Chemical Storage: Myths vs. Reality

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Introduction

A large number of resources explaining proper chemical storage are available. These resources include books, databases/tables, and articles that explain various aspects of chemical storage including compatible chemical storage, signage, and regulatory requirements. Another source is the chemical manufacturer or distributor who provides storage information in the form of icons or color coding schemes on container labels. Despite the availability of these resources, chemical accidents stemming from improper storage, make up almost 25% of all chemical accidents (1) (2). This relatively high percentage of chemical storage accidents suggests that these publications and color coding schemes although helpful, still provide insufficient information to completely mitigate storage risks. This paper will explore data gaps in published storage information, examine the associated risks, and suggest methods to help further eliminate chemical storage risks.

Compatible Chemical Storage Methods

Compatibility is the subject that gets the most attention during discussions of chemical storage. The two methods most commonly cited as a cure to solve incompatibility storage issues are to provide a listing of compatibilities by chemical class or to provide a compatibility listing by chemical. A third method that is not usually cited in the literature is to use the manufacturer's compatibility scheme. All three methods have their limitations.

Compatibility Listings by Chemical Class

A common approach used to define chemical compatibilities for storage purposes comes from determining each chemical's class and then determining the proper compatibility group based upon that class from a table. Tables of compatibility groupings include the U.S. Coast Guards Cargo Compatibility Chart (3), the U. S. Environmental Protection Agency (EPA) Method 600 Compatibility Chart (4) which was ultimately used as the basis for the National Oceanic and Atmospheric Administration (NOAA) Chemical Reactivity Worksheet (5), and a multitude of "Home-Grown" charts tailored to the needs of the specific location. While the approach to classify chemical compatibilities by chemical class appears at first glance to be a good method that can be used to ensure compatible chemical storage, it is only marginally better than storing chemicals alphabetically. There are several reasons for this.

1) This method can create hazardous situations. Many chemicals belong to more than one hazard class. This can lead to confusion as to which class is appropriate for the chemical in question. For example, nitric acid is both an acid and an oxidizer. If one stores it as an acid, then there is the potential that it will be stored with organic acids such as acetic or formic acid, which, if mixed, can lead to a significant adverse reaction. Acetic acid is not only an acid, but is also a combustible liquid. Acetic anhydride is flammable, corrosive, and water reactive. Storing them with flammable liquids such as methanol would not be a problem. It should be noted that some compatibility schemes state that organic acids are incompatible with alcohols, but this is rarely the case. (4)

2) Storage schemes based upon hazard classes are prone to failure because some hazard classes are not listed. Sulfuric acid is a strong mineral acid, but it is also a strong dehydrating agent. Few, if any, classification schemes include dehydration as a chemical class and yet it can be significant. If one inadvertently mixed another strong acid such as hydrofluoric or hydrochloric acid with sulfuric acid, the sulfuric acid would immediately dehydrate the hydrochloric or hydrofluoric acid. The result of this reaction would be a large amount of heat generation and the immediate off gassing of either hydrogen chloride or hydrogen fluoride due to the removal of water as a solvent.

3) Classification schemes do not work well because not all chemicals in a given class are compatible. Sodium dichloroisocyanurate and calcium hypochlorite are both oxidizers and belong to no other class of chemical, yet the mixing of these two materials can lead to the formation of nitrogen trichloride, a shock sensitive explosive (National Fire Protection Association (NFPA) 49, *Hazardous Chemicals Data*.(6)

4) Classification schemes do not lend themselves toward consistent application between work areas. If a worker spends part of his time in a work area where nitric acid is defined as an oxidizer and the rest of his time where nitric acid is classed as an inorganic acid, then the worker can become confused as to which storage practice is used in which area. Confusing storage schemes can lead to unsafe storage practices.

5) Classification schemes are based upon chemical classes such as esters, aromatic amines, non-oxidizing mineral acids, etc. While this classification scheme may be interpretable by a chemist, most workers are not chemists and would find these classifications confusing. Some classes such as non-oxidizing mineral acid could even confuse a chemist when the conditions present will determine whether an acid, such as sulfuric acid, is an oxidizer or not. As confusion increases, so does the potential for a mistake.

Chemical Storage Listings

Another method in use to ensure compatible chemical storage is to use compatibility listings or charts. These documents list various chemicals and those chemicals with which they are compatible. Some, such as the American Chemical Society (ACS) publication *Safety in Academic Laboratories* (7), are fairly short, while others are more extensive. The primary difficulty with using these lists/charts is that they are limited. None provide information for every chemical or chemical product and, many times, some incompatible interactions are not noted. If one were to rely upon one of these charts, then it might provide a false sense of security if one assumes the listing is comprehensive. Another difficulty with these charts is that one does not always know the type of interaction or the conditions being described which cause the mixture to be incompatible nor is the applicability always apparent. For example, solutions of analytical reagents made up in dilute acids and bases may not represent a significant issue even though the listing indicates that it is incompatible. A last issue concerning the difficulty in using these lists is that their use requires a certain amount of expertise and different users will have differing opinions as to how the listings should be applied. Variations in expertise or differences in opinion can lead to inconsistent applications of the storage scheme, which could become a problem if workers move from one work location to another.

<u>Manufacturer's Storage Schemes</u>

Blindly using manufacturer's schemes can also lead to incompatible storage situations or storage situations that potentially violate regulations. Two well known manufacturer's or distributors of chemicals have similar color coded storage schemes. In both schemes, the color red is used to denote flammable storage, white is used to denote acid storage and yellow is used to denote oxidizer storage. If one looks at how various acids are classified according to these two schemes, one can immediately see numerous issues (Table 1).

Manufacturer 1		Manufacturer 2	
Chemical	Compatibility Code	Chemical	Compatibility Code
Hydrofluoric Acid	White	Hydrofluoric Acid	White
Sulfuric Acid	White	Sulfuric Acid	White
Hydrochloric Acid	White	Hydrochloric Acid	White
Phosphoric Acid	White	Phosphoric Acid	White
Oxalic Acid	White	Oxalic Acid	White
Formic Acid	White	Formic Acid	White
Acetic Acid	Red	Acetic Acid	Red
Nitric Acid	Yellow	Nitric Acid	White
Perchloric Acid	Yellow	Perchloric Acid	White

Table 1. Storage classification of acids using two similar manufacturer's storage schemes.

1) Incompatibilities exist within each storage scheme. Both manufacturers indicate that sulfuric acid can be stored compatibly with hydrochloric acid or hydrofluoric acid which has been shown not to be the case (see (2) above). Additionally, Manufacturer 2 incorrectly indicates that the oxiding nitric and perchloric acids are compatible with the organic formic and oxalic acids. Both manufacturers recommended acetic acid be stored

as a flammable liquid while neither recommended it for formic acid. Both formic and acetic acids are classified as combustible liquids. This may require them to be stored in flammable liquids storage cabinets depending on the quantity of material on-hand and the limits imposed on the facility by codes or standards.

2) The two systems appear to be similar, but it would take a well trained individual to realize that they are different and what those differences are. If no compatibility scheme exists or the user is relying upon the manufacturer to provide the compatibility information on each chemical container, then using chemicals from more than one manufacturer could lead to incompatible chemical storage as the worker gets the various schemes confused.

3) Most locations do not limit the chemicals present to those offered or classified by one manufacturer. If no other compatibility scheme exists, then how does one store a chemical that is not classified by the manufacturer?

4) Manufacturer's compatibility schemes are not designed to address regulations which set facility limits on the quantity of specific chemicals that may be stored. For example, OSHA in 29CFR 1910.106 "Flammable and combustible liquids" or locally enforced fire codes such as NFPA 1 "Uniform Fire Code" limit how much of a flammable or combustible liquid may be stored in various locations such as outside of a flammable liquids storage cabinet. Storing organic acids that are not identified as being a flammable or combustible liquid could cause one to become noncompliant with flammable and combustible liquids storage requirements.

Other Chemical Storage Considerations

Storage areas are rarely discussed to any depth in chemical safety references. When they are discussed, topics such as provisions for bonding and grounding of flammable liquids, separation distances, storage unit (i.e. shelves or cabinet) types, or ventilation are usually covered. Several other important issues are rarely covered.

Compatibility

When discussing compatibility the issue is usually exclusively limited to compatibilities between chemicals being stored. What is just as important is the issue of compatibility of chemicals being stored with their environment. Examples of improper storage conditions would include:

- Storage of oxidizers on unpainted wooden, shelves is prohibited (for example, NFPA 432 *Code for the Storage of Organic Peroxide Formulations*, 2002 Edition (8) also prohibits the storage of hydrogen peroxide [concentrations greater than 27.5%] on wooden pallets since oxidizer impregnated wood is prone to spontaneous combustion) (see Figure 1).
- Chemicals should not be stored above face level due to the potential of spills falling into a person's face (see Figure 2).

- Storage of water reactive chemicals in a facility with a water-based fire suppression system (due to potentially adverse chemical reactions during a fire response),
- Corrosives stored on unpainted shelves (since corrosion which can weaken shelves or hydrogen gas generation can occur) (see Figure 3) ,
- Acid storage in rooms with unpainted cement floors and/or cement or concrete block walls (due to the reaction between acids and cement), and
- Oxidizers cannot be stored where they will come into contact with heating units, piping or ducts (since some oxidizers will violently decompose upon heating).

Figure 1. (photo by Ken Niswonger, Chief Chemist Hazardous Materials Division, Colorado Department of Public Health and Environment) **Storage of chemicals on wooden shelves**. Are any chemicals stored here oxidizers? Note the flammable liquid loading on the right. This shelving arrangement would not last should a fire occur even with fire sprinkler activation.

Figure 2. (photo by Ken Niswonger) **Chemicals stored above face level**. Many chemicals are stored above face level have the potential for spilling into a worker's face during their removal or placement on the shelf. Some chemicals shown on the upper shelves have ground glass or cork stoppers. One should note the good practice of having a lip on chemical storage shelves to protect from containers falling off from vibrations due to seismic activity, road traffic, building work, etc.

Figure 3. (photos by Ken Niswonger) **Storage of Acids in Cabinets**. Perchloric acid stored in a cabinet designed for acids (left) shows no corrosion while perchloric acid stored in a metal cabinet (right) shows extensive corrosion even when stored in a plastic secondary container and the metal is painted. Note the cracked cap on the container (right).

<u>Maintenance</u>

Another issue that is rarely discussed is the need to control those activities performed in a storage area. Because chemical storage areas are inherently unsafe, all activities to be performed there must be reviewed for safety. This means that activities such as maintenance, building modifications, etc., must all be carefully controlled and reviewed to ensure that these activities can be performed safely.

Chemical Storage Requirements

There are many requirements that regulate the storage of chemicals. These requirements may come from federal or local governments or may be from consensus standards such as those from the NFPA and the Compressed Gas Association (CGA) (9-15). These requirements are continuously evolving. For example, the recently revised NFPA 55, *Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders, and Tanks* 2003 Edition (10), greatly expanded its scope by including extensive requirements for cryogenic liquids.

<u>Compatible Chemical Storage</u>

Occasionally, one will hear an argument about how compatible chemical storage is a good idea, but can be taken too far. An example of this argument is how some solid oxidizers, such as nitrates, do not need to be segregated from organics. The argument is that a reaction between nitrates and solid organics will not occur under any condition and that requiring their segregation during storage is not justified (16). While this may be true from a technical point of view, fire codes, building codes, and various NFPA standards require their segregation.

Facility Limits

Locally enforced fire/building code requires facilities to limit the amount of hazardous material stored there. To meet this requirement each facility must classify each chemical according to their hazards. Examples of hazards include class 1, 2, 3 and 4 oxidizer; toxic; highly toxic, pyrophoric gas; etc. There are approximately forty hazard classifications and a chemical is likely to be classified as having more than one hazard. Fire code limits how many pounds of a liquid or solid and cubic feet of a gas of a given hazard classification can be stored in a facility. If these limits are exceeded then the local authority having jurisdiction may suspend the facility's occupancy permit until limits are attained. If quantities greater that those listed need to be stored, then specialized structures meeting various building and fire codes can be constructed for that purpose.

Security

Security should be a priority for all chemical storage areas. Security is required and is essential for many reasons.

First, basic chemical inventory and management principles require secured storage. If free access to chemical storage areas is allowed, then users will wander in and out with chemicals and the ability to track and keep an accurate inventory will be lost or made much more difficult. Controls can be put in place to monitor when users remove chemicals, but this can incorporate uncertainty into the chemical management process.

Second, unrestrained access to chemical storage areas can endanger the quality of chemical storage. If personnel are allowed to remove chemicals from a common storage area such as a stockroom and then return them after use, then a question of product quality arises. Incorrect dispensing techniques can result in contaminated or impure chemicals and future users may not want to risk using impure chemicals that could negatively affect their work. This results in opened chemicals accumulating in the storage as fewer users will risk using them. Eventually, these accumulated chemicals must be removed as costly unused/unspent waste.

Third, unrestricted access can result in people placing chemicals in the store room in the wrong, incompatible location, which can increase the danger of an accident in the chemical storage area. Lastly, chemicals represent feedstocks or source materials for illegal activities such as illicit drug manufacturing, bomb making, etc. Unrestricted access can result in pilferage and increased liability. Finally, there are some chemicals which may require increased scrutiny due to other reasons such as being on the Drug Enforcement Administration (DEA) watch list (17) for chemicals used in illegal drug manufacturing.

Time-Sensitive Storage:

Some chemical products are sensitive to the length of time they are stored. One reason a chemical may be time-sensitive is safety. Some chemicals can generate additional hazards such as the formation of explosive peroxides (e.g., ethers) or toxic gases (e.g., chloroform), while others develop explosion from the evaporation of water (e.g., picric acid) or the generation of gases (e.g., anhydrous HF) (18). These chemicals must be identified and properly managed.

Another reason why chemicals may be sensitive to the length of time they are stored is quality. Some products deteriorate over time which affects their quality and their ability to perform a task.

Signage

Signage is an integral part of chemical storage. Signage serves to notify emergency responders and visitors, as well as remind employees of the hazards associated with a particular location. For example, there are specific signage requirements for Compressed Gases (9, 10), No Smoking signs (11 -13), Oxidizers (8), and Flammables (15), as well as those for the NFPA 704 placard.

Recommendations

Is there a cookbook for chemical storage? The answer is no. Safe chemical storage cannot be reduced to a list or chart. Proper chemical storage should not exist as a list or chart, but should be a process consisting of several major steps that are designed for the size and complexity of the inventory. These steps are:

Step 1: Classify All Chemical Products Present

The first step is to classify all chemical products present. Classification comes in two forms. The first is the initial classification of the initial or existing inventory. As the size of the existing inventory increases, the size and expense of this task increases. The second form is the ongoing classification of new or incoming products. It is imperative that new or incoming chemicals are classified prior to their arrival at the facility. This generally requires a pre-review process to be performed to determine the compatibility classification, but this pre-review process must be timely and not hold up the procurement of the product.

In performing these compatibility classifications it is very important to obtain the help of a knowledgeable chemist to classify chemicals in the scheme for several reasons. One reason to obtain the help of a knowledgeable chemist to help classify chemicals according to the compatibility scheme is that many chemicals can fall into multiple hazard or compatibility groupings. For example, nitric acid could be classified as an acid, corrosive, or an oxidizer; acetic acid could be classified as a flammable/combustible liquid, acid, or corrosive; benzoyl chloride could be classified as a combustible liquid, water reactive, unstable (reactive), corrosive, or lachrymator; and acrolein could be classified as a flammable liquid, unstable (reactive), highly toxic, sensitizer, or time sensitive (peroxide former). Determining which class is the most significant is not always easy. While approximately 90% of all chemicals will be simple to classify, the remaining 10% can fall into multiple classification groups and it is important to ensure that these chemicals are correctly classified. What can complicate this determination is the need to look at other chemical classed in a given grouping and ensuring that any new chemical classed in that group does not cause an incompatibility issue to arise.

Another reason to obtain the help of a knowledgeable chemist is that not all chemicals in a given class can be stored together. For example a common pool chemical, sodium dichloroisocyanurate, is an oxidizer, but cannot be mixed with chlorine based oxidizers. If these are mixed, then the explosively unstable nitrogen trichloride is formed. Few, other than a knowledgeable chemist, would be cognizant of this or other incompatible mixtures.

A third reason to obtain the help of a knowledgeable chemist is that the regulations sometimes appear to be contradictory. Someone needs to understand the intent behind the regulation to divine what the regulation is attempting to accomplish in light of the chemistry of the products being managed or stored. An example is the prohibition of storing acids and bases together. While this is a good practice, it is not practical when one has numerous atomic absorption standards made up in dilute nitric acid and a few made up in dilute ammonium hydroxide. Clearly, mixing these acid and base solutions will not result in a hazardous reaction and forcing workers to store such standards separately is inconvenient and unnecessary.

Step 2: Determine the Proper Storage Area

While finding a proper storage area is a task that becomes more complex as the size of the chemical inventory increases, the basic principles remain the same. Some considerations to be aware of when determining a proper storage area are:

Size

One principle is to ensure that the storage area is large enough. For small inventories this is a simple task, but this task becomes more difficult as the inventory size increases especially for facilities where space comes at a premium. To determine the proper size of the storage area, one must have some idea of both the classes of chemicals one is to store and the volume of each. One must also be knowledgeable of the locally enforced building and fire codes. First, each chemical must be classified according to building/fire code hazard definitions and then the estimated quantity of each hazard class compared to locally enforced fire/building code limits. When the quantity of a given hazard is over a limit specified in the building/fire code, then either the quantity must be reduced or a specialized facility must be found or constructed. Second, segregation distances and principles must be obeyed. Some chemical classes must be segregated from other chemical classes by either a specific distance or by structural barriers such as berms or fire walls. Once again, knowledge of fire/building code will be required for complaint storage practices. Third, sufficient area should be allowed so that chemical storage is not cramped. Cramped storage leads to unsafe practices such as storing chemicals above face level (especially toxics or corrosives), overloading shelves making it difficult to inspect chemical containers or obtain containers from the back of shelves, storing chemicals on the floors in aisles, stacking chemical containers on each other, etc.

Compatibility

When the issue of chemical compatibility comes up, most think that this issue refers to one chemical being compatible with another. While this is an important issue in chemical storage, it is equally important to ensure that each chemical is compatible with the storage area itself. Chemicals for which this is particularly important are those that are reactive such as acids, bases, oxidizers, water reactives, etc. Typical mistakes that are made and their solutions are listed in Table 1.

Chemical Class	Incorrect Storage Practice	Correct Storage Practice
Oxidizers	Stored on wooden shelves which can absorb spilled product.	Store on wood coated with an impregnable material such as epoxy paint.
Unstable (Reactive), Oxidizer, Compressed Gases	Stored near heating vents/pipes, in direct sunlight, or other sources of heating.	Store in cool dry area out of direct sunlight.
Water Reactive	Stored in the open in an area covered by a water based fire suppression system (sprinklers).	Store in plainly marked cabinets that meet code requirements.
Acids, Bases	Stored on metal shelves that either have exposed metal or where the paint is easily scratched to expose bare metal.	Store on shelves that are chemical and abrasion resistant such as epoxy painted, wooden shelves.
Organic Peroxides	Stored on shelves with no temperature control.	Store in area such as a refrigerator where the temperature will remain below the self accelerating decomposition temperature (locally enforced building/fire codes should be checked for temperature control and alarm requirements).

Table 2. Typical mistakes made and solutions in determining proper chemical storage areas.

Some compatibility issues are straight forward. For example, if oxidizers are stored on wooden shelves then the wood can absorb spilled oxidizer especially if the oxidizer is in a liquid form. Absorbed oxidizer can then react with the wood to cause a fire or explosion when subjected to compression or shock that could come from placing a container on the spill area. Another example of an obvious compatibility issue concerns the storage of acids or bases on metal shelves. Acids or bases can react with the metal to form hydrogen gas or can corrode the shelf and weaken it. Other compatibility issues are less straight forward. Most do not consider sources of heat when determining a storage area, but heat can cause compressed gas cylinders to overheat and fail, or can cause some oxidizers, organic peroxides, or unstable (reactive) chemicals to undergo an energetic thermal decomposition reaction. Another issue that is commonly overlooked is the storage of water reactive products in a sprinklered area. This practice can cause significant issues during a fire when the sprinklers are activated and containers of water reactive materials could be broken during the response.

Also consider the compatibility of the chemicals with other containers around it. Hexadimethylsilazane is incompatible with steel. If a chemical of the same class is stored in a steel can, the steel can will corrode.

Figure 4 Steel containers incompatible with surrounding chemicals.

<u>Ventilation</u>

Some chemical hazard classes such as flammable liquids require special ventilation when prescribed limits are reached. These requirements include a minimum of one cubic foot of air per minute per square foot floor space and air returns located near the floor. While there are no formal requirements, proper ventilation can eliminate or reduce hazards and potential difficulties. Having adequate ventilation can reduce or eliminate many of the odors associated with chemical storage areas and makes it a more comfortable place to work. Some chemicals should be stored in a room that is at a slightly negative pressure to the rest of the facility with the exhaust being directly vented to the outside. Chemicals in this group would be those with high vapor pressures that can react. This would include acids such hydrochloric acid and bases such as ammonium hydroxide. Vapors from these can react to form ammonium chloride which will cover all surfaces including glass with a white film. This white film can make it difficult to see through the glass on a cabinet door to determine the cabinet's contents. Other types of chemicals that could be stored in this type of room would be those that are a stench hazard (e.g., putrescine, cadavarine), lachrymators (e.g., benzoyl chloride), or toxic with a high vapor pressure (e.g., formaldehyde).

Other Issues

Numerous other issues should be taken into account when looking for a proper chemical storage area. Shelves used for chemical storage should be braced and anchored to prevent their tipping over. Shelves should also be of a substantial construction and have a lip or other means present to prevent chemicals from falling off the shelf. Aisles should typically be a minimum of four feet wide and appropriate illumination should be followed. Floors of storage areas should be made of a noncombustible material and provisions should be available for secondary containment should a spill occur. Locations and room for storage cabinets should be factored into the determination of a chemical storage area. Storage cabinets that might be required include flammable liquids storage cabinets, gas cabinets, and acid cabinets. Likewise, the need and room for gloveboxes, refrigerators and freezers should also be considered. Regulations should be researched to determine what signs need to be posted to alert both every day users and emergency responders and access requirements for the storage area determined. Lastly, the allowing of chemical dispensing in the storage area should be considered. Allowing chemical dispensing could result in additional requirements such as bonding and grounding, specialized ventilation, etc. A fire protection engineer should be consulted to determine these additional requirements.

Step 3: Determine a Chemical Compatibility Scheme

The complexity of determining a chemical compatibility scheme is dependent upon the size of the inventory. Small inventories are the easiest and complexity increases as the inventory increases. Small simple inventories are not likely to contain significant number of products that require special concern. For these inventories, one can simply adopt the labeling scheme present on the manufacturer's label if one is present. This will work well if one procures all chemical products from the one manufacturer, but could present issues if other vendors are used. Another possibility is to develop a simple compatibility scheme and use it. As the size of the inventory increases so do potential problems and the complexity of the compatibility scheme.

Step 4: Publish Chemical Compatibility Classifications

It is important to communicate the chemical compatibility classifications in use. If chemical compatibility determinations are not communicated, then employees will not know how to properly store their chemicals. Equally important with publishing the compatibility determination is to publish these determinations in an easily accessed location(s) and in a format that leaves no question as to the compatibility determination. All the above cited work will be in vain if the workers are not informed of compatibility classifications so classifications must be easily accessible and readily understood.

Step 5: Develop Time-Sensitive Chemical Storage Program

A time-sensitive chemical storage program according to Bailey et. al. (18) should be developed. Elements of this program would include a) identification of time-sensitive chemicals, b) tracking, c) defining proper storage conditions, d) determine inspection periods, e) define when time-sensitive chemicals become “unsafe”, and f) managing “unsafe” time-sensitive chemicals.

Step 6: Feedback

Feedback is very important for the health of the compatibility system. One must always know how the system is working in the field so that classification errors or problems can be identified and fixed before they become insurmountable problems.

Conclusion

Compatible chemical storage is a complex and demanding task that is impacted by regulations, chemical properties, storage conditions and chemical reactivities. This complexity is so great that one can rely on simple solutions for small simple applications. Larger storage applications require a more complex approach that includes individually evaluating each chemical for its proper storage condition, control over the storage area, and implementing a unambiguous chemical storage scheme that is readily communicated to all employees.

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