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Abstract

Supercritical Carbon Dioxide (S-CO2) is emerging as a potential working fluid in power-production Brayton cycles. As a result, concerns have been raised regarding fluid purity within the power cycle loops. Additionally, investigations into the longevity of the S-CO2 power cycle materials are being conducted to quantify the advantages of using S-CO2 versus other fluids, since S-CO2 promises substantially higher efficiencies. One potential issue with S-CO2 systems is intergrannular corrosion [1]. At this time, Sandia National Laboratories (SNL) is establishing a materials baseline through the analysis of 1) “as received” stainless steel piping and 2) piping exposed to S-CO2 under typical operating conditions with SNL’s Brayton systems. Results from ongoing investigations are presented.

A second issue that SNL has discovered involves substantial erosion in the turbine blade and inlet nozzle. It is believed that this is caused by small particulates that originate from different materials around the loop that are entrained by the S-CO2 to the nozzle, where they impact the inlet nozzle vanes, causing erosion. We believe that, in some way, this is linked to the purity of the S-CO2, the corrosion contaminants, and the metal particulates that are present in the loop and its components.

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NOMENCLATURE

BEI	Backscatter Electron Imaging
°C	Degrees Centigrade
CO2	Carbon Dioxide
DOE-NE	U.S. Department of Energy – Office of Nuclear Energy
EDS	Energy Dispersive Spectroscopy
GEN IV	Generation IV
IA	Intergrannular Attack
IN	Inconel
Ni	Nickel
PCHE	Printed Circuit Heat Exchanger
±	Plus or Minus
RCBC	Recompression Closed Loop Brayton Cycle
SEM	Scanning Electron Microscopy
S-CO2	Supercritical Carbon Dioxide
SNL	Sandia National Laboratories
SS	Stainless Steel
TAC	Turbine Alternator Compressor
µm	Micrometer
XS	Cross-sectional

1. INTRODUCTION

The Department of Energy, Office of Nuclear Energy (DOE-NE) has successfully completed the construction of the 1 MWth S-CO2 Recompression Closed Loop Brayton Cycle (RCBC) testing platform, and testing is well underway with some successful results to date [2]. As more hours of operation are applied to the RCBC power loop, uncertainty in the long term reliability of various components has become more visible. More testing and analysis should be done in order to complete a rigorous assessment.

Preventive maintenance practices are utilized at SNL to avoid untimely failures [3]. Practices such as periodic bore scope inspection and time-lapsed comparison of components and piping are employed. Recently, as part of this effort, Sandia extracted the piping used in the RCBC through September, 2012, and subjected it to standard metallurgical analyses: optical microscopy, scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS).

Ultimately, Sandia established a program to actively monitor the corrosion characteristics of components from the start of service to the end of service lifetime. Results to date have demonstrated the need for this investigative program. During visual turbomachinery inspections, it was noted that the turbine nozzles appeared eroded, with no precise root cause identified. The nozzles had suffered severe erosion, which resulted in geometrical changes that were visually observed. The turbine also showed visual evidence of wear, but this wear was often ignored because the actual “life span” of the turbine was so unpredictable. The nozzle and turbine components were ultimately removed from service and analyzed with microscopy. Materials issues are of concern given the following reasons 1) the solvent nature of S-CO2 [4], and 2) its ability to transport small, dissolved particles throughout the loop, the combination of which causes erosion at high gas-velocity locations, such as the turbine inlet.

2. PIPE ANALYSIS

Material samples of 316L from the GENIV RCBC loop were obtained from 3” diameter, schedule 160 piping that had been replaced. The various samples had accumulated approximately 200 hours of operation at temperatures ranging between 20°C and 500°C. The CO2 fluid states were “subcritical gas” and “supercritical”.

This analysis showed that the in-service pipe contained evidence of intergrannular attack along the grain boundaries and pitting on the grain surfaces, as shown in Figure **2-1**. These conditions were identified using a low-energy Backscatter electron imaging (BEI) SEM. There was a noticeable deposit in the intergrannular trenches. Upon further analysis with EDS, the material was concluded to be carbonaceous. These results raised concerns that S-CO2 may be influencing the apparent materials degradation observed. Additional preventative maintenance pipe sampling were planned to gain further insight into these data.

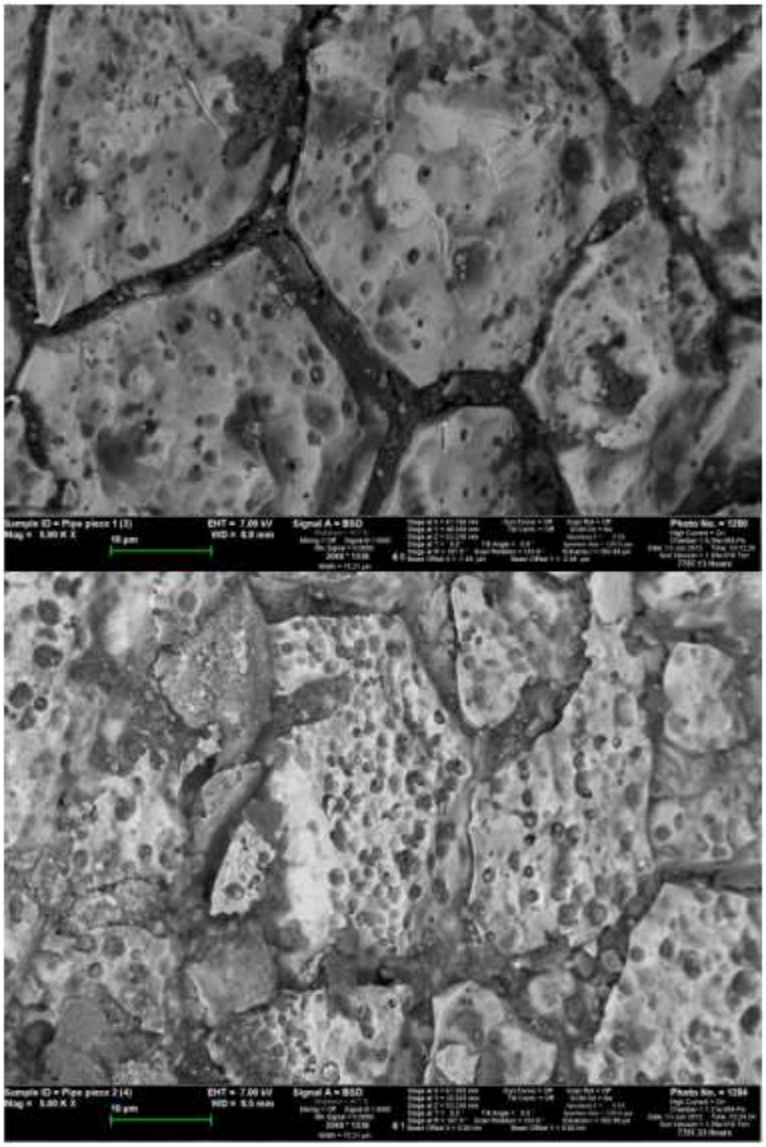
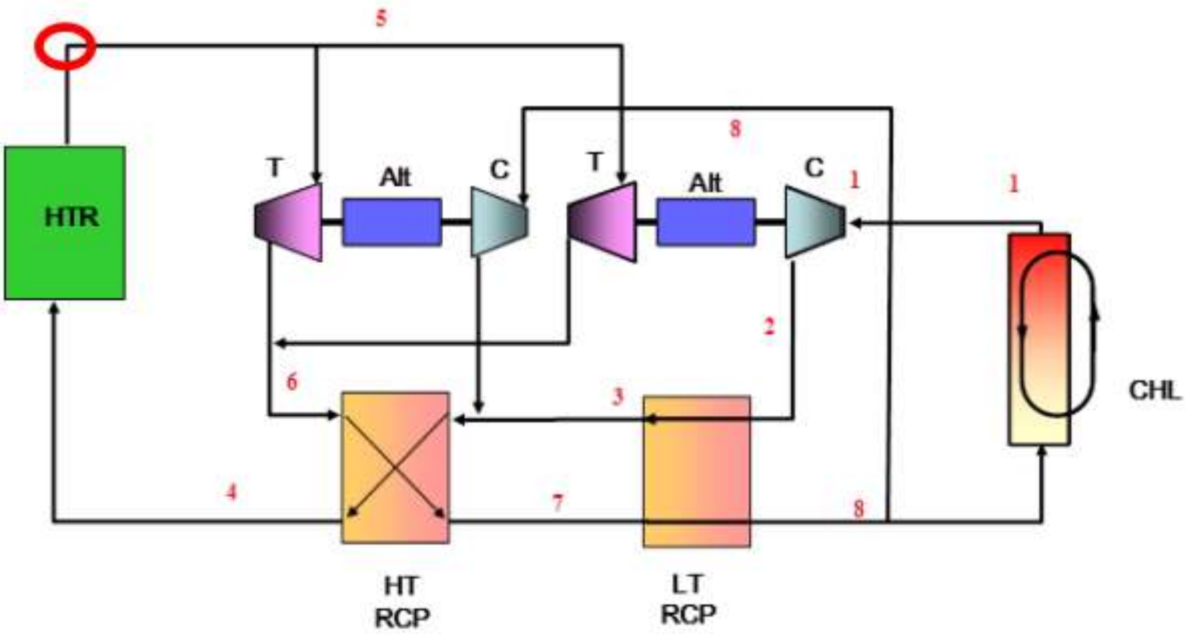
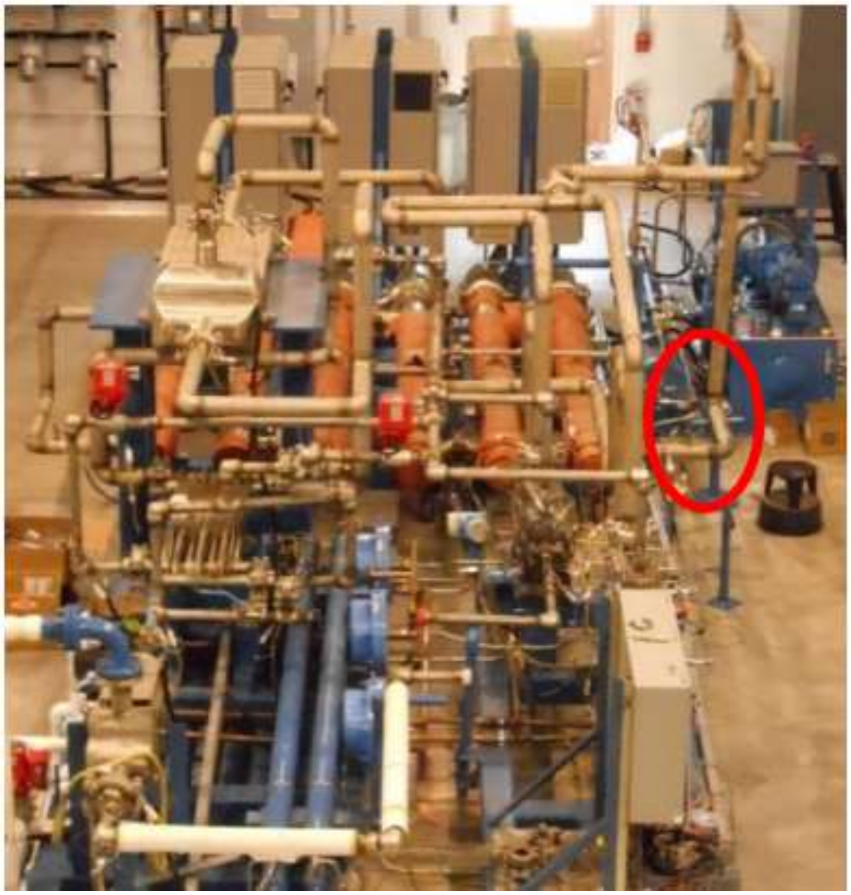


Figure 2-1: Two SEM images of the in-service SS 316L piping showing significant intergrannular corrosion and pitting.

In early May 2013, the Brayton team decided to obtain a sample from the GEN IV S-CO2 RCBC loop. It was determined that the leg that had the highest temperature should represent conditions where corrosion would be the most severe in the loop. The sample was taken from the heater outlet indicated by the red circle in Figure **2-2** (a). The sample was cut using a low-speed reciprocating saw to avoid sample contamination from cutting oils. Cross-sectional microscopy was used to gauge the depth of the affected base material to quantify the depth of the intergrannular attack initially found in fresh pipe Figure **2-2** (b) shows the physical location of the sample taken from the loop and the actual sample is shown in Figure **2-2** (c).



(2a)



(2b)

(2c)

Figure 2-2: Sample location in schematic view (a) Sample location in physical view (b), corrosion sample removed (c).

It was apparent that the inside diameter of the pipe exhibited uniform intergrannular attack to a depth of 15µm ± 4µm. When analyzing the sample at 500x, small amount of surface scale on the inside diameters (IDs) of the pipe were noticeable. Scale was not uniform, and only presented itself in small amounts on the IDs of the pipe, which indicated that corrosion was insignificant over the range of conditions and durations that the 316L were exposed to during system operation. Furthermore, the scale was not found in the intergrannular trenches, but rather only on the surface, as shown in Figure **2-3**.

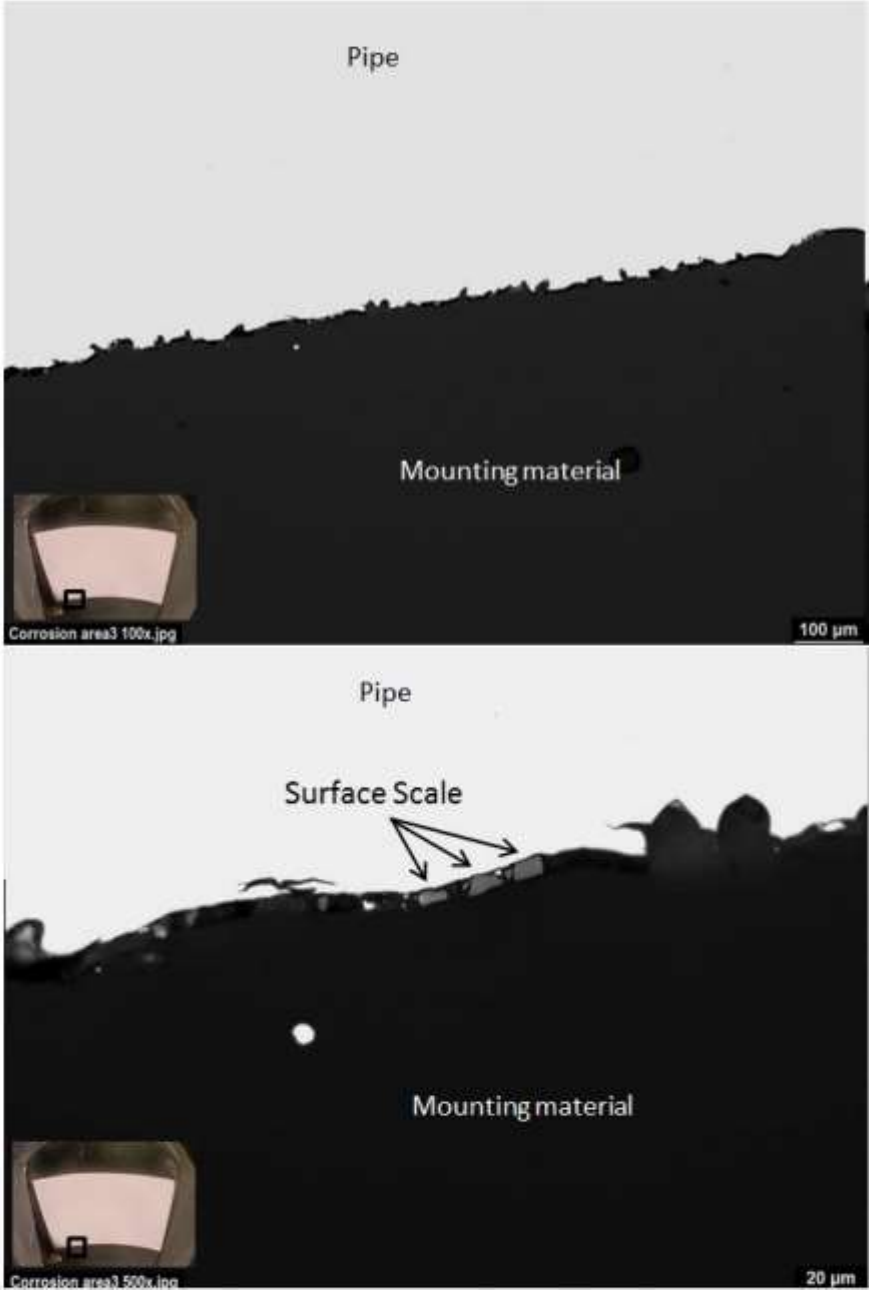


Figure 2-3: 100x (upper) and 500x (lower) images indicate surface features indicative of intergrannular attack. Some surface scale was observed and will be identified using electron spectroscopy techniques.

Observations during the piping analysis raised questions regarding the as-received material quality and specifications obtained on the 316L piping. The original GEN IV piping is thought to be of lesser quality than domestic US piping material and possibly a counterfeit material. Details about the source of the piping and the level of manufacturing quality control are still uncertain. A pre-exposed material sample to establish a baseline was not secured, despite repeated requests of the manufacturer. In spite of this lack of baseline data it is thought that the picking process, used in removing surface scales during manufacturing, resulted in the grain boundary trenching.

Pickling of stainless steels is a multi-step process that must be done after alloys are hot-worked to remove oxide scales that develop on the surface. Due to their high chromium content, stainless steels typically develop adherent, robust chromium oxide scales, which are difficult to remove. Pickle liquors for stainless steels are thus required to utilize a variety of acid mixtures that typically contain various concentrations or mixtures of three acids: sulfuric, nitric, and hydrofluoric acid [5]. Lack of control during picking can result in pitting and increase in surface roughness. Hydrofluoric acid has been shown to induce significant intergrannular attacked and pitting on 304SS, which is compositionally similar to 316SS, in only 42 seconds [6].

In view of this information, SNL has currently benchmarked all newly installed SS 316L pipes in the RCBC loop to keep track of the number of hours in service and will continue periodic materials sampling. It will provide information for material requirements and pipe quality standards related to S-CO2 systems. A mass spectrometer (Pfeiffer Vacuum Omni-Star) was installed downstream of the heater discharge and the turbine inlet to actively monitor the relative elemental compositions of materials being transported throughout the loop. These tests were initially benchmarked, and the details of these tests will be presented.

3. EROSION SAMPLES

During the rebuild of the turbomachinery, it was noticed that the turbine wheel and nozzles showed significant erosion, which was thought to be due to particulate matter in the flow stream. The turbomachinery continued operation for five months until it was removed to undergo analyses that included microscopy, SEM, and EDS. Figure **3-1** shows the substantial amount of erosion on the turbine nozzle and turbine. Another area of high velocity flow and erosion is the compressor discharge. Inspection of these components revealed an absence of erosion as shown in Figure **3-2**. It is very important to note that were two-phase flow conditions exist such as the compressor inlet there has been no visible signs of erosion.

Figure 3-1: Turbine nozzle with substantial amount of erosion, and turbine wheel with placement inside turbine nozzle.

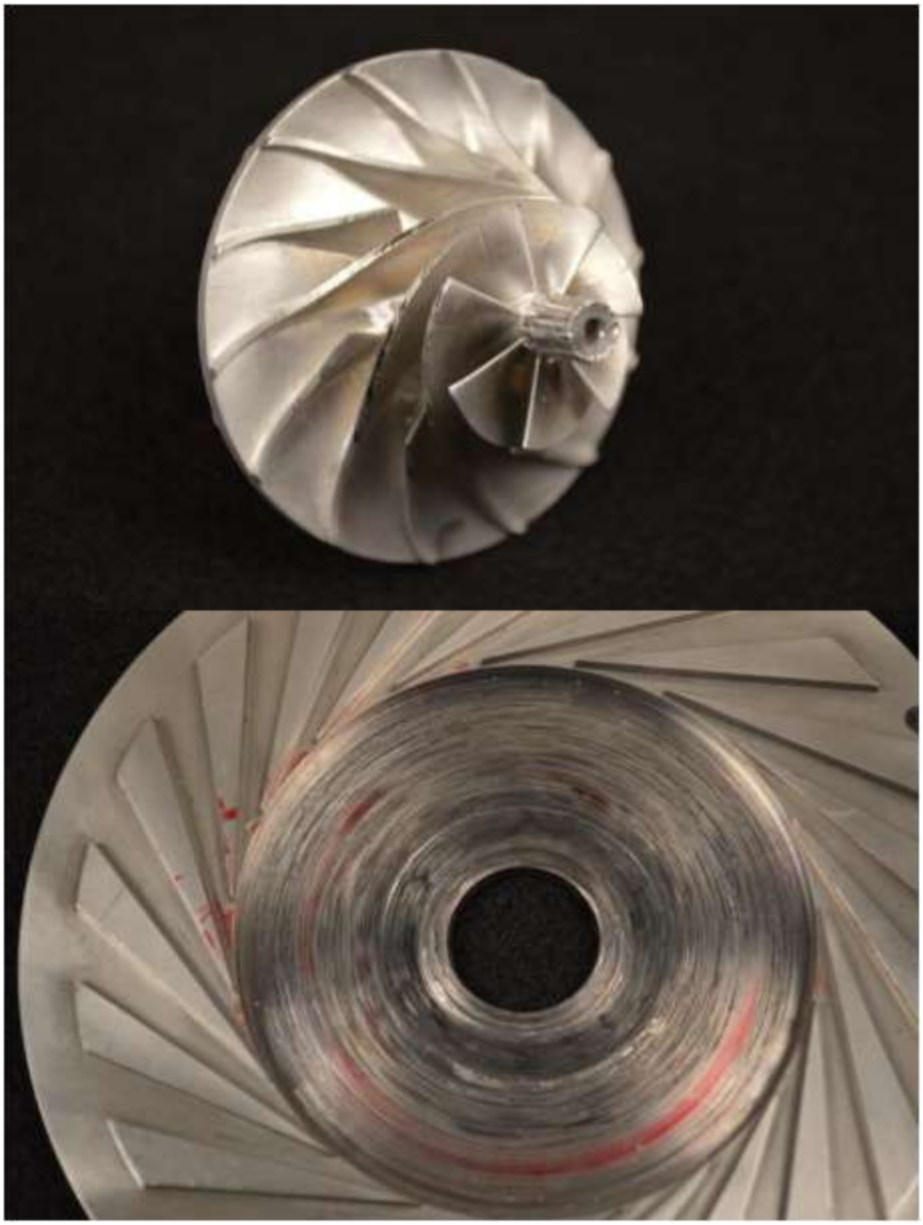


Figure 3-2: Compressor and compressor diffuser showing signs
of no erosion or liquid impingent.

Turbine analysis was accomplished using microscopy and SEM/EDS. The results from microscopy showed substantial amounts of erosion. In addition, the inlet of the turbine wheel showed erosion that was apparently purely mechanical, resulting from particulate erosion, as seen in Figure **3-3**. The reasoning behind the assumption of mechanical caused erosion is the fact that we operate with high temperatures that are far in excess of the critical temperature precluding the possibility of two-phase conditions that might lead to liquid impingement. Furthermore, erosion occurred primarily on the suction side of the blade.

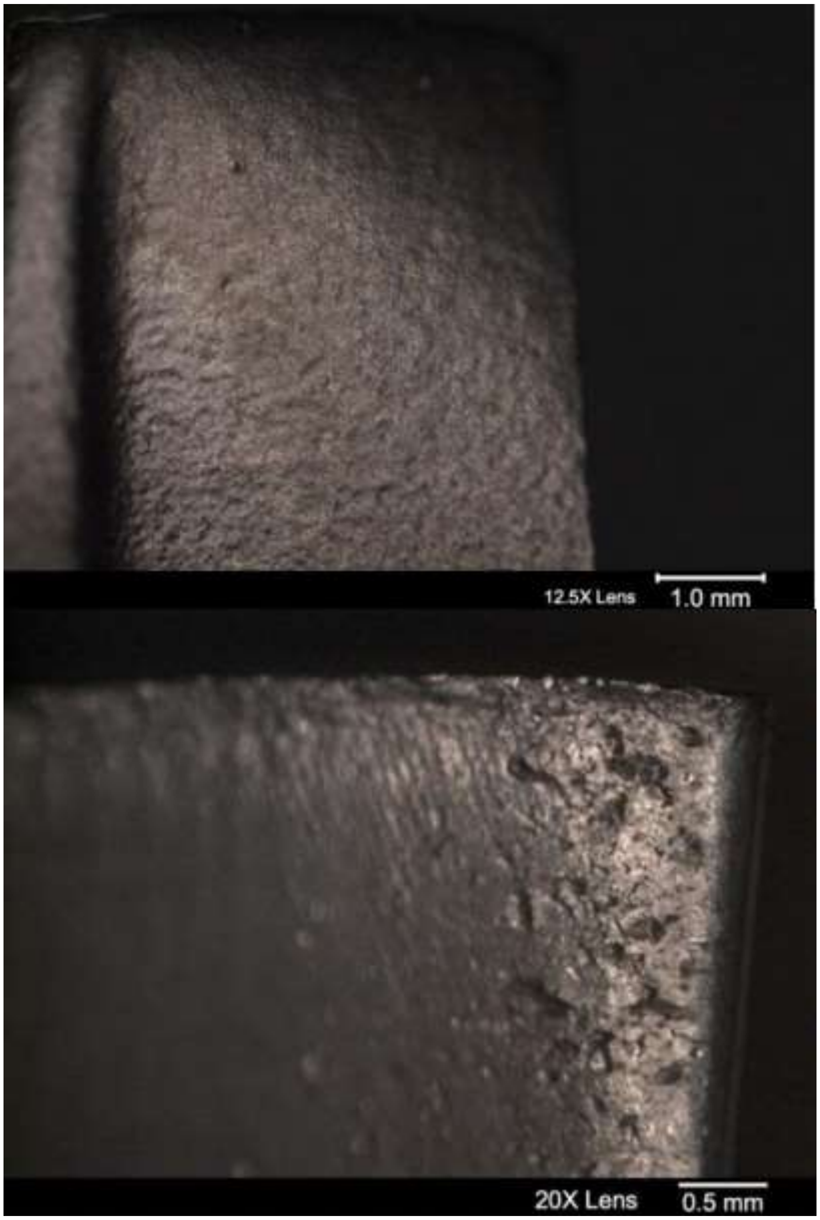


Figure 3-3: Erosion on the Turbine, particulate erosion on turbine blade

Results from the SEM, displayed in Figure **3-4**, showed a different microstructure than what had been expected. There are indications of plastic deformation from abrasion, potentially due to a plastically deformed layer of some metal. To accurately identify the material causing abrasion, the material composition of C-22 (the material from which the turbine was constructed) was researched and compared it to the EDS measurement, as shown in Table **3-1**. There was a high amount of Fe present on the surface of the turbine. The current best hypothesis is that small shavings of Ferritic steel may be the cause of the erosion.

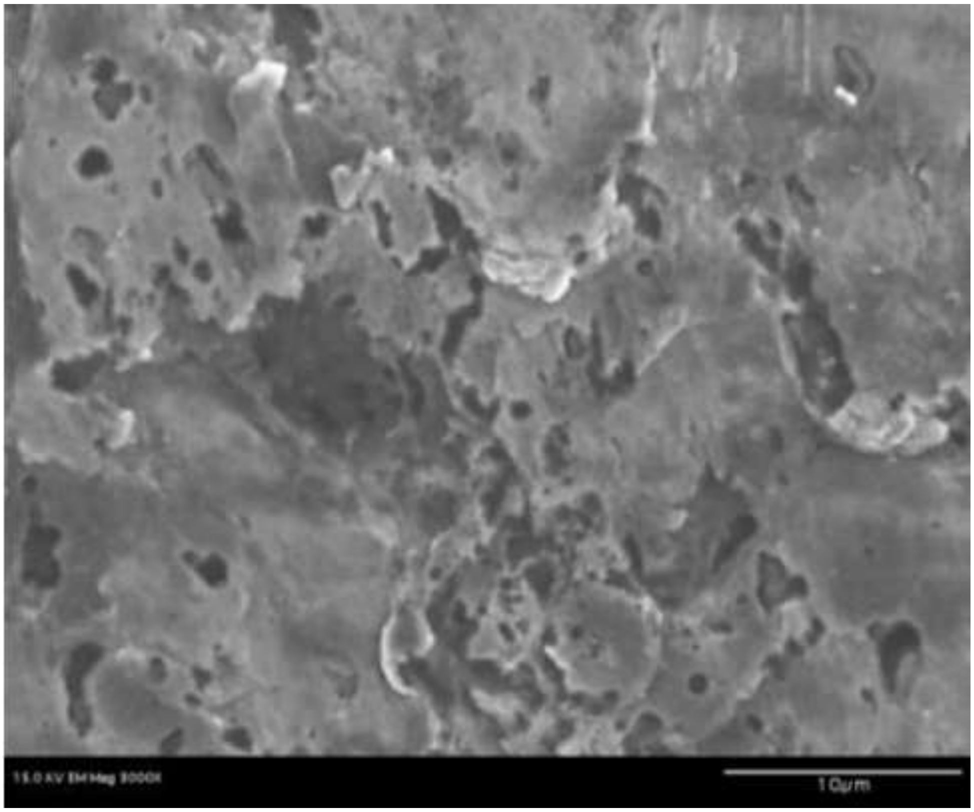


Figure 3-4: SEM showing different microstructure

Table 3-1. EDS comparison: IN C-22 vs. actual on turbine wheel

*max **bal	C	Si	V	Mn	Cr	Fe	Ni**	Mo	Co	W
C-22	0.010*	0.08*	0.35*	0.50*	22	3	56	13	2.5*	3
EDS					19.8	11.6	56.9	9.2		2.1

4. NOZZLE ANALYSIS

Erosion has been present in the S-CO2 Brayton loop at least since 2010. Mechanical abrasion has been noted on both the nozzles and the turbines. Initially, it was thought that the erosion was a temporary problem associated with the fabrication of the loop, but the erosion has not stopped or lessened in severity. There was concern of erosion in the high temperature heat exchanger because of the erosion that had been happening in the turbine nozzle. Due to the proprietary nature of Heatric PCHEs, it is not possible to cut open the heat exchangers, therefore a similar candidate, the turbine nozzle, was selected to undergo the same analysis.

Advanced microscopy was selected as the way to visually examine the nozzle. This examination noted particulate erosion, much like that associated with the turbine, but with a more aggressive behavior. Once this particulate erosion was identified, EDS analysis was performed to try to understand its origin and nature.

Visual inspection of the sample showed extreme wastage. Figure **4-1** shows a channel eroded out of the nozzle the height of the inlet of the turbine vane.

Figure 4-1: Turbine Nozzle with undercut and the EDS sample location represented by red square

Following these initial observations, the nozzle underwent analysis using EDS on the undercut of the nozzle. Because time would not permit sectioning the nozzle with a cutting technique, a similar location was chosen for analysis (See Figure **4-1**). The EDS analysis showed that there was significant iron enrichment present on the surface, as well as a decrease in Ni. As shown in Table 4-1, the iron content was 40.7 by percent, which was significantly higher than the expected 23.8 percent.

Table 4-1. EDS comparison: IN 718 vs. actual on nozzle

*max **bal	C	Si	V	Mn	Cr	Fe	Ni**	Mo	Co	Ti	Nb+Ta
IN 718	0.008*	0.35	0.35-0.80	0.35*	17-21	11.5-23.8	50-55	2.8-2.2	1.0*	0.65-1.15	4.75-5.50
EDS					19	40.7	35.8	3.1			

5. CONCLUSION

Sandia National Laboratories is currently investigating erosion mechanisms in the recompression closed Brayton cycle. It was found that there is currently an absence of corrosion in the S-CO2 cycle components. The initial speculation of the intergrannular attack was suspected to be corrosion, but after careful consideration it was found the intergrannular attack was caused by an ASTM 312 and 376 processes in which the pipe was pickle passivated in order to remove any surface scale that had formed during the fabrication of the pipe. Testing will continue to look for signs of intergrannular corrosion with well documented (hours of operation) 316L schedule 160 pipe samples.

After investigating the erosion samples from the turbine and turbine nozzle, a stronger level of effort will be placed on the identification of the source of this damage. Currently, it is thought that the erosion is caused by iron particulates, which are believed to come either from the machining of loop components or from the mild steel inventory tanks. The investigation is not limited to these sources, but it has been determined that the erosion particles are high in iron content.

Several general strategies are being employed to respond to erosion in S-CO2 power cycles. This includes installation of an in-situ Thermostar mass spectrometer to identify loop contaminates. Also, erosion-resistant materials and coatings for use on the turbines and turbine nozzles associated with these prototype systems are being investigated.

6. ACKNOWLEDGEMENTS

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