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Effects of Extreme and Unusual Conditions on LANA Alloys:

Year-End Report, FY14

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1.0 Introduction

In early FY14, funding was offered to allow pursuit of the objectives outlined in "Effects of Extreme and Unusual Conditions on LANA Alloys: Task Technical and Quality Plan (U)", SRNL-RP-2013-00778 (herein called the "TTP"[1]). This report addresses the milestone "Write Year-End Report". Herein, a summary of the research results obtained through Sept. 30, 2014 will be presented. Funding for this project has been continued in FY15, therefore activities and obstacles to be expected for meeting the existing and modified TTP milestones will be reported.

2.0 Background

As noted in the TTP, previous scouting work on samples of a LANA85 material procured by SRNL for the prototype Four-Inch Short Hydride (FISH) bed has suggested that there is a change in material performance when it is heated at slightly higher than normal temperatures at high hydrogen loadings. (Note that LANA = Lanthanum-nickel-aluminum, where the trailing digits are taken from the 'x' value in the generic formula, $LaNi_{(5-x)}Al_x$, i.e. $LaNi_{4.15}Al_{0.85}$ is abbreviated LANA85 and can also be written as LANA0.85.)

Previously, 4 samples were loaded to 4 different loading levels and heated for ~1 year at 240^{o}C. After the treatment, the material's isotherms showed slight losses in working capacity in proportion to the loading level. The most highly loaded sample showed the formation of a dual plateau isotherm (see Figure 1). Subsequently, a single sample of the same material was prepared and heated at 240^{o}C with high H loading for short periods of time, whereupon the isotherms were determined on the treated material. These studies showed a continuous plateau pressure decrease, which was reasonably rapid during the first month of treatment, but slowed down considerably in subsequent months of treatment up to a total treatment time approaching 6 months. These studies were continued under the current TTP. A plot of the 240^{o}C desorption isotherm plateau pressure vs. the treatment time is given in Figure 2 (both the aging and isotherm determination were performed at 240^{o}C on this sample) out to ~10 months.

Generally, this effect has previously been observed in Pd alloys[2], and the process of heating a fully loaded hydride material under 'high' pressure is called Hydrogen Heat Treatment, or HHT. 'High' is not explicitly defined but typically is significantly over the plateau pressure. One of the objectives of this study is to determine the effects of varying the treatment temperature and overpressure conditions.

The TTP proposed research aimed at determining the following objectives:

a) the rate at which these changes occur and the effect of initial conditions, especially in the early phases of HHT,

b) whether or not different LANA alloys would show similar effects, and

c) whether common contaminants/poisons impact LANA alloy hydride chemistry similarly to what had been found for Pd and Pd-alloy hydride chemistry.

In prior SRNL work, it has been noted that pre- or co-adsorption of CO on Pd alloys can almost completely block H absorption[3,4]. Similarly, from the open literature, S pre-adsorption can completely block H absorption in many metals and alloys. CO has also been noted to block hydrogen absorption in LANA alloys[5,6,7]. Additionally, it would be useful to determine a method to remove contaminants from the LANA material in a manner that might be implemented in the Tritium Facility (TF).

3.0 Objectives A and B – Characterize Rates and Conditions Causing HHT Effects

3.1 Experimental Approach

The previous scoping studies used a LANA85 material procured for the prototype FISH bed development program. Raw alloy was obtained in ingot form from GfE (Gesellschaft für Elektrometallurgie), crushed for SRNL by Ergenics, and subsequently solution alloyed for SRNL by Hydrogen Components, Inc. Substantial prior work on the virgin material had established its isotherm properties. Herein, this material will simply be referred to as the 'GfE' material.

Initially, to address objective B, 5 new samples of other LANA materials were prepared and studied. One of the samples was a second type of LANA85 procured in the 1980's, which has since been stored under ambient inside conditions (Ergenics lot number 1138-V-2, sample designation LANA85_EXOP1). Two samples were different lots of LANA75 material: one was material that had also been procured in the 1980's and stored (Ergenics lot 1316-V-2, sample designation LANA75_EXOP2), and the second was taken from archival material of LANA75 that had been procured for the TCON (Tritium CONsolidation) project of the mid-2000's. This lot of material was manufactured by Ergenics and was comprised of a blend of 3 heats, designated as V-200767, V-200797, and V-200322 (sample designation LANA75_EXOP3). This material was used in the replacement LANA75 beds installed in the TF in 2004 and will be hereafter referred to as the 'TCON blend' material.

For the Interim Report, the first 3 samples (LANA85_EXOP1, LANA75_EXOP2, and LANA75_EXOP3) were loaded and heated at 240^{o}C for ~1 month to compare to the second scoping sample study results mentioned above. One additional sample of each of the LANA75 materials was also prepared (sample designation LANA75_EXOP4, lot 1316-V-2; sample designation LANA75_EXOP5, TCON blend) and hydrogen heat treated for ~1 week. Diagnostic isotherms were then recorded on these 5 samples. After completing these isotherms, the samples aged for 1 month were returned for an additional month of HHT. At the end of the reporting period of the Interim Report, the 1 week samples were nearing completion of isotherm acquisition and the 1 month samples had just begun their 2nd month of HHT. However, a Safety Stand-down interrupted this work and all HHT was placed on hold. Subsequently, it was determined that additional overtemperature detection devices were required for unattended operation and that the laboratory eHAP needed to be updated. The additional devices were ordered and received and the eHAP was updated during a 3-month operations hold.

The original scoping study (see Fig. 1) samples were initially loaded on the PCTPro with H_2 to 195, 241, and 374 psia (13.1, 16.2, 25.1 bar, respectively) for the LOW, MID, and HIGH loading levels, respectively. Subsequent sample loadings were also performed on the PCTPro, typically to pressures of ~40 bar (~580 psia) +/- 1 bar (14.51 psia), with the following exceptions:

1. Sample LANA75_EXOP3 was loaded to 44.3 bar (638 psia) for its first HHT.
2. Sample LANA85_GFE5 was initially loaded to lower pressures, 25-35 bar (363-508 psia), whereas the last 2 loadings were at 40-42 bar (580-609 psia).

Because of significant equipment and administrative issues, progress on LANA85_GFE5 was minimal. The 8^{th} loading/aging and subsequent isotherm collection was completed, and the sample was reloaded with H_2 for the 9^{th} aging period. Only LANA85_GFE5 has been loaded with D_2. Out of 9 charges, the first 4 and the last 2 were performed with H_2, and the remaining 3 with D_2. The isotope effect causes D_2 plateaux to occur at higher pressures than for H_2. In Figure 2, the D_2 values are artificially lowered to the same point as the H_2 values, which illustrates that the general trend observed is not significantly different when using D_2 for the HHT. The samples typically showed a slight drop in pressure over the HHT; however, it is not clear if this is a result of leaks or some other factor(s).

Despite being impacted by the difficulties mentioned above, progress has also been made on the other 5 samples prepared in the first half of FY14. EXOP1, 2, and 3 have completed their second aging period , isotherms have been collected, and the samples are now aging again. For EXOP4, in addition to completion of its second aging period/isotherm collection, its third aging period has also been completed and is awaiting isotherm collection. Likewise, EXOP5 has completed its second aging period/isotherm collection and is awaiting reloading for the third aging period. The results from these samples are presented below.

In addition, 6 more samples have been prepared: two remain untouched, one has been activated only, one is being used to collect virgin material isotherms for the TCON blend material, and two have been used to determine if HHT at 150 ^oC will induce similar changes in isotherms. To aid in recalling sample designations and processing parameters, Table 1 shows the sample designation, material source, aging conditions ('HHT protocol' = period duration and aging temperature (^oC)), whether or not the last aging period isotherms have been collected, and the current sample status. All samples currently aging will be ready for isotherm determination in the first two weeks of October. Results are discussed in the next section.

Table 1. Sample ID and status as of FY14 end

Sample ID	Material	HHT Protocol	Aging Periods Completed	Last Period Isotherm Complete?	Current Status
LANA85_GFE5	GfE LANA85	monthly, 240°C	8	Y	Aging
LANA85_EXOP1	Erg. Lot 1138	monthly, 240°C	2	Y	Aging
LANA75_EXOP2	Erg. Lot 1316	monthly, 240°C	2	Y	Aging
LANA75_EXOP3	TCON blend	monthly, 240°C	2	Y	Aging
LANA75_EXOP4	Erg. Lot 1316	weekly, 240°C	2	Y	Ready for Isos
LANA75_EXOP5	TCON blend	weekly, 240°C	2	Y	Ready to Load
LANA85_EXOP6	GfE LANA85	monthly, 150°C	2	Y	Aging
LANA85_EXOP7	Erg. Lot 1138	-	0	NA	Assembled
LANA75_EXOP8	TCON blend	monthly, 150°C	2	Y	Aging
LANA75_EXOP9	Erg. Lot 1316	-	0	NA	Assembled
LANA85_EXOP10	GfE LANA85	-	0	NA	Activated
LANA75_EXOP11	TCON blend	-	0	NA	Virgin Isos

3.2 Results and Discussion

Isotherm (Equilibrium) Results

The reader should be aware that all Figures presented herein use Excel graphics with the 'dot-to-dot' method of drawing connecting lines on isotherms. In some cases this produces some issues as the density of data points is insufficient to show all the curve's details, especially when looking at expanded portions of the isotherms. (A particularly good example of this can be found in Figure 8b near the D/M value of 0.4.) However, no other method available does substantially better, so the default dot-to-dot method was utilized.

For comparison, the previous results of the 350-day aging of 4 GfE LANA85 samples at 240°C are shown in Figure 1. The results illustrate a small capacity drop proportional to the HHT loading pressure and the severe change in shape of the hydrogen desorption isotherm for the 'fully' loaded sample, i.e. where the loading was high enough for the sample to be fully in the β–phase. (All 4 of these samples have been retired.) This severe drop in plateau pressure and the formation of a double-plateau isotherm are what originally stimulated interest in studying these effects.

Figure 1. 80°C H_2 Isotherms on Four LANA85 Samples Thermally Aged for ~1 year

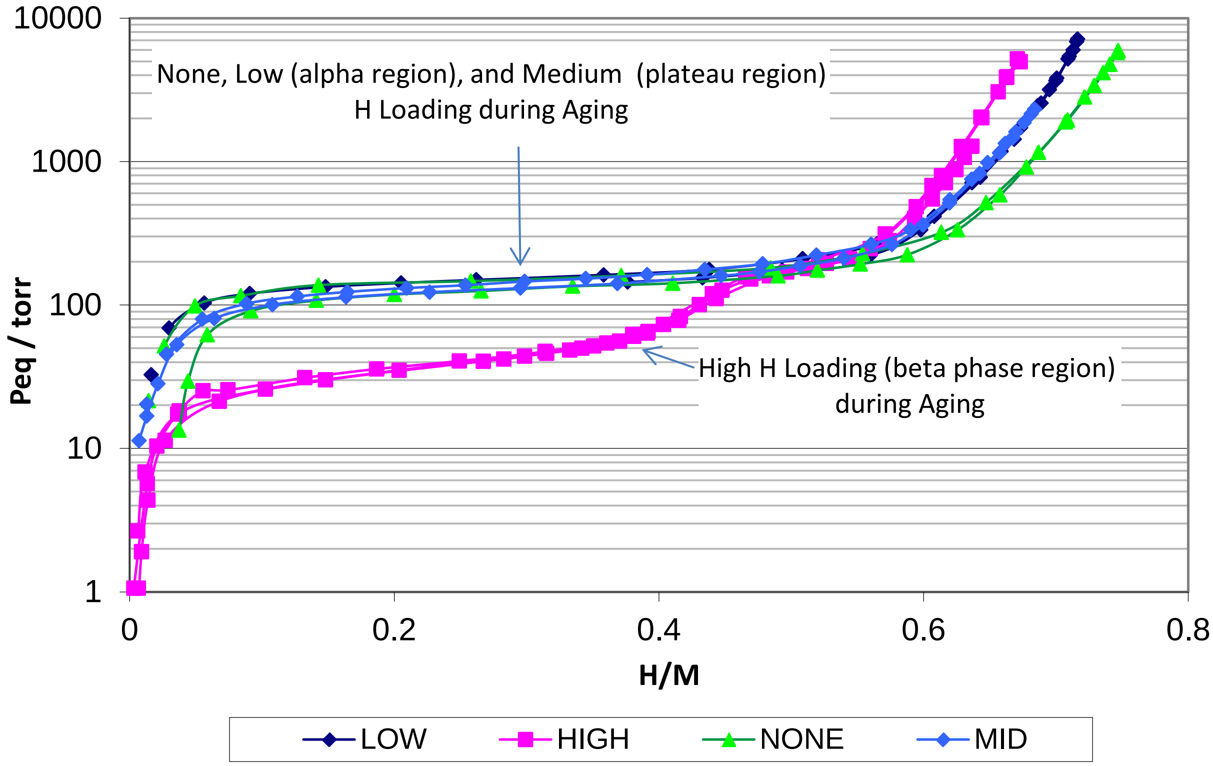
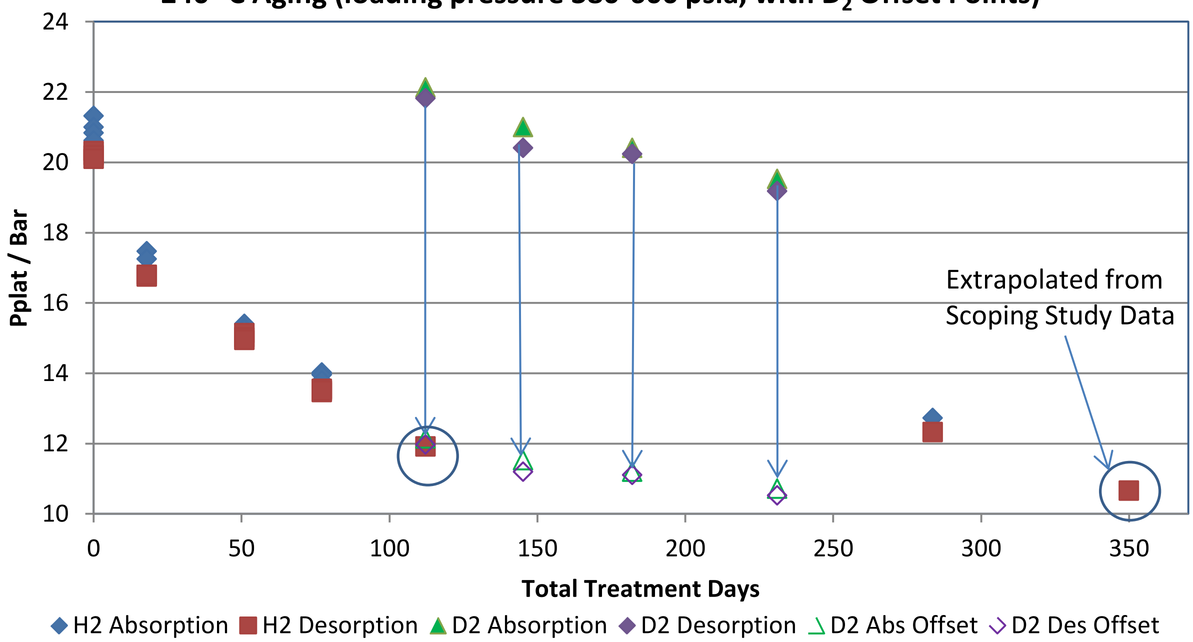


Figure 2 plots the 240°C desorption isotherm plateau pressure of the GfE LANA85 material (LANA85_GFE5) that was heated at 240°C for ~9 months under full loading (periodically interrupted for isotherm determinations). The isotherm results obtained on the fully loaded sample in the scoping study (Fig. 1) were extrapolated via a van't Hoff relationship to predict the 240°C desorption isotherm plateau pressure, which is indicated in the Figure as the last point (circled).

Also shown are four points derived from deuterium isotherms. The latter three points were obtained after D_2 HHT, using D_2 for the isotherms. These results show the well-known isotope effect in which the D_2 plateau pressures are higher than H_2 plateau pressures. In the Figure, these points have been arbitrarily lowered by ~10 bar in order to evaluate the impact of using D_2 for the HHT. The D_2 isotherm pressure values obtained after the 4th HHT cycle were lowered to approximately match those of the H_2 isotherms taken at the same point (circled, at day ~112). Those points then make a smooth and continuous extension of the prior H_2-based data, implying that the use of D_2 for HHT had no impact on the aging behavior.

Figure 2. H_2 & D_2 Plateau Pressures over LANA85_GFE5 after X days of 240 °C Aging (loading pressure 380-600 psia, with D_2 Offset Points)

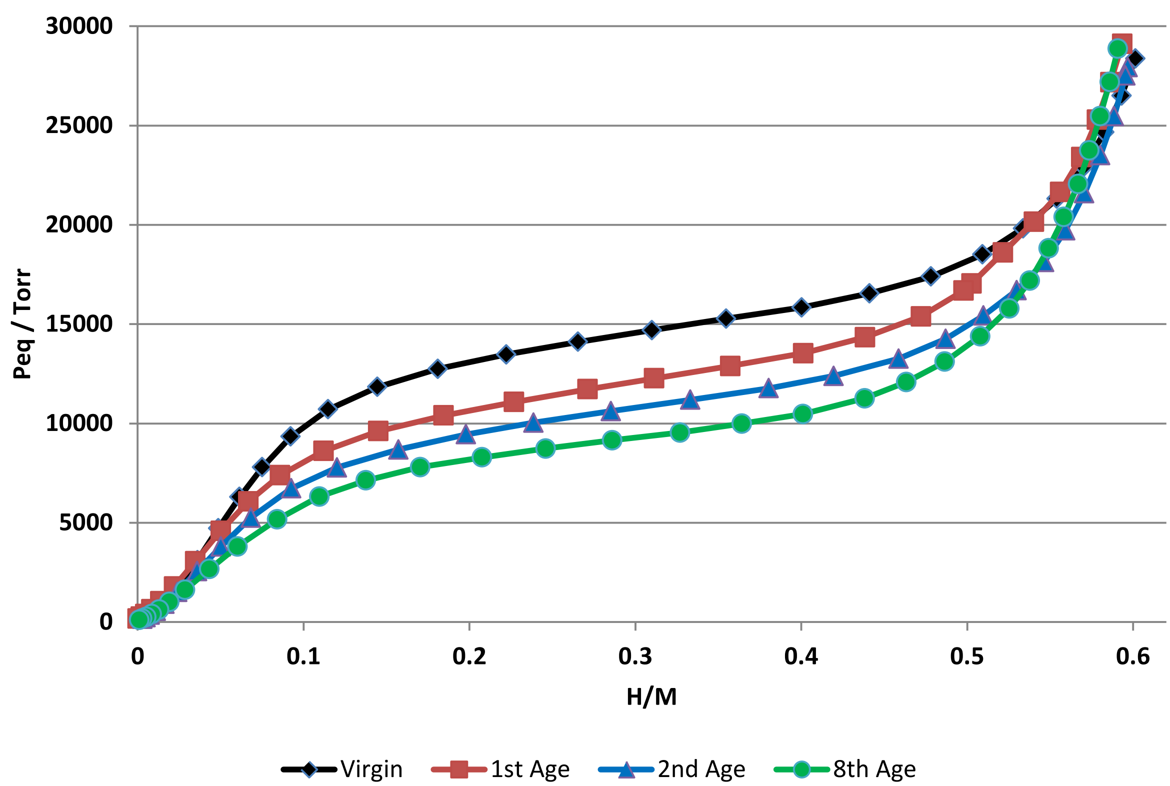


Taken together, the data now appear to represent a reasonably smooth decreasing curve that asymptotically approaches the 'final' pressure obtained for the largest portion of the isotherms obtained in the scoping study. Figure 3 shows 240°C H_2 desorption isotherms from virgin LANA85_GFE5 and those obtained after the 1st, 2nd, and 8th HHT. The plateau pressure depression is clearly observed; furthermore, the approximately same decrease between the 1st and 2nd HHTs and the 2nd and 8th indicates the decrease in the lowering rate.

As mentioned in the Interim Report, the early pressure depression (<~120 days) extrapolated to zero before the age of the scoping sample was reached. Since one cannot obtain a zero pressure, it is expected that the pressure would level off at some value, but the apparent development of the dual plateau at that time is unique. It remains to be seen if the behavior is replicated in LANA_GFE5 and if more of the sample will convert to the higher plateau pressure material if the age of the scoping sample is extended.

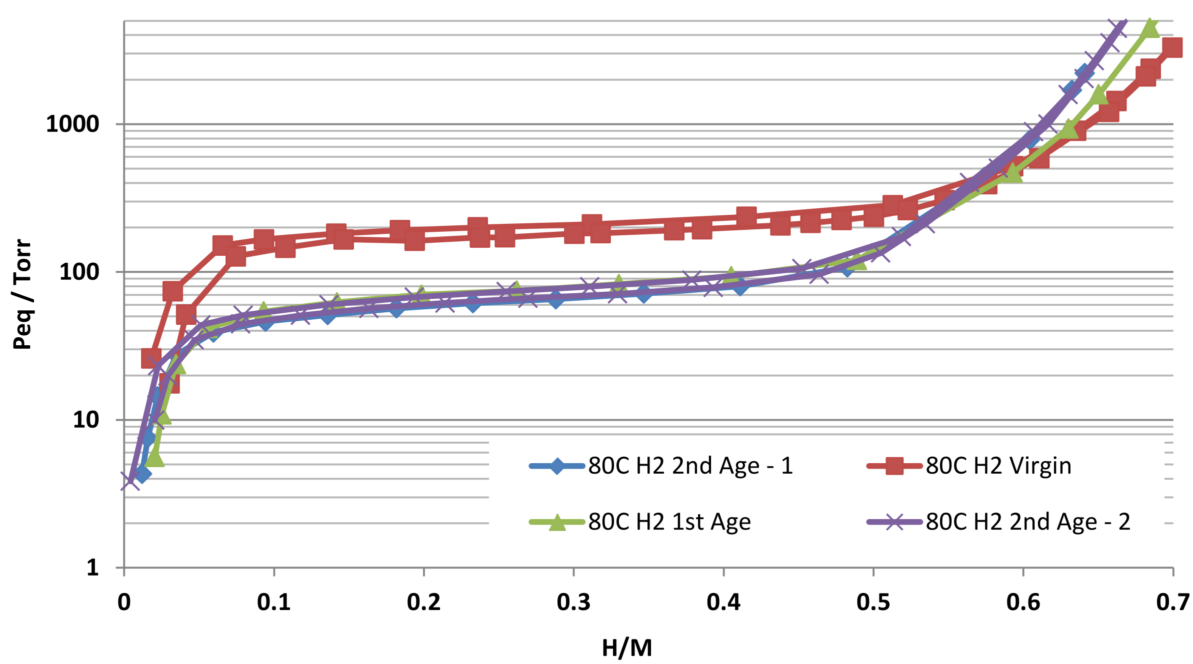
HHT cycle 8 produced the data points at day ~284, which appear to be higher than expected based on extrapolation of the prior data. Because the extrapolation seemed to be well aligned with the van't Hoff calculation results shown at day ~350, the behavior at ~284 days is somewhat anomalous. However, it should be noted that the sample was held at room temperature under ~40 bar of H_2 for several months while equipment and administrative issues were being resolved, which may have allowed for a small recovery. Such a recovery could be analogous to the 'healing' observed in tritium-aged samples when some of the ^{3}He decay product is observed to escape the sample. The sample is currently undergoing its 9th HHT and will produce points approximately halfway between those of the 8th HHT and the extrapolated values, which will certainly be of interest. Continued HHT beyond 350 days is planned for this sample in FY15.

Figure 3. H_2 240°C Desorption Isotherms from Virgin and Aged GfE LANA85

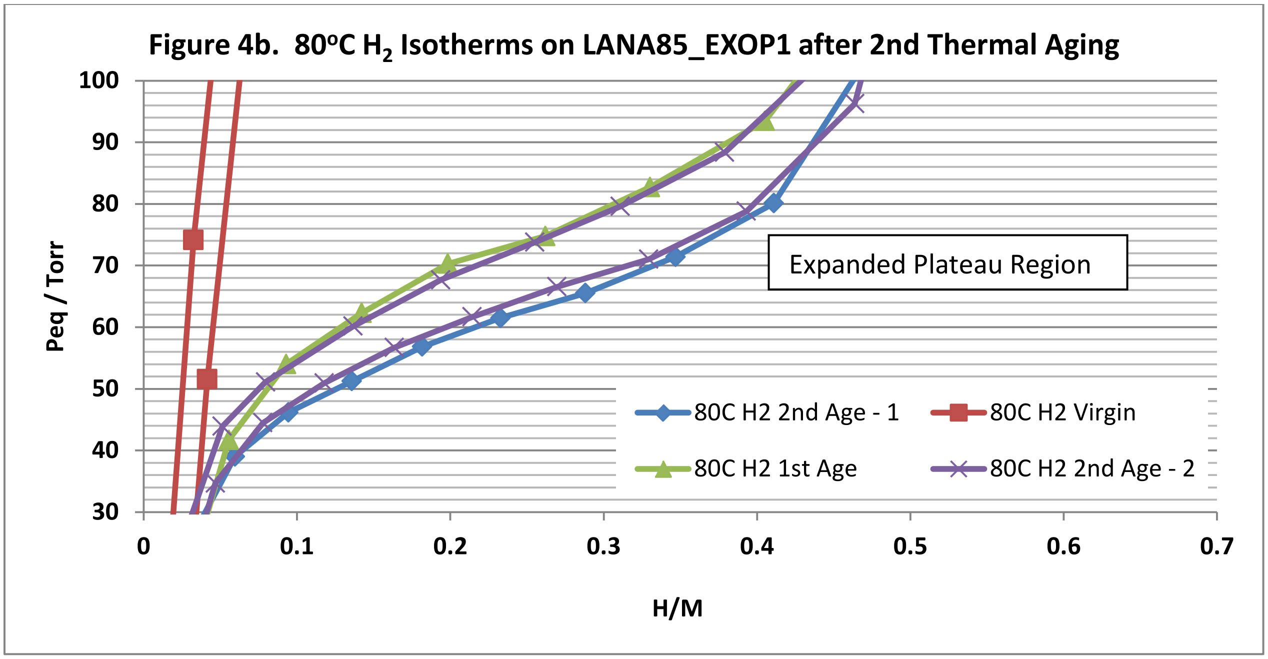


Sample LANA85_EXOP1 is composed of a different LANA85 material and is being HHT aged in monthly intervals to compare its behavior to that of LANA85_GFE5. Figures 4a and b show the virgin material H_2 absorption and desorption isotherms taken at 80°C, along with the isotherms obtained after the first and second month-long HHT (Figure 4b represents an expansion of the plateau region of the HHT results). A plateau pressure depression is evident, but unlike the GfE LANA (shown in Figure 3 for 240°C isotherms), there is minimal change between the 1st and 2nd HHT results. The curves "80C H2 1st Age" and "80C H2 2nd Age-1" were both obtained by opening the aged sample to the manifold and performing an immediate desorption isotherm. A slight additional depression was observed to be induced by the 2nd HHT. Curve "80C H2 2nd Age-2" was obtained by evacuating the sample overnight after the 1st desorption isotherm was completed, followed by a full absorption/desorption cycle. The desorption obtained in this cycle matched the first desorption, indicating that the isotherm acquisition process was not altering the curves (unlike what is frequently the case in tritium aging studies). There may be a change in working capacity as indicated by the equilibrium pressure at 1000 torr (as an example); however, this may only be a result of experimental error and subsequent results should clarify this.

Figure 4a. 80°C H_2 Isotherms on LANA85_EXOP1 after 2nd Thermal Aging

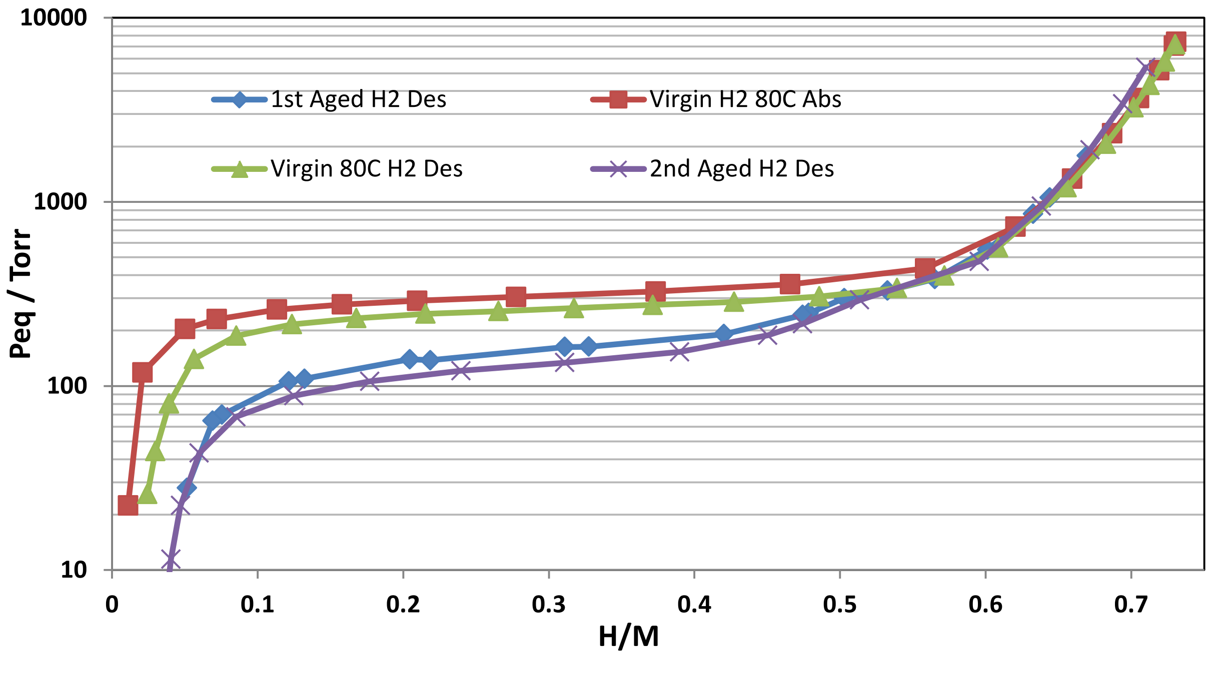


The 80 °C desorption plateau pressure for virgin LANA85_EXOP1 is somewhat higher than that of the virgin GFE material (~180 torr vs ~120 torr, respectively), which likely arises from the slight composition difference.



As noted in Table 1, samples LAN75_EXOP2 and LANA75_EXOP3 are from two different lots of LANA75 materials. Both samples were treated for ~30 day periods. Figure 5 shows the HHT results for LANA75_EXOP2 (lot 1316). In addition to the clear plateau pressure depression and loss of capacity in this material, the formation of a dual plateau structure is also observed upon HHT. In this Figure, the isotherms have been matched in the beta-phase region, thus the typical capacity loss observed during HHT emerges as a difference in the location of the alpha-phase region of the isotherms. Again, there are minor changes in the plateaus of the depressed region between the virgin material and 1st HHT and the 1st and 2nd HHTs.

Figure 5. 80^{o}C H_2 Desorption Isotherms of Virgin and Thermally Aged LANA75_EXOP2



Figures 6a, b, and c show the results for LANA75_EXOP3 (the TCON blend sample), where Figure 6b is an expanded view of the plateau region shown in Figure 6a. Isotherms for the virgin material and the material that underwent 1 and 2 month long HHT periods are shown in Figures 6a and b. Additionally, an isotherm from LANA75_EXOP5 obtained after 2 week-long aging periods is included to illustrate the smooth development of the plateau pressure depression and the fact that the depression rate decreases as noted in the GfE LANA85 material. Figure 6c compares isotherms of the virgin (EXOP11 sample for the D_2 data) and aged material (1 HHT period) obtained with pure H_2 and D_2 for comparison, illustrating the minimal isotope effect at 80^{o}C obtained with this material. The HHT treatment seems to have slightly increased the extent of the isotope effect.

By comparing Figures 5 and 6a, the virgin material plateau pressures are observed to be slightly different (~50 torr) and both are slightly higher than the plateau pressures from the LANA85 samples. Both LANA75 samples show plateau pressure depression, capacity loss (on more aged sample), and a dual plateau structure. The D_2 isotherm from the aged TCON material (1 HHT period, Figure 6c) shows some anomalous points at higher pressures, which are likely a result of experimental error.

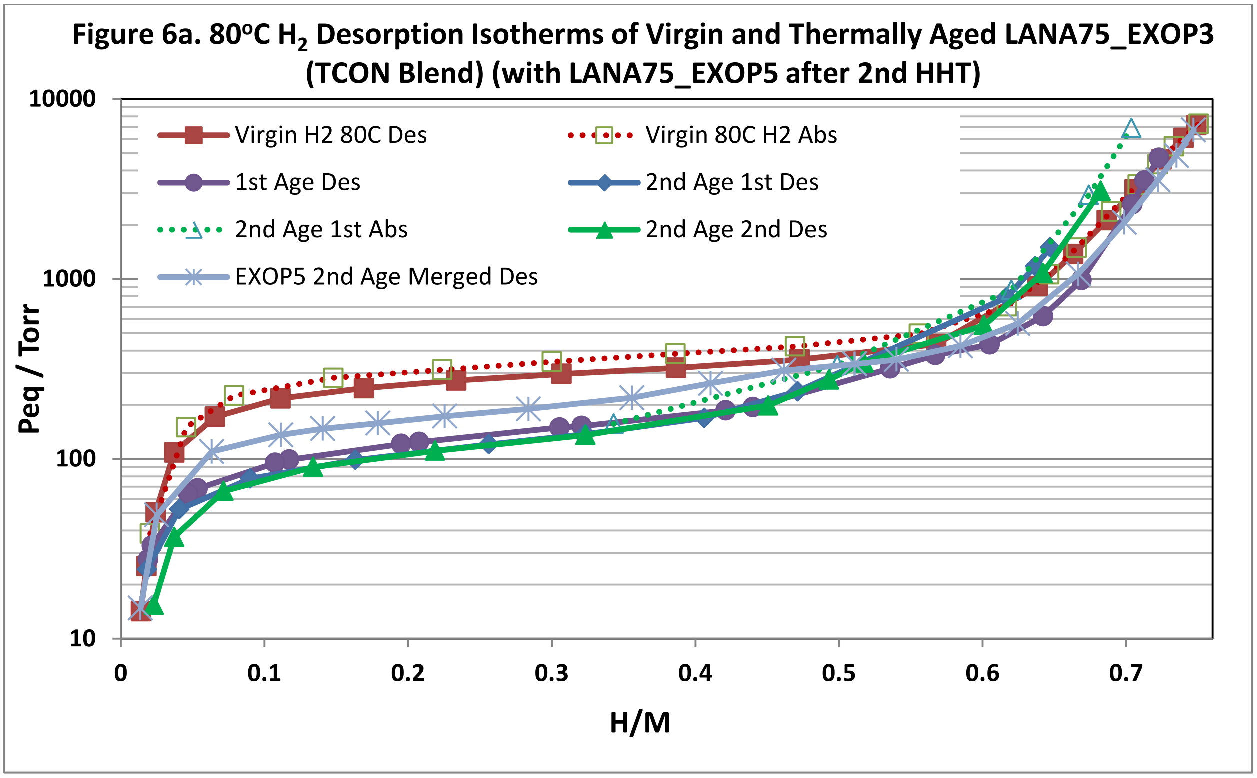


Figure 6a. 80^{o}C H_2 Desorption Isotherms of Virgin and Thermally Aged LANA75_EXOP3 (TCON Blend) (with LANA75_EXOP5 after 2nd HHT)
10000
1000
100
10
Peq / Torr
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
H/M
Virgin H2 80C Des
Virgin 80C H2 Abs
1st Age Des
2nd Age 1st Des
2nd Age 1st Abs
2nd Age 2nd Des
EXOP5 2nd Age Merged Des

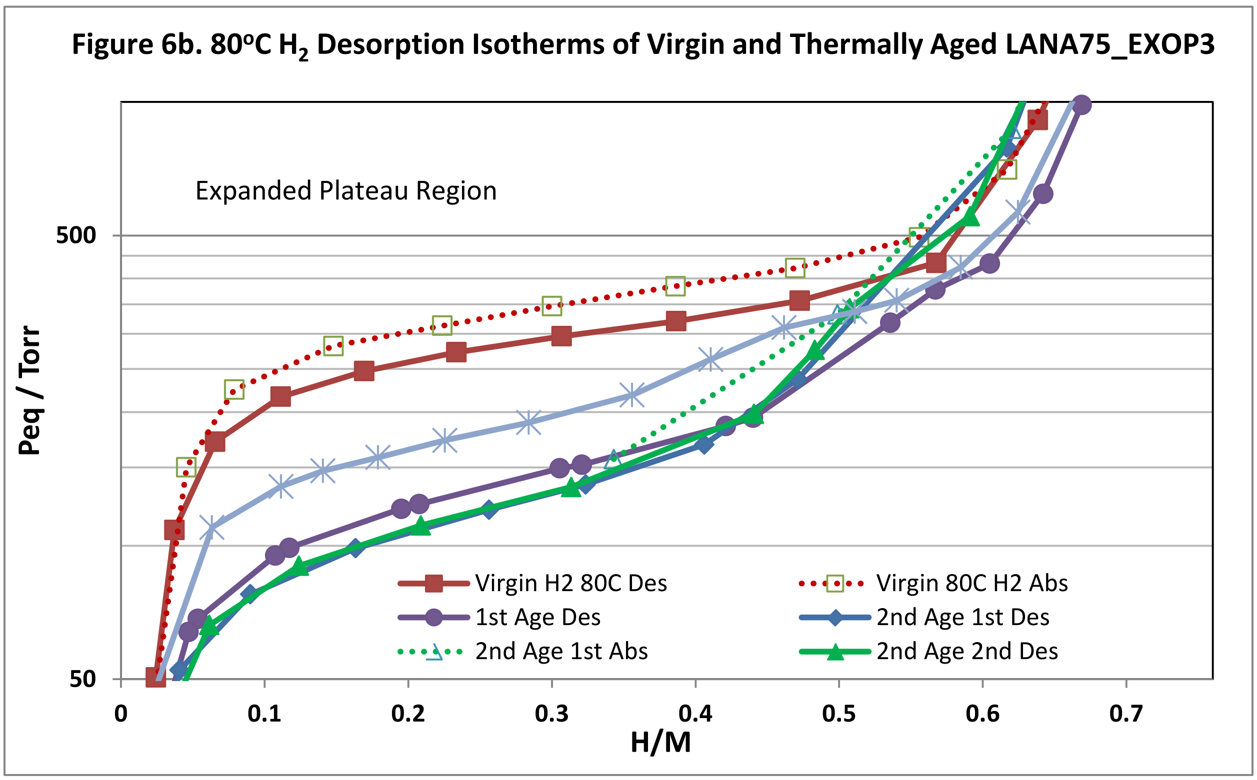


Figure 6b. 80^{o}C H_2 Desorption Isotherms of Virgin and Thermally Aged LANA75_EXOP3
Expanded Plateau Region
500
50
Peq / Torr
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
H/M
Virgin H2 80C Des
Virgin 80C H2 Abs
1st Age Des
2nd Age 1st Des
2nd Age 1st Abs
2nd Age 2nd Des

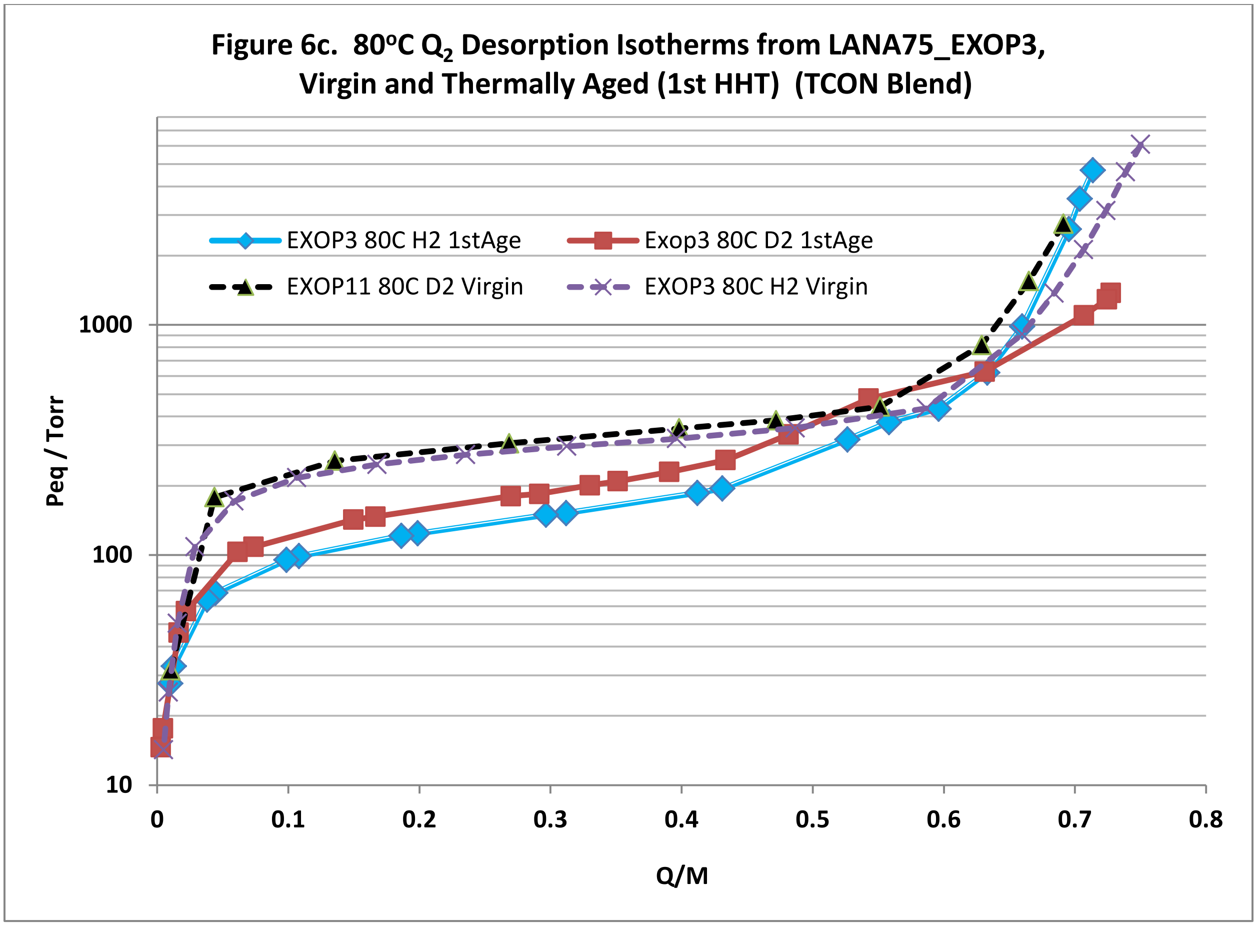


Figure 6d plots the H_2 isotherm plateau pressure for desorption as a function of total HHT time for the combined data plotted in Figure 6a and b. As was observed with the GFE LANA85 sample, there is an initial rapid decrease which then slows. Further aging will be conducted to determine how much further, if any, the pressure will be lowered.

Samples LANA75_EXOP4 (1316) and _EXOP5 (TCON blend) are being studied in short intervals (typically ~1 week of aging at a time) in an attempt to determine details of the aging process during the first one to three months. Figure 7a and 7b show the results for LANA75_EXOP4. HHT was only conducted on this sample for ~1 week at 240°C, in which very little impact is observed (Figure 7a). At most, the low Q/M portion of the isotherm may be slightly lowered (Figure 7b), and the beginnings of a dual plateau structure with a transition point near D/M = 0.2-0.3 may be observed. This is significantly lower than that shown in earlier Figures where HHT had occurred on a monthly interval. Further week-long HHTs are planned for this sample in the hopes of observing more details of the process.

Figure 6d. 80°C H_2 Desorption Isotherm Plateau Pressure for Aged TCON LANA75

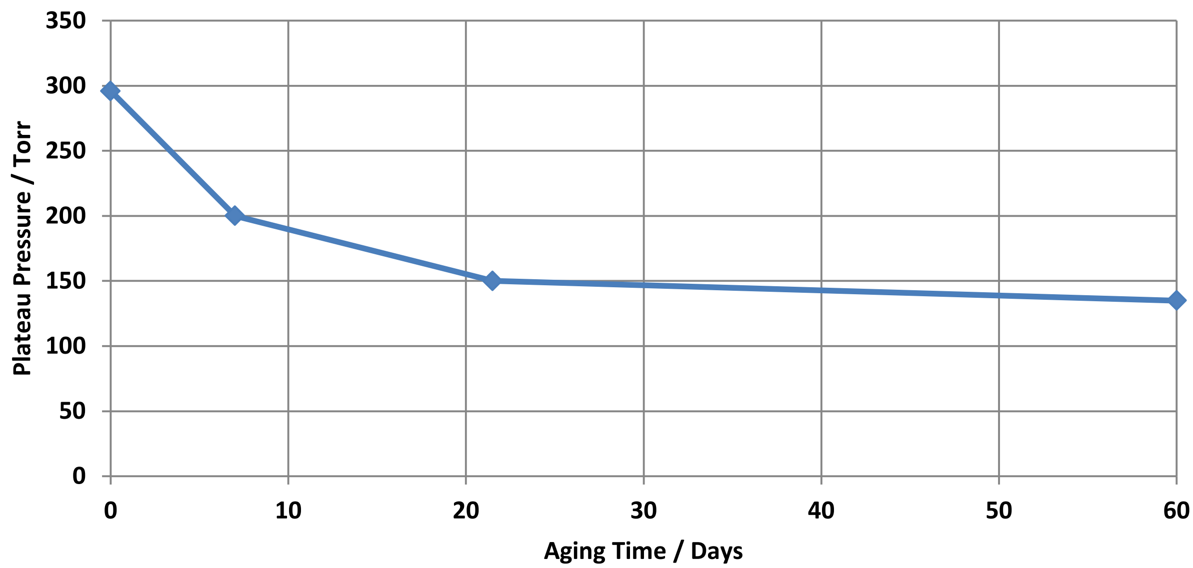


Figure 7a. 80°C D_2 Isotherms of Virgin and Thermally Aged LANA75_EXOP4

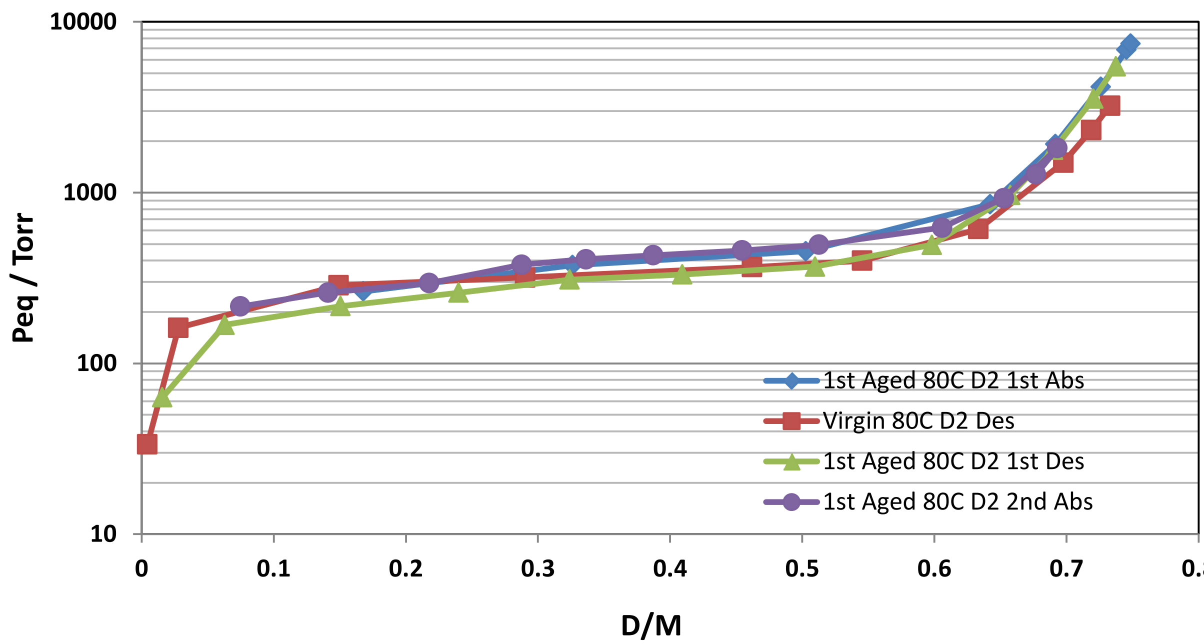
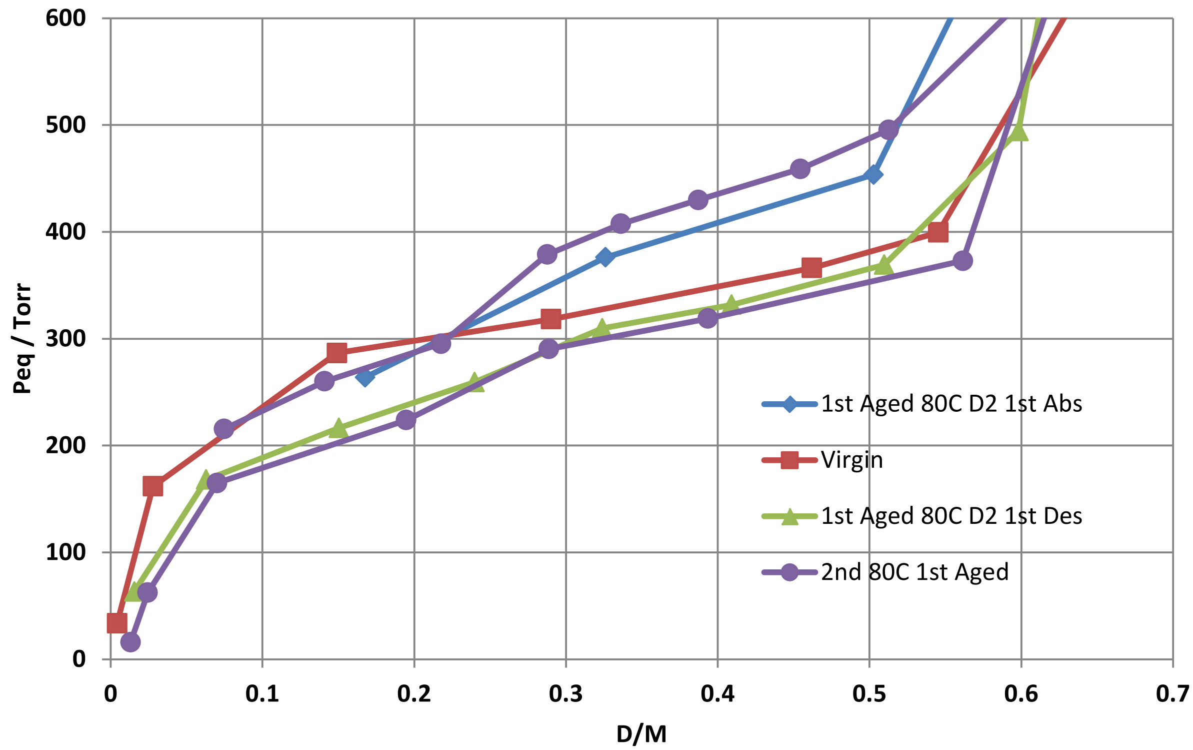


Figure 7b. 80°C D_2 Isotherms After 1st Thermal Aging of LANA75_EXOP4



Figures 8a, b, c, and d present data for LANA75_EXOP5, which has undergone week-long aging cycles at 240°C. Figures 8a and b show the 150°C and 80°C D_2 isotherms obtained from the sample after the first HHT. Both Figures illustrate the slight plateau pressure depression and the formation of a dual-plateau with a transition point at ~0.38 Q/M. The 150°C data are less cluttered, but the 80°C data shows 2 replicate runs illustrating the reproducibility of the data. Figure 8c shows the 80°C H_2 isotherms obtained after the 2^{nd} HHT. Apparently, not much additional depression is noted over the 1^{st} HHT cycle. The inclusion of the flat virgin material 80°C H_2 isotherms shows that the dual plateau structure develops because of the HHT. Figure 8d is an expansion of the middle pressure range of Figure 8c, which shows that the transition point on the dual plateau increased to H/M=~0.4. The virgin 80°C H_2 data are from LANA75_EXOP3.

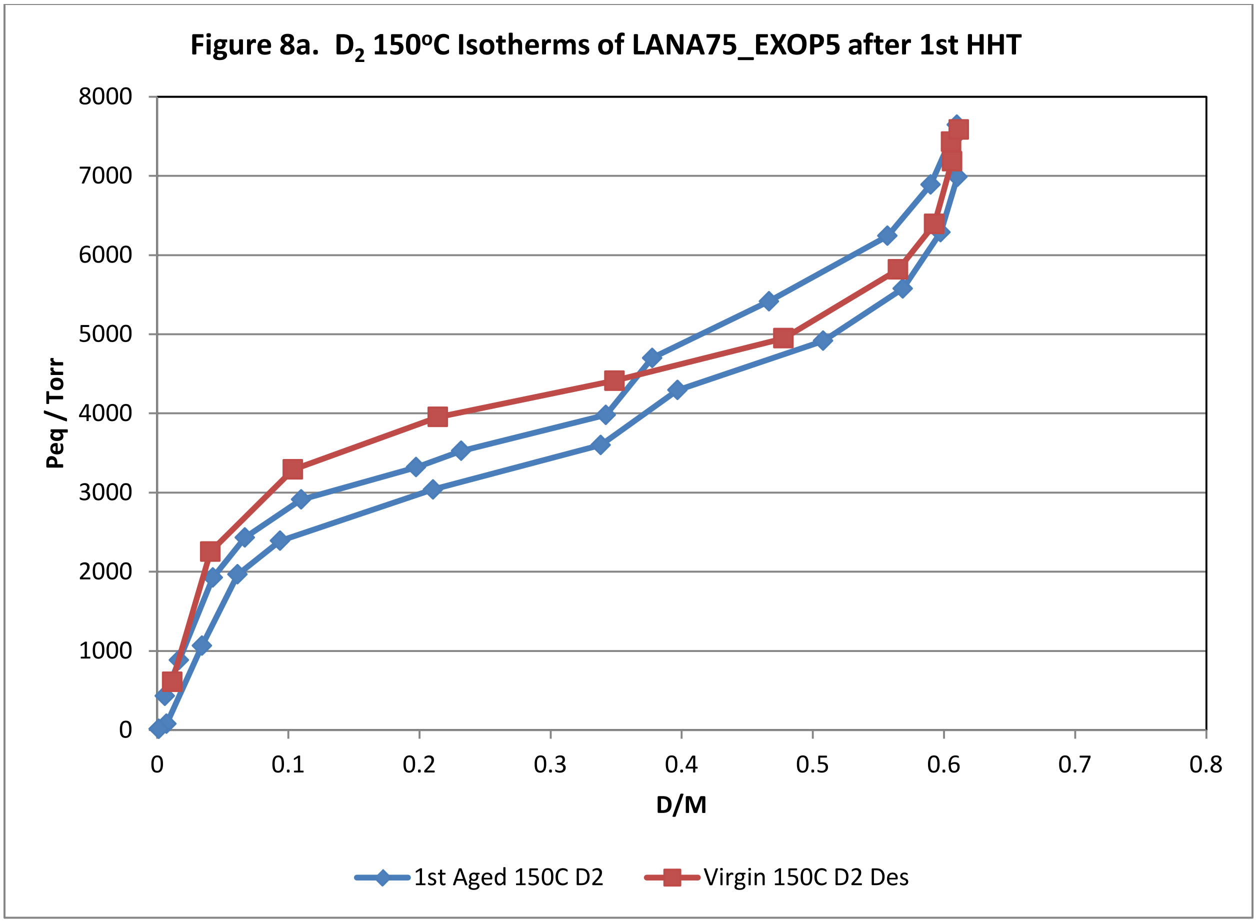


Figure 8a. D2 150oC Isotherms of LANA75_EXOP5 after 1st HHT
8000
7000
6000
5000
4000
3000
2000
1000
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Peq / Torr
D/M
1st Aged 150C D2
Virgin 150C D2 Des

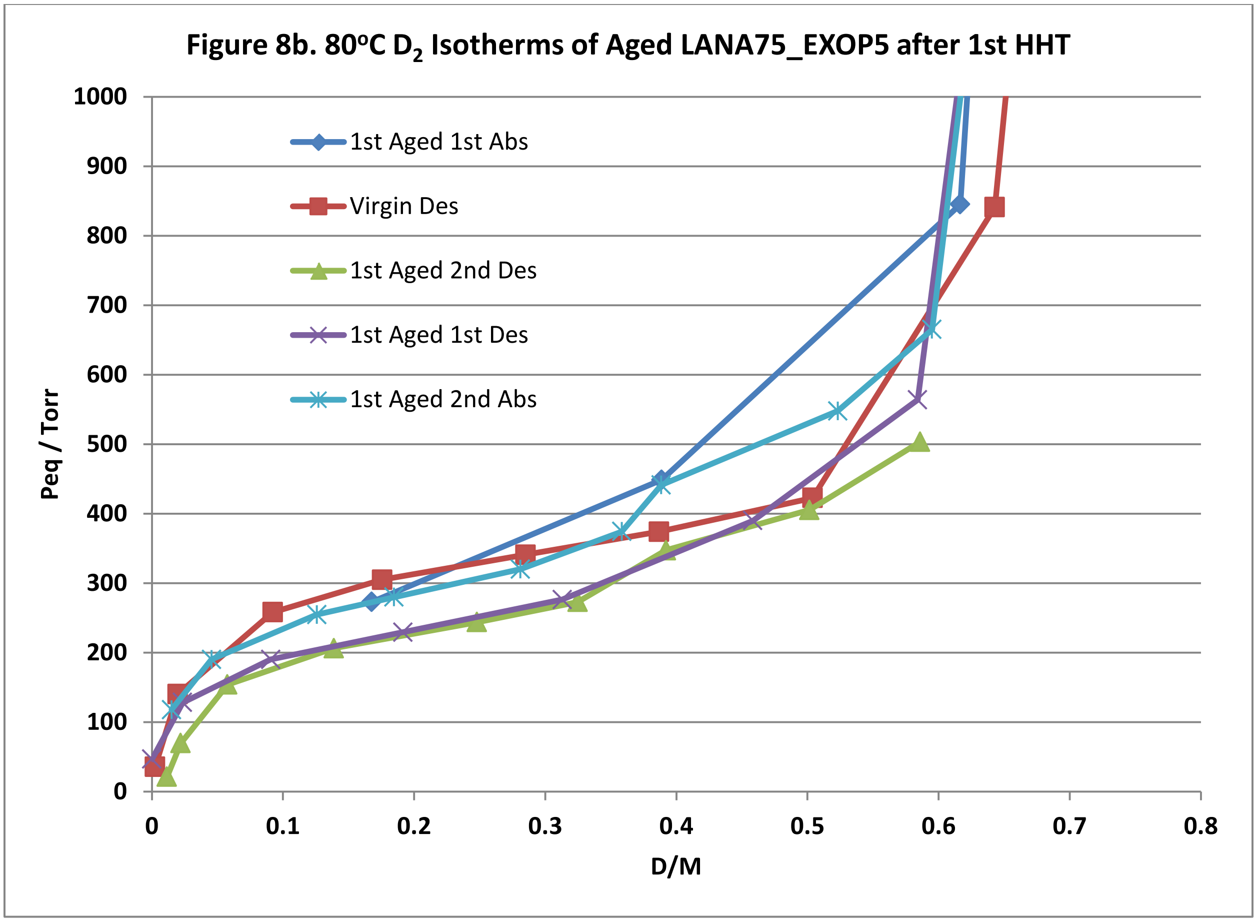


Figure 8b. 80°C D2 Isotherms of Aged LANA75_EXOP5 after 1st HHT
1st Aged 1st Abs
Virgin Des
1st Aged 2nd Des
1st Aged 1st Des
1st Aged 2nd Abs
Peq / Torr
D/M
0
100
200
300
400
500
600
700
800
900
1000
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8

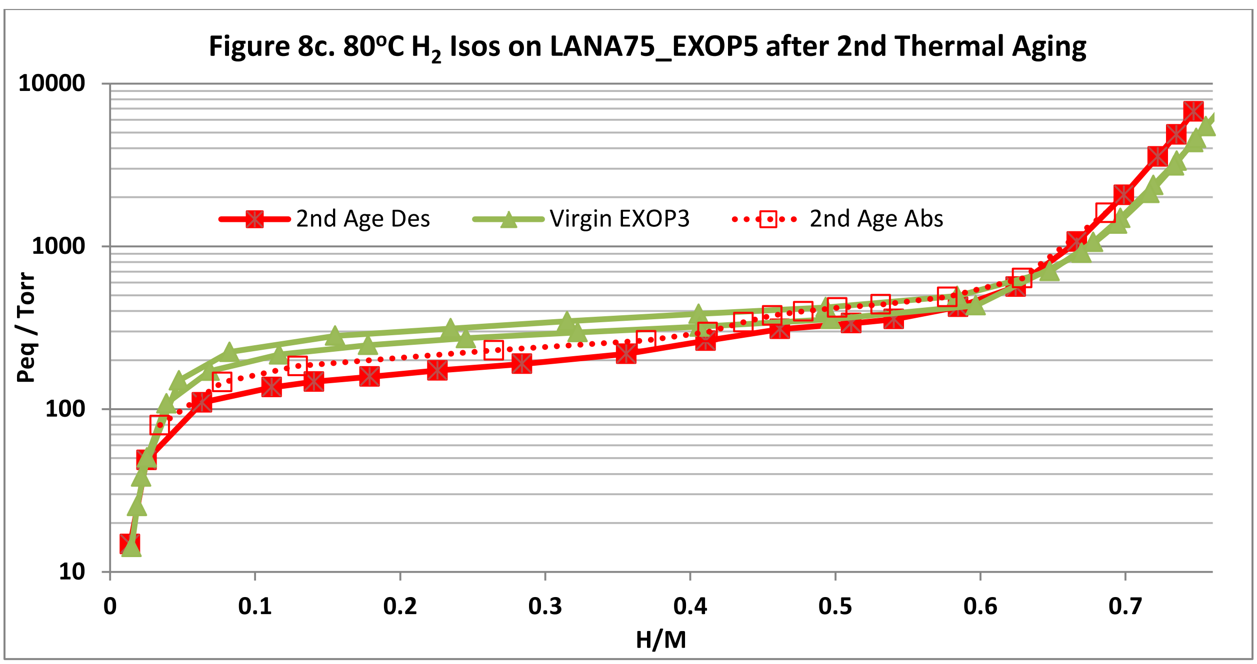
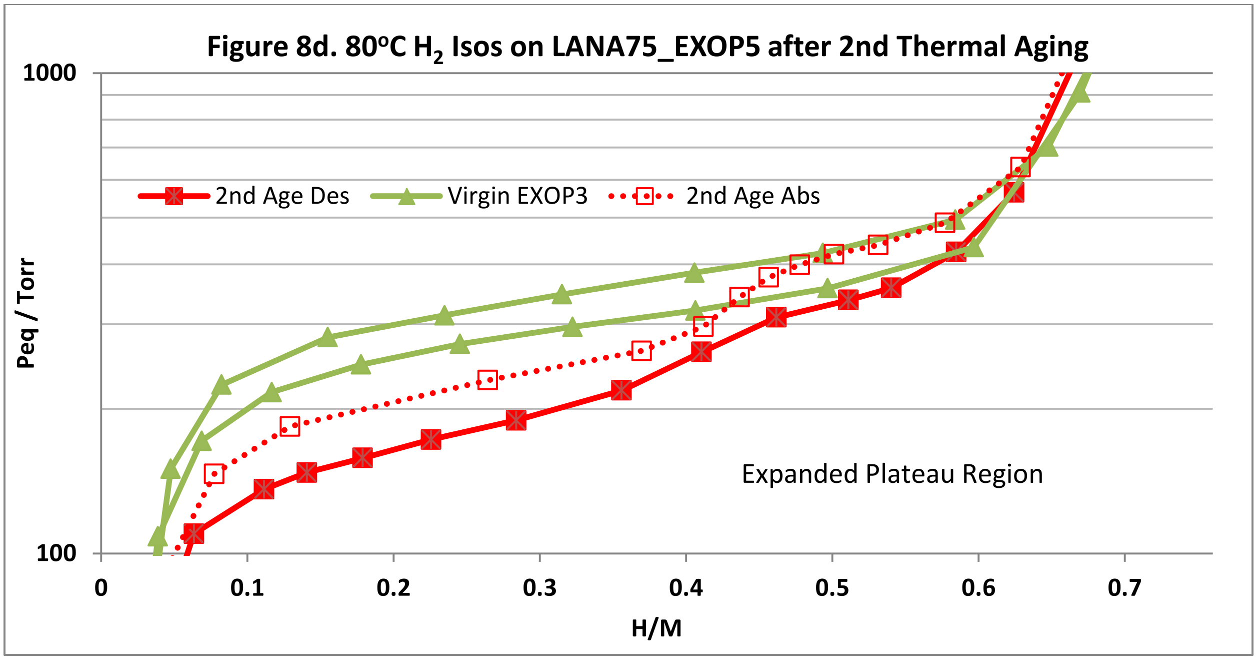


Figure 8c. 80°C H2 Isos on LANA75_EXOP5 after 2nd Thermal Aging
2nd Age Des
Virgin EXOP3
2nd Age Abs
Peq / Torr
H/M
10
100
1000
10000
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7



Samples LANA85_EXOP6 (GfE material) and LANA75_EXOP8 (TCON Material) were aged at 150°C for ~1 month. Figure 9 presents the results for LANA85_EXOP6, and shows no significant change in the plateau pressure, but a large decrease in capacity. It is unclear at this time if this result is real or an experimental artifact.

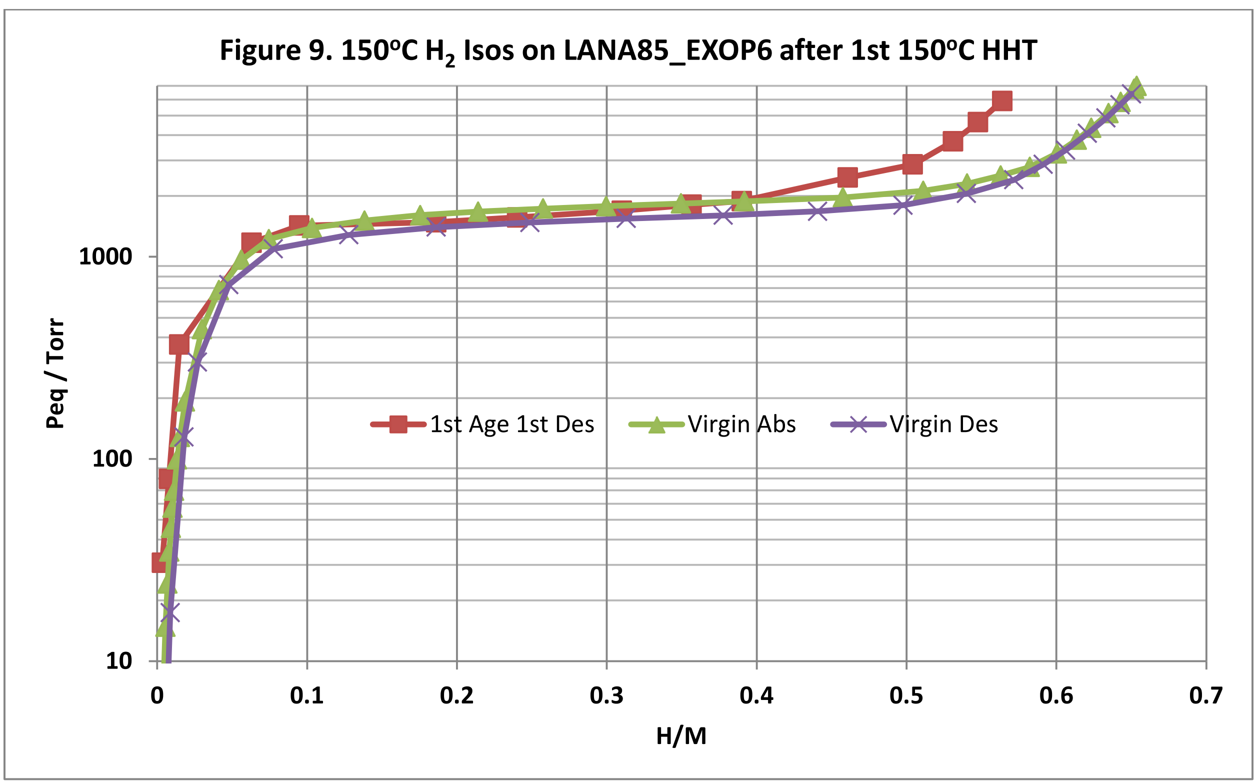


Figure 10 shows a 'merged' isotherm formed by combining data from several isotherms from LANA75_EXOP8. A slight plateau pressure depression is noted and a trace of a transition point to the dual plateau structure is seen at H/M=~0.47-0.48. Virgin data were obtained from LANA75_EXOP11.

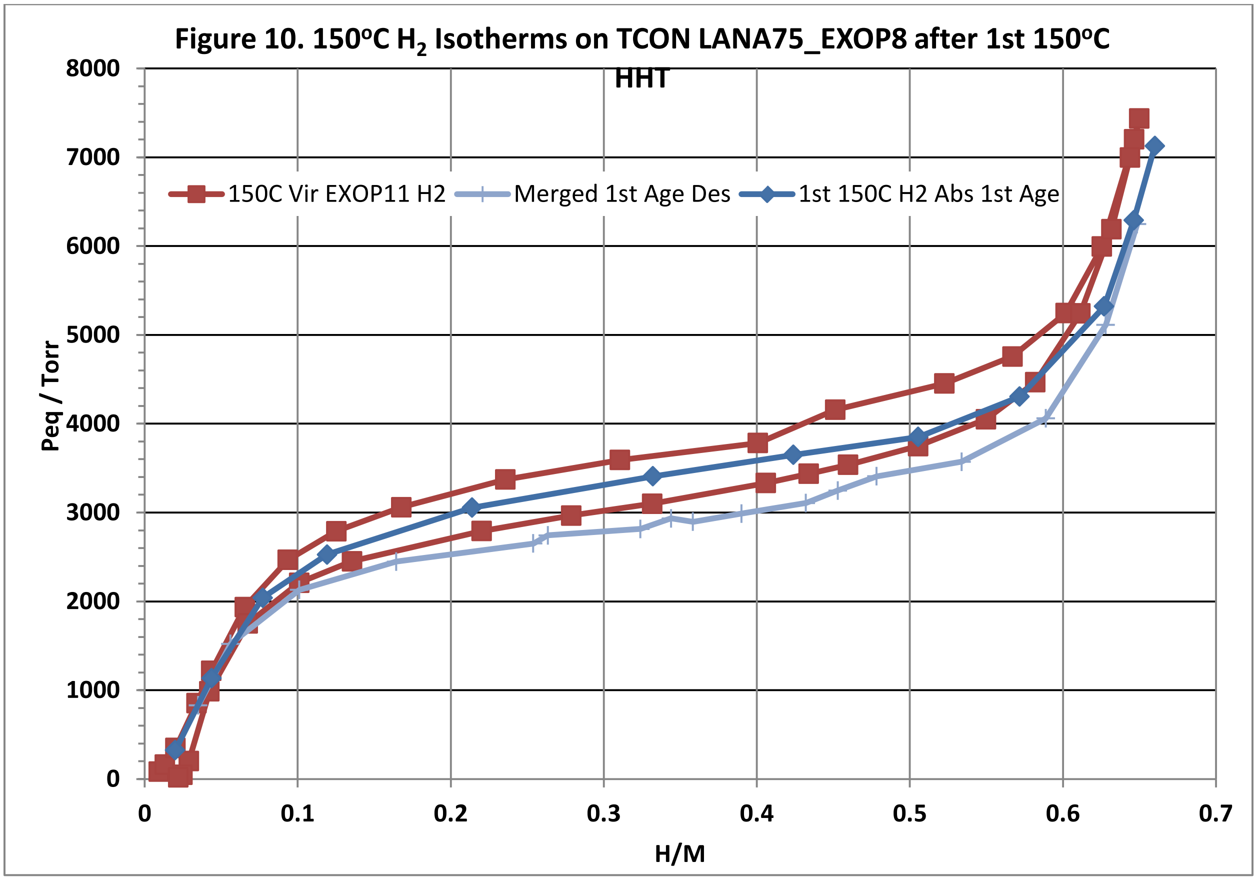
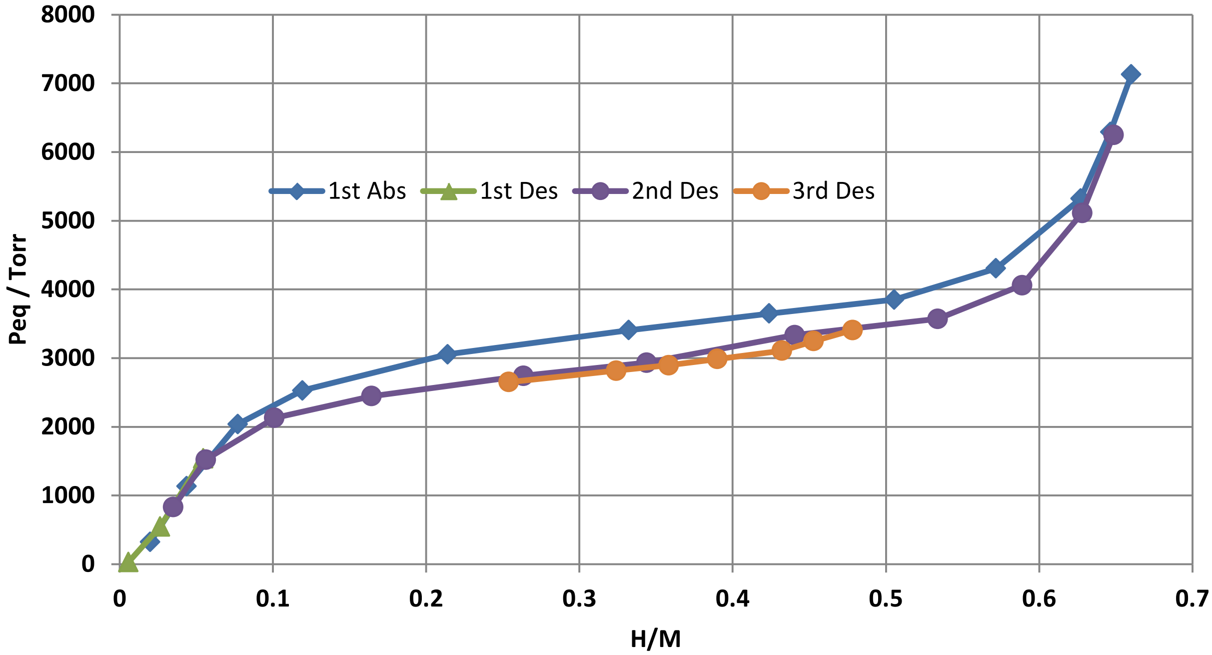


Figure 11 shows the 3 isotherms that were combined to form the 'merged' isotherm shown in Figure 10. The isotherm collection sequence consisted of an initial desorption directly after aging was terminated, followed by a complete absorption/desorption cycle, which produced the "1^{st} 150C H2 Abs 1^{st} Age" and the second 150C H_2 desorption. Because a slight inflection was noted at approximately H/M=0.45, a one-step load was conducted to return the loading to H/M~0.5, and another desorption using smaller steps was conducted to give the 3^{rd} desorption isotherm. The reproducibility of the data allowed for combining them to clearly illustrate the inflection point, which did not become clear until the 3^{rd} isotherm was collected.

The merging process consists of taking all the data from the three isotherms and sorting them into a steadily decreasing H/M value. This produces an 'isotherm' that typically appears to have more noise than the individual isotherms; however, this variability was already present in the separate isotherms and is just clarified in the merged one. In fact, one point was deleted from the merged isotherm from the 2^{nd} desorption located right at the inflection point simply to clarify the shape. The deflection at the inflection point can be seen barely above the noise level, and thus will need confirmation from more experimentation, but does seem to follow the pattern of the other samples.

Figure 11. "Unmerged" 150 °C H_2 Isotherms from Aged LANA75_EXOP8



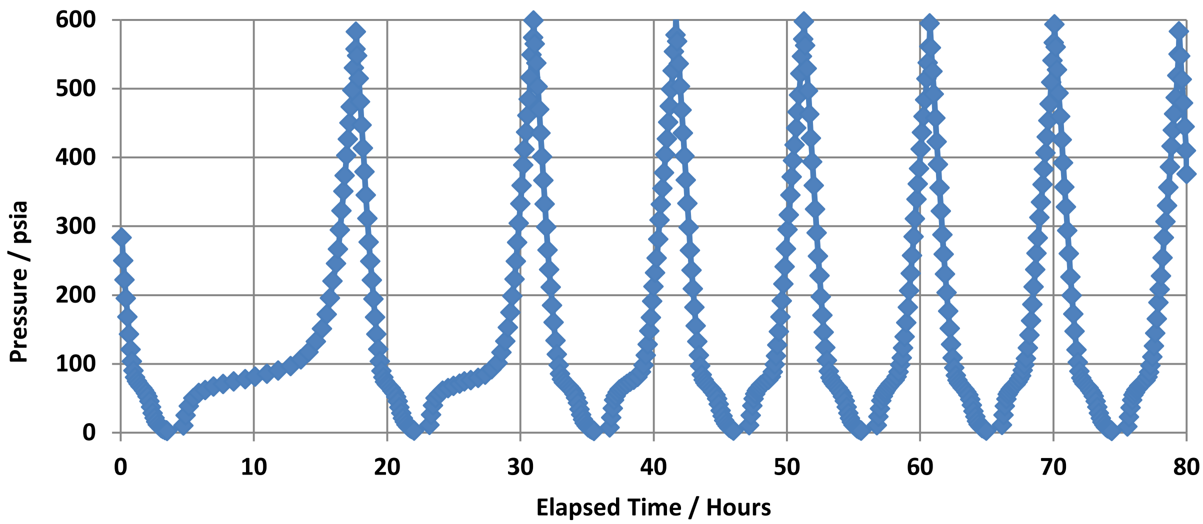
Kinetics (Dynamic) Results

Experimental work on the LANA85_GFE5 sample has shown that the absorption/desorption kinetics of the material at the lower isotherm temperatures slowed down considerably after multiple HHTs. The 80°C isotherm determination is no longer feasible on this sample as the observed equilibration time was on the order of 24 hours. Therefore, higher temperature isotherms are being examined, which has led to an effort to obtain some high temperature data on the new samples in preparation for being unable to obtain low temperature isotherms later in the program. Of course, higher temperatures means higher pressures and the primary isotherm determination manifold in HTRL Lab 134 is limited to 150 psia feed pressures. Strategies have been implemented to load at low temperature and then study the sample at high temperature; however, this essentially limits the ability to obtain high temperature absorption data. Later, the samples may be transferred to our high pressure manifold, a commercial instrument called the PCTPro, to obtain the absorption isotherms.

The PCTPro instrument presents a new capability in that it is significantly easier to obtain multiple isotherm cycles in a given period and thus it becomes possible to note cycle-to-cycle changes. One unexpected observation has been made based on this capability. Figure 12 shows the plot of *all* of the pressure vs. time data collected by the PCTPro from the LANA85_GFE5 sample after completing the 8th aging period. Six full absorption/desorption cycles are shown along with the initial desorption from the sample at the end of the aging period including a final partial cycle that was terminated during the desorption process.

The time needed to complete the first absorption process is clearly longer compared to that of the 4th through 7th absorptions. The second absorption likewise requires a longer time, but less than the first cycle. The 3rd cycle requires only a slightly longer time than the final cycles, and the latter cycles appear to be stable at a uniform time. This observation was unexpected, and an objective for FY15 will be to examine this phenomenon in more detail.

Figure 12. Pressure vesus Time for 200°C D_2 Isotherms from LANA85_GFE5 after 8th Aging Period



Summary

The newly added data clearly show a continuation of the results presented in the Interim Report. With multiple samples from each of the 4 types of hydride materials used, more details can be observed. The longest running data set is for the GfE LANA85 material. With ~280 days of HHT, the GfE material still has not developed the dual plateau structure seen in the 1-year scoping study sample. However, the prior extrapolation suggested the current age of the sample is near to the point where that may occur, and that is supported by the flattening out of the plateau pressure vs. aging time curve (Fig. 2). Presumably, the dual plateau will be observed in the next set of data acquired, or perhaps the following one. The observed difference in cycle time (Fig. 12) likewise promises interesting results from the upcoming work.

The 'other' LANA85 material seems to be behaving similarly to the GfE LANA85 material. It has shown plateau pressure depression but no formation of a dual plateau structure yet. However, the rate at which the depression advances seems slower, as there were only very small changes in the effects between the first and second aging periods.

The TCON LANA75 samples (EXOP3, 5, 8, and 11) have illustrated several features: (a) the existence of a dual plateau structure only in the absorption isotherm of virgin material, (b) plateau pressure depression and formation of a dual plateau structure in desorption isotherms at two temperatures (80 and 150°C), and (c) the *disappearance* of the dual plateau structure in the 150°C absorption isotherms upon HHT (Fig. 10).

The second LANA75 material is also showing effects similar to the TCON LANA75 material. However, more data are required from this material before extensive conclusions can be drawn.

As noted in the Interim Report, the explicit origin of the dual plateau structure is unknown. The dual plateau can indicate two different chemical phases present in the material, brought on by HHT. This might imply different chemical composition in different parts of the material. In the untreated material with a single plateau, the isotherms are interpreted with a picture that has the β-phase forming precipitates in the majority α-phase until the α–phase has been fully consumed, which presumes the formation of the hexahydride, $LaNi_{5-x}Al_xH_6$. However, literature data also indicate that some researchers[8] have observed the formation of the intermediate trihydride, $LaNi_{5-x}Al_xH_3$, which produces a dual plateau isotherm with a transition point at ~50% of full loading, i.e. Q/M~0.3-0.4, depending on the full capacity of the material.

In several of the samples, however, the transition between the two plateaus occurs in the Q/M region of 0.4 to 0.5, which is higher than expected for a differentiation based on observing the trihydride species. That would tend to suggest instead that some fraction of the samples is completely converting to a new structure with different characteristics. Presumably, more data would show the transition point moving higher or lower as the fraction converted changed with aging.

An example of this may be found with samples LANA75_EXOP2 and EXOP4. Both samples are based on the Ergenics Lot 1316 LANA75 material and both are being aged at 240°C. Sample EXOP2 has been subjected to 2 month-long aging periods, whereas EXOP4 has experienced a single week-long aging period. In EXOP4, the transition point is located near H/M~0.3, whereas in both sets of data from EXOP2, the transition appears to occur at H/M~0.5.

Samples LANA75_EXOP3 and EXOP5 are similarly related, both coming from the same lot of material (TCON blend) and both aged at 240°C. EXOP3 has been subjected to two month-long aging periods, whereas EXOP5 has experienced two week-long aging periods. The results are somewhat more complex with this material in that the 80°C D_2 isotherms of a 1 week aged EXOP5 show a transition only on the absorption isotherm at D/M~0.35-0.45 (Fig. 8b), whereas the D_2 isotherms at 150°C have transitions in both absorption and desorption curves at the same D/M values (Fig. 8a). After an additional week of aging, the 80°C H_2 isotherms (Fig. 8c,d) now show the transition point in both absorption and desorption isotherms at the same or perhaps slightly higher H/M (combined with a slightly greater plateau pressure depression). EXOP3 (see Fig. 6) was subjected to two month-long aging periods and shows a transition between plateaus at H/M~0.4-0.5. The transition point in EXOP5 appears to move up slightly between the first and second week-long aging periods, from H/M~0.35-0.40 to 0.45-0.50, whereas the transition observed after a month long aging period in EXOP3 occurs near H/M~0.5. See Figure 6b for a comparison of transition point location after 2 weeks (EXOP5 2nd HHT), 1 month (EXOP3 1 HHT), and 2 months of HHT (EXOP2 2 HHT).

3.3 Conclusions

The Interim Report's preliminary conclusions have been sustained with the new data obtained in the second half of FY14, which are repeated/updated as follows:

1.) LANA75 materials and other LANA85 material show HHT effects
2.) HHT effects occur differently in LANA75 than in LANA85, but the second lot of LANA85 mimicked the first in that only plateau pressure depression is noted to occur early on (possibly up to ~6 months of HHT). Therefore, dual plateau isotherms must develop later.
3.) The differences in HHT response suggest sensitivity to composition, which includes changes found from lot-to-lot in the same nominal material

The project as a whole progressed somewhat more slowly than originally envisioned. However, a large quantity of new information has been obtained and new conclusions are being drawn that are potentially important to the TF in terms of operating conditions and procurement specifications for replacement LANA materials, which meets the intent of this effort.

<u>3.4 Equipment Considerations</u>

This project has required the simultaneous running of multiple samples. The HTRL Lab 134 Manual Manifold 1 (MM1) had 6 test ports split evenly between two sides, but only 1 pressure transducer per side, limiting simultaneous operations to two samples. During this project, additional in-hand pressure transducers have been installed on sub-manifolds that have allowed the simultaneous examination of 4 samples on the MM1. In addition, the gas-inlet manifold connected to the Pfeiffer-Balzers High resolution GAM400 Mass Spectrometer System (which uses air-actuated valves) has been reconfigured to form 2 new submanifolds (Air-Actuated Manifold 1 &2, AAM1 & AAM2), adding the potential to run 2 more simultaneous samples. The laboratory eHAP was modified to allow operation of these new manifolds and to modify operational restraints to conform to current policies. These operational restraints required 12-15 new overtemperature protection devices to be ordered. In addition, several new PID-based heater controllers have been ordered, of which 2 have been received.

The high pressure capability of HTRL Lab 134 is limited to the commercial instrument known as the PCTPro. Although the other manifolds are limited to 150 psia feed pressures, which limits obtaining higher P and T absorption data, the PCTPro is capable of handling up to 3000 psi. Unfortunately, this instrument is becoming aged, and has recently suffered some equipment issues (resolved prior to this fiscal year). One item of particular potential significance is the fact that the PCTPro control software is a commercial product that runs on Windows XP, which has just stopped being supported by this Site and the manufacturer. In addition, part of the issues noted above was a computer crash because of a failed motherboard. We are currently operating using an old laptop running XP, but we have no backup identified (we were unsuccessful in getting the software to run on Windows 7). If this computer fails, we will be unable to continue this project until an alternate solution is found and implemented, as the PCTPro is used to charge the samples to 30-40 bar (430-580 psia) in the HHT treatments. Software upgrades for the PCTPro software are available and may be ordered in FY15. If so, some downtime will be experienced while installing and testing the upgrades.

The vacuum pump used to evacuate the PCTPro is nearing its maximum lifetime and is becoming noisy (a sign of imminent failure). A replacement pump is available, but it was recently discovered when the MM1 manifold vacuum pump was replaced with an identical unit that the pump leaks hydrogen to the room and sets off the PCTPro hydrogen leak detector, which immediately shuts the PCTPro down. Furthermore, the new pump, a Varian SH-110, does not appear to work well while pumping hydrogen in that when it pumps hydrogen it subsequently is unable to attain its normal base pressure. On the MM1, this can be overcome by allowing some air to go to the pump via a manifold vent line and be pumped away. Subsequently, the pump recovers its baseline. However, that approach will not be possible with the PCTPro, especially during unattended operation. Therefore, a better pump will have to be identified and ordered to replace the current aging one.

The data acquisition system used on MM1 needs to be upgraded, particularly for monitoring more temperatures, perhaps even from thermally aging samples. This is not likely to be too difficult because a second FieldPoint unit had been added previously for temperature monitoring in another project. The thermocouple wires from that unit simply need to be repositioned and connected, which will hopefully be completed in early in FY15. However, the current MM1 software was modified to handle additional Paroscientific pressure transducers, thus the Labview program that ran the extra thermocouple monitoring must have the same modifications performed on it.

4.0 Contaminant Effects: Objective C – Impact of Common Contaminants/Poisons

4.1 Background

Contaminants such as carbon monoxide (CO) and sulfur (S) are known to cause hydrogen absorption/desorption issues in Pd-based materials. Some new materials were developed here at SRNL through joint research with Prof. T. Flanagan from the U. of Vermont to address CO contamination[2]. The CO effect could be induced either by adding CO to the hydrogen or by pre-exposing the Pd-material to CO. The CO would be retained even after evacuation, as was shown by the continued loss of absorption ability. However, heating the material with or without additional oxygen often reverses the problem. Unfortunately, S is known from the literature to be very difficult to deal with once it has appeared on the Pd material. Also, there has been a study[6] of the impact of a continuous feed of a CO-contaminated hydrogen feed to a LANA material that showed it also hampered hydrogen absorption. The goal of this part of the project is to determine the importance of these factors to TF-type LANA materials. To that end, several experiments were outlined in the TTP to investigate these issues.

4.2 Progress

To be able to handle CO and S derived from H_2S, a separate gas handling manifold was constructed, which was placed inside a chemical fume hood for toxicological control in the event of leaks or releases. The manifold uses a scroll pump and air-operated valves. An air-actuated valve controller has been installed that will allow remote valve operation either manually or via computer control. The assembled manifold has been vacuum tested and the remaining critical activity that needs to be completed is to obtain permission to proceed via a signed eHAP. This process is currently awaiting completion of the pressure protection calculation for sizing rupture disks/relief valves, at which point they can be ordered and installed. Subsequently, the eHAP can be completed and permission to operate can then be obtained. At that point, the plan is to first work with CO, as it has little memory effect, to determine its effect on LANA characteristics, followed by the use of H_2S to deposit S on the LANA samples. Excess CO and H_2S have been located and are in the process of being transferred to the hood in HTRL Lab 134.

5.0 Conclusions and Path Forward

To date, significant progress has been made despite setbacks as a result of unexpected shutdowns and experimental difficulties due to capability expansion. The following conclusions can be drawn from the results obtained thus far: all LANA materials show plateau pressure depression as a result of HHT effects; different LANA materials show additional effects to differing extents; and these responses indicate minor compositional variation, which can result in noticeably different behavior over time, indicating that lot-to-lot variations can be important. We have also observed an interesting kinetics issue in which the first few absorption/desorption cycles on the LANA85_GFE5 sample show hindered absorption, which disappears at a certain point only to reappear after more aging.

One reason to study HHT effects is to mimic the plateau pressure depressions that occur as a result of tritium aging effects. This has become even more apparent at the end of FY14, as the plateau depression seems to be reaching a maximum, which is also similar to tritium aging effects on LANA75 (where the plateau pressure drops and a heel grows in to a point, but afterwards the isotherm shape becomes less and less 'plateau-like'). Thus, the implication that lot-to-lot variations may be important in HHT can potentially infer that tritium aging effects may show such dependencies as well. This aspect has not been thoroughly investigated in the Tritium Exposure Program.

In FY15, work continues to quantify these behaviors and to build and implement a manifold for handling and studying the effects of toxic substances known to be poisons for hydrogen absorption in LANA materials. We will also be continuing to upgrade and replace components of our research hardware and software. A new FY15 TTP will be written and submitted for approval detailing the planned FY15 efforts.

6.0 References

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