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Reactive Material Hazards

What You Need To Know

SAFETY ALERT

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Reactive Material Hazards

What You Need To Know

Many facilities have chemically reactive materials and systems without knowing the hazards they pose. Others are aware of the hazards, but have inadequate safeguards. Still others have situations where materials are adequately controlled individually, but the potential for a major incident exists if materials are inadvertently combined. Here are five examples:

- Rainwater leaked into a room where hundreds of drums of dry swimming pool chemicals were stored, causing an explosion. The explosion and resulting fire set off the sprinkler system that soaked the remaining drums. The fire, explosions and chlorine releases lasted three days. Over 25,000 people were evacuated, and 275 people went to the hospital with skin burns and respiratory problems.
- Twenty-three people were sent to the hospital after a chemical release at a resort casino. Two cleaning agents were apparently mixed together in the basement of the building, generating vapors that permeated part of the resort.
- A runaway reaction and reactor explosion occurred in a resins production facility that killed one worker and injured four others. To control the reaction rate, an operating procedure called for the slow addition of one of the raw materials to the reactor. The runaway was triggered when the raw materials and catalysts were improperly charged to the reactor simultaneously, followed by heat addition.
- A massive explosion and fire occurred at an agricultural chemical packaging facility in Arkansas, killing three firefighters and injuring a fourth. The likely cause was a supersack of azinphos-methyl (an insecticide) being placed near a hot compressor exhaust pipe.
- Five workers were killed when a blender exploded. The blender was used to mix several dry powders, including aluminum powder and sodium hydrosulfite. The likely cause of the explosion was the unintentional introduction of water into the blender, possibly through a leaking water-cooled seal.

This document is intended as an introduction to reactive material issues for people whose main business is ***not*** reactive materials and systems. Further, it does ***not*** replace any of the more extensive guides and references that deal with this topic in detail, or eliminate the need for competent expert analysis in dealing with these issues. The last section of this document lists references and sources of information that readers are strongly encouraged to use.

Reactivity is the tendency of a material or combination of materials to undergo chemical change under the right conditions. Chemical reactivity is a highly desirable trait that permits a wide variety of useful materials to be synthesized. It also allows products to be made under relatively moderate conditions of pressure and temperature, saving energy and reducing the physical risks of high-temperature and/or high-pressure equipment. Even some consumer products such as swimming pool chemicals have reactive properties. On the other hand, it is these properties that make reactive materials so useful that also pose hazards to health and property, and reactions are not limited to intended and controlled situations.

You may find it helpful to identify and control reactivity hazards in two broad categories: ***reactive materials*** and ***reactive interactions.*** ***Reactive materials*** are commonly regarded as those materials that can be hazardous by themselves when caused to react by heat, pressure, shock, friction, a catalyst, or by contact with air or water. ***Reactive interactions*** require the combining of two or more materials to pose a hazardous situation by chemical reaction.

So, what *do* you need to know about reactive materials and interactions? The following diagram will guide you through the four key questions that you must be able to answer. The best time to consider these questions is when designing a new operation or facility, but they should be answered for existing operations as well, particularly when making changes or bringing in new materials.

1 Do we handle REACTIVE MATERIALS?

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2 Can we have REACTIVE INTERACTIONS involving materials that we handle?

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If **1** and/or **2** are answered YES, then your reactivity hazards must be contained and controlled throughout the entire lifetime of your facility to avoid loss/injury incidents.

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3 What DATA do we need to control these hazards?

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4 What SAFEGUARDS do we need to control these hazards?

These questions are addressed in turn on the following pages.

1 Do We Handle Reactive Materials?

Chemical reactivity has many different names, such as reactive materials, runaway reaction hazards, instability, thermal sensitivity, and incompatibility. Flammability, toxicity, and corrosion are also forms of reactivity. Since these topics are addressed elsewhere, our focus here will be on those reactions that fall outside the normal definitions of flammable or toxic and that generally occur far more rapidly than corrosion.

To decide if we handle reactive materials, we want to identify those materials that can cause a dangerous release, such as of heat, blast energy, toxic vapors, or gases that could rupture a container, when exposed to conditions that may reasonably occur in normal or abnormal situations. This step is sometimes called an *intrinsic* evaluation, as the information we are seeking relates to a property of the material itself.

Material Safety Data Sheets (MSDSs) are a good place to begin identifying reactive materials. You should have an MSDS from your supplier for every hazardous material you have on hand. While formats vary, there should be a section titled "Reactivity Data," "Stability and Reactivity," or similar, which outlines the material's main reactivity hazards. This will not tell you everything you need to know, but it should give you an immediate warning of a major reactivity hazard associated with the material. Other clues may be found in MSDS sections dealing with fire fighting measures or explosion data.

Be aware that MSDSs for the same material but from different sources can vary considerably in what they report as hazards. For this reason, it is wise to consult multiple MSDSs and other sources before concluding that a material is or is not hazardous. In addition to MSDSs, there are many other readily available references that can provide similar information, often in more detail than the MSDS. Several are listed in the "Where Can I Get More Help?" section of this document, under Reactive Materials.

Here are some intrinsic reactivity hazards and their definitions. *Incompatible materials* will be considered in the next section of this document, as reactive interactions.

Reactivity Hazard	General Definition	Examples
UNSTABLE (DECOMPOSING, THERMALLY SENSITIVE, SHOCK SENSITIVE, EXPLOSIVE)	Has the tendency to break down (decompose) over time or when exposed to conditions such as heat, sunlight, shock, friction, or a catalyst with the resulting decomposition products often being toxic or flammable. Decomposition can be rapid enough to give an explosive energy release and can generate enough heat and gases for fires/explosions.	Trinitrotoluene (TNT), dibenzoyl peroxide, ethylene oxide, acetylene, picric acid, hydrogen peroxide (concentrated)
POLYMERIZING	Has the tendency to self-react to form larger molecules, while possibly generating enough heat/gases to burst a container	Acrylic acid, styrene, 1,3-butadiene
PYROPHORIC	Will ignite spontaneously when exposed to air	Phosphorus, silane
PEROXIDE FORMER	Has the tendency to slowly react with oxygen, such as from being exposed to air, to form unstable organic peroxides	1,3-Butadiene, isopropyl ether
WATER REACTIVE	Will react with water or moisture. Some react slowly; others violently. Heat and flammable/toxic gases may be produced.	Sodium, sulfuric acid, acetic anhydride
OXIDIZER	Will give up oxygen easily or readily oxidize other materials.	Chlorine, nitric acid

2 Can We Have Reactive Interactions?

Many materials that are not considered "reactive materials" can nevertheless react dangerously with other, incompatible materials. The other material may be there intentionally (addition of the right material, but in the wrong amount) or by accident (such as contaminants like rust or lubricants). Conditions under which the materials are used (pressure, temperature, humidity, concentration, etc.) can also change the reactive behavior dramatically. For these reasons, identifying reactivity hazards involving the mixing of two or more materials is highly situation-dependent and not readily addressable using a "cookbook" list, or rule-based prescriptive approach. This section presents an *extrinsic* approach to identifying reactive interactions that goes beyond the intrinsic properties of the individual materials that may be associated with your business.

Determining the potential for dangerous interactions is not always easy. Take concentrated sulfuric acid as an example. By itself, it is very stable unless heated to high temperatures. It is non-flammable, and has a fairly low vapor pressure. However, mix it with water, or worse, a caustic solution, and it can rupture a tank in seconds. The key to evaluating the reactive hazard in this example is to first **identify** that both concentrated sulfuric acid and caustic are present. Then, safeguards can be put in place to ensure the two materials do not come into uncontrolled contact.

The first thing to do is determine what you have on site, and then determine which materials are reactive with which other materials. There are some easy-to-use tools that can help in this analysis, and one of the best is called a *compatibility chart*. Other references may call this a *chemical compatibility chart*, a *chemical interactivity chart*, or a *chemical interaction matrix*.

A hypothetical example of such a chart is shown below. All intended chemicals and common contaminants (such as utility streams that might leak in) are listed on both the horizontal and vertical axes. Each box in the chart represents the interaction of the two gridded components. Each half of the chart represents all possible binary (two-component) mixtures. Therefore, only one half of the matrix needs to be filled out to assess possible two-component combinations. This kind of simple analysis does not consider order of mixing (X mixing into Y is treated the same as Y mixing into X), which may be an important consideration such as when handling strong acids.

Example Compatibility Chart for an Acetic Anhydride Handling Facility

Will These Two Materials React?	Acetic Acid	Acetic Anhydride	Cooling Water	Sulfuric Acid	50% Caustic	Lube Oil	Cleaning Solution
Acetic Acid							
Acetic Anhydride	***Reactive***						
Cooling Water	***Not reactive***	***Reactive***					
Concentrated Sulfuric Acid	***Reactive***	***Reactive***	***Reactive***				
50% Caustic	***Reactive***	***Reactive***	***Reactive***	***Reactive***			
Lube Oil	***Not reactive***	***Not reactive***	***Not reactive***	***Reactive***	***Reactive***		
Cleaning Solution	*Find out what the cleaning solution contains, then determine reactions*						

Note that some of the "reactions" indicated by the chart are combinations where the heat generated by diluting a material may cause pressurization of an enclosure. Note also that more information is needed about the chemical composition of the cleaning solution before its compatibility with the other materials can be determined.

At this point, we are not trying to decide how likely it is for the two materials to come together. We are only identifying what combinations pose a reactivity hazard. The questions addressed in the next two sections of this document will lead you to consider what data are needed to determine the severity of an interaction and whether safeguards are adequate to keep incompatible materials from being combined in an uncontrolled manner.

Completing a compatibility chart often requires persistence and determination. You or someone in your organization may be able to readily answer whether most combinations are reactive or not. A few combinations may take more work. One way to do a quick check on chemical combinations is to use a method such as the **Chemical Reactivity Worksheet**, available free of charge (see the Where Can We Get More Help? section of this document under Reactive Interactions). This program has over 6,000 chemicals in its database, and predicts the results of two-chemical mixtures by reactive group combinations. The Worksheet not only indicates possible hazardous interactions, it also sets up a compatibility chart and indicates potential consequences of the interactions (e.g., "Heat generation by chemical reaction, may cause pressurization").

Some other important considerations at this stage:

- MSDSs and the literature may not provide the information needed, especially if the chemicals being used are not common or are new materials under development. In these situations, specific testing may be needed to provide enough information to accurately fill out the compatibility chart.

- A compatibility chart only considers two-component mixtures. Consider also whether any interactions among three materials are hazardous; e.g., one acting as a catalyst for the reaction of two others.

- Check with your purchasing people to find out what materials are brought on site.

- Do not overlook materials that are produced on site, including chemical intermediates.

- Be careful about ruling out materials on the basis of quantity alone. Mixing liquid waste materials in 55-gallon drums has resulted in numerous incidents. Acetylene in contact with copper can produce shock-sensitive copper acetylides, which can be dangerous in very small quantities.

- Consider materials such as air, water, oil, or foreign objects that could be left inside equipment during cleaning or maintenance operations. Physical processing conditions, such as temperature, pressure, humidity, and oxygen content should also be considered.

- Be sure to consider the possibility of mixing materials in your waste disposal or sewer system.

3 What Data Do We Need to Control These Hazards?

Now that you know where the reactive material and interaction hazards are at your facility, you will need to ensure all of the hazards are contained and controlled on an ongoing basis.

Reactive Materials. You can get most of the data you need to safely handle many reactive materials from material suppliers. Depending on the nature of the material and how you will be storing and using it, the needed data for each reactive material will likely include:

- Materials of construction to use and to avoid
- Common materials and contaminants to avoid (e.g., air, water, rust, oil, acids, caustic)
- Storage configurations, maximum quantities, and minimum/maximum storage temperatures
- Shelf life considerations
- What to do in the event of a leak or spill
- What to do if an unwanted reaction starts
- How to fight a fire involving the material
- Possible toxic/corrosive/flammable products of reaction or decomposition
- Any special considerations (e.g., "light-sensitive" or "forms unstable byproducts over time")

You should be able to find some of this information on the MSDS, such as how to respond to a spill or fire. In some cases, suppliers have developed technical bulletins that provide very detailed engineering information. You should ask for and use these bulletins if they are available.

If you are producing a unique material, you or an experienced reactive materials testing company will need to do your own material assessments. This may include testing for water reactivity, shock sensitivity, dust explosivity, and thermal stability in actual storage and handling configurations, as well as finding out all of the items in the list above.

Reactive Interactions. Likewise, your material supplier may not be much help for reactive interactions on your compatibility chart. For these combinations, the first thing you need to know is how much heat or gas can be generated. In some cases, this can be as simple as using the heat of mixing published in a technical reference book. In others, it may involve use of special equipment to accurately measure the amount of heat and pressure generated during a complex chemical reaction.

In addition, you will need to know under what conditions a reaction will occur, whether an explosive mixture can result, and whether the reaction products (e.g., off-gases) are hazardous.

A number of sophisticated tools can be of assistance in these areas. Two of the more common tools are the Differential Scanning Calorimeter (DSC) and the Accelerating Rate Calorimeter (ARC). The resulting data can then be used to properly size heat transfer equipment and relief devices, as well as establish safe limits of operation. You may need to get professional assistance to gather the data you require.

A word of warning: be very careful in the use of information from small-scale tests. For example, the maximum storage temperature for a temperature-sensitive material will vary, depending on the storage quantity and configuration. Safe operating limits may also change such as with differing sizes and shapes of mixing vessels.

4 What Safeguards Do We Need to Control These Hazards?

Many materials in common use today have obvious reactivity hazards, for example, explosives, laboratory chemicals, and raw materials to make plastics and other useful products. Yet they are handled safely every day. How? Their hazards have been recognized and controlled so that undesirable events (those which can cause loss and harm) do not happen. Your first source of information for controlling hazards should always be your material supplier.

Inherently Safer. If you can eliminate the use of reactive materials, substitute materials with less reactivity potential, reduce inventories of materials, and/or reduce the severity of operating conditions, then you will be moving in the direction of an inherently safer operation. Be very careful that one hazard is not just substituted for another when making these kinds of changes.

Codes and Standards. Where some reactivity hazards have been handled for many years by companies in similar ways, industry codes and standards have been developed that specify needed safeguards. After your material supplier, these codes and standards should be your next point of reference for controlling hazards. For example, organic peroxides are commonly used as initiators and curing agents. If you handle organic peroxides, NFPA 432 (formerly NFPA 43B), *Code for the Storage of Organic Peroxide Formulations,* gives safe storage and handling considerations.

Reactivity Safeguards. When reactivity hazards are unavoidable, multiple safeguards can be set up as lines of defense. These safeguards can prevent abnormal situations, keep abnormal situations from leading to incidents such as fires and explosions, and reduce the severity of consequences if an incident does occur. To be effective, safeguards, such as those listed below, must be carefully designed, properly installed, and maintained in working order throughout the lifetime of your facility.

- Train all personnel to be aware of reactivity hazards and incompatibilities and to know maximum storage temperatures and quantities
- Design storage and handling equipment with all compatible materials of construction
- Avoid heating coils, space heaters, and all other heat sources for thermally sensitive materials
- Avoid confinement when possible; otherwise, provide adequate emergency relief protection
- Avoid the possibility of pumping a liquid reactive material against a closed or plugged line
- Locate storage areas away from operating areas in secured and monitored locations
- Monitor material and building temperatures where feasible with high temperature alarms
- Clearly label and identify all reactive materials, and what must be avoided (e.g., heat, water)
- Positively segregate and separate incompatible materials using dedicated equipment if possible
- Use dedicated fittings and connections to avoid unloading a material to the wrong storage tank
- Rotate inventories for materials that can degrade or react over time
- Pay close attention to housekeeping and fire prevention around storage and handling areas
- Some operations will need to be contained within special blast-resistant enclosures
- Have an emergency response plan in place and conduct periodic drills

Each of these considerations will not, of course, apply to every material and situation. To look at your operation in a systematic, rigorous way with a knowledgeable group of people, a *process hazard analysis* can be conducted. Books and outside consulting resources are available that can provide guidance and professional assistance when needed.

Where Can We Get More Help?

You may find the following references useful in getting the information you need to identify and control reactivity hazards. References marked with an asterisk (*) can be obtained from the American Institute of Chemical Engineers – Center for Chemical Process Safety, 1-800-AIChemE, www.aiche.org/ccps/products.

Reactive Materials

MSDSs from suppliers and via internet; www.ilpi.com/msds links to many MSDS sites

Lewis, *Sax's Dangerous Properties of Industrial Materials,* ISBN 0471354066

NFPA 49: Hazardous Chemicals Data, www.nfpa.org

U.S. Dept. of Transportation. *Emergency Response Guidebook*, http://hazmat.dot.gov

Reactive Interactions

Bretherick's Handbook of Reactive Chemical Hazards, can be searched from www.chemweb.com after free registration

NFPA 491: Guide for Hazardous Chemical Reactions, www.nfpa.org

U.S. National Oceanic and Atmospheric Administration (NOAA), *Chemical Reactivity Worksheet*, http://response.restoration.noaa.gov/chemaids/react.html

American Society for Testing and Materials (ASTM), *Guide E2012-00, Standard Guide for Preparation of Binary Chemical Compatibility Chart*, www.astm.org

Reactivity Data

**Guidelines for Chemical Reactivity Evaluation and Application to Process Design*

Yoshida, Wada and Foster, *Safety of Reactive Chemicals and Pyrotechnics,* ISBN 0444886567

Analysis and Safeguards

*Lees, *Loss Prevention in the Process Industries* ISBN 0750615478

**Guidelines for Safe Storage and Handling of Reactive Materials*

**Guidelines for Process Safety in Batch Reaction Systems*

**Guidelines for Hazard Evaluation Procedures, Second Edition with Worked Examples*

Professional Assistance

Professional Assistance Directory of Process Safety Consultants. See the CCPS website at www.aiche.org/ccps/pdad/profdr.asp

Government Agencies

The U.S. Environmental Protection Agency (www.epa.gov/ceppo) shares information on preventing and preparing for chemical emergencies.

The U.S. Occupational Safety and Health Administration (*www.osha.gov*) has additional information related to process safety management.

The U.S. Chemical Safety and Hazard Investigation Board (www.chemsafety.gov) publishes investigation reports, such as on major incidents and reactive chemical hazards

The Center for Chemical Process Safety was established by the American Institute of Chemical Engineers in 1985 to focus on the engineering and management practices to prevent and mitigate major incidents involving the release of hazardous chemicals and hydrocarbons. CCPS is active worldwide through its comprehensive publishing program, annual technical conference, research, and instructional material for undergraduate engineering education.

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American Institute of Chemical Engineers
3 Park Avenue
New York, New York 10016

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A final word, quoted from The Dow Chemical Company, a leader in the field of reactive chemistry:

"We recognized long ago that virtually any chemical can be reactive if involved in the wrong situation or scenario. We therefore do not limit our hazard assessments to any specific list of chemicals. Some companies limit the scope of their reactive chemicals hazard assessments to scenarios that involve only inadvertent mixing of chemicals. While this type of scenario is an important part of any reactive chemicals program, it is far from all of what needs to be considered in a total reactive chemicals hazard assessment effort. Companies whose work is just chemical handling may find it appropriate to only address inadvertent mixing, but additional dimensions need to be included for companies involved with processing or reacting chemicals. Some additional types of scenarios beyond inadvertent mixing of chemicals that need to be included in a comprehensive Reactive Chemicals program include:

- Reactor loss of control scenarios and lines of defense
- Inadvertent lack of mixing of things like reaction inhibitors in reactors or storage tanks
- Accelerated corrosion and loss of containment due to material incompatibility
- Special scenarios that result in loss of stability of chemicals."

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