Sensors and Technologies for Monitoring Waste Package Corrosion in a Geologic Repository.

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Imagination at work.

Areas of Interest for NWTRB

i. What are the key parameters to monitor to confirm waste package performance in a geologic repository for high-level radioactive waste and spent nuclear fuel?

ii. What is the state of the art in sensors and technologies that can be used to monitor those key parameters?

iii. What are the technical challenges in applying those sensors and technologies to monitor waste package performance?

iv. What are the main areas for improvement in currently available sensors and technologies?

The US Nuclear Waste Geologic Repository Stakeholders.

Blue Ribbon Commission Recommendations

Congress

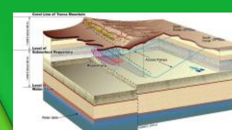
Reactor Owners

NEI

Courts

US Department of Energy - DOE

Geologic Repository Yucca Mountain



US Nuclear Regulatory Commission - NRC

US Nuclear Waste Technical Review Board - NWTRB

State of Nevada

EPA

Public Opinion

Courts

Nuclear Waste Fund ~ $40 billion

Plan for YMP

Performance Confirmation Starts at Licensing

1987
Yucca Mountain Designated as Repository Site

1998
Viability Assessment

2002
Site Recommendation

2008
License Application

2020
First Nuclear Waste Shipment Arrives on Site

2010? to ~2100?
Performance Confirmation

Performance Confirmation documents were initially written in 1997, and then revised numerous times up to the License Application submittal of 2008.

Evolution of Waste Package Design to Engineered Barriers.

Design times
300-1000 years

1970s
300 mm thick wall
Carbon Steel or Cast iron
Self shielded concept

~1982
20 mm thickwall
Carbon Steel or Cast iron
Paper bag concept – Thermal Barrier concept

Environment oxidizing – passivating materials desired.

Less emphasis on the mountain, more demands on the package.

1996 = 825
1997 = 625
1998 = C-22

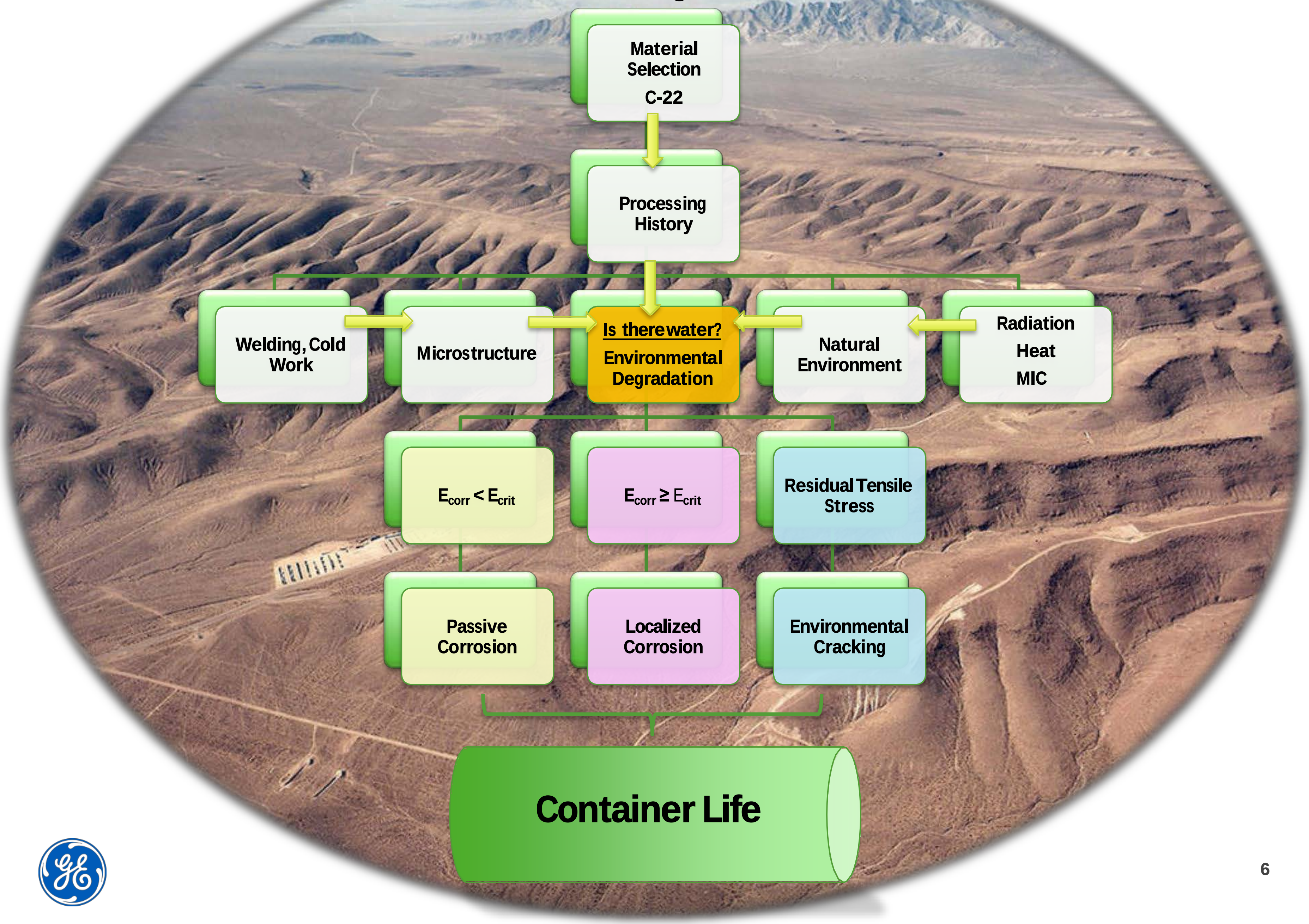
10,000 to
1,000,000 years

Ti Drip Shield

1991
Double walled container
Carbon Steel outside (100 mm)
Corrosion resistant alloy inside (20 mm)

1999
Double walled container
Alloy 22 outside (20 mm)
316L SS inside (127mm)

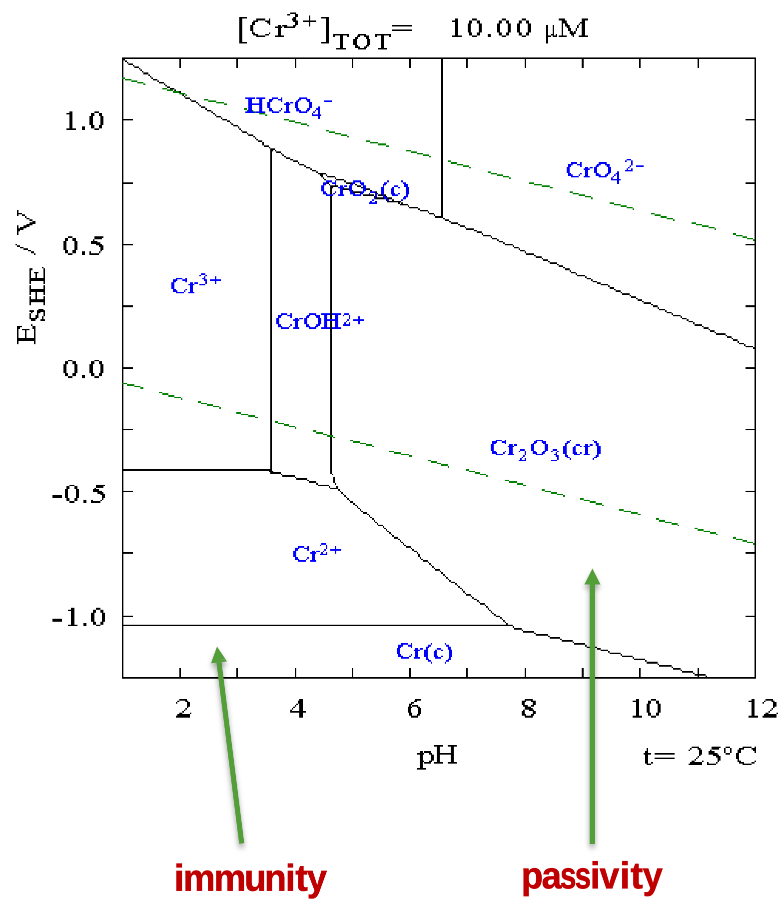
Model For Environmental Degradation of Waste Containers



Conditions for Corrosion or Environmental Degradation

1) **Corrosion is the degradation of materials by interaction with the environment.**
2) **For the temperature ranges of the engineered barriers, measurable corrosion may happen only if condensed water is present.**
3) No water, no corrosion.
4) **All the metals in the engineered barriers came from minerals.**
5) **Thermodynamically the metals want to go back to minerals.**
6) **Through engineering it is possible to slow down the return to minerals process.**
7) **Passivation means slow kinetics.**
8) **Example is stainless steels or Hastelloy C-22**

Pourbaix diagram for Cr



Long Term Corrosion Test Facility
(Lawrence Livermore National Laboratory)

Test facility tanks

Test specimen rack

Evaluation of General, Localized, Galvanic and Stress Corrosion
Over 20,000 specimens tested over 10 years.

14 Alloys Were Tested at LLNL for Corrosion

Label	Alloy	ASTM Standard	UNS
A	Incoloy 825	B424	N08825
B	Hastelloy G-3	B582	N06985
C	Hastelloy C-4	B575	N06455
D	Hastelloy C-22	B575	N06022
E	Titanium Grade 12	B265	R53400
F	Titanium Grade 16	B265	R52402
G	Monel 400	B127	N04400
H	CDA 715 (70Cu-30Ni)	B171	C71500
I	Low Alloy Steel Grade 22	A387	K21590
J	Carbon Steel Grade 55	A516	K01800
K	Cast Steel Grade 70-40	A27	J02501
L	Inconel 625	B443	N06625
M	Inconel 686	B575	N06686
N	Titanium Grade 7	B265	R52400

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Sensors and Sensing

Package/Drift Monitoring in Performance Confirmation.

1) Once the license is granted by NRC, it is understood that a Performance Confirmation period will start.
2) The PC period may last 100 years or more.
3) Monitoring the condition of waste packages (or engineered barriers) is the key component of PC.
4) Key variables to monitor may include
    a) Temperature
    b) Relative humidity
    c) Condensation, electrolyte conductivity, ionic species present
    d) Radioactivity, identity of radionuclides
    e) Changes in the chemistry of the atmosphere
    f) Accumulation of solid chemical species, microbial activity
    g) Package surface stresses

Sensors and Sensing

1) There was a surge in the sensors development race, mainly since 9/11, at first driven by Homeland Security for detection of substances.
2) Sensors currently control self driven vehicles in the US. Therefore, using sensors to monitor environmental degradation of static metallic packages in Yucca Mountain should be achievable.

3) Sensors should be developed for each specific application.

4) In the case of Yucca Mountain, the monitored changes may be extremely small while time periods are extraordinarily long.
5) Other specific YM characteristics may include the presence of an irradiation field and changing temperatures.
6) Many of the Yucca Mountain sensors may need to be static or mounted on the packages. Others can travel the tunnels on fixed rails or even attached to drones.

The Anatomy of Sensors and Sensing

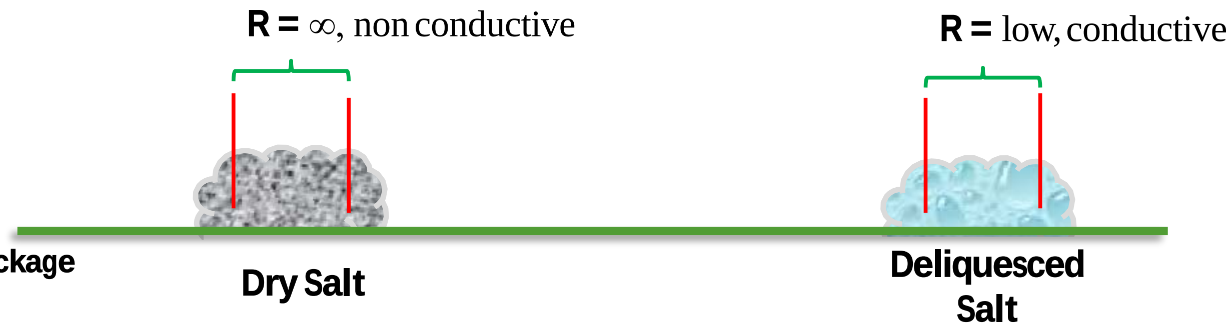
1) **A sensor is an instrument for detecting a quantity or quality, for example temperature or motion, and returning an electrical output. How does a sensor** work? Generally via a ‘sensing’ device and a transducer.
2) **A good sensor would obey certain rules (selectivity and stability are important)**
   - it is sensitive to the measured property
   - it is insensitive to any other property likely to be encountered, and
   - it does not influence the measured property.
3) **Sensors should be developed for the specific application, in the case of Yucca Mountain, changes may be extremely small but the time periods are long.**
4) **Newer electronic noses include Multivariable Sensors such as MPN (Monolayer Protected Nanoparticles) – may provide several independent responses.**
   - ✓ **Conjugated or conductive polymers – through change in density or carrier mobility.**
   - ✓ **Metal Oxides – using principles of physisorption or chemisorption.**
   - ✓ **Carbon allotropes – such as graphene can act as main component or as additives.**

Industries with Prevalent Sensing

1) "Long" term sensing is already used in some industries but none to the extent of **Yucca Mountain.**
   - ✓ **For civil engineering (bridges) sensors may last 100 years**
   - ✓ **For Oil & Gas they are designed to last 20 years**
   - ✓ **For appliances they need only 10 years**
2) **Sensors resistant to radiation are used in industries such as Healthcare (medical) and Agricultural (food) through the need of sterilization.**
3) Corrosion sensors may measure "direct" changes in metal strips, such as resistance and impedance. "Indirect" measurements can be the detection of Al_2O_3 in aircrafts, or pH changes. This means "soft sensing" or "inferential sensing."
4) **Healthcare, Aviation, Transportation, Oil and Gas, are GE industries which use sensors on a daily basis.**
5) **Homeland Security.**

One example of YM sensing

1) Maximum temperature of the external skin of the waste packages may be ~200°C.
2) No appreciable corrosion will occur until water condenses on the surface of the container. Water or electrolyte are needed to separate anodic and cathodic sites on the surface of the container for the corrosion to proceed.
3) At what temperature the water may condensate on the surface is a function of the relative humidity, the dew point.
4) Some salts such as mixtures of nitrates could absorb water, deliquesce, at lower relative humidity than the dew point.



No corrosion

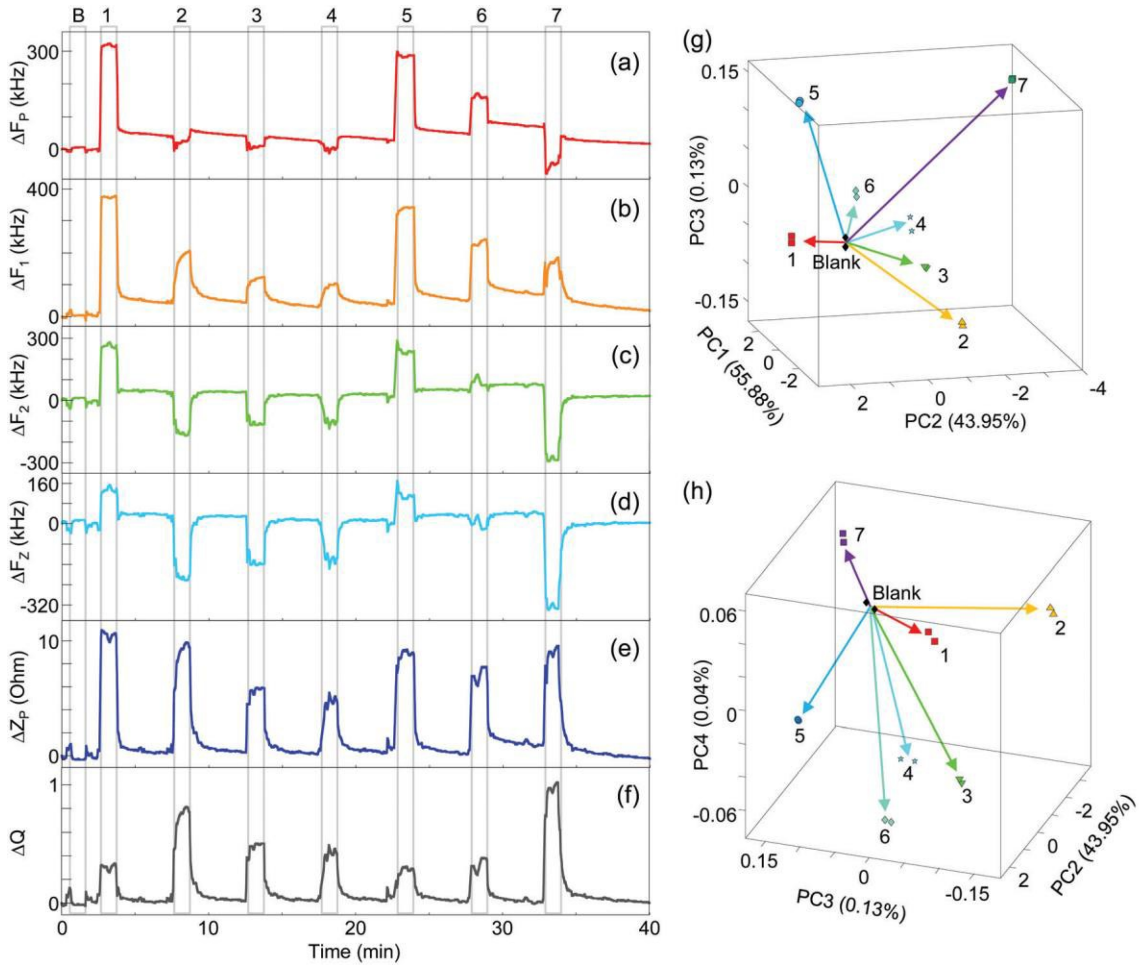
Corrosion may be possible

Challenges in Sensors and Sensing

1) The growing number of disciplines involved in building innovative sensor systems is truly impressive. Materials science, nanotechnology, and biological chemistry are foundations for new sensors.
2) The main limitations of sensors are
   - ✓ Lack of sensitivity
   - ✓ Drift changes
3) Despite the rapid recent development in sensors and sensing, their long term reliability is still unknown.
4) Some transducers under development may increase the sensitivity of sensors from 6 to 9 orders of magnitude.
5) Common current sensors are built with discrete amount of materials, using commonly nanotechnology. Therefore their long term stability needs to be tested and confirmed.

Example of Modern Sensing

Reference: Radislav A. Potyrailo, GE Research, Chem. Soc. Rev., 2017, 46, 5311



Discrimination of complex aromas from 7 (seven) teas in jars with 40% RH using a multivariable resonant impedance sensor with 1-mercapto-(triethylene glycol) methyl ether-capped gold nanoparticles.

(a–f) Diversity of Fp, F1, F2, FZ, Zp, and Q responses of the sensor. Scores plots of the developed Principal Component Analysis (PCA) model (g) PC1 vs. PC2 vs. PC3 and (h) PC2 vs. PC3 vs. PC4.

Labels: (B) Blank ambient laboratory air, (1) Robert Roberts Blackcurrant Tea, (2) Dilmah Moroccan Mint Green Tea, (3) Bigelow Green Tea With Lemon, (4) Dilmah Pure Camomile Flowers Tea, (5) Bewley's Pure Rooibos Tea, (6) Numi Organic Jasmine Green Tea, and (7) Dilmah Earl Grey Tea.

Recommendations Sensors & Sensing

1) There is a bright future for sensors.
2) Using Nuclear Waste Funds, DOE should engage the private sector to develop unique sensing capabilities for the specific YMP application.
3) It is important not to rely solely in sensors (indirect detection), but also to use coupons of several alloys (with a range of corrosion resistance) that can be extracted at intervals of decades and assess changes in the actual coupons.
   - ✓ Flat Coupons, creviced coupons
   - ✓ Welded and non-welded coupons, as-welded and surface treated or HT
   - ✓ Stressed specimens for EAC
4) Even though the Performance Confirmation period of 100 years may seem long, it represents only 0.01% of the expected life of the containers.

Recommendations on Coupon Testing

1) **Several materials with increasing degree of corrosion resistance should be selected to make coupons. This will increase the confidence in the data**
2) **For example,**

For Container Performance	For Drip Shield Performance
Carbon Steel, e.g. A516	Ti Gr 2
2.25Cr + 1Mo steel, F22	Ti + 6V + 4Al
13Cr steel	Ti Gr 7
Type 316 SS	
Inconel 625	
Hastelloy C-22	

3) **Remove coupons at 10, 20, 40, 80, and 160 years for studies and analyses.**
4) **Correlate changes observed in the coupons with changes in drift conditions.**

Monitoring in Dry Cask Storage Systems - DCSS

Reference: X. He et al. Available Methods for Functional Monitoring of Dry Cask Storage Systems, November 2014 Report from Center for Nuclear Waste Regulatory Analysis, NRC.

1) The U.S. Nuclear Regulatory Commission (NRC) has licensed DCSSs, in addition to pools, to be used for storage of spent nuclear fuel (SNF).
2) DCSSs were first licensed in the mid-1980s, which were intended to provide additional SNF storage capacity and allow operating plants to maintain capacity in the spent fuel pools.
3) These independent spent fuel storage installations (ISFSI) with DCSSs were initially licensed for up to 20 years, but currently due to the absence of a permanent repository, ISFSIs have applied for and received license renewals for up to an additional 40 years, and may eventually require periods beyond 60 years.
4) Monitoring methods in DCSSs include temperature, relative humidity, chloride deposition, and microbial activity.

What are Other Countries doing on Monitoring?

Sweden (SKB) submitted their License Application for the Forsmark geologic repository in 2011.

For the containers deposited first, there will be systems for measuring different parameters (pressure, temperature, moisture content, radiation level, etc.) in deposition holes and deposition tunnels.

Shafts, ramp, access tunnels and maintenance areas in the deep repository will naturally be kept open and accessible throughout the operating period.

When the time comes to the closing of the repository the initially deposited canisters would have been observed for several decades. [Ref. Monica Hammarström and Fred Karlsson, The planned Swedish Repository for spent fuel, 1998].

France (Andra), is planning to monitor its La Manche facility (1969-1994) of low and intermediate waste for 300 years.

Andra has an underground research laboratory (URL) in Haute-Marne since 2007, which is 490 m deep in 160 million year old clay. Monitoring is currently on going.

If licensed for permanent storage, the Andra site will be called Cigéo (Centre industriel de stockage géologique). Construction may start in 2022.

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Summary and Conclusions

Summary and Conclusions

1) Performance Confirmation is a period starting from licensing of the YM repository. It may last 100 years.
2) During the PC period, the engineered barriers (including the containers) will be monitored for performance.
3) Monitoring may include direct (coupons) or indirect (sensors) evaluations.
4) Typical monitored variables include temperature, relative humidity, type of solids deposited (salts), radioactivity, microbial activity.
5) The development of sensors is currently booming mainly due to advances in nanomaterials and functional compounds.
6) Sensors should be specifically developed for Yucca Mountain applications, for small changes of monitored variables over extended periods.

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Additional Slides

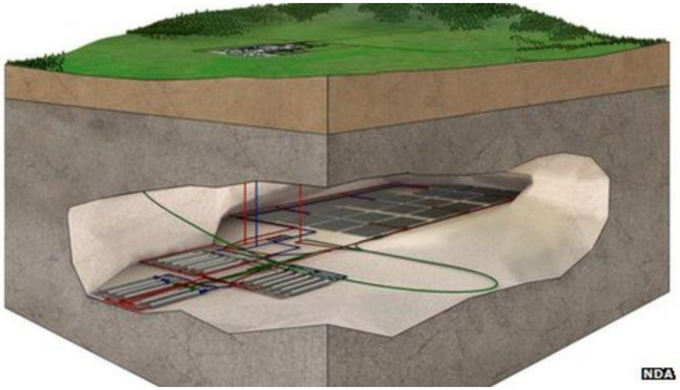
Main Modes of Corrosion in Nuclear Systems

Power Generation

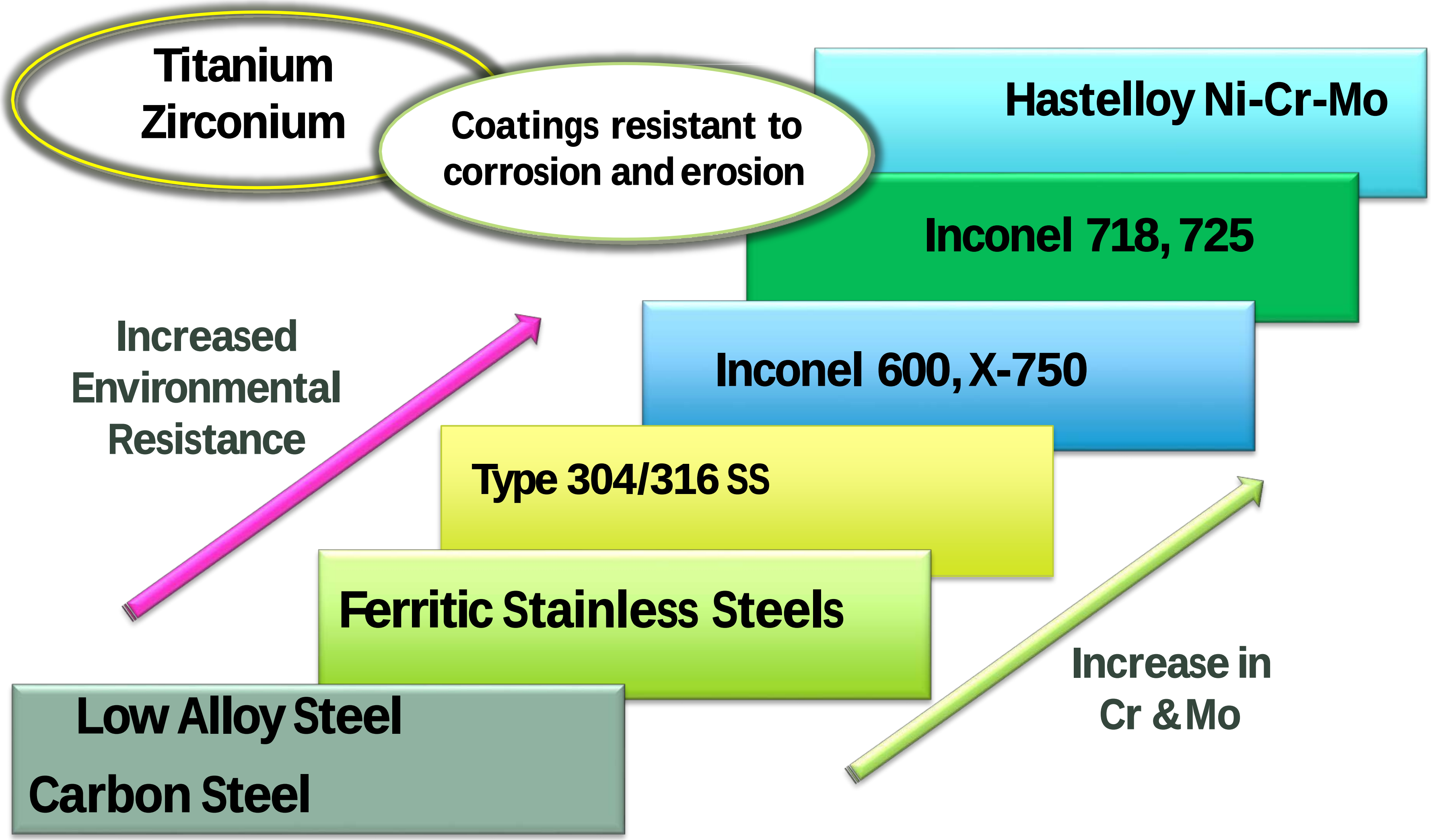
1. Stress Corrosion Cracking
2. General Corrosion
3. Localized Corrosion

Waste Disposition

1. Localized Corrosion
2. Stress Corrosion Cracking
3. General Corrosion



General Ranking of Materials by Corrosion Resistance



Pitting Resistance Equivalent (PRE) - Localized Corrosion

1) It was empirically developed for stainless steels in chloride media
2) Later applied to passive nickel and cobalt alloys
3) Alloys with PRE higher than 40 are considered resistant to localized corrosion

$$PRE = \%Cr + 3.3(\%Mo + 0.5\%W)$$

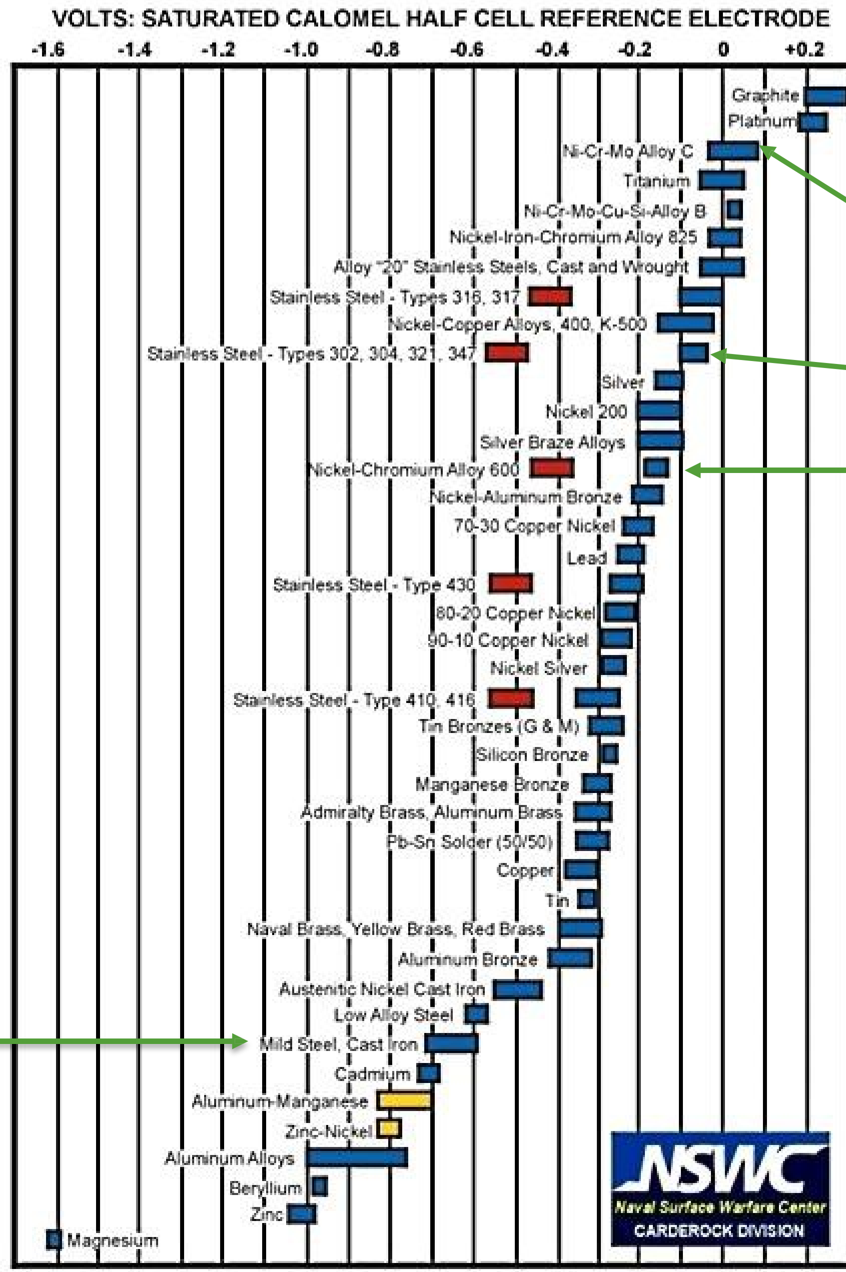
Alloy	PRE
304SS	18
316SS	25
X-750	15
Inconel 600	16
Inconel 718	28
Inconel 725	47
Inconel 625	51
Hastelloy C-22	70

The higher PRE the higher the resistance to localized corrosion

Galvanic Series for Corrosion Behavior

ASTM G82 – 98(2014)

Standard Guide for Development and Use of a Galvanic Series for Predicting Galvanic Corrosion Performance



More Noble

Higher Corrosion Resistance

e.g. C-22

304SS

Inconel 600

Steel

Less Noble

Lower Corrosion Resistance