TPA Training Course

Corrosion Management in the Oil & Gas Industry

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Part 2

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Corrosion Management in the Oil & Gas Industry

Main families of corrosion cases in the Oil & Gas Industry and their Prevention
Corrosion Management in the Oil & Gas Industry

CO$_2$ (and H$_2$S) Corrosion
CO₂ Corrosion

- CO₂ corrosion is the most often encountered corrosion type
- It is a very complex phenomenon
- CO₂ corrosion is a kind of acidic corrosion, influenced by $P_{CO₂}$, temperature and chemical composition of water (acetates, pH, Ca⁺⁺,...)

Localised corrosions at locations where iron carbonate deposits lose their protective character: Metallurgical heterogeneities, hydrodynamic effects, ...
CO$_2$ corrosion: When? How fast?

Some examples:

- Norway, gas field, 0.3% CO$_2$: ~ 25 yrs…
- Offshore Netherlands gas fields, 2- 3% CO$_2$: 8 months
- Gabon oil fields, 1- 2% CO$_2$: 1 to 3 yrs
- Cameroon, Indonesia, Nigeria oil fields: 2 to 6% CO$_2$: >> 20 years

Whatever its name, "CO$_2$ corrosion" is not only dependent on the CO$_2$ content.
CO$_2$ Corrosion on piping flanges
Corrosion by $\text{CO}_2$ in a tubing from an oil well

Corrosion rate: 7 mm/y
CO$_2$ and H$_2$S corrosion

Sweet corrosion

Fe + CO$_2$ + H$_2$O $\rightarrow$ FeCO$_3$ + H$_2$

Corrosion product: Iron carbonate

Sour corrosion

Fe + H$_2$S $\rightarrow$ FeS + H$_2$

Corrosion product: Mackinawite (Iron sulphide)

H$_2$S reduces corrosion rate if $P_{H2S} > 0.5$ to 2 % $P_{CO2}$ but induces metallurgical requirements ("Sour service")
Corrosion prediction models

- There is no generally accepted prediction model
- For Total, CORPLUS treats pH calculations and corrosion prediction in wells and lines, without H$_2$S. It is based on a large field data base
- It addresses physico-chemical equilibria, electrochemical kinetics of corrosion, thermodynamics, hydrodynamics, water/oil wetting, protectivity of corrosion layers
- It gives a "corrosion assessment" about CO$_2$ corrosion (with a complete account of the effect of acidic organic species), erosion-corrosion
- Precise pH and water chemistry evaluation, definition of "Sour service" conditions.
**CO₂ corrosion risks in wells producing reservoir water (CORPLUS)**

<table>
<thead>
<tr>
<th>Condition</th>
<th>P$_{CO₂}$ max (bars)</th>
<th>C.P. (mm/an)</th>
<th>pH in situ</th>
<th>Ca$^{++}$/HCO$_3^-$ (meq/meq)</th>
<th>HAc (meq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Très faibles*</td>
<td>&lt; 0.05</td>
<td>&lt; 0.2</td>
<td>&gt; 5.6</td>
<td>&lt; 10</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>Very low</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moyens*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Medium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt; 1000</td>
</tr>
<tr>
<td>Importants</td>
<td>Pour toutes les autres conditions</td>
<td>For all other conditions</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* : Condition VRAIE si l’une au moins des propositions est vérifiée  
(1 proposition = 1 ligne)  **True when one of these conditions is fulfilled**
CO₂ corrosion risks in wells producing condensed water (CORPLUS)

<table>
<thead>
<tr>
<th></th>
<th>( P_{\text{CO}_2} ) max (bars)</th>
<th>C.P. (mm/an)</th>
<th>HAc (meq)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Very low</strong></td>
<td>&lt; 0.05</td>
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<td><strong>Très faibles</strong></td>
<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td><strong>Moyens</strong></td>
<td>0.2&lt; 5</td>
<td></td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td><strong>Importants</strong></td>
<td>Pour toutes les autres conditions</td>
<td></td>
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</tr>
</tbody>
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(1 proposition = 1 ligne)

**True when one of these conditions is fulfilled**
Flow management for corrosion-erosion prevention

RESPECT OF CRITICAL FLOW RATES ($V_{cr}$)

$$V_{cr} = \frac{C}{\sqrt{\rho_m}}$$  \hspace{1cm} \text{(API RP 14-E)}

$\rho_m$ : Mean volumic weight of fluid

- non inhibited corrosive polyphasic fluids : $C=100$ to 130 (US units)
- inhibited corrosive polyphasic fluids : $C=130$ to 160
- inhibited wet gas : $C=160$ to 200
- water free fluids: $C>200$
- De-aerated inhibited injection water: $C= 200$ to 250
- stainless steels: $V_{cr} > 50$ m/s

without solid particules
Flow management for corrosion-erosion prevention

Presence of solids is a major parameter for damage of equipment.

The «right» prevention against solid erosion is when ensured «at the origin», at the well bottom.

If not possible:
- choose moderate flow rates
  - long radius elbows
  - hard coatings (ceramics), mainly for choke valves
  - sand traps
  - monitoring (coupons, ultrasonic probes)
  - CRA (Corrosion Resistant Alloys).
Methods of internal corrosion prevention in wells

- **Chemical treatment:** Inhibition
  - **Difficult,** often not reliable and not cost effective for wells, especially offshore
  - May be implemented with continuous injection, batches or squeezes

- **Corrosion Resisting Alloys (CRAs):**
  - 13% **Cr Stainless steel:** often the best solution for tubings, generally enough for resistance to CO$_2$ corrosion (limited for SSC)
  - More alloyed stainless steels necessary for the most severe cases (high temperature, H$_2$S level, high Cl$^-$ content)
## Methods of internal corrosion prevention in wells: CRA's

<table>
<thead>
<tr>
<th>Material</th>
<th>Cost*</th>
<th>Advantages</th>
<th>Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard steel</td>
<td>1*</td>
<td>Cheaper cost</td>
<td>No corrosion resistance</td>
</tr>
<tr>
<td>13% Cr</td>
<td>1* : Near 100 k$ for 3500 m tubing 4”1/2</td>
<td>Good corrosion resistance</td>
<td>Grade max : C95 Sensible H2S</td>
</tr>
<tr>
<td>Duplex 22% Cr</td>
<td>8</td>
<td>Grades C75 à Q125</td>
<td>Sensible H2S for grades &gt; C75 Very expensive</td>
</tr>
<tr>
<td>22% Cr, 5% Ni, 3% Mo</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duplex 25% Cr</td>
<td>10</td>
<td>Grades N80 à Q140</td>
<td>Idem</td>
</tr>
<tr>
<td>25% Cr, 7% Ni, 3% Mo</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aust. 28% Cr</td>
<td>12-15</td>
<td>Very good corrosion resistance incl. with H2S</td>
<td>Cost</td>
</tr>
<tr>
<td>28% Cr, 31% Ni, 4% Mo</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Methods of internal corrosion prevention in surface equipment: Piping

- In case of significant corrosion risk, the use of **stainless steels** (SS) is common because inhibition is difficult and/or expensive to realize for short distances.

- Mainly "**Duplex**" (22% Cr- 5 Ni%) or "**super-duplex**" (25% Cr-7%Ni) austeno-ferritic SS are used for ensuring the best compromise between corrosion resistance and higher mechanical strength as compared with austenitic SS.
Methods of internal corrosion prevention in surface equipment: Vessels

- Most often **internal coating** constitute the prevention systems of pressure vessels (separators, scrubbers, ...) in process and water environments.

- They are limited in pressure (disbonding with pressure variations) and temperature.

- Epoxy limited to 60°C and 50 to 80 bars.

- Heat cured phenolic paints, Glass flakes vinyl esters and other composite or hybrid systems more resistant.

- Paint linings do not prevent SSC risks.
Methods of internal corrosion prevention in surface equipment: Vessels

- Eventually anodes are installed at the bottom when enough continuous water phase exists for preventing corrosion at coating defects.

- Clad materials are selected for the most severe conditions, using 2 to 3mm thick stainless steels (316L, 904L) or nickel alloys (Alloy 825, Alloy 625,…), depending on the corrosion risks (e.g. SCC).

- SS claddings prevent SSC risks.

- If found more economical, solid SS vessels are used.
Methods of internal corrosion prevention of oil pipelines

- No safe solution exists today with coatings to ensure a complete continuity for corrosion protection (initial defects, technical difficulty and cost to apply and check internal girth weld coatings, damage in service when pigging, prevention of any efficient in-line inspection, …)

- No parallel possible between combination of external coatings and CP and internal coatings and inhibition as it is necessary to inject roughly the same concentration of inhibitor to ensure its efficiency at coating defects, hence no OPEX savings
Methods of internal corrosion prevention of oil pipelines

- **Inhibition** is the conventional solution using continuous injection.
- Inhibition at temperature higher than 100 °C is difficult to achieve.
- When inhibition is too difficult or safe enough, other solutions are available:
  - **Corrosion Resisting Alloys (CRAs):**
    - Austenitic and Duplex Stainless steels: expensive, currently used for piping and short length flow-lines.
    - Weldable Supermartensitic 13% Cr Stainless steels: several failures due to sensitivity to H embrittlement.
  - **Flexible pipes:** -> Offshore flow-lines often competitive for short lengths.
  - **Composites (GRP):** -> competitive cost for flow-lines, but specific cases.
Methods of internal corrosion prevention of wet gas pipelines

- If re-circulated regenerated glycol is used for hydrate prevention, pH stabilization of glycol is the most efficient solution when feasible, i.e. total acidity to neutralize not too high and no reservoir water.

- Inhibition is the conventional solution when hydrate prevention is not necessary or pH stabilization of re-circulated glycol not possible (use of hydrate inhibitors).

- When all these methods are not possible or safe enough, solid, lined or clad Corrosion Resisting Alloys (CRA), flexible pipes or composites (GRP) are used.
Corrosion inhibition

- Different mechanisms:
  - Anodic inhibitor
  - Cathodic inhibitor
  - Film forming inhibitor

- Solubility / Partitioning
  - Oil soluble C.I
  - Water soluble C.I
  - C.I repartition in hydrocarbon phase and in water phase

- Foaming tendency and Emulsion tendency
  - Hydrocarbon quality, Discharge water quality
Qualification testing of corrosion inhibitors

Measurement equipment

Corrosion cells
Simulation of field corrosion

Static
mono phase
results

Static
Two phases results
Simulation of field corrosion

Turbulent flow: Jet impingement test

(High shear stress)
Simulation of field corrosion

Dynamic test results

- C.R mm/y
- Shear stress 70 Pa
- C.I. addition
- inhibitor X
- selected C.I.
- Time (hour)
Corrosion inhibition treatments

Continuous injection

- The most used treatment system. Typical injection rates
  - 5 to 15 l/ Mm³ gas for pipelines of gas with condensate
  - 10 ppm/water for T < 40 °C
  - 20 à 30 ppm/water for 40 °C < T < 60°C
  - 50 ppm/water for 60°C < T < 90 °C
  - 100 à 150 ppm above…

Generally, "water soluble inhibitors", or "preferentially soluble in water inhibitors" are preferred

Need of evolution towards "greener" products, often less efficient
pH stabilization of re-circulated glycol (without $H_2S$)

- **PH stabilization** (pH target 6) consists in adding a neutraliser (MDEA, MBTNa, NaOH, $HCO_3^-$, ...) to water-glycol re-circulated after regeneration.

- Long experience (near 40 years) with very corrosive gases without $H_2S$ (Italy, Netherlands, Norway, etc).

- Recent full demonstration of absence of any trace of corrosion (including at top-of-line) through ILI (In-Line Inspection) of a pipeline offshore Netherlands after 25 years operation (100 °C, very high potential corrosivity).
pH stabilization of re-circulated glycol (with H$_2$S)

- First use on long wet gas pipeline containing CO$_2$ and H$_2$S for pipelines in Iran, South Pars 2/3, (pH target 7 instead of 6)
- Problems encountered with salt deposits (CaCO$_3$) due to unforeseen produced field water containing Ca$^{++}$ not removed upstream pipeline inlet, causing problems for executing ILI. Project of MEG purification unit
- PH stabilization no more economically feasible when CO$_2$ and H$_2$S contents are too high (3 to 5%). This led to selection of inhibition through the re-circulated MEG after qualification of inhibitor resisting to regenerator temperature
Top of line corrosion in hot wet acidic gas lines

Corrosion rate: 1 to 2.5 mm/y

Iron carbonate
Top of line corrosion in hot wet acidic gas lines

TLC corrosion is promoted by:

- Laminar flow in gas lines
- High temperature effluent (typically >50°C)
- External cooling by sea water, cold air, etc.
- High partial pressure of CO₂
- High organic acid content
- Water condensation rate > Critical water condensation rate (typically from 0.025 to 0.25 ml/m²s, depending on organic acid content, without H₂S)
Prevention of top of line corrosion in hot wet acidic gas lines

Top of line corrosion shall be prevented by proper design:

- Thermal insulation or burial of pipeline

- When thermal insulation is applied, care must be taken to avoid cold spots at for instance field joint areas (infill necessary with concrete weight coating)

- When pipeline burial, attention must be paid to unburied parts such as doglegs as well as to upheaval buckling.

- Cooling of effluent at pipeline departure

- Internal cladding in the first part of the pipeline on a sufficient length (generally not economical)
Mitigation of top of line corrosion in hot wet acidic gas lines

In case TLC is appearing during operation, following methods may be applied for mitigation:

- Batch treatment with "oil soluble" corrosion inhibitor with high remanence on the surface
- Continuous injection of MDEA to increase the pH, avoiding deposits
- Use of special pig to disperse inhibitor at top of line

Monitoring to be done by:
- Intelligent pigging
- Air cooled Electrical Resistance probe located at top of line on topsides
Corrosion Management in the Oil & Gas Industry

$\text{H}_2\text{S}$ cracking phenomena ("Sour service")
H₂S cracking ("Sour" service)

- One of the **hydrogen embrittlement** phenomena
- **H₂S** (in fact adsorbed HS⁻) promotes penetration in steel of H produced by corrosion on surface
- **Risk lower when temperature higher**
- A contact of liquid water with the steel surface is necessary for the damage risks to exist.
- This water has to produce acidic corrosion (with H formation on cathodic zones), therefore must contain acidic species like CO₂ or H₂S (**influence of pH**)
- **H₂S** concentration in this water must be sufficient to produce enough H flux into steel (**influence of P_{H₂S}**)
H₂S cracking ("Sour" service)

- 3 main forms of damage: SSC, HIC, SOHIC
- "SSC" (Sulphide Stress Cracking)
  - a case of delayed rupture (such as Stress Corrosion Cracking) in presence of mechanical stress
  - H in solid solution reduces ductility and can lead to quick ruptures through transverse cracks (perpendicular to stresses) after a very short incubation time (the most dangerous)
  - concerns mainly high mechanical resistance steels (well tubings and casings, high hardness welds, ...): $R_{p0.2} > 660$ MPa (95ksi), hardness $> 22$ HRC for not or low alloy steels
Fissurations en présence de $\text{H}_2\text{S}$ humide

- **Hydrogen Induced Cracking (HIC)**
  - internal decohesion without stresses, after incubation
  - precipitation of gaseous $\text{H}_2$ at heterogeneities such as interfaces ferrite/ MnS inclusions or ferrite/bands of perlite
  - problem with extruded steels (welded pipes, vessels,...)
  - 2 kinds of patterns:
    - **Blistering**: blisters when "soft" steel
    - **SWC** (Step Wise Cracking) when steel “harder”
  - "SOHIC" (Stress Oriented Hydrogen Induced Cracking)
  - hybrid phenomena leading to transversal cracks under stresses (mainly in weld areas)
Patterns of H2S cracking ("Sour" service)

- SSC
- HIC / blisters
- HIC / SWC
- SOHIC
H$_2$S cracking ("Sour" service): SSC
Prevention of $\text{H}_2\text{S}$ cracking

- Use a $\text{H}_2\text{S}$ resistant material as soon as cracking risks exist

- For preventing SSC: Acceptable mechanical characteristics, Heat treatments (relaxation of stresses), precautions in welding (control of hardness and stresses)

- For preventing HIC: Chemical composition (low level of impurities), Control of manufacture (improvement of micro-structural homogeneity)

- Presence of a coating or inhibition is favourable for HIC (but monitoring mandatory), but not safe enough for SSC (too quick process when failure of corrosion prevention)
There are international standards and recommendations:

- **Former NACE MR 01-75** (for SSC only)
- **EFC Publication n°16** (unalloyed or low alloyed steels)
- **EFC Publication n°17** (CRAs = Corrosion Resisting Alloys)
- **ISO 15156/NACE MR 01-75**

Total General Specification **GS EP COR 170** is more precise on some aspects (e.g. low pH / low $P_{\text{H}_2\text{S}}$)
Severity domains for sour service

- **Area 0 “Sweet Service”**: no specific precautions - tubings → API Q125
- **Area 1 “Mild Sour Service”**: Nothing special for pipelines and vessels - tubings → API P110
- **Area 2 “Intermediate Sour Service”**: HV5 hardness at girth welds < 280 at weld root and 300 at weld cap - tubings → API N80
- **Area 3 “Severe Sour Service”**: HV5 hardness at girth welds < 250 at weld root and 280 at weld cap - tubings → API L80 / C90
"Microbiologically Influenced Corrosion" (MIC)
Severe metal loss corrosion (craters) when sulphidogenic (= H₂S producing) bacteria develop on steel surface.

These bacteria develop when conditions are locally favorable: anaerobia (absence of oxygen), pH near neutrality, temperature between 20 and 80 °C, presence of nutrients (C sources) and specific ions ensuring "breathing" for their metabolism.
MIC (Microbiologically Induced Corrosion)

- Two types of Bacteria in oil & gas corrosion:
  - **SRB**: Sulphate Reducing Bacteria which reduce sulphate into sulphide:
    \[ \text{SO}_4^{2-} \rightarrow \text{S}^{2-} \]
    Typically craters from 2 to 3 mm/yr
  - **TRB**: Thiosulphate Reducing Bacteria which reduce thiosulphate into sulphide:
    \[ \text{S}_2\text{O}_3^{2-} \rightarrow \text{S}^{2-} \]
    Typically craters from 10 to 15 mm/yr

  Generally \( \text{S}_2\text{O}_3^{2-} \) results from \( \text{H}_2\text{S} \) and \( \text{O}_2 \):

  \[ 2\text{H}_2\text{S} + 3/2\text{O}_2 \rightarrow \text{S}_2\text{O}_3^{2-} + 4\text{H}^+ \]

- MIC prevention carried out by adapted monitoring and biocide treatment when necessary
MIC due to SRB
MIC due to TRB

Craters up to 15 mm / yr
Risks of MIC caused by contaminations through introduction of water

- Contamination of facilities during hydrotests or when cleaning raw water is introduced is a permanent threat because presence of bacteria in river or sea waters
- The use of non treated water, for instance for flushing or cleaning vessels, may contaminate facilities for the remaining of their life, especially in dead areas, valves and under deposits.
- Bacteria may then develop and are very difficult to kill with chemical treatments.
- E.g. in Argentina, 2 oil pipelines contaminated during laying have leaked after 1 year of operation.
Risks of MIC during operations

- MIC develops under deposits: it is of utmost importance to keep oil pipelines clean through cleaning pigs, even when water cut is low.

- MIC failures may be very rapid when parameters of operation are modified without taking this change into account in the Corrosion management program.

- E.g.: change in quality of water feeding injection water system (introduction of a new water containing traces of hydrocarbons, SRB, sulfate ions, …)
Biocide treatments

◆ Control of MIC:
  ▪ SRB and TRB,
  ▪ present on the metallic surface (sessile)...
  ▪ ...and not those present in the liquid volume (planctonic),
  except for "reservoir souring" prevention.

◆ Sessile bacteria live:
  ▪ In synergy with other bacteria,
  ▪ Protected by a "biofilm", sometimes thick deposits (sulphides, sand...)

◆ Biocide efficiency = Reduction of bacteria population by 100 000 \( (10^5) \)
Biocide treatments

◆ Biocides
  - Formaldehyde, glutaraldehyde
  - quaternary ammoniums
  - T.H.P.S. (Tetrakis Hydroxymethyl Phosphonium Sulfate),

◆ Treatment basis
  - High dosage (basis: 500 ppm/water)
  - During a limited time => discontinued treatment (5 hrs)
  - Periodically renewed (typically 2 weeks)

◆ Change of biocides on a monthly basis. When risks of TRB, THPS to be used alternatively with glutaraldehyde (efficient for SRB only)

◆ Use of pigs (cups or plates) before injection of product
Monitoring of bacteria

- Culture of bacteria using special media which consists of mixtures of different nutrients for bacteria.
- API bottles ("test-kits")
- More specialised and quick "test-kits" for SRB and TRB developed by Labège R&D Centre and commercialised by CFG
- Serial dilution methods (1/10 x n) and McGrady table
- Rapid analysis (Sani check, Rapid check, Hydrogenase etc.): analysis of enzymes or other substance produced by bacteria (indicator of bacteria activity)
- Installation of "Bioprobases" (coupons) either directly in the line or in a side stream device.
Monitoring of bacteria: Serial dilution method
Corrosion Management in the Oil & Gas Industry

$O_2$ Corrosion inside facilities
Oxygen corrosion

Oxygen corrosion is important in the following systems:

- **sea water systems**:
  - injection for pressure maintenance
  - fire fighting systems
  - cooling water systems
- **water containing process fluids** when in contact with air or aerated water

As to the hydrotesting, this is **not a major issue** as the dissolved oxygen will be consumed and corrosion will stop (**MIC risk to be prevented**).
Detrimental role of oxygen in process fluids

- Oxygen = Additional oxidising power
- With $H_2S : O_2 + H_2S \rightarrow$ Thiosulphates :
  «thiosulphato-reducing» bacteria are very dangerous
- Inhibitors efficiency : Oxygen degrades the efficiency of a lot of inhibitors \(\rightarrow\) localised corrosion

Oxygen ingress must be as much as possible prevented in process fluids
Oxygen corrosion in sea water injection systems

• Sea water is:
  • chlorinated during pumping from the sea
  • filtered
  • physically deoxygenated in a de-aeration tower (vacuum or gas stripping)
  • then deoxygenated by oxygen scavenger injection down to less than 30 ppb

• **Upstream** of the de-aeration tower:
  • corrosion resistant materials like GRE or copper-nickel alloys are generally used
  • internal coating may be used but many problems were experienced. Internal cathodic protection should be used together with internal coating for large diameter pipes.

• **Downstream** of the de-aeration tower:
  • carbon steel is the only material used for the lines and equipment (eventually with thin epoxy paint coating for cleanliness).
Oxygen scavenger treatments

- Practically only sodium or ammonium bi-sulphite or sulphite
  - Basic chemical products ==> low price.
  - Oxygen reduction by oxidation of sulphite ==> sulphate
  - Often catalysed for increasing reaction rate
  - Care to take: Bisulphite = acidic product corrosive in high concentration

- Produced waters
  - In case of permanent aeration: continuous injection of 15 to 20 ppm/ O₂

- Utility or slop waters
  - Deaeration to get O₂ < 30 ppb
  - Multi-functional product (O₂ scavanger and biocide)
Oxygen corrosion in sea water fire-fighting and cooling systems

• Fire-fighting systems:
  • Corrosion resistant materials like GRP (mainly in "wet section" and copper-nickel alloys (mainly in "dry section") are generally used.

• Cooling systems
  • Chlorinated during pumping from the sea
  • Corrosion resistant materials (CRA) like Cu-Ni alloys or GRP are used for piping.
  • Internally cement lines lines can be used for large diameter lines onshore.
  • Nickel - Co - Mo alloys (Alloy C 276 or C22) and titanium alloys are generally used for heat exchangers to prevent pitting, crevice corrosion and stress corrosion cracking.
Corrosion resistance of stainless steels in sea water

Selection of corrosion resistant alloys uses PRE:

\[ \text{PRE}_N = \% \text{Cr} + 3.3 \% \text{Mo} + 16 \% \text{N} + 0.5 \% \text{Ni} + 1.7 \% \text{W} \]

- The PRE should be higher than 35 to resist pitting corrosion in the flowing sea water up to 50°C.
- The PRE values should be higher than 42 for temperatures up to 80°C and in stagnant water.

The residual chlorine content of the water should not exceed 0.5 ppm to prevent severe pitting and crevice corrosion of stainless steels.
Corrosion – erosion of copper alloys in seawater
Types of anticorrosion chemicals

**CORROSION INHIBITORS:**
- long chain amines, imidazolines, phosphoric esters...

- Oil, gas, water circuits

**BIOCIDES:**
- glutaraldehyde,
- quaternary ammonium,
- THPS...

- All contaminated circuits

**OXYGEN SCAVENGERS:**
- sulfites, bi-sulfites

- Aerated injection waters
- Various aerated waters

**pH STABILISERS:**
- MDEA, MBTNa, HCO₃⁻...

- Gas transportation pipelines with hydrate prevention
Corrosion Management in the Oil & Gas Industry

Monitoring of internal corrosion
Monitoring the treatment efficiency and residual corrosivity

Major tools and methods:

- Water analysis for:
  - iron counts
  - Residual corrosion inhibitor content
  - pH
- Coupons
- ERP (Electrical Resistance Probe)
- LPR (Linear Polarisation Resistance probe)
- Bioprobes
- Flexible UT mats
Iron counts vs time

Average ppm iron vs S1 temperature
Corrosion Monitoring: coupons and probes

- Electrical Resistance
- LPR probes
- Coupons

- Cylindrical intrusive (RCS data sheet)
- Flush
- Intrusive (Cormon data sheet)
- Flush (Corrocean data sheet)

Bioprobes

Flush (Cormon data sheet)
Internal corrosion monitoring: recovered probes and coupons
Corrosion Monitoring: Access fittings

Corrocean type  (from Corrocean data sheet)

Standard R/C type  (from Cormon data sheet)
Corrosion Monitoring: HP extractors for probes

Mechanical system (Rohrback-Cosasco)  Hydraulic system (Corrocean)
Internal corrosion monitoring
Measurement of corrosivity (LPR)

Field testing new inhibitor

Product anomaly

Velocidades de Corrosión Medidas en S1

- Vcorr 2-ECP-0124
- Vcorr 2-ECP-0124(acumulada)
- Vcorr 2-CC-0124

Date:
- 20-09-04
- 21-09-04
- 22-09-04
- 23-09-04
- 24-09-04
- 25-09-04
- 26-09-04
- 27-09-04
- 28-09-04
- 29-09-04
- 30-09-04
- 01-10-04
- 02-10-04
- 03-10-04
- 04-10-04
- 05-10-04
- 06-10-04
- 07-10-04
- 08-10-04
- 09-10-04
- 10-10-04
- 11-10-04
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- 29-10-04
- 30-10-04
- 31-10-04
- 01-11-04
- 02-11-04
- 03-11-04
- 04-11-04
- 05-11-04

Graphical representation of corrosion velocity measurements with key dates and annotations.
Measurement of corrosion rate with ERP

Date Range Graphed: 21/09/2004 to 21/03/2006
Corrosion monitoring: UT measurements at specific locations
Corrosion Management in the Oil & Gas Industry

Corrosion-related Inspection
The challenge of inspection

Monitoring is not sufficient!

Only INSPECTION allows direct information on physical status of equipment.

Risque de dégradation du composant

negligible

faible

important

INSPECTION
The evolution of approach

PREVIOUSLY ➔ Prescriptive, regulated and not selective ("Time-based Inspection")

- Mandatory systematic inspections, without taking into account operating conditions
- High Maintenance and Operation costs (need of shutdowns)

TODAY ➔ Risk Based Inspection (RBI) approach

- A selective verification, based on probable risks
- Potential savings associated to a better availability of facilities
RBI (Risk Based Inspection)

A definition
The establishment of optimised inspection programmes, adapted to the risks facing the facilities

A methodology
A structured approach involving:
- Assessment of consequences of failures (explosivity, flammability, toxicity, pollution, …)
- Assessment of degradation modes (corrosion, fatigue, etc.)
- Physical status of equipment (previous results of inspections)
and delivering quantified and auditable results

A tool: For Total, FAME+
A software allowing quick compilation and management of a great number of parameters
RBI (Risk Based Inspection): Calculation of consequences

- EVALUATION OF CONSEQUENCES
  - EXPLOSION, FIRE POLLUTION, TOXICITY
- COMPENSATION PROTECTION
- DETERMINATION OF CONSEQUENCE FACTOR

Components:
- ESDV
- DCS

Diagram showing risk assessment process.
RBI (Risk Based Inspection): Calculation of probability of damage

- Conditions of operation (fluid, P, T, environment...)
- Materials and design

Identification of potential degradation modes

Specific data for each mode

Calculation of corrosion rates and/or sensibilities

Determination of identified damage probabilities

- Thickness thinning
- Cracking
- Localised Corrosion
- Embrittlement
RBI (Risk Based Inspection): Calculation of Criticity

**Calculation Criticity**

- Degradation Mode 2
- Degradation Mode 1

Probabilities of failure

Consequences in case of failure

Impact on production

Level of Criticity

Strategy of inspection for each mode of degradation
RBI (Risk Based Inspection): Strategy of inspection

For each mode of degradation

- **Inspection reports**
  - Determine status parameter

- **Basic Inspection intervals**
  - Effectiveness of inspection
  - Level of Criticity

- **Optimised Inspection intervals**
  - For each mode of degradation
  - Determine intermediate inspections

- **Number and types of inspections**
  - Parameter of confidence
Inspection methods for corrosion: pressure vessels, piping

- Ultrasonic measurements (Internal corrosion, cracks)
- Magnetoscopy, Dye penetrant, Eddy currents (superficial cracks)
- Radiographies (Internal corrosion, welds)
- Hydrotest (Construction, verification of repairs, regulatory aspects)
- Verification of materials (Hardness, Composition, …)
- Internal and external visual examinations
UT measurements

Previously: measurements on specific locations at periodical intervals
Better: performing **scanning** on critical areas
   (recording of **minimum value of thickness**)
Advanced inspection techniques: Acoustic emission

Main applications:

- Evaluation of internal corrosion of tank bottoms
- Detection of cracks in pressure vessels
Other advanced inspection techniques

- Corrosion under insulation
  - Thermography
  - Numerical Gammagraphy
- Long range Ultrasonic testing
Inspection techniques of offshore structures

Surface structures

*Visual inspection*
*Detection of cracks through NDT*

Underwater structures

*Visual inspection (ROV, Divers)*
*Cathodic Protection*
*FMD (Flooded Members Detection)*
*Detection of cracks through NDT*
Methods for inspection of corrosion: well tubings, pipelines

- **Calipers** for tubings (geometrical fingers or magnetic systems)

- **Intelligent (smart) pigs** for internal inspection of pipelines ("In-Line Inspection", ILI)
  - Self propelled pigs, autonomous
  - Tethered pigs propelled by the fluid
  - Tethered pigs propelled by crawlers
  - Magnetic tools ("MFL", Magnetic Flux Leakage)
  - Ultrasonic tools ("UT")
In-Line Inspection (ILI) of pipelines: MFL Intelligent pigs

**Advantages:**
- Applicable whatever the fluid
- High level of detection (continuous measurement)

**Drawbacks:**
- Imperfect sizing of defects (not a direct measurement of thickness)
- Evaluation to be checked by direct measurements
In-Line Inspection (ILI) of pipelines: MFL Intelligent pigs

- Magnets
- Primary detector
- Secondary detector
- Data storage
# Example of report

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<th>Insp. Sheet Number</th>
<th>Absolute Distance (metres)</th>
<th>Ext. or Int.</th>
<th>Predicted Dimensions</th>
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Example of corrosion image (MFL)
Sizing of defects
Corrosions vs. distance to girth welds
An example of external corrosion under disbodied coatings on the hottest end
In-Line Inspection (ILI) of pipelines: UT intelligent pigs

**Advantages:**
- High accuracy of sizing of defects (direct measurement)

**Drawbacks:**
- Not applicable in gas or heterogeneous fluids
- May miss small defects (discontinuous measurements)
In-Line Inspection (ILI) of pipelines: UT intelligent pigs

Ultrasonic tool
TPA Training Course

Corrosion Management in the Oil & Gas Industry

End of Part 2