Degradation Mechanisms in the Oilsands Industry

A.I. (Sandy) Williamson, P.Eng.
Ammonite Corrosion Eng. Inc.
Calgary, AB

Outline

- Identification of process conditions
- Classification of Degradation Mechanisms
- References

Identification of Process Conditions

- Normal Operation vs. Upset vs. Stand-by
- Accuracy of analyses
- Presence of contaminants
- Presence of process additives
Classification of Degradation Mechanisms

- Mechanical and Metallurgical
- Uniform or Localized Loss of Thickness
- High Temperature Corrosion (>400°F)
- Environment-Assisted Cracking
- Other

Uniform or Localized Loss of Thickness
- Atmospheric Corrosion
- Caustic Corrosion
- CO₂ Corrosion
- Corrosion Under Insulation (CUI)
- Crevice Corrosion
- Erosion Corrosion
- Galvanic Corrosion
- Microbiologically Induced Corrosion (MIC)
- Raw water and Recycle water Corrosion
- Soil Corrosion

Environment-Assisted Cracking
- Caustic Stress Corrosion Cracking (Caustic Embrittlement)
- Chloride-Induced Stress Corrosion Cracking (CISCC)
Atmospheric Corrosion

- The most common material of construction is carbon steel. Carbon steel will corrode when exposed to water and oxygen from the atmosphere. Impurities in the water may make the water a better electrolyte which in turn will increase the rate of corrosion. Protective coatings are normally used to prevent water from contacting the steel; however, there may be circumstances where the humidity levels are low enough to leave the steel uncoated. Under 60 percent humidity, corrosion of steel is negligible and the lower the amount of oxygen absorbed in the water, the lower the corrosion rate.

- Structural steelwork in slurry preparation towers are commonly protected from atmospheric corrosion through the use of hot-dip galvanizing. This is necessary due to the splash over and misting of the process water (recycle water) which is an aggressive corrosion agent of carbon steel. Inorganic zinc primer is also used to protect structural steel from atmospheric corrosion in high humidity areas.

Caustic Corrosion

- Caustic corrosion is a localized form of corrosion due to the concentration of caustic or alkaline salts that usually occurs under evaporative or high heat transfer conditions. However, general corrosion can also occur depending on alkali or caustic solution strength.
- Carbon steel, low alloy steels and 300 Series SS can all be subject to caustic corrosion.
- Caustic injection may occur in the slurry preparation area of an Ore Process Plant (OPP) as caustic is often injected into the first process water stream prior to the primary pump (PP). One needs to ensure that there is good distribution of caustic by using an injection quill in the first process water stream.
**CO₂ Corrosion**

- Carbon dioxide combined with water forms carbonic acid. Carbon dioxide may come from two sources: 1) from the decomposition of bicarbonates contained in, or added to the bitumen; and 2) from steam used in the plants. The corrosion rate of carbon dioxide corrosion depends on partial pressure and temperature. In steam condensate systems, corrosion from carbon dioxide can be prevented by injecting special corrosion inhibitors.

**Corrosion Under Insulation**

- Cracks in insulation or insulation barriers may allow moisture to penetrate to the steel, where corrosion can occur. The most severe corrosion occurs in situations where the equipment or piping is operating in the 175 to 250°F range. Protective coatings are used to prevent contact of water with the metal surface.
Corrosion Under Insulation

Crevice Corrosion
- Crevices or cracks occur between the mating surfaces of metal-to-metal and nonmetal-to-metal components. Environmental conditions in a crevice can become quite different to those on a nearby clean, exposed surface. The difference in concentrations of salt, metal ions, hydrogen ions, and oxygen will set up a concentration cell. This cell can cause a flow of electrons, causing corrosion at the anode. Crevices commonly exist at gaskets, lap joints, bolts, rivets, etc. They are also created by deposits, corrosion products, scratches in paint films, etc.
- Some materials are more susceptible than others: namely those that depend on an air-formed oxide film to achieve their corrosion resistance, such as stainless steel, aluminum, and titanium.
- Some examples of crevice corrosion found in Bitumen Production are:
  - Corrosion of pumpbox shell plates beneath liner plates
  - Corrosion of vibrating screen beams beneath the screen cloths
  - Corrosion beneath adhering deposits of bitumen

Erosion-Corrosion
- The movement of a corrosive medium over a metal surface increases the rate of attack due to mechanical wear and corrosion. A number of process streams in Bitumen Production plants contain high solids loadings and water that provide the wear component and the corrosion component, respectively. The erosion-corrosion synergy can vary from 100% corrosion/0% erosion (e.g., wet quiescent systems) to 0% corrosion/100% erosion (e.g., flowing dry feed). The majority of systems lie somewhere between the two extremes.
- Erosion-corrosion is usually attributed to the removal of protective surface films, i.e., protective oxide films or adherent corrosion products. The rate of removal of these protective oxide films will depend on the amount, size distribution, and geometry of the solids in the process stream as well as the velocity and turbulence of the process.
Some examples of erosion-corrosion found in Bitumen Production are:

- Mixing Box liners
- Vibrating screen and screen cloths
- Pump box nozzles
- Straight run slurry pipe showing accelerated metal loss at flange connections
- Slurry pipe bends
- Galvanic pair

Galvanic Corrosion

Galvanic corrosion occurs when two dissimilar metals are in contact and exposed to a conductive solution. A difference in electric potential exists between different metals and is the driving force to pass current through the conductive solution. The larger the potential difference, the greater the corrosion. Corrosion of the less resistant metal is usually increased, and attack of the more resistant material is decreased compared to when the metals are not in contact. The less resistant metal becomes anodic and the more resistant metal becomes cathodic.

Galvanic corrosion can be avoided by insulating the metals, or by restricting the use of metals together that have a large potential difference. Since galvanic corrosion is especially severe if the area of the anode (corroding metal) is considerably smaller than that of the cathode, making the anode bigger will reduce the corrosion current effect.

Galvanic corrosion is not common in Bitumen Production as there are few metallic couples present in the equipment and piping.

Galvanic Corrosion

<table>
<thead>
<tr>
<th>Corroded End – Anodic or Less Noble (Electronegative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
</tr>
<tr>
<td>Zinc</td>
</tr>
<tr>
<td>Aluminium</td>
</tr>
<tr>
<td>Cadmium</td>
</tr>
<tr>
<td>Tin or Steel</td>
</tr>
<tr>
<td>Tungsten</td>
</tr>
<tr>
<td>Brass</td>
</tr>
<tr>
<td>Stainless</td>
</tr>
<tr>
<td>Nickel-copper alloys</td>
</tr>
<tr>
<td>Metal</td>
</tr>
<tr>
<td>Copper</td>
</tr>
<tr>
<td>Nickel</td>
</tr>
<tr>
<td>Silver</td>
</tr>
<tr>
<td>Gold</td>
</tr>
</tbody>
</table>

| Protected End – Cathodic or Most Noble (Electropositive) |
Microbiologically Influenced Corrosion (MIC) is a form of corrosion caused by living organisms such as bacteria, algae or fungi. It is often associated with the presence of tubercles or slimy organic substances. MIC is usually found in aqueous environments or services where water is always or sometimes present, especially where stagnant or low-flow conditions allow or promote the growth of microorganisms. Because there are several types, organisms can survive and grow under severe conditions including lack of oxygen, light or dark, high salinity, pH range of 0 to 12, and temperatures from 0°F to 235°F (−17°C to 113°C). Different organisms thrive on different nutrients including inorganic substances (e.g., sulfur, ammonia, H2S) and organic substances (e.g., hydrocarbons, sugars, acids). Additionally, organisms require a source of carbon, nitrogen, and phosphorous for growth. Leakage of process contaminants such as hydrocarbons or H2S may facilitate the growth of microorganisms.

MIC is most often found in heat exchangers, bottom waters of storage tanks, piping with stagnant or low flow, and piping in contact with soils. MIC is also found in equipment where the hydrogen sulfide has not been removed or in equipment that has been left inactive and unprotected.
Raw/Recycle Water Corrosion

- The presence of dissolved oxygen in water accelerates corrosion of steel. Increasing temperature will also increase the corrosion rate of this mechanism. In most cases, a protective oxide layer will form which slows down the rate of corrosion. In cases where deposits are allowed to accumulate, the area under the deposit is low in oxygen content relative to the rest of the steel surface. This creates an oxygen concentration cell which leads to pitting under the deposits.
- The concentration of chloride ion increases the aggressiveness of the water towards steel. Oilsands operators have seen a dramatic increase in corrosion problems when the chloride concentration reaches around 1,000 ppm.

Soil Corrosion

- The deterioration of metals exposed to soils is referred to as soil corrosion. Carbon steel, stainless steel, cast iron and ductile iron are all affected and therefore all buried piping is protected by external coating and application of cathodic protection.
- The severity of soil corrosion is determined by many factors including operating temperature, moisture and oxygen availability, soil resistivity (soil condition and characteristics), soil type, water drainage, and homogeneity (variation in soil type), cathodic protection, stray current drainage, coating type, age, and condition. Soils having high moisture content, high dissolved salt concentrations, and high acidity are usually the most corrosive. Soils in the Fort McMurray area are known to contain aggressive corrodents, e.g., Replacement of City of Fort McMurray cast iron water pipes in 1990. Use of aggressive backfill should be used for buried pipelines in lieu of the original soil.
Caustic Embrittlement

- Caustic embrittlement is a form of stress corrosion cracking characterized by surface-initiated cracks that occur in piping and equipment exposed to caustic, primarily adjacent to non-petroleum treated welds. Carbon steel, low alloy steel, and 300 Series SS are susceptible. Nickel base alloys are more resistant.
- Susceptibility to caustic embrittlement in caustic soda solutions is a function of caustic strength, metal temperature, and stress levels.
- Some examples of caustic embrittlement are:
  - Poisoning of steam lines due to excess concentration of caustic, which is exacerbated by wet/dry cycles and ensuing further concentration.
  - Caustic tanks can be put at risk due to process transients of temperature and concentration. Operations need to be aware of the serious implications of accidental poisoning and physical damage.

Chloride Stress Corrosion Cracking

- In the case of chloride SCC of austenitic (300 series) stainless steels, there are several environmental factors that are necessary for cracking to occur:
  - Chloride concentration
  - Elevated temperature, >150°F
  - Stress, what the minimum stress level is not exactly known
  - Oxygen must be present.

- The recycle water used for slurry preparation and various other uses in the Bitumen Production contains chlorides which precludes the use of austenitic stainless steels. Aluminum bronze should be used in lieu of austenitic stainless steel for hot water base lines.
Brittle fracture is the sudden rapid fracture under stress (residual or applied) where the material exhibits little or no evidence of ductility or plastic deformation. Carbon steels and low alloy steels are of prime concern, particularly older steels. 400 Series SS are also susceptible.

In most cases, brittle fracture occurs only at temperatures below the Charpy impact transition temperature (or ductile-to-brittle transition temperature), the point at which the toughness of the material drops off sharply.
Cavitation

Cavitation is deterioration due to the formation and collapse of vapor bubbles at the metal surface. The vapor bubbles can form in local turbulent zones where the pressure drops to below the liquid’s vapor pressure. The vapor bubbles collapse with considerable energy. The high pressures produced by this collapse can deform the metal, remove protective films, etc. Cavitation occurs on pump impellers, agitators, piping, etc.

Corrosion Fatigue

A corrosive will sometimes lower by half the stress normally required to cause fatigue in dry air. Methods of avoiding corrosion fatigue usually attempt to prevent a fatigue crack from starting — e.g. design changes, protection, inhibitors, etc. — since it is difficult to stop a crack from propagating once initiated. Shot peening has been used to avoid/delay the onset of corrosion fatigue.

The significance of pitting to the initiation of corrosion-induced fatigue is shown in the example of vibrating screen foundation springs. The following times to failure are shown by three materials:

- Martensitic spring steel: 4 weeks
- Pearlite spring steel: 6 months
- 17-4PH spring steel: 3 years

The service life of the above materials is directly proportional to the rate of pitting in recycle water.
**Dissimilar Metal Weld Cracking**

- Dissimilar metal weld cracking is most common when ferritic materials such as carbon steel and low alloy steels are welded to the austenitic stainless steels and exposed to high operating temperatures. It can also occur when metals with widely differing thermal expansion coefficients are welded together.
- Important factors include the type of filler metal used to join the materials, heating and cooling rate, metal temperature, time at temperature, weld geometry and thermal cycling. As the temperature increases, differential thermal expansion between the metals results in increasing stress at the weldment, particularly if a 300 Series SS weld metal is used. Thermal cycling aggravates the problem.
- Although there are some examples of dissimilar metal welds in Bitumen Production, weld cracking is less of an issue due to the relatively lower operating temperatures found in Bitumen Production equipment and piping.

**Mechanical Fatigue**

- Fatigue cracking is a mechanical form of degradation that occurs when a component is exposed to cyclic stresses for an extended period, often resulting in sudden, unexpected failure. These stresses can arise from either mechanical loading or thermal cycling and are typically well below the yield strength of the material. All engineering alloys are subject to fatigue cracking although the stress levels and number of cycles necessary to cause failure vary by material.
- Geometry, stress level, number of cycles, and material properties (strength, hardness, microstructure) are the predominant factors in determining the fatigue resistance of a component.
- Several common surface features can lead to the initiation of fatigue cracks as they can act as stress concentrations:
  - Mechanical notches (sharp corners or grooves); Key holes on drive shafts of rotating equipment; Weld joint, flaws and/or mismatches; Quench nozzle areas; Tool markings; Grinding marks; Lips on drilled holes; Thrust root notches; Corrosion.
Overloading

Overloading is defined as loads in excess of the maximum permitted by the design of the equipment under consideration. Overloading can result in immediate structural failure which may be brittle or ductile in nature. Both are very serious but fortunately very infrequent events. Particular care must be taken with oils where it can build up within an enclosure and result in overload of the supporting structural steel, e.g., enclosed conveyor galleries.

Overpressure

Overpressure can occur due to the thermal expansion of fluids, freezing of lines or pressure transients in the system. Overpressure protection is commonly afforded through the use of a pressure safety valve (PSV) or pressure relief valve (PRV).

Thermal Shock

A form of thermal fatigue cracking – thermal shock – can occur when high and non-uniform thermal stresses develop over a relatively short time in a piece of equipment due to differential expansion or contraction. If this thermal expansion/contraction is restrained, stresses above the yield strength of the material can result. Thermal shock usually occurs when a colder liquid contacts a warmer metal surface.

The magnitude of the temperature differential and the coefficient of thermal expansion of the material determine the magnitude of the stress. Cyclic stresses generated by temperature cycling of the material may also initiate fatigue cracks. Stainless steels have higher coefficients of thermal expansion than carbon and alloy steels, so in most cases they are more likely to see higher stresses.
Low Stress Abrasion

- This is the predominant wear mechanism in oilsands mining. It occurs when the oil sands pass over a surface with relatively low contact force, for example when it slides down a hopper wall or along a truck box floor during dumping. The abrasive remains substantially intact and material is generally removed from the wear part surface by a micro-cutting action.
- The main characteristic required in a protective material is very high hardness.
- The wear rate varies as the square of the particle velocity. A practical demonstration of this is the large difference in the wear rates at the following two locations: 1) Double Roll Crusher apron feeder channel, and 2) DRC exit hopper. The softer AR400 plate provides good abrasion resistance on the walls of the apron feeder channel. The harder feed is moving relatively slow and the additional impetus due to gravitational acceleration and the additional impetus applied by the rotating rolls. The increase in the feed velocity requires the use of 1 inch thick chrome white iron wear tiles.

High Stress Abrasion

- High stress abrasion usually occurs when abrasive oil sand particles are trapped and crushed between two hard surfaces in moving contact. Material removal is by a combination of scratching, fracture, and ploughing on a microscopic scale. Abrasion resistance is influenced by the relative hardnesses of the oil sands solids and the wear surface. Protective materials should ideally be significantly harder than 65 HRC (740 HB) which is the approximate value reported for quartz. Prevailing high stress contact however usually imposes large bulk forces that demand structural integrity, toughness, and strength. As these attributes cannot be provided reliably by very hard but generally brittle wear materials typified by ceramic and cermet options, the compromise selections are mainly high strength alloys with hardnesses up to 600 HB. Examples of components exposed to severe attack are tractor undercarriage parts and dragline chain links.
High Stress Abrasion

This occurs in a severe stress system when abrasive lumps are driven into a surface with sufficient force to plow out material by plastic flow. The rate of loading may be quite rapid which necessitates a requirement for adequate fracture toughness to resist shock and shearing forces. This must be combined with high hardness or work hardening capability to withstand gross penetration. Because large stresses are imposed materials of choice must also have good bulk strength. Feeder breakers and the double roll crusher are equipment affected most by gouging.

Gouging Abrasion

- This occurs in a severe stress system when abrasive lumps are driven into a surface with sufficient force to plow out material by plastic flow. The rate of loading may be quite rapid which necessitates a requirement for adequate fracture toughness to resist shock and shearing forces. This must be combined with high hardness or work hardening capability to withstand gross penetration. Because large stresses are imposed materials of choice must also have good bulk strength. Feeder breakers and the double roll crusher are equipment affected most by gouging.

Erosion

- Erosion occurs when a dense concentration of solid particles carried in a flowing liquid or gas, impact and/or slide against a wear surface. There are numerous areas that are severely affected in the bitumen extraction area. Screens, pumps, piping products and valves in aqueous slurry transportation are some examples. It also causes chronic attack in centrifuges and in systems handling high temperature hydrocarbon streams in upgrading operations.
- Very high hardness protective options are usually selected for low impingement angles where material removal occurs by microcutting. Increased toughness capabilities are required at high contact angles when microcutting predominates. Relatively soft elastomers are used in applications where the combinations of flow velocity and particle mass result in impacts which only cause elastic deformation.
Erosion

Rolling Contact Wear/Fatigue

- This occurs where many cycles of oscillating high stress contact, for example in bearing components, cause sub-surface fractures to initiate and propagate leading to spalling and delamination.

Fretting

- This occurs over many cycles of very low amplitude, oscillating slip between contacting surfaces. This can result in wear damaged layers which are susceptible to fatigue fracture under the prevailing stress conditions. Bolted connections, keyways, bearing/Shaft interfaces and multi-strand wire rope are locations which have a propensity to fretting attack.
Adhesion, galling or scuffing

- These processes occur where relatively clean metal surfaces come into contact and the prevailing forces are sufficient to cause solid state welding at small discrete areas. Shearing and material transfer occurs as these intermittently bonded surfaces are displaced relative to one another.

References

- ASM Handbook - Corrosion, Volume 33

Summary

- Get involved in TEG 341X – Oil sands Information Exchange Group to further understanding of degradation mechanisms.