PARAMETERS CONTROLLING HYDROGEN INGRESS DURING CORROSION OF PRESSURE TUBE MATERIAL

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Abstract

In general, pressure tube material (currently Zr-2.5% weight Nb) picks up hydrogen (or its isotope deuterium) in reactor primary heat transport system coolant during aqueous corrosion raising the possibility of hydride formation and delayed hydride cracking at high levels of hydrogen concentration. As a result, the build up of hydrogen in pressure tubes due to corrosion could be life limiting. The objective of this work was to identify the parameters controlling the percentage of hydrogen, generated during corrosion, being absorbed by pressure tube material in order to increase the understanding of the pickup phenomena.

Corrosion coupons taken from two different pressure tubes (β-quenched and non-β-quenched Zr-2.5Nb) were corroded under different conditions for 30 days following a test matrix designed to examine the effect of the corroding environment, the lithium concentration and the temperature on the percentage hydrogen uptake. The results show that the percentage uptake is higher in aqueous environment than in steam. However, adding lithium to the aqueous solution results in significant decrease in the value of the percentage uptake with increasing lithium concentration. The percentage uptake also decreases with increasing temperature in the range from 250°C to 360°C, which includes reactor operating temperatures. In general, the percentage uptake appears to decrease as the oxide thickness increases.

1. Introduction

The Zr-2.5 wt.% Nb alloy is currently used in the fabrication of pressure tubes (PTs) in CANDU® (Canada Deuterium Uranium)[1] reactors. This is due to its special properties including low neutron cross-section and intrinsic corrosion resistance. The inside surface of pressure tubes corrodes slowly due to exposure to the primary heat transport coolant at relatively high temperatures (~ 250°C to 300°C). During corrosion deuterium (D) is picked up by the bulk alloy raising the possibility of hydride formation and delayed hydride cracking at high D levels. The lifetime average rates of corrosion and deuterium ingress in pressure tubes are reasonably low (~ 1μm/year and 2 mg/kg/year, respectively). However, after approximately a decade of operation, indications of accelerated corrosion

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rates and high D uptake have been observed [1-2]. Therefore, the build up of D in pressure tubes due to corrosion could be life limiting.

The overall understanding of the phenomena is that the interaction of water molecules (H_2O or D_2O) with Zr surfaces results in the formation of an oxide and the liberation of H or D gas according to the following overall equation:

$$Zr + 2H_2O \rightarrow ZrO_2 + 2\ H_2$$

The majority of the generated H_2 (following recombination) dissolves into the corroding solution as H_2 gas except for a small percentage that is absorbed by the bulk alloy constituting what is known as percentage theoretical H uptake (% H uptake) where,

$$\%\ H\ uptake = (H\ entering\ alloy/\ H\ from\ corrosion) \times 100$$

The steady or lifetime average % H uptake could vary significantly (ranging from 5 to 40%) depending on the Zr alloy and operating conditions. For example for Zircaloy-2, it is known to be roughly 40%, while for Zr-2.5Nb it is generally found to be in the range between ~5-10% [3]. However, the instantaneous value could vary in a much more significant fashion. The parameters that actually affect this % H uptake value have never been determined explicitly. The objective of this work was to examine the influence of several parameters on the value of the % H uptake due to the corrosion of Zr-2.5Nb. Parameters such as the nature of the environment (aqueous, steam or air), the temperature and the lithium concentration were examined.

2. Experimental

The basic idea for these experiments was to expose sets of similar samples to different corrosion conditions for the same period of time followed by measurements of the grown oxide thickness and the change in the concentration of H in each coupon. In this section, the materials for the samples, the experimental methodology and the experimental matrix are described.

2.1 Materials

The tested materials in this study are from two slightly different Zr-2.5Nb pressure tubes; PT- H1587, which is a β-quenched tube and PT-E402, which is a non-β-quenched tube with typical compositions. The two types are currently used in operating CANDU reactors. Corrosion coupons (8x8x4 mm) were machined from the two pressure tubes with the original curvature preserved (no electrical discharge machining, EDM, was used). The surface finish on both sides of the coupons was as-received machined surface with only the air-formed oxide. This allows for the initial fast oxidation kinetics to be captured. Before exposure, all coupons were cleaned ultrasonically and weighed using a Mettler AE163 scale. For each test two sets of samples (of 4-5 coupons each), one set from each tube, were used.

2.2. Laboratory Set-up

Four to five coupons from each pressure tube were exposed in each experiment as per the experimental matrix in Table 1. Aqueous exposures were conducted in Inconel-600 PARR 1.9 litre static autoclaves using different solutions and at several temperatures as per Table 1. Prior to heating up the autoclaves, the solutions were purged by bubbling through nitrogen gas for 2-4 hours at room temperature to minimize any dissolved oxygen. The room temperature pH as well as the lithium concentration was adjusted using lithium hydroxide. The steam exposure was conducted in a four litre Inconnel-600 "Autoclave Engineers (AE)" static autoclave dedicated only for steam autoclaving to eliminate any possibility of contamination. The air exposure was carried out in a thermally controlled THERMOLYNE 48000 furnace.

Following each exposure for 30 days, the coupons were removed after being cooled to room temperature, cleaned in an ultrasonic bath, dried, weighed using a Mettler AE163 scale and then sent to Nu-Tech (a company with a facility for hydrogen analysis on small samples of zirconium alloys) for hydrogen analysis. Nu-Tech uses a LECO RH-404, EF-400 Automatic Hydrogen Determinator instrument. This destructive technique involves heating of the sample in a crucible to drive off gases. Sample gases (hydrogen and other gases) are flushed into the carrier gas stream and filtered through glass wool to remove carbon and metal particulates. Gases next flow through Schutze reagent, which converts carbon monoxide to carbon dioxide. After passing through a final Lecosorb/AnhydroneTM filter, gases are separated in a molecular sieve column. Gases with lower molecular weights (e.g. hydrogen) pass through the column more quickly than heavier gases (e.g. nitrogen). After hydrogen is separated in the molecular sieve column, it is detected in a thermal conductivity cell.

3. Results

A summary of the weight gain results converted to oxide thickness from all post exposure coupons corroded under different conditions from PT-H1587 and PT-E402 are shown in Table 2. The oxide thickness was estimated from the weight gain for each coupon assuming a uniform oxide thickness. The post-exposure hydrogen analysis results from all corroded coupons are also summarized in the same Table. The total hydrogen uptake for each coupon was estimated from the difference between the post-exposure [H] and the determined average initial [H] for each PT. The average initial [H] for each tube was determined by analyzing five coupons at Nu-Tech. The average oxide thickness and the average hydrogen uptake were used to determine the percentage of the hydrogen liberated from the corrosion process that was picked up by the bulk alloy known as the percentage uptake. The determined percentage uptake values for the sets from PT-H1587 and PT-E402 are also included in Table 2.

The oxidation and H pickup results for coupons from both PTs in all tested environments are illustrated in Figures 1-3. The determined values for percentage uptake from both PTs are compared in Figures 4-6 for all corroding environments.

4. Discussion

In view of Figure 1 (a&b), it appears that the oxide grown in air, steam and H_2O at 300^oC for 30 days is approximately similar in thickness for each alloy. However, in general, the non-β-quenched coupons (from PT-E402 shown in Figure 1b) seem to corrode faster than β-quenched coupons (from PT-EH1587 shown in Figure 1a). Only when Li is added (as LiOH) to adjust the pH to ~ 10.2 (~ 1 ppm of [Li]), the resulting oxide is slightly thicker. This is clearer in PT-E402 than in PT-H1587. Increasing the [Li] from ~ 1 ppm to ~ 200 ppm appears to have a larger effect for coupons from PT-E402 (Figure 2a) than those from PT-H1587 (Figure 2b), while the effect of a 1000 ppm [Li] is significant for both tubes as illustrated in Figure 2(a&b). The effect of temperature on oxide growth, illustrated in Figure 3(a&b), shows a small difference when temperature was increased from 250^oC to 300 ^oC, but a larger difference for a temperature increase from 300 ^oC to 360^oC (as expected for an Arrhenius dependancy). However, in general, again, PT-E402 corrodes faster than PT-H1587.

In terms of total H pickup, corroding in steam or air is generally associated with less H uptake when compared to aqueous corrosion. However, increasing [Li] in aqueous corrosion does not seem to have a significant effect on the total H pickup as depicted in Figures 1& 2(a&b). The effect of temperature on the total H pickup also appears to be insignificant as illustrated in Figure 3(a&b). Only for the non-β-quenched coupons (from PT-E402 shown in Figure 3b), the total H pickup seems to increase only at the highest temperature (360^oC). This observation may allude to more than expected pickup at the inlet of operating PTs (~ 250^oC) and less than expected pickup at the outlet higher temperature (~ 300^oC). In other words the usually assumed Arrhenius behavior for D pickup, based on corrosion and an assumed constant percentage uptake, may be too conservative.

In Figure 4 the effect of different corroding environments on the percentage uptake appears to be scattered. In general, it seems to be higher for β-quenched PT material than the non-β-quenched material. For the non-β-quenched coupons, the percentage uptake appears to increase from air to steam to aqueous, but starts to drop when Li is added. This trend is not clear for the β-quenched coupons. Increasing the [Li] results in a significant drop in the percentage uptake as illustrated in Figure 5. Also, increasing the corroding temperature appears to decrease the percentage uptake as shown in Figure 6. The effect of increasing [Li] as well as increasing temperature on the percentage uptake may possibly be explained by the associated increase in oxide thickness resulting in a diminishing access to the metal-oxide interface where the uptake of hydrogen atoms by the bulk alloy may be occurring.

5. Conclusions

•The growth of oxide thickness at 300°C is slightly slower in steam than aqueous environment. This is relevant to the case of possible boiling at the outlet. In air the rate is close to steam but more scattered.

•In general, non-β-quenched pressure tubes corrode faster than β-quenched pressure tubes. However, the percentage uptake is generally higher in β-quenched than in non-β-quenched pressure tubes.

•The percentage uptake is usually higher in aqueous environment than steam. However, adding lithium to the aqueous solution results in significant decrease in the value of the percentage uptake with increasing [Li]. The percentage uptake also decreases with increasing temperature in the range from 250°C to 360°C.

•In general, the percentage uptake appears to decrease as the oxide thickness increases.

6. Acknowledgements

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7. References

[1] Warr, B.D., “Review and Predictions of Corrosion and Deuterium Uptake in the Body of Operating Reactor Pressure Tubes”, OH Report No. A-FC-97-113-P, AECL Report No. 00-31100-200-005, Revision 0, 1998 July.

[2] Warr, B.D., Ramasubramanian, N., Elmoselhi, M.B., Greening, F.R., Lin, Y-P and Lichtenberger, P.C., “Hydrogen Ingress in Pressure Tubes”, Ontario Hydro Research Review, No.8, August 1993.

[3] M. B. Elmoselhi, B. D. Warr, N. S. McIntyre, "A Study of the Hydrogen Uptake Mechanism in Zirconium Alloys", proceedings of the 10th Int. Symp. on "Zirconium in the Nuclear Industry". ASTM, STP 1245, Baltimore, MD, USA, June 21-24, 1993.

Table 1 Summary of the Experimental Test Matrix

Step No.	Experimental Description	Experiment 1	Experiment 2	Experiment 3	Experiment 4
1	Effect of the environment	Air @300°C	Steam@300°C	Aqueous,H_2O @ 300°C No Li added	Aqueous,H_2O, pH ~ 10.2 ~ 1 ppm [Li]
2	Effect of Li concentration (Aqueous (@300°C)	~ 1 ppm [Li]	~200 ppm [Li]	~ 1000 ppm [Li]	
3	Effect of temperature Aqueous, H_2O, pH~ 10.2/LiOH (~ 1 ppm [Li])	250°C	300°C	360°C	
4	Post autoclaving analyses include: (1) Hydrogen concentration using the LECO system at Nu-Tech. (2) Oxide thickness using weight gain	X	X	X	X

Table 2 Summary of results for coupons from PT-H1587*/PT-E402**

Environment	Average Oxide Thickness (micron)	Standard Deviation (micron)	Average Δ[H] (ppm)	Standard Deviation (ppm)	% Uptake
300° in Air	0.82/1.13	0.13/0.28	3.61/1.88	0.50/0.86	15.21/5.72
300° Steam	0.87/1.08	0.13/0.13	3.02/2.58	1.28/0.95	12.01/8.21
300° Aqueous (no Li added)	0.92/1.13	0.20/0.33	3.93/3.15	0.75/0.52	14.84/9.59
300° C lithiated H_2O, pH~10.2 (~ 1 ppm [Li])	0.92/1.27	0.11/0.20	4.28/3.17	0.90/0.60	16.14/8.54
250° C lithiated H_2O , pH ~10.2 (~ 1 ppm [Li])	0.58/0.54	0.13/0.11	4.13/2.95	0.78/0.80	24.70/18.77
360° C lithiated H_2O , pH ~10.2 (~ 1 ppm [Li])	2.61/2.94	0.11/0.17	4.39/4.34	0.06/1.30	5.82/5.07
300°C lithiated H_2O 200 ppm [Li]	2.08/4.21	0.22/0.44	4.52/4.10	2.02/0.41	7.54/3.34
300°C lithiated H_2O 1000 ppm [Li]	47.11/55.70	5.55/16.86	3.99/5.97	2.54/2.15	0.29/0.37

* Average initial [H] for PT-H1587 was determined to be 3.94 ppm (with a standard deviation of 0.82 ppm)

** Average initial [H] for PT-E402 was determined to be 4.12 ppm (with a standard deviation of 0.87 ppm)

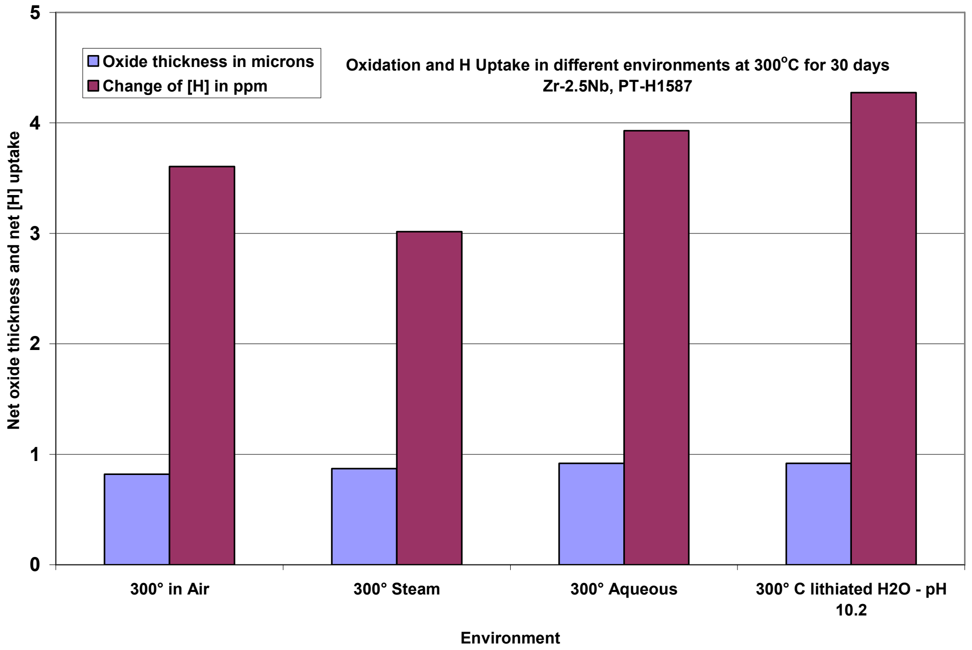

Figure 1a Oxidation and H pickup results for coupons from PT-H1587 corroded in different environments for 30 days.

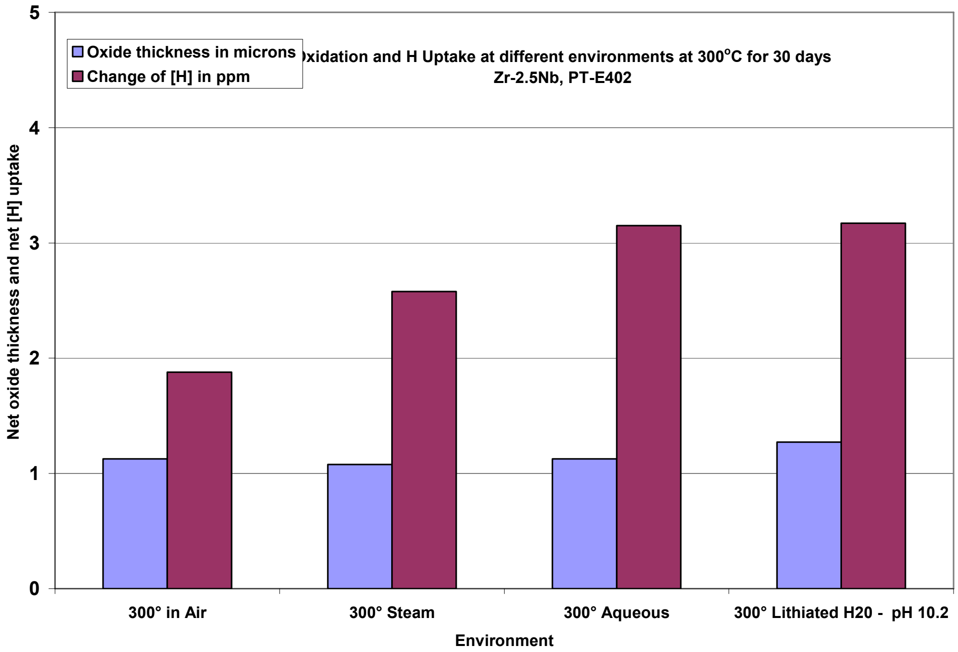

Figure 1b Oxidation and H pickup results for coupons from PT-E402 corroded in different environments for 30 days.

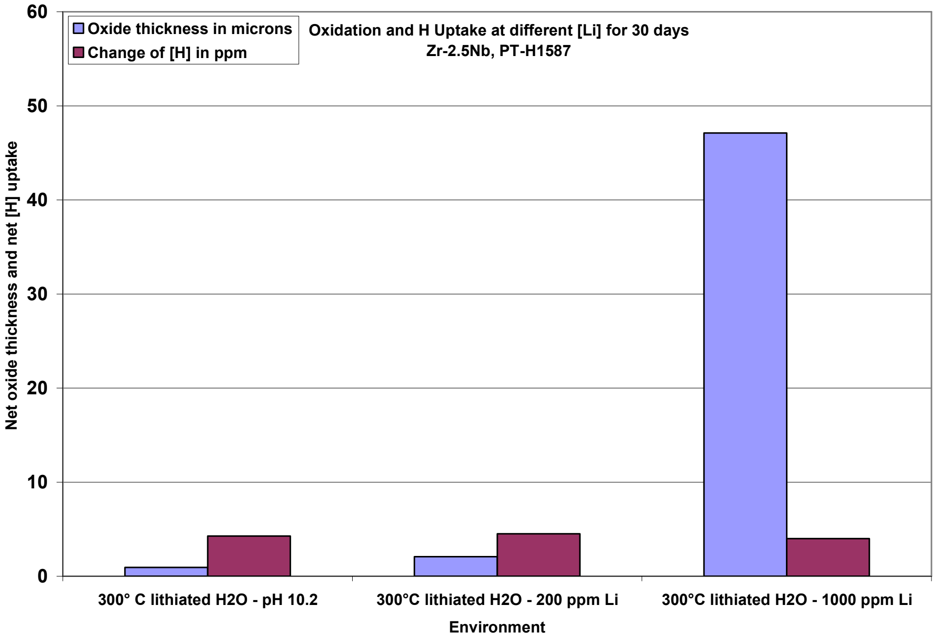

Figure 2a Oxidation and H pickup results for coupons from PT-H1587 corroded in aqueous solution with increasing [Li] for 30 days.

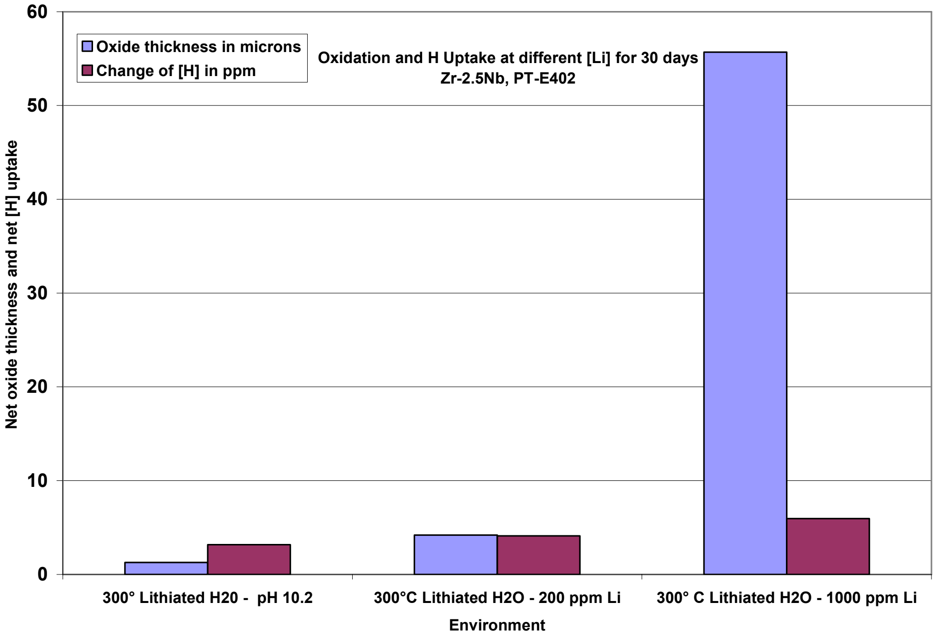

Figure 2b Oxidation and H pickup results for coupons from PT-E402 corroded in aqueous solution with increasing [Li] for 30 days.

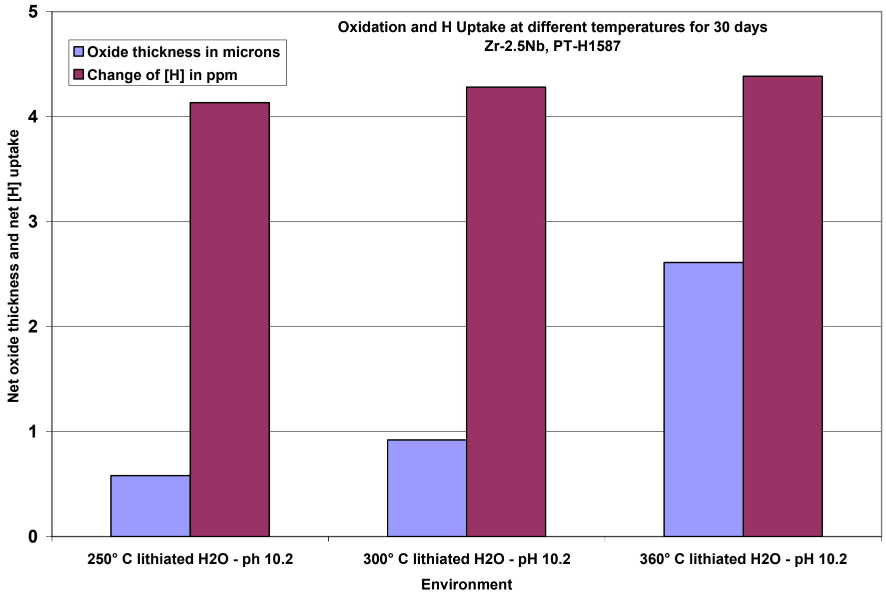

Figure 3a Oxidation and H pickup results for coupons from PT-H1587 corroded in aqueous solution at increasing temperature for 30 days.

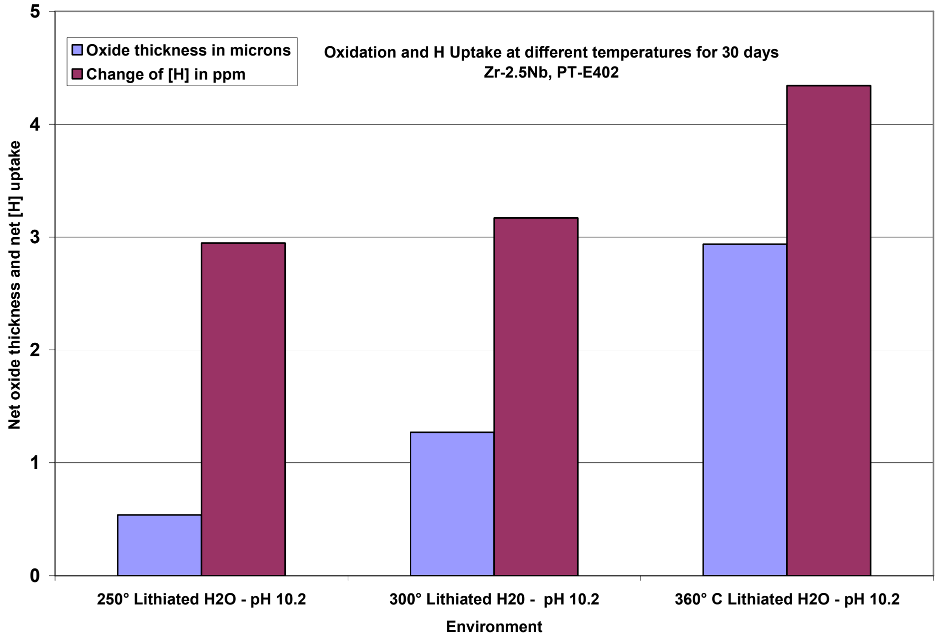

Figure 3b Oxidation and H pickup results for coupons from PT-E402 corroded in aqueous solution at increasing temperature for 30 days.

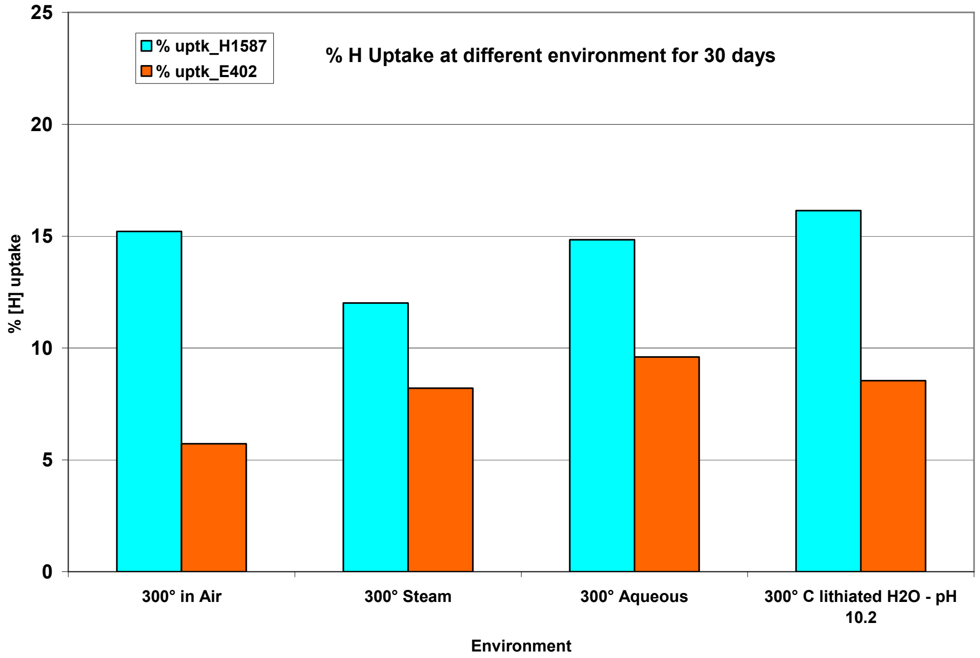

Figure 4 Percentage H uptake for coupons from both PTs (H1587 and E402) corroded under different environments for 30 days.

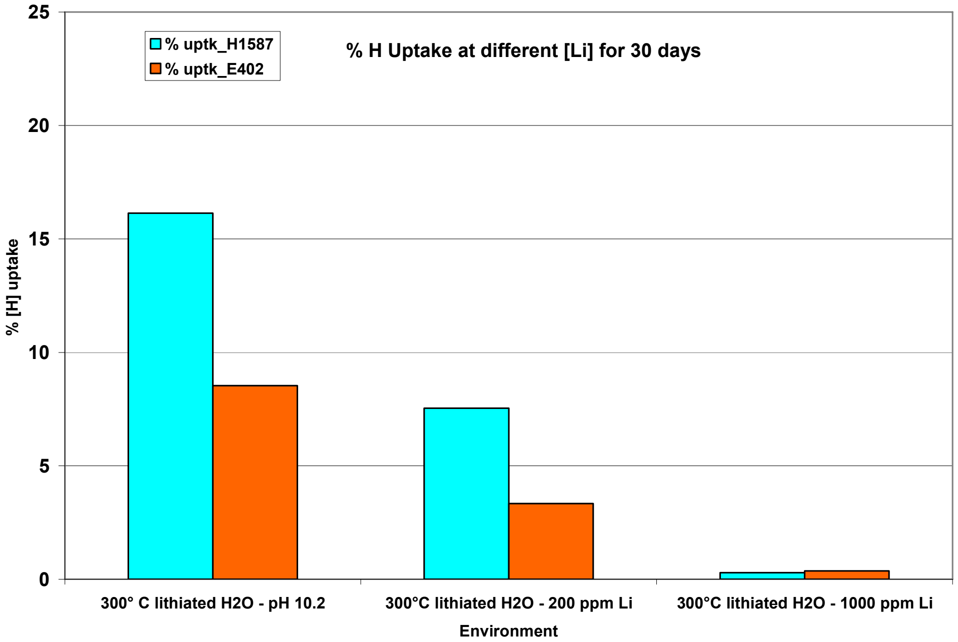

Figure 5 Percentage H uptake for coupons from both PTs (H1587 and E402) corroded in aqueous solution with increasing [Li] for 30 days.

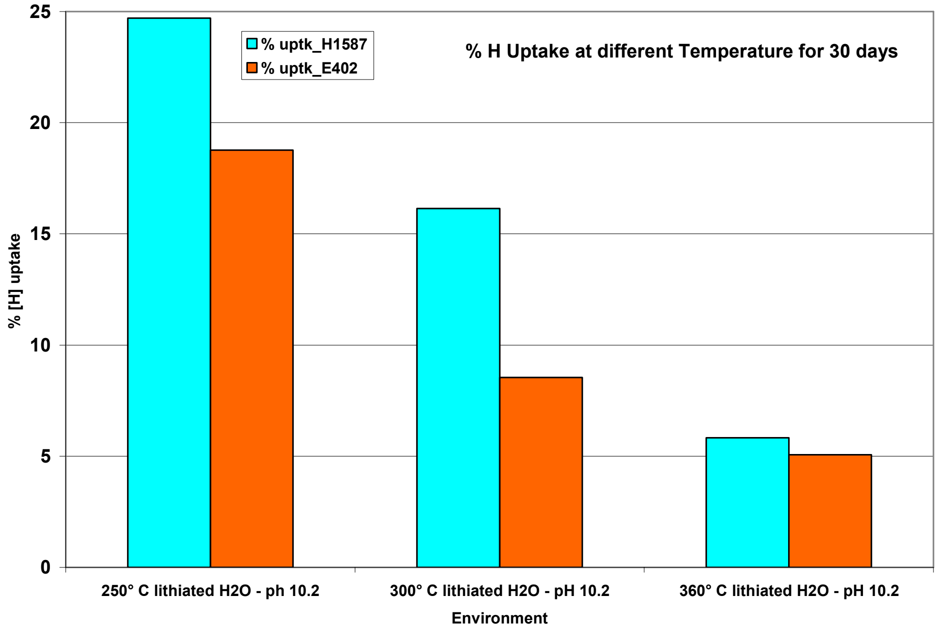

Figure 6 Percentage H uptake for coupons from both PTs (H1587 and E402) corroded in aqueous solution at increasing temperature for 30 days.