Corrosion of Titanium Grades 7 and 29 Under Dripping of Seepage Water

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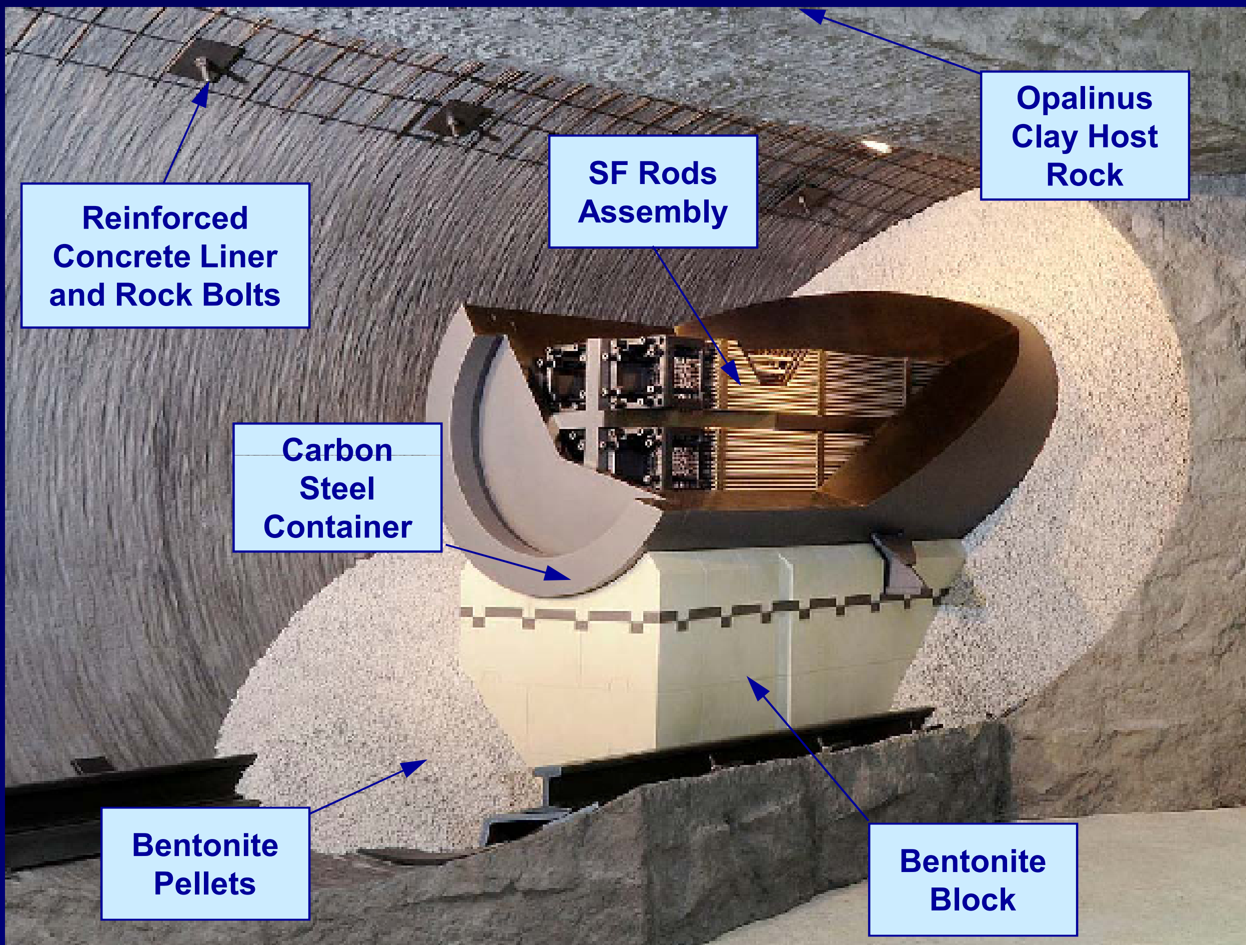
Outline

- Background
- Objective
- Experimental methods
- Results and discussion
- Summary

Background: Engineered Barrier System for Geologic Waste Disposal



Swiss Engineered Barrier System Concept

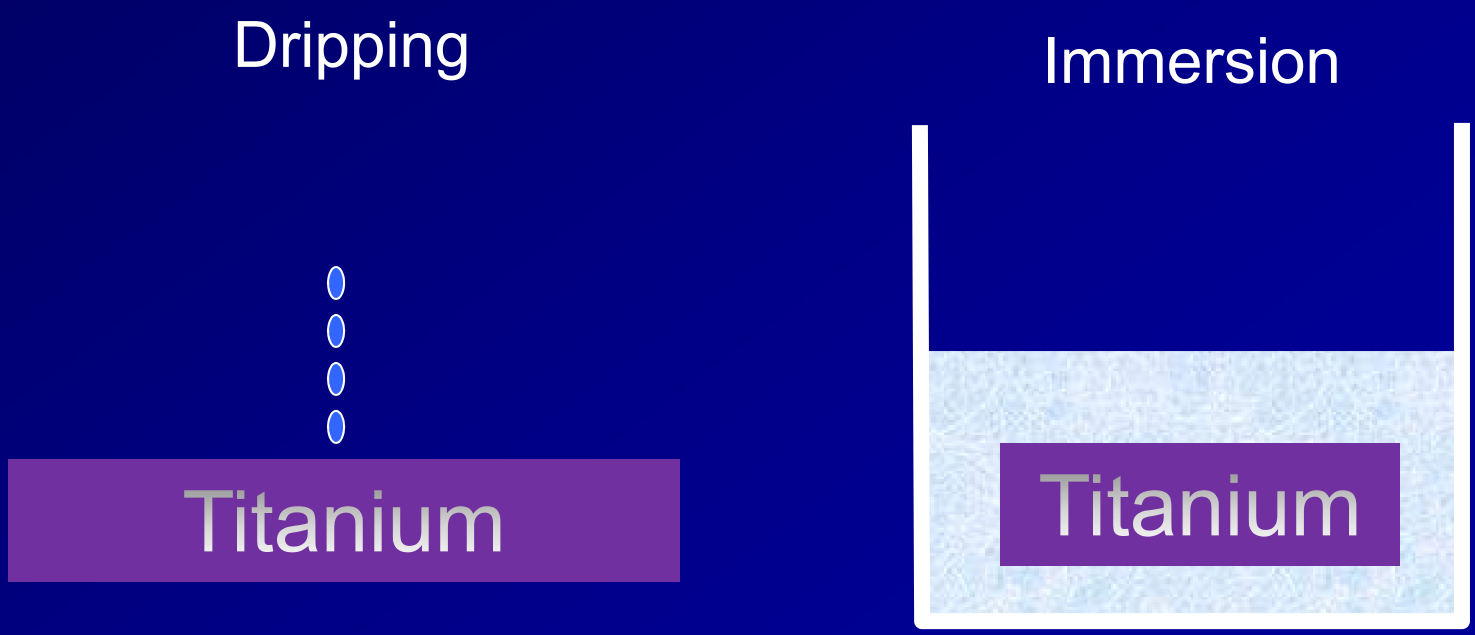
- In geologic waste disposal systems, an engineered barrier system is intended to work with the natural geological system to protect the environment and human health

Background: Titanium in Geologic Waste Disposal

- Titanium is one of the proposed corrosion-resistant engineered barrier materials in several countries
  - Early studies for the waste disposal program in Canada (Shoesmith, et al., 1997)
  - Rock-salt media in Germany (Smailos and Köster, 1987)
  - Transuranic waste disposal in deep underground in Japan (Nakayama, et al., 2008)
  - Drip shield material in the proposed Yucca Mountain repository in U.S. (Sandia National Laboratories, 2008)
  - Candidate materials in several other countries: Belgium, Sweden, UK, Japan (Kursten, et al., 2004)

Objective

- Dripping tests were conducted to understand how the results may differ from tests conducted in the literature, which were performed under immersion conditions

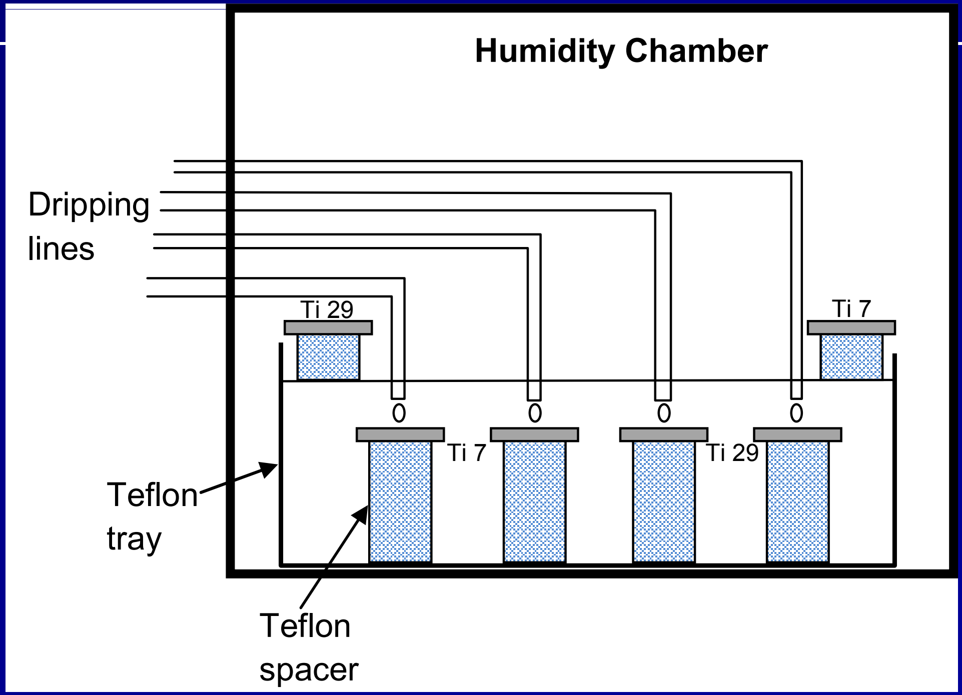


Titanium Alloys Dripping Tests

- Materials: Ti Grade 7 and Grade 29 with dimensions 4 cm × 4 cm × 0.6 cm

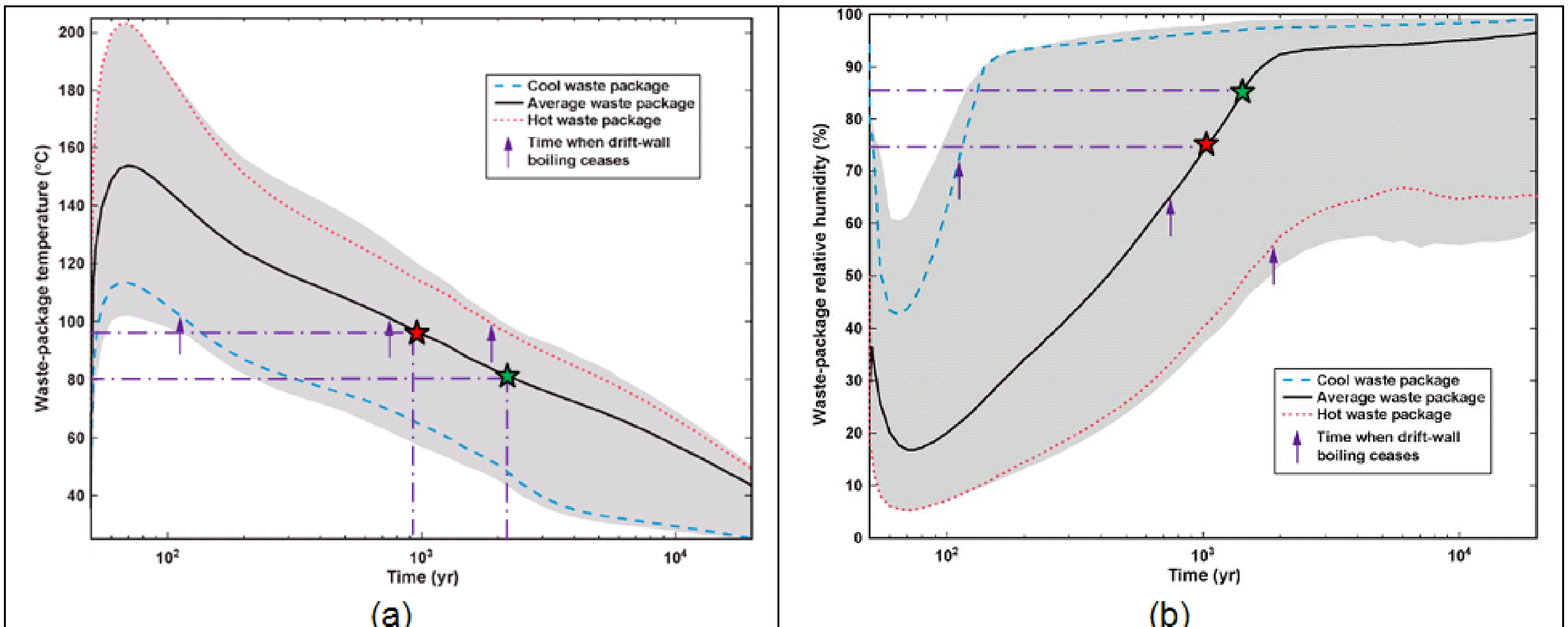
Chemical Composition of Titanium Grades 7 and 29 (in Weight Percent)										
Material	Ti*	Pd*	Fe*	C*	N*	O*	H*	Al*	V*	Ru*
Titanium Grade 7 Heat CN2775	Bal.	0.16	0.08	0.01	0.01	0.13	0.001	NA	NA	NA
Titanium Grade 29 Heat 00192DB	Bal.	NA	0.19	0.04	0.006	0.109	0.0021	5.62	4.16	0.10
*Ti—titanium, Pd—palladium, Fe—iron, C—carbon, N—nitrogen, O—oxygen, H—hydrogen, Al—aluminum, V—vanadium, Ru—ruthenium										

- Tests conducted in humidity chamber with controlled temperature and relative humidity



Dripping Conditions

	Temperature and Relative Humidity (RH)	Water Dripping Rate	Test Duration
1st Batch	80 °C, 85% RH	80 mL/day	181 Days
2nd Batch	95 °C, 75% RH	65 mL/day	64 Days

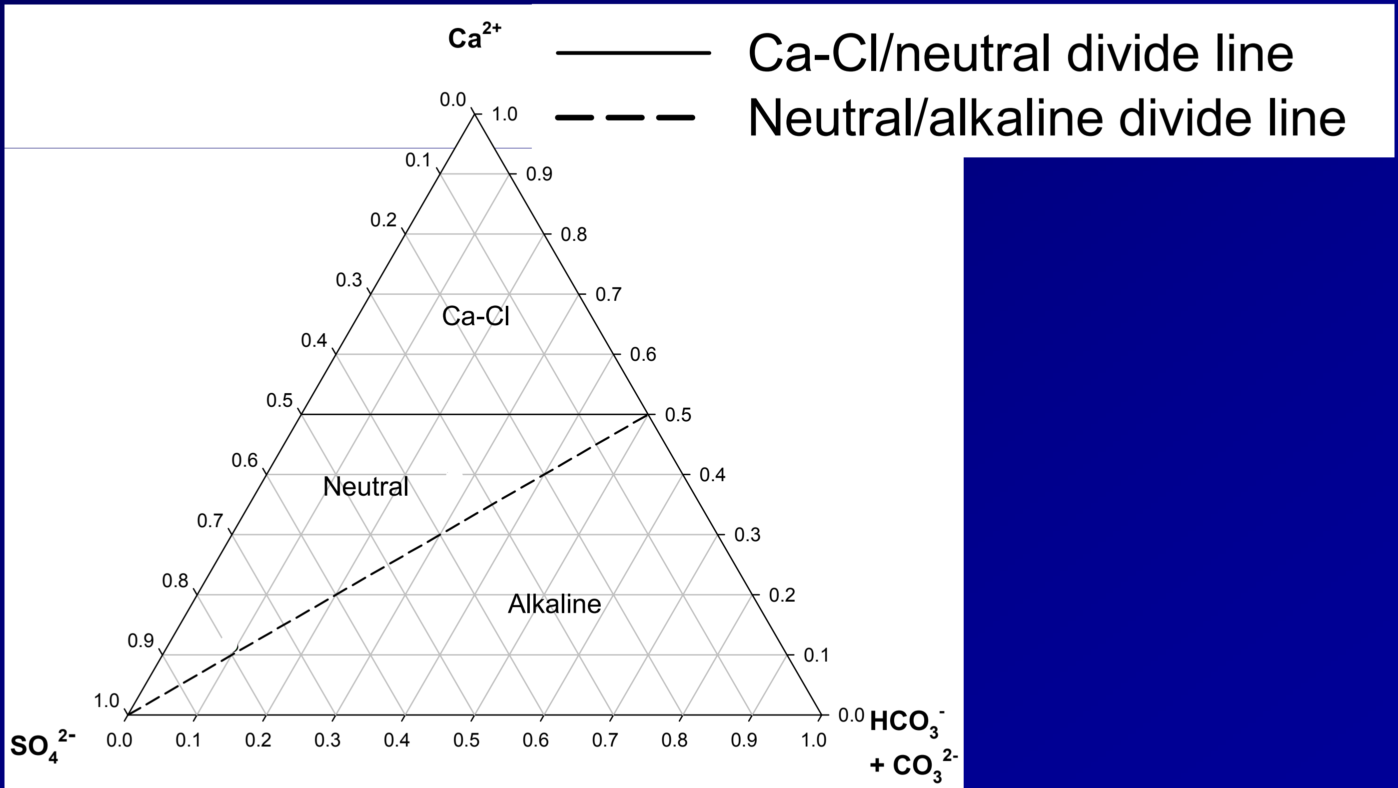


Range of (a) Waste Package Temperature and (b) Relative Humidity Versus Time
Note: The stars indicate the test conditions selected for the completed tests

(Sandia National Laboratories, 2008)

Dripping Water — Simulated Neutral Type Water

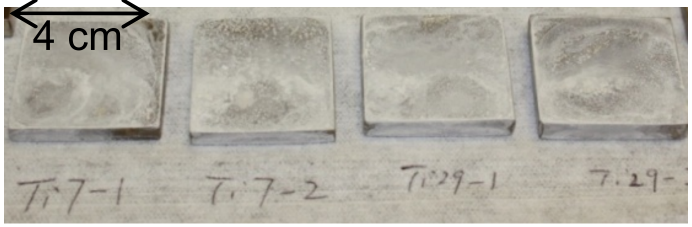
Chemical Composition of Simulated Seepage Water (Neutral Type)									
Ion	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	NO_3^-	HCO_3^-	CO_3^{2-}
mol/L (M)	1.5×10^{-2}	1.7×10^{-4}	4.9×10^{-4}	9.9×10^{-4}	7.7×10^{-4}	7.0×10^{-3}	1.5×10^{-3}	1.7×10^{-3}	1.7×10^{-5}



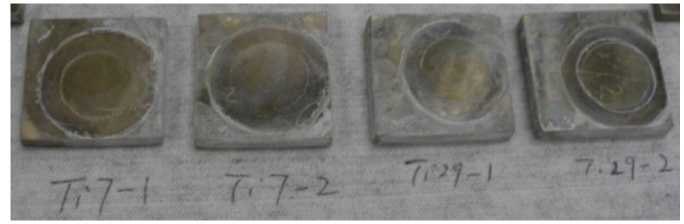
Posttest Samples of 1st Batch Test

Specimens Subject to Dripping

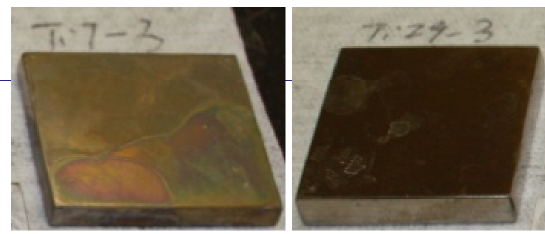
Front Side



Back Side



Reference Specimens Without Dripping

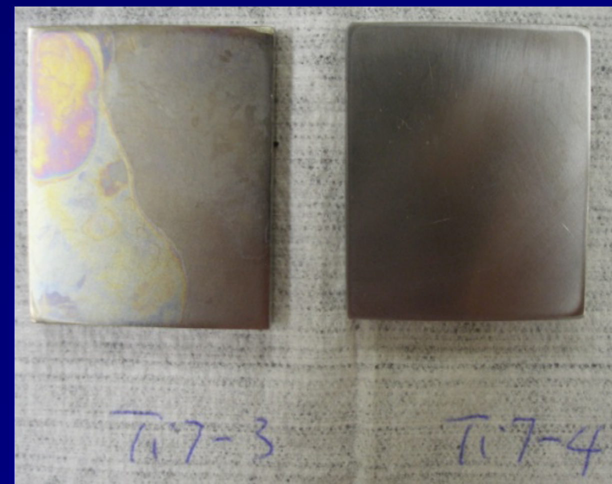


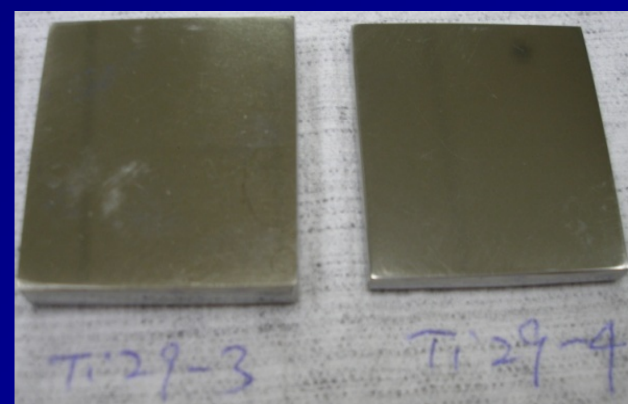
- Dripping side covered with a layer of tightly adhered white deposits
- Chemical analysis showed that white deposits consist of calcium, carbon, oxygen, silicon, sulfur, aluminum, and magnesium

Posttest Chemical Cleaning for Weight Loss

- HCl solution cleaning
  - Clean in 1.8 M HCl for 2 minutes
  - During each cleaning, one new coupon not included in corrosion test, but with the same surface finish as the test specimen, was cleaned as a control specimen along with the corroded specimen
  - After each cleaning, the specimen was ultrasonically cleaned in deionized water, then dried and weighed
  - Cleaned three times

Optical Photos After 1^{st} HCl Solution Cleaning



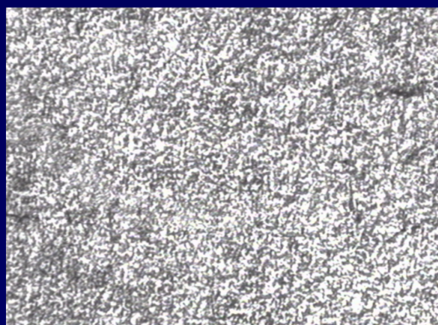


Note: The dimensions of the specimens are about 4 cm × 4 cm × 0.6 cm

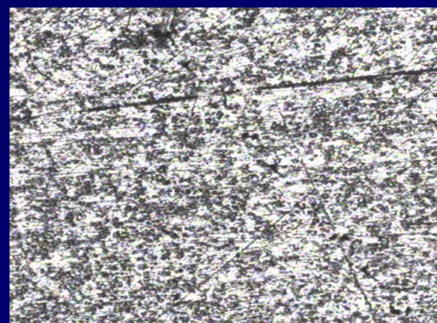
- White deposits dissolved, but thick oxide still remained
- Weight analysis showed weight gain

Optical Photos under Higher Magnification of 3rd HCl Cleaned Specimens

Ti7-1 front side

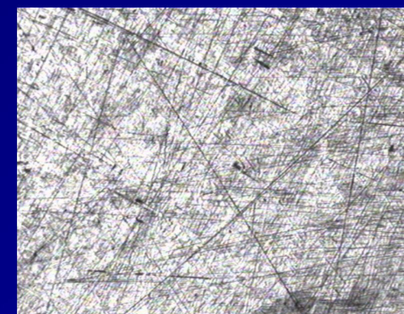


Ti7-1 back side

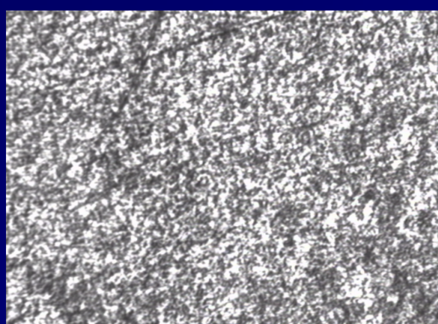


Ti29-1 front side

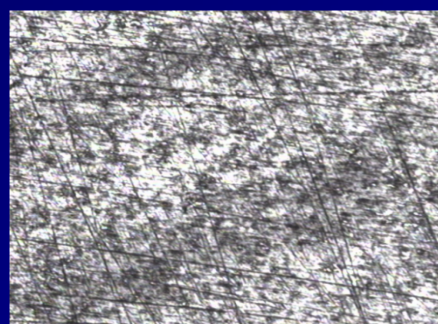
Ti29-1 back side



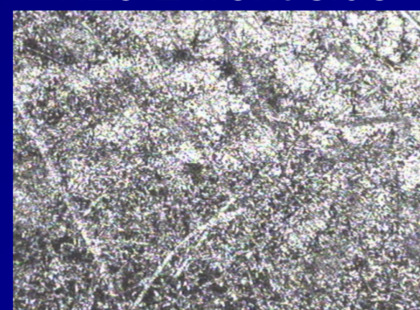
Ti7-2 front side



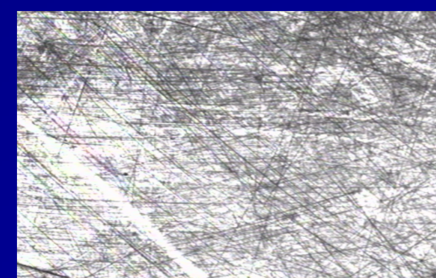
Ti7-2 back side



Ti29-2 front side



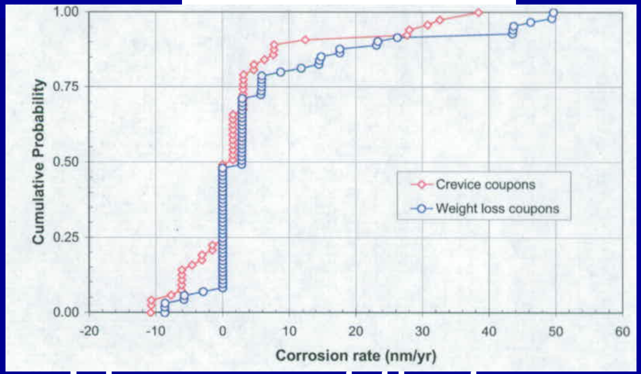
Ti29-2 back side



- More general corrosion at the front side subjected to dripping as evidenced by a smoother surface, compared to more evident polishing scratches at the back side

General Corrosion Rates at 80 °C and 85% Relative Humidity

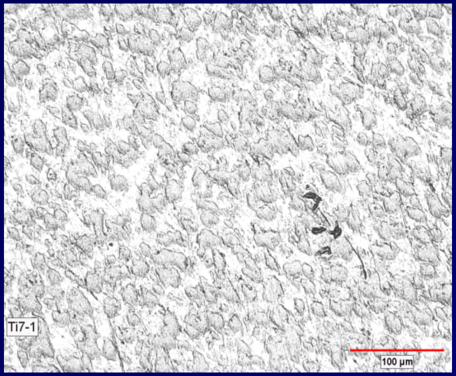
Sample Identification	Ti 7-1	Ti 7-2	Ti 7-3	Ti 29-1	Ti 29-2	Ti 29-3
	Subject to Dripping		Without Dripping	Subject to Dripping		Without Dripping
Initial weight, g	43.85001	42.33159	43.11402	52.63078	53.48684	53.57979
Weight loss, g	0.00038	0.00027	0.00067	0.00023	0.00035	0.00016
Corrosion rate, nm/yr	49.5	35.9	69.9	28.7	43.7	15.9
	Average: 43±10			Average: 36±11		



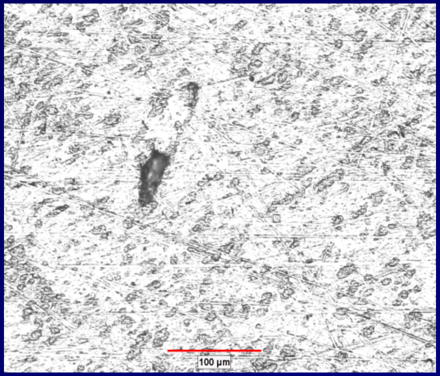
- General corrosion rates under dripping are close to upper bound of literature data under immersion conditions (Sandia National Laboratories, 2007)
- Higher corrosion rates without dripping could suggest that dry oxidation without deposits from dripping water covering the surface could lead to higher corrosion rates

Some Local Features Observed on the Surface

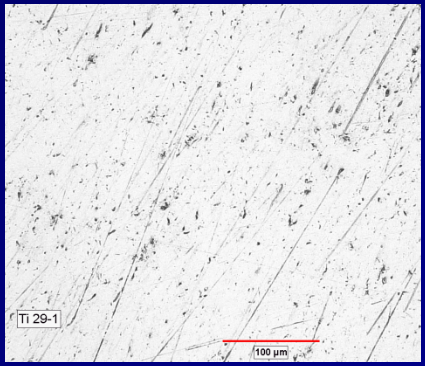
Ti7-1 front side



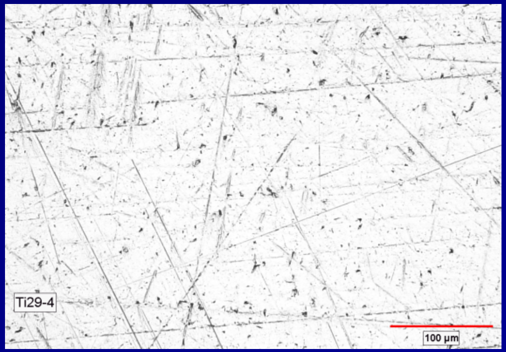
Ti7-4 control specimen



Ti29-1 front side



Ti29-4 control specimen

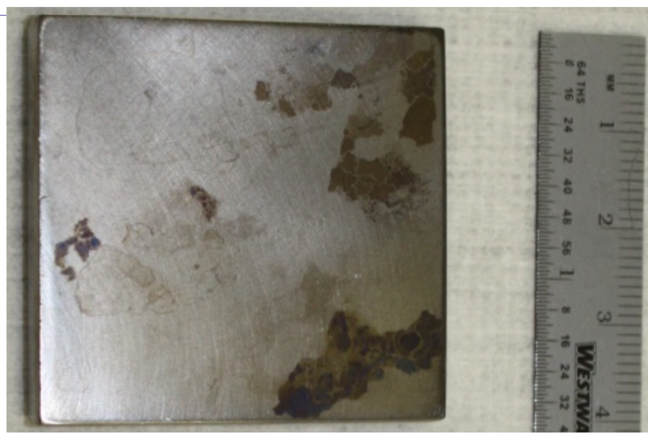


- Both the tested and control specimens showed some localized features protruding on the surface, and they persisted through the cleaning process.
- These features are not pits or any other localized corrosion form generated from the dripping process. They are features of the material from the manufacturing process or from the surface preparation process.

Second Batch of Posttest (a) Titanium Grade 7 and (b) Titanium Grade 29 Specimens at Temperature of 95 °C [203 °F] and Relative Humidity of 75 Percent

Subject to Dripping

Subject to Dripping



Without Dripping

Without Dripping

(a) Titanium Grade 7

(b) Titanium Grade 29

General Corrosion Rates of 2nd Batch of Samples at 90 °C and 75% Relative Humidity

Samples	Titanium Grade 7				Titanium Grade 29			
	Subject to Dripping			Without Dripping	Subject to Dripping			Without Dripping
Initial weight, g	42.97176	42.36883	42.63832	42.62994	53.31863	33.63283	34.32682	34.14560
Weight loss, g	0.00101	0.00036	0.00091	0.00162	0.00148	0.00086	0.00069	0.00249
Corrosion rate, nm/yr	372	133	336	473	521	333	267	755

Average: 280±130

Average: 370±130

- Corrosion rates were higher than what was measured from the first batch of tests at 80 °C and 85% relative humidity
- Higher corrosion rates without dripping could suggest that dry oxidation without deposits from dripping water covering the surface could lead to higher corrosion rates

Summary

- The first batch of tests at 80 °C and 85% relative humidity for 181 days showed that
  - The corrosion rates of the specimens subjected to dripping ranged from 29–50 nm/yr, close to the upper bound of that reported in the literature under immersion condition
  - No statistically significant difference in corrosion rate and no differences in corrosion features observed between Titanium Grades 7 and 29
  - The front side, which was subjected to direct dripping, corroded more than the back side, which was not subjected to direct dripping

Summary (continued)

- The second batch of tests at 95 °C and 75% relative humidity for 64 days showed that the corrosion rates for Titanium Grades 7 and 29 under dripping were 130–370 nm/yr and 270–520 nm/yr, respectively
- No localized corrosion was observed on either material from the two batches of tests

References

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