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CCPS
Center for Chemical Process Safety

Process Safety Beacon

http://www.aiche.org/CCPS/Publications/Beacon/index.aspx
Messages for Manufacturing Personnel

CCPS Sponsors, the Beacon Committee, and volunteer Beacon translators wish all Beacon readers a happy, prosperous ***and safe*** New Year 2010.

Corrosion and Erosion

January 2010

Mechanical integrity is one of the biggest challenges for an effective process safety management program. Think about it – in your plant, there may be hundreds of vessels, thousands of feet of pipe, and hundreds of pumps, compressors, instruments, and other equipment. All of it must be kept in good operating condition to ensure safe, reliable, and profitable operation. Management of corrosion and erosion of process piping and equipment must be a major component of any effective mechanical integrity program.

The pictures show some examples of corrosion and erosion problems which were identified in plant inspections. (1) and (2) – external corrosion of pipes in a plant; (3) – close up of erosion damage to the face of a flange; (4) – close up of eroded body and seat of a gate valve; (5) – erosion damage on the body of a valve.

Do you know?

- ***Corrosion*** is the deterioration of metal by electro-chemical reaction with substances or microbes in its environment. These substances can be process materials contained in a vessel, pipe, or other equipment, or materials in the outside environment – for example, water, salt, or contaminants in the atmosphere. The rusting of steel is an example of corrosion.
- ***Erosion Corrosion*** is the degradation of material surface due to mechanical action, often by impinging liquid, abrasion by a slurry, or particles, bubbles, or droplets suspended in fast flowing liquid or gas.
- Corrosion has been responsible for major losses in the process industries. For example, in 2006, part of a major oil field had to be shut down for several months because of multiple oil spills resulting from severe pipeline corrosion.

What can you do?

- Understand mechanical integrity programs in your plant, and your role in ensuring that these programs are effective.
- Observe pipes, vessels, and other equipment when you are working in the plant. Look for stains on the outside of insulated lines and other signs of damaged or corroded equipment. Follow up to make sure that repairs are made.
- If you are taking equipment or piping apart, look for evidence of corrosion damage – for example, corrosion under insulation, internal corrosion in pipes or other equipment, damage to flanges or valves.
- When replacing pipes, valves, or other equipment, be careful to use the same material of construction.
- Understand the corrosion and erosion corrosion properties of the materials in your plant, and what you must do to minimize corrosion problems.

Watch out for corrosion and keep the chemicals inside the equipment!

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Introduction:

Type of Facility:	Unspecified
Hazard(s):	Unspecified
Hazardous Material(s) Involved:	Unspecified
Equipment Involved:	Any
Initiating Cause / Event:	Unspecified
Most Relevant RBPS Elements:	Process Knowledge Management; Operating Procedures; Asset Integrity and Reliability, Management of Change

Additional Information for Technical and Management Staff

What Happened?

Corrosion and erosion damage materials. Objects subjected to such damages can fail, such as:

- Mobile components that get stuck by corrosion or loosened by erosion, as in valves, hinges, etc.
- Functional parts get destroyed, such as springs, wiring, electrical contacts
- Supporting structures buckle and collapse
- Pipes, vessels, and rupture discs leak or break

The outcome of such failures depends on the function the part had to fulfill. The photographs in this Beacon show findings during inspections—Near Miss incidents.

Elsewhere, corrosion damages became serious incidents. See, for instance, the Beacon of May 2017, "Corroded Tanks", and these CSB reports:

1) The rupture of a pipe, its wall thinned by sulfidation corrosion, released flammable gas oil, which ignited. There were no fatalities or serious injuries, but 15,000 people from surrounding communities sought medical treatment later. Approximately 20 were hospitalized [1].

2) Workers repaired a catwalk above a tank farm storing sulfuric acid when a spark from hot work ignited flammable vapors in one of the tanks having holes due to corrosion. The tank collapsed; there was one fatality; eight others were injured. Sulfuric acid was released [2]

3) A steam explosion shot a steel vessel weighing some 2,000 lbs. into the air. The explosion caused on fatality and critically injured another worker. Coming down several hundred feet away, the vessel caused three fatalities. Corrosion had thinned the pressure vessel at its bottom [3].

And, as alluded to in this Beacon's "Do you know?" section, there were the oil spills and the shut-down of a major oilfield due to corrosion at Prudhoe Bay, Alaska, in 2006 [4].

Did You Know?

Corrosion and erosion are different phenomena but may occur jointly, Corroded parts erode easier; erosion removes protective coating. Corrosion is a chemical process, and erosion is a physical, mechanical process.

Some Erosion Facts:

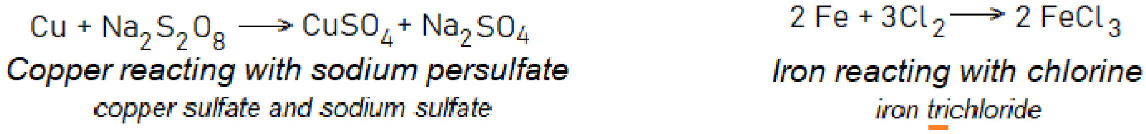
Erosion involves collision with solids or liquids which grind off parts of the surface (erosion, translated literally from Latin, means gnawing out). Wind that carries solids, e.g., sand (as done on purpose with sandblasting) and water – not only as a fast or high-pressure jet but even as the "constant dripping [that] wears away a stone [5]" – not only form landscapes but may damage buildings and other installations. Inside apparatus and pipes there may be abrasion from solids suspended in slurries or in pneumatic conveying. Droplets in gas streams, bubbles in liquids, especially those forming and collapsing by cavitation, may cause damages too.

Some Corrosion Facts;

The focus in this section is the corrosion of metals, which is an oxidation process. Concrete and stones, plastics as well as glass and ceramics are corroded by breaking of chemical bonds; this is addressed in the last paragraphs of this section.

1) Corrosion by Oxidation Chemistry: Oxidation means a process where atoms, molecules, or ions of substance A lose electrons to atoms, molecules, or ions of substance B, for which this means a reduction ("you can't have one without the other").

Oxidizers, depending on their strength labelled with the "flame-crowned O", usually transfer bound oxygen or halogen to the metal, converting it into an oxide/hydroxide or halide, or into some other salt depending on the specific oxidizer. Halogens (fluorine and chlorine also have the O-Label, bromine and iodine don't) form halide salts directly with metals.



$$Cu + Na_2S_2O_8 \longrightarrow CuSO_4 + Na_2SO_4$$

$$2\,Fe + 3Cl_2 \longrightarrow 2\,FeCl_3$$

Figure 1001-1: Direct oxidation

Acids, neutral water, and alkalis, depending on the metal, form hydrogen <u>and</u> salts (including oxides, hydroxide) at the same time. Aluminum reacts with some heated alcohols, forming hydrogen and alcoholates.

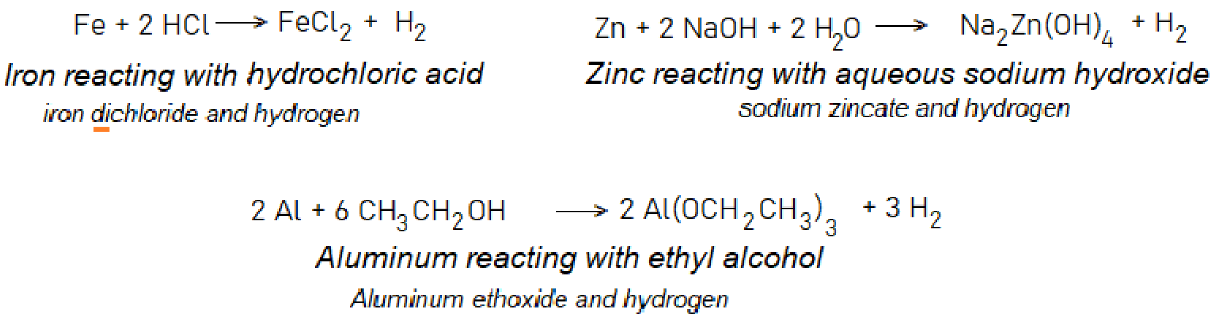


Figure 1001-2: Reactions with acid, alkali, and alcohol

Note that the hazard "corrosivity" has two meanings, both indicated on the pictogram: one is corrosivity to metal, the other is corrosivity to organic tissue.

Figure 1001-3: Labels for oxidizing and for corrosive substances (Globally Harmonized System, GHS)

Inside pipes, vessels, etc., oxidation is caused by the medium contained or conveyed within. On the outside of structures and apparatus corrosion usually is due to air and water, but there may also be corrosive gases or leakages of corrosive liquids affecting them. Water, as stated earlier, may oxidize metals. There may be acids present in rain and in water from wells, rivers, lakes, etc. Generally, they are carbon dioxide and, from industrial activities and volcanoes, sulfurous and sulfuric acid ("acid rain"). Bacterial action may break down biological wastes into organic acids. The resulting metal ions form hydroxides or salts with whatever acid is present, e.g., sulfates with sulfuric acid.

Oxygen, from air, forms oxides and/or hydroxides plus carbonates from moisture and carbon dioxide. The mixed oxide/hydroxide/carbonate of iron is known as "rust". Rust has a sponge-like structure that does not protect the metal it covers. Copper and its alloys bronze, brass, form verdigris, which is a mixed hydroxide/carbonate (also chloride, sulfide, sulfate, depending on the environment) and may be a more compact, somewhat protective layer, patina.

Hydrogen sulfide (H_2S) is present in oil [1] and in water available in volcanic areas. In biological processes it comes from bacterial reduction of sulfate or from degradation of sulfur-containing amino acids, not only in sludge but also at home – silverware gets black with time. While silver tarnishes because sulfide formation supports the oxidation by oxygen, in other cases H_2S produces metal sulfides and hydrogen, analogous to the reaction of metal and water. H_2S can be oxidized to sulfurous/sulfuric acid and thus indirectly attack substrates that do not react with it.

2) Some Corrosion Physical Chemistry: The ease with which atoms, molecules, and ions lose electrons (get oxidized) or gain electrons (get reduced) is expressed by their standard electrode potentials. Tables of them are found in textbooks and reference books of physical chemistry. The CRC Handbook of Chemistry and Physics [6] calls them Standard Reduction Potentials and lists them under Electrochemical Series. Potentials are measured against the Standard Hydrogen Electrode (SHE), setting the reaction of hydrogen cations (as in water) to hydrogen at zero. Metals like magnesium and aluminum have about -2.4 V and -1.7 V, respectively; zinc -0.76 V, iron -0.45 V: these metals **can** be attacked by water. Gold has a potential of +1.4 V; it resists many oxidizers.

"Can" is underlined to indicate inert behavior: a reaction would occur because it yields energy, but does not do so spontaneously, see Figure 1001-1.

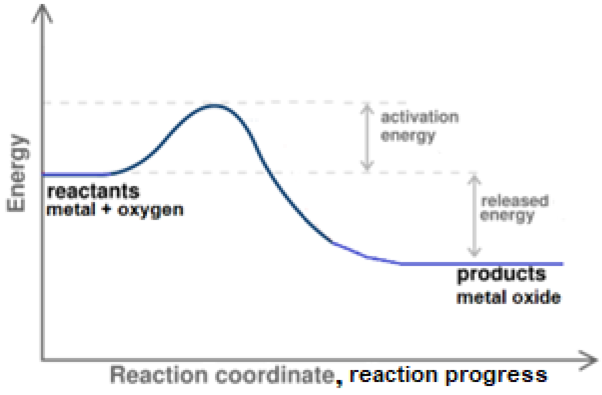


Figure 1001-4: Graph of an exothermic reaction with activation barrier

Another cause is that magnesium, aluminum, and zinc form thin and compact oxide layers that protect the metal underneath. Iron in steel alloys is protected similarly: the accompanying elements may raise the activation barrier and help the formation of a compact oxide layer. An oxide layer is also created intentionally, e.g., by bluing of steel or anodizing; this is called passivation. The layer may "heal" after scratching, yet it can be destroyed. For example, aluminum forms soluble hydroxides with caustic (sodium hydroxide), and so does zinc. Contamination of anodized aluminum with mercury can interfere with the oxide layer and additionally form a galvanic couple (see below); one can literally watch bristles of aluminum oxide growing on aluminum that has been exposed to mercury (own observation).

The pH-value and in particular the presence of so-called complexing agents can change standard potentials. Cyanide makes gold susceptible to oxygen (used in recovering gold from ores); chloride has a similar effect on many metals too. Thus, presence of chloride damages many "stainless" steel alloys.

For practical application the Galvanic Series is more common than the electrochemical series. Lists and tables are provided by many suppliers of metal pipes etc., by engineering service organizations, and in ASTM G82. This series shows potentials for materials used in engineering: graphite/carbon, metals, and alloys. The potentials are measured against the SHE or the Saturated Calomel Electrode (SCE; its zero is at +0.24 on the SHE scale). It is the difference between values for different materials that matters, just use the same scale when you compare materials. Two materials with different potentials, connected with each other by direct contact or an electrically conductive intermediary, form a galvanic couple. With an electrolyte present, such as water with salts or acids (e.g., carbon dioxide), a process starts whereby the more "noble" metal with the higher number gets electrons via that connection, which reduces hydrogen cations in the solution, from the more "base" metal, which is oxidized and releases its cations into the electrolyte [7].

Hence, the presence of nobler metals like gold, silver, or more commonly copper and its alloys, makes steel more susceptible to corrosion. A special case of galvanic corrosion was the iron-copper couple inside the Statue of Liberty [8] found and remedied during its restoration in the mid-1980s: the insulation between wrought iron parts of the skeleton and the copper skin had failed locally after a century and promoted corrosion to the iron. Another example is the different behavior of steel depending on what it is coated with: Tin-coated steel (tinplate) that has been scratched will rust easily. Because tin, with standard electrode potential of -0.14 V, is the nobler part in the galvanic couple, it facilitates corrosion of the exposed steel. Zinc-coated ("galvanized") steel is not perceptibly affected, because iron is the nobler metal here. Iron will be protected for as long as there is zinc to be oxidized.

3) Corrosion by Breaking Chemical Bonds: Building materials containing calcium carbonate (marble, limestone, sand-lime bricks, mortar, concrete) are attacked by acids. By this, stagnant water containing carbon dioxide has a faster effect than erosion by a flowing river would. Acid rain or acids from spills take shorter time. The process changes calcium carbonate to soluble salts that wash away: calcium bicarbonate, or calcium sulfate from sulfuric acid, or calcium chloride from hydrochloric acid, etc. Glass and ceramics are harder than many steels, and they are stable against a very wide range of chemicals. Glass and porcelain are very common in laboratories; glass lined reaction vessels are also used in industry. But there are conditions that break down the silicon-oxygen network in glass, quartz, and silicate ceramics, in particular hydrofluoric acid, which forms volatile silicon tetrafluoride, and hot, concentrated alkalis. Glass lining shares this hazard with other protective coatings that mechanical damages or attack by dissolving agents expose the metal underneath.

Plastics may not be resistant against erosion, but they can be used with many chemicals. Polyolefins, also halogenated polymers like PVC and PTFE, are very stable, while polyesters, polyamides, polyurethanes have backbone chains based on ester and amide links that can be broken by acids and alkalis. Sunlight, UV radiation, breaks chlorine-carbon bonds in PVC, this initiates further degradation. Carbon-carbon bonds in polymer chains are less and varyingly susceptible but can be affected by UV too. Solvents may simply dissolve plastic, or they may be absorbed by it (this can be described as solvent being dissolved in the plastic) just as water is absorbed by the biopolymers starch or gelatin, forming a jelly. This deteriorates the mechanical properties; the plastic part, for instance a washer or gasket, may fail directly or because the material swells and gets damaged during normal use, e.g., O-rings at a valve.

What Can You Do?

The first step is the right choice of material for your equipment and installations. What substances and conditions are in your process? What environmental conditions, including local emissions, can affect your equipment? Is there already know-how for the process and its equipment? Manufacturers of pipes, vessels, hoses, gaskets, etc., may have tables with data from their own or contracted test laboratories that inform you how well their materials withstand a series of reagents, mostly the raw materials and often the products in your process. This information should not only state what substance will be resisted, but also the temperature range and the concentrations for which this information is valid; for instance, a material that is good for a storage tank at ambient temperature may not be adequate for a distillation column or a reactor running at high temperatures. But also ask technical experts, as the tables may not cover what your process is about. Manufacturers of your raw materials know from experience what your equipment should, or may not, be made of to handle them. Obtaining this information is an aspect of **Process Knowledge Management**.

Consequently, also ensure that only approved materials are used in modifications as well as in repairs and replacement; include this in your **Management of Change** process.

Maybe the equipment you already have, or the one that is accessible for you to install, is not the ideal one for your process. Possibly it is known to be reliable in your process only under some conditions, or it was selected by drawing conclusions from similar processes. Perhaps your facility is made only of parts that are manufactured from materials highly recommended for your process, but occasionally there may be hidden defects in some parts, or some parts may be joined together not quite as properly as they ought to be. And even a properly run process, with careful use and handling, will affect your equipment with time. All these considerations tell you that a régime of inspections, maintenance, and repairs [9] is needed to ensure **Asset Integrity and Reliability**.

Operating Procedures should consider safe operating limits also with a view to conditions that affect the operability of your equipment: e.g., a valve will fail because some elastomer part softens at too high temperature. Operators – they are around more often than maintenance persons – should report if something does not look normal, like discolorations or crusts forming on equipment, or damages to anti-corrosion coatings. Managers and supervisors should set an example by walk-through inspections. If dust collects on equipment, these deviations cannot be seen at an early stage, so keeping equipment tidy is required even if the dust is not combustible, which is a different problem (see Beacon of May 2006, Dust Explosion Hazards). Take note if there are places where water, rain, or released condensate repeatedly impinge on equipment and concrete.

On turnarounds in continuous processes or after a defined number of batches the equipment should be inspected on the inside to check for signs of erosion and corrosion. Deposits of decomposed material and process waste should be removed, as they could promote corrosion underneath.

If a leakage, also rainwater, gets into insulation or fireproofing, it will stay there and collect at the locally lowest point. If the liquid has some corrosive property, this will have an enhanced effect as exposure now persists for a long time (see CSB Report [10], section "Oleum Release"). Read the article on the Beacon of February 2005, "Insulation does NOT Prevent Corrosion", and follow the recommendations there. Something comparable to corrosion under insulation occurred due to label taped on a PTFE-lined stainless-steel hose. Small quantities of phosgene slowly diffused through the plastic and would have evaporated at an acceptable rate under the conditions through the metal braid, but below the label some was trapped. Phosgene forms hydrochloric acid. This caused faster and hidden corrosion here, the hose failed (see Beacon of October 2011 "Hose Hazards" and CSB report [10], section "Phosgene Release", and video [11].

The effect of galvanic coupling can be used to protect equipment. Just like zinc on the outside of galvanized steel (discussed earlier) undergoes oxidation readily to the benefit of iron, "sacrificial anodes" of zinc, magnesium and aluminum can be connected to steel equipment and prevent corrosion there. Discuss with your specialist if and where cathodic protection systems could be useful. If you have such systems, make sure your operators know about them so they do not damage or interfere with them – and report if this should happen.

Other Lessons:

Here are two examples of damages that are not due to failure of the corroded part itself:

1. When reinforcing steel that is used in concrete ("rebar") oxidizes, its volume increases. This expansion may crack the surrounding concrete, and while the structure need not yet collapse, parts of it will already drop off. Fissures give water access to the steel, wider cracks form by

this process and let in even more water. The corrosion rate is particularly high when there is much chloride in the concrete.

2. With iron being nobler than aluminum and magnesium, iron oxides can be reduced by these light metals. This is the very exothermic process known as thermite reaction and can inadvertently occur when aluminum or magnesium rub or strike against rusty steel [12], creating an ignition source. In one instance this happened when a mild steel valve was forcibly screwed onto an aluminum pipe; in another instance a sacrificial magnesium anode impacted on rusty steel, leading to ignition and explosion in a tanker.

Resources:

Other Closely Related Beacons:

- July 2004: Misalignment + Corrosion = Failure!
- February 2005: Insulation does NOT Prevent Corrosion
- May 2009: Mechanical integrity
- April 2011: Don't let a small leak become a big leak!
- June 2019: Corrosion under insulation
- June 2022: Some mistakes take time to become incidents!

Key Words for this Beacon:

Corrosion, Leaks and Spills, Maintenance, Asset Integrity, Piping

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