Hydrogen Embrittlement In Titanium Steam Surface Condenser Tubing

Truths, Myths & Misnomers

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ABSTRACT

With more than 600 million feet of Grade 2 titanium steam surface condenser tubing in service around the world operating without a single reported corrosion event since 1972, few if any competing materials can make such a dramatic claim. However, without proper design, operation and maintenance of the cathodic system envelope, embrittlement or hydriding of titanium surface condenser tubing can occur when solubility limits of nascent hydrogen are exceeded. The results of such an excursion can, in the case of titanium and other materials, induce the formation of brittle hydrides. This corrosion event can ultimately lead to a loss of structural integrity of the material.

Additional contributing factors may include elevated temperature, pH extremes and other parameter anomalies. Since the typical powerplant steam surface condenser tube/tubesheet interface is continually passivated by circulating water, (CIR$H_2$0) and the operating temperatures remain relatively low, the solubility limit of hydrogen is rarely threatened. Indeed, the mere existence of hydrogen embrittlement in a surface condenser environment has been infrequent reportedly occurring only several times over the past 40+ years of powerplant condenser tube service. Conversely, industries such as the CPI (chemical process industry), which can expose the heat exchanger to elevated temperatures, pH extremes and high levels of hydrogen charging without the benefit of passivation have reported hydrogen embrittlement damage.

Notwithstanding the infrequency of this form of corrosion in powerplant condenser service, recently identified activity has surfaced that warrants further investigation of this phenomenon. This paper will identify and research several case studies associated with

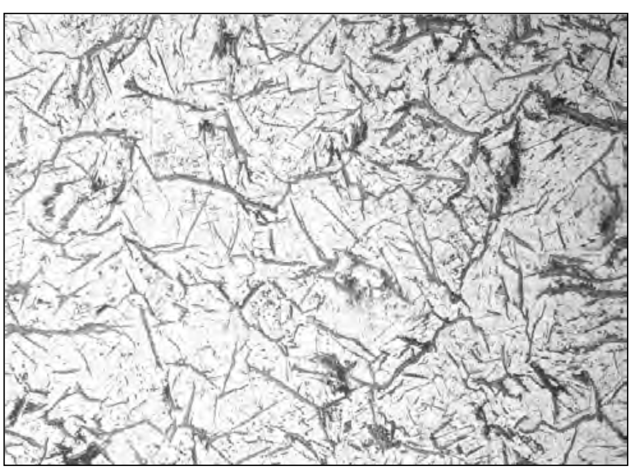
hydrogen embrittlement. An in-depth investigation of each will provide a practical benchmark for future lessons learned operating experience. Since there appears to be a common denominator to most if not all of the reported hydrogen damage, the paper will attempt to clear the air in terms of apparent confusion surrounding merely the innocuous hydrogen charging of certain materials vs. actual embrittlement damage.

Key Words: *hydriding, titanium tubing, powerplant surface condenser, impressed current systems (I-C), saturated calomel electrode, (SCE), silver/silver-chloride electrode (Ag/AgCl), cathodic protection systems (CP), sustained load cracking.*

INTRODUCTION and BACKGROUND

The phenomenon of hydrogen absorption or charging can occur in many materials but is typically more common to aluminum, carbon steel, titanium and ferritic stainless steels. The yellow metals and austenitic stainless series appear less susceptible. Much of both purported and actual corrosion or embrittlement damage (Figure 1) has been attributed to improper design and/or miss-operation of the cathodic protection (CP) or impressed current (IC) protective systems. These systems have been historically problematic appearing to be the singular and leading cause of embrittlement damage.

Figure 1
CP Titanium Hydride Needle



An inability to properly control SCE voltage, use of improper sacrificial materials and challenges in responding to changing water/salinity conditions have been directly connected to embrittlement damage. It should also be noted however that if the improper operating anomalies are discovered early on, corrective action can and has, successfully mitigated damage. As we shall see during an examination of Case Study 1, historical precedence exists demonstrating this action has not only halted the corrosion but allowed the equipment to successfully operate to this day.

Hydriding 101

The study of hydriding or hydrogen embrittlement associated with power plant surface condensers is a study of the galvanic environment that exists within the surface condenser steam cycle. However, the term hydriding can be a misnomer. More correctly, and given the enormous difference between hydrogen charging or absorption (which is more common) and hydrogen embrittlement where actual cracking and/or fracture can occur, care must be exercised when callously assigning hydriding as a “catch all term” for this activity in the condenser.

Hydrogen absorption is a common occurrence and exists naturally within many condenser circuits. Merely the discovery of classic hydride needle formation within the titanium matrix is not an indictment of the integrity of the material. However, hydrogen embrittlement can and has occurred with damaging results in the chemical process industry (CPI) where heat exchangers are routinely exposed to elevated temperatures, pH extremes and high levels of hydrogen charging without the benefit of passivation.

As expected, much of the hydrogen absorption occurs in high conductivity sea or brackish water conditions. In these environments, hydrogen can be produced at the cathode by galvanic coupling to a dissimilar metal such as zinc or aluminum which are very active (low) in the galvanic series. Coupling to carbon steel or other metals higher in the galvanic series generally does not generate hydrogen in neutral solutions even though corrosion is progressing on the dissimilar metal. It is speculated that the presence of hydrogen sulfide, which acts as a recombination poison, apparently increases the absorption of hydrogen on titanium and stainless steel materials.

With the powerplant surface condenser tube/tubesheet interface continually passivated in circulating water (CIRH20), the solubility limit of hydrogen is rarely threatened. Laboratory work [7, 8] has demonstrated that the presence of as little as 2% moisture in hydrogen gas effectively passivates titanium so that absorption does not take place. (Table 1)

Table 1
Effect of Moisture Absorption Of Hydrogen

%H_2O	Hydrogen Pickup (ppm)
0	4.480
0.5	51,000
1.0	700
2.0	7
3.3	10
5.3	17
10.2	11
22.5	0
37.5	0
56.2	0
600ºF (316ºC @ 800 psi – 96 Hours Exposure	

As noted earlier, the mere existence of hydrogen embrittlement in a surface condenser environment is exceedingly rare. Furthermore, the surface oxide film on titanium acts as a highly effective and tenacious barrier to penetration by hydrogen. Disruption of the oxide film however, may allow penetration by hydrogen. As noted earlier, when the solubility limit of hydrogen is exceeded, hydrides begin to precipitate. Excessive absorption of hydrogen results in possible embrittlement and the possibility of cracking and fracture under conditions of stress. Laboratory experiments [2] have shown that four (4) conditions noted below usually exist simultaneously for hydriding to occur.

1. The pH of the solution is less than 3 or greater than 12 (this would not typically exist in a steam surface condenser environment).

2. Impressed potentials are significantly more negative than - O.75V (vs. SCE).

3. The temperature is above 176°F (80°C) (this phenomenon would not typically exist in a surface condenser). Below this temperature only surface hydride films will form which, experience indicates, do not seriously affect the properties of the metal. Failures due to hydriding are rarely encountered below this temperature.

4. There must be some mechanism for generating hydrogen. This may be a galvanic couple, cathodic protection by impressed current, corrosion of titanium or dynamic abrasion of the surface with sufficient intensity to depress the metal potential below that required for spontaneous evolution of hydrogen.

Within the range of pH 3 to 12, the oxide film on titanium is generally stable and presents a good barrier to penetration by hydrogen. Efforts at cathodically charging hydrogen into this pH range have been unsuccessful in short-term tests at voltages more positive than - O.75V (vs. SCE). If pH is below 3 or above 12, the oxide film is believed to be unstable and can breakdown, permitting easy access of available hydrogen to the underlying titanium metal. Mechanical disruption of the film (i.e., iron smeared into the surface) allows entry of hydrogen at any level provided the temperature is above 176ºF (80ºC).

Case Study 1

The 1987 thru 1989 window produced possibly the first and certainly, at the time, the most comprehensive benchmark study of powerplant surface condenser tube hydriding. Two papers identified significant titanium-tubed surface condenser tube cracking at the Florida Power and Light (FP&L)[1] nuclear units St. Lucie 1 (840 MW) (Figure 2) and Turkey Point 3 (666 MW) (Figure 3).

Figure 2
St. Lucie Nuclear Power Station

Figure 3
Turkey Point Nuclear Power Station

The first paper, presented at the 1987 International Joint PowerGen Conference (IJPGC) [2] addressed a root cause analysis while the second 1989 NACE publication identified remedial action guidelines and lessons learned. As of this writing, both Turkey Point units have completed extensive power uprate and license extension efforts wherein steam generators, MSR's, feedwater heaters, surface condensers (titanium-tubed modules) and other components have been upgraded. St. Lucie Units 1 and 2 continue to operate in its current state. Since concentrated sea water was causing severe cooling water corrosion issues at both plant locations, the original Foster Wheeler [3] - installed aluminum brass condenser tubes were replaced with Gr. 2 titanium in 1976. The St. Lucie unit followed a similar path in 1979 replacing the Westinghouse [4] - installed, OEM aluminum brass tubes again with Gr. 2 titanium. At the time, both units were retrofitted with manually-controlled, impressed current (IC) rectifiers generating - 900mV/-.90V_{SCE} (saturated calomel electrode).

In 1986/87, eddy current (EC) testing suggested possible localized tube wall loss and cracking located near or in proximity to the tubesheet face. However, no tube joint leakage was observed and subsequent removal and flattening, tensile, hydrostatic and hoop stress testing of sample tubes demonstrated little effect on as-manufactured mechanical properties [*] and no hydride-related failures were observed. It should be noted that severe hydriding and subsequent wall thinning can have a detrimental effect on cyclic fatigue properties. Testing by Hartt and Liu [*] completed in 1992 demonstrated that fatigue strength and endurance limits for in-service hydrided condenser tubes investigated decreased with increasing hydride penetration depth in the range of 0 – 50%.

The IC system was suspected as the cause of the hydriding. In both cases, the manual system was overdriven to a point where free or nascent atomic hydrogen formed on the surface of the tubing far exceeding the absorption limit even when fully passivated. The estimated -1.5 to - 2.0V_{SCE} voltage range resulted in excess of 2 – 3,000 ppm hydrogen representing orders of magnitude higher than traditional breakthrough saturation numbers. Even to this point of concentration, no tube cracking or failure was reported. As an immediate corrective measure, the existing, manually controlled IC system was upgraded to automatic potential control. The unit was restored to successful service and operates today some 24 years the event.

A second paper presented at the NACE 1989 Conference [*] undertook extensive laboratory testing to determine, among other parameters, the threshold where hydrogen absorption and penetration would take place. These

[1] Trade Name – Florida Power and Light Corporation
[2] Trade Name – International Joint Power Generation Conference
[3] Trade Name – Foster Wheeler Energy Corporation

[4] Trade Name – Westinghouse Electric Corporation

observations are identified in the following paragraph.

- Laboratory testing confirms hydriding of Gr. 2 titanium does not occur up to potentials of ≤ $-1.20V_{SCE}$
- Under the same testing, hydride layers are detected at potentials of greater than > $-1.20V_{SCE}$
- ST. Lucie outlet tubesheet potentials estimated @ $-1.60V_{SCE}$ to $-2.00V_{SCE}$
- Predicted threshold potential for hydrogen @ $-1.20\ V_{SCE}$ to $-1.40\ V_{SCE}$
- Residual stress (typical) influences hydride phase orientation but does not any effect hydrogen absorption or penetration rate

The following paragraph highlights the investigators recommendations which were implemented at both plants.

- Automatic potential-controlled IC system with continuous feedback installed
- Rec. voltage @ -1.0_{SCE}. Actual IC voltage potential set point @ $-0.7V_{SCE}$
- Coating all seawater tubesheet surfaces
- Installation of reference electrodes and modify anode to eliminate tubesheet "hotspots"
- All tubes were to be plugged where EC indications are >50%

Case Study 2

The NB Power [5], Point Lepreau nuclear plant is a single, 635 MW CANDU heavy water reactor located in New Brunswick Canada (Figure 4). The unit was officially commissioned in February 1983 and has been offline beginning in March, 2008 for Life Extension Project Modifications. As of November 23, 2012, the unit was returned to full power. Among other major modifications was a near complete rebuild of the steam surface condenser. The rebuild consisted of new titanium tubes and titanium tubesheets and a protective epoxy coating applied to the waterboxes. No upgraded or modified IC system was included nor used in the rebuild. As of this writing the project has been successfully completed.

Figure 4
Point Lepreau Nuclear Station

The condenser is a once-thru design cooled with sea water taken from the Bay of Fundy. It was recognized during the initial plant design phase that suitable precautions had to be incorporated in the condenser circuit due to the aggressive corrosion effects of the sea water and galvanic differences between the construction materials. Table 2 below identifies the principal al construction materials and design considerations utilized, at the time to limit potentially damaging nascent hydrogen and mitigate predicted corrosion and galvanic concerns.

Table 2
Major Condenser Construction Materials

ITEM	MATERIAL
Condenser Tubes	UNS[6] R50400 - ASTM[7] B-338 Gr. 2 Titanium
Condenser Tubesheet	ASTM B171-UNS 61400 Aluminum Bronze Epoxy Coated
Water Boxes	Carbon Steel (Neoprene Rubber Lined)
Impressed Current System	Automatic Potential Control

[5] Trade Name – New Brunswick Power Company

[6] UNS Numbering Systems for Metals and Alloys (UNS –S). UNS numbers are listed in Metals and Alloys in the Unified Numbering System, 10th ed. (Warrendale, PA: SAE International and West Conshohocken, PA: ASTM International 2004).

It is noteworthy that the IC system was, at the time of initial construction, considered state-of-the-art. The anode current could be varied based on operating and environmental parameters such as plant load, water temperature, flow rate, salinity and oxygen levels. A 100% failure of the coating was considered a worst case operational scenario and design set points for the IC system were operated accordingly (Table 3).

Table 3
IC System Design Set Points

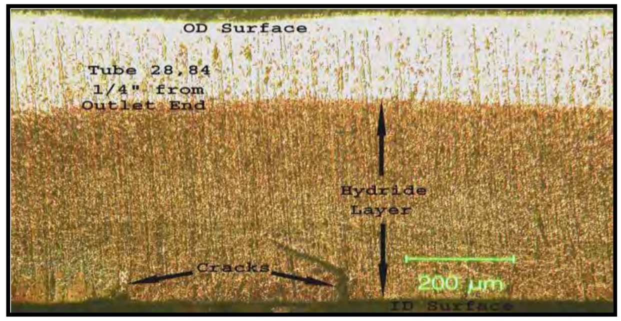
INITIAL DESIGN IC SET POINTS	
TUBESHEET	-0.7 to -0.9 V Ag/AgCl
WATERBOX	-1.0 V Ag/AgCl

Overpolarization of the tubesheet and tubes (tube ends) was not initially considered as a threat given the as-built coating of the inlet tubesheets and waterboxes and subsequent coating of the outlet tubesheets in 1999. In fact, the coating operation likely contributed to an increase in hydriding as a result of increased current collected in the form of increased overpolarization at the tube ends. Without precise individual waterbox control of the voltage to more suitable values, this overprotection value was later calculated at a -1.23 V Ag/AgCl (silver/silver-chloride reference electrodes).

At the direction of the utility, an extensive research study was undertaken in 2008 by among others, DNV [*] following reported suspicious calcareous (calcium and magnesium salts) deposits on unprotected tubesheet areas and suspected hydriding of peripheral titanium tube ends. Further examination determined that several of these tubes had hydride formations up to and in some cases, exceeding 80% of the tube wall thickness (Figure 5).

[7] ASTM International (ASTM) 100 Bar Harbor Drive, West Conshohocken, PA 19428-2959

Figure 5
Tube Hydride Layer

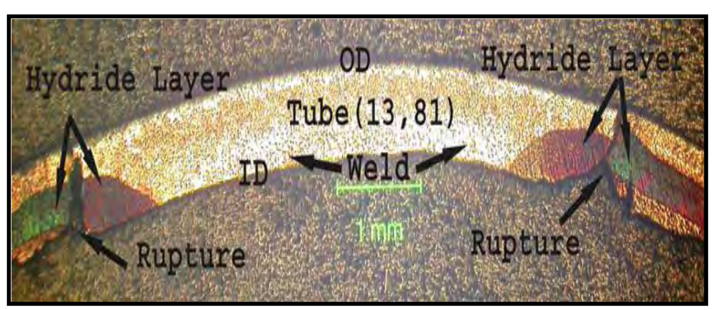


As a cautionary note, do not be confused when eddy current (EC) testing hydrided tubing. Typically, wall loss is not a product of hydriding and EC signals, which resemble wall loss, are actually a change in electrical resistivity in the hydrided layer. Further to this point, the EPRI Charlotte NDE Group [9] will be examining hydrided tube samples from the Pt. Lepreau station to determine if there is a meaningful method of determining hydriding in titanium tubing. Results of this investigation should be available in 2013 or 2014.

Localized tube cracking was also observed. It was suggested that excessive applied cathodic potential could have caused the hydriding. Subsequent computer simulations identified voltages in the range of -1.345 V_{SCE} to -1.36 V_{SCE} were applied to the titanium outlet tubesheet tube ends – the area of highest concentration of wall hydriding.

It is well understood that titanium hydrides generally exhibit very low ductility and are highly susceptible to brittle fracture under the influence of high internal stress. The suspect tubing showed numerous small cracks or fissures in the relatively thick hydride layers. These cracks can act as a notch (stress riser) in the initiation of a tube rupture (Figure 6).

Figure 6
Hydride Layer and Rupture



An additional rhetorical sidebar to the investigation is an analysis of the tube weld itself which appears immune to hydrogen absorption (Figure 6) [*]. Hydriding appears to congregate on either side of the weld where ultimately, the rupture occurs.

At this point in the discussion, it is notable that within the typical pH range of sea water (~ 8), the theoretical hydrogen evolution potential is ~ - 700mV$_{SCE}$ [*]. However, when driven to a potential of - 1030 mV$_{SCE}$ or greater, the pH is ~ 13.5 and the theoretical hydrogen evolution potential meet. These values support the direct field experience where hydriding occurred at potentials more negative than a – 1000 mV$_{SCE}$ and under the calcareous deposits which typically have a pH of over 10.

Several other issues also appeared to influence the degradation of some of the tube ends. The calcareous deposits were determined to have been directly formed by the overpolarization of the IC system resulting in significant deposit formation in particular, the protruding tube ends of the condenser outlet tubesheet. The net effect of these deposits resulted in a significant change in pH at this location. This excursion allowed hydriding to take place which was camouflaged by the hard scale deposits. When the scale was removed, the true hydrided condition of the tube ends was exposed. Removing the scale uncovered not only the ruptured/near-ruptured areas of the tube but the scale removal process was sufficiently aggressive that thru-wall failures ensued.

Another operational anomaly is the plants proximity to excessive 32 ft. (9.75m) Bay of Fundy tide swings – arguably one of the highest in the world. During plant outages, these tidal excursions would flood the condenser waterboxes which were located below the high tide level. The 60” butterfly valves were not capable of full isolation and as a result, stagnant water accumulated under full-on cathodic (cp system) charging and CCW pumps shutdown. The lack of circulating water allowed hydrogen to accumulate at the cathodic surface (tubes) thus removing the continual passivation capability of circulation water significantly increasing the solubility limit of hydrogen.

Clearly, in both the Case 1 and Case 2 studies, there were significant excursions from industry norms. Both units identified in the Case 1 studies units operated with manual control and exceeded IC industry guidelines while the Case 2 study, designed and operating with an even more sophisticated automatic system, experienced both IC potential excesses and corrosion product buildup to degrade system metallurgy both during an on-line and off-line condition.

The lack of a consistent preventative maintenance program appeared as an additional contributing cause of failure. The use of an automatically controlled IC system is one thing – it is quite another to properly inspect, maintain and replace electrodes, regularly calibrate equipment and insure timely replacement of control cards, etc. It would appear that even though elevated temperatures were not a contributor to the formation of hydrides, over polarization and significant changes in pH beyond normal operational bandwidth were suspect in inducing damage.

Case Study 3

The Hawaii Electric[8] (HECO), Kahe 1 Generating Unit (Figure 7) is a sea water cooled, 82 MW unit that entered commercial service in 1963. The unit was retubed with Gr. 2 titanium in 1976 to arrest significant tube ID erosion due to suspended sand in the cooling water. From the late 1980’s to 2008, the unit experienced a number of condenser tube failures.

[8] Trade Name: Hawaii Electric Company

Figure 7
Kahe Unit 1 Generating Station

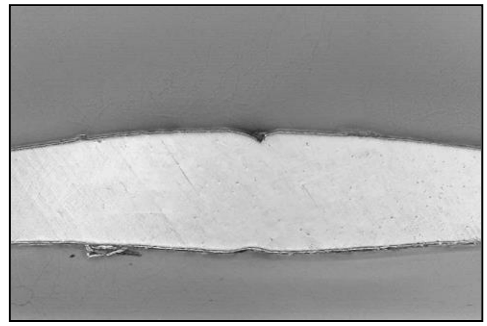
Eddy Current testing at the time indicated possible weld defects and wall thinning [12, 15]. Even more troubling was the discovery of circumferential cracks within the confined annulus space within the tube/tubesheet joint area. This cracking was determined to be hydriding as a result of over rolling the tube joint and an excessively applied IC system.

To ameliorate the situation, a sleeving process was undertaken in 2008. This operation appeared to have prevented further leaks at the tube joint but inhibited future effective cleaning activities which ultimately affected the plant heat rate. Ultimately a titanium-tubed modular changeout with proper IC protection was ordered for installation in 2012.

Several issues come into play here. The first relates to the suspect tube welds that were discovered during EC testing.

Figure 8
Tube Section Suspect Weld Deformity

Figure 9
Tube Section
Weld Deformity Cross-Section



The original tube manufacturer was contacted directly relative to these anomalies and while it was confirmed all tubing passed ASTM-required tests at the time of manufacture (EC and pressure test), an ultrasonic test (UT) was not performed (Figure 8 and Figure 9).

ASTM did not require a UT at the time and indeed, had this test been performed, weld deformities may have been discovered. It is notable however that no leaks were directly attributable to the weld anomalies. Second, the circumferential cracking attributable to hydriding exhibited classic characteristics including high stress concentrations presumably from an over roll conditions during the first retube and an overactive IC system. It would appear that there are similarities between the Kahe and Pt. Lepreau units in terms of a highly stressed environment acting in concert with an overactive IC system. It was further reported that neglect of the IC system and selection and use of an improper anode material compounded the problem.

Since the Kahe unit is forecast to operate until 2035 and the current number of renewable energy projects do not provide the equivalent 82 MW capacity reserve, HECO has decided to install titanium tube and tubesheet modules and an upgraded IC system.

Case Study 4 - Other Hydriding Myths and Misnomers

It is axiomatic that the Laws of Physics are generally fixed. However, there are always gray areas and hydriding has its own peculiarities that sometimes defy explanation.

Following extensive research, recent analysis of several Gr. 2 titanium powerplant surface condenser tube samples revealed a phenomenon identified as "longitudinal, OD initiated, hydride-assisted cracking". The consensus was that hydrogen migrated over time to the highest stress regions – which are the areas of the tube scored during installation and more importantly, areas of highest hoop stresses. Once the local hydrogen concentrations exceeded the solubility limit, they precipitated as hydride needles. This phenomenon has been identified by third party investigation [17] where hydrides oriented themselves in the radial direction under a stress field. The testing laboratory suggested that this phenomenon allowed a crack to initiate and propagate under an increased stress. It should be noted that this failure mechanism is not the more classic hydrogen induced cracking or hydriding where some source of hydrogen exceeding accepted solubility limits is present. What continued to be perplexing in this example demonstrated the presence of hydriding with no apparent source of free system hydrogen. Even more perplexing in this case study was the confirmation that the condenser did not employ any IC or CP system which could generate hydrogen.

Excessive residual hoop stress was initially considered as a potential contributor to the hydride assisted cracking identified above. At the time the tubes were manufactured (early 80"s), an as-produced 10 - 15 ksi (69 – 103 MPa) residual hoop stress was the accepted norm. Actual extracted samples were measured at 18 ksi (124 MPa). Today, the residual stress values more approximate 5-7ksi (44 – 48 MPa).

Given the 18 ksi (124 MPa) residual hoop stress, there would need to be some additional stress applied in the hoop direction of the tube in order to exceed yield. Even under a fatigue failure scenario, a typical run out stress for commercially pure Grade 2 titanium (cp) is about 50% of UTS, or roughly 30+ksi (207 MPa). The presence of the hydrides could reduce the total stress needed for a crack to form. The study however, could not predict what level would be required to bridge fatigue failure, if any. Only a few isolated hydride needles were present in the samples and no signs of embrittlement or crack propagation. Cracking as a result of high residual hoop stresses in hydrided environment was therefore dismissed.

It was also proposed that some form of pressurization could have imparted the required additional stress so as to approach fatigue run-out levels. This pressurization could originate from an overzealous cleaning system such as hydrolyzing, hydraulically driven mechanical scraper plugs or sponge balls. A strong case could be made for hydrolyzing as deleterious events took place in the UK some years ago where expanded end tube failures took place upon withdrawal of the cleaning wand undermined the mechanically expanded tube joint. A second cleaning process utilizing mechanical scrapers is also purported to be safe. However, never let it be said that a hydraulic scraper will never impart scratches to the tube ID, never experience a shut-off pump head pressure spike or cause other events that could endanger the integrity of the tube.

Another scenario in pursuit of the case of hydride assisted cracking introduces the possibility of a thermal stress gradient between the tube OD and the ID. This event could conceivably take place at plant startup-up, upset or trip condition where a high temperature thermal dump or bypass were to impinge higher temperature steam on the condenser tube bundle that may not have circulating present. However, as opposed to fossil units, nuclear units cannot produce the elevated steam temperatures required for the necessary thermal gradient. This study will therefore dismiss this action an illegitimate case of failure.

At one time, nuclear units were once thought to be a potential source of nascent hydrogen within the feedwater/condensate system. However, unless it was a boiling water reactor (BWR), and even there, radiolithic hydrogen concentrations are very low, typical pressurized water reactor (PWR) or fossil system condensate would not contain sufficient hydrogen to approach or exceed any dangerous threshold.

SEM analysis has ruled out more traditional and documented failure mechanisms including corrosion and, due to the longitudinal orientation of the crack, flow or other induced vibration. One could speculate that after nearly 40 [*] years of operational service, these failures are isolated incidents or aberrations caused by the introduction of additional stress levels to the tube resulting in hydride-assisted cracking. Similarly, we believe the classic, fatigue-induced vibration and/or IC/sacrificial-induced hydriding as not sponsoring the failures.

This author suggests that generalizing the use of catchy terms such as “hydride assisted cracking” may be highly premature and inaccurate falling into the myth and misnomer category. Further photographic and investigative research conclusively suggests a more plausible explanation to the cracking is not at all related to hydrogen attack but in fact, fatigue initiated by installation scratches imparted to the tube during a retube operation that took place 25 years prior.

Additionally, “sustained load cracking” has been identified as a condition that has emerged as another potential failure mechanism. Research however would suggest that this phenomenon typically applies to the alloy titanium grades vs. the cp (commercially pure) family [19] and systemic crack propagation from this condition has not taken place as predicted. It is also suggested that since cp titanium condenser tubing has successfully operated in hostile environments for more than 40 years without one reported failure, [18] this industry message must be examined more thoroughly before any final conclusions can be drawn.

However, as noted earlier, these failure mechanisms, however obscure, cannot be entirely discounted. A systematic and ongoing NDE testing program can assist in proper data gathering and is recommended with suspect areas supported by actual sampling.

Conclusions and Recommendations

It was stated earlier in this paper that since the powerplant surface condenser tube/tubesheet interface is continually passivated in circulating water ($CIRH_20$), the operating temperature is below any likely damage threshold and the pH remains relatively neutral, the solubility limit of hydrogen is rarely threatened. However, reactive metals such as titanium can form brittle hydrides when exposed to excessive hydrogen charging.

The case studies presented in this paper clearly document a consistent and common denominator as the root cause for hydrogen embrittlement. Improper design and/or miss-operation of the CP (cathodic protection) or IC (impressed current) protective systems emerge as the common link in most if not all damage reports. These systems have been historically problematic and continue to be the singular and leading cause of embrittlement damage. Should a cathodic protection (cp) or sacrificial system be considered, the following guidelines should be followed.

- Anodes should be selected to produce negative potentials of ≤ - $0.90V_{SCE}$ to - $1.0V_{SCE}$ (-1.2V max) for titanium
- Cast iron or aluminum is preferred for sacrificial systems. Zinc can also be considered
- Magnesium should be avoided due to its high negative potential
- Anodes should not be placed closer than 30 inches from the tubesheet

This paper has also developed special notes for the reader that can be useful in evaluating the performance of an existing systems or examining design parameters for a new installation.

1. Varying CP systems polarization limits to one value at the tubesheet and another value at the waterbox may be ideal but due to condenser dynamics, all but impossible.

2. Individual rectifiers are recommended for each waterbox. More accurate of the respective polarization values based on individual condition assessment.

3. In the NB Power Case Study, the condenser was completely upgraded without the benefit of either an IC or sacrificial system rather relying entirely in the integrity of a full waterbox coating.

In conclusion, hydriding can be avoided if proper consideration is given to equipment design and service conditions to eliminate detrimental galvanic couples or other conditions that will promote the condition. If, in the unusually rare instance, hydriding is suspected, we suggest the following procedures be followed.

- Perform a thorough operational check of the IC or sacrificial system
- Confirm the presence of hydriding through destructive analysis
- Compare ID surface replication process for initial identification
- Confirm hydriding presence - I.E., a white, to calcareous, flowered appearance powder
- Confirm hydriding presence - Normal gunmetal gray color to a silvery appearance
- An ID RFT EC should be performed
- SEM can identify the fracture morphology
- Develop and implement consistent and accountable maintenance programs

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of

Because it is n ble to an
uses and op conditions,
you to consult h technical ser
your particular applic

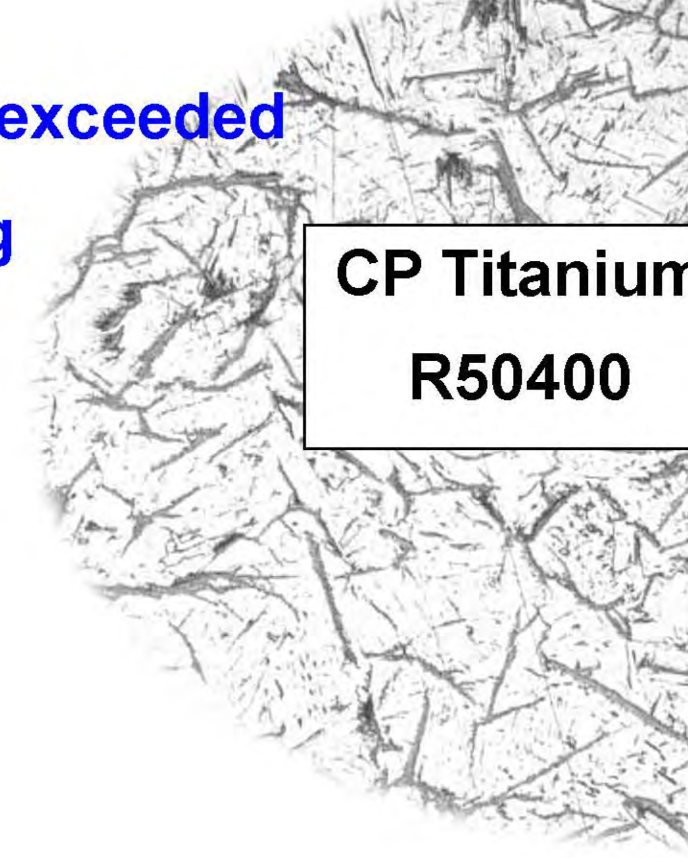
blah, blah, bl

riding 101	***What It Is and What It's No***
e Study 1	***FP&L St. Lucie/Turkey Poi***
e Study 2	***NB Power Pt. Lepreau***
e Study 3	***HECO Kahe***
e Study 4	***Hydriding Myths & Misnom***
maries	

What is it??? Solubility of H_2 in metals is exceeded

Formation of Brittle Hydrides & Cracking

oss of Structural Integrity



/hat is it??? Solubility of H_2 in metals is exceeded

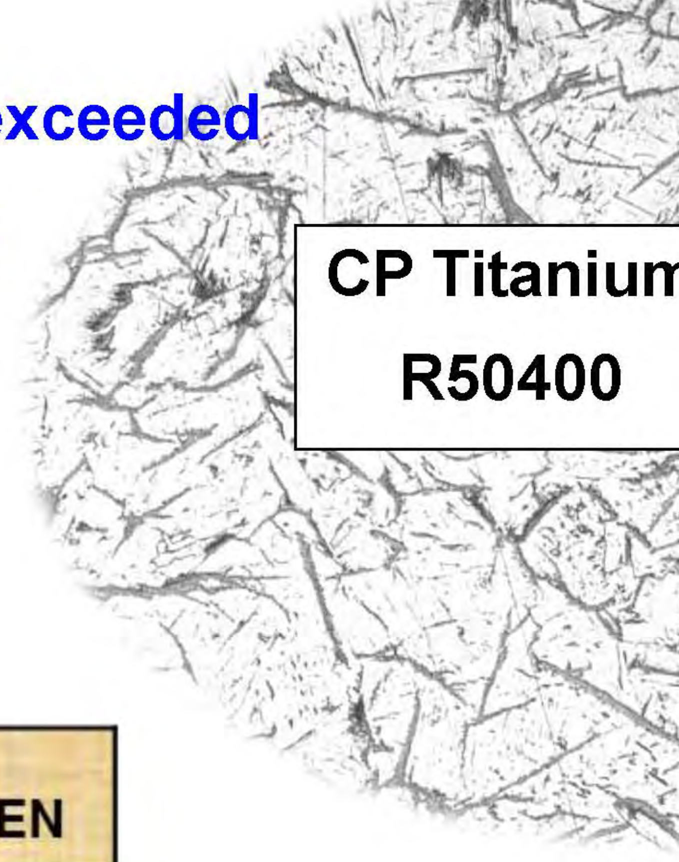
Formation of Brittle Hydrides & Cracking

ss of Structural Integrity

currence

Temps Too Low

s Passivation



EFFECT of MOISTURE ABSORPTION of HYDROGEN	
%H_2O	Hydrogen Pickup (ppm)
0	4.480
0.5	51,000
1.0	700
2.0	7
3.3	10
5.3	17
10.2	11

What is it??? Solubility of H_2 in metals is exceeded

- Formation of Brittle Hydrides & Cracking

Loss of Structural Integrity

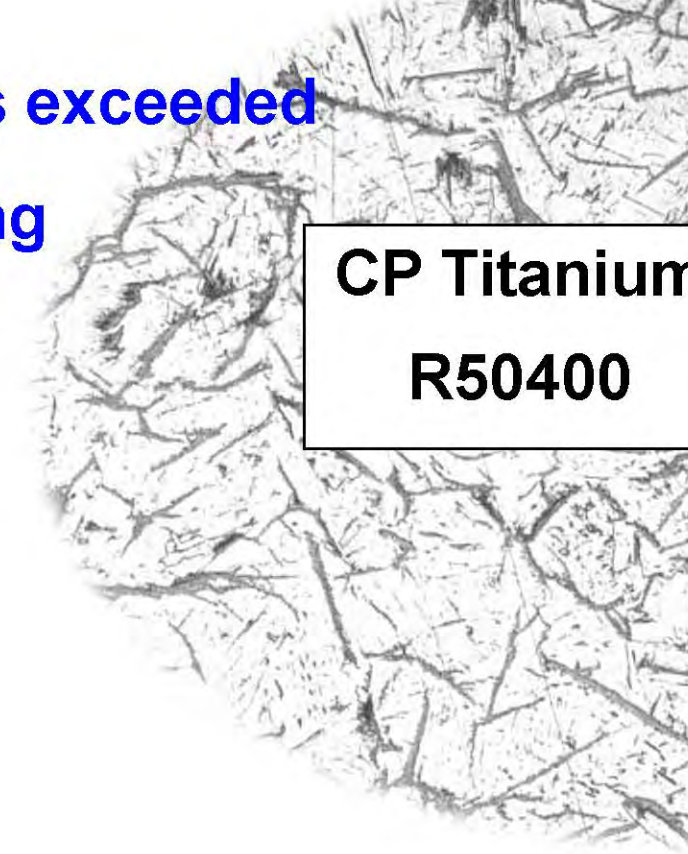
ccurrence

Temps Too Low

us Passivation

harging/Absorption vs. Actual Hydriding

vs. Damaging



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Temps Too Low

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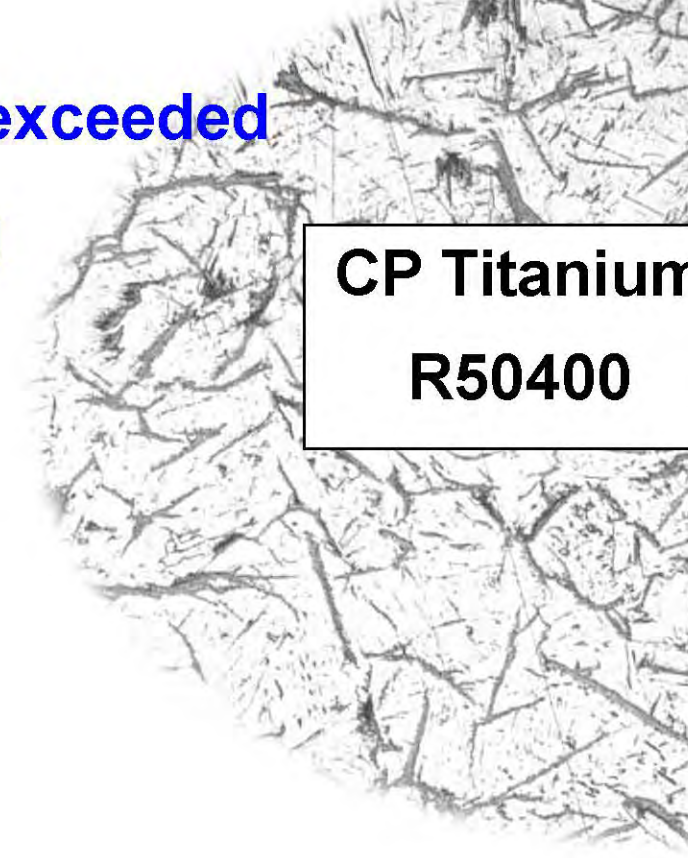
arging/Absorption vs. Actual Hydriding

s. Damaging

t Cause

P (Cathodic Protection)/IC (Impressed Current) Design

tion of Same



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Formation of Brittle Hydrides & Cracking

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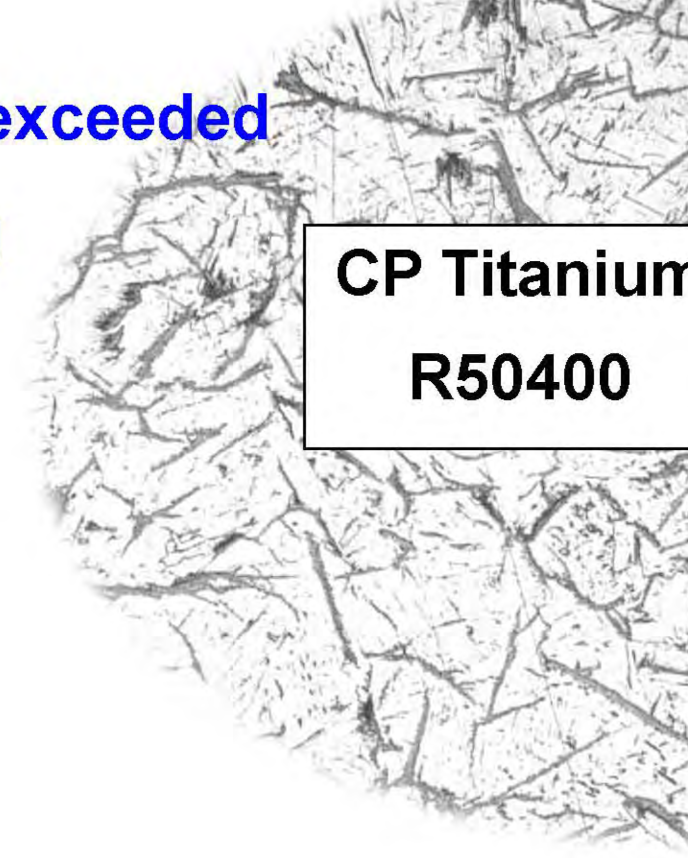
aterials



lydriding
ur?

ntials

mp

The pH of the solution is le
greater than 12

The metal surface is dam
abrasion, or impressed pot
significantly more neg
than -O.75V (vs. SC

The temperature is above

There must be some mec

Study & Publications

NACE 89

Study & Publications
NACE 89

enser Ti Retube 1976
denser Ti Retube 1979

7 & NACE 89

ondenser Ti Retube 1976
Condenser Ti Retube 1979

Hydriding Confirmed via EC Testing
Manual Control IC System
tage est. @ -1.5 – 2.0V
m (est.) Breakthrough Saturation

udy & Publications
ACE 89

nser Ti Retube 1976
nser Ti Retube 1979

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t.) Breakthrough Saturation

ailures
esting OK.
e to Automatic Potential Control

nser Ti Retube 1976
enser Ti Retube 1979

riding Confirmed via EC Testing
ual Control IC System
Est. @ -1.5 – 2.0V
st.) Breakthrough Saturation

Failures
esting OK.
e to Automatic Potential Control

s
ower Uprate – New Hardware
Change

ase Study 2

t Is It?

- 635 MW CANDU Heavy Water (Deuterium) Reactor Commissioned
- Current Life Extension Project Window 2008 thru 2012
- Original Condenser Construction Materials
- State-of-the-art IC System

ITEM	MATERIAL
Condenser Tubes	ASTM B-338 Gr. 2 Titanium
Condenser Tubesheet	ASTM B171-61400 Aluminum Bronze – Epoxy Co
Water Boxes	Carbon Steel (Neoprene Rubber Lined)
Impressed Current System	Automatic Potential Control

at Is It?

- # 635 MW CANDU Heavy Water (Deuterium) Reactor Commission
- # Current Life Extension Project Window 2008 thru 2012
- # Original Condenser Construction Materials
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Impressed Current System	Automatic Potential Control

- # Original IC System Set Points

INITIAL IC DESIGN SET POINTS	
TUBESHEET	-0.7 to -0.9 V

Study 2

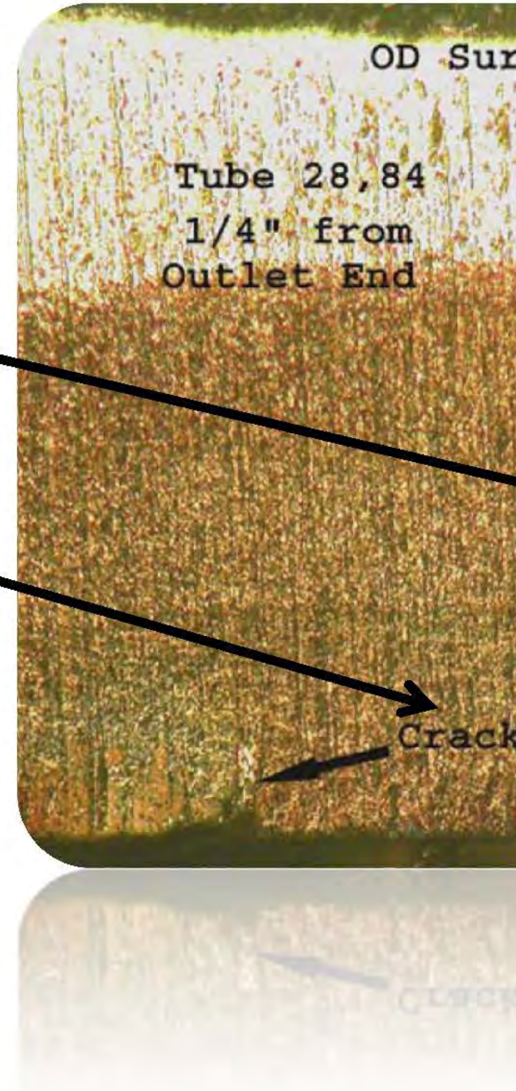
appened?

- reous Deposits (calcium & magnesium)
- neral Titanium Tubing Hydriding
- zed Tube Cracking

se Study 2

t Happened?

- Calcareous Deposits (calcium & magnesium)
- Peripheral Titanium Tubing Hydriding
- Localized Tube Cracking



t Caused It?

- Excessive Cathodic Potential Voltages

ACTUAL IC OPERATING POINTS (CALCULATED)	
TUBESHEET	-1.345 V_{SCE} to -1.36 V_{SCE} OR -1.23 V Ag/AgCl

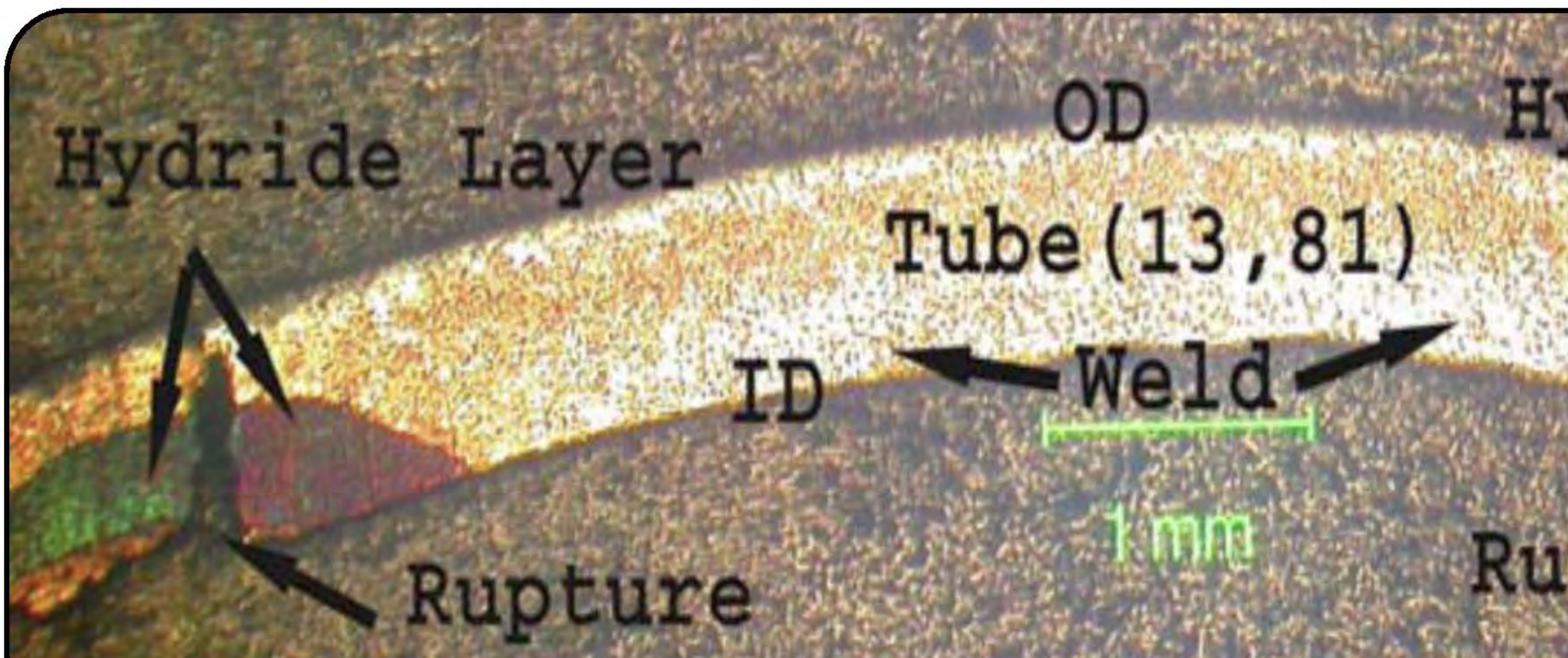
'as The Fix???????

- ' Gr. 2 Titanium Condenser Tubes
- Cp Gr. 1 Kinetically Clad Titanium T
- All-Welded Tube-Tubesheet Joint
- ➢ Plural Component Epoxy Clad W

Condenser Tubes
y Clad Titanium Tubesheets
ubesheet Joints
Epoxy Clad Waterboxes, etc.

ne

ck



hat did they have?

mmercial 1963

g CuNi Cond Tube – Erosion Suspended Solids/Sand

anium Retube 1976

be Leaks 1980's thru 2008

* EC Testing Begun
* Possible Wall Thinning
* Circumferential Cracks in the T.S. Expanded Zone

fety Sleeving Operation Undertaken

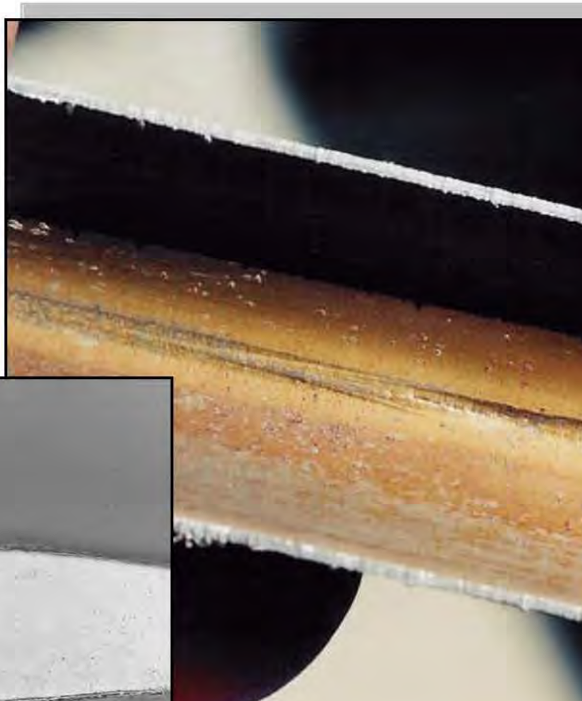
sion Suspended Solids/Sand

08

ning
acks in the T.S. Expanded Zone
Undertaken

ered?

dentified
s (ASTM did not require this test)
o weld anomalies
xpanded Zone due to overrolling



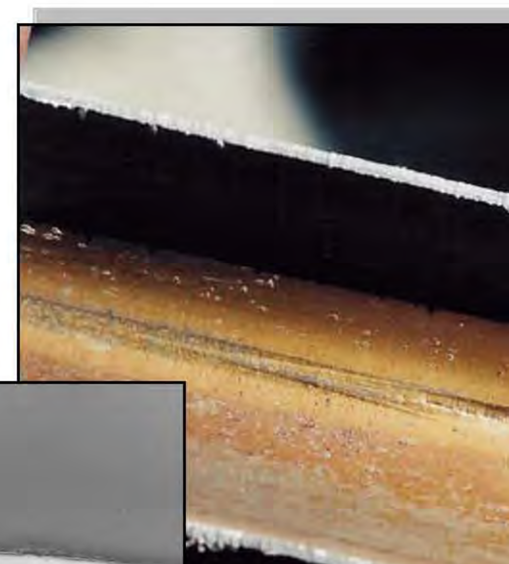
Erosion Suspended Solids/Sand

2008
gun
hinning
Cracks in the T.S. Expanded Zone
on Undertaken

overed?

on Identified
ubes (ASTM did not require this test)
le to weld anomalies
n Expanded Zone due to overrolling

emented?



Condenser Changeout (2012)

Other Hydriding Facts, Myths & Misnon

n”, Longitudinal, OD-Initiated, Hydride Assisted

- Only nukes
- Hydrides appear to align radially direction under a st
- Vibration ruled out
- No IC or sacrificial system present to generate hydro
- Minor hydride needles present
- Radiolithic hydrogen (BWR’s) ruled out
- Residual Stress levels normal (10 – 15 ksi)

Other Hydriding Facts, Myths & Misnom

", Longitudinal, OD-Initiated, Hydride Assisted T

Failure Mechanism ????

Stress Riser/Fatigue/Thru-Wall

How Did It Happen???????

Initiated by installation scratches imp to the tube during a retube operation years prior.

ndom", Longitudinal, OD-Initiated, Hydride Assi

Failure Mechanism

Stress Riser/Fatigue

How Did It Happen??????

Initiated by installation scratches imparted
tube during a retube operation 25 years pri

Generalizing the use of catchy terms suc "hydride assisted cracking" may be high premature and inaccurate falling into the and misnomer category.

ng Summary
ons Learned

ck for it???...........

!!! Check IC or CP System

ctive Analysis

e Replication (Comparison) Process)

nspection (I.E., White, Calcareous, Flowered Appearance

Change to Gray or Silvery Appearance

driding Summary
Lessons Learned

Avoid it???

- roper Equipment Design.
- iminate Detrimental Galvanic Couples.
- dividual rectifiers are recommended for each waterbox. M
- onsistent, accountable maintenance programs.

ling Summary
sons Learned

sons Learned ....

systems polarization limits to one value at the
nd another value at the waterbox may be ideal
ondenser dynamics, all but impossible.

uld be selected to produce negative potentials of:

V_{SCE} to $-1.0V_{SCE}$ (-1.20 max) for titanium

Note: EC signals may resemble wall loss but actually represents a c
esistivity.

Thank you f
attenti

Question