Coatings and Corrosion in the Nuclear Industry

Presented by
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The Context

- The use of coatings to prevent corrosion has some very specific conditions attached, when applied to the nuclear industry.

- The two main considerations are that
  - The plant generally represents high value assets where no corrosion-generated failure is acceptable.
  - The environment is one where many conventional coatings or corrosion inhibitors are impractical.

- Accordingly, many systems are specified in terms of highly corrosion resistant materials, that do not need a coating.
The Environmental Context

- A number of challenging environments exist within the nuclear industry.

- These are associated with various stages in the nuclear fuel cycle.
The nuclear fuel cycle

The Nuclear Fuel Cycle

Fuel fabrication

Fuel rods

3-5% U-235

Depleted uranium

MOX

Plutonium

Reactor

Used fuel

Storage

Conversion to UF₆

Reprocessed uranium

Reprocessing

0.7% U-235

Wastes

U₃O₈

Vitrification

Mining

Disposal

Tailings
Environmental requirements – (1) Radiation

• One of the general requirements is that plant / components / materials have to operate in an environment where ionising radiation is present.
• Radiation will generally break up molecules, e.g. organics, making conventional coatings such as oil-based paint impracticable.
• Radiation will also decompose many other molecular species – e.g. water – to give hydrogen and oxygen, and they can interact with coatings.
Environmental requirements – (2) Chemicals

The fuel cycle introduces many demanding environment requirements, associated with chemicals.

• Fuel production uses fluorine gas to produce UF$_6$.
• Inside a nuclear reactor conditions the coolant chemistry may involve chemical additives (LWR) besides the physical conditions.
• Spent fuel handling / shipping containers – chemical dosing to control water chemistry.
• Reprocessing – highly acidic environments for UO$_2$ dissolution.
• Waste encapsulation – cement and high pH.
**Environmental requirements – (3) Physical**

The fuel cycle introduces many harsh environment requirements, associated with physical conditions.

- Inside a nuclear reactor conditions are extremely harsh – temperatures in the hundreds of °C, pressures in the many tens of bar, very high radiation fields.
- Plant may not be accessible for repair or maintenance, once it has “gone active”.
- Fuel production has strict QA controls and no foreign material (e.g. coating debris) would be permitted.
- Geological disposal – systems need to retain integrity for very long timescales.
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Roadmap for this presentation

• Basic principles & constraints. ✓
• Case examples where coatings have been used or considered in order to minimise corrosion in key items of plant in the industry.
  • These case examples will include:
    • Underground buried pipework at nuclear power stations.
    • Nuclear fuel cladding.
    • Spent fuel transport and storage containers.
    • Exposed / painted steel surfaces.

There could be many more, but time does not allow!
**Buried Nuclear Pipework - 1**

- Internationally, the problem of buried pipework at nuclear plants becoming corroded (and leaking!) has begun to attract significant attention.
- EPRI identified the issue in 2007 and work has been intensifying since then.
- NACE has a dedicated subject study team looking at this, and it has merited its own session at a major Corrosion conference.
- In the UK, relatively low priority has been given to this (as far as can be established). There may well be reasons associated with more corrosion resistant materials, compared with US plant.
In 2010 the “Beyond Nuclear” environmental campaign group publicised the following issues.

- Tritium releases from corrosion-generated leaks in underground pipework (in the USA) were claimed to be increasing.
- Eight particular incidents, at different plants in the USA, were identified.
- The pipework under a plant was described as a “spaghetti bowl” of assorted materials, diameters, lengths of pipe.
Buried Nuclear Pipework - 2

- Buried pipework as a wide topic, was addressed at the 2010 CED Event at Buxton. No nuclear aspect.
- Corrosion of pipework can be either a result of general corrosion, or localised corrosion. Opportunities exist for both types of mechanism.
- Buried nuclear pipework materials are (in the USA) often carbon steel, protected by an appropriate coating or using cathodic protection.
- In nuclear plant, pipe runs are often short and electrically grounded, making CP more complex to implement. More emphasis on materials & coating.
**Buried Nuclear Pipework - 3**

General corrosion can be caused by

(1) a protective coating that does not provide complete coverage of the pipe or other structure,

(2) a pipe or other structure exposed to the environment for too long without proper coating maintenance, or

(3) an attack from a corrosive environment which the protective coating was not designed to withstand.
Buried Nuclear Pipework - 4
Localised corrosion can be caused by
(1) Materials susceptible to pitting.
(2) Stress corrosion cracking.
(3) Hydrogen induced cracking.
(4) Erosion / corrosion & cavitation.
(5) Crevices where sleeves or similar do not provide a watertight cover.
(6) Welding of T-joints where heat affected zone is susceptible.
(7) Galvanic attack from dissimilar materials.
(8) Microbially induced corrosion – e.g. at optimum temperature along a line.

Image: EPRI
**Buried Nuclear Pipework - 5**

Many different forms of protective coating are commonly available for pipework – e.g.

- 2-layer polyethylene
- 3-layer polyethylene
- Fusion-bonded epoxy
- Adhesive Tape
- Heat shrink sleeves – for joints
- Polyurethane foam half-shells
- Foam injection
- Liquid epoxies

Image of heat-shrink sleeves:
NACE “Pipeline Mainline and Field Joint Coatings” Chapter 19, 2010
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*Buried Nuclear Pipework - 6*

Coatings technology on the outside of the pipework can only mitigate external corrosion! (Statement of the obvious, but a reminder that its not a silver bullet to fix all the problems).

That leaves a number of internal corrosion mechanisms still in play.

Hence the general requirement to also use appropriate materials. Getting the right combination of material, coatings approach, economics, design lifetime right is becoming more challenging. Plant lifetime / safestore extension issues.
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**Nuclear Fuel cladding - 1**
When a Light-Water Reactor (LWR) experiences a severe reactor accident, one of the possible consequences is that the fuel cladding, usually a zirconium alloy, interacts with high temperature steam to produce hydrogen.

Hydrogen can then explode, as seen at Fukushima, Chernobyl, Three Mile Island.

[Image: Fukushima Dai-ichi after explosion]
Photo credit Digital Globe / Wikipedia commons
Nuclear Fuel cladding - 2

The problem is the reaction

\[ \text{Zr} + 2 \text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2 \text{H}_2 \]

So the thought has been entertained – can we protect the surface of the fuel, to prevent this reaction from happening?

(NB in PWRs the control rods are also clad in (Zr) metal).
Nuclear Fuel cladding - 3

A number of previous efforts have involved sheathing the zirconium alloy with other metals.

A constraint is that other metals generally have much higher neutron capture cross-sections than Zr, and interfere with the neutron economy needed to sustain a criticality. This significantly limits the options.

Concept of sputtering the Zr surface with Hf ions.

Various alternative materials have been considered.

A current front-runner is the use of silicon carbide as an alternative cladding material.

MIT (among others) are working towards a practicable design.

MIT Conceptual design with UO2 pellet (centre) surrounded by a gas gap, dense SiC, SiC fibers infused with SiC, outermost dense SiC.

MIT News July 26 2013.
Spent fuel transport & storage - 1

Magnox reactors are now (all-but-one) shut down.

Spent fuel was* discharged to a pond, where it cooled until suitable for transport for reprocessing.

* (The one remaining Magnox reactor at Wylfa uses dry storage, not a pond)

Wylfa power station, North Wales
Photo credit NDA website
Spent fuel transport & storage - 2

For wet storage and transport, spent Magnox fuel elements are placed in a cube-shaped “skip”, made of painted carbon steel. The skip fits inside a cuboid transport flask.

Cuboid Magnox flask being lifted
Photo credit NDA website

Magnox fuel rod
Photo credit Science & Society Picture Gallery
Spent fuel transport & storage - 3

The painted skips have a finite usage time – the fuel is intended to be reprocessed, following which the skips can be cleaned and refurbished.

The paint is an epoxy formulation and quite resistant to radiation. Its role is to prevent contact between the steel and the Mg alloy fuel cladding.

Cutaway of analogous AGR cuboid, showing skip at the centre

Image credit Greenpeace website
Spent fuel transport & storage - 4

Before shipment the painted skips (containing fuel) are stored in ponds at the power station. After shipment the fuel is transferred to pond skips and stored at Sellafield. This procedure has been used since the 1960s. The paint formulation has changed a few times. In 2002 it was decided to take another look at the effect of radiation.

First Generation Magnox Storage Pond, Sellafield

Photo credit Sellafield Ltd website
Steel specimens were coated with the current formula paint, then subject to irradiation whilst underwater.

The leachate was chemically analysed.

It found negligible chloride or organics, but some unexpected sulphate.
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Spent fuel transport & storage - 6

And the moral of the story is: –

When it comes to radiation effects, learn to expect the unexpected!
Painted steel surfaces - 1

Most of the UK nuclear plant (both power stations and reprocessing) is located at coastal locations.

Corrosion in a near-marine environment is prevalent.

Surfaces are usually painted, but there are issues.

Sellafield, Cumbria
Photo credit Aztec Research website
Painted steel surfaces - 2

- In near-coastal locations, the role of salt aerosols is well recognised.

- There is growing recognition of the role of organic-derived material in the aerosol burden, as much as 50% by weight.

- They can also have a role in corrosion. And coatings need to resist their activity.
Painted steel surfaces - 3

- There are well known compilations of data for corrosion rates of bare mild steel (as a common structural / building material) in marine / industrial / urban / rural locations.

- This has classically been interpreted in terms of enhancement by salt deposits.

- Much of that data may need reassessment in light of the role of organics, both as MIC and the role of surface contaminants.
**Painted steel surfaces - 4**

The problem is exemplified in the instance of Iron Oxidising Bacteria (FeOB) as studied by McBeth et al. in field and laboratory experiments in nearshore environments.

Mariprofundus sp. strain GSB2 was grown on both metallic iron substrates and with Fe(II)(aq) nutrients. It was concluded that the distribution of such FeOB was far greater than previously thought.

Painted steel surfaces - 5

- One of background the problems is that structures are often assembled on-site (e.g. by welding) and painted after assembly.
- If care is not taken to protect the material before welding, this can mean that the bio-organism is underneath the paint, and can remain dormant until the paint degrades sufficiently to allow water to penetrate.

Image: Footage.shutterstock.com
Summary

- This talk has illustrated a few areas where coatings of various sorts have become important (and are currently still under development) in support of the nuclear industry.
- We have recognised the (sometimes unique) nature of the environment presented.
- The example areas have included
  - Buried nuclear pipework
  - Coatings for fuel rods
  - The effect of radiation on paint
  - Painted steel surfaces
- The message is: continue to be vigilant and this is still an area for development and improvement.
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