

Thomas A. Summers, Acting Chairman
Jessie H. Roberson
Joyce L. Connery

**DEFENSE NUCLEAR FACILITIES
SAFETY BOARD**

Washington, DC 20004-2901



The Honorable Dan Brouillette
Secretary of Energy
US Department of Energy
1000 Independence Avenue, SW
Washington, DC 20585-1000

Dear Secretary Brouillette:

We received a letter from the Department of Energy's Office of River Protection on August 30, 2019, regarding open Board issues related to erosion and corrosion wear allowances for the design of piping, process vessels, and pulse-jet mixers at the Hanford Site's Waste Treatment and Immobilization Plant (WTP). The Department's letter stated that these issues, which were expressed in our January 20, 2012, letter have been resolved. The 2019 letter also included an attachment summarizing the technical work performed by the Department to support this conclusion. We agree that the Department has identified acceptable strategies for resolution of these issues and acknowledge that the work performed adds significant technical rigor to the designs for erosion and corrosion wear allowances. Consequently, we concur with the Department's position that these issues are resolved.

Separately from the issues described in the Department's letter, we would like to stress the importance of additional proposed (but not yet fully implemented) Pretreatment Facility flowsheet changes. In particular, the WTP project team has stated that it intends to reduce the maximum allowed temperature within the ultrafiltration feed vessels during caustic leaching.

We consider this an important change, as the project team's general corrosion allowance for stainless steel process vessels may be non-conservative at higher operating temperatures and caustic concentrations. The proposed reduction in the allowed temperature would resolve any concerns in this area. The enclosure provides further analysis for your information and use during the design process.

Yours truly,

Thomas A. Summers
Acting Chairman

Enclosure

c: The Honorable William I. White
Mr. Brian Vance
Mr. Joe Olencz

DEFENSE NUCLEAR FACILITIES SAFETY BOARD

Staff Report

May 19, 2020

General Corrosion Allowance for 304L and 316L Stainless Steel in the Waste Treatment and Immobilization Plant

Summary. Early in the design process, Waste Treatment and Immobilization Plant (WTP) project personnel performed a literature study to determine localized corrosion design limits and general (uniform) corrosion allowances for WTP stainless steel and nickel alloys that will be used to process the Hanford tank waste [1]. Most WTP piping and vessels are constructed from 304L or 316L stainless steel. WTP project personnel determined that the general corrosion rate for 304L and 316L stainless steel under all WTP operating conditions is less than 0.6 mils per year (mpy) [1 – 3]. Therefore, WTP project personnel established a general corrosion allowance of 0.6 mpy for 304L and 316L stainless steel for the 40-year design life of the WTP facilities (i.e., overall material loss of 24 mils) [1 – 3].

At the time, a Defense Nuclear Facilities Safety Board's (Board) staff team independently reviewed the literature and identified additional stainless steel corrosion rate data that suggests the WTP project's corrosion allowance of 0.6 mpy for 304/304L and 316/316L stainless steel may be non-conservative at the upper bounds (in the initial design) of operating temperatures (158–194°F) and sodium hydroxide (NaOH) concentration limits (50 weight percent, wt%) in the Pretreatment Facility caustic leaching ultrafiltration vessels.

During an October 29, 2018, teleconference with the Board's staff team, the Department of Energy's (DOE) Office of River Protection (ORP) personnel stated they had removed the oxidative leaching process in these ultrafiltration vessels, and lowered the maximum operating temperature of caustic leaching processes in the Pretreatment Facility to 140°Fahrenheit (F). While the stated reason for lowering the temperature was to reduce the potential for caustic stress corrosion cracking and corrosion pitting in the processing vessels, this reduction in peak temperature resolves concerns regarding non-conservatism in the general corrosion allowance.

The staff team understands that, while these changes have not yet been reflected in the WTP Basis of Design or formally included in the WTP contract documentation, these actions will be completed when full design work resumes on the Pretreatment Facility. In the meantime, this report documents the Board's staff team's assessment, for use if ORP should later decide to revert the WTP waste operating temperatures to above 158°F.

Background and Discussion. The following discussion is divided into sections that address *WTP Project's Reported Data* [1], *Data from the Literature* identified by the Board's staff team, *Determining Corrosion Rate as a Function of Temperature*, *Determining Activation Energy for Corrosion*, *Plotting Mean Corrosion Rate as a Function of Temperature*, and *Impact of Potentially Higher Corrosion Rates on Ultrafiltration Vessels*.

WTP Project's Reported Data—General corrosion rates in mpy for 304L and 316L stainless steel in solutions relevant to Hanford tank waste as reported by the WTP project are listed in Table 7-1 of Reference 1. The WTP project states that NaOH concentrations in the waste feed vary from a few percent to 50 wt% in the stainless steel process vessels and piping [1]. In the initial design, the highest expected temperature for caustic waste processing in stainless steel vessels and piping, excluding melters, was 194°F (90°C), but waste temperatures in all but two vessels should not have exceeded 158°F (70°C) [1]. Both are ultrafiltration vessels. One of these, UFP-VSL-00002A/B, was limited to 158°F during normal operations but could operate at temperatures up to 194°F for limited durations of eight to twenty-four hours per caustic leaching cycle [1]. This vessel is fabricated from 304L stainless steel [4, 5] even though Table 1-2 of Reference 1 lists the maximum operating temperature for 304L stainless steel exposed to caustic solutions as 150°F (66°C).

Reference 5 states that the other ultrafiltration vessel, UFP-VSL-00001A/B, can operate at temperatures up to 185°F (85°C) for limited durations, while References 4 and 6 state this vessel operates at temperatures up to 194°F. This vessel is fabricated from 316L stainless steel [4, 5]. Table 1-2 of Reference 1 lists the maximum operating temperature for 316L stainless steel exposed to caustic solutions as 200°F (93°C). Therefore, operating at 185–194°F would be within the maximum allowable temperature for 316L stainless steel [1].

WTP project documentation states that the 0.6 mpy general corrosion allowance is conservative because it accounts for any uncertainty in corrosion rates at higher waste temperatures and NaOH concentrations [1]. The general corrosion rates in Table 7-1 [1] support the WTP project's conclusion that a general corrosion allowance of 0.6 mpy bounds the measured corrosion rates for 304L and 316L stainless steel in nitric acid, and in NaOH and tank waste solutions with their designed maximum chemistry concentrations and temperature limits up to approximately 150°F. However, Table 7-1 (first row) shows one measured corrosion rate for 304/304L stainless steel of up to 1 mpy at 203°F in a 50 wt% NaOH concentrated solution.

Corrosion rates for 304/304L and 316/316L stainless steel were similar at comparable temperature and solution conditions shown in Table 7-1. The WTP project did not report any measured corrosion rates for 316/316L stainless steel at the highest expected WTP waste temperature (194°F) and maximum NaOH concentration (50 wt%). Assuming the corrosion rates for 304/304L and 316/316L stainless steel are similar at 194°F and 50 wt% NaOH concentration, then the ~1 mpy 304/304L data point suggests the 0.6 mpy general corrosion allowance may not bound corrosion rates for 316L stainless steel in caustic solutions at the highest allowable WTP waste temperatures and NaOH concentrations.

Data from the Literature—Table 1 below shows 27 general corrosion rate data points for 304/304L and 316/316L stainless steel in 50 wt% NaOH solutions: 24 data points from the literature and three data points reported by the WTP project in Table 7-1 of Reference 1. The data show that corrosion rates measured near the highest allowable WTP waste temperatures exceed the WTP project's general corrosion allowance of 0.6 mpy. Table 1 also lists reported corrosion rates in 50 wt% NaOH solutions measured near or at the boiling point (~295°F). Although this is well above the maximum expected caustic waste temperature of 194°F, the data

shows how corrosion rates accelerate with increasing temperature above 200°F and allows interpolating predicted corrosion rates at WTP maximum operating temperatures of 150–200°F where limited test data is available.

Table 1. *Stainless steel corrosion rates in 50 wt% NaOH solutions from the literature and Reference 1.*

304/304L Stainless Steel			316/316L Stainless Steel		
Corrosion Rate (mpy)	NaOH Concentration (wt%)	Temperature (°F)	Corrosion Rate (mpy)	NaOH Concentration (wt%)	Temperature (°F)
15 ¹	50	295	59 ²	50	298
0.1 ¹	50	149	< 0.1 ³	50	95
< 0.1 ¹	50	136	< 0.1 ³	50	85
150 ²	50	298	3.3 ³	50	190
< 0.1 ³	50	95	< 0.1 ³	50	130
< 0.1 ³	50	85	< 0.2 ³	50	104
1.1 ³	50	190	< 0.1 ³	50	72
< 0.1 ³	50	130	5 ⁴	50	194
0.1 ³	50	104	15 ⁴	50	290
< 0.1 ³	50	72	77.6 ⁴	50	295
5 ⁴	50	185	124 ⁴	50	295
71 ⁴	50	295	0.1–0.2 ⁵	50	136
118 ⁴	50	295			
0.1–0.2 ⁵	50	136			
< 1 ⁶	50	203			

¹ INCO Ltd., *Corrosion Resistance of the Austenitic Chromium-Nickel Stainless Steels in Chemical Environments*, Publication No. 2828, Distributed by Nickel Development Institute, 1964.

² Yasuda, M., et al., “On the Active Dissolution of Metals and Alloys in Hot Concentrated Caustic Soda,” *Corrosion*, Vol. 43(8), pp 492–498, August 1987.

³ INCO Ltd., *Corrosion Resistance of the Nickel and Nickel-Containing Alloys in Caustic Soda and Other Alkalies*, Publication No. 281 (CEB-2), Distributed by Nickel Development Institute, Circa 1970.

⁴ Davies, M., *Corrosion by Alkalies*, in *Corrosion: Environments and Industries*, Vol 13C, ASM Handbook, ASM International, pp 710–726, 2006.

⁵ Craig, B.D., (Ed), *Handbook of Corrosion Data*, ASM International, Metals Park, OH, 1989, from Reference 1, Table 7-1.

⁶ BNFL proprietary data, from Reference 1, Table 7-1.

Determining Corrosion Rate as a Function of Temperature—Corrosion of stainless steel is a thermally activated process and therefore an Arrhenius equation is generally used to predict the exponential effect of temperature on corrosion rate [1]. Figure 1 below shows the general corrosion rate data from Table 1 plotted on a logarithmic scale as a function of reciprocal temperature. The solid line is a regression fit to an Arrhenius equation of the combined 304/304L and 316/316L stainless steel data:

$$CR = A \exp(-E_a/RT), \quad (1)$$

where CR is corrosion rate, A is a normalized constant corrosion rate, E_a is the activation energy for corrosion, R is the gas constant, and T is absolute temperature. The correlation coefficient, $r = 0.943$ ($r^2 = 0.888$), implies a linear relationship between $\log(CR)$ and $1/T$ and supports the premise that the rate-controlling mechanism for corrosion remains constant over the temperature range of Figure 1.

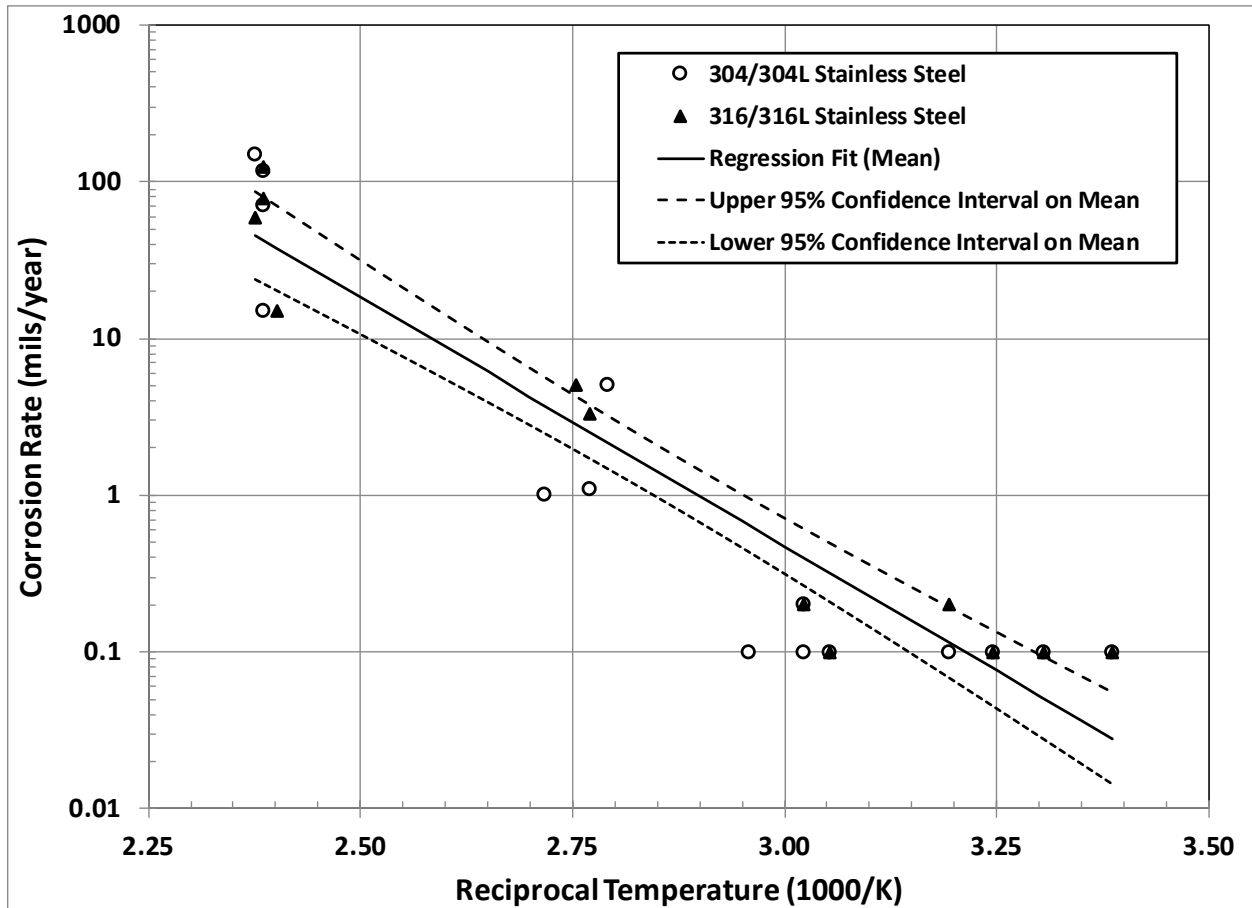


Figure 1. Arrhenius plot of corrosion rates for stainless steel in 50 wt% NaOH solutions.

The 304/304L and 316/316L stainless steel data have been combined to derive the Arrhenius equation. This should be a valid approach because most of the caustic solution or caustic tank waste data showed little difference in general corrosion rates between 304/304L and 316/316L stainless steel even though 316 stainless steel is known to have better chloride corrosion resistance than 304 stainless steel. The WTP project concluded that chloride concentration has little effect on general corrosion rates of 304/304L and 316/316L stainless steel in caustic solutions and that the addition of molybdenum in 316/316L stainless steel and AL-6XN super austenitic stainless steel serves principally to increase pitting corrosion resistance at higher chloride concentrations [1]. The dashed lines in Figure 1 represent the 95 percent confidence interval for the regression fit or mean value of corrosion rate at (reciprocal)

temperature. The upper 95 percent confidence interval on the mean slope and intercept represents the highest mean values of corrosion rate at each value of (reciprocal) temperature and the lower 95 percent confidence interval represents the lowest mean values of corrosion rate.

Determining Activation Energy for Corrosion—The slope of the solid line in Figure 1 represents the activation energy for corrosion (divided by the gas constant, R), which can be compared with results reported in the literature. The activation energy in Figure 1 is 61 kilojoules (kJ)/mol, a relatively high value that reflects the large increase in measured corrosion rates for data tested at temperatures above approximately 185°F (less than 1000/Kelvin (K) = 2.79 in Figure 1). The standard deviation of the activation energy is 4.3 kJ/mol and the 95 percent confidence interval on the activation energy is 61 ± 8.9 kJ/mol, which corresponds to a 95 percent confidence that the activation energy range is between 52–70 kJ/mol. Reference 7 lists 316L stainless steel corrosion rate data reported in Reference 8 from tests in 0.1 M (0.4 wt%) NaOH concentrated alkaline (pH = 13) solutions at three different temperatures. A survey of corrosion data reported in Reference 9 shows an Arrhenius plot of the three 0.4 wt% NaOH solution data points tested at temperatures of 86–176°F as reported in References 7 and 8. The corrosion rates were very low (< 0.01 mpy), as would be expected for such a low NaOH concentrated alkaline solution at these temperatures. The activation energy for corrosion of 316L stainless steel calculated from this data is 50 kJ/mol [9].

Plotting Mean Corrosion Rate as a Function of Temperature—Figures 2a and 2b below show the corrosion rate data from Figure 1 plotted as a linear function of temperature. Figure 2a shows all data at temperatures up to the boiling point of 50 wt% NaOH solution (~295°F), while Figure 2b shows the corrosion rate data only in the range of WTP allowable operating temperatures (< 200°F) for 316L stainless steel. The solid line in Figures 2a and 2b is the regression fit to the Arrhenius equation from Figure 1, which shows how the mean (expected) corrosion rate increases with temperature. The dashed lines show the upper and lower 95 percent confidence interval representing the highest and lowest mean values of corrosion rate at each value of temperature.

There is a relatively large amount of scatter in the corrosion rate data of Figure 2a measured at the boiling point and a relatively large variation of 1–5 mpy in the corrosion rate data of Figure 2b measured at 185–194°F. This is typical of the natural variability in experimental data that increases exponentially with temperature. The scatter is shown to be more uniform over the entire temperature range when the data is presented on a semi-log scale in an Arrhenius plot as shown in Figure 1 above. Because the regression fit is derived by minimizing the sum of the squares of the errors or scatter in the data, the solid line is the statistical best fit to the data. Approximately half of the data points lie above the regression fit (solid line) and approximately half lie below the solid line in Figures 1 and 2. The dotted line in Figure 2b shows WTP project's general corrosion allowance of 0.6 mpy.

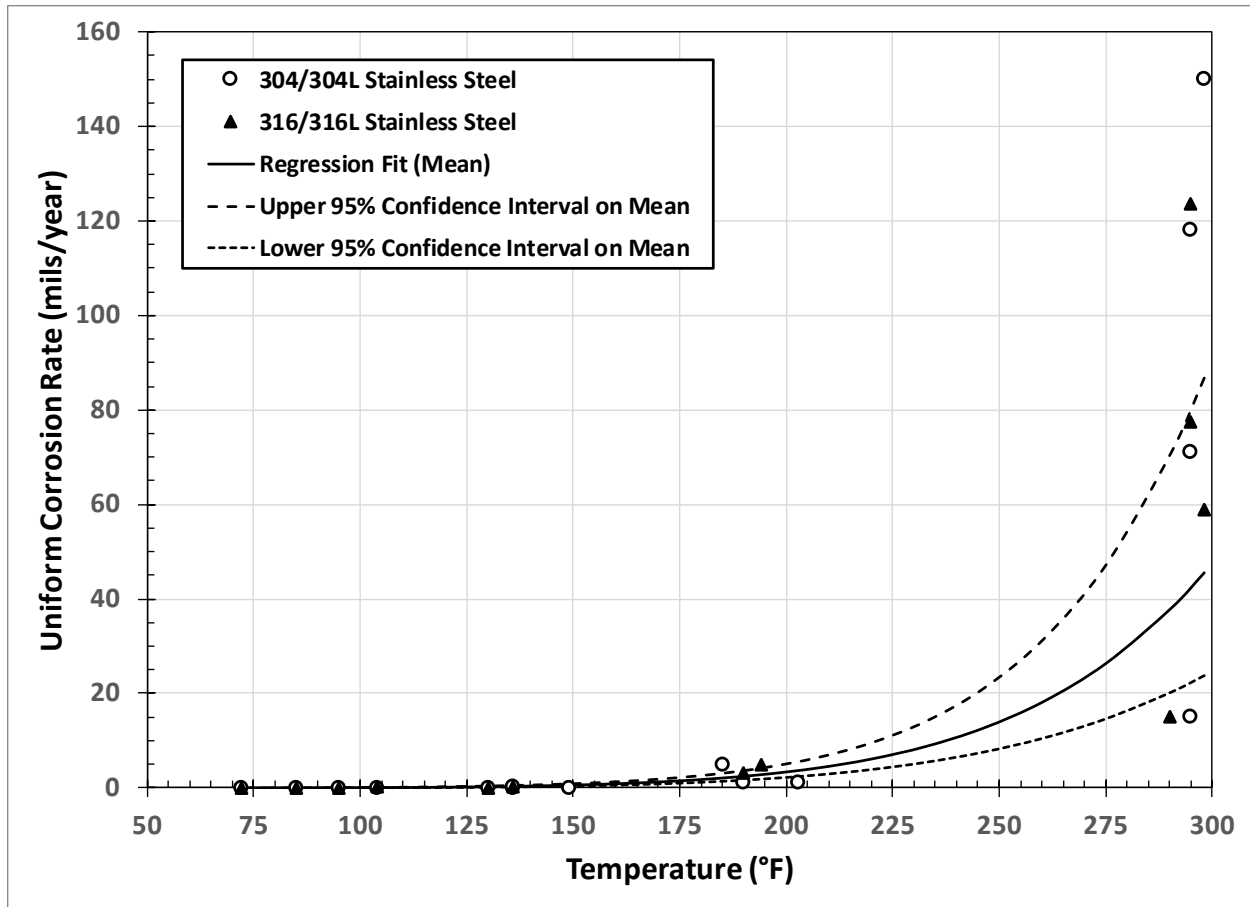


Figure 2a. Corrosion rates for stainless steel in 50 wt% NaOH solutions up to the boiling point.

Figure 2b shows that all four of the corrosion rate data points from 185–194°F exceed WTP project’s general corrosion allowance of 0.6 mpy. Although the sole data point (149°F) from 137–184°F is well below the regression fit solid line, this data point is inconsistent with the corrosion rate data from 130–136°F and is essentially the same rate measured at 72–95°F. The corrosion rate is expected to increase exponentially with temperature as most of the other data in Figure 2 shows. The regression fit (solid line) in Figure 2b predicts the mean corrosion rate exceeds WTP project’s general corrosion allowance of 0.6 mpy (dotted line) at temperatures above ~147°F. The mean corrosion rate is predicted to be ~3 mpy in a 50 wt% NaOH solution at 194°F based on a regression fit to an Arrhenius equation of all the data measured from 72–298°F. The lower 95 percent confidence interval (short dashed line) in Figure 2b predicts with 95 percent confidence that the mean corrosion rate exceeds 0.6 mpy at temperatures above ~158°F. This is significant because the solid line is the predicted mean corrosion rate for 304L/316L stainless steel whereas the dotted line is WTP project’s bounding corrosion rate of 0.6 mpy for 304L stainless steel at temperatures up to 150°F and for 316L stainless steel at temperatures up to 200°F. The mean corrosion rate is predicted with 95 percent confidence to be at least ~2 mpy in a 50 wt% NaOH solution at 194°F based on a regression fit to an Arrhenius equation of all the data measured from 72–298°F.

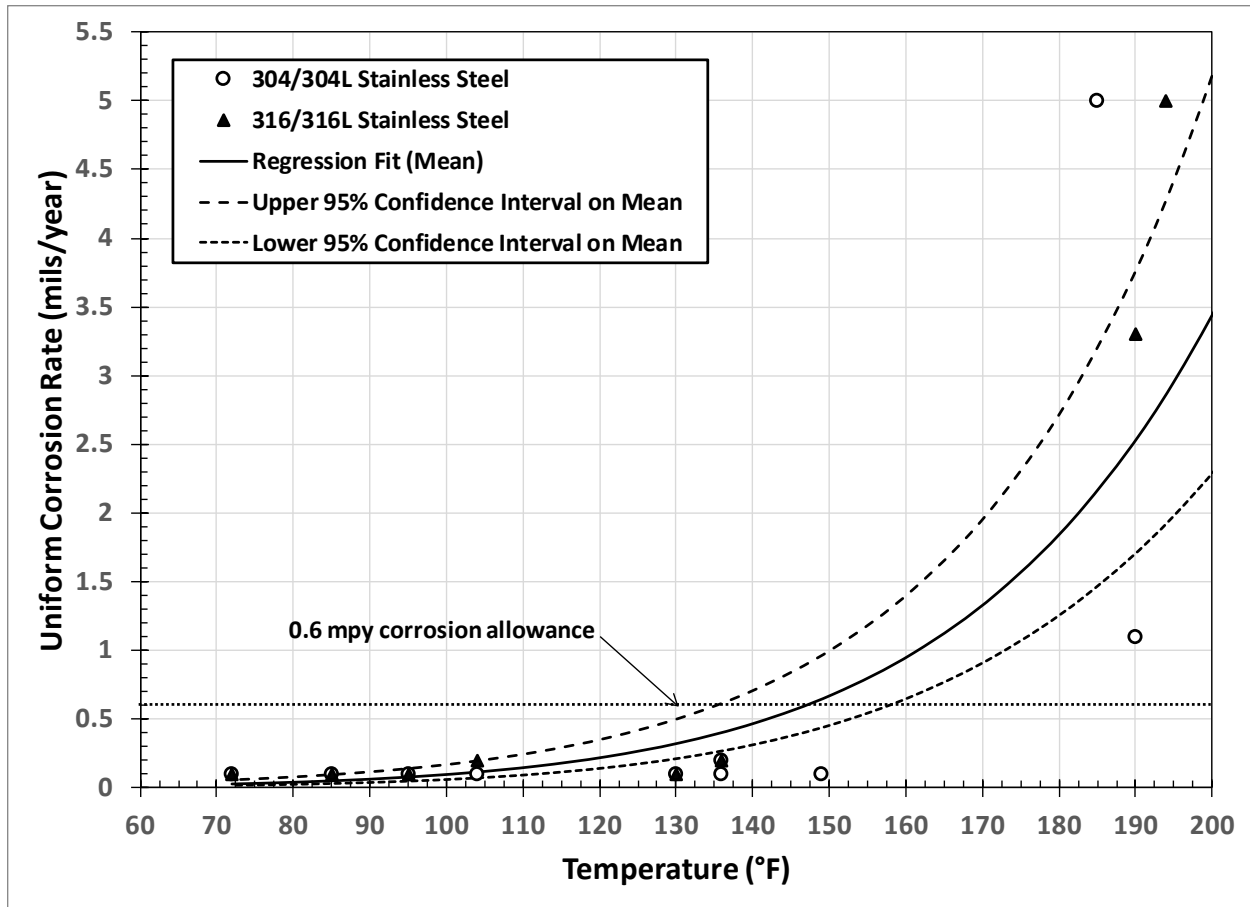


Figure 2b. Corrosion rates for stainless steel in 50 wt% NaOH solutions at WTP operating temperatures.

The WTP project notes that the general corrosion rate of stainless steel in solutions at temperatures below 194°F is low: less than 0.2 mpy for caustic NaOH concentrations up to 50 wt% and less than 0.4 mpy for nitric acid solutions [1]. The project also notes that the general corrosion rate of stainless steel only exceeds 1 mpy above 194°F and suggests this may be due to a thinning of the passive film (chromium oxide) at temperatures somewhere above this value [1]. WTP project documentation [1] cites a study [10] showing the general corrosion rate for 304L stainless steel at 190°F in 12–14 wt% NaOH solutions is less than 0.2 mpy and increases to 0.4 mpy in a 23 wt% NaOH solution at this same temperature.

This increase in stainless steel corrosion rate with increasing NaOH concentration is consistent with 304 stainless steel potentiodynamic anodic polarization data from the literature showing increasing current density and shifting of corrosion potential in the active direction with increasing NaOH concentration from 10⁻³ M (0.004 wt%) to 2.5 M (10 wt%) [11]. The regression fit of all the data measured from 72–298°F in 50 wt% NaOH solutions shown in Figures 1 and 2 predicts a mean general corrosion rate of 2.5 mpy with a lower 95 percent confidence interval of 1.7 mpy for 304/304L or 316/316L stainless steel at 190°F. This is well above the WTP project’s general corrosion allowance of 0.6 mpy. The four general corrosion rate data points at 185–194°F in 50 wt% NaOH solutions vary from 1–5 mpy in Figure 2b,

consistent with the regression fit prediction of the mean general corrosion rate of 2.5 mpy at 190°F.

WTP subcontractor personnel have recently reported corrosion tests of 304L stainless steel in caustic ($\text{pH} \geq 9$) NaOH solutions at temperatures of $\sim 100^\circ\text{C}$ ($\sim 212^\circ\text{F}$) [12]. Although the percent NaOH solution is not given, the reported boiling point of 103°C (217°F) for the pH 14 solution should correspond with slightly less than a 10 wt% (2.5 M) NaOH solution [13]. Corrosion rates of 304L stainless steel tested at temperatures of $95\text{--}100^\circ\text{C}$ ($203\text{--}212^\circ\text{F}$) varied from 0.35–1.62 mpy [12]. These corrosion rates are lower than those for 304L/316L stainless steel tested in 50 wt% NaOH solutions at $185\text{--}194^\circ\text{F}$ as shown in Figure 2b. Lower corrosion rates would be expected for 304L stainless steel tested in a 10 wt% NaOH solution compared with 304L/316L stainless steel tested at comparable temperatures in a 50 wt% NaOH solution [10, 11].

Impact of Potentially Higher Corrosion Rates on Ultrafiltration Vessels—Uncertainty in corrosion rates at the highest operating temperatures and NaOH concentrations may only affect the design allowance for certain vessels that operate at temperatures up to 194°F . As noted earlier, ultrafiltration vessels UFP-VSL-00001A/B and UFP-VSL-00002A/B exceed 158°F and periodically operate at temperatures up to 194°F [1, 4, 5]. Also as noted earlier, vessel UFP-VSL-00002A/B is fabricated from 304L stainless steel [4, 5] even though Table 1-2 of Reference 1 lists the maximum operating temperature for 304L stainless steel exposed to caustic solutions as 150°F . Ultrafiltration vessel UFP-VSL-00001A/B is fabricated from 316L stainless steel [4, 5] and therefore will be below the maximum operating temperature (200°F) for 316L stainless steel exposed to caustic solutions. As discussed above, general corrosion rates could exceed the 0.6 mpy allowance in high NaOH concentration waste at high WTP operating temperatures. Depending on what the actual duty and usage cycles of these two 304L/316L stainless steel vessels will be, higher corrosion rates could result in overall material loss exceeding the general corrosion allowance of 24 mils during the 40-year design life.

Path Forward for Resolution. On November 16, 2017, BNI completed the *PT Facility Standard High-Solids Vessel Concept Design Alternative Study* [14]. Project personnel developed this collection of technical assessments to resolve a wide range of long-standing technical issues at WTP, including (but not limited to) erosion and corrosion. A portion of this study recommended flowsheet changes to the Pretreatment Facility, including a reduction in the peak temperature allowance for caustic leaching in the ultrafiltration vessels from $80\text{--}90^\circ\text{C}$ to 60°C (140°F). While this change was specifically proposed to reduce caustic stress corrosion cracking in the ultrafiltration vessels, it also resolves the aforementioned concerns with the generalized corrosion rate.

BNI reported to ORP in letters dated December 20, 2017, [15] and June 20, 2019, [16] that incorporating the standard high-solids vessel design [14] would resolve all major technical issues including open Board issues related to erosion and corrosion wear allowances at WTP. On July 16, 2019, ORP agreed that Pretreatment Facility technical issues had been resolved [17]. Corresponding changes have not yet been incorporated into the Basis of Design or WTP contractual documents. The staff team understands that these changes will be made prior to resumption of Pretreatment Facility design activities.

Conclusion. During the staff team's review of the WTP erosion and corrosion control strategy, the team identified potential non-conservatism with the project's generalized corrosion rate and associated general corrosion allowances. In particular, the Pretreatment Facility's ultrafiltration process, which was initially designed to operate at 160°F or above, could have experienced corrosion rates exceeding the design allowance.

The project team has since lowered the maximum operating temperature of this process; however, it took this action to resolve other technical issues, rather than explicitly to resolve concerns related to generalized corrosion rates in WTP. Therefore, while the staff team acknowledges that the generalized corrosion allowance in WTP is no longer an issue, it is important to understand fully the technical basis associated with this conclusion to ensure DOE and its contractors have the information necessary to make informed decisions on design in the future.

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AFFIRMATION OF BOARD VOTING RECORD

SUBJECT: Erosion and Corrosion Wear Allowances in Hanford WTP

Doc Control#: 2020-100-0054

The Board acted on the above document on 09/25/2020. The document was Approved.

The votes were recorded as:

	APRVD	DISAPRVD	ABSTAIN	NOT PARTICIPATING	COMMENT	DATE
Thomas Summers	✓	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	09/25/2020
Jessie H. Roberson	✓	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	09/24/2020
Joyce L. Connery	✓	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	09/24/2020

This Record contains a summary of voting on this matter together with the individual vote sheets, views and comments of the Board Members.

Shelby Qualls

Executive Secretary to the Board

Attachments:

1. Voting Summary
2. Board Member Vote Sheets

DEFENSE NUCLEAR FACILITIES SAFETY BOARD
NOTATIONAL VOTE RESPONSE SHEET

FROM: Thomas Summers

SUBJECT: Erosion and Corrosion Wear Allowances in Hanford WTP

Doc Control#: 2020-100-0054

DATE: 09/25/2020

VOTE: Approved

COMMENTS:

None

Thomas Summers

DEFENSE NUCLEAR FACILITIES SAFETY BOARD
NOTATIONAL VOTE RESPONSE SHEET

FROM: Jessie H. Roberson

SUBJECT: Erosion and Corrosion Wear Allowances in Hanford WTP

Doc Control#: 2020-100-0054

DATE: 09/24/2020

VOTE: Approved

Member voted by email.

COMMENTS:

None

Jessie H. Roberson

DEFENSE NUCLEAR FACILITIES SAFETY BOARD

NOTATIONAL VOTE RESPONSE SHEET

FROM: Joyce L. Connery

SUBJECT: Erosion and Corrosion Wear Allowances in Hanford WTP

Doc Control#: 2020-100-0054

DATE: 09/24/2020

VOTE: Approved

COMMENTS:

None

Joyce L. Connery