Corrosion Offshore – It’s a Battle Out There

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Charlie Speed Bio

Originally from Montreal, Canada, Charlie first worked in the aerospace and nondestructive testing industries. For the last 30 years Charlie has provided materials, corrosion, inspection engineering and chemical support for the Gulf of Mexico operations of major oil companies. (Exxon: 14yrs, Mobil: 5 yrs, & Shell as a Consultant Chemical Engineer for >10 yrs. Currently consulting in Houston at SBM Offshore.

Charlie has a BS in Materials Engineering from Auburn University and a MBA from William Carey University.

Charlie is Past Chair of the New Orleans Section of the American Society for Nondestructive Testing (ASNT); Past Chair for NACE, The Corrosion Society New Orleans and an active member of API, SPE, ASM and the Gideon’s International.
Forming: Stage 1 of Team Growth
When a team first forms, team members are like hesitant swimmers standing by the side of the pool and nibbling their toes in the water.

Storming: Stage 2 of Team Growth
As team members start to realize the amount of work that lies ahead, it is normal for them to almost panic. Now they are like swimmers who have jumped into the water, think they are about to drown, and start thrashing about.

Norming: Stage 3 of Team Growth
As team members get used to working together, their initial resistance fades away. They start helping each other stay afloat rather than competing with one another.

Performing: Stage 4 of Team Growth
As team members become more comfortable with each other, and better understand the project and what is expected of them, they become a more effective unit with everyone working in concert.
Corrosion Offshore – It’s a Battle Out There

Abstract

• Corrosion seriously damages the wealth of a nation.

• Ever since 1763 when the British Admiralty clearly reported on bi-metallic corrosion of copper sheathing and iron rivets aboard the Royal Navy’s Vessel HMS Alarm, there has been a constant battle to prevent or mitigate corrosion.

• This presentation shares a number of corrosion related failures that designers and engineers working in the Offshore Oil and Gas Industry need to be aware of so these failures will not be continually be repeated.
Oilfield Corrosion Experiences

1. Corrosion Threats
2. Corrosion Barriers
3. MCI Experiences/Learnings
Forms of Corrosion (“Threats” you can see)

1. Uniform Attack or General Corrosion
2. Localized or Pitting
3. Crevice Corrosion (Pitting)
4. Galvanic – Dissimilar materials
5. Velocity Effects – Erosion Corrosion
6. Cavitation
7. Fretting
8. De-alloying or Selective Leaching
9. Environmental Corrosion
10. Stress Corrosion Cracking (Corrosion Fatigue)
11. Hydrogen Damage
12. High Temperature
13. Degradation of non-metallics (resins and composites)
“Corrosion” Threats

Acid Gas Corrosion

Microbiologically Induced Corrosion

Acid Attack

Environmental Cracking

Oxygen Attack

Erosion/Corrosion
CORROSION BARRIERS

1. Materials Selection and Designing for Corrosion Control (DCC)
2. Chemical Treating (CT)
3. Protective Coatings and Linings (PCL)
4. Cathodic Protection (CP)
5. Process Control (PC)
6. Preventative Maintenance (PM)

Corrosion Barrier Assurances

1. Monitoring & Sampling and
2. Inspection (Visual & NDE)
Learn from your Mistakes

- British Navy Ships and Plans
- Instrument Tubing
- WBHRIZ
- Acidizing
- Packer Fluids
- Inspection Nondestructive Testing (if time)
HMSW Alarm, the royal Navy frigate which in 1763 was the subject of the first recorded study of bimetallic corrosion.
McArthur’s Universal Corrective Map of the World
In 1982, the nose wheels failed on two Royal Navy Sea Harriers Aircraft. The cause was attributed to bimetallic corrosion between the magnesium hub and its stainless steel bearing.
Cost of Corrosion

Royal Navy Sea Harrier suffered nose wheel collapse because of bimetallic corrosion between the bearing and the wheel.

Remains of steel bolts which in 1962 had been used to hold a copper alloy end plate on to an evaporator on board a Royal Navy submarine

Ref. Corrosion For Students of Science & Engineering . Trethewey & Chamberlain
Materials Selection and Designing for Corrosion Control
What are these used for?
Under Deposit Corrosion  (Ref Corrosion in Action)

Crevice Corrosion (2004)
Preventing and Mitigating Corrosion of Stainless Steel Instrumentation Tubing
Pitting corrosion
• Breakdown of passive oxide layer
• Formation of localized shallow pits
• Pits grow deeper in time
• Can penetrate tubing

\[
Fe \rightarrow Fe^{++} + 2e^- \quad \text{(anode)}
\]

\[
Fe^{++} + O_2 \rightarrow Fe-oxide
\]
Corrosion of Instrumentation Tubing

2507 superduplex tubing: no pitting corrosion, minor crevice corrosion (no leaks) with inadequate tubing clamps

316 tubing: pitting and crevice corrosion (leaks)
Aluminum to the Rescue (1984)

- Marine grade aluminum strips mated against both tubing surfaces mitigate crevice corrosion

First Installed on EUSA MC-280 LENA til 1994 (VR-164 BAT)
“Aluma Rack” for Eliminating Tubing Movement (1994)

First Installation 1994 on EUSA SM-99B “Cupid”
Encapsulated Instrument Tubing
I-Rod Tubing Assembly
NOT RECOMMENDED

- Thermoplastic I-Rod spacer
- marine grade aluminum alloy strip
- 316 SS sheet metal tubing spacers
Offshore retrofit using ITA concept

I-Rod Tubing Assembly
NOT RECOMMENDED
I-Rod Tubing Assembly
NOT RECOMMENDED
Properly installed U-bolt clamp with I-Rod and double locking nuts.
Another Good Idea
Three Ways To Do It
Some People Think Zinc Stinks
Question

Which Coating System Do You Want?
Observations

When you have coating breakdown with a typical top coated inorganic zinc marine coating system there is a good chance that you would see corrosion that penetrates the pipe wall.

This does not happen with un-topped coated (single coat) Inorganic Zinc?
Australia: Inventor Victor Nightingall

- **Post-cured Zinc Silicate** originated in Australia when **Victor Nightingall** experimented with combinations of zinc & sodium silicates attempting to emulate zinc-iron silicate ores.

- **Zinc dust, alkaline sodium silicate, & a little lead** was applied to 250 mi. Morgan-Whyalla pipeline in 1942.

Inorganic Coatings, Inc. videoed fifty miles after 48 years of marine coastal exposure, the **pipeline was in perfect condition**, even on difficult areas like joint welds.
Chuck Munger of Ameron, joined forces with Nightingale to produce **Dimetcote**.

**Dimetcote 3**, first acid post-cured zinc silicate

**Dimetcote 4**, the first self-cure zinc silicate coating (low ratio). Their success further proved the great protection provided by zinc silicate chemistry.

**Offshore Jack – Up Mr Gus With Post-cure Zinc Silicate at 12 Years.**
Esso/Humble (ExxonMobil) Developed Similar Products

How Esso Research makes a "permanent" primer last even longer!

New RUST-BAN 191 is sometimes called a "permanent" primer because it eliminates repeated repriming and lasts as long as some equipment. This unique, self-curing inorganic zinc silicate can last even longer—in special coating systems developed by Humble. These systems combine the remarkable underfilm protection of RUST-BAN 191 with the extra surface protection of Humble epoxy, vinyl, chlorinated rubber and other special-service topcoats. Significant savings have been realized from our experience with over 10 million square feet of inorganic zinc silicate coatings on our own equipment. For more information about RUST-BAN 191 and these coating systems, call our local Sales Representative, or write to our Industrial Sales Department in Houston, Texas.

IT PAYS TO DO BUSINESS WITH HUMBLE ... AMERICA'S LEADING ENERGY COMPANY

January 1964
Mobilzinc coating. Like dipping your steel structures in a galvanic bath.

Brushing or spraying steel with Mobilzinc gives the same protection as dipping it in a galvanic bath. That's why "Zinc-rich" Mobilzinc gives the most effective, longest lasting, easiest applying cathodic protection of any coating. Mobilzinc leaves a tough coating of zinc on steel substrates. During immersion, or in highly caustic environments, the steel becomes cathodic and Mobilzinc becomes anodic. If the steel becomes exposed by damage, the zinc film is quickly restored, protecting the steel.

No demanding application techniques are necessary with Mobilzinc. It brushes or sprays on like ordinary paint. Its eye-appealing green color provides an easy-to-see contrast to unpainted surfaces. Setting time is just twenty minutes.

Extensive testing proved Mobilzinc effective for adverse marine and industrial environments, including bridges, offshore rigs, pulp and paper mills, chemical plants, caustic environments, and areas exposed to heavy abrasion or high temperatures.

For expert advice on the best Mobilzinc coating for you, see your favorite Mobil oilfield supplier, or write to Mobil Chemical, Maintenance & Marine Coatings Dept., Edison, N.J., the largest supplier of maintenance coatings to the drilling industry.
Kennedy Space Center Beach Corrosion Test Site

- Untopcoated inorganic zinc
- Topcoated inorganic zinc (right steel panel) with epoxy/urethane

After 8 years of atmospheric exposure at the Beach Corrosion Test Site

NASA Corrosion 2003 # 03208
• In general topcoats were found to be detrimental to long term performance

• Results from coating evaluation studies at KSC have shown that inorganic ZRPs outperform organic ZRPs in the KSC seacoast environment

• Inorganic ZRPs are the best choice to provide long term protection of launch equipment and ground support structures
Some People Think Zinc Stinks - I Don’t!

8 Year NASA KSC Scribe Test

Which Coating System Do You Want?
Comprehensive study on the performance of Single-coat IZS vs multi-coat systems found:

• All the different types of single coat inorganic zinc silicate systems performed equally well, and very much better than their top coated counterparts
• Faster turnaround of work
• Less handling damage; easier & simpler maintenance;
• *No unacceptable solvent-containing top coats*
Esso Australia 1992 Recommendation

• **Permanently** replace the multi coat systems with the single coat, high ratio zinc system for new construction and maintenance work onshore and offshore.
Pontoons In (Immersion) Service
Pontoons In Service

(Courtesy of Earl Ramlow Polyset)
Major Wellhead Manufacturer
Coating Specialists (1992)

These Folks Like Water Borne Zinc! It Does Not Stink
Maintenance Coating Test

• In 1993 a Major E&P Company tested WB-HR-IOZ by choosing one of the oldest platform in the Gulf of Mexico being recoated.

• Half was coated with WB-HR-IOZ and the other half with a 3 coat Maintenance Epoxy/Epoxy/ Polyurethane Coating System
Three Coat Epoxy/PU vs WB-HR-IOZ (after 11 years)
Water Borne High Ratio Inorganic Zinc Silicate Transition to 3 Coat Epoxy/Epoxy/Polyurethane Maintenance System

Rust reported to be from above
Three Coat Epoxy/PU vs WB-HR-IOZ (after 11 years)
GOM Test - Three Coat Epoxy/PU vs WB-HR-IOZ (after 11 years)
Epoxy Side of Test After 11 Years
GOM Test - Three Coat Epoxy/PU vs WB-HR-IOZ (after 11 years)
In 1986, the 100th birthday of the Statue of Liberty was marked with a complete refurbishment of the statue.

A protective water borne high ratio inorganic zinc silicate (WB-HR-IOZ) coating called IC 531 was used to provide corrosion protection for the interior of the statue.

The coating originated with research on corrosion resistant materials conducted by NASA's Goddard Space Flight Center.

http://er.jsc.nasa.gov/seh/spacepupnew.pdf
Metallic Solutions

• Use of Corrosion Resistant Alloys (CRA)
  – 9Cr1Mo
  – Martensitic Stainless 13 Cr, Super 13Cr
  – 17-4 PH
  – Duplex Stainless 2205, 2207
  – Ni-Fe-Cr-Mo Sanicro 28, A-825, NIC 42
  – Ni-Fe-Cr-Mo 2550, G-3 G-50, 718, 925, NIC 52
  – Ni-Cr-Mo C-276, A-625, NIC 60,
  – Titanium
Well Pressure and Temperature Profile as Reinhardt, OGJ 4/28/88

An extreme effort needs to be made to ensure that the mixture compositions are as accurate as possible in developing phase diagrams.
For a TLP Waterflood Reservoir souring was a concern with existing well materials.

ISO15156/NACE MR0175 protocol for SSCC allows qualification basis pH testing.

Needed to define cracking resistance at normal exposure.

However, exposure may change: during operations & workovers.

For TLP, @ 0.07 psi projected H2S from souring:
1. Normal Flow with formation water pH = 5
2. Shut-in, with condensing water, pH = 4

When tested at shut-in conditions, 4 out of 5 materials presently in well failed!
Brine Fluids For Stainless Materials

Brine qualification testing with stainless materials
Normal Tests:

- Deoxygenated brine in corrosion-resistant alloy (CRA)-carbon steel annulus

- When initial completion is left for 1-2 months, brine plus produced gas in tubing; if tubing leaks them brine plus produced gas in CRA-carbon steel annulus

- And if completion work not quite just right Brine plus too much or no scavenger

If air is allowed into annulus top during a well cool-down before well restart and normal annulus re-pressure to 1500 psi Brine plus 30 psi oxygen

Avoid by System Design
Oxygen Exposure in Annulus

- Nitrogen injected into TLP well annulus below mudline to increase well temperature to address wax deposition.
- Platform nitrogen contains 1-2% oxygen.
- At 150 psi (10 atm.), partial pressure would be equal to atmospheric exposure of oxygen content.
- Air exposure of normal available height in tubing spool – inches – is OK as mass of oxygen in air cannot corrode much mass of steel.
- 3000’ of “air”, focusing damage on small brine interface area could possibly part the casing.

• Commercially pure grade (99.99%) nitrogen is recommended.
Duplex Stainless Steels Significantly Damaged by HCl

Acid inhibitor effectiveness also varies with martensitic stainless steel chemistry
13Cr Enhanced Metallurgy

Acid inhibitor effectiveness varies with martensitic stainless steel chemistry

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<tr>
<th>IDENTIFICATION</th>
<th>Nominal Chemistry</th>
<th>Unified Number</th>
<th>Description</th>
<th>API-5CT (Seamless)</th>
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Chemical Solutions

Chemical Inhibitors As Solutions For Corrosion

• Produced Fluids
  – Application method is key performance indicator
    • Continuous (CDIS), batch-pump, batch & fall, squeezes
  – Chemical type must match need
    • For e.g., gas well, high shear, high water cut,
  – Other Issues:
    • Environmental (toxicity), phase behavior throughout well, partitioning into water phase, compatibility and stability

• Special Fluids
  – Inhibitors for brines, stimulation fluids
  – pH buffers for brines
Chemical Barrier DSS Failure

- Chemical Stability
- In a HPHT well, the brine supplier company used a thiocyanate inhibitor in the annulus brine.
- In service, the high temperature in the well degraded the NaSCN to additional H2S in the annulus.
- Upon well recovery operations, the initial failure was found to be externally initiated cracks, occurring deep in the well, beginning on the outside of the 22Cr Duplex stainless tubing.
- The H2S generated exceeded the service limits of the material!

Eight months later, in another hotter HPHT field, when asked if the proposed additives were thermally stable, a supply company had no answer, despite vendor notifications.
718 CRA Microstructure

- To provide protection against CO$_2$ and H$_2$S, an entire HPHT well was constructed of CRA materials
- N07718, a Ni-Cr PH (precipitation hardened) proven material, was used for the hanger
- After very limited service the hanger failed
- Analysis indicated the crack had originated at the hanger threads, out of contact of both the annulus brine or the produced fluids! (An almost “pure” low cycle fatigue failure)
- Microstructural examination revealed an unsuitable aircraft grade of 718 was used!
Wireline Barb Scatcher Damage of Downhole Tubulars
Questions? Did I forget Anything?
ANY QUESTIONS?

I think we better better learn by our mistakes.
Extra Stuff
Scale & Internal Crsn
External Corrosion

Active External Corrosion
Profile Radiography (RTp) Of External Wall Loss Can Sometimes Be Used to Measure Wall Thickness Under Corrosion Product This is Typically Used When the Corrosion Product Cannot Be Safely Removed
Radiographic Profile (RTp) of External Wall Loss

Illustrates Importance of Alignment of Film & Radiation Beam

Any misalignment could result in the appearance of more external wall loss.
Internal Corrosion to be Proved up with UTpu

Wall thickness< .187”
Profile Radiography, RTp

Is a Routine Method Used to **Locate** Internal Corrosion

Black & Grey Boxes Represents Degree of Darkening on Radiograph

Radiation beams

Hole in Pipe

Film ===>

New Orleans ASME May 13, 2009
**Use Best NDT Methods**  Radiographic Profile for Internal Wall Loss Must Include Ultrasonic Prove-up (UTpu) of Any Indication

All Internal Wall Loss Must be Measured Using Best NDE Method (UTpu is preferred)
• EXTRA SLIDES
Internal Corrosion Considerations

• Three Gasses
  – Oxygen (O2), (The Invader)
  – Carbon Dioxide (CO2) (Soda Pop) and
  – Hydrogen Sulfide (H2S) (The Killer)

• Water (The electrolyte)
  – Condensed Water (De ionized)
  – Brine (Dissolved Salts)

  – Organic Acids
  – Bacteria

pH & (Water) Wettability
External Corrosion Considerations

• The Atmosphere (Gas)
  – Oxygen (O2), (CO₂ & H₂S)

• Water (The electrolyte)
  – Fresh/Condensed Water
  – Brine

pH & Water Wettability
What is included?

• **The production environment**
  – Pressure
    • Partial pressure CO2, H2S
  – Temperature
    • Phase behavior
      – Oil & water condensation
    • Corrosion acceleration & scales
    • Cracking tendencies
  – Oil:water ratio
    • Water or oil continuous
  – pH (Pourbaix)
  – Flow regime/velocity
    • Water separation
    • Erosive flow (solids)
    • Mass transfer rate of corrodents
Continuous Improvement Method
(Causes and Effect)

- Organic Acids
- H2S
- CO2
- Low pH
- Coatings & Linings
- CRA
- Materials Considerations
- Prod Rate
- Solids
- Water Wet
- Flow Regime
- Velocity
- Chemicals
- Operations/Workovers
- Acid Stim
- Lack to Treating
- Failure Analysis
- Communication
- Poor Design
- Lack to Treating
- Internal Corrosion

New Orleans AICHE Jan 12, 2010
Monitoring in Wellheads
Christmas Trees

Simple Weight Loss
Rod Coupons
Manufacturer Demonstrated that Previous Clamps & Clips Caused Crevice Corrosion
Limitations of Single Coat Inorganic Zinc

• Require greater steel surface cleanliness than other coatings (All coatings require near white metal blast)
• Must be applied by a skilled applicator using a constantly agitated pot to keep the heavy zinc particles suspended. (Can be trained in a few hours)
• Requires more inspection and application care (than when used as a primer) (One coat? Less man power)
• If applied too thick, may mud crack. Generally applied at less than 5 mils DFT, although some products can successfully be applied at greater thicknesses. (Not So, used over pitted steel and does not mud-crack)
Limitations of Single Coat Inorganic Zinc

• Problems may occur when topcoating with organic coatings. Small bubbles of air or solvent vapors escaping from the porous silicate film may create holidays. WB cure fast and have good performances without topcoating. **Best not to topcoat.**

• The zinc is attacked by acid - **Silicate holds up to lower and higher pH than and alkali older IOZ**

• **Often not recommended in continuous water immersion because of concern for their limited period of protection.** **NEXSTEEL SLIDE PLEASE**