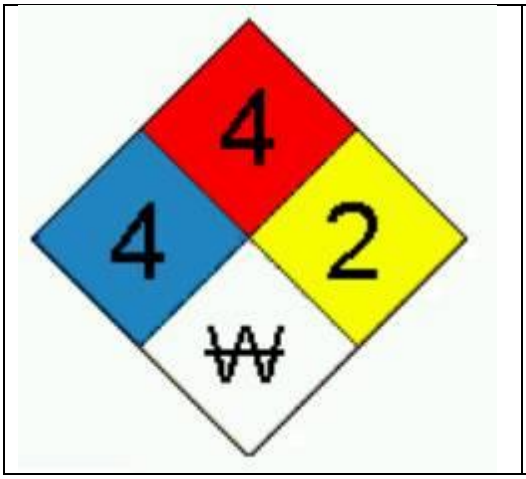
There are many chemicals to which water should not be used in the cleanup or wash down of a spill or in fighting a fire. This may come as a surprise to first responders and to firefighters.

Some chemicals if they are wetted may give off enough heat that they might ignite nearby combustibles. Some chemicals react with water and give off toxic or flammable gases.

This article takes a closer look at water-reactive chemicals and why they behave that way.

NFPA Code

The National Fire Protection Agency Code is one place to look to see which chemicals are water-reactive. The example shown below is the NFPA Code for aluminum phosphide.



Aluminum phosphide is given a "4" rating for both health (the blue diamond) and flammability (the red diamond). And for good reason.

Aluminum phosphide will react with water to produce a flammable and toxic gas. The water could come from the humidity in the air or even the lining of the throat and lungs if any dust is inhaled. The symbol W or the words "no water" are added to the white diamond. The flammable and toxic gas given off is phosphine.

Emergency Response Guidebook

The Emergency Response Guidebook (ERG), published jointly by the U.S. Department of Transportation, Transport Canada, and Secretariat of Communications and Transportation of Mexico, is an excellent source to learn about water-reactive chemicals. This Guidebook is updated every four years. A copy of the 2004 ERG can be downloaded off the Internet as a pdf file at http://hazmat.dot.gov/erg2004/erg2004.pdf.

Various chemicals or dangerous goods are assigned a four digit ID Number in this Guidebook. This number must appear on a placard or shipping document or package when the material is transported. Associated with each 4-digit number is a guide number which gives instruction on what to do if the chemical is spilled or involved in a fire or if first aid needs to be rendered. Several guide numbers are reserved for water-reactive chemicals.

Guide 137: Substances -Water Reactive – Corrosive

Guide 138: Substances - Water Reactive (Emitting Flammable Gases)

Guide 139: Substances – Water Reactive (Emitting Flammable and Toxic Gases)

Guide 144: Oxidizers (Water Reactive)

Guide #	Examples
137	Acetic anhydride, anhydrous hydrogen bromide, benzene phosphorus dichloride, benzyl chloroformate, chlorosulfonic acid, methyl phosphonic dichloride, phosphorus oxychloride, pyrosulfuryl chloride, sulfuric acid, sulfur trioxide, titanium tetrachloride
138	Aluminum hydride, barium, calcium carbide, cesium, lithium, lithium nitride, potassium metal, potassium borohydride, sodium metal, sodium aluminum hydride, sodium borohydride, zirconium hydride
139	Aluminum phosphide, ethyldichlorosilane, ferrosilicon, lithium amide, phosphorus heptasulfide, trichlorosilane
144	Bromine pentafluoride, bromine trifluoride, iodine pentafluoride, sodium peroxide

Guide #137 (water reactive, corrosive) means that the material (the chemical) can cause severe burns to human flesh or if inhaled as it reacts with the water in the human body, often with the generation of heat. For example, if water is added to concentrated sulfuric acid, enough heat will be generated to cause the material to boil. Concentrated sulfuric acid added to organic materials containing water (or hydrogen and oxygen as in sugar) may even result in the material catching fire. Many of these materials also generate acids when they react with water.

Guide #138 (water reactive, emitting flammable gases) produce flammable gases on contact with water. They may even ignite on contact with water or moist air. Lithium, for example, reacts with water producing the flammable and explosive gas hydrogen.

Guide # 139 (water reactive, emits flammable and toxic gases) produces toxic and flammable gases on contact with water. The gases produced depend on the material. Aluminum phosphide on contact with water produces phosphine gas which is both flammable and toxic.

Guide # 144 (Oxidizers, Water-Reactive) produces toxic and/or corrosive substances upon contact with water. The material (chemical) is also a strong oxidizer. Bromine pentafluoride and bromine trifluoride react with water to produce the toxic gases hydrogen fluoride and bromine. Iodine pentafluoride also produces hydrogen fluoride. Sodium peroxide reacts with a small amount of water producing considerable heat, sometimes enough to start a fire if combustibles or certain other materials are present. The toxic sodium peroxide aerosols generated in sodium fires can result in severe burns to the respiratory tract.

Some materials are water reactive but less so than the materials (chemicals) linked to guides 137, 138, and 139. When contacted with water, they may release toxic or corrosive and/or flammable gases but maybe with less vigor. If other chemicals are present in the water such as acid, they could be much more dangerous. The Emergency Response Guidebook uses the words, "water sensitive", to cover these materials. Most are also toxic or dangerous because of other attributes.

Guide #155: Substances – Toxic and/or Corrosive (Flammable/Water-sensitive)

Guide #156: Substances – Toxic and/or Corrosive (Combustible/Water-sensitive)

Guide #157: Substances – Toxic and/or Corrosive (Non-Combustible/Water-sensitive)

Guide #166: Radioactive Materials – Corrosive (Uranium hexafluoride/Water-sensitive)

Guide #	Examples
155	Acetyl chloride, allyl isothiocyanate, amyltrichlorosilane, butyl isocyanate, diethyldichlorosilane, ethylchlorothioformate, isochloroformate, phenyl isocyanate, n-propyl chloroformate, trimethylchlorosilane
156	Alkylsulfuric acids, butyric anhydride, cyclohexyl isocyanate, dichlorophenyltrichlorosilane, dimethyl sulfate, ethylsulfuric acid, malenic anhydride, phenyltrichlorosilane
157	Aluminum phosphide pesticide, antimony pentafluoride, arsenic chloride, barium cyanide, barium oxide, calcium cyanide, calcium oxide, ferric chloride, hydrofluoric acid, perchloromethyl mercaptan, phosphorus trioxide, potassium cyanide, sodium cyanide, vanadium trichloride
166	Uranium hexafluoride

Acetyl chloride when contacted with water or air moisture produces the corrosive hydrochloric acid and acetic acid; it can produce skin burns; a 2 ppm concentration in air is irritating. Acetyl chloride is also flammable. Allyl isothiocyanate, which is also flammable, is a violent irritant if inhaled and is a powerful lachrymator; if contacted with acid, toxic hydrogen cyanide is released. Amyltrichlorosilane is also flammable and releases toxic hydrogen chloride (or hydrochloric acid) on contact with water.

N-propyl chloroformate is also a flammable liquid; if the chemical is mixed with water including moisture in the air it will hydrolyze [react with water] to form hydrochloric acid and various other chemicals. The reaction time is not quick (about half of the chemical will be converted within 30 minutes), but it is fast enough for the chemical to be very irritating to the eyes and mucous membranes.

Dimethyl sulfate is a combustible liquid that can react with water to form methyl alcohol and sulfuric acid. These chemicals are irritating and can cause severe burns to the eyes, skin, and respiratory tract.

Aluminum phosphide pesticide typically contains about 55% active ingredient and 45% inert ingredients and is typically in the form of pellets or tablets. If wetted, some phosphine is given off but at a slower rate compared with the pure chemical. The pesticide itself is not combustible.

Calcium oxide releases considerable heat when mixed with water. Calcium cyanide, potassium cyanide, sodium cyanide, etc., form the toxic hydrogen cyanide when mixed with water. Cyanide compounds are deadly if inhaled or ingested. If the water is made acidic or is heated, the hydrogen cyanide will be released as a toxic gas.

Uranium hexafluoride releases the toxic gas, hydrogen fluoride, if contacted with water or moisture in the air. The residual, a white-colored uranium compound, is soluble in water.

There are several other guide numbers in the ERG that include substances which can react violently with water and/or produces toxic gases if spilled in water even though the term, water reactive or water sensitive is not used in the guide heading. These include: guide #170, metals (powders, dusts, etc.); guide #171 (a miscellaneous category covering low to moderate hazard substances), and guide #143, unstable oxidizers. For example, zinc dithionite and zinc hydrosulfite under guide #171 produces hydrogen sulfide and sulfur dioxide if spilled in water. Frozen chlorine dioxide under guide # 143 produces chlorine if spilled in water.

Many chemicals will react with a small amount of water generating enough heat that possibly nearby combustibles might be ignited, or result in an explosion is the chemical is confined in a container.

The ERG provides a list of water-reactive materials which produce a large amount of toxic gases when spilled in water. This list is near the end of the Guidebook. The list of toxic gases generated include ammonia, bromine, chlorine, hydrogen bromide, hydrogen chloride, hydrogen cyanide, hydrogen fluoride, hydrogen sulfide, phosphine, sulfur dioxide, and sulfur trioxide.

The ERG also provides a table listing initial isolation zones and protective action distances for many chemicals. For those chemicals which produce toxic gases if spilled in water, the category "when spilled in water" is created. The initial isolation zone and protective action distances are based on inhaling the toxic gases produced from water reactions and not in inhaling the original chemical. Obviously, large spills (> 55 gallon container) are going to result in greater protection action distances than small spills. The greater night time protective action distances assumes that the air is more stable on the average during the night; as a result, the toxic chemical is less likely to disperse and can travel a greater distance downwind.

Example: Chlorine Chemical Fire Accident at Springfield, MA, June 17-19, 1988.

Advanced Laboratories in Springfield MA purchased the chemical trichloroisocyanuric acid in bulk and blended it with buffers and other materials and sold the product in small packages for use as a disinfectant in swimming pools. The use of trichloroisocyanuric acid in formulations such as prepared by Advance Laboratories is considered a much safer alternative to disinfecting swimming pools than use of chlorine or sodium hypochlorite solutions. Trichloroisocyanuric acid is a white crystalline powder or granules which Advanced Laboratories purchased in 300 lb cardboard drums. If a small amount of chemical formulation is added to a large volume of water as in a swimming pool, the chlorine released accomplishes the disinfection.

However, if the raw material trichloroisocyanuric acid is wetted with a small amount of water, chlorine and the explosive gas nitrogen trichloride is released along with considerable heat. It was believed that some of the bulk chemical became moistened from rain entering an open door or window on 17 June resulting in the release of chlorine [with accompanying heat]. The fire department ordered evacuation within a quarter mile from the plant and ordered windows on all sides to be broken to ventilate the building.

Later a thunderstorm caused rain to enter the broken windows wetting more material, this time the heat generated resulted in a fire. The automatic sprinkler system was set off wetting additional chemicals. A second evacuation was ordered encompassing a radius of 1 mile from the plant. The situation was later declared under control, and people were allowed to return home.

However, water that had accumulated caused one or more of the drums containing the chemical to collapse. Fire broke out again and spread to combustible materials stored nearby. The release of chlorine, hydrogen chloride, and NOx , resulted in the evacuation of 20,000 to 30,000 people, on 19 June. Most of the fire-fighting efforts were directed towards saving nearby facilities and directing the chlorine plume up into the air. The facility itself was a total loss.

When this writer (John Nordin) interviewed the Fire Department and City Officials several weeks after the incident, they said that the company had not disclosed what chemicals or hazards of what was stored (a requirement under Community Right-to-Know laws), and what was known about the hazards was pieced together afterwards.

ERG Guide #141 (Oxidizers –toxic) applies to trichloroisocyanuric acid. The chemical may explode from heat or contamination, and can ignite combustibles.