Supercritical CO2 Heat Exchanger Fouling

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His current research interests are related to materials compatibility, selection, and performance related to energy production applications.

ABSTRACT

Supercritical CO_2 power cycles rely heavily upon heat transfer for ensuring efficient cycle performance. Current state of the art utilizes printed circuit heat exchangers that are effective due to the large surface area available for heat transfer. The recompression closed Brayton cycle, located at Sandia National Laboratories, has experienced some minor fouling of the channel inlets during short term operation (hundreds of hours). Products were determined to be a combination of dirt, metal corrosion products, and hydrocarbon materials. The system operates with oil-free components (i.e. pumps) and the source of the hydrocarbon material may arise from the industrial grade CO_2 (99.9% purity) utilized during previous experiments with future experiments using 99.95% purity.

INTRODUCTION

Energy efficiency continues to be an important consideration in power production, and highly efficient cycles require less heat, which costs less from an energy source standpoint. However, levelized cost of electricity also requires minimizing capital costs and maintenance costs. With this perspective in mind, many supercritical fluids are being considered for their potential to achieve high energy efficiency and small footprint [1-3].

The U.S. Department of Energy Office of Nuclear Energy (DOE-NE) supercritical carbon dioxide recompression closed Brayton cycle (RCBC) test assembly (TA) construction has been completed to its original design and resides at Sandia National Laboratories (SNL) in New Mexico. The cycle configuration is shown in Figure 1. Each component is subjected to different fluid conditions that may result in differing performance related concerns. Component lifetime will continue to be a heavily researched area as supercritical carbon dioxide (SCO_2) continues to emerge as a working fluid for power cycles.

Previous work showed erosion of turbine blades during the operation of the RCBC [4]. Currently, this degradation is thought to occur by entrainment of iron oxide particles through the turbine blade. Formation of corrosion products, like iron oxide, even in the presence of very pure CO_2, has been observed in the literature [5-12]. Mitigation of corrosion and corrosion product entrainment must be addressed as RCBC technology matures so as to increase lifetime of the turbomachinery.

In continuing to disseminate component related performance concerns, this report is a compilation of observations made related to heat exchanger fouling, causes of fouling and its relation to fluid purity, and mitigation methods being pursued at present.
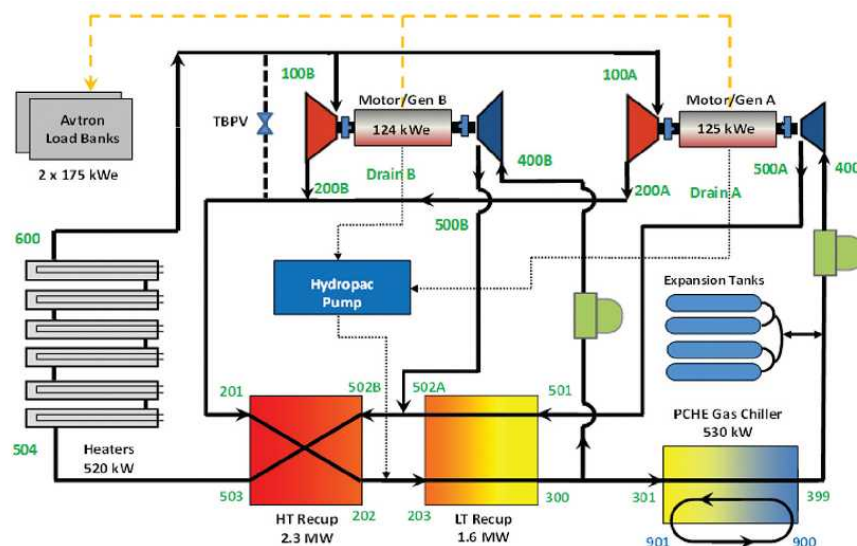

Figure 1: Schematic diagram of the SCO2 RCBC test article.

Compact Heat Exchanger Fouling

Fouling in heat exchangers describes the build-up of material along the heat transfer surface within fluid channels, which degrades thermal performance and increases hydraulic resistance through the unit. This generally occurs more slowly and to a lower degree in compact heat exchangers, but is more likely to cause channel plugging. Cleaning methods for compact units become more difficult due to the small channel diameters and complex passages, therefore prevention of fouling mechanisms and monitoring of heat exchanger performance will be critical to achieving high capacity factors in SCO_2 Brayton cycle power systems.

This material build-up in fouling can arise from one or more factors related to precipitation fouling, particulate fouling, chemical fouling, corrosion fouling, and solidification fouling. The potential impact of these different fouling mechanisms in the supercritical carbon dioxide Brayton cycle test article are listed in Table 1. Examples of fouling in more typical applications are reviewed by Shah [1] and Hesselgreaves [2].

Fouling of a heat exchanger is a transient process that occurs over the service life of the unit and is closely coupled to the cleaning regimen it undergoes. Material build-up usually proceeds along one of the paths in Figure 2 from Shah [1] under steady operating conditions but can exhibit more complex behavior under the conditions encountered in a test system.

An initial delay period is seen as nucleation of fouling material occurs across the heat transfer surface. The length of the delay is affected by the interactions between the process fluid, surface chemistry, and surface morphology. Increasing surface temperature, roughness, and compatibility of the surface material with the foulant can all decrease this delay time.

This delay is followed by a complex period of foulant deposition, removal, and aging mechanisms. Deposition of fouling material generally increases with temperature, surface roughness, and impurity concentration while removal increases with higher wall shear stresses or flow velocities and proper surface design. Compact heat exchangers such as the Printed Circuit Heat Exchangers (PCHEs) used in the Sandia test article have relatively high wall shear stresses as well as complex flow paths that help scour fouling deposits away, leading to almost an order of magnitude reduction in fouling factors as compared to shell and tube units [3]. Corrosion fouling by a stable oxide is a common example of asymptotic fouling behavior where interaction with the process fluid builds a thin, stable oxide layer that

eventually reaches an equilibrium condition. Precipitation fouling in compact heat exchangers on the other hand will exhibit a fairly linear dependence as individual channels quickly fill and plug with precipitate.

The degradation in heat exchanger performance due to fouling can be observed over time by monitoring the pressure drop and overall heat transfer coefficient of a unit under steady operating conditions. Gas-like flows will tend to indicate fouling first from an increase in component pressure drop as they typically have poor local heat transfer coefficients already, while liquid-like flows tend to indicate fouling first from a decrease in overall heat transfer coefficient. Heatric™ recommends monitoring these metrics for an increase in component pressure drop above 120% of the expected value or a decrease in temperature efficiency below 90% of the expected value [4].

Table 1: Examples of several fouling phenomena and potential SCO2 Brayton impacts.

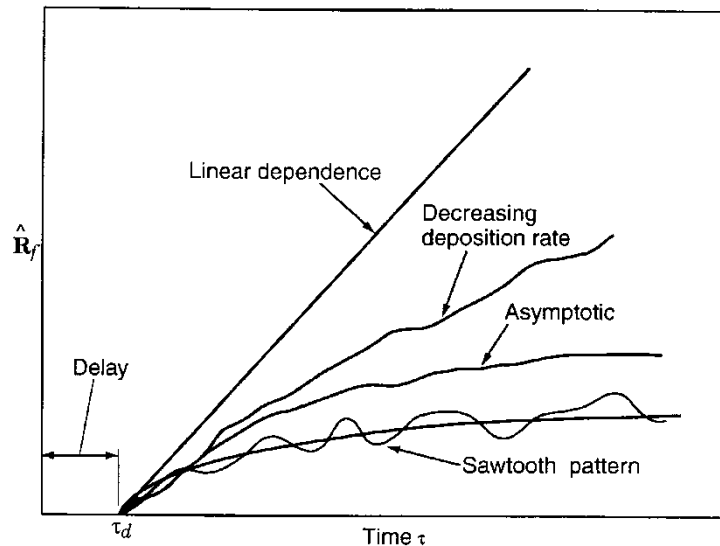| Type	Examples	Potential SCO2 Brayton Impacts
Precipitation	Salt Scale (H2O) Oil Transport (CO2)	1. Decreased heat exchanger performance. 2. Cleaning / replacement of heat exchangers. 3. Local thermodynamic property variation.
Particulate	Fabrication Shavings	1. Erosion of surfaces and sharp corners. 2. Sedimentation of piping, headers. 3. Plugging of heat exchanger channels.
Chemical Reaction	Coking	1. Reduced heat exchanger performance 2. Localized hot-spots from high emissivity.
Corrosion	Oxide Formation	1. Reduction of material thickness. 2. Spallation of weak oxide layers. 3. Reduced heat exchanger performance.
Solidification	Vent Line Freeze-up	1. Blockage of vent lines and over-pressurization of other system components. 2. Mechanical failure due to cold temperatures. 3. Stuck mechanisms from material shrinkage.

Figure 2: Typical fouling behavior trends for heat exchangers [1].

Sealed compact heat exchangers are not recommended for high-fouling service because frequent and aggressive cleaning is impractical without direct access to heat transfer surfaces. However, chemical and mechanical cleaning techniques are still possible. Chemical and solvent cleaning can remove even tenacious fouling materials where the heat exchanger core and other components are not damaged by

the additive. SCO_2 itself is an excellent solvent and will dissolve many materials in the system, with normal solubility species such as oils precipitating on cold surfaces similar to compressor oil in refrigeration systems and inverse solubility species precipitating on high-temperature surfaces. Back puffing is a moderately-aggressive mechanical cleaning technique where the heat exchanger is taken out of service, fitted with a burst disk on the inlet side where particulate tend to accumulate, and pressurized until the burst disk releases the pressure. The high-velocity gas expanding through the unit can clear particulates from even small channels. If a solvent gas, such as SCO_2, is used additional precipitates can be removed. Heatric™ recommends this method for PCHEs as a second cleaning step when chemical methods fail [5]. Finally, ultra-high pressure water jetting can be used to remove especially tough deposits such as calcium carbonate from severely fouled heat exchangers. Water at pressures above 1700 bar have been used to clean PCHEs even if the unit has a lower maximum allowable working pressure because the pressure is not actually held within the channels [6].

Product Fouling Analysis

Heat Exchanger Fouling Analysis

Analysis of the fouling product from Figure 3**Error! Reference source not found.** was performed using energy dispersive spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FT-IR), and Nuclear Magnetic Resonance Spectroscopy (NMR).

EDS analysis, shown in Figure 4, determined a variety of elements, which are likely extracted from different loop components. Metal from loop piping, graphite, and dirt were found in the analysis.

RCBC piping is fabricated from 316L (nominal max: Fe-18Cr-14Ni-3Mo-2Mn-0.75Si + minor), thus iron, chromium, and nickel rich products are thought to be from the loop piping. Uncalibrated EDS has large uncertainty when used for low Z (atomic number) elements, specifically carbon and oxygen. Regardless of this uncertainty, appreciable quantities of carbon and oxygen were detected and are likely due to graphite used in labyrinth seals on the TAC. Calcium and sodium were found and are commonly associated with compositions of dirt.

Samples were quite small and were of insufficient quantity to perform extensive analytical chemical analysis. FT-IR of the sample (Figure 5) indicated that organic products were present in the sample, but nothing more than characteristic peaks could be clearly determined from this analysis.
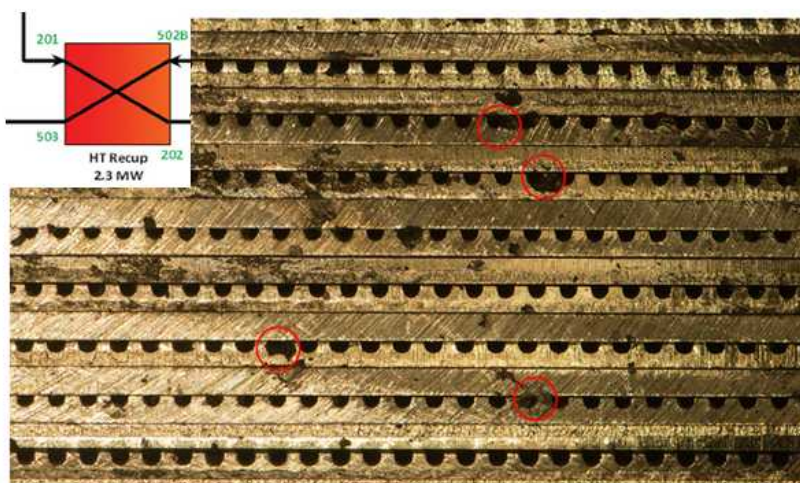

Figure 3: Picture of high pressure, low temperature (location 502B) recuperator outlet, showing fouling and possible plugging of channels.
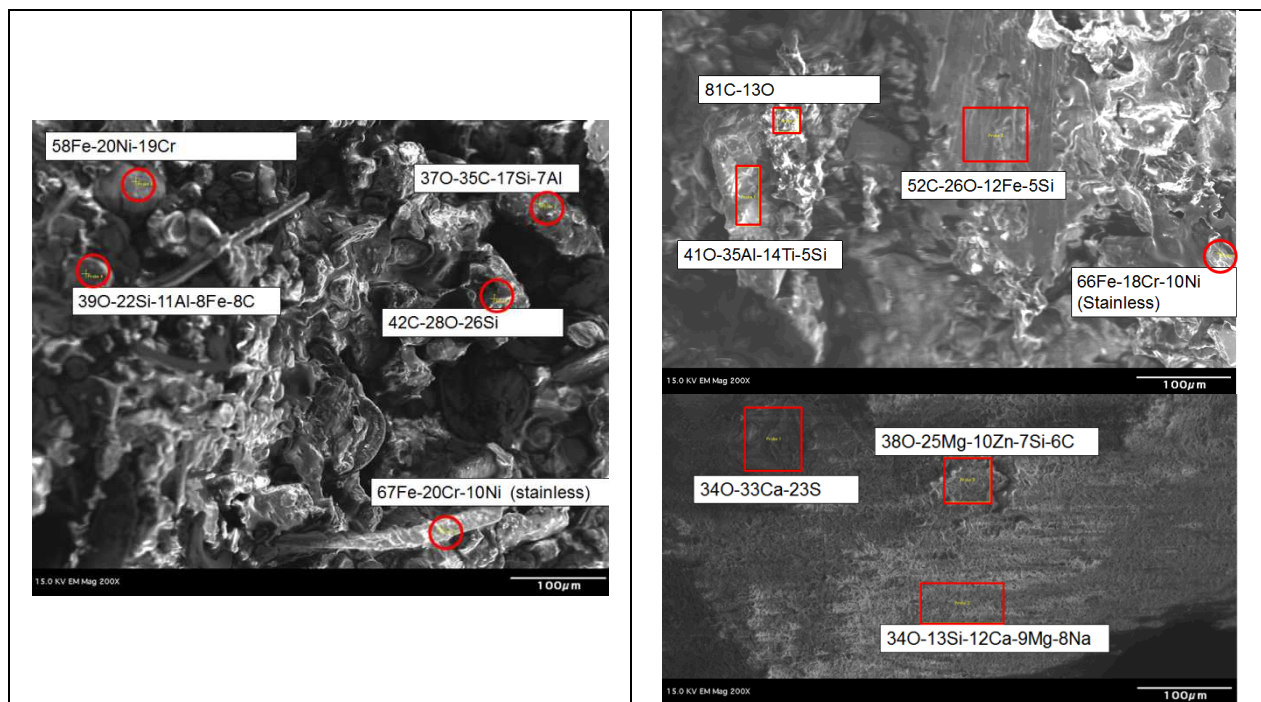
Figure 4: EDS analysis of fouling product removed from heat exchanger. Elemental composition provided in weight percent.
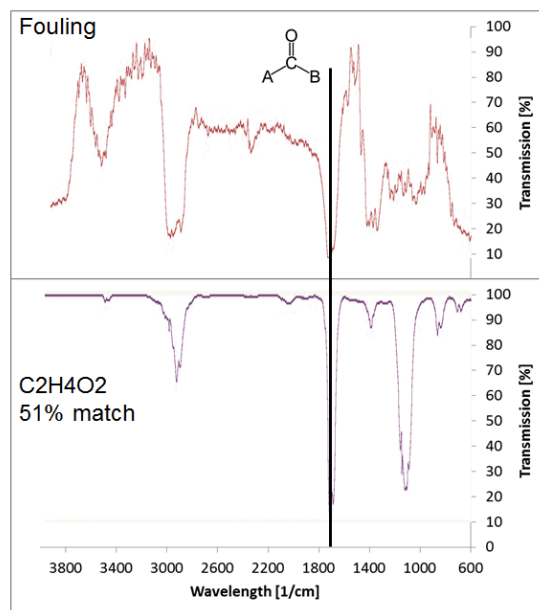

Figure 5: FTIR data that yielded no clear matches. Carbonyl peak could be determined based on characteristic responses as shown in $C_2H_4O_2$, hence confirming presence of organic products.
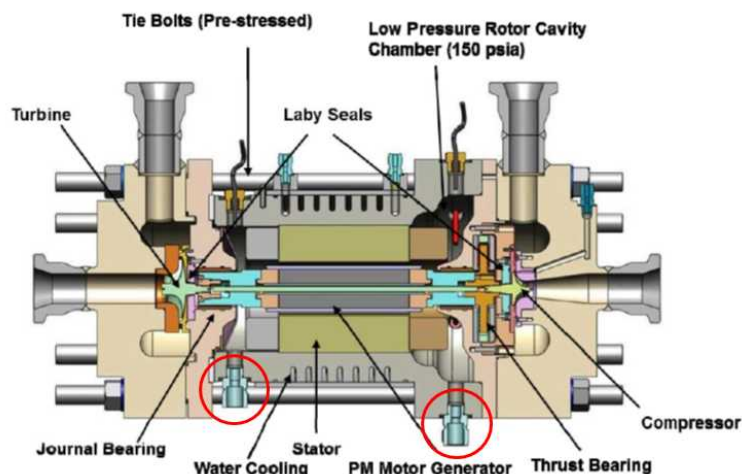
Figure 6: A cross-sectional diagram of the turbo-alternator-compressor (TAC) unit. Two drain locations are shown on the bottom of the unit (circled in red), with one drain line currently unused and closed off by the Swagelok fitting shown in Figure 7

Figure 7: Swagelok cap with fouling product from the turbo-alternator-compressor (TAC) unit in the RCBC.

Swagelok Tar Analysis

Tar was found in a Swagelok fitting (Figure 7) during routine inspection and maintenance. It should be noted that all pumps are oil-free and cleaning all SCO_2 wetted surfaces are done prior to installation, thus the finding of this tar was unexpected. This fitting is located on an unused drain line in one of the turbo-alternator-compressors (TACs), one of two available for draining the rotor cavity as shown in Figure 6.

Various compounds were separated using differential solubility. The product was subjected to six different chemical solvents sequentially to extract fractions of material out of the original tar. Those solvents were hexane, diethyl ether, toluene, acetone, dimethylformamide, and dimethylsulfoxide. After extracting the tar, solid black flakes remained. Only solvents of hexane and dimethylformamide yielded any reportable extracts.

Hexane solvent is a hydrocarbon, similar in chemical structure to gasoline or kerosene, and it is low boiling (easy to evaporate and remove without further contamination). We evaporated the low boiling hexane solvent leaving behind a colorless, oily residue. This residue was then analyzed using nuclear magnetic resonance (NMR) techniques, which can detect the presence of hydrogen atoms in a material and determine the identity of the other atoms that surround that hydrogen atom. Figure 8 shows the NMR spectrum of the colorless, oily residue. If no hydrogen atoms were present, the spectrum would be a flat baseline. However, there are two features that show up in what is called the "alkane region" (1.3 ppm and 0.9 ppm). This is an indicator of either hydrocarbon oil or grease.

In order to provide evidence for this hypothesis, a sample of Welch DuoSeal Pump Oil was tested (Figure 9). The NMR spectrum of pump oil shows two features, which are unmistakable as a long-chain

hydrocarbon (oil). These features are also present in the extract, which confirms that they are also some form of hydrocarbon oil.

However, the NMR spectrum of the extract has additional features, specifically showing up around 0.1 ppm. Peaks in this region are characteristic of silicon-containing hydrocarbons. Figure 10 shows the spectrum of Fisherbrand Silicone Oil, and silicone oil shows a sharp peak at roughly 0.1 ppm.
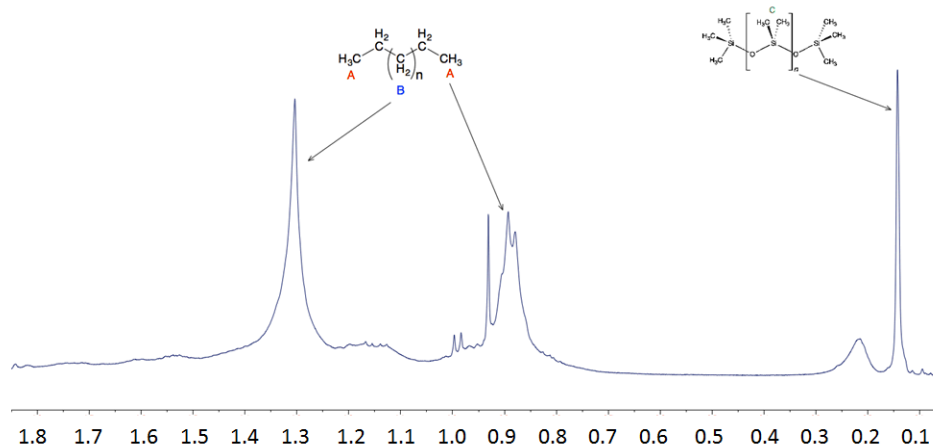

Figure 8: NMR spectrum of tar dissolved in hexane. The first two peaks to correspond to a hydrocarbon oil such as Welch DuoSeal Pump Oil as shown in the spectrum of the oil alone in Figure 9. The third peak corresponds to silicone oil such as Fisherbrand Silicone Oil shown alone in the spectrum in Figure 10.
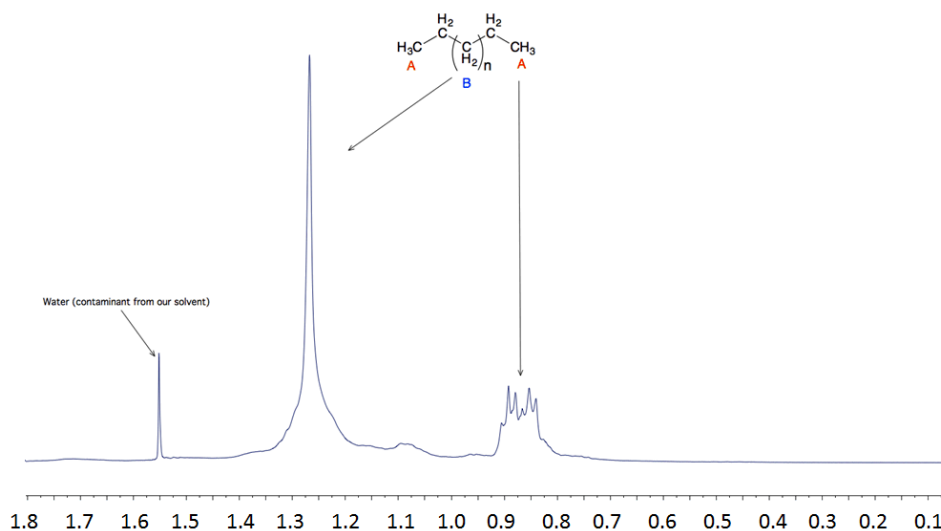

Figure 9: NMR spectrum of Welch DuoSeal Pump Oil with characteristic peaks at 1.3 ppm and 0.9 ppm in the "Alkane" region. The peak at 1.55 indicates water contamination in the solvent.

The hexanes solvent extracted both hydrocarbon oil and silicone oil from the tar, and these were confidently identified based on known literature values and also standards (Welch Pump Oil and Fisher Silicone Oil).

Since oil-free equipment is used in the RCBC the source of the hydrocarbon is unknown. Hydrocarbon impurities are present to some extent in the CO_2 used for experiments. 99.9% CO_2 purity currently used in the RCBC and, between tests, the CO_2 is vented. Successive fills of the RCBC may be sufficient to cause

an accumulation over time of hydrocarbon material. Estimations, based on the number of fills and 5ppm of total hydrocarbon, would contribute 22 grams of hydrocarbons over the operation lifetime of the RCBC.
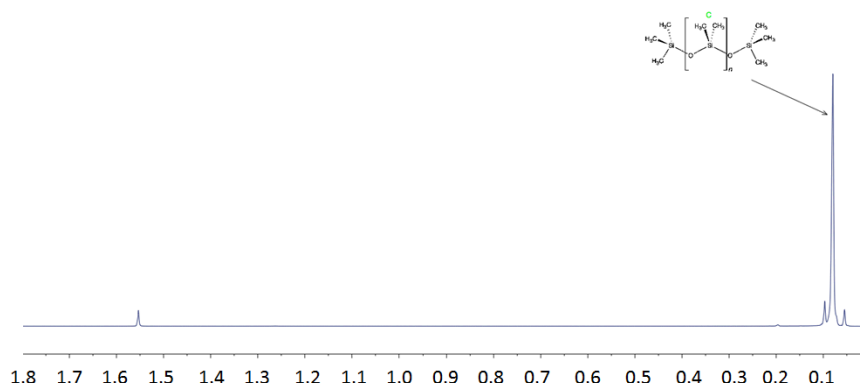

Figure 10: NMR spectrum of Fisherbrand Silicone Oil with a characteristic peak near 0.1.

Dimethylformamide as a solvent was also used. Before evaporation of this fraction, there was an obvious discoloration present. The color was difficult to see, but it was compared visually to another sample of clean dimethylformamide and the difference was apparent.

Upon evaporation of the solvent, a reddish solid was obtained. No signals could be found in the NMR spectrum, and the infrared spectroscopy showed no obvious features. These data and the color are indicative of an inorganic compound, like iron oxide. No further analysis was performed, but iron oxide is likely as shown in the heat exchanger fouling analysis.

CONCLUSIONS

Fouling and build-up materials were found in the high pressure, low temperature inlet of the high temperature recuperative heat exchanger on the RCBC located at Sandia National Laboratories. Fouling products are composed of dirt, stainless steel, and hydrocarbon material. PCHEs behave as filters for agglomerates, where hydrocarbon contamination traps exfoliation products from piping and any dirt contamination that enters the system.

Locations in the system that have low pressures, specifically in cavity of the turbine alternator compressor, any hydrocarbon contamination accumulates. Calculations indicate that this product is likely from impurities in the CO_2 used for experiments.

NOMENCLATURE

CO_2 = Carbon Dioxide
DOE = Department of Energy
EDS = Energy Dispersive Spectroscopy
FT-IR = Fourier Transform Infrared Spectroscopy
NMR = Nuclear Magnetic Resonance Spectroscopy
RCBC = Recompression Closed Brayton Cycle
SCO_2 = Supercritical Carbon Dioxide
SNL = Sandia National Laboratories
TAC = Turbine Alternator Compressor

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