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SR19021 Tritium Aging of Regenerated LANA.75 Final Project Report

G. C. Staack

S. P. Reynolds September 2021

SRNL-STI-2021-00485, Revision 0

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PREFACE OR ACKNOWLEDGEMENTS

The authors would like to thank the Savannah River Tritium Enterprises (SRTE) Engineering and Operations, Savannah River Field Office, and National Nuclear Security Administration (NNSA) Office of Engineering and Technology Maturation (NA-115) for the Plant Directed Research and Development (PDRD) program for funding this project. In addition, the authors gratefully acknowledge the assistance of the many people within the Tritium Facilities and SRNL who helped perform this work. In the Tritium Facilities: Zack Trotter for being the Tritium Facility co-sponsor for this project, Tracy Franklin for being the SAS system engineer, Dante Pilgrim and Dakota Hooker for performing the hands-on work on the SAS manifold. In SRNL: Kirk Shanahan for the guidance and training that he provided for the new lab workers in the proper use of the Manual Manifold, and David Missimer and Henry Ajo for their work performing particle size analysis, ICP, XRD, and SEM analysis of the thermal stability samples.

EXECUTIVE SUMMARY

The Savannah River Tritium Enterprise (SRTE) has used the metal hydride $LaNi_{4.25}Al_{0.75}$ (LANA.75) in the Tritium Facilities for over two decades. LANA.75 beds store significant quantities of tritium but have a limited service life due to the radiolytic decay of tritium to He-3 within the metal matrix. It has been shown that heating tritium-aged LANA.75 under vacuum can reverse tritium aging effects, eliminating the heel of trapped hydrogen, and restoring the reversible capacity. Additional investigation is needed to ensure there are no unexpected changes to the hydride before this restoration technique is employed in full scale beds in the Tritium Facilities.

This project was to be comprised of three distinct scopes: obtain tritium aging data on the sample regenerated in 2018, regenerate a tritium-aged sample at 600 °C, and perform thermal stability testing on a non-tritiated sample. Isotherms were collected on the previously regenerated sample after approximately two years of tritium aging. Isotherms were collected at 80, 100, and 120 °C. As expected, there was a decrease in the plateau pressure, an increase in plateau slope, and a portion of the "heel" of tritium trapped in the metal had been reestablished. Unexpectedly, it appeared that the plateau had shortened at the higher tritium to metal ratios as well. This is typically seen in older samples.

The second scope, to regenerate a second tritium-aged LANA.75 sample, was not completed. A Task Technical and Quality Assurance Plan was written and approved, a high temperature test cell was fabricated, several pre-job briefs were held, and the hydride sample was passivated with air. Despite these successes, the hydride sample was not recovered from the legacy test cell.

The third scope was to perform thermal stability testing on a "cold" LANA.75 sample. A non-tritiated sample of LANA.75 was held at 750 °C under vacuum for 200 hours to simulate exposure to multiple regeneration evolutions. Hydride isotherm performance, chemical composition, crystallinity, particle size, and morphology are compared between the pre- and post-regeneration samples. No significant changes were observed in composition, crystallinity, or particle size. Comparison of before and after isotherms showed that performance improved rather than deteriorated during the evolution. Scanning Electron Microscopy (SEM) analysis showed small growths on the particle surface after exposure to regeneration conditions. Additional testing will be required to determine the cause of these growths.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Al	Aluminum
Ca	Calcium
Ci	Curie
EDS	Energy Dispersive X-ray Spectroscopy
FE-SEM	Field Emission Scanning Electron Microscope
H/M	Hydrogen to Metal Atomic Ratio
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
JMC	Japan Metals and Chemicals
La	Lanthanum
LANA.75	$LaNi_{4.25}Al_{0.75}$
LPM	Low Pressure Manifold
MA	Mean Area
Mg	Magnesium
MN	Mean Number
MV	Mean Volume
Ni	Nickel
PVT	Pressure, Volume, and Temperature
SAS	Sample Assay System
SEM	Scanning Electron Microscope
SRNL	Savannah River National Laboratory
SRTE	Savannah River Tritium Enterprise
T/M	Tritium to Metal Atomic Ratio
XRD	X-ray Diffraction
Z	Atomic Number

1.0 Introduction

The Savannah River Tritium Enterprise (SRTE) has used $LaNi_{4.25}Al_{0.75}$ (LANA.75) hydride to store hydrogen isotopes, including tritium, for over two decades. The hydride beds store significant quantities of tritium but have a limited service life due to the radiolytic decay to He-3 within the metal matrix. He-3 is larger than atomic hydrogen and has a very low solubility in the metal, so it becomes trapped within the lattice and alters the crystal structure of the hydride. The altered structure, in turn, causes the formation of a heel of trapped hydrogen isotopes and reduces the reversible capacity of the hydride under normal processing conditions. [1] [2] With sufficient tritium exposure, the bed will lose its ability to deliver He-3 free tritium. Whenever a bed's reversible capacity impacts the process throughput or the bed can no longer deliver He-3 free tritium, it must be replaced at significant cost and effort to the facility. This is typically after 8-12 years of service.

One strategy to reduce the cost and effort of having to replace the beds is to regenerate the beds in place. Nobile et al. [3] saw that the He-3 formed in the lattice due to the radiolytic decay from tritium caused (1) decreased tritium desorption pressures, (2) increased slopes of the desorption isotherm plateau, and (3) small quantities of irreversibly held tritium. However, those effects were partially reversed by briefly heating the samples to 350 °C. Staack et al. [4] showed that the majority of the He-3 was released in two separate peaks (one near 220 °C and the other near 490 °C). Essentially all the gas from a tritium-aged sample had been released by 600 °C. Later, Staack and James [5] showed that heating a tritium-aged LANA.75 sample to 450 °C moderately restored the performance while heating the sample to 600 °C significantly improved the performance. This improvement between 450 and 600 °C was likely due to the release of the second He-3 peak. Additional heating to 750 °C produced modest improvements over 600 °C. Interestingly, the regenerated sample had a plateau pressure higher than anticipated.

The objective of this project was to expand upon the understanding of LANA.75 regeneration. Three distinct scopes were identified: monitor tritium aging of the single sample regenerated, regenerate a second tritium-aged sample, and perform thermal stability testing on a non-tritiated sample of LANA.75.

2.0 Experimental Procedure

As mentioned, this project consisted of three distinct scopes. First, isotherms were collected on the single sample regenerated in 2018 to ensure no unexpected behaviors were observed. Second, a tritium-aged LANA.75 sample was to be regenerated at the maximum expected facility regeneration temperature of 600 °C. Third, thermal stability testing was performed on non-tritiated LANA.75 to ensure that prolonged exposure to high temperatures would not adversely change the composition, morphology, or behavior of the hydride.

2.1 Monitor Tritium Aging

Isotherms are pressure vs. composition graphs of the metal hydride/gas system at constant temperature. The composition of a hydride is typically expressed as the hydrogen to metal atomic ratio, H/M (or T/M for tritium). For an absorption isotherm, equilibrium pressure measurements are taken after an aliquot of gas is added to the system. Likewise, for a desorption isotherm, equilibrium pressure measurements are taken after an aliquot of gas is removed from the system. The quantity of tritium absorbed or desorbed by the hydride is inferred from differences in before and after pressure, volume, and temperature (PVT) measurements of the gas phase. Isotherms reveal the plateau pressure, reversible capacity, and heel of a material for a given hydrogen isotope.

Four tritium desorption isotherms were collected on the sample regenerated at 750 °C in 2018. Isotherms were collected in 2020, after approximately 2 years of aging, using the Sample Assay System (SAS) in the

Tritium Facilities. The first two isotherms were at 120 °C, the third at 100 °C, and the fourth at 80 °C. The repeating of the 120 °C isotherm was to determine sample stability. After testing was complete, the sample was reloaded with tritium for continued aging.

2.2 Regenerate a Second Sample

A legacy tritium-aged LANA.75 sample (LANA75-SP2) was to be isotope exchanged to reduce total tritium content to less than 5 Ci, passivated by controlled exposure to air, and the hydride transferred to a new, high temperature compatible test cell. The new sample was to be isotope exchanged, isotherm performance evaluated, and heated under vacuum to 600 °C. Tritium isotherm performance would be compared to baseline results after selected durations at 600 °C. After testing, the sample was to be reloaded with tritium to monitor aging. Testing was intended to provide a second data point for Bed Life Extension.

2.3 Thermal Stability Testing

A non-tritiated sample of LANA.75 previously purchased from Japan Metals and Chemicals (JMC), USA and characterized previously by Shanahan [6] was used for thermal stability testing. A portion of the hydride was loaded into the sample cell and another portion was set aside for chemical analysis. The LANA.75 in the sample cell was activated at 80 °C using 99.9999% pure hydrogen and load/unload cycled a total of 10 times to decrepitate. Heat was provided by (3) 300 Watt cartridge heater set into a nickel block with the sample cell. After activation and cycling, a baseline desorption isotherm was collected.

After obtaining the baseline isotherm, the sample was cooled to ambient temperature and passivated by introducing small aliquots of air into the test cell. The test cell was then opened, and a portion of the LANA.75 was recovered for additional analyses. The remaining material in the sample cell was re-activated at 80 °C with protium and cycled three (3) times to re-activate the material. Once re-activated, pre-anneal desorption isotherms at 80, 100, and 120 °C were collected.

After the pre-anneal desorption isotherms were complete, the hydride was heated under vacuum (absolute pressure less than 1 torr) to 750 °C and held for a total of 200 hours over two weeks – the system was under dynamic vacuum for 2 weeks, but the heat was removed during the weekend. After reaching 200 hours, the sample cell was cooled, and the material was reloaded with hydrogen. Desorption isotherms were collected again at 80, 100, and 120 °C. Following the post-anneal desorption isotherms, the sample was passivated so that a portion of the post-anneal material could be collected for additional analyses.

3.0 Results and Discussion

Testing of the regenerated LANA.75 sample demonstrated typical tritium aging characteristics, a reduced plateau pressure, increased plateau slope, and formation of a “heel” of trapped tritium. Thermal stability testing demonstrated that the heating process yielded flatter isotherm plateaus but promoted nanometer sized growths on the LANA.75 surfaces.

3.1 Tritium Aging of the 2018 Sample

The sample regenerated at 750 °C in 2018 was connected to the Low Pressure Manifold (LPM) of the SAS in the Tritium Facilities for isotherm collection. The manifold was charged with tritium to ensure the first desorption data points remained on the beta portion of the isotherm, the sample was opened to the manifold, and was then heated to 120 °C. After completion of this isotherm, the sample was reloaded with tritium and the isotherm repeated to verify stability. Two additional isotherms were collected, one at 100 °C and the other at 80 °C. Results are shown in Figure 3-1 with the exception of the repeated isotherm.

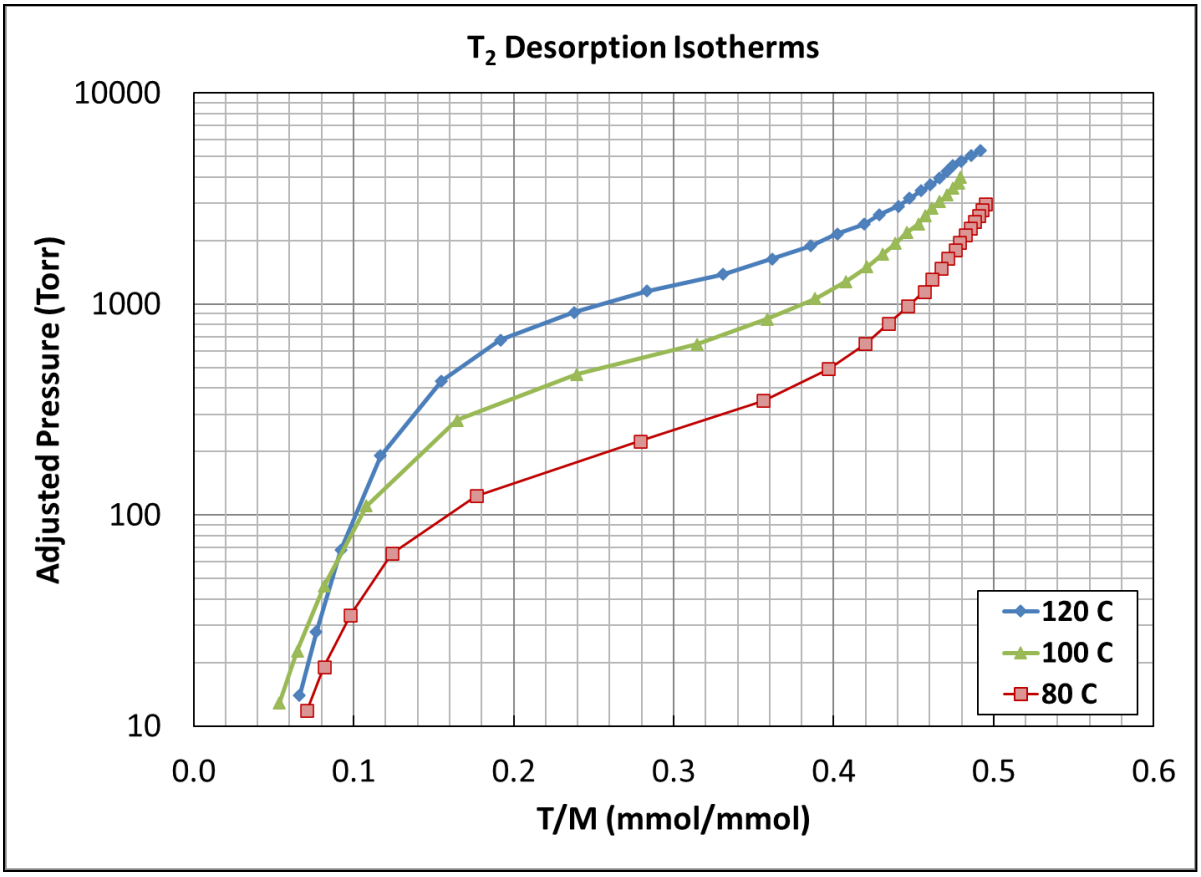


Figure 3-1: Tritium Desorption Isotherms after 2 Years of Aging

As can be seen, the isotherms have maintained their typical alpha, alpha + beta, and beta regimes, though tritium aging has induced formation of a heel, a slope in the plateau, and a decreased reversible capacity. These effects were anticipated, though appear to be forming somewhat faster than for a "virgin" sample. Figure 3-2 compares 80 °C desorption isotherms from the sample before regeneration, immediately after regeneration, and after 2 years of tritium aging. Of particular note is the contraction of the plateau region.

Plateaus normally initially contract on the alpha side of the isotherm with the buildup of the heel, then with additional aging, the beta phase shifts towards lower T/M values. Though the sample maintains significantly higher reversible capacity than pre-regeneration, a portion of the capacity has been lost.

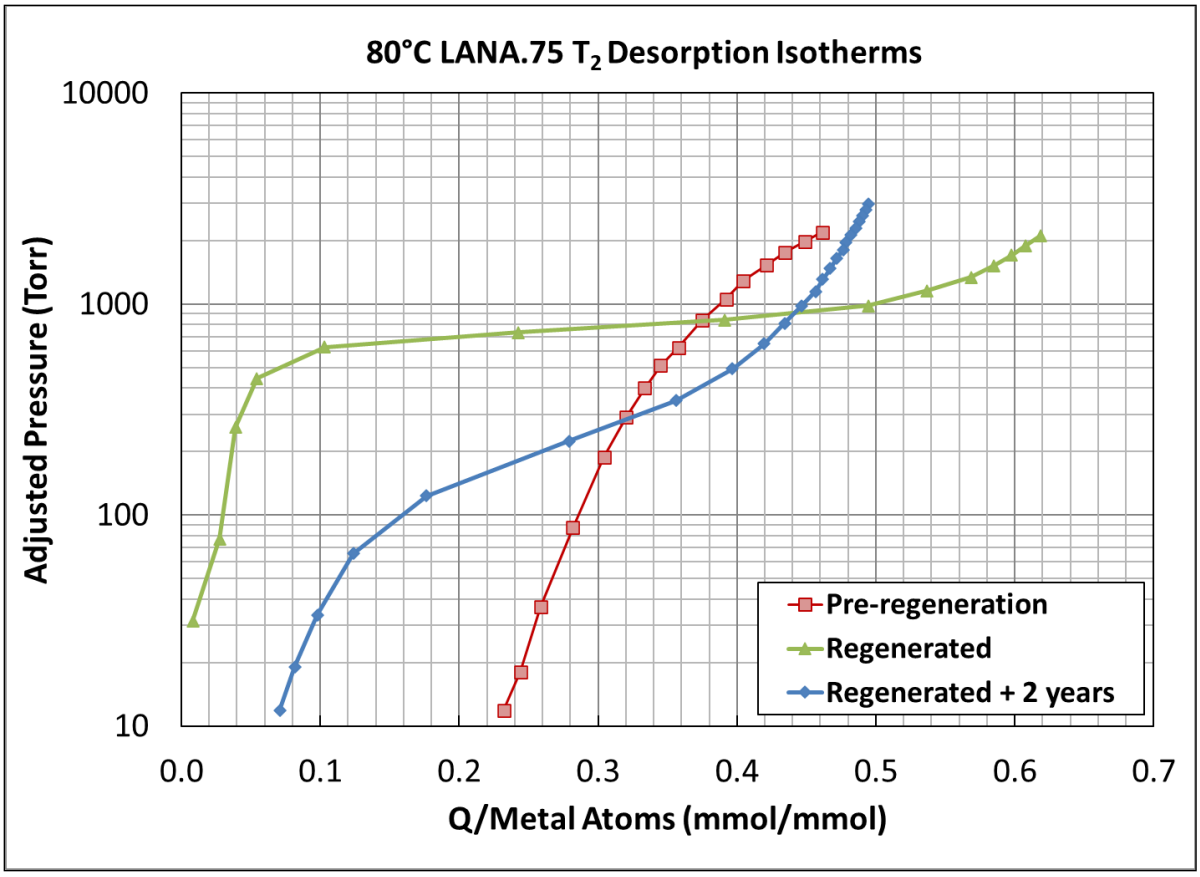


Figure 3-2: Pre, Post, and Aged 80 °C Isotherms

3.2 Regeneration of a 2nd LANA.75 Sample

A legacy LANA.75 sample, LANA75-SP2 was selected for regeneration at 600 °C. A high temperature test cell was fabricated and Task Technical and Quality Assurance Plan [7] was written and approved to support this activity. Despite these successes, the sample was not regenerated.

The path taken for the sample regenerated in 2018 consisted of first performing an isotope exchange on the "heel" to reduce the residual tritium content to less than 5 Ci. The hydride was then passivated with air to ensure it would not react with trace oxygen in the glovebox during recovery. It was then moved to another room for recovery and transfer of the hydride to the high temperature test cell. The recovered hydride and cell were then transferred back to SAS. Finally, another isotope exchange was performed to repopulate the heel with tritium for an "apples to apples" comparison with future tritium isotherms.

This path was not available for the new sample for two reasons. The first involved no longer being able to connect the sample to the SAS manifold. With no access to the manifold, no isotope exchange could take place and no reliable estimate of the residual tritium content could be made. The passivation procedure was changed to allow passivation of the sample with an unknown residual tritium content. The second reason is that the room historically used to recover legacy hydride samples could not receive an item containing an unknown, albeit low, amount of tritium. A path to recover future samples is needed if additional regeneration testing is to be performed.

3.3 Thermal Stability Testing

3.3.1 Isotherms

The initial verification isotherm collected showed that the material behaved similarly to the previous JMC sample tested by Shanahan [6]. After passivation and recovery of a portion of the activated pre-anneal sample, additional desorption isotherms were collected at 80, 100, and 120 °C, Figure 3-3. A second isotherm was collected at 120 °C to show reproducibility. The isotherms showed a slightly sloped plateau at all temperatures, and the second isotherm at 120 °C showed that the experiment was reproducible.

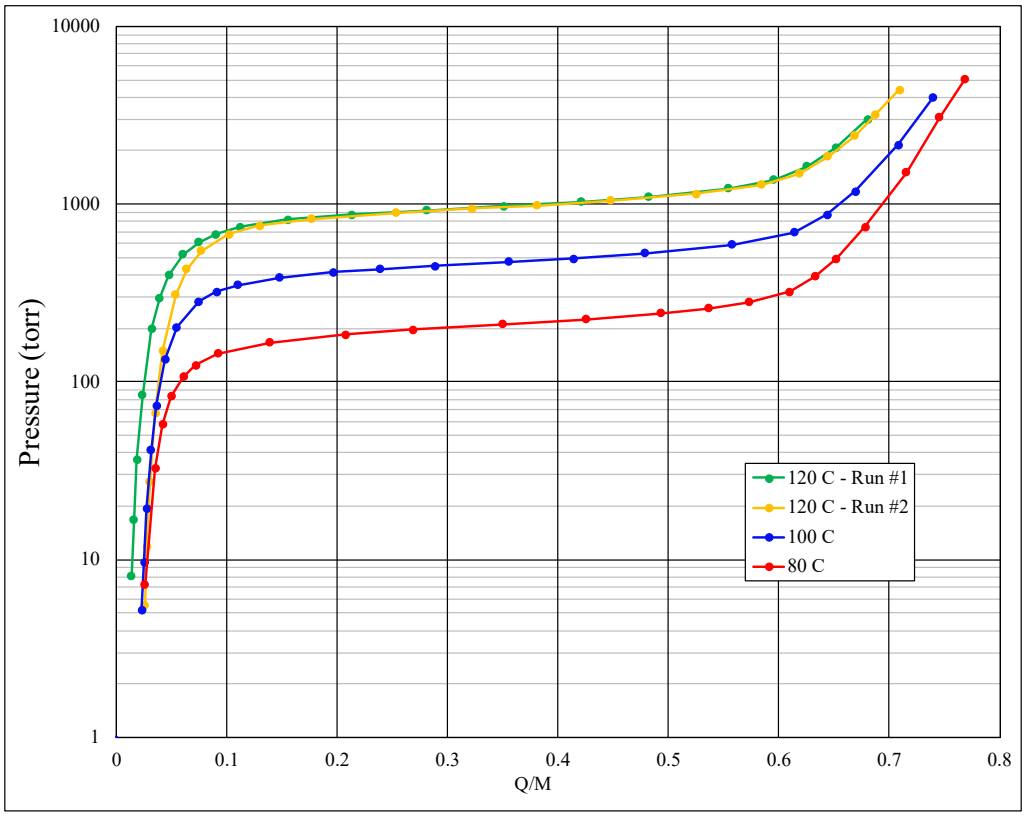


Figure 3-3. Pre-annealing isotherms of LANA.75 at 80, 100, and 120 °C.

The final set of desorption isotherms were collected after the annealing process. Isotherms were collected at 80, 100, and 120 °C. These isotherms, along with the pre-annealed isotherms, are shown in Figure 3-4. The post-anneal isotherms have a similar shape in the alpha and beta phases and have similar transition points to/from the plateau as the pre-anneal isotherms. However, the plateau regions for each temperature are flatter for the post-annealed material. This plateau shape is reminiscent of the material "healing" itself, which can be useful when dealing with tritium aging damage.

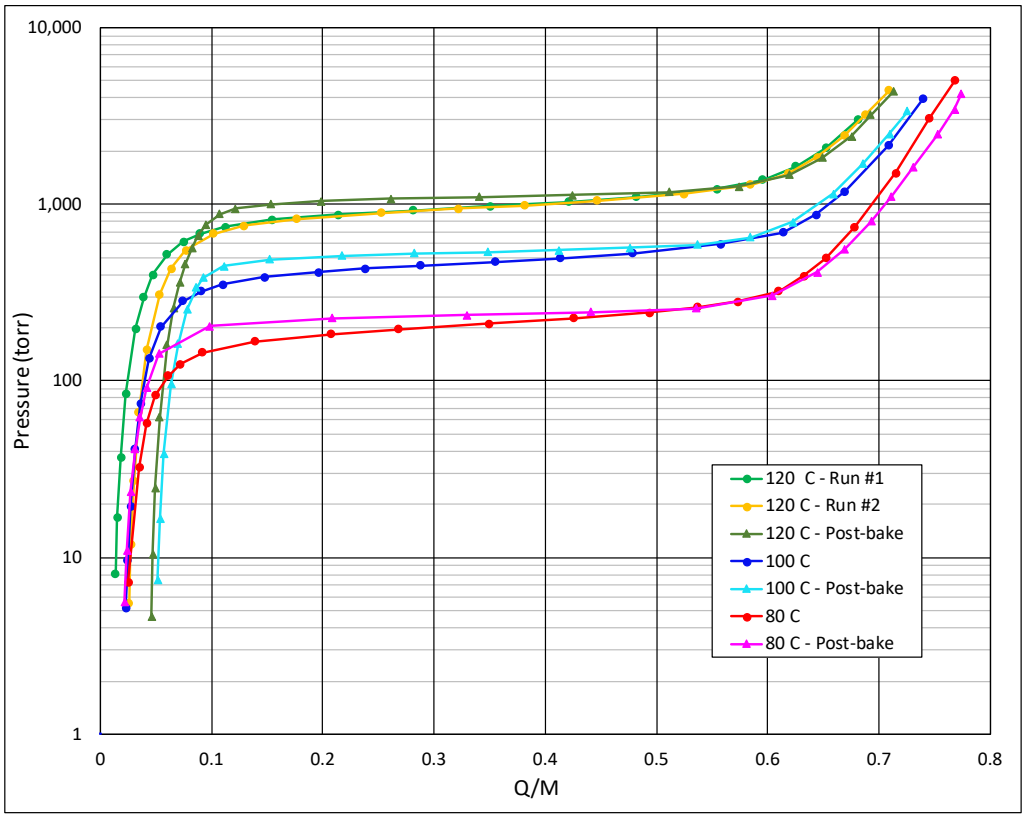


Figure 3-4. Comparison between LANA.75 pre-anneal and post-anneal isotherms.

Another difference noted between the isotherms is that there appears to be a slight heel in the alpha region in the post-anneal material. This is shown in the isotherms at 100 and 120 °C. However, it does not appear in the isotherm at 80 °C. This is likely due to accumulation of small errors in the pressure, temperature, or volume measurements during isotherm collection. As Shanahan [8] has shown with LANA.10, the standard deviation shows a 3-4% variation in the reproducibility in the alpha region H/M.

3.3.2 Particle Size Analysis

The particle size of the material was measured using a Microtrac S3500. The Microtrac passes a laser through a dispersion of particles in air or in liquid. The resulting "halo" of diffracted light is related to the particle size. The angle of diffraction increases as the particle size decreases.

The particles are typically not perfect spheres, and thus cannot be defined by a single dimension. Therefore, the particle size is usually defined by the concept of equivalent spheres. So, the particle size is defined by the diameter of an equivalent sphere having the same volume as the subject particle.

The way the particle size is represented is done with respect to the weighting of individual particles. In a volume weighted distribution, the contribution of each particle relates to its volume. The mean volume (MV) is the point where the cumulative volumes for all diameters less than or equal to the equivalent diameter is 50% of the total volume. In other words, it is where 50% of the total volume has a diameter less than or equal to the equivalent diameter. In an area weighted distribution, the contribution of each particle relates to its area. The mean area (MA) is the point where the cumulative area for all diameters less than or equal to the equivalent diameter is 50% of the total area. In other words, it is where 50% of the total area has a diameter less than or equal to the equivalent diameter. In a number weighted distribution, all particles have the same contribution independent of their equivalent diameter. The mean number (MN) is the point where 50% of the total diameters are less than or equal to the equivalent diameter.

Table 3-1 shows the particle size analysis results. As can be seen in the table, the virgin material particles are much larger than either the pre-anneal or post-anneal particles. This is because the material has not been activated, and thus it has not decrepitated due to hydrogen exposure. Interestingly, the post-anneal particulate appears to be slightly larger than the pre-anneal particulate. The full particle size analysis results can be seen in Reynolds et al. [9]

Table 3-1. LANA.75 particle size analysis results.

	MV (μm)	MA (μm)	MN (μm)	σ (μm)
Virgin Material	548.6	474.6	148.5	120.1
Pre-anneal Material	17.98	14.45	9.04	8.17
Post-anneal Material	21.37	18.83	13.42	6.97

3.3.3 Elemental Analysis

Elemental analysis was performed via inductively coupled plasma emission spectroscopy (ICP-ES). The ICP-ES results (see Reynolds et al. [9] for full analytical results) show that the composition is very close to the expected value with a slight excess of La. This result corresponds with Shanahan. [6] Prior to each analysis, a "blank" sample is run to ensure that any contaminants are not an artifact of the instrument. All three samples detected both Ca and Mg present above the instrument detection limits. Concentrations for both, though, are 3-5 orders of magnitude lower than those for La, Ni, and Al.

Table 3-2 shows the resulting compositions when La is forced to 1.

Table 3-2. LANA.75 Composition when La is forced to 1.

	Composition
Virgin Material	$LaNi_{4.21}Al_{0.77}$
Pre-anneal Material	$LaNi_{4.20}Al_{0.74}$
Post Anneal Material	$LaNi_{4.24}Al_{0.72}$

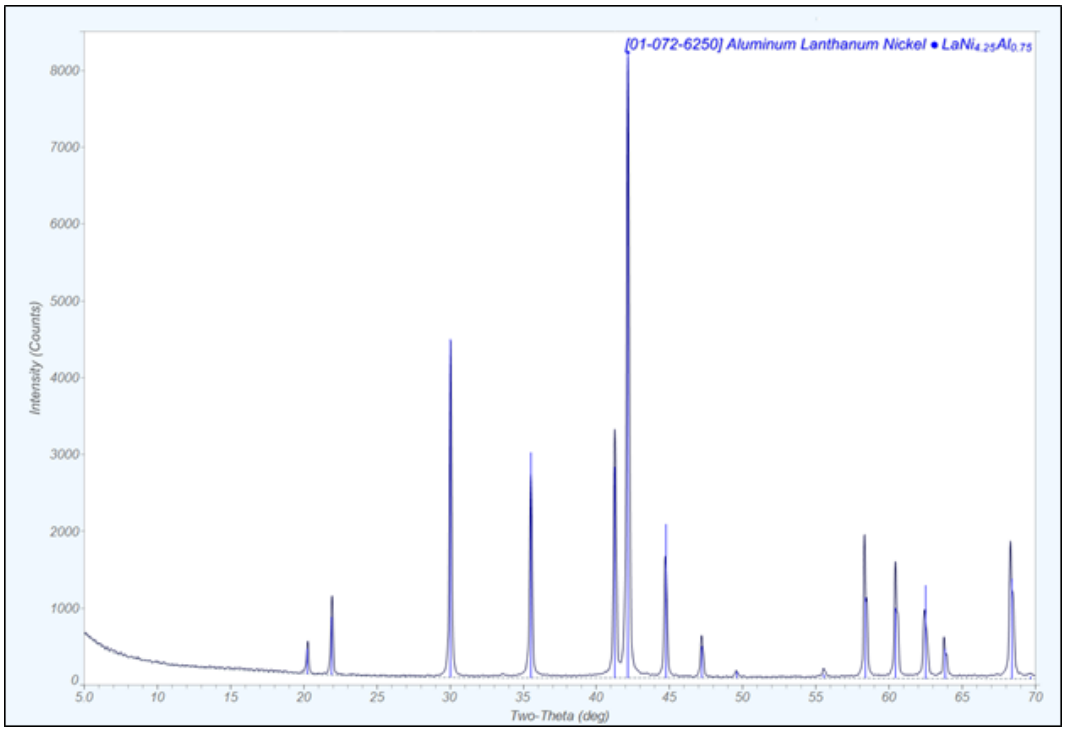
These numbers show the average of a small amount (0.05 to 0.26 g) of digested material; the material may, however, have compositional microvariations throughout the sample, which may be seen more easily by SEM or XRD. The values in Table 3-2 show that no gross changes were caused by the regeneration process.

3.3.4 X-ray Diffraction Analysis

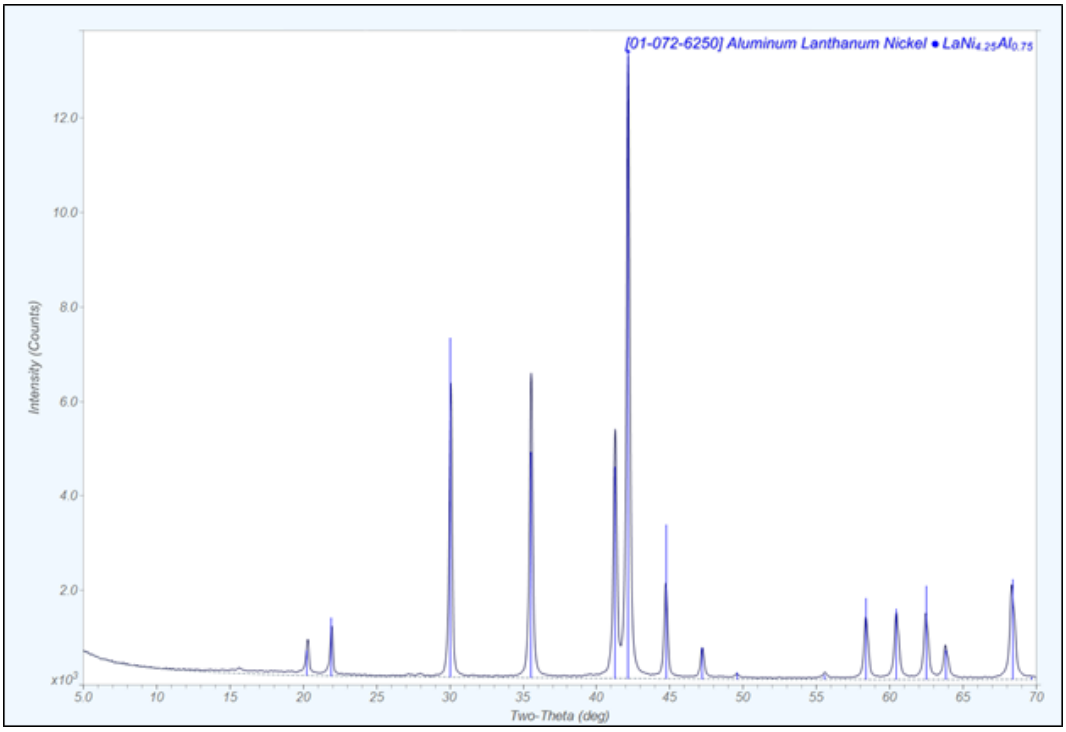
X-ray diffraction (XRD) is a scattering of X-rays by the atoms of a crystal that produces an interference effect. The resulting diffraction pattern provides information on the structure of the crystal or the identity of the crystalline substance.

The spectra shown in Figure 3-5 indicate that there were no material changes between the virgin, pre-anneal, and post-anneal materials. In addition, there were no spurious peaks detected, and the observed peaks were sharp.

a)


[01-072-6250] Aluminum Lanthanum Nickel • LaNi4.25Al0.75
Intensity (Counts)
Two-Theta (deg)

b)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Intensity (Counts)
x10^3
Two-Theta (deg)

c)

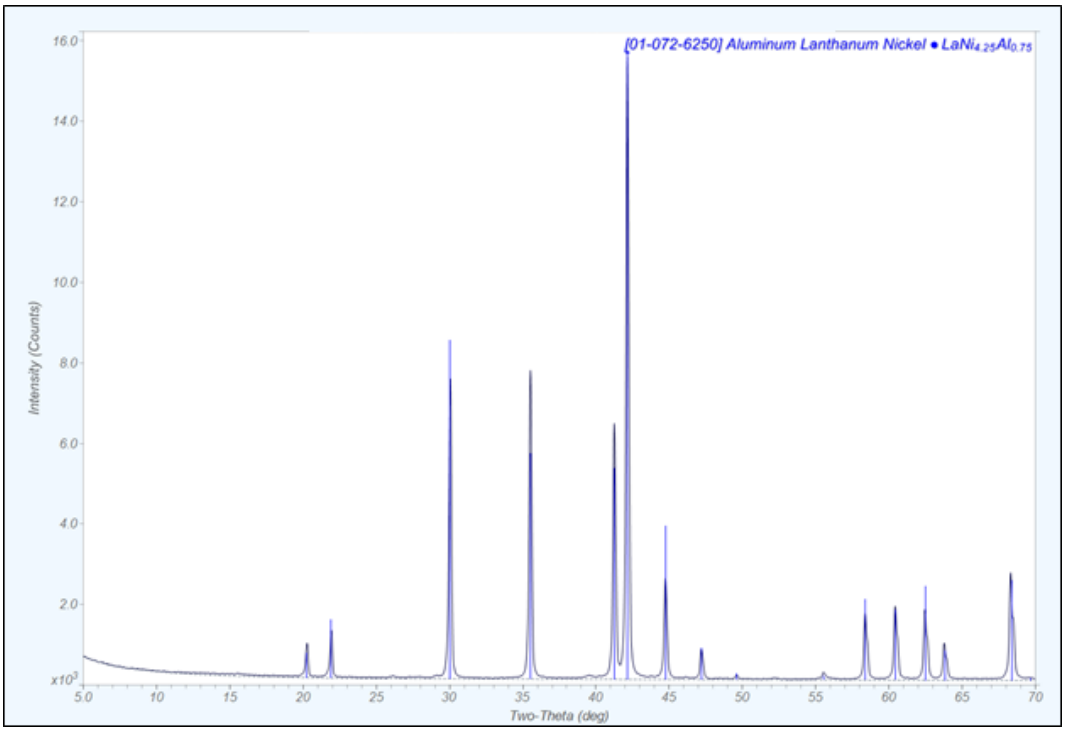


Figure 3-5. XRD patterns for a) virgin material, b) pre-anneal material, and c) post-anneal material.

The ICP-ES results showed that there was very little contamination in the material. For XRD spectra, contaminants, either other phases, or elements, would lead to broadening of the peaks and/or peak shoulders. This was not observed in the XRD spectra in Figure 3-5. Thus, this result reinforced the ICP-ES result that there was little to no contamination of the material.

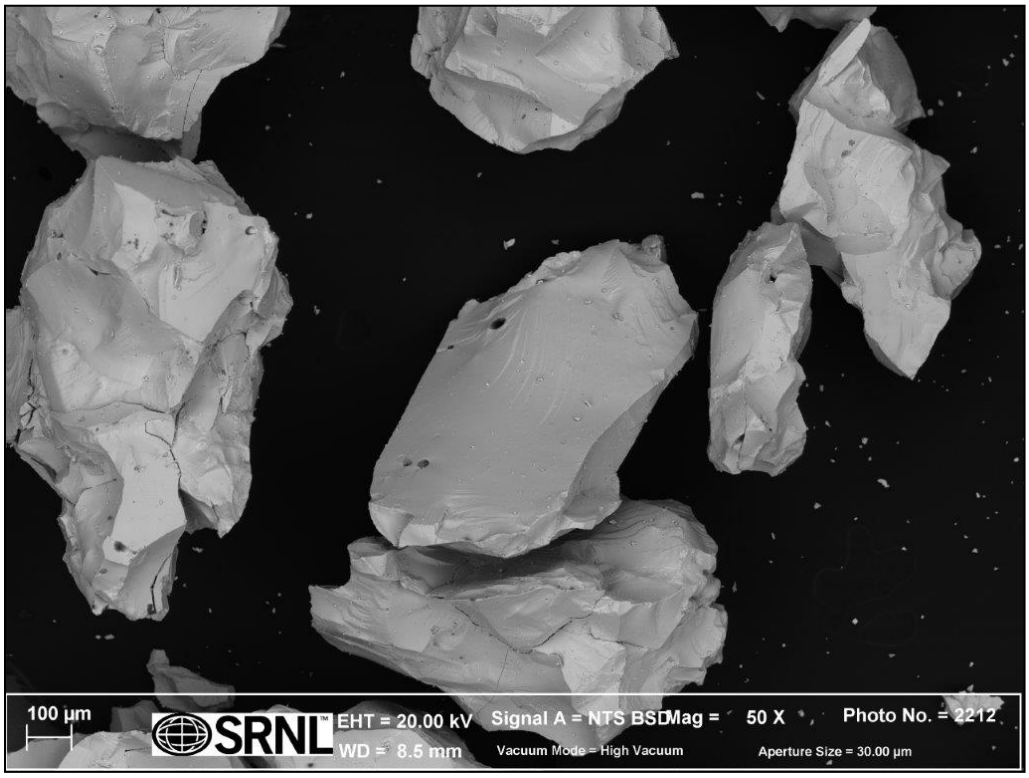
3.3.5 Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy Analysis

The scanning electron microscope (SEM) produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample providing information about the surface topography and composition of the sample. A Carl Zeiss Microscopy LLC Sigma VP field emission scanning electron microscope (FE-SEM) was used to image these samples. It is equipped with secondary electron, backscattered electron, and in-lens secondary electron detectors. It has an imaging capability up to 500,000X.

Energy dispersive X-ray spectroscopy (EDS) is an analytical technique used for elemental analysis or chemical characterization of small surfaces of a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks in its electromagnetic emission spectrum. For the Carl Zeiss SEM, the EDS is performed using an Oxford Instruments X-Max 20 silicon drift detector to detect elements greater than atomic number 3 (Z>3). EDS data and maps are analyzed by Oxford Instruments' INCA 4.15 data analysis software.

Figure 3-6 show several SEM images each of the virgin, pre-anneal, and post-anneal material. One observation from the photos is that the virgin material is much larger than either the pre-anneal or post-anneal material. The scale shown on the image of the virgin material (Figure 3-6) is an order of magnitude larger than the images of the pre-anneal (Figure 3-7) and post-anneal material (Figure 3-8). Another observation is that the virgin material does not have any cracks. The smaller size and the cracks seen on the pre-anneal and post-anneal material is due to the decrepitation caused by the absorption and desorption of hydrogen. See Reynolds et al. [9] for the full sets of virgin, pre-anneal, and post-anneal SEM.

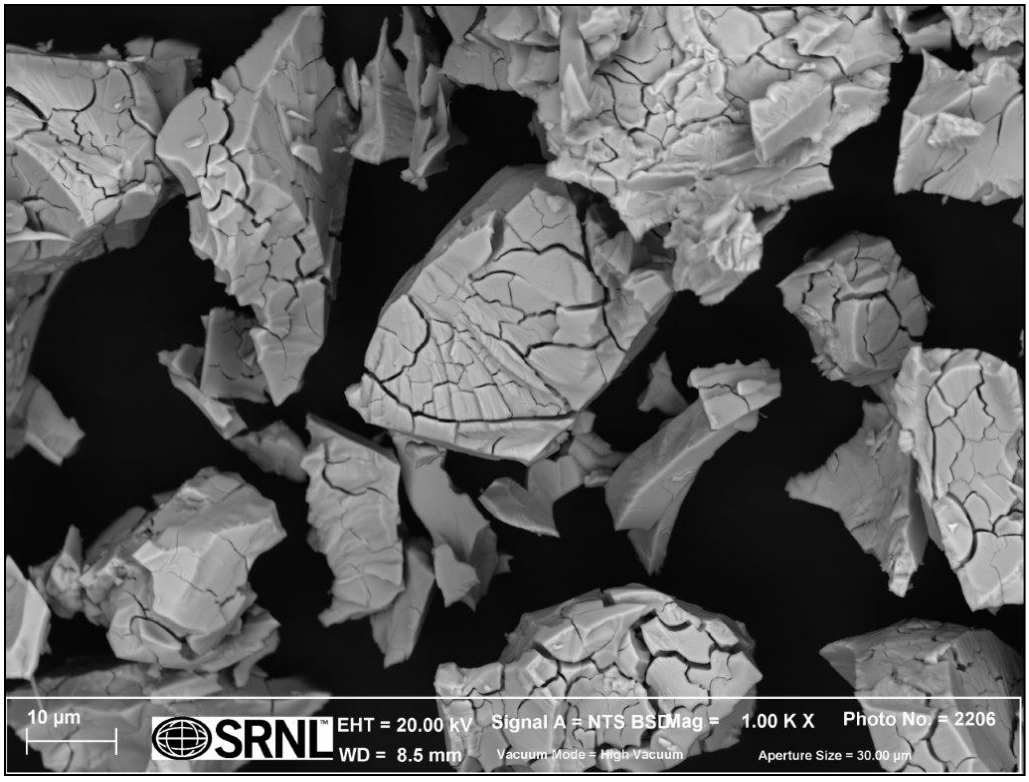
a)



b)

Figure 3-6. SEM images of virgin material at a) 50X and b) 500X magnification.

a)



b)

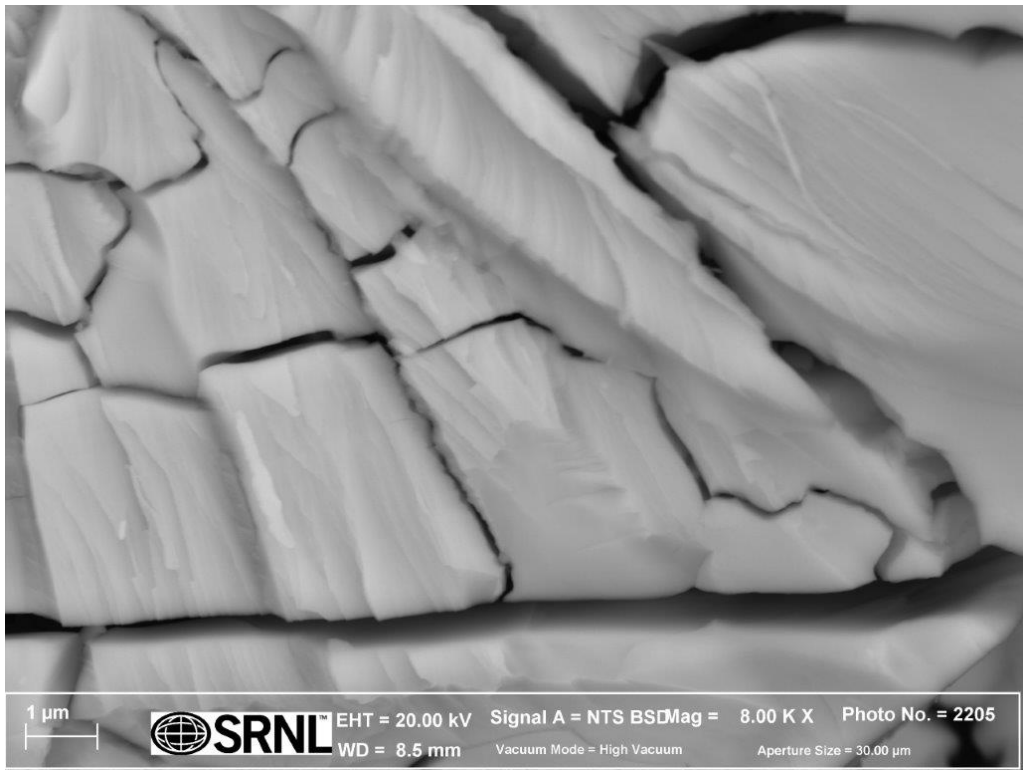
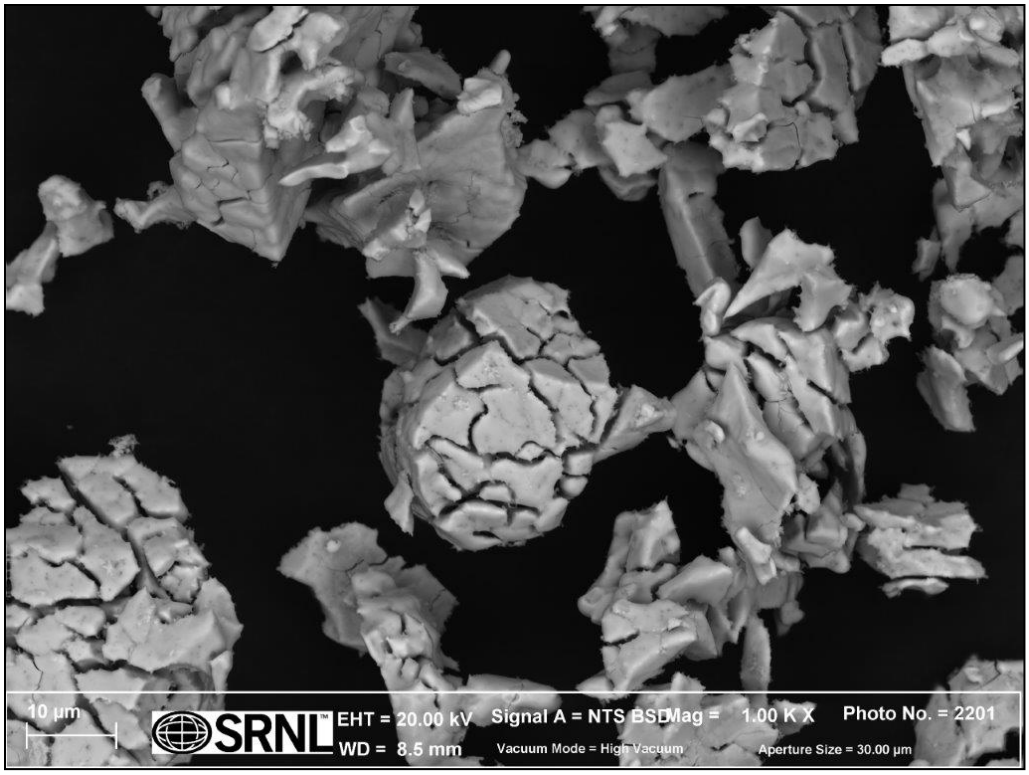


Figure 3-7. SEM images of a) pre-anneal material at a) 1,000X and b) 8,000X magnification.

a)



b)

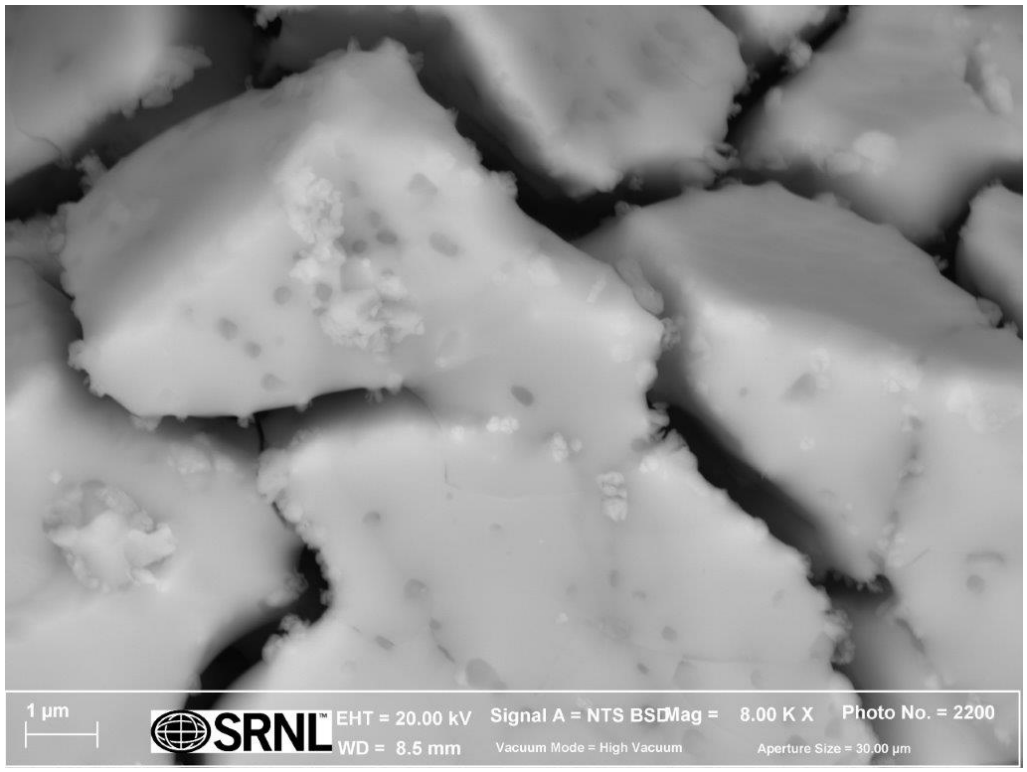


Figure 3-8. SEM images of post-anneal material at a) 1,000X and B) 8,000X magnification.

A difference is seen between the pre-anneal and post-anneal materials. The image for the pre-anneal material appears to be sharper (i.e., less fuzzy) than the image for the post-anneal material. When the

magnification is increased on the post-anneal material, it becomes evident that growths resembling potato eyes (Kartoffelaugen) have formed on the particle surface at some point between sample recoveries. These growths are better seen in Figure 3-9. The appearance of the growths was unexpected, but they did not appear to adversely impact isotherm performance.

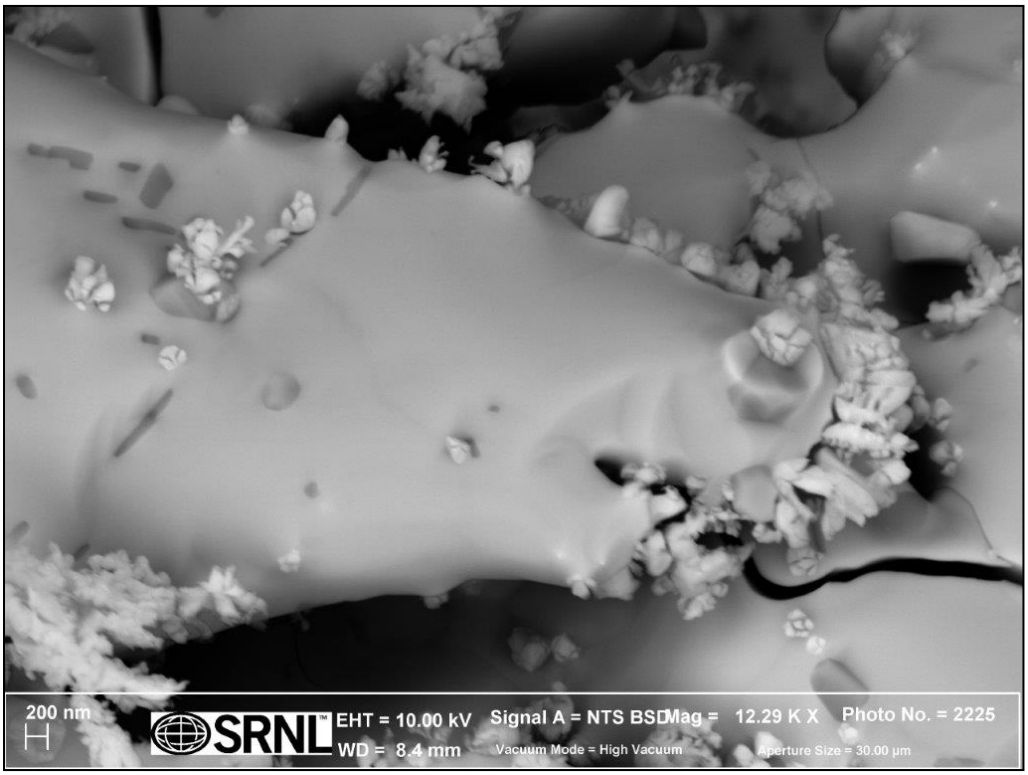
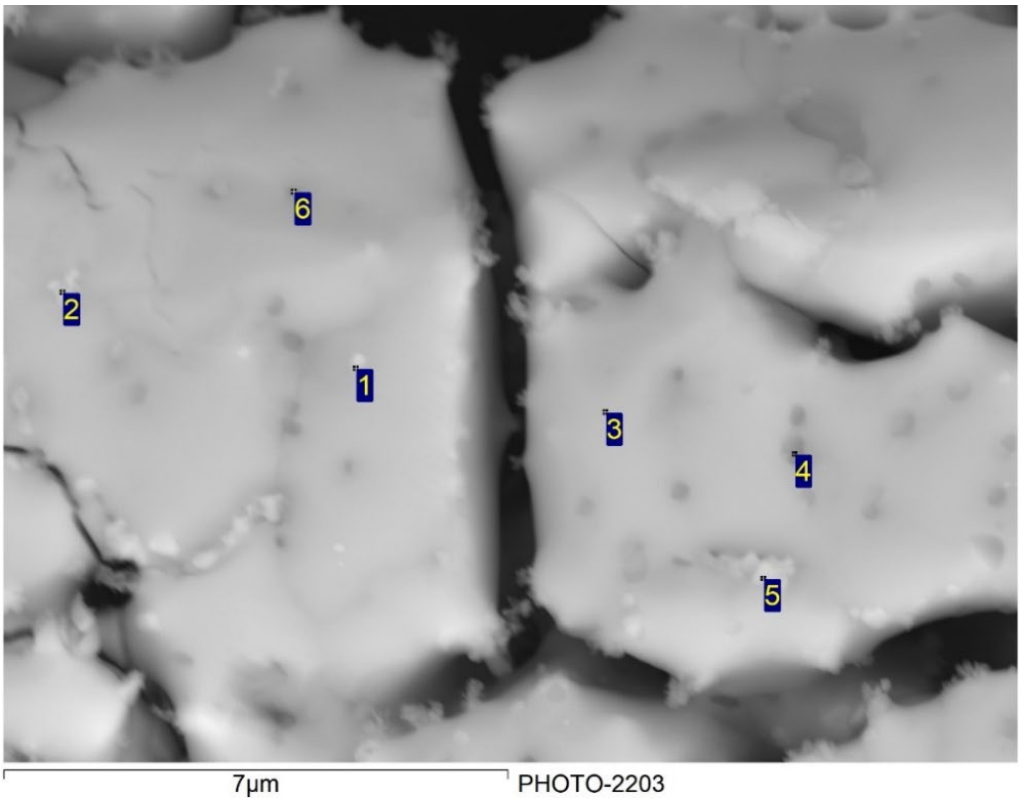


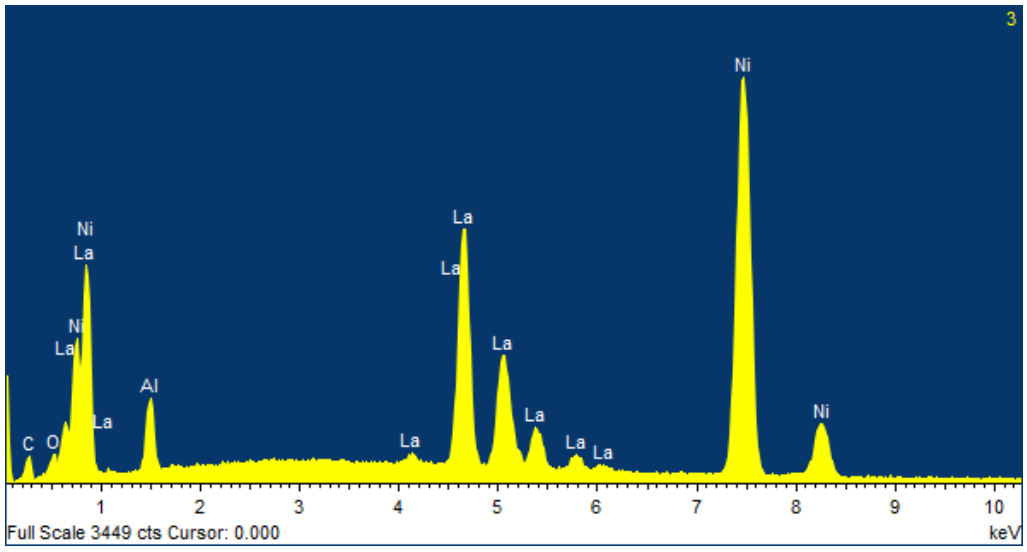
Figure 3-9. SEM image of LANA.75 post-anneal at a magnification of 12,290X.

EDS was performed by focusing 20 kV electrons on specific areas of the SEM image. See Reynolds et al. [9] for the full sets of virgin, pre-anneal, and post anneal EDS spectra. All the spectra show some carbon (C) and oxygen (O) present. Carbon is due to epoxy from the sticky tape that is used to hold the particles. Oxygen is likely from oxides on the surface of the metal that are formed during sample passivation with air. EDS was performed on the surface of the material as well as the growths. As shown in Figure 3-10, the growths tend to have a higher oxygen content than the surface. This tendency is consistent with the growths seen on the virgin material. It is assumed that this happened either during the reactivation step or the simulated regeneration. It is unknown whether these growths are due solely to temperature or rearrangement of lanthanum, nickel, or aluminum oxides formed during passivation.

a)


6
2
1
3
4
5
7µm
PHOTO-2203

b)


3
Ni
La
Ni
La
Ni
La
Al
C
O
La
La
La
La
La
La
La
La
Ni
1
2
3
4
5
6
7
8
9
10
Full Scale 3449 cts Cursor: 0.000
keV

c)

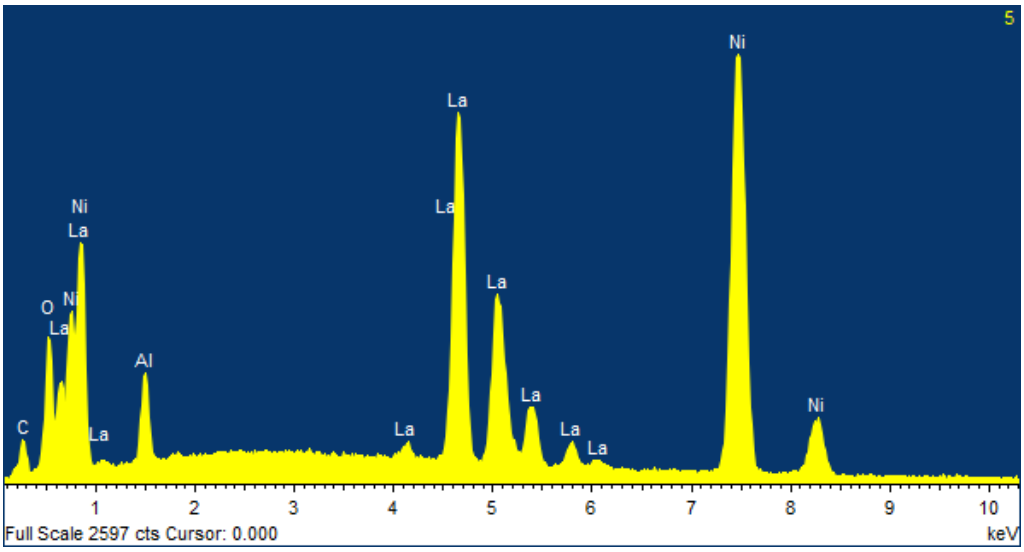


Figure 3-10. Post-anneal material showing a) SEM image, b) EDS image of Point #3, and c) EDS image of Point #5.

4.0 Conclusions

No grossly unexpected behaviors were observed in the isotherms of the sample regenerated in 2018. The sample may be experiencing somewhat accelerated tritium aging, but that is difficult to say conclusively. Thermal stability testing demonstrated that annealing the sample under vacuum slightly flattened the plateau region of subsequent isotherms, had negligible effect on particle size and chemical composition, but did appear to affect morphology. Specifically, SEM images showed the post annealed sample appeared to have fewer cracks than the pre annealed sample and the annealing process appears to have caused growths reminiscent of potato eyes (Kartoffelaugen) on the surface. EDS of these Kartoffelaugen suggest that they are agglomerations of oxides. These oxides likely formed during passivation of the sample after re-activation, but additional work is needed to verify this hypothesis.

5.0 Recommendations, Path Forward or Future Work

It is recommended that tritium aging continue to be monitored on the single regenerated LANA.75 sample. When the sample has aged sufficiently, it should undergo regeneration testing a second time. Monitoring tritium aging and performing secondary regeneration testing is important to ensure any undesirable effects are detected on a bench scale sample prior to being observed in the facility. Further, additional LANA.75 samples should be regenerated and monitored. This will ensure that various samples with diverse backgrounds regenerate in a similar manner. Finally, it is recommended that the growths formed during the annealing process be investigated further. While they do not appear to adversely impact isotherm performance, they are not desirable. It is unknown how robust these tens of nanometer sized growths are or whether they can spall off the surface and migrate throughout the process.

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