

PREDICTING SERVICE LIFE OF 347 STAINLESS STEEL PIPES BY CARBURIZATION  
RATE MEASUREMENT

Tyler Sura

Sponsored by Chevron Corporation

June 12, 2017

## **Abstract**

Chevron Corporation and other refiners face challenges predicting the service life of piping in coker furnaces. This is largely due to a build up coke on a single surface of the piping. This coke build up results in carbon penetration into the surface of the 347 stainless steel used for the pipes. Carbon penetration can lead to degradation of the surface and ultimately, the failure of the pipe. Current modeling software has difficulty predicting the influence of sulfur on the carbon penetration rate. This study aims to provide a baseline for further study into the subject. The carbon penetration rate of 347 stainless steel was investigated at four temperatures ranging from 900°F to 1400°F on a bed of activated charcoal over a period of 100 to 200 hours. It is expected that higher temperatures and longer times will allow for greater diffusion of carbon into austenite, although some chromium carbide may form at the surface. Apart from chromium carbide formation, the carbon absorption into the austenitic matrix should remain a single phase process. Carburization rate was characterized by EDS, metallographic analysis, and microhardness measurements. Results will lead to determination of the non-steady state diffusion coefficient for carbon into 347 stainless steel.

## Background

### *Coker Furnaces*

Delayed cokers are employed in the petrochemical industry to thermally crack heavy oils into lighter compounds and to produce petroleum coke. This processing takes material that would otherwise be used for asphalt and processes it into intermediaries for other refining processes and into coke. Coke is a solid form of carbon, similar to coal in many respects. It can be used in some metallurgical processes if the sulfur content is low enough. Metals and other elements that act as catalytic poisons for later processing are captured in coke. During the firing cycles of coker furnaces, coke builds up inside the pipes of the equipment. This accumulation of coke results in a temperature increase inside the furnace, as the coke can act like an insulator. Normally, coker furnaces operate near 900°F. Once a sufficient amount of coke has built up, the temperatures can rise to upward of 1400°F. This temperature increase results in a loss of efficiency in the production of desired products<sup>1</sup>. Once the efficiency drops below acceptable values, the coke layer must be removed.

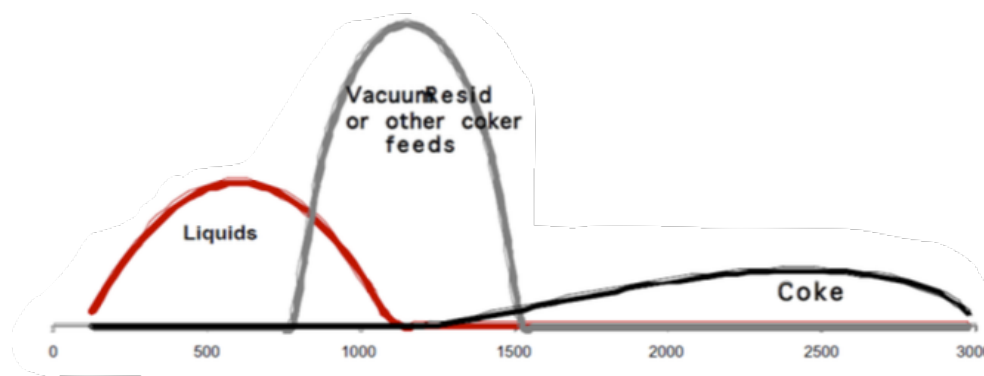


Figure 1. A depiction of the outputs of thermal cracking across different temperatures. Horizontal axis is temperature in degrees Fahrenheit, vertical axis is yield distributions<sup>1</sup>.

Cleaning of the coker furnace, called decoking, is performed in order to return the efficiency to optimal conditions. This is done by either of two methods, pigging or on-line spalling. Pigging involves taking a mechanical plug that abrades the interior

surface of the pipe or coke layer in order to remove coke build up. On-line spalling uses thermal cycling to spall, or flake off. High temperature steam is flushed through the pipes to heat them to approximately 1250°F then the pipes are cooled to near 700°F<sup>2</sup>. The thermal expansion and contraction differences between the pipe and the coke leads to the breaking up of the coke layer, and the steam flushes out the waste.

### *347 Stainless Steel*

Stainless steel is widely used in the refining industry for piping in coker furnaces. This specific stainless steel is AISI 347 stainless steel. It is employed largely within the petrochemical industry for high temperature applications. Its chemical and thermal resistance comes from its chemical composition (Table I).

Table I- The Chemical Composition of AISI 347 Stainless Steel, wt%

The bulk of its resistance to carbon penetration comes from the chromium content and nickel content (Figure 2). Silicon provides an effective barrier to carbon diffusion, but content above 2% results in weldability and rupture strength issues. 347 stainless steel would lie on this graph near the 18/8Si point.

The data in Figure 2 may not be fully indicative of the carbon absorption of 347, as other elements in 347 not included in the figure's test may affect the rate at which carbon is absorbed. The major difference that this steel has over similar grades is the addition of niobium. Niobium is used in austenitic stainless

Ni	11%
Cr	18%
Si	1%
Mn	2%
C	0.08%
P	0.045%
S	0.030%
Nb	.8%
Fe	Bal.

steels, such as 347, to reduce intergranular corrosion<sup>4</sup>. 347 stainless was developed with the goal to reduce intergranular corrosion in the temperature range of 800°F to 1500°F, as these are temperatures common to chromium carbide formation.



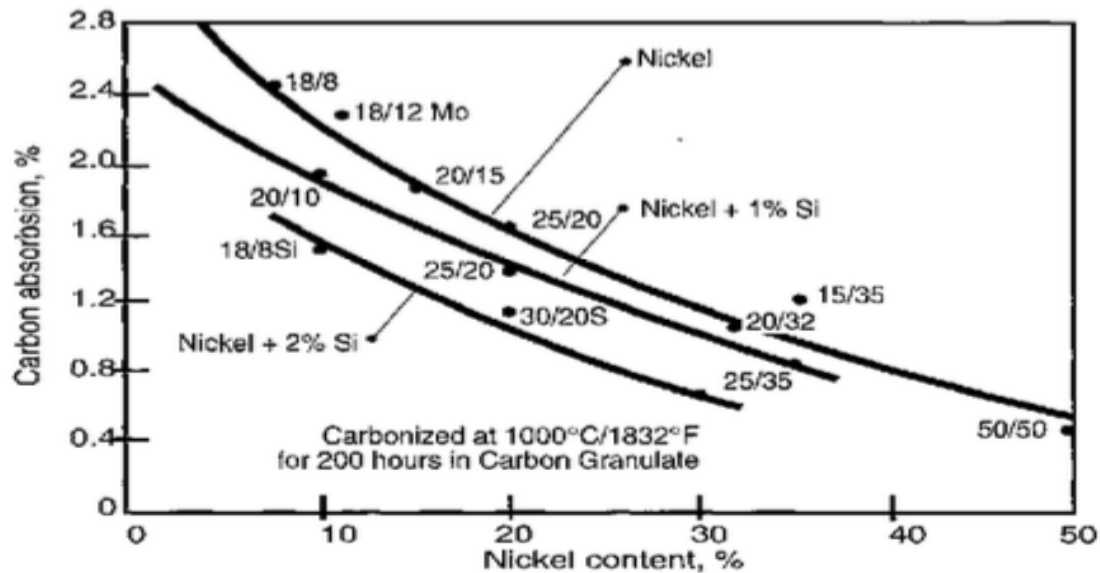


Figure 2. Carbon absorption plotted against nickel content. 347 stainless steel lies near the 18/8Si point on the graph, but will have 11% nickel content<sup>3</sup>.

### *Carburization*

Carburization is the absorption of carbon into steels and irons. This process is thermally activated. Additionally, a high concentration of carbon is necessary at the surface for carburization to occur. In some cases, carburization is intentionally induced on a part in order to enhance mechanical properties at the surface. This process is called case hardening. In other circumstances, these very same property changes are detrimental to a parts service life, rendering carburization an unwanted process. The mechanical changes that happen to carburized parts include surfaces hardening and embrittlement of the carburized layer. This can be problematic when decoking, as embrittled layers are prone to abrading or spalling off. Over the lifetime of piping in coker furnaces, repeated spalling results in reduced diameters of the piping itself. Once the pipe walls are thin enough, the pipes will need replacing.

### *Sulfidation*

Another corrosion phenomena that occurs at elevated temperatures is sulfidation. The temperature ranges that are most susceptible to sulfidation are from 450°F to 1000°F<sup>4</sup>. It occurs in the presence of sulfur, typically in the form of hydrogen sulfide.

This is an ever-present problem at refineries, as most all oil feeds contain sulfurous compounds. During the processing of the input feeds, sulfur content can be trapped inside the coke formed. Sulfidation corrodes irons and steels by forming iron sulfide.

### *Problems at Chevron*

Chevron is experiencing an unexpected carburization rate inside their coker furnaces. The predicted service life, from their computer models, does not accurately reflect the found service life of the piping. They believe that their software is inadequately modeling the effect of sulfur concentration in the feeds. There is likely a competitive effect between carburization and sulfidation that is not being accounted for. Chevron is presenting a need for testing to identify the effect of sulfur on carburization rates of 347 stainless steel. Due to the noxious nature of sulfurous gasses that can be formed on heating sulfur, this experiment is testing the baseline carburization rate of 347 stainless steel for Chevron.

### **Methods**

Corrosion samples of 347 stainless steel were exposed to a high temperature, carbon rich environment for varying times in order to carburize the samples. The temperatures tested at were: 900°F, 1075°F, 1200°F, and 1400°F. For each temperature a sample was carburized for 100, 150 and 200 hours. Some variance in time occurred, but can be accounted for in mathematical models. Maintaining a carburizing environment for the duration of each test was done by assembling a test chamber from black iron schedule 40 pipe fittings (Figure 3).

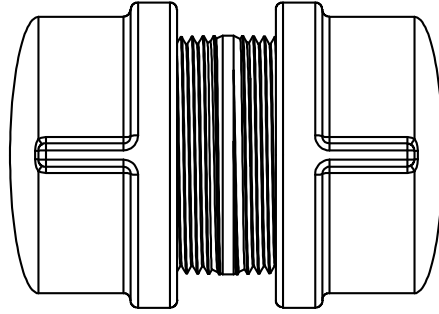


Figure 3. Drawing of test chamber. A 1/8" hole was drilled into one of the endcap's top faces. A 1/8" hole was drilled into one of the endcaps in order to equalize any pressure changes that might occur during the testing. Once assembled the test vessels were partially filled with activated charcoal powder. One sample was placed on top of the bed of charcoal, as to better simulate the one directional diffusion of carbon that would be present in coker furnaces. After each sample reached its test time, the sample and its test vessel were removed from the furnace to air cool. Once cool, the samples were prepared for metallographic examination. Adler's reagent was used in order to etch the samples.

## Results

Three methods of examining the carburization rate of the tested samples were performed: energy dispersive x-ray spectroscopy (EDS), microhardness testing, and measuring the case depth by optical microscopy.

### *EDS*

EDS measurements were taken to quantitatively find the amount of carbon that penetrated into the material during testing. An example measurement can be seen in Figure 4. This data is from a sample tested at 1400°F for 200 hours. All measurements were using the linear spacing tool so that each measurement was equidistant from its neighbors. Measurements started at five or less micrometers from the surface.

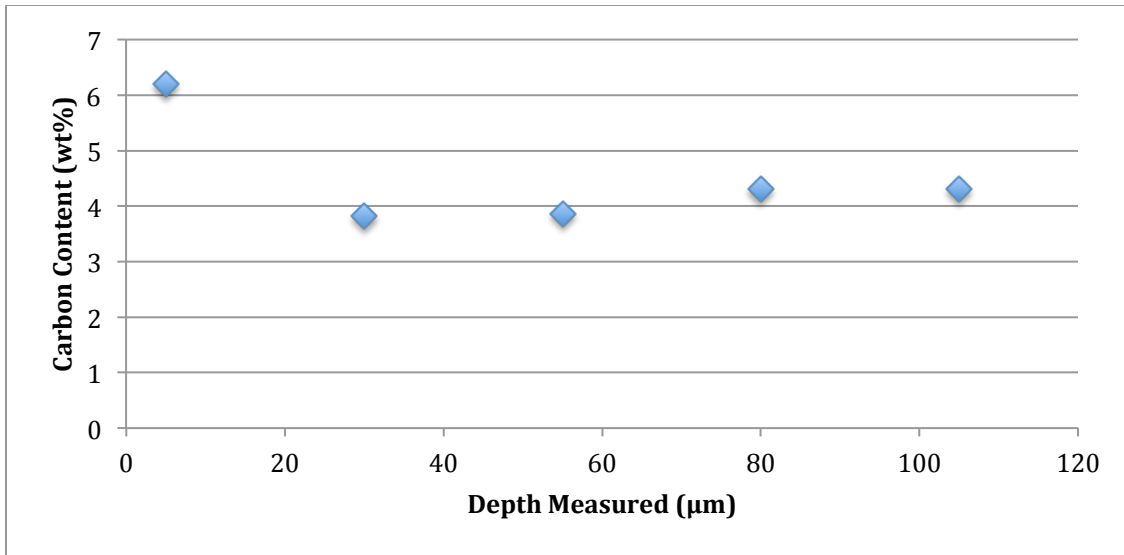


Figure 4. EDS data collected, showing carbon concentration as a function of depth.

### *Microhardness*

Microhardness measurements were taken of the samples inward from the carburized edge. Figure 5 shows the collected microhardness values for all samples tested at 1200°F. The force used for this test was 100 gf.

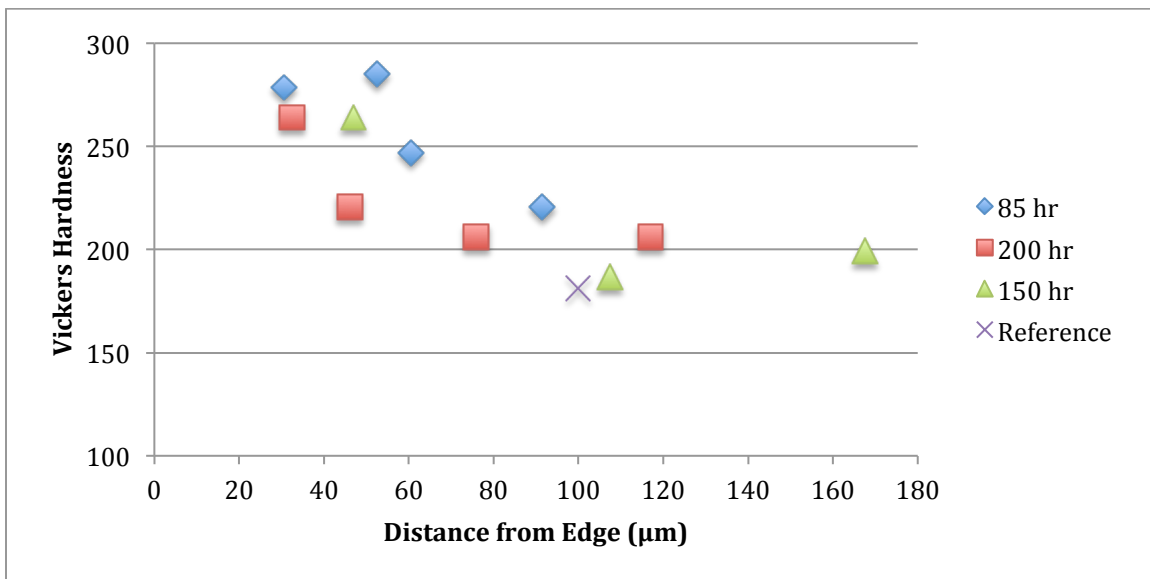


Figure 5. Microhardness measurements from all samples tested at 1200°F.

### Optical Measurements

Optical measurements of the case depth were taken of all samples (Figure 6). The point of transition between case depth and base metal was consistently defined as the point at which the sample transitioned from mostly darkened to mostly lighter material. In most cases this was obvious.

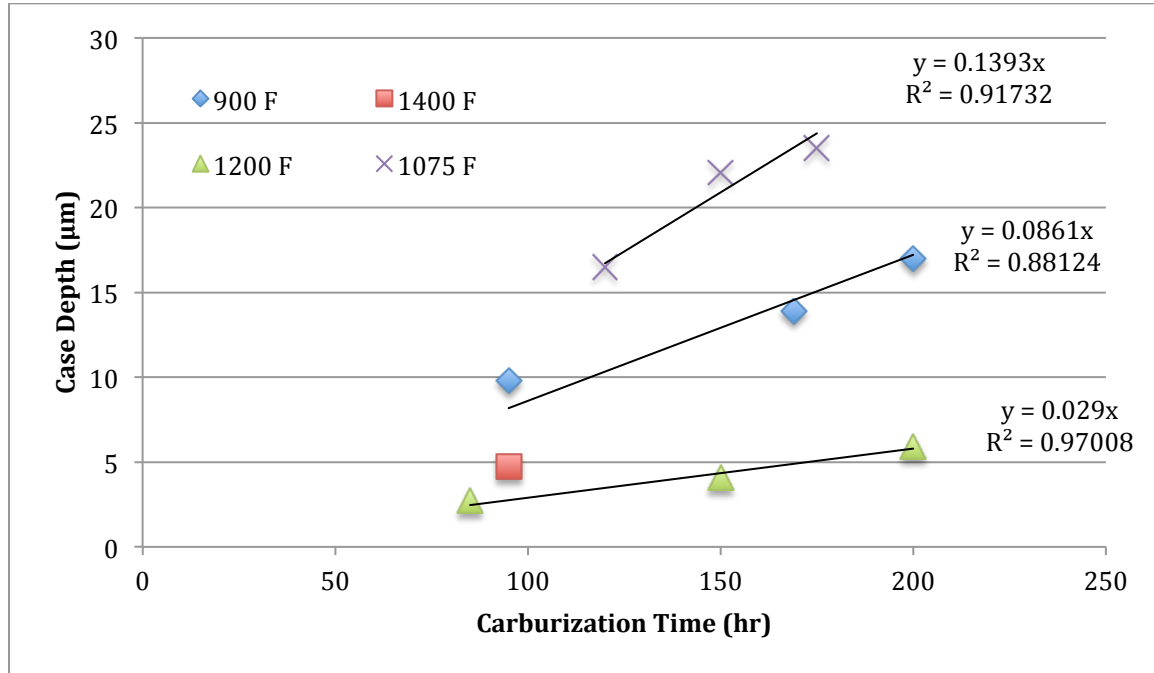


Figure 6. Case depth as a function of time spent carburizing. The 1400°F times above 100hrs presented no case depth.

One notable observation is that the times above 100 hours for the 1400°F test showed no case depth.

## Discussion

### Mathematical Modeling

The overall goal of the experiment was to find the activation energy of diffusion for the carbon 347 stainless steel system. This can be done by modeling the system using Fick's Second Law of diffusion (Eq. 1). Fick's Second Law is used for cases of diffusion that involve non steady-state conditions.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \text{Eq. 1}$$

C: concentration

D: diffusivity constant at a given temperature

x: distance

t: time

This equation can be solved to Eq. 2, treating the source of carbon as near infinite and the well to diffuse into as near infinite. These are reasonable assumptions to make, as the carbon present was significant to the expected amount to be diffused into the metal. The one dimensional diffusion direction chosen for the experimental setup was to allow for the second assumption.

$$C(x, t) = C_{surface} \operatorname{erfc} \left( \frac{x}{2\sqrt{Dt}} \right) \quad \text{Eq. 2}$$

erfc: the complementary error function

Quantitative data can be used along with Eq. 2 to find the diffusivity constant for a given temperature. To remove temperature dependence, Eq. 3 can be linearized to form Eq. 4.

$$D = D_o e^{-\frac{Q_d}{RT}} \quad \text{Eq. 3}$$

D<sub>o</sub>: temperature independent diffusivity constant

Q<sub>d</sub>: activation energy of diffusion

R: gas constant

T: temperature

$$\ln D = \ln D_o - \frac{Q_d}{R} \left( \frac{1}{T} \right) \quad \text{Eq. 4}$$

Eq. 4 can be plotted using ln D as the vertical axis and 1/T as the horizontal axis.

When plotted as such, the slope of the line is Q<sub>d</sub>/R. This requires multiple temperatures to be tested in order to properly find the linearization.

### EDS

The EDS instrument available was not producing accurate results, even after calibration. This is evident in the far depth concentration found was beyond what was expected. The order of magnitude of the mass change between before testing and after testing is 10<sup>-2</sup> grams. That amount of mass change is near .04wt% carbon for the samples. As can be seen in Figure 4, the weight percent carbon was

measured at 4 wt%, where the expected value should be .12 wt% carbon at the highest. More accurate data is required to properly use the mathematical models presented in above.

#### *Microhardness*

Microhardness trends also showed to be inconsistent with expected results. In general, for a given depth, the hardness should increase with longer carburization times. The found trends seem to inverse this relationship. Otherwise the values are appropriate for hardened austenitic stainless steels<sup>5</sup>.

#### *Optical Measurements*

The highest case layer growth rate occurred in the sample carburized at 1075°F. Optical measurements indicated that the two higher temperatures resulted in lower case depths than the two lower temperatures (Table II).

Table II. Linearized case layer growth rates

	900°F	1075°F	1200°F	1400°F
Case Depth Growth Rate ( $\mu\text{m/hr}$ )	.09	.14	.03	N/A

This can be explained as two different mechanisms of case layer formation occurring. Apart from the differing case depth growth rates, there is visual evidence of a differing mechanism occurring (Figure 7).

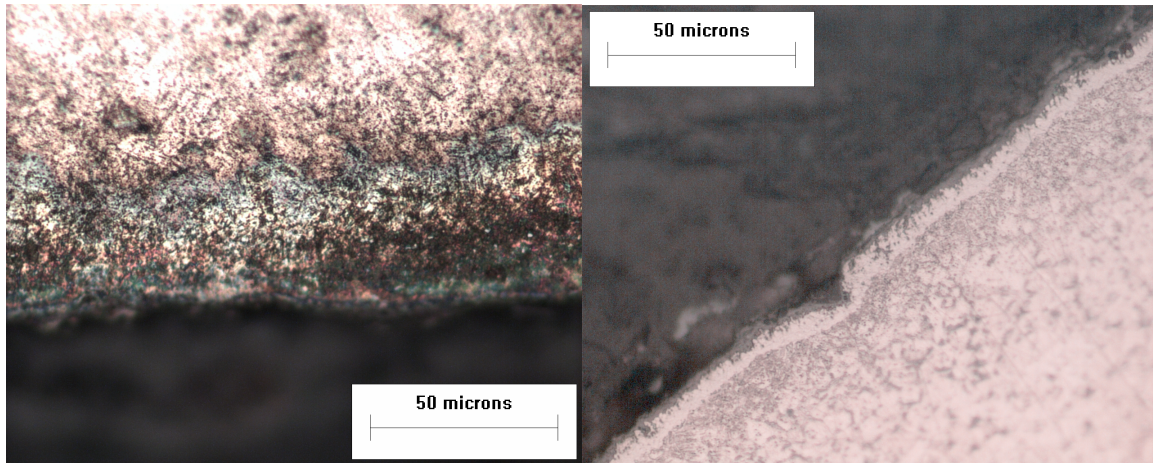


Figure 7. The left image shows the case depth from a sample carburized at 1075°F, while the right image shows the case depth from a sample carburized at 1200°F.

The sample treated at 1075°F resulted in a much thicker case depth, not only that, the region next to the case shows a significant, vibrant color change. The higher temperature sample showed a color change that is indicative of a depletion layer. The higher temperature carburization is likely to have formed chromium carbide. With a formula of  $\text{Cr}_3\text{C}_2$ , chromium carbide contains twice the carbon content of cementite per mole. Either the increased temperature made chromium carbide formation preferential, or the increased amounts of carbon allowed for chromium carbide to form. Additionally, chromium carbide might allow carbon to diffuse through the forming layer at a differing rate than cementite. Further research is necessary to draw conclusions.

## Conclusions

1. There was a peak case depth growth rate of .14 micrometers per hour.
2. There is a likely carburization mechanism change between 1075°F and 1200°F.



## References

- [1] Sayles, Romero, "Comparison of thermal cracking and hydrocracking yield distributions", from  
[http://www.digitalrefining.com/article\\_1000070.pdf](http://www.digitalrefining.com/article_1000070.pdf)
- [2] Gregory, 2007, "System and method for on-line spalling of a coker",  
United States Patent and Trademark Office, US 7597797 B2
- [3] Tillack, Guthrie, "Wrought and cast heat-resistant stainless steels and nickel alloys for the refining and petrochemical industries", Nickel Development Institute
- [4] US Chemical Safety and Hazard Investigation Board, "Final Investigation Report: Chevron Richmond Refinery Pipe Rupture and Fire", US Chemical Safety and Hazard Investigation Board
- [5] Valencia, López-Callejas, Muñoz-Castro, Barocio, Chávez, Godoy-Cabrera, "Nitriding of AISI 304 stainless steel by PIII in DC and RF toroidal discharges", Brazilian Journal of Physics