

## CORROSIVE CHEMICAL HAZARDS & RISK MINIMIZATION

(For assistance, please contact EHS at (402) 472-4925, or visit our web site at <http://ehs.unl.edu/>)

### Background

The Globally Harmonized System (GHS) of classification and labeling of chemicals has two separate classifications for corrosives. These are 'corrosive to metal' and 'skin corrosion.' The two definitions are as follows:

- *A substance or a mixture, which by chemical action will materially damage, or even destroy, metals.*
- *A substance or mixture that will cause irreversible damage to the skin; namely, visible necrosis through the epidermis and into the dermis.*

Corrosive chemicals will be identified with the pictogram shown below. In addition, Section 2 of the Safety Data Sheet (SDS) will include one or more of the hazard statements indicated below.



- H290 May be corrosive to metals
- H314 Causes severe skin burns and eye damage.
- H318 Causes serious eye damage

### pH

Aqueous solutions of acids and bases are compared using the logarithmic pH scale. By definition, pH is the negative logarithm of the hydrogen ion concentration found in the solution and uses a scale from 1 to 14. Because it is a logarithmic scale, a solution with a pH of 1.0 has 10 times more  $H^+$  ions in it than does a solution with a pH of 2.0. Above pH 7, conditions are reversed and pH is an indicator of  $OH^-$  ions. A solution with a pH of 12 has 100 times more  $OH^-$  ions than a solution with a pH of 10. Thus, a pH of 1 is strongly acidic, 14 strongly basic, and 7 neutral.

### Strength and Concentration

Two concepts that are important to understand when analyzing the hazards of corrosive materials are the strength and concentration. Both of these influence the pH of a solution.

1. *Strength* - the percentage of ionization that occurs when an acid or base is mixed with water, expressed in terms of weak and strong.
2. *Concentration* - the amount of acid or base that is mixed with a certain amount of water (a ratio of material to water), expressed as a weight or volume ratio.

A strong acid or base will totally, or almost totally, ionize when mixed with water resulting in a greater amount of  $H^+$  (acid) or  $OH^-$  (base) ions. A weak acid or base will ionize only partially when mixed with water. The tendency to dissociate (ionize) is expressed as a dissociation

constant ( $K_a$  for acids and  $K_b$  for bases). Strong acids have a  $K_a > 1$ ; strong bases have a  $K_b > 1$ .  $K_a$  and  $K_b$  are related to pH in that the greater the dissociation constant, the more extreme the pH of the resulting solution

For example, hydrochloric acid (HCl) is a strong acid; it has a  $K_a$  of  $1.3 \times 10^6$ . Acetic acid is a weak acid; it has a  $K_a$   $1.76 \times 10^{-5}$ . HCl will produce more  $H^+$  ions in solution than an equal amount of acetic acid, and exhibit a lower pH. A 0.35 molar solution of HCl will have a pH of 0.5, while a 0.35 molar solution of acetic acid will have a pH of 2.6. This example demonstrates the influence of “strength” on pH.

The concentration of acid or base in solution also influences pH. For example, as indicated in the example above, a dilute (0.35 molar) solution of acetic acid has a pH of 2.6. But, concentrated acetic acid (>95%) has a pH < 0.01. There are many different terms used to describe concentration such as percent, molar, formal, normal, etc. The information that all of them provide is basically the same, that is, the ratio of the amount of a material to a given amount of water.

### **Ionization**

The degree of ionization (influenced either by strength or concentration) tends to drive reactions whether in a solution or on skin because it is the ions that are reacting, not the whole chemical. In contact with the skin, acetic acid begins to ionize and react with anything that will accept a hydrogen ion. In this reaction, skin is a base. The reaction will continue as long as acetic acid ions are available. Areas that are moister (i.e., the eyes) are more rapidly damaged since there is more water present to allow the corrosive to ionize.

Ionization is an exothermic reaction and is known by the term ‘heat of dissociation.’ This is why concentrated mineral acids react violently if water is added to them and explains the axiom that acids are added to water and not the reverse. In this way, the heat absorbing capacity of water can help keep the reaction from being violent. It also accounts for the need for the water to be stirred as the addition is made. The addition of acid can cause localized areas to be so hot as to melt plastic.

Associated with ionization are corrosives in nonpolar solvents. Since the corrosive cannot ionize in nonpolar solvent, the solution will not exhibit a pH but will still present a skin corrosion hazard in contact with the skin.

### **Hazards to Tissue**

Strong acids and bases are so corrosive that even momentary exposure to the skin will produce severe damage. Weak acids and bases can also produce severe corrosion of the skin, but generally require higher concentrations or longer contact times.

Acids and bases damage tissue in different ways. Acids generally damage proteins while bases saponify (e.g., dissolve) both proteins and fats. Damage from acids is generally felt at the outset of exposure. Damage from bases may not become painful for some time. Because bases act on both proteins and fats and are not as immediately painful, exposure to bases can cause more damage.

The two greatest exceptions to acids causing immediate pain are hydrofluoric acid (HF) and trifluoroacetic acid. Trifluoroacetic acid reacts with water to form hydrofluoric acid. For both, it

can take several hours for any symptoms to develop (e.g., pain, redness). By this time, significant tissue damage can occur as well damage to bone tissue. See the EHS SOP, **Hydrofluoric Acid** for additional information and precautions.

While most skin exposure to corrosives is from liquids, dusts from some of the solid corrosives are capable of producing both internal and/or external injuries. The same is true for corrosives that produce vapors as well as corrosive gases. Of internal injuries, inhalation is the greatest concern. Corrosives that damage lung tissue will cause chemically induced pulmonary edema. The lungs can fill with fluids making breathing difficult or even impossible.

### **Mitigating the Risks of Corrosives**

First and foremost, conduct a general hazard analysis/risk assessment of the work to be conducted and verify that a written, comprehensive project-specific risk/assessment with additional oversight is not in order, as described in the companion EHS SOP, **Chemical Hazard Assessment and Risk Minimization**. General risk mitigation measures are as follows:

- Conduct a thorough literature search, including review of Safety Data Sheets, to establish a thorough understanding of the properties of the corrosives to be handled with particular consideration given to the procedures and tasks to be conducted. If working with compressed gas cylinders, observe the safety precautions detailed in the EHS SOP, **Gases Under Pressure Hazards & Risk Minimization** and review the archive Laboratory Safety Colloquium presentation titled **Flammable-Corrosive-Toxic Gas Safety** on the EHS web page.
- Follow general safe chemical handling practices as described in the EHS SOP, **General Guidance for Chemical Ordering, Receipt, Distribution, Use and Storage**.
- Observe all specific safety procedures established for the laboratory/procedure.
- Wear appropriate PPE. See EHS SOP, **Personal Protective Equipment for Chemical Exposures**. In addition:
  - Wear gloves at all times, even when handling closed containers. For incidental contact, nitrile is generally acceptable.
  - Wear face shields when doing work where splashes can occur and when making the initial dilutions of concentrated acids to protect against splatters caused by vigorous reaction. Face shields are in addition to safety goggles.
- Where available, purchase liquid corrosives in shatter proof bottles (i.e., glass coated in plastic). Dropped bottles can shatter and cause splashing of corrosives.
- Transport bottles of corrosive liquids in buckets or some other form of protective secondary containment.
- Where possible, use dilute solutions of corrosives to reduce how rapidly they can damage tissue.
- Always add acid to water, and not the reverse. When making initial dilutions of concentrated acids, use cold water (i.e. in an ice bath) and keep the water mixing during the addition. Make additions to the center of the container so that the heat is most rapidly dispersed.
- Use a fume hood for any:
  - Work involving corrosive gases
  - Liquids that produce corrosive vapors
  - Operations that generate vapors or mists
  - Corrosive dusts
  - Refluxing

- Allow heated (i.e., refluxed) containers to cool before handling. Allowing it to cool eliminates the risk that the container will be dropped because it was hot, as well as making the corrosive less active.
- Heated work (e.g., refluxing) using perchloric acid must be conducted only in a specially-designed, wash-down perchloric acid fume hood.
- Know what actions to take in the event of an exposure.
  - Initial first aid for contact with the skin consists of flushing with copious amounts of water. The water should be applied with little or no pressure to avoid further damaging injured tissue. The application should be started as soon as possible after the exposure has occurred. A victim of such an exposure may be in great pain and may require forceful aid while flushing is taking place.
  - If the exposure occurs to the eyes, the eye lids must be held open for flushing to be effective.
  - The standard for flushing is a minimum of 15 minutes. This applies to the eyes as well. Seek medical attention as necessary following flushing.
  - For inhalation exposures, medical attention should be sought immediately. The full effects of the exposure may not be evident for several hours. Thus, medical observation/assistance during this time is important.
  - Special precautions apply to hydrofluoric acid exposure. See EHS SOP, ***Hydrofluoric Acid***.