Characterization of the β-phase Region of the SAS Compressor Bed 1 Material (LANA10)

Kirk L. Shanahan

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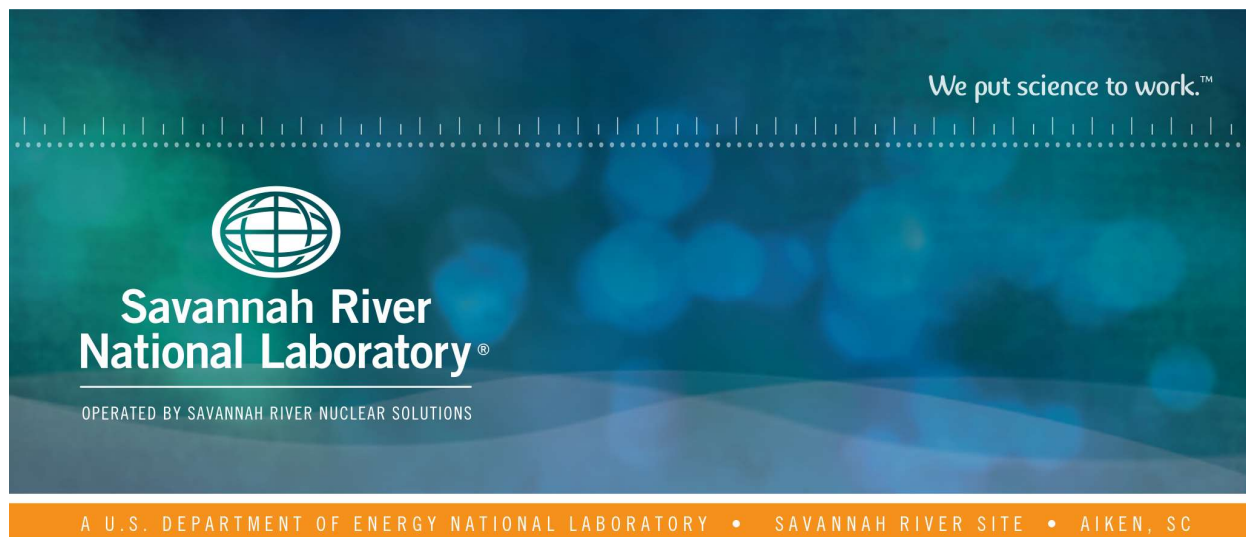
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EXECUTIVE SUMMARY

Isotherm data have been acquired and analyzed on the SAS Compressor Bed 1 material in order to define a method to set the initial bed Q/M value when freshly filled after inventory. β-phase data from eleven protium and two deuterium isotherms have been combined to determine a method for calculating the bed Q/M value given a β-phase equilibrium pressure at temperature. This method is a two-step method; first, the plateau pressure is calculated based on the isotope used and the temperature of the bed, and second, the measured equilibrium pressure is divided by the computed plateau pressure to obtain the reduced pressure, which is then inserted into the β-phase equation to calculate the bed's Q/M value. Error sources and effects are discussed, with the conclusion that the 'true' reduced isotherm has been determined in the β-phase which will allow virgin bed inventory to be determined to ~3-4% accuracy.

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LIST OF ABBREVIATIONS

SRNL	Savannah River National Laboratory
TF	Tritium Facilities
SAS	Sample Assay System
LANA	La-Ni-Al Alloy
CB	Compressor Bed
H	Hydrogen Isotope Protium
D	Hydrogen Isotope Deuterium
T	Hydrogen Isotope Tritium
Q	All Hydrogen Isotopes (H + D + T)
M	Metal Atom
Q/M	Hydrogen (all isotopes) Concentration in solid hydride material
Peq	Equilibrium Pressure (in Torr)
P_{plat}	Equilibrium Plateau Pressure (in Torr)
SS	Stainless Steel

1.0 Introduction

The SAS Compressor Bed (CB) is to be included in the physical inventory reconciliation performed once every 2 years in the Tritium Facilities (TF). It is desired to use the SAS Storage Bed Inventory methodology to accomplish this, which fills the bed with a known amount of gas, measures the equilibrium pressure, and computes the bed Q/M value based on the isotherm characteristics of the bed's hydride material. This point then becomes the starting point for the subsequent T transfers into and out of the bed. The bed material information that would allow that to be done for the SAS Compressor Bed was not available, however. Therefore, a sample of the bed material was prepared and protium (H_2) and some deuterium (D_2) isotherms were determined on the material at ~25, 30, 45, 50, and 60 °C. The isotherms were converted to 'reduced pressure' isotherms by dividing the equilibrium pressure values by the plateau pressure determined at Q/M=0.5, which collapses the isotherms on top of each other.

The series of reduced isotherms shows 3-4% variation in their absolute H/M values. Standard Propagation of Error calculations indicate this is consistent with error bars computed from instrument errors typically observed in practice. However, the resulting spread in the β-phase region produced statistical fits of the data that were of low quality. Therefore, strictly to produce a reasonable mathematical model, the isotherms were arbitrarily shifted on the H/M axis to reduce the spread and allow the extraction of a mathematical equation representing the isotherm in the β-phase region. The shifts utilized in this process were equal to or less than the error size noted in the raw data. This generic equation is then assumed to give H/M values accurate to the 3-4% level found in the original data. It is entirely possible to choose a different degree of arbitrary shift, and thus to shift the computed Q/M values slightly. The optimum value must be determined in the actual application. The details and results of this effort are described below.

2.0 Experimental Procedure

The SAS CB material is reported to be nominally a LANA05 ($LaNi_{4.95}Al_{0.05}$) material. This material was purchased from Ergenics, Inc sometime in the 1980's and is designated as lot 1500-V-2. This material was previously studied at higher temperatures (~50-250 °C) for another project, the Unloading Line B Project (ULBP). However chemical analysis of it for the ULBP showed that it was actually closer to a $LaNi_{4.9}Al_{0.1}$ (LANA10) material[1]. It was observed to be a slightly La-poor, which was a typical manufacturing specification used during that time period. The large difference in melting point between Al (660 °C) and Ni (1455 °C) (La – 920 °C) allows Al loss to occur during the alloy formation process and makes it somewhat difficult to control the final Al content of an alloy. Herein the material will be referred to as LANA10 material.

Isotherms were determined in an all-SS, manual Sieverts' apparatus. Volume calibrations were done with argon at several temperatures between 20-70 °C. Cell volumes for the isotherm determinations were calculated from a straight line fit of that data. The usual spreadsheet isotherm calculation was conducted with a single, temperature dependent test cell volume. In one case, an anomalous result was obtained at one point that caused the desorption β-phase to shift suddenly to lower Q/M (the desorption isotherm should overlay the absorption in theory). After attempting several minor changes to the data, it was found that the only thing that corrected the shift was a temperature adjustment of 0.05 °C at one point, which is within the electronic noise of the thermocouple. (Other adjustments would fix the single point, but the subsequent ones remained shifted.) For this project, the corrected value was used. This extreme sensitivity to the exact numbers used in the calculations has been noted before. Because of this observation, a modified

spreadsheet calculation that calculated the test cell volume from the linear fit was used for each individual equilibrium point. This was not found to significantly alter the results, so it was not employed in this analysis.

Pressures were measured with either a calibrated MKS Baratron or a Paroscientfic pressure transducer. Pressures were routinely corrected for zero offset. Sample temperature was measured with a calibrated type K thermocouple placed in a thermocouple well that penetrated the side of the barrel shaped sample cell. It is likely the thermocouple well did not extend into the hydride powder. Temperature deviations of a few tenths to a few degrees were observed during isotherm determinations. The room temperature reading of the sample thermocouple agreed closely with several other thermocouples concurrently measuring room temperature, thus no significant manufacturing offset in reading is anticipated, and temperatures are used as recorded by the data logging system and in the lab notebook (WSRC-NB-98-00260, sample ID LANA10_SASCB1). Likewise, manifold temperatures were also measured with type K thermocouples fastened to the ¼" SS manifold tubing. The manifold was constructed of Swagelok and Cajon parts fitted with 4-VCR (metal-to-metal gasket) fittings. All gaskets used were SS. The sample, which decrepitates into small particulates that can be entrained in the gas flow, was isolated and contained with a 0.5 micron filter gasket.

The material had been stored inside a plastic bag held in a paint can from the time of purchase. 3.242 grams of the material were placed in a standard SS sample cell and assembled with a valve and SS stand-off tube into a usual test cell assembly. The sample was activated initially with mixed H/D gas of unknown composition by heating up to 100 °C under hydrogen pressure, followed by cooling to room temperature. Hydrogen absorption began on the first activation cycle. Two additional cycles were used to complete the activation. Following that, duplicate protium isotherms at ~25 and 30 °C were determined, followed by duplicate deuterium isotherms at ~30 °C, for a total of 6 full absorption-desorption isotherm cycles.

The isotherms never completely closed the mass balance. Upon cycling through an absorption/desorption cycle, there routinely was a 0.01-0.02 gap in the alpha phase branches. This is thought to be due to accumulated measurement errors arising from the various sensors. A propagation of errors calculation conducted elsewhere on isotherm data supports this conclusion. This leads to the need to decide how to handle the impact of these errors. In the analysis below, primarily desorption data is used, and thus the desorption data will be shifted on the Q/M axis towards more theoretically correct positions, i.e. where the Sieverts' plots of the low pressure α-phase data intersect the (0,0) point. More detailed discussion of what was done is given below.

Analysis of the initial set of isotherms suggested a 1-2% (0.01-0.02 H/M units) variation in the β-phase region of the isotherm. Subsequent discussion led to the belief that higher temperature isotherms were needed as well since the CB was to contain tritium, and the tritium decay heat would raise the bed temperature somewhat. Therefore, higher temperature isotherms were determined. Attempts to collect isotherms at 70 °C were abandoned as the plateau pressure was too high to give good β-phase results given the 150 psia pressure limit of the apparatus. 60 °C isotherms gave some information in the useful region of the β-phase part of the isotherm (typically at least ~2X the desorption plateau pressure) and two desorption isotherms were determined at that temperature. In addition, a 45 and a 50 °C isotherm were determined in order to produce sufficient data for a good van't Hoff plot. Since the first 60 °C reduced isotherm disagreed slightly with the prior 25 and 30 °C isotherms, an additional 3 isotherms were determined at ~30 °C for comparison to the prior runs at that temperature.

The chronological sequence of runs (and run labels) is illustrated in the row order presented in Table 1. Two levels of manipulation were required to develop the model equation for the β-phase region and details of this process are discussed below. Some adjustments were made to the raw data in order to improve the fitting process (which is not to be taken as altering or improving the variation in the raw data) and these adjustments ('alpha phase' and 'beta phase') are noted in Table 1 as well (details described later). As noted, the cumulative error leads to a failure to close the isotherms completely in the low Q/M region. Therefore, it should be expected that the 'alpha-phase' adjustments would be negative in order to move the termination point of the isotherm towards the (0,0) point. The beta-phase adjustments also appear as all negative, however of more importance is the difference between the alpha- and beta-phase adjustment for a given isotherm. That value is always zero or positive in this study. It is possible that the average beta-phase adjustment (0.0225) should have been centered on zero, however the maximum addition was 0.045 Q/M units, and thus falls within the expected random error. If a different offset is determined to be preferred, the difference in the offsets can simply be added or subtracted from the model proposed in this report.

The study temperatures were chosen to be close to the nominal glovebox operating temperatures. Fully unloading the material at the study temperatures is difficult due to diffusional limitations. Full unloading would normally involve heating the sample under vacuum to over 100 °C, but this imposed a large experimental delay (>24 hrs.) due to the time it took to recover the isotherm temperature because of the thermal mass of the GlasCol beaker heater used to heat the sample used for some of the isotherm determinations. The remainder of the determinations used a Neslab RTE-111 constant temperature bath which used a thermal fluid limited to below ~90 °C. Therefore, it was decided to forego the bake outs of the sample.

In some cases, sample evacuation lasting at least overnight (sometimes longer) at temperature was conducted. No evacuation was performed after the 1st 30°C H_2 run, and only a 2-hour evacuation was performed after the 2nd 30°C H_2 run. Similarly, for the 2nd 30 °C D_2 run, the 2nd 60 °C run, and the 50 °C run, the sample was not evacuated prior to beginning that isotherm. The following isotherms were simply started at the prior run's endpoint. This did not appear to affect the β-phase or plateau region results noticeably compared to using prior evacuation.

The absorption isotherms were not as fully determined in the α and plateau regions as in the β-phase regions. This makes the plateau pressure determination for the D_2 absorption isotherms more problematic, but the final results in the β-phase region were consistent with the H_2 results (see below). The D_2 desorption and H_2 absorption and desorption plateau pressures were determined by selecting several points from the plateau region and fitting them with a least-squares routine (Excel). Then the plateau pressure was calculated from that fit for Q/M = 0.5. Those plateau values were used to divide the pressure values for all the isotherm to compute the individual reduced pressures. The natural log of reduced pressure for the β-phase regions were all combined to derive a quadratic and cubic fit predicting Q/M as a function of $\ln(P/P_{plat})$, again with least-squares regression. Issues relating to precision and accuracy and the ability to extrapolate the data will be discussed below.

In developing an equation describing the β-phase region a reduced pressure isotherm technique was used. This follows the work of Suda, et al[2], who attempted to fit full reduced isotherms with a complex 6-parameter model. The 'reduced pressure' approach requires that the pressure values of the isotherm data points be divided by the plateau pressure of that isotherm. Of course, the plateau pressure shows hysteresis effects between absorption and desorption. This introduces a difficulty in the β-phase region (and the α-phase as well), since the absorption and desorption branches theoretically overlap and dividing the overlapped data by different plateau pressures will separate

the lines, not merge them. Therefore, only desorption data were actually used in developing the β-phase model.

3.0 Results and Discussion

Because of the failure to close the mass balance on the real isotherms, herein we will use the alpha-adjusted desorption isotherms as the initial basis to examine the data. This will shift the absorption isotherms as well, and in some cases will cause the first point or two on the low Q/M end of the absorption isotherm to fall at negative H/M values, which is physically unreal. However, in computing reduced pressure isotherms, dividing the absorption isotherm by its plateau pressure causes the β-phase region to fall below that of the desorption isotherm, which is also theoretically incorrect. The procedure used in developing the β-phase region equation will therefore be restricted to using the desorption data. In principle, the β-phase region absorption isotherm data could potentially have been treated as if it were desorption data, since the isotherms theoretically and experimentally overlay (barring noise) in the β-phase region, and could have been divided by the desorption plateau pressure, but that requires selecting which points of the absorption data could be included or not, adding another layer of complexity to the model development. Having more data points would theoretically improve the equation fits, but *it needs to be remembered that the error band of this method is not related to the end quality of the fit equation since that is being artificially improved.*

These issues are perhaps best illustrated graphically. To begin, in Figure 1 all of the raw (unadjusted) isotherms are presented on a semi-log plot. Because of the random variation, the isotherms show a considerable spread that makes fitting the β-phase region problematic. To facilitate the fitting process, adjusting the desorption isotherms by adjusting their position on the Q/M axis was desirable. The method used first was to plot the final 3 or 4 data points from a desorption isotherm on a Sieverts plot, which uses the square root of the pressure on the Y axis. That portion of the isotherm is theoretically supposed to form a straight line whose origin is (0,0). When that line in the real data did not go to (0,0), the isotherm was shifted by adding an appropriate constant so that the intercept was (0,0).   Those additions are listed in Table 1 as the 'alpha phase' adjustment. All but one are negative, an expected result give the accumulation of random error as the isotherm determination progressed. These adjustments were then applied to the whole isotherm.

The alpha-adjusted isotherms are shown in Figure 2. Note the compression of spread in the alpha region, basically into two subsets, absorption and desorption, and the translation of the variation into the beta region. This is illustrated more clearly by expanding the low Q/M portion of the isotherms as shown in Figure 3 (which is derived from Figure 2). This process shifts the raw data variation primarily into the β-phase region, as illustrated in Figure 4.

It is worth noting that the lines connecting the data points on the graphs are simple dot-to-dot connections and do not reflect the underlying isotherm curve shape. In Figure 4, examination of the '60C-2' curve shows a final point at a substantially different position from the rest of the isotherm, This is due to the fact that this last point was obtained by cooling the sample from 60 ºC to 30 ºC without any addition or removal of hydrogen. Thus, this last point represents a checkpoint on the other 30 ºC isotherms. Similarly, the absorption portion of the '30C-4' isotherm is acquired at elevated temperature, but the desorption portion is at the stated temperature. (Note that this means there is no absorption data at the designated temperature for those isotherms.)

The final Q/M values obtained from the alpha-adjusted pressure isotherms at Peq=7000 ranged from 0.94 to 1.02. However, that data includes the standard temperature dependencies of hydrogen isotherms, which will shift the isotherms acquired at higher temperatures down on the Q/M axis for a given pressure. This effect can be compensated for by using the reduced pressure approach mentioned previously, which requires knowledge of the plateau pressures at different temperatures. That information can be extracted from the data in the following manner. Note that at this point all Figures will utilize alpha-adjusted data. However, none of the following manipulations will reduce the inherent error levels present in the raw data.

Plateau pressures (P_{plat}) were determined by fitting the plateau region data with a linear fit and then computing the P_{plat} at Q/M = 0.5 from the fit equation whenever possible. The D_2 absorption isotherms did not have enough plateau pressure points to do this. In fact, the '30C-1 D2' plot had only 1 such point and the '30C-2 D2' plot had two. The single point value is used for the 1st 30ºC D_2 absorption plateau value. The average of the two points from the '30C-2 D2' data is reported and employed herein for the 2nd 30ºC D_2 isotherm. An interesting effect was noted in the second 30 ºC D2 desorption isotherm, known in the literature as 'the large aliquot effect'. Essentially what happens is that lower equilibrium pressures are obtained on the plateau when small aliquots (resulting in small Q/M changes) are taken as compared to values obtained when large aliquots are used. Figure 5 shows the '30C-D2' desorption isotherm. When subsequent plateau points are close together it can be seen that the equilibrium pressures are lower. Since the anticipated use of the model developed herein will utilize a large aliquot change, the van't Hoff analysis used the large aliquot values for the equilibrium plateau pressure (the three points at ~D/M values of .3, .45, and .6).

The different plateau pressures determined are noted in Table 2, along with the average temperature recorded with the plateau data. These values are then used to construct a van't Hoff plot, which can then be used to predict the plateau pressure obtained at any pressure. Such a plot with statistical fit of the data is shown in Figure 6a for desorption and 6b for absorption. Of note is the fact that the D_2 data (triangles, not used in fit) differs from the H_2 data, illustrating that a small isotope effect exists. This difference is removed via the reduced pressure approach. When the model is applied to tritium data, the tritium plateau pressures will have to be known as well.

Once the plateau pressures are determined, the adjusted alpha-phase data can be divided by those values and the reduced alpha-phase adjusted data computed. The resulting reduced isotherms are shown in Figure 7 (note that the D_2 data is included). The expanded alpha-phase region of the reduced pressure plot is shown in Figure 8. Note that the span at the reduced pressure of 0.1 is now <0.01 Q/M units. This is primarily because these are the desorption isotherms only. The spread in the beta region is now ~0.04 H/M units (see Figure 9), which is a decrease from the spread seen in Figure 4. In theory, that occurred because the temperature dependence in the data has now been removed. In any case, the residual variation presents difficulties to the modeling effort.

The first choice that has to be made in the modeling effort is how much of the data is to be modeled. Since there is such a change in curve characteristics in going from the plateau region (which can be sloped slightly or greatly) to the β-phase region, selecting the subset of data with which to construct a β-phase model requires some consideration. Secondly, the effect of the residual variation in the alpha-phase adjusted reduced data has an effect as well. In Figure 10 the natural logarithms of the β-phase reduced pressure, alpha-adjusted data for Q/M values > 0.9 are fit with linear, quadratic, and cubic fits. Clearly the cubic fit is not extrapolatable to reasonable values, while both the linear and quadratic form seem to behave much better. Statistically they all present very similar R^2 values, none being particularly promising. Restricting the included data to higher minimum Q/M values only seemed to hurt the fit quality.

Examination of the underlying data indicates that the different isotherms are not overlaying well and suggests that an adjustment of the sort used to match the alpha phase data would yield better fits. Again, this would not improve the overall error limits of the model but would just make it easier to decide on the form of the model. Figure 11 presents 'beta-matched' data with statistical fits (cubic – dashed line, quadratic – dotted line). The 'beta-match' was achieved by shifting the Q/M values of the raw data to provide good overlay off the resulting isotherms and is strictly arbitrary. The only driving concern was to keep the shift on the order of the raw data error bars and to try to keep the high-end Q/M values close to 1.0. The final shifts in the Q/M values used to create the 'beta-matched data are shown in Table 1 as the 'beta phase' adjustment.

Quadratic and cubic fits are shown in Figure 11, as the curvature eliminated linear fits from comparison. The R^2 values are much better, *but as a reminder are strictly fictitious at this point for anything relating to the actual error bars of the method being developed herein*. The fits are shown extrapolated to slightly higher and lower Q/M. Clearly the cubic fit fails once the plateau is reached. Likewise, the quadratic fit has too many points above the fit line in the 0.85-0.95 region. The problem is trying to fit the plateau into the model. A better fit is made by restricting the data to higher Q/M values as is shown in Figure 12 for a quadratic fit.

Finally, we are now able to invert the data and develop a model which predicts the Q/M value given an equilibrium pressure, a plateau pressure, and the relevant isotherm temperature. Figure 13 shows the results. The plateau region of the data was further excluded by using only the data for Q/M>0.95 and the cubic and quadratic fits to that data were essentially statistically indistinguishable. Since the statistical fit quality of the model is irrelevant to the overall precision and accuracy of that model, being controlled by the raw data's variation, the only criterion used to choose which fit was 'better' was the ability to extrapolate the data, particularly in the high Q/M region. The cubic fit seems to better predict the subsequent points at Q/M values exceeding the data range, so that model is thereby recommended for use in determining the CB initial Q/M following accountability measurements.

The solid lines lying to either side of the data are computed from the cubic fit equation by increasing and decreasing the values by 2%, giving a 4% band around the data and fit lines. Thus, for $\ln(P_{red})$ = 1.0 (which equates to $P_{red} \sim 2.7$, the Q/M band is ~0.97-1.01, i.e., a 0.04 Q/M unit spread. This is approximately the same spread observed in the data presented in Figure 9 at $P_{red} = 3$, therefore the model equation shown on Figure 13 is determined to be a good candidate for the desired SAS CB material model. That equation is:

$$Q/M = 0.003085*(\ln(P_{red}))^3 - 0.02283*(\ln(P_{red}))^2 + 0.07524*\ln(P_{red}) + 0.9364 \qquad (1)$$

The precision of this model is limited to the precision demonstrated for the alpha-adjusted data, since the subsequent 'beta adjustment' was not driven by objective or statistical considerations. The model's accuracy depends on how well the beta adjustment relates to the real data, which is very difficult to determine without additional data to use for cross-checking. The above model can also be shifted on the Q/M axis by altering the additive constant at the end of the equation. Model users will have to determine if such a shift is required in their application.

One additional precision and accuracy issue needs a brief examination. In a prior effort[1], additional isotherms were determined in a different apparatus capable of automated isotherm determination, i.e. cycling, on the same material. In Figure 14 a comparison is made between a 52 °C isotherm obtained from the other instrument with the 50 °C and one 30 °C isotherm from this study. The

isotherms have been 'beta adjusted' to force an overlay with the cubic model predictions. (The β-phase adjustments used in Fig. 14 were: ULB -.041, 50C +.025, 30C -.0114.)

The isotherms obtained for this study fit the model well, as would be expected. However, the isotherm from the other instrument has a slightly different β-phase slope. This can occur from several possible sources, one of which is an error in volume determinations. This highlights one limitation inherent in this study, namely that all data were collected from one apparatus by a single researcher. That can often result in a limited estimate of error. Often, when additional researchers and equipment are utilized to increase the database, there will be a concomitant increase in error magnitude. In some cases, with considerable effort that error can be reduced. Whether that is necessary in this case remains in the purview of the model users to decide.

There is a deuterium isotope effect explicit in the data. However, by adopting the reduced isotherm approach, the reduced isotherms overlap well. It is expected the same model developed with the H_2 data will apply to the D_2 data, even in the case of different temperature isotherms. Tritium will likewise show an isotope effect, but there are no data available to assess the magnitude of it at this point. The tritium isotope effect on virgin material will need to be either estimated or measured.

Tritium aging effects are more problematic. At least in the early phases of tritium aging, the primary effect has been observed in LANA75 to be a slight lowering of plateau pressure and an in-growth of a low T/M heel. The β-phase curve should not change significantly due to this initially, therefore measurement of the desorption plateau pressure would still suffice. Eventually however, the β-phase curve will be impacted and this method will be invalidated. Actual tritium aging of a LANA10 sample is recommended to assess the seriousness of this problem.

4.0 Conclusions and Recommendations

To summarize, a model, given as equation 1 above, using reduced pressure to compute the Q/M value obtained when a LANA10 hydride material is loaded to a given pressure, as long as that reduced pressure exceeds ~1.3, has been developed. Two 30 $^{\circ}$C D_2 isotherms were also collected and confirmed that while there is an isotope effect, it can be compensated for with the reduced pressure approach used in the model presented. Applying the model to tritium isotherms is anticipated to work, however, the desorption plateau pressures for tritium isotherms must be known either by measurement or estimation. Additionally, advanced tritium aging is expected to invalidate the model due to anticipated isotherm shape changes. The severity of this problem is unknown at this time.

Estimation of the tritium isotope effect in this material could be accomplished by comparing tritium isotope effects from other LANA alloys such as LANA75, for which more of this type of data exists, and assuming the same magnitude of response would exist in LANA10. Conversely, a fresh LANA10 sample could potentially be prepared and the isotope effect on a virgin sample determined. Finally, the desorption plateau pressure of the actual SAS bed could be determined and used in computing the reduced pressure isotherm point needed for the Q/M model. This latter method may be the quickest way to allow model implementation, although it will require some effort as it is the desorption pressures that are needed.

5.0 Path Forward and Future Work

The results and conclusions reported herein will allow the Tritium Facilities to determine the SAS Compressor Bed 1 loading given the equilibrated temperature of and pressure over the bed, once

the tritium isotope effect is estimated or measured, in a manner directly analogous to that in the TF procedure SOP 233-50040, Rev. 3, "SAS Storage Bed Inventory (U)". The most significant remaining issue is how to determine the tritium isotope effect. The tritium aging effect is a problem that can likely be deferred for the immediate time frame.

The most accurate, although perhaps not the easiest, method for this would to be to approximately half-load the bed and then conduct a small desorption. Allowing the bed to equilibrate at that point would allow the direct measurement of the plateau pressure. Following, another half-load to fullness would reach the final pressure. Tritium Facilities personnel should assess the work required to accomplish the proposed measurements in relation to accountability requirements to determine if that path is viable.

Alternatively, the current LANA10 data might be compared to literature data and other related LANA data, especially that relating to tritium isotope effects, to develop an estimation of the desorption isotherm plateau pressures for the anticipated temperature span. These estimated plateau pressures would then be used to divide the actual bed data to compute an estimated reduced pressure. It is unknown at this point if such a process can be developed or how accurate it would be.

The slowest method for obtaining the necessary data would be to prepare a new LANA10 sample (or perhaps more than 1) for tritium isotherm determination. It would likely require approximately 3 months to get the necessary data for virgin material. Subsequently the sample would need to undergo tritium aging studies in order to assess how severe the aging problem would be.

Our recommendation is in fact to do all three. The 'paper study' on the isotope effect should proceed as quickly as possible, but the actual measurement of the data should also be performed, as it will give the highest degree of accuracy. However, the model's veracity with respect to whether the proposed equation fits the tritium data can only be determined by actually obtaining the comparison data. Timing may require the faster interim approximate methods to be employed.

6.0 References

1. Kirk L. Shanahan, "Materials Characterization for the Unloading Line B Project (U)", March 24, 2011, SRNL-STI-2011-00750.
2. H. Bjurstrom, S. Suda, and D. Lewis, "A Numerical Expression for the P-C-T Properties of Metal Hydrides," J. Less-Common Metals, **130**, 365 (1987).
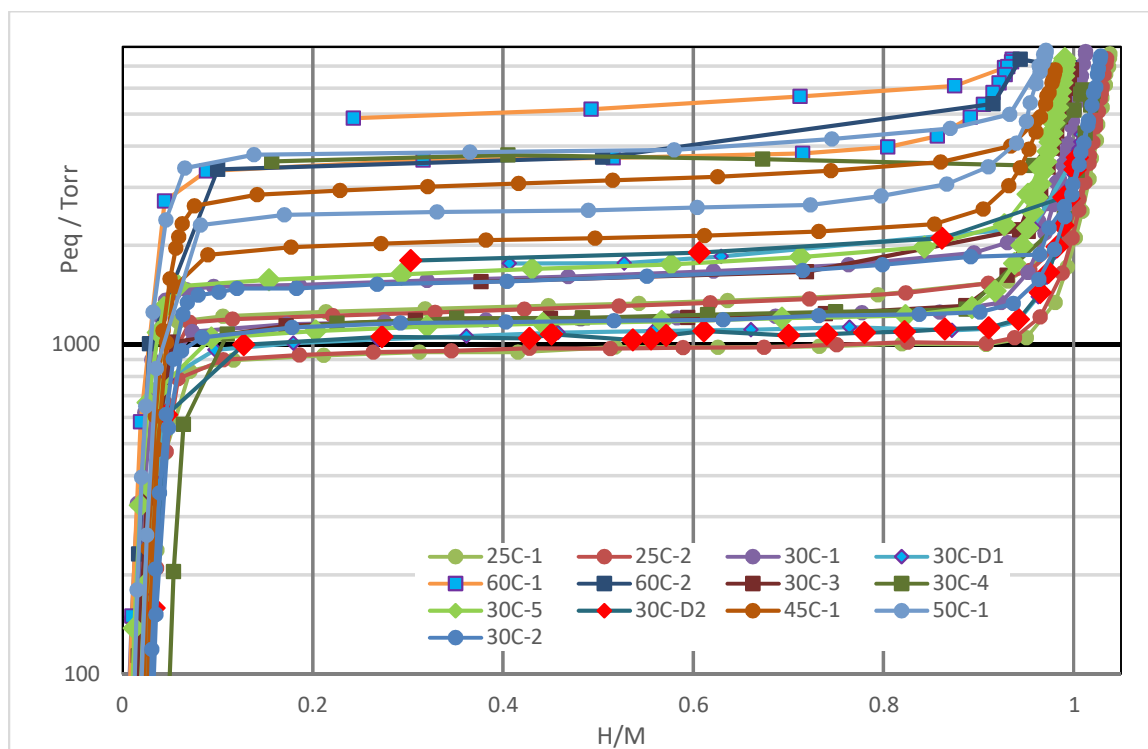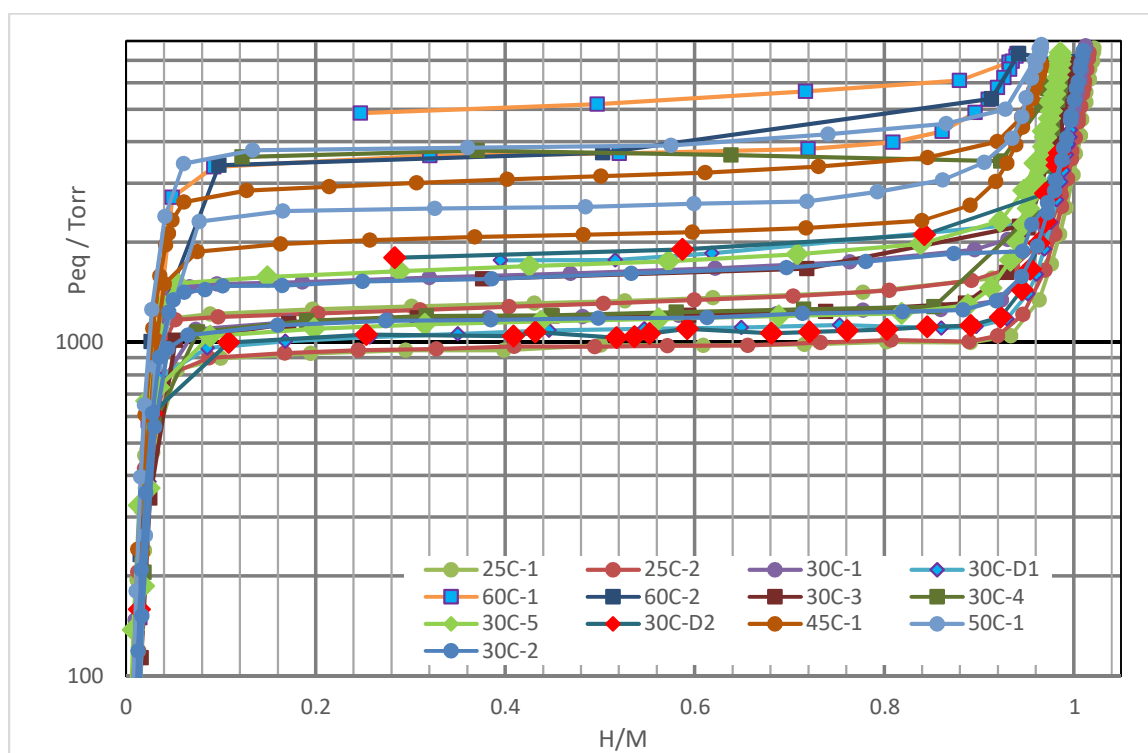
Figure 1. Raw H₂ absorption/desorption isotherms from LANA10 Lot 1500-V-2

Figure 2. Alpha-adjusted H₂ absorption/desorption isotherms from LANA10 Lot 1500-V-2

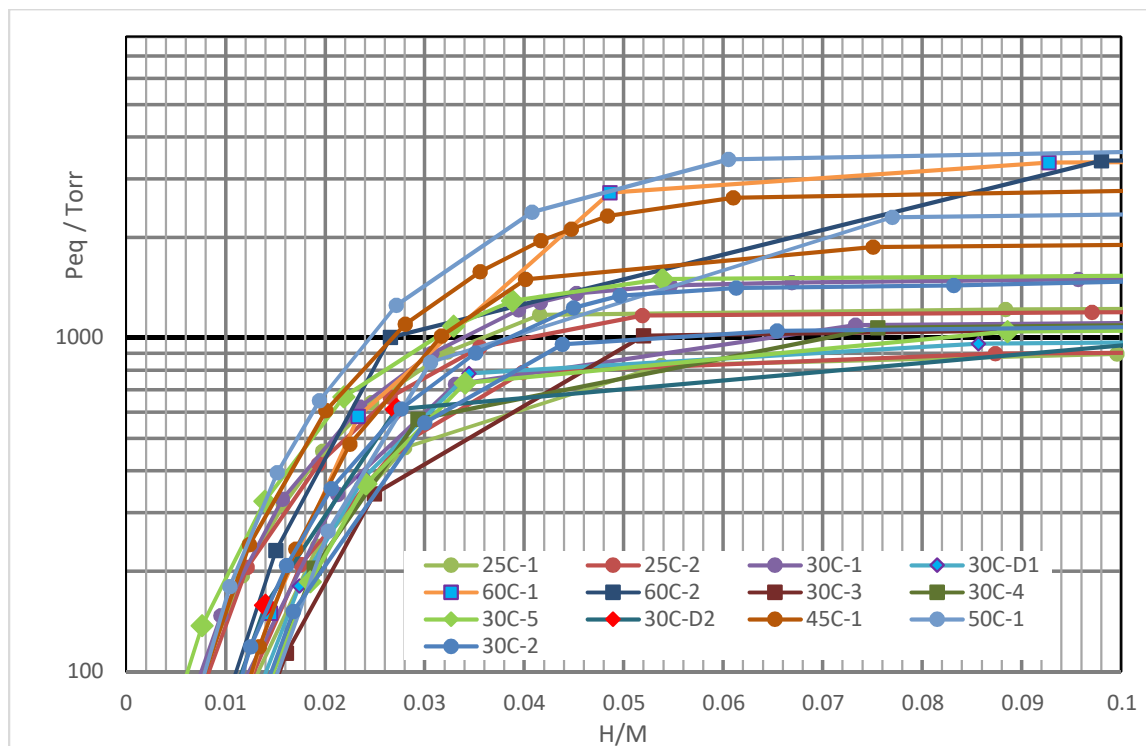**Figure 3. Expanded alpha region of H₂/D₂ alpha-adjusted absorption/desorption isotherms**

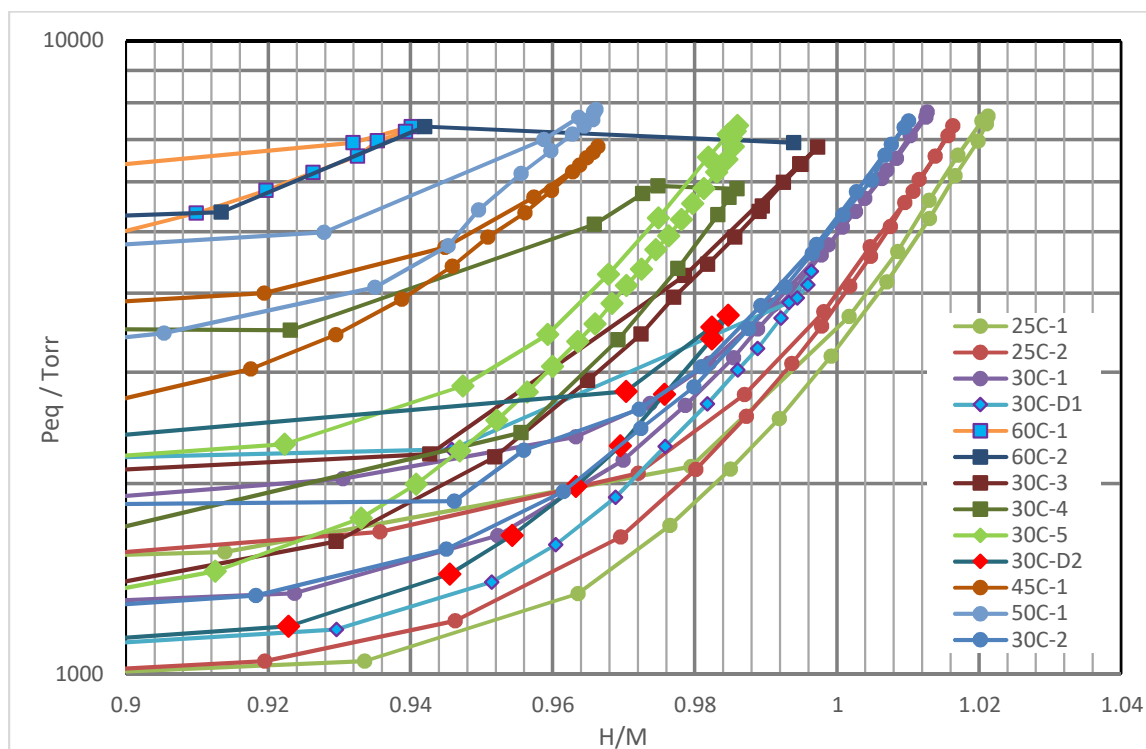**Figure 4. Expanded beta region of H₂/D₂ alpha-adjusted absorption/desorption isotherms**

Figure 5. '30C-D2' Desorption Isotherm Plateau illustrating the 'large aliquot effect'
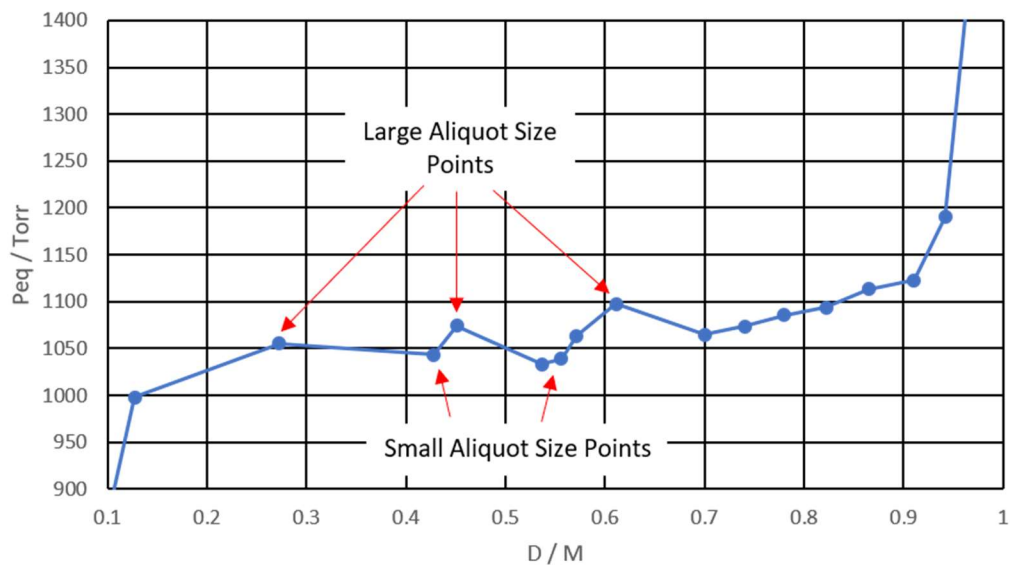

Figure 6a. Van't Hoff Plot with Linear Fit of H_2 Desorption Data (2 D_2 points shown, overlapping triangles)
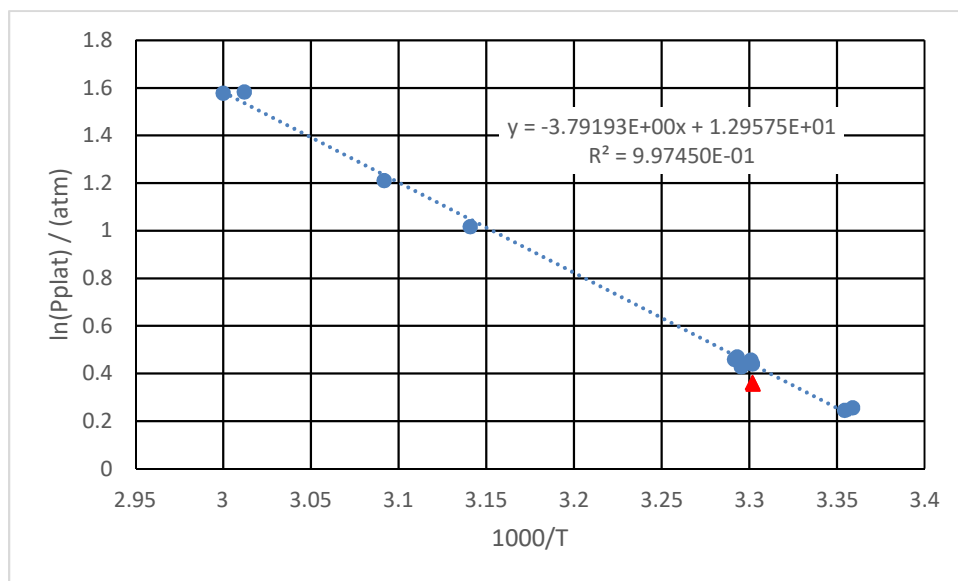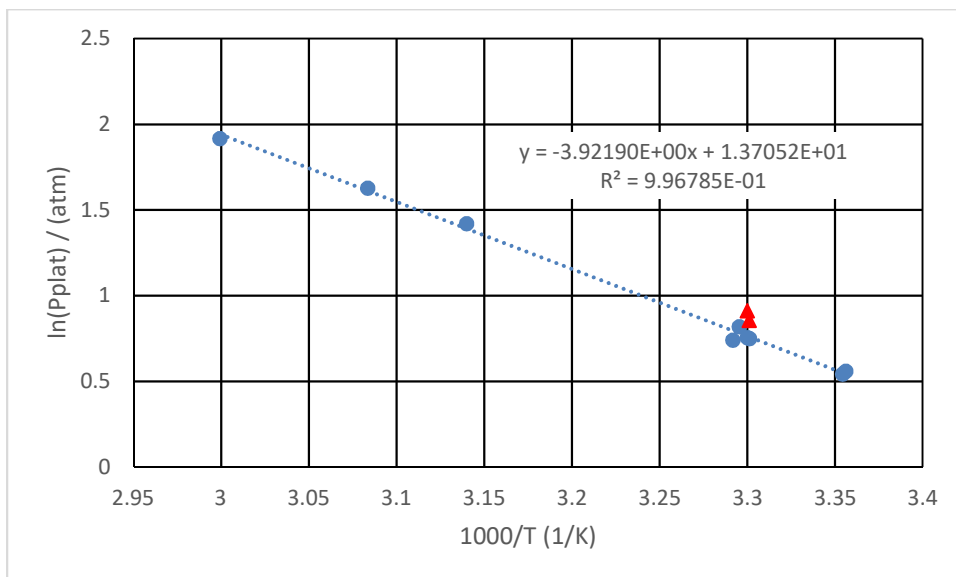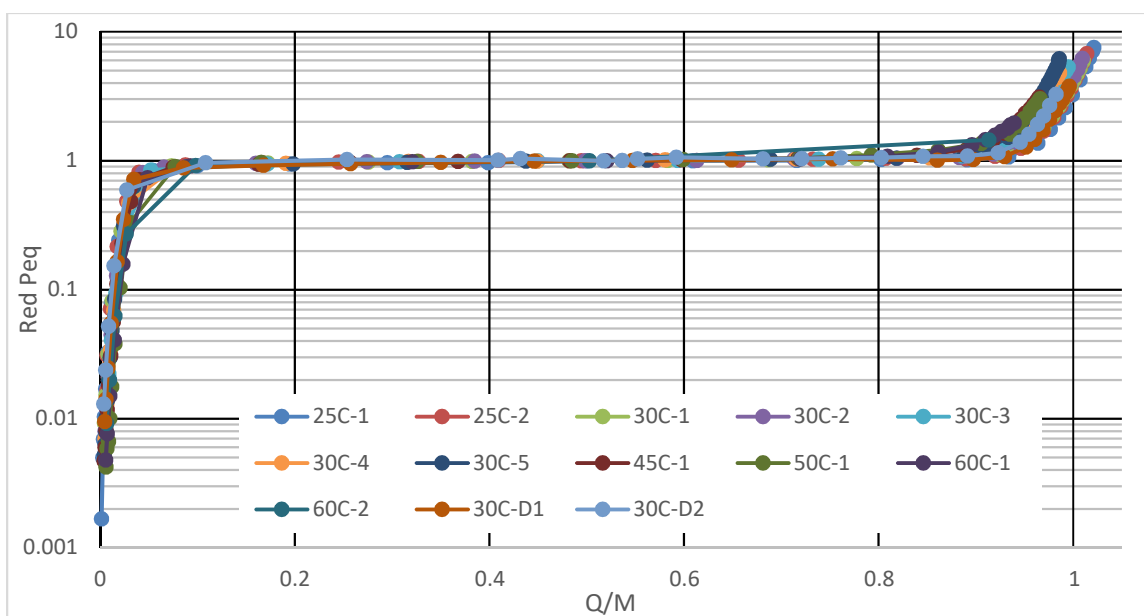
Figure 6b. Van't Hoff Plot with Linear Fit of H₂ Absorption Data (D₂ points shown, triangles)

$$y = -3.92190E+00x + 1.37052E+01$$
$$R^2 = 9.96785E-01$$

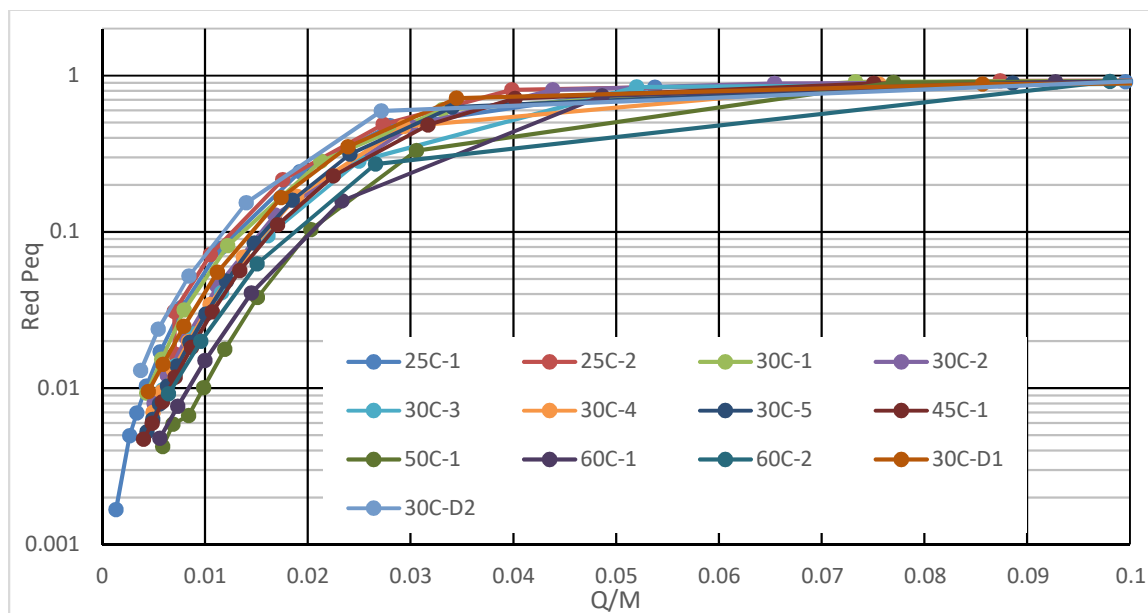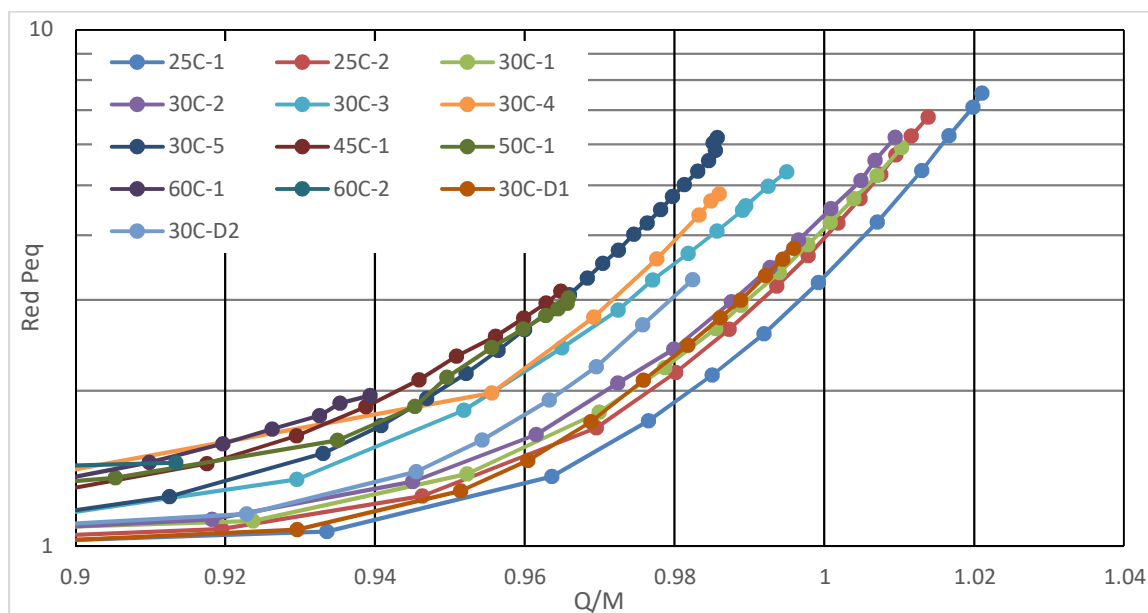**Figure 7. Reduced Alpha-phase Adjusted Desorption Isotherms**

Figure 8. Expanded Alpha Region of Reduced Alpha-phase Adjusted Desorption Isotherms

Figure 9. Expanded Beta Region of Reduced Alpha-phase Adjusted Desorption Isotherms

Figure 10. Statistical Fits of the Beta-phase region alpha-adjusted isotherm data.

$y = 31.039x^2 - 44.116x + 14.609$
$R^2 = 0.7551$

$y = -1048.3x^3 + 3064.2x^2 - 2967.6x + 953.29$
$R^2 = 0.7577$
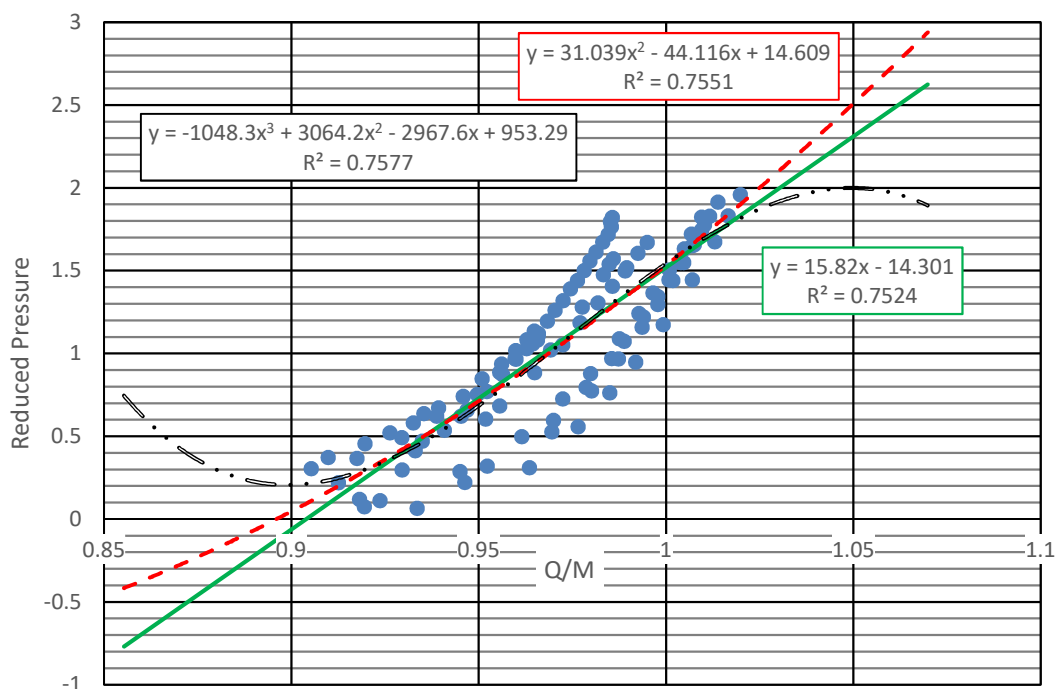
$y = 15.82x - 14.301$
$R^2 = 0.7524$

Figure 11. Statistical Fits of the Beta-phase region beta-matched isotherm data (Quadratic – dots, Cubic – dashes).

$y = 166.46x^2 - 304.45x + 139.24$
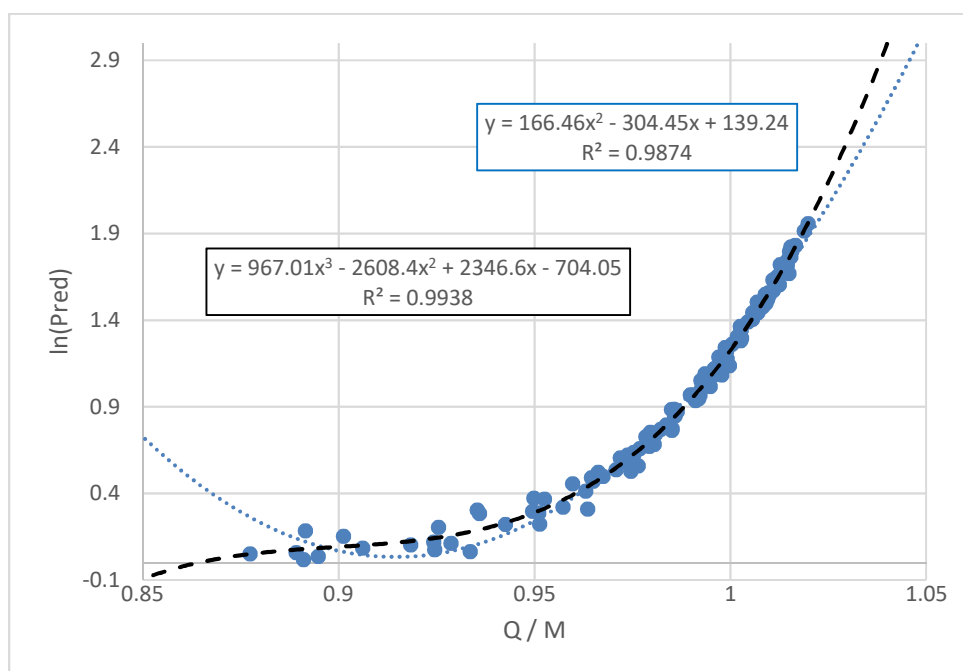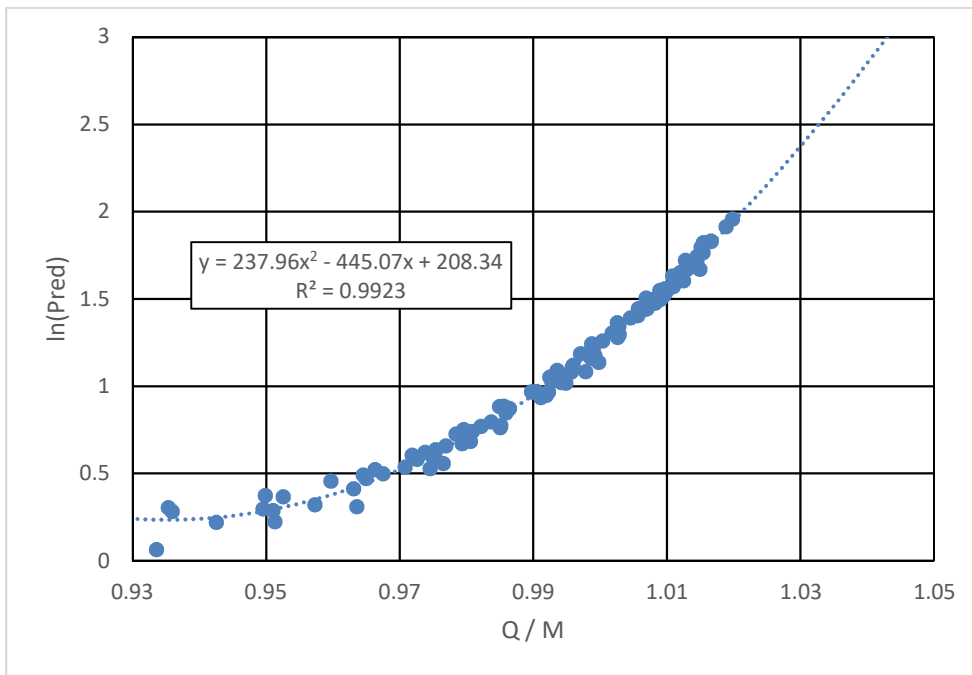$R^2 = 0.9874$

$y = 967.01x^3 - 2608.4x^2 + 2346.6x - 704.05$
$R^2 = 0.9938$

Figure 12. Statistical Fit of beta-matched data at >0.93 Q/M

Figure 12. Statistical Fit of beta-matched data at >0.93 Q/M

$y = 237.96x^2 - 445.07x + 208.34$
$R^2 = 0.9923$

Figure 13. Inverted Statistical Fit of beta-matched data at >0.95 Q/M, with +/- 2% lines from cubic fit (dotted line, dashed = quadratic)

$y = -1.221E-02x^2 + 6.412E-02x + 9.398E-01$
$R^2 = 9.882E-01$

$y = 3.085E-03x^3 - 2.283E-02x^2 + 7.524E-02x + 9.364E-01$
$R^2 = 9.884E-01$
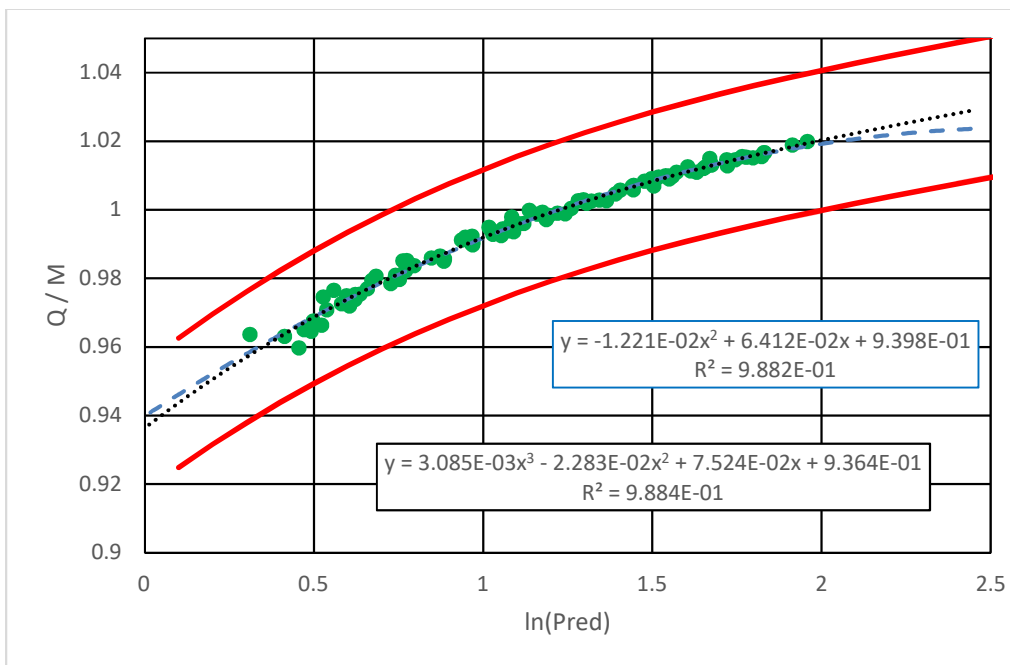
Figure 14. 52ºC LANA10 H$_2$ Isotherm from a different instrument vs. 50 and 30 ºC (30C-3) isotherm from this study. 'Beta' adjustment to force overlay for comparison to cubic model. (Adjustments: ULB -.041, 50C-1 +.025, 30C-3 -.0114) Note the slight slope difference in β-phase.
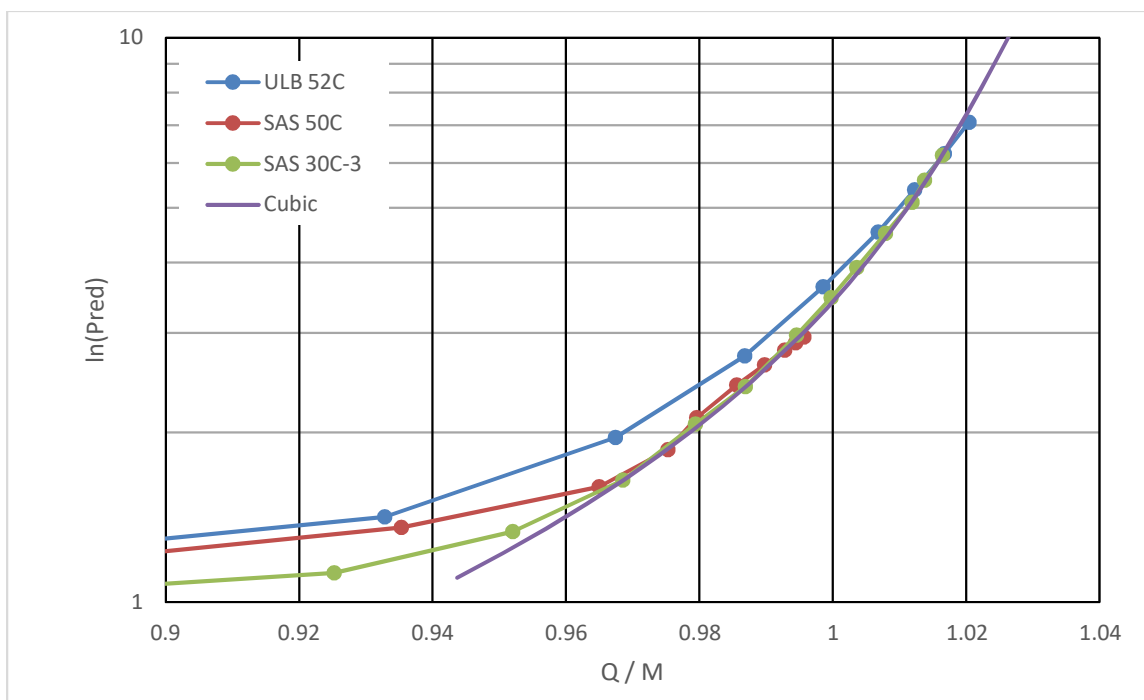
Table 1. Run Sequence Numbers and Identifiers, and Offsets Used in Data Analysis

Run Seq#	Label	Alpha Adj,	Beta Adj.
1	25C-1	-0.017	-0.017
2	25C-2	-0.0185	-0.0135
3	30C-1	-0.0186	-0.0086
4	30C-2	-0.0184	-0.0034
9	30C-3	-0.0007	0.0243
10	30C-4	-0.0348	-0.0098
12	30C-5	-0.0048	0.0302
13	45C-1	-0.0145	0.0255
11	50C-1	-0.005	0.03
7	60C-1	0.0044	0.0494
8	60C-2	-0.002	0.025
5	30C-D1	-0.0116	-0.0016
6	30C-D2	-0.0193	0.0007

Table 2. Van't Hoff Parameters

Label	$P_{plat, a}$ (Torr)	Abs. T (C)	$P_{plat, d}$ (Torr)	Des. T (C)
25C-1	1330	24.80	982	24.56
25C-2	1308	24.96	971	24.97
30C-1	1618	29.88	1199	29.79
30C-2	1609	29.77	1181	29.72
30C-3	1594	30.63	1203	30.66
30C-4	na	na	1215	30.52
30C-5	1722	30.30	1166	30.29
45C-1	3147	45.33	2102	45.24
50C-1	3871	51.16	2550	50.28
60C-1	5173	60.27	3683	60.19
60C-2	na	na	3702	58.85
30C-D1	1765	29.61	1092	29.71
30C-D2	1858	29.91	1032	29.68