REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* 01/3/2023	**2. REPORT TYPE** Technical Report	**3. DATES COVERED** *(From - To)* Dec, 2020 - Oct, 2022

4. TITLE AND SUBTITLE
Characterization of Increased Silicon and Chromium Impact on Premature Heat Tape Failure from Decreased Inconel C-276 Thermal Conductivity

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
6.1

6. AUTHOR(S)
Theodore E. Burye
Talia M. Sebastian

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
US Army CCDC Ground Vehicle Systems Center (GVSC)
Ground Vehicle Power and Mobility (GVPM)
Force Projection Technology (FPT)
6501 E. 11 Mile Road
Warren, MI 48397

8. PERFORMING ORGANIZATION REPORT NUMBER
OPSEC 7139

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
US Army CCDC Ground Vehicle Systems Center (GVSC)
Ground Vehicle Power and Mobility (GVPM)
Force Projection Technology (FPT)
6501 E. 11 Mile Road
Warren, MI 48397

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT
DISTRIBUTION A. Approved for public release; distribution unlimited. OPSEC #7139

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The purpose of this effort was to investigate the proposed hypothesis in our previous report that the heat tape used to heat the Inconel C-276 reactor vessel was prematurely failing due to an increased concentration of silicon and/or chromium on the reactor vessel's outer surface. The outer surface of the reactor vessel is exposed to air when being heated by the heat tape, and the increased silicon and/or chromium would produce increased silicon oxide, chromium oxide or an oxide layer with a combination of those two elements. An silicon/chromium oxide layer between the heat tape and outer reactor vessel surface is thought/hypothesized to reduce the thermal conductivity of the Inconel C-276 material due to silicon oxide and/or chromium oxide having a significantly lower thermal conductivity, which has been shown in literature to be as lower as 1.2-2.0 W/mK. This is close to a 91% reduction in thermal conductivity compared to the reported 21.9 W/mK (700°C) of Inconel C-276, which may result in the heat tape increasing in temperature (at localized spots) to the point of premature failure.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF: Available for Public Release			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Theodore Burye
a. REPORT UNCLS	**b. ABSTRACT** UNCLAS	**c. THIS PAGE** UNCLAS	Same as Report (SAR)	19	**19b. TELEPHONE NUMBER** *(include area code)* 586-282-3047

Characterization of Increased Silicon and Chromium Impact on Premature Heat Tape Failure from Decreased Inconel C-276 Thermal Conductivity

Theodore Burye[a] & Talia Sebastian[b]
U.S. Army Combat Capabilities Development Command Ground Vehicle Systems Center
Ground Vehicle Power & Mobility[a], Force Projection Technology[b]

Prepared by:

Dr. Theodore Burye
Chemical Engineer
theodore.e.burye2.civ@army.mil
Fuel Cell Technologies
Ground Vehicle Power and Mobility (GVPM)
Combat Capabilities Development Command (CCDC) Ground Vehicle Systems Center (GVSC)

Dr. Talia Sebastian
Research Chemist
talia.m.sebastian.civ@army.mil
Fuels and Lubricants Branch
Force Protection Technology (FPT)
Combat Capabilities Development Command (CCDC) Ground Vehicle Systems Center (GVSC)

DISCLAIMER

Acknowledgements

Energy Dispersive Spectroscopy (EDS) results were acquired from the Ground Vehicle Systems Centers (GVSC's) Metallurgy Laboratory, while thermal conductivity results were acquired from the Elastomer Laboratory. Bill Roland, from the Characterization & Failure Analysis group, conducted the thermal conductivity characterization tests.

Table of Contents

List of Figures

1.0 Introduction

The purpose of this effort was to investigate the proposed hypothesis in our previous report [1] that the heat tape used to heat the Inconel C-276 reactor vessel was prematurely failing due to an increased concentration of silicon and/or chromium on the reactor vessel's outer surface. The outer surface of the reactor vessel is exposed to air when being heated by the heat tape, and the increased silicon and/or chromium would produce increased silicon oxide, chromium oxide or an oxide layer with a combination of those two elements. An silicon/chromium oxide layer between the heat tape and outer reactor vessel surface is thought/hypothesized to reduce the thermal conductivity of the Inconel C-276 material due to silicon oxide and/or chromium oxide having a significantly lower thermal conductivity, which has been shown in literature to be as lower as 1.2-2.0 W/mK [2]. This is close to a 91% reduction in thermal conductivity compared to the reported 21.9 W/mK (700°C) [3] of Inconel C-276, which may result in the heat tape increasing in temperature (at localized spots) to the point of premature failure.

This study investigates different mechanisms that might occur during powder exposure experiments (such as elemental diffusion or leaching) that would increase the reactor vessel's surface silicon and/or chromium concentrations and determine each mechanisms effectiveness at increasing those elements. Thermal conductivity measurements of the reactor vessel were investigated in tandem with the mechanistic experiments above to conclude whether the actual thermal conductivity was statistically reduced such that the heat tape may fail prematurely.

2.0 Experimental Methods

2.1 Experimental Inconel C-276 Sample Preparation for Thermal Conductivity Measurements

Samples from the Inconel C-276 reactor vessel, shown in Figure 1 and Figure 2, were taken from the lid and side of the body, respectively. Points 5 and 8 were used to sample from the lid and two different radial locations at point 12 elevation were used to sample from the body. Samples were cut from their respective locations using a composite saw blade. Samples were cut with a length and width at least 20mm. Samples from the body had a thickness greater than or equal to 12mm, while samples from the lid had thicknesses between 7.8mm and 9.0mm. The lid of the reactor vessel is thinner than 12mm, which limited its maximum sampling thickness. The samples from the body had a slight curvature due to the body being manufactured from a round bar-stock. The original oxide coating on each sample was untouched while the sides and backside had exposed Inconel C-276 bare metal.

Samples from the reactor vessel lid were machined as flat as possible for analysis. The oxidized surface was placed flat facing down and the bare Inconel surface was machined parallel to the oxidized surface to within five one-thousands of an inch. The two curved samples from the reactor vessel body were more complicated to make flat. Those samples were first placed oxide surface down and allowed to rest in their natural resting position. Once each sample did not move, they were clamped in place and the bare metal backside was machined flat.

2.2 Experimental Hastelloy X Sample Preparation for Thermal Conductivity Measurements

Samples of Hastelloy X (a high nickel content alloy with similar properties to Inconel C-276) with different thicknesses were cut from a piece of 1 inch diameter bar stock. Samples had thicknesses of 5mm, 7mm, 9mm, 12mm, and 15mm.

Samples were machined as flat as possible. The top and bottom surfaces were machined parallel to each other within one one-thousands of an inch.

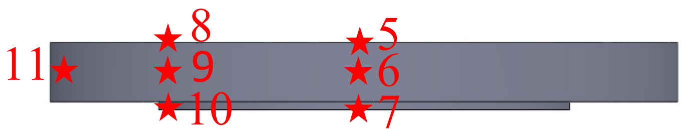

Figure 1: Inconel C-276 Reactor Lid Analysis Locations

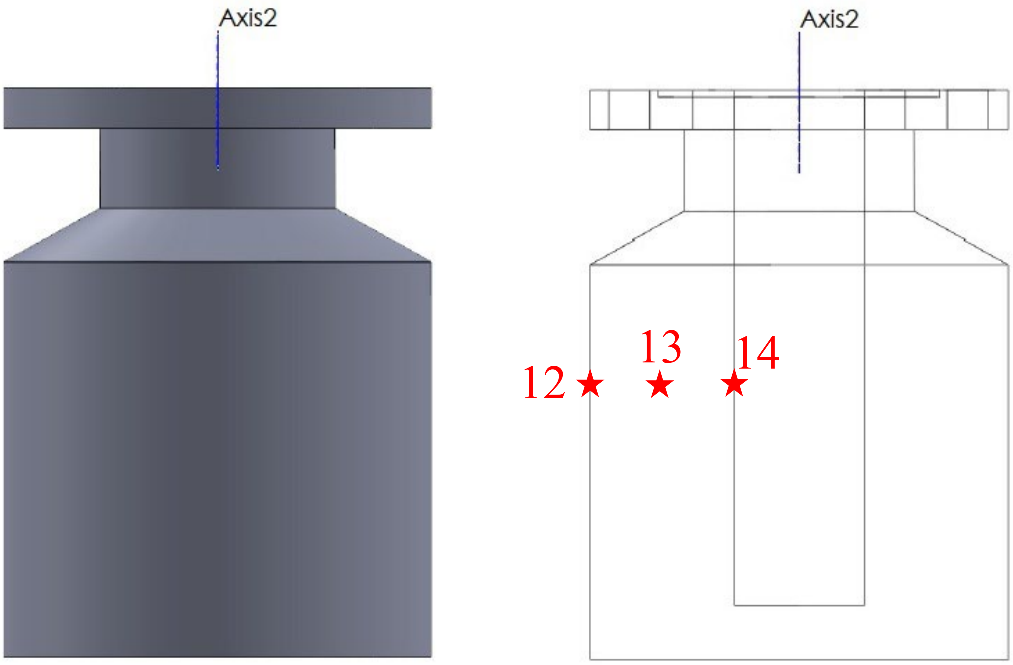

Figure 2: Inconel C-276 Reactor Body Analysis Locations

2.3 Experimental Inconel C-276 Sample Preparation and Testing Parameters for Silicon and Chromium EDS Measurements

Additional samples from the Inconel C-276 reactor vessel, shown in Figure 2, from three different radial locations at point 13 elevation, were also taken. Samples were cut from their respective locations using a composite saw blade. Samples were cut with a length and width at least 20mm and a thickness greater than 12mm.

Each sample first had a physical notch placed on one side to indicate the surface being characterized using Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and/or Thermal Conductivity measurements. The first sample was placed with its notched surface facing upwards not touching any other material. The second sample had its notched surface placed downwards on heat tape (Model BW0101020L from BriskHeat, Columbus, OH, USA) mentioned in the previous report [1]. The final sample had its notched surface facing downwards on a piece of high-temperature insulation described in the previous report [1]. All three samples were tested simultaneously and placed inside a muffle furnace. They were heated in air to 700°C using a ramp rate of 10°C/min and held at that temperature for 5 hours before being cooled back to room temperature. All three samples had their notched surfaces characterized after every 10 hours of heating using the EDS. All three samples were heated for 50 hours in total, each, with each sample being characterized six times (which includes the baselines measurement).

3.0 Characterization Methods

3.1 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) Experiments

The wt% concentrations of multiple elements were identified and measured before and after each experiment in Section 2.3 using a Hitachi SEM (Hitachi; Krefeld, Germany) with an Oxford Instruments EDS detector (Oxford Instruments; Concord, MA, USA). EDS measurements were taken using a beam voltage of 20.0 kV, a 30 μm aperture, a 512 s scan speed, a 10 mm working distance, and a 100x magnification. At least four measurements were taken for each sample and averaged to account for sample composition variations. While the operating parameters each sample was exposed to did appear to significantly impact the wt% concentration of multiple elements, the silicon and chromium concentrations were focused on for the purpose of this report as those are related to the hypothesis being explored in Section 1.

3.2 Thermal Conductivity Experiments

Thermal conductivity was used to characterize changes to the heat transfer of the different Inconel samples cut from the lid and body of the reactor during post-mortem analysis. A C-THERM Technologies Trident thermal conductivity instrument (C-Therm Technologies Ltd.; Fredericton, New Brunswick, CA) was used to acquire these measurements. Measurements were taken at room temperature (~23°) and 200°C using a ceramics calibration. Thermal paste was used as a contact agent between the sample and thermal conductivity instrument sensor. Each sample made optimal contact between its testing surface and the sensor for best results.

Measurements at 200°C were acquired first by heating the muffle furnace to 200°C and allowing the furnace to thermally equilibrate for 1 hour. The thermal conductivity instrument was placed inside the heated furnace, then the sample was placed on the instrument sensor, and finally a weight was placed on the top of each sample. The furnace was then closed and allowed to thermally equilibrate at 200°C for an additional 30 minutes before measurements were taken. Samples tests at room temperature were not placed inside the furnace and held in place on the sensor using a weight during each measurement.

4.0 Results

4.1 Inconel C-276 Elemental Characterization

The following analysis first characterizes the most probable mechanism that would produce elevated silicon and/or chromium surface concentrations in the Inconel C-276 material, which uses operating conditions similar to those as the reactor vessel underwent during powder exposure experiments. As mentioned in Section 2.3, three reactor vessel samples were characterized to determine whether air alone, in contact with the heat tape or contact with the high-temperature insulation, resulted in the highest elevated silicon and/or chromium surface concentrations. The sample exposed only to air is meant to test if self-diffusion is the dominant mechanism. The sample in contact with the heat tape will test if the heat tape influenced elemental levels or whether the sample in contact with the insulation had a greater influence on elemental levels.

4.1.1 Chromium Element Measurements

Figure 3 details the surface chromium wt% from sample 1, which was exposed to air alone while being heated. The baseline measurement of chromium was 16.32 wt% at 0 hours of testing. The chromium wt% increased after 10 hours to 17.66 wt% and ended at 19.06 wt% after 50 hours of testing. Chromium wt% values did statistically increase between the baseline measurement and 10 hours of heating, but remained statistically similar between the 10 and 50 hour measurements.

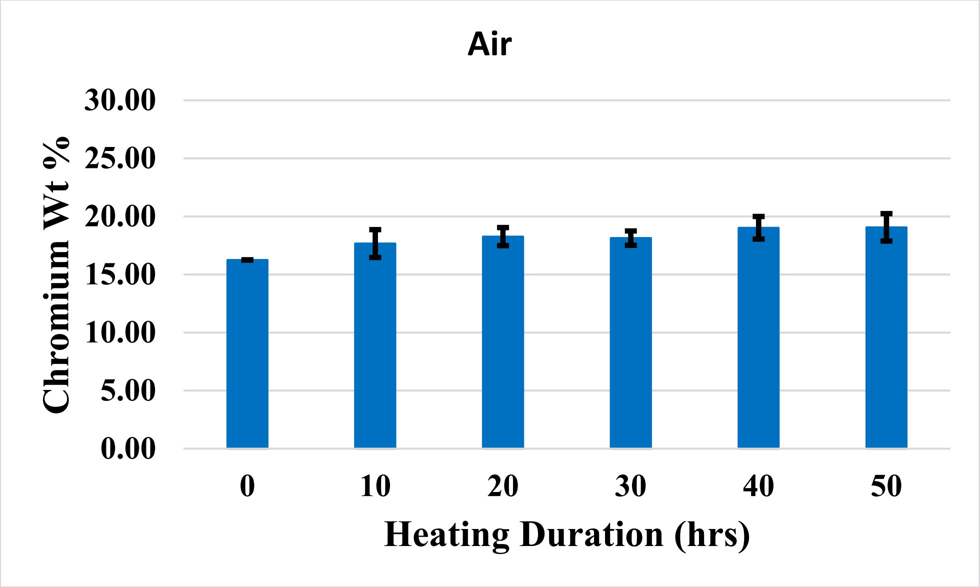

Figure 3: Chromium Wt% Results for Sample 1 in Air

Figure 4 details the surface chromium wt% results from sample 2, which was in contact with the heat tape while being heated. The baseline measurement of chromium was 16.34 wt% at 0 hours of testing. The chromium wt% increased after 10 hours to 19.11 wt% and ended at 19.66 wt% after 50 hours of testing. There was some variability over the 50 hours of testing and the chromium wt% was observed to reach a value as high as 20.62 wt% after 30 hours, but it still was statistically similar to the 50 hour measurement.

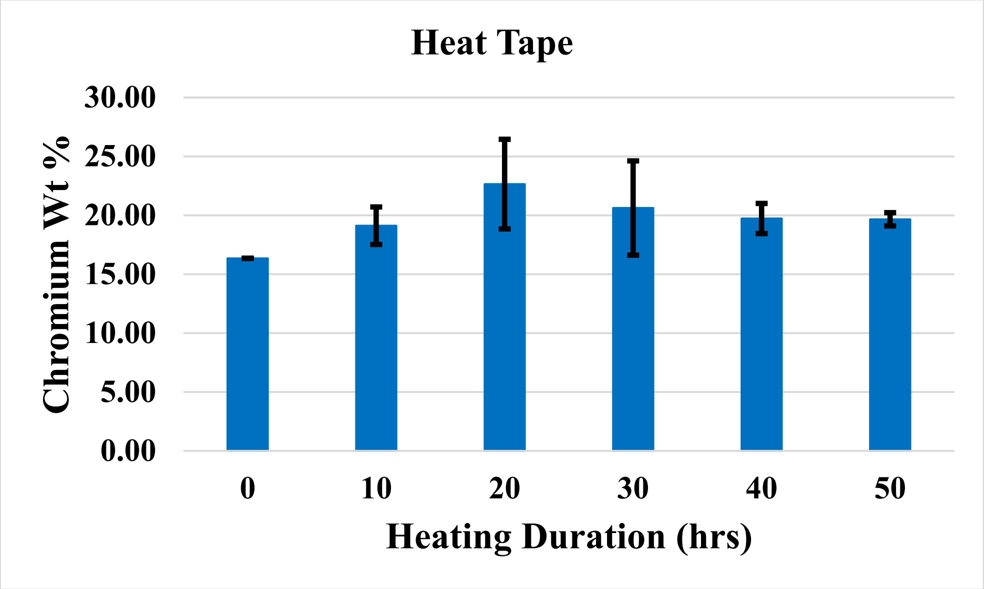

Figure 4: Chromium Wt% Results for Sample 2 in Contact with Heat Tape

Figure 5 details the surface chromium wt% results from sample 3, which was in contact with the insulation while being heated. The baseline measurement of chromium was 16.29 wt% at 0 hours of testing. The chromium wt% increased after 10 hours to 18.30 wt% and ended at 20.33 wt% after 50 hours of testing. As with the other two samples the final 50 hour measurement was statistically similar to the 10 hour measurement.

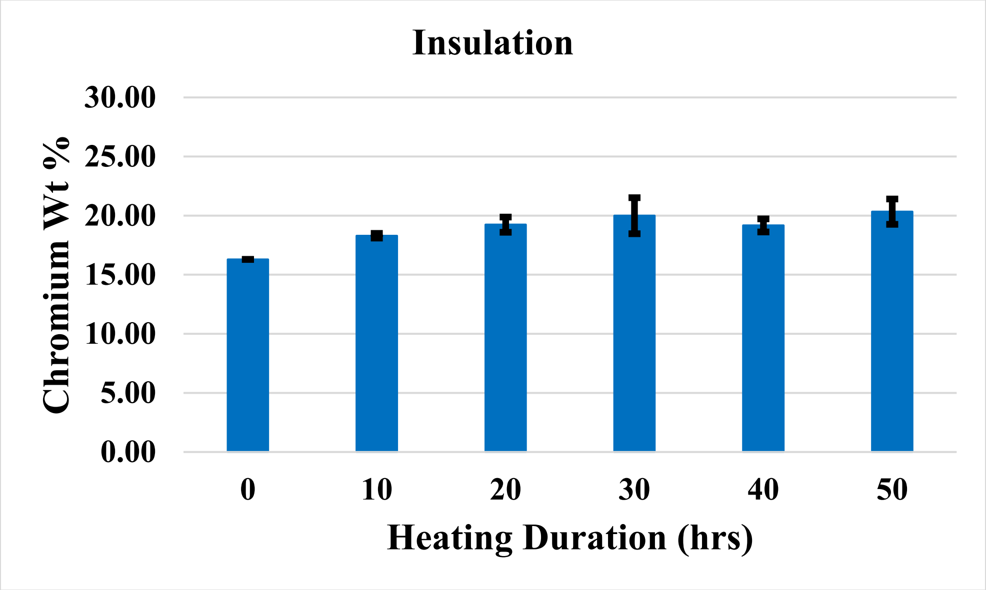

Figure 5: Chromium Wt% Results for Sample 3 in Contact with Insulation

After comparing all three samples, it appears they have statistically similar chromium wt% values after 50 hours of testing. It is possible additional time may increase the surface chromium even further, but this one specific mechanism did not appear to dominate significantly.

4.1.2 Silicon Element Measurements

Figure 6 shows the surface silicon wt% results from sample 1, which was exposed to air alone while being heated. The baseline measurement of silicon was 0.00 wt% at 0 hours of testing. The silicon wt% increased after 10 hours to 0.06 wt% and ended at 0.08 wt% after 50 hours of testing. There was a small amount of silicon that was initially brought to the surface, but it appears to have stayed constant over the duration of testing.

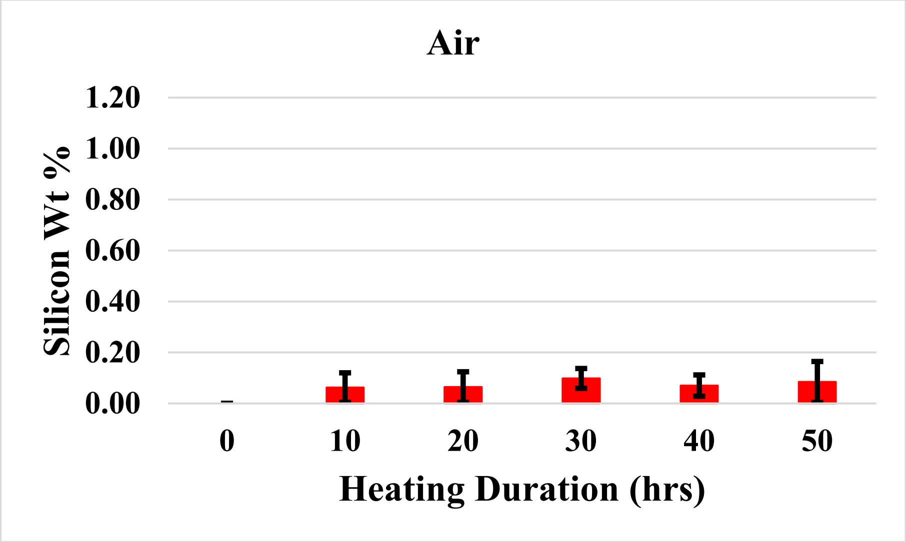

Figure 6: Silicon Wt% Results for Sample 1 in Air

Figure 7 details the surface silicon wt% results from sample 2, which was in contact with the heat tape while being heated. The baseline measurement of silicon was 0.00 wt% at 0 hours of testing. The silicon wt% increased after 10 hours to 0.12 wt% and ended at 0.77 wt% after 50 hours of testing. Unlike all the other measurements beforehand these results show a clear, statistically significant increase in silicon as the heating duration was increased.

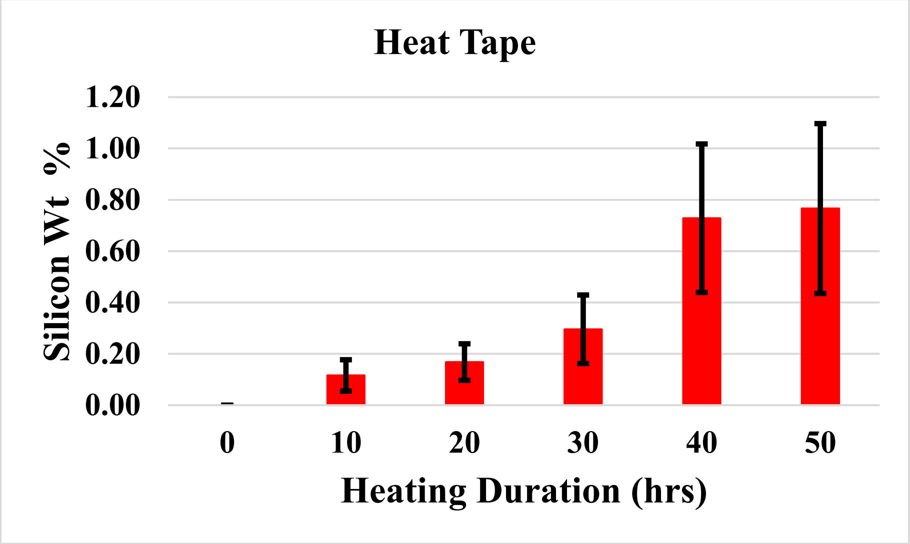

Figure 7: Silicon Wt% Results for Sample 2 in Contact with Heat Tape

Figure 8 details the surface silicon wt% results from sample 3, which was in contact with the insulation while being heated. The baseline measurement of silicon was 0.00 wt% at 0 hours of testing. The silicon wt% increased after 10 hours to 0.13 wt% and ended at 0.14 wt% after 50 hours of testing. There was a slightly higher silicon wt% at the 49 hour mark, which was 0.29 wt%, but was statistically similar all the previous results and the 50 hour measure reduced the silicon wt%, which indicated this was not a trend.

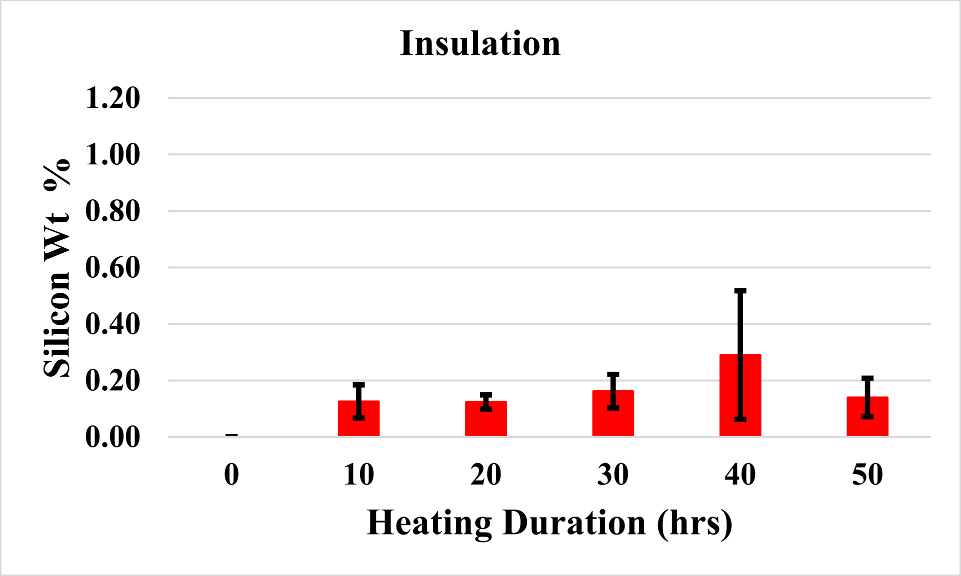

Figure 8: Silicon Wt% Results for Sample 3 in Contact with Insulation

After comparing all three samples, it appears the only mechanism that increased the surface silicon content in a significant manner, was contact with the heat tape. These results align well with our previous paper, wherein silicon was observed to have the largest wt% where the heat tape was present. As well, the insulation in this study was observed to have a noticeable increase in both the reactor vessel body and lid.

The next section will characterize samples from the previous report [1], mentioned in Section 2.1 and 2.2, to determine if their thermal conductivity was statistically reduced from what literature has reported.

4.2 Thermal Conductivity Characterization

This section will explore the thermal conductivity of the different sample types mentioned in Section 2. The different samples obtained from the reactor vessel had different thicknesses based on where they were obtained. This was primarily a problem with the lid, as it was significantly thinner than the amount of material available from the body. Based on specifications from the thermal conductivity instrument, when using a ceramics calibration curve, samples need to be at least 4mm thick, which conveniently all samples used in this study were. However, Inconel is a metal, and the instrument could also be tested using a "Low Metal" calibration curve (metals with <90 W/mK), but those measurements would require samples to have a minimum thickness of 12mm, which these tested samples do not meet. Inconel C-276 has a relatively low thermal conductivity, compared to other metals, and its measured values fit more in the middle of the ceramics calibration and are close to the edge of the low metal calibration. The fact the Inconel is so close to the edge of the low metal calibration may influence results.

The ambiguity in which calibration to use, combined with whether the samples were lower than the minimum thickness, lead to some additional necessary testing, shown below, to characterize the impact sample thickness had on material thermal conductivity measurements compared to reported literature values. The following section analyzes the thermal conductivity of the alloy Hastelloy X, which has a similar thermal conductivity profile, using different sample thickness between 5mm and 15mm at room temperature. These samples were first tested using the low metal calibration and then tested using the ceramics calibration to see both which matched literature the closest and which deviated more from literature as a function of sample thickness.

4.2.1 Inconel C-276 and Hastelloy X Thermal Conductivity Thickness Dependence

This next section discusses the Inconel C-276 metal used in the lid and body of the reactor vessel. This material is much more resistant to corrosion, so material degradation is expected to be less, but still may have occurred and needs to be characterized.

Figure 9 shows the reported thermal conductivity for untested Inconel C-276 [3] and Hastelloy X from 20°C to 900°C [4]. The grey squares represent Inconel, the black circles represent Hastelloy X, and the red triangle is the calculated thermal conductivity at 200°C using a linear trendline from the reported data. Both sets of data are nearly identical and show a nice linear trend within the temperature range used in our previous report (400-700°C).

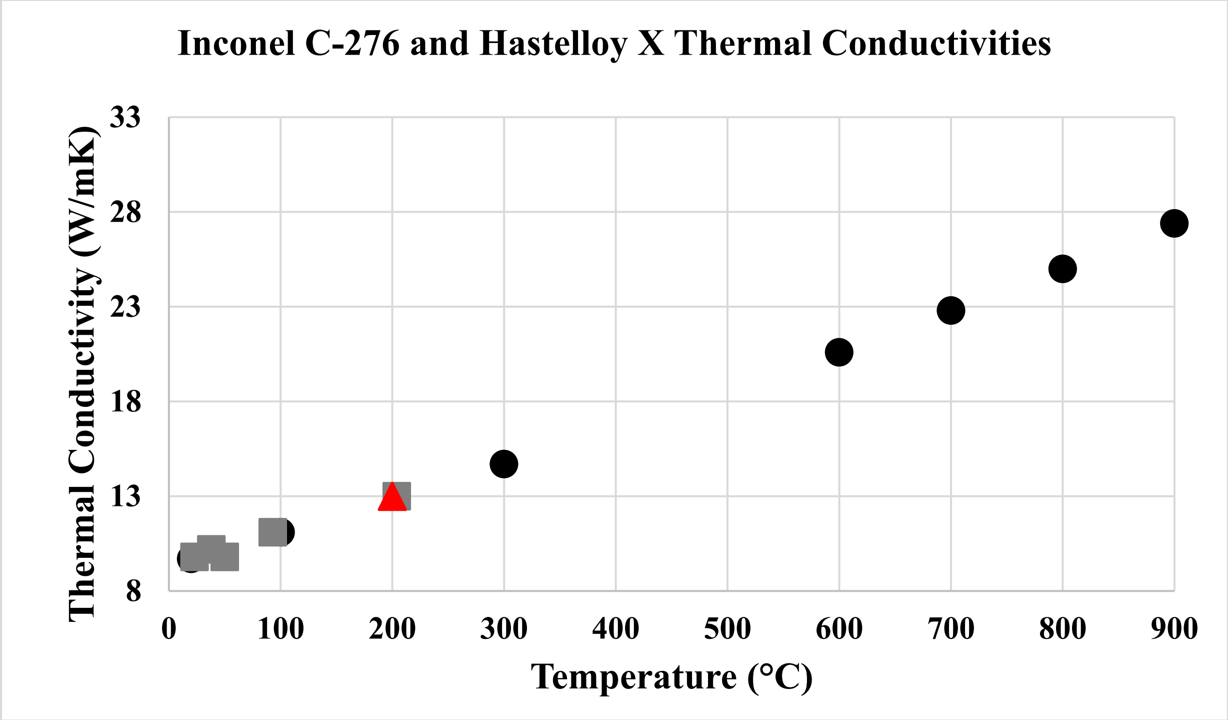

Figure 9: Literature Baseline Values for Inconel C-276 and Hastelloy X Thermal Conductivity

These literature results were used as a reference against the tested Hastelloy X samples using different testing calibrations and different sample thicknesses.

Initially the Hastelloy X samples were tested at room temperature (~23°C) using the Low Metal and Ceramic calibrations to determine which calibration resulted in values closer to the reported literature values and if sample thickness influenced the determined thermal conductivity.

Figure 10 and Figure 11 detail the thermal conductivity values for Hastelloy X measured at room temperature using the low metal and ceramic calibrations, respectively. It was observed that at room temperature, the sample thickness did not impact the measured results, using either calibration. It is not apparent which calibration produced results consistent with literature since both have nearly the same deviation. The only observed difference was the low metal calibration had values lower than literature and the ceramic calibration had values greater than literature. Neat Inconel C-276 was investigated next using the low metal and ceramic calibrations to determine if the material produced a noticeable difference.

Figure 12 shows the thermal conductivity of neat, untested, Inconel C-276 at room temperature using the low metal and ceramic calibrations, compared to literature. While the ceramic calibration is still elevated compared to the Inconel literature value it is still statistically similar and is significantly closer to literature than the low metal results.

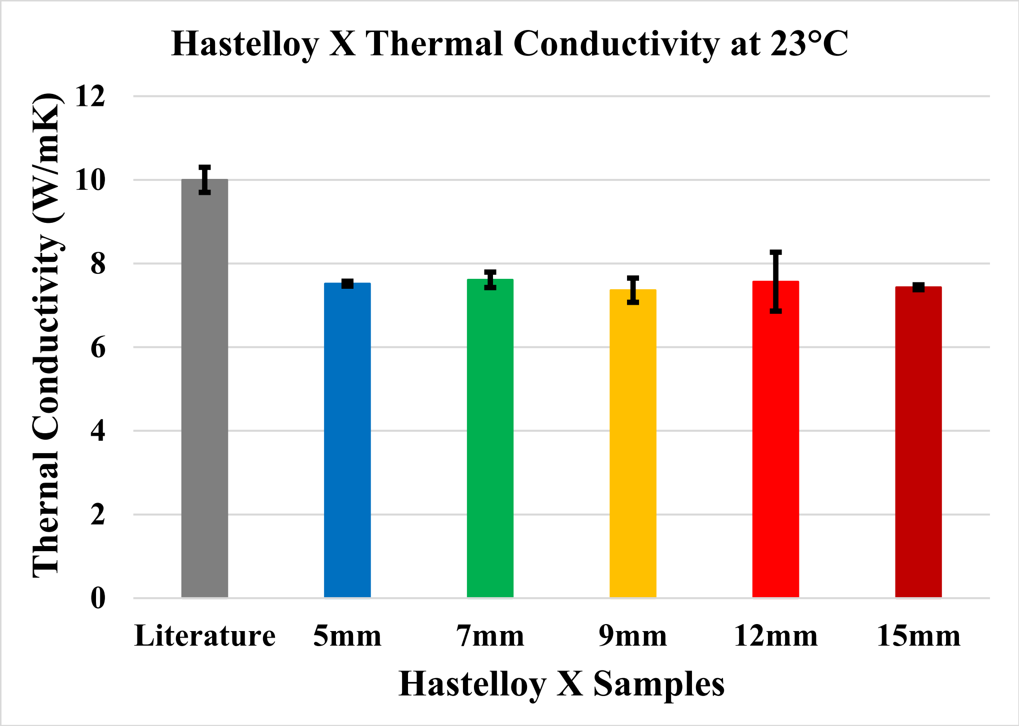

Figure 10: Hastelloy X Thermal Conductivity at 23°C with Varying Sample Thicknesses using the Low Metal Calibration Compared to Literature.

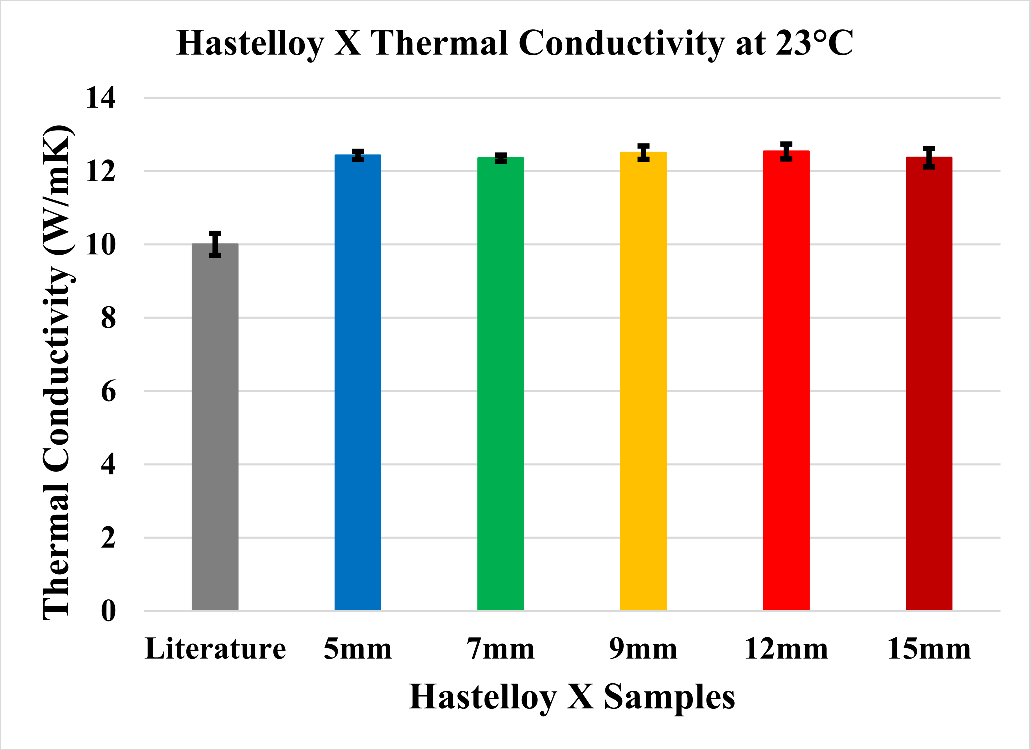

Figure 11: Hastelloy X Thermal Conductivity at 23°C with Varying Sample Thicknesses using the Ceramic Calibration Compared to Literature.

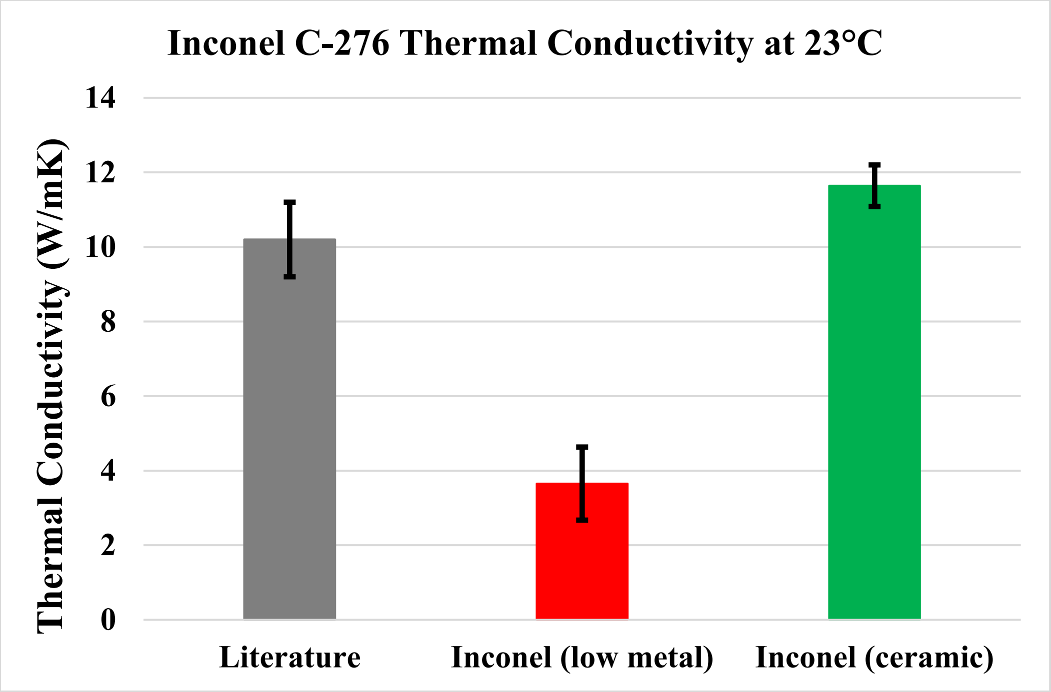

Figure 12: Untested Inconel C-276 Thermal Conductivity at 23°C using the Low Metal and Ceramic Calibrations Compared to Literature.

Based on these results the ceramic calibration was used for sample testing as it showed the closest results compared to literature; however, it was still inconclusive whether sample thickness varied results. Elevated temperature measurements, closer to the operating temperatures used in the previous report (400-700°C), may result in more varied thermal conductivities with respect to sample thickness. Next, the Hastelloy X samples were tested at 200°C and compared to literature.

Figure 13 details the thermal conductivity values for Hastelloy X measured at 200°C using the ceramic calibration. At elevated temperatures it was not observed that thinner samples statistically deviated from literature. Experimental results show samples 9mm or thicker statistically are the same as the reported literature values. Samples sizes as thin as 8mm are also statistically similar based on interpolation of the data between 7mm and 9mm. The sample thickness where thermal conductivity deviates from literature may change at even greater temperatures, but 200°C is the highest the testing instrument could reach. These results, when compared equally at these same conditions, do at least provide statistically similar results compared to literature and was viewed as a good comparison.

Inconel C-276 lid samples mentioned in Section 2.1 were determined to be thick enough, based on the results shown in Figure 13. Those two samples were tested at ~23°C and 200°C and compared to literature.

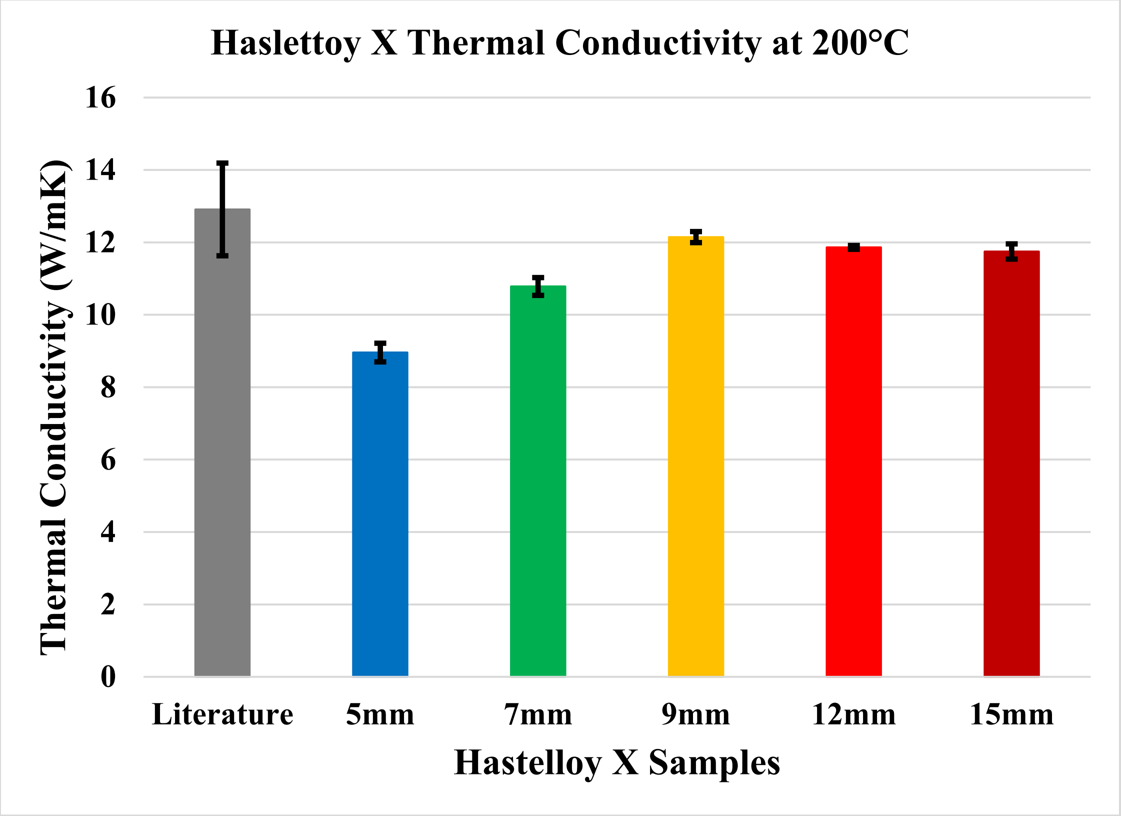

Figure 13: Hastelloy X Thermal Conductivity at 200°C with Varying Sample Thicknesses using the Ceramic Calibration Compared to Literature.

4.2.2 Inconel C-276 Lid and Body Thermal Conductivity Measurements

Both the Inconel reactor vessel lid and body samples, mentioned in Section 2.1, were measured at room temperature (~23°C) and 200°C. Results from the two lid samples were usable, however, the curvature of the samples from the body did not allow enough contact area to touch the instrument and those results were unusable.

Figure 14 details thermal conductivity values for the two lid samples and untested Inconel C-276 measured at 23°C using the ceramic calibration, compared to the reported literature value. As with the Hastelloy X samples, these are all statistically similar to the reported literature value. At room temperature the oxide coating on the two lid samples did not influence the results significantly, which is to be expected.

Figure 15 details thermal conductivity values for the two lid samples and untested Inconel C-276 measured at 200°C using the ceramic calibration, compared to the reported literature value. The untested sample had slightly lower thermal conductivity than at 23°C but was still statistically similar to the literature result. The two oxidized lid samples, however, did show a significant change compared to literature. They were both observed to be similar to each other and were both approximately 35.90% lower than literature, which is significantly outside the standard deviation of literature or any other measured sample in this report.

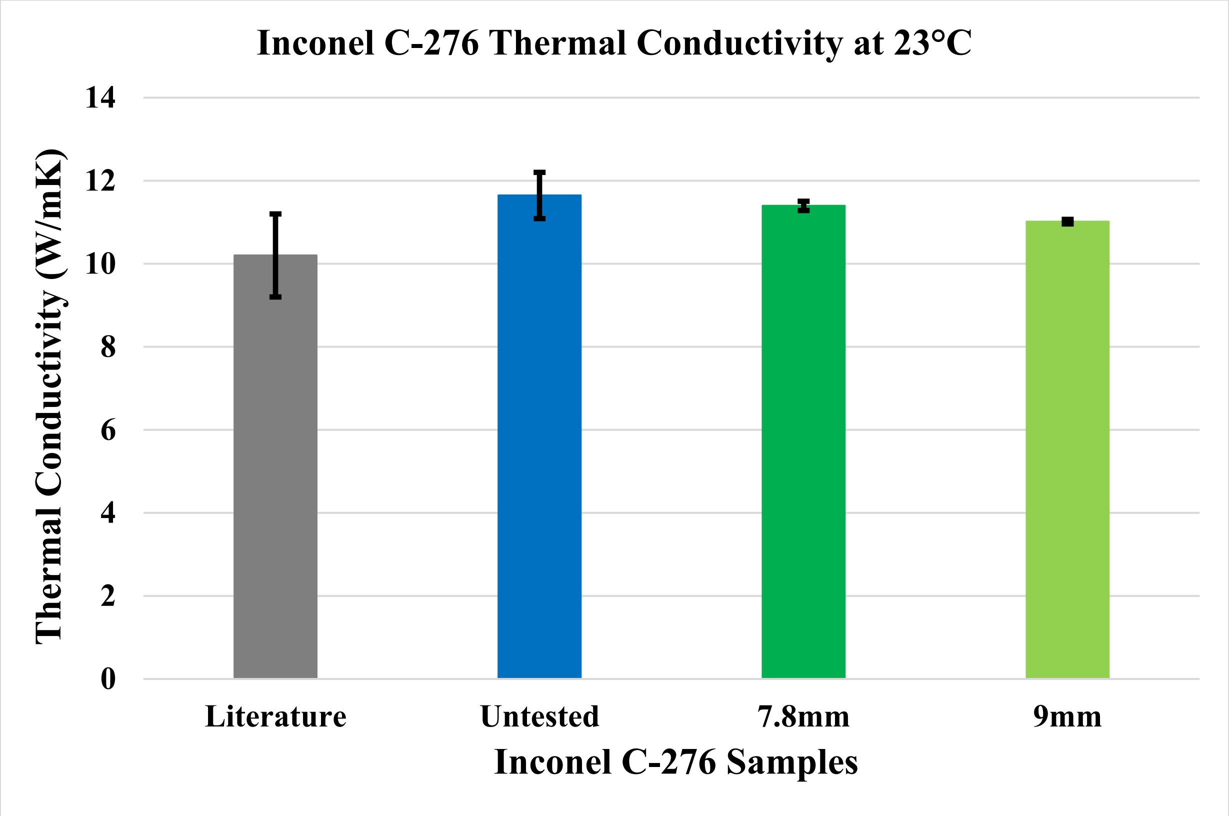

Figure 14: Untested and Lid Inconel C-276 Sample Thermal Conductivity at 23°C using Ceramic Calibration Compared to Literature.

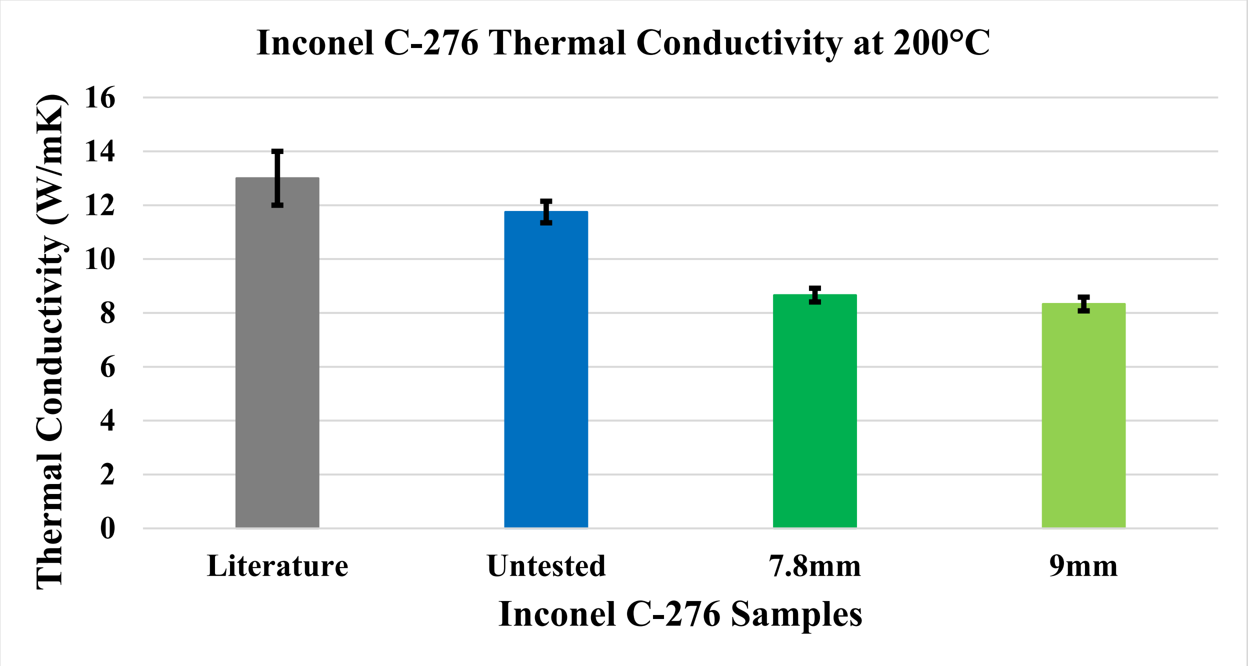

Figure 15: Untested and Lid Inconel C-276 Sample Thermal Conductivity at 200°C using Ceramic Calibration Compared to Literature.

5.0 Discussion and Conclusions

Overall, these results strongly support the hypothesis that a silicon and/or chromium oxide layer on the Inconel vessel surface reduced its thermal conductivity. These findings point to silicon deposition through contact with the heat tape and/or high-temperature insulation being a realistic mechanism for increasing the silicon content on the vessel surface, forming silicon dioxide, and decreasing the Inconel C-276's thermal conductivity. As silicon dioxide is a strongly insulating material, coupled with the fact silicon was significantly elevated on the Inconel surface in an oxidizing environment, point to a strong likelihood this contributed to lowering the Inconel thermal conductivity. Elevated chromium on the reactor vessel's surface, detailed in the previous report [1], could also be a contributing factor, as this study found it could be diffused to the Inconel C-276 surface from its bulk interior through an increased operating temperature.

While it was not possible to take thermal conductivity measurements above 200°C using the conductivity instrument in this study, a statistically significant difference between the Inconel C-276 lid samples and reported literature values at 200°C was established. The two lid samples had similar thermal conductivities which were about 35.90% lower than what literature has reported at 200°C. This difference in thermal conductivity, at 200°C, may not be large enough to produce failures in the heat tape, but operational heat tape failures in the previous study [1] occurred at temperatures between 600-700°C. Differences between measured thermal conductivities in this report and literature would be expected to be even larger at those increased temperatures, thus increasing the potential for heat tape failure further. An additional point to mention is that the silicon content was greater on the reactor vessel's body than the lid, where the heat tape was located. The previous report [1] detailed that the silicon content of the reactor vessel's body was

45 wt%, compared to 1.5 wt% on the lid. While the reactor vessel's body samples could not be accurately tested (due to the sample curvature), it is viewed as likely and probable the increased silicon in those samples would have lowered those thermal conductivity measurements further; however, it is difficult to approximate how much lower the thermal conductivity would be with increased silicon.

In conclusion, this report details that increased silicon and chromium levels can be formed using operating conditions, such as those that the Inconel C-276 reactor vessel experienced, detailed in our previous report [1]. The elevated silicon and chromium individually, or together, (in the form of an oxide material) appear to have resulted in statistically lowering the thermal conductivity of the Inconel C-276 below reported literature values at 200°C by 35.90%. This reduction in thermal conductivity is thought to increase further when at operating temperatures of 600-700°C, which was experienced by the Inconel samples. Finally, while the curved samples from the body could not be accurately tested, the increased silicon content observed on those samples is also viewed as likely to decrease the thermal conductivity further yet. While these findings may not result in the heat tape immediately failing catastrophically, they support the hypothesis the heat tape life expectancy is reduced significantly. Based on these findings it is recommended that future experiments should remove the surface coating from the Inconel that is in contact with the heat tape. Simple abrasion of the surface may be sufficient to reduce or completely remove the elevated silicon and chromium levels and extend the life of the heat tape.

References

[1] T. Burye and T. Sebastian, "Characterization of 316 Stainless Steel and Inconel C-276 Degradation after Exposure up to 10 vol% H_2S at High-Temperatures up to 100 Hours," *DTIC,* pp. 1-46, 2022.

[2] W. Zhu, G. Zheng, S. Cao and H. He, "Thermal Conductivity of Amorphous SiO_2 Thin Film: A Molecular Dynamic Study," *Scientific Reports,* vol. 8, p. 10537, 2018.

[3] H. T. Metals, "High Temp Metals," 2022. [Online]. Available: https://www.hightempmetals.com/techdata/hightempHastC276data.php.

[4] H. T. Metals, "High Temp Metals," 2022. [Online]. Available: www.hightempmetals.com/techdata/hitempHastXdata.php.