Chemical Characterisation in the Safe Handling of Acids and Caustics

Employers must be aware of workplace hazards facing their employees and take appropriate action to minimise or eliminate exposure to these hazards. This paper discusses the hazards and the precautions that can prevent serious health risks to workers due to exposure to corrosives. Corrosive chemicals are essential to many work processes; however, they can enter the body through ingestion, inhalation, or contact with the skin and eyes.

Employee exposure to corrosives must be evaluated to determine the need for engineering and administrative controls as well as the need for personal protective equipment. The results from injuries can be severe and even fatal. Mists produced by liquids can result in lung damage if inhaled, serious burns or irritation can be the result of accidental contact to the skin or eyes, and lung and skin cancer have been linked to chromic acid. Additional threats to employees are posed by the ease with which many corrosive chemicals ignite, explode or react with incompatible substances.

Acids and caustics have two common key properties; they are all corrosive and are extremely common in industry. Taking the time to ensure that acids and caustics are managed appropriately is critical to process safety. They can damage human tissue, and attack many other materials as well. They can react with metals, producing hydrogen gas which is highly flammable. Many acids and some caustics may have toxic properties, and they may release corrosive vapours at room temperature when in a concentrated form, such as nitric acid and hydrochloric acid. Some chemicals turn corrosive when they come into contact with water or humidity; for example, 1, 2-dichloroethane attacks iron and some other metals in the presence of moisture at high temperatures. Corrosive substances widely used in industry can be grouped into general classes, such as those that are listed below, in order to facilitate training and organising process safety information:

- Acids and acidic anhydrides
- Alkalis (bases/caustics)
- Halogens and halogen salts
- Organic halides, organic acid halides, esters, and salts
- Miscellaneous corrosive substances (substances that are widely used but do not fall into the above-mentioned classes)

Due to potentially hazardous properties, it is extremely important to fully characterise all process stream raw materials, intermediates, by-products, products, and residuals/wastes that are corrosive or have the potential to generate corrosives. The characterisation should be used to develop prevention and control strategies in the programs such as mechanical integrity, management of change, process safety, hazard communication, personal protective equipment, industrial hygiene, engineering controls, uncontrolled emissions, permitting, and emergency response planning.

Characterisation, Use, and Handing of Acids & Caustics

The common term `corrosive substances' originated in the United Nations Committee of Experts on the Transport of Dangerous Goods. In 1956, these were defined as: `These are substances which, by chemical action, will cause severe damage when in contact with living tissue or, in case of leakage, will materially damage or even destroy other goods or the means of transport; they may also cause other hazards'.

Corrosive material may be in the form of: Gas (chlorine, nitrogen oxides, and ammonia); Liquid (sulphuric acid, and hypochlorite solutions); or Solid (sodium hydroxide, and aluminium chloride).

Groups of substances with corrosive properties include:

- Acids and Anhydrides such as Acetic Acid and Acetic Anhydride; Phosphoric Acid and Phosphorous Trioxide; Sulphuric Acid and Sulphur Trioxide.
- Alkalis (bases/caustics such as Sodium Hydroxide; Aqua Ammonia; Organic Amines such as Ethanolamine
- Halogens and Acid Halides such as Chlorine gas; Iron (Ferric) Chloride; Chlorite solutions; Acetyl Iodide
- Other Compounds such as Mercury; Ammonium Polysulfide; Hydrazine; Peroxides

The US Department of Transportation (DOT) regulations consider a corrosive material to be a liquid or solid that causes visible destruction or irreversible alterations in human skin tissue at the site of contact or in the case of leakage from its packaging, a liquid that has a severe corrosion rate on steel. The DOT further develops this definition by offering the following: A liquid is considered to have a severe corrosion rate if its corrosion rate exceeds 1/4 inch per year on SAE 1020 low-carbon steel at a test temperature of 130^0 F.

The pH scale is used to compare the level of acidity or alkalinity of various acids and bases and their diluted solutions. The pH value is related to the amount of hydrogen ions present in the solution. The pH of a neutral solution or substance is 7. Acids have a pH of that is less than 7, and

Substance	Concentration in Water	Effect on Concrete
Acetic Acid	Up to 10%	Negligible
Acetic Acid	10% and Above	Corrosive; Rate depends on Concentration
Acetic Anhydride	Concentrated	Slow decomposition
Ammonium Hydroxide	All Concentrations	None
Arsenic Acid	All Concentrations	None
Barium Hydroxide	All Concentrations	None
Boric Acid	All Concentrations	Negligible
Calcium Hydroxide	All Concentrations	None
Carbon Disulfide	Up to 99.8%	None
Formic acid	Up to 10%	Negligible
Formic acid	10% and Above	Slow decomposition
Hydrogen chloride	Up to 37% [Saturation]	Corrosive; Rate depends on Concentration
Hydrogen fluoride	All Concentrations	Corrosive; Rate depends on Concentration
Nitric acid	All Concentrations	Corrosive; Rate depends on Concentration
Oxalic acid	Up to 9% [Saturation]	Negligible
Perchloric acid	All Concentrations	Corrosive; Rate depends on Concentration
Potassium hydroxide	Up to 5%	Negligible
Potassium hydroxide	5% to 53% [Saturation]	Corrosive
Sodium hydroxide	Up to 1%	Negligible
Sodium hydroxide	1% to 52% [Saturation]	Corrosive
Sulphuric acid	All Concentrations	Corrosive; Rate depends on Concentration
Tartaric Acid	Up to 17% [Saturation]	None

Table 1: Effects of Some Corrosive Liquids on Concrete

bases have a pH that is greater than 7. The pH scale is logarithmic, and for every whole number increase or decrease, the pH changes 10-fold. For example, the alkalinity of wet cement is 30 million times higher than the pH of skin; a pH of 13, as compared to 5.5 for human skin. Strong acids may have a pH that is less than 1.0, and strong alkaline solutions can have pH values above 14.

The health effects of acids and caustics resemble those caused by heat. Effects of direct contact vary from irritation causing inflammation, to a corrosive effect causing ulceration, and, in severe cases, chemical burns. Occupational hazards due to contact with corrosives mostly affect skin, eyes and the respiratory tract. The tissues most susceptible to rapid, severe, and often irreversible damage are those of the eyes. The effect depends on the properties of the substance, on its concentration, and the time of contact with acid or caustic. Even a dilute solution may cause irritation with prolonged or repeated contact, for example with skin.

Controlling the Hazards of Acids and Caustics

Engineering and administrative controls can be used to reduce employee exposure to corrosive liquids, and mists or dusts in the air and – in particular – to lessen the hazard of direct contact of corrosive materials with the eyes, lungs, and skin.

Engineering controls include: Eliminating the use of a corrosive liquid, or replacing it with a liquid that is less corrosive; Containment of acids and caustics, in equipment that is constructed from materials that can resist corrosion, or where a corrosion allowance is provided for a known corrosion rate; Limitation of process temperatures to minimise corrosion rates; and Local exhaust ventilation (hoods, or process enclosures) to limit personnel exposures to corrosive vapours.

Administrative controls include: Operating procedures and training to reduce unplanned or uncontrolled releases associated with the handling, transporting, processing, and storing of corrosive liquids; Safety procedures – including lock-out and confined-space entry – to reduce employees' exposure duration to liquids, mists, and vapours; and Hazard Analysis to identify unrecognised sources of exposure to corrosive liquids. .

The characteristics of corrosive materials are both general and specific. Effective process safety management includes both the toxic and physical hazards associated with process chemicals. Information on the properties of a given substance should be obtained before handling. The use of testing and screening tools such as corrosivity and compatibility tables (Tables 1 to 4), safety data sheets, and/or chemical safety cards can be helpful in evaluating chemicals prior to purchase and process changes. Proper hazard assessment is key

Plastics	Max. Temp. (oC)	Typical Uses
PVDF (polyvinylidene fluoride)	90 85 70 70 100	Storage tanks and pipes for sulphuric acid, nitric acid, hydrogen chloride, hydrogen fluoride Vaporisers Drying tower for chlorine Scrubbers and pipes for sulphuric acid, phosphoric acid, hydrogen chloride, hydrogen fluoride Dilution tank for sulphuric acid
FEP (fluorinated ethylene propylene; tetrafluoro ethylene)	95 120 90 90 100	Electrolytic bath Pipes Equipment for sulphuric acid regeneration Tanks containing chlorine Pipes for chlorine
LPE (linear high density polyethylene)	Room temperature	Laboratory bottles
PP (polypropylene)	80 80 70 70 70 60	Pipes for sulphuric acid, hydrogen chloride, hydrogen fluoride Entrainment separator for sulphuric acid, phosphoric acid, hydrogen fluoride Storage tanks for sulphuric acid, hydrogen chloride Gas pipes for sulphuric acid, sulphur dioxide, sulphur trioxide Scrubbers of sulphuric acid, phosphoric acid Blowers, fans
PVC (polyvinyl chloride, rigid)	50 50 50 30 40	Surface treatment baths and pipes Entrainment separator for sulphuric acid, chromic acid Pipes for sodium chlorate Storage tanks for hydrogen chloride Blowers, fans

Table 2: Uses of Plastics for Corrosive Liquids

to process safety, which includes support – upstream and downstream – processes, materials, and activities. It is important to ensure that receiving, warehousing, and logistics employees are able to stage and properly store chemicals upon arrival. In addition, a hazard evaluation checklist can be used in the change-control process to identify potential hazards within operations where these chemicals may be processed and/or generated.

The Manufacture, Storage and Import of Hazardous Chemicals (MSIHC) Rules require specific preventive actions that the employers need to implement. The occupier is responsible to ensure safe operation and adequate engineering and administrative control to provide safe operating facility to its employees and neighbouring population. The Process Safety Management (PSM) provides good guidance for gauging process safety awareness. Chilworth offers PSM gap analysis, training, process hazard reviews and audits to assist clients in proactively managing process hazards on a global basis, including India.

Storage of Corrosive Raw Materials and Corrosive Wastes

Taking the time to ensure that acids and caustics are managed appropriately is critical to process safety. Also, it is important to characterise process-stream raw materials, intermediates, products, by-products, and wastes or residuals that are corrosive or can react with moisture or air to generate corrosives.

All containers need to be properly labelled so that the contents can be readily identified.

Pay close attention to expiration dates, making sure that unstable acids and caustics are disposed of on or before the expiration date.

Additional factors that should be taken into consideration when storing acids and caustics include: First and foremost is to make sure that acid and caustics are not stored together. If there were to be a spill, chemical reactions could occur if they are stored in the same storage area. Second, make sure you check the MSDS of the acid or caustic to determine concentrations and any other storage conditions which must be maintained such as temperature or low moisture, etc.

Anticipating acidic and caustic constituents in residual waste streams is also very important. Aerosols of solid or liquid corrosive substances are air pollutants, and so are corrosive gases, and they may require control measures subject to permitting. Changes in the level of acidity and alkalinity affect the flora and fauna in soil and water. For example, acidity of pH 4 can be lethal to crickets and frogs. Some alkalis such as ammonia also have an acute toxic effect on fish. Soil may be classified as contaminated due to acidity when at a

Substance	Incompatible With:
Acetic Acid	Chromic acid, nitric acid, hydroxyl compounds, ethylene glycol, perchloric acid, peroxides, permanganates
Ammonia (Anhydrous)	Mercury, chlorine, bromine, iodine, calcium hypochlorite, hydrofluoric acid (anhydrous)
Bromine; Chlorine	Ammonia, acetylene, butadiene, butane, methane, petroleum gases, hydrogen, sodium carbide, benzene, finely divided metals, turpentine
Chromic Acid	Acetic acid, naphthalene, camphor, glycerol, alcohols, flammables
Fluorine	A wide range of substances and construction materials
Nitric Acid	Acetic acid, aniline, chromic acid, cyanides, sulfides, flammable solids, liquids or gases, copper, brass, heavy metals
Sodium Hydroxide; Potassium Hydroxide	Aluminum, zinc, or galvanised metals: produce flammable gases: hydrogen and dichloroacetylene.
Sodium Nitrite	Ammonium nitrate and other ammonium salts
Sulphuric Acid	Potassium chlorate, potassium perchlorate, potassium permanganate and similar compounds of sodium, magnesium and lithium

Table 3: Uses of Plastics for Corrosive Liquids

pH value of 4 to 5 and heavily contaminated when the pH is 2 to 4. When soil has a pH value of 9 to10, it is contaminated due to alkalinity and, at a pH value10 to 12, it may be classified as heavily contaminated. Neutralisation does not always remove the hazards to the environment, as the salts produced in this reaction may also be harmful.

Checklist for the Handling of Corrosive Materials

The following aspects can be incorporated into a preliminary hazard review or checklist and should be considered when planning or organising the use, storage and handling of corrosives at your facility:

1. The physical and chemical properties of materials, from ingredients to wastes.
2. The level of acidity or alkalinity of acids and bases and their diluted solutions, as expressed by the pH value.
3. The occupational exposure limits required to control and prevent adverse effects of acids and bases on health.
4. Incompatible materials and conditions such as illustrated in the Example Tables in Figures 1 to 4.
5. Materials of construction for storage tanks, to resist internal and external corrosion.
6. The potential mixing points, such as process vessels, mixers, pumps, and other equipment.
7. The need for isolation of piping that contains incompatible materials.
8. The need for procedures such as lockout, vessel entry, and line-breaking.
9. Consideration of alternative materials of construction, piping configurations, equipment design, and accessibility for maintenance, inspection, and testing.
10. Minimising the hazard to workers and to the surroundings, using distance or barricades.
11. Gas and vapour sensors or monitors, with alarms.
12. Dikes, trenches, sumps, or reservoirs to collect spillage of hazardous liquids.
13. Ventilation to limit the extent of gas and vapour releases.
14. Emergency planning, training, and drills.
15. Spill-response teams and equipment, including sampling and monitoring, and personnel control.
16. Personal protective equipment, particularly for members of the spill-response teams.
17. Hazard markings for all tanks and containers, including appropriate dating.
18. Compliance with national, international, and local regulations, codes and standards.
19. Internal and external inspections and/or tests, with permanent record of findings.
20. A file for each process vessel that contains – or could contain – corrosive material, to include equipment drawings, materials of construction, welder's certificates, heat treatment, vessel supports and/or foundations, maintenance procedures, inspection and test schedules, and changes made since fabrication and installation. ■

References

1. National Institute for Occupational Safety and Health, "Pocket Guide to Chemical Hazards".
2. Jernkontoret [Stockholm], "Corrosion Tables" (1979).
3. Dillon, C. P., "Materials Selection for the Chemical Process Industries", McGraw-Hill, Inc., (1992).
4. North Carolina Department of Labor Education, Training and Technical Assistance Bureau, "Industry Guide #30" (September, 2011)

Author's Details

Richard W. Prugh
Principal Process Safety Specialist Chilworth Technology
E: safety-usa@chilworthglobal.com

Jitendra Kumar
Senior Process Safety Specialist Chilworth Technology
E: jitendra.kumar@dekra.com