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Estimation of Metal Loss by Corrosion Process in Heat Exchangers Applied to Hydrotreating Systems

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It is well known that among of all the components of hydrotreating systems used in the industrial processes, the heat exchangers that pre-heat the reactor suffer the greatest degree of degradation by pitting corrosion due to extreme temperature exposure. Typically, two different mathematical analysis were used to estimate the probability of failure by metal loss as a consequence of pitting corrosion mechanism: short-term and long-term corrosion rate (STCR and LTCR, respectively), as designated by API 510 standard method. However, the results are often misunderstood when the difference between the calculated data of STCR and LTCR is large. For this reason, in this research the STCRs and LTCRs models were fitted to a generalized extreme value distribution (GEVD) to characterize the metal loss that take place in four heat exchangers, as well as to determine what kind of corrosion rate model is better for predicting the metal loss estimation. According to the results obtained in this research, the STCR model appears to be the most appropriate analysis for estimating future metal loss by pitting corrosion for the heat exchangers reactors used in hydrotreating systems.

Keywords: metal loss, corrosion rate, heat exchanger, hydrotreating systems, extreme value distribution, mathematical analysis.

1. INTRODUCTION

The global demand for diesel fuel has been rising rapidly, even faster than for gasoline transportation vehicles [1]. The principal reason for this, undoubtedly, is the fuel efficiency of diesel engines, which are 25-40% more fuel-efficient than gasoline engines. However, untreated diesel typically has a relatively high sulfur content [2]. This high sulfur content leads to SOx formation when the fuel is burned. During the last part of the twentieth century, in Mexico, the diesel was hydrotreated in the oil refineries to reduce the sulfur content to 500 ppm. However, the Mexican government has recently established lower maximum sulfur content of 15 ppm for diesel, which is referred to as ultra-low sulfur diesel (ULSD) [3]. To produce ULSD, Pemex (a Mexican state-owned and gas company) considers it necessary to renew 17 of the existing plants throughout the country [4].

To improvement these plants, it is necessary to carry out a mechanical integrity study of the pressure vessels that will keep working to produce ULSD. Among the vessels to be studied, the two heat exchangers handling the reactor effluent, which are exposed to the highest fluid temperatures, are the most susceptible to corrosion damage. This is due to the severe conditions that these heat exchangers are exposed during their service operation (approximately 350°C, a high sulfur content of about 60 kg/cm^2 of gauge pressure). For monitoring the equipment damage, an ultrasonic test may be performed to determine the wall thickness.

According to the Nernst equation [5], corrosion is an electrochemical process that occurs spontaneously, that means that this process takes place in a thermodynamically most stable state of energy. For this reason, it is not possible to avoid the corrosion process; one can only reduce & control the degradation rate using corrosion inhibitors, cathodic protection or a physical barrier to prevent electron flow from the anode to the cathode [6]. Examples of such organic coatings, claddings or linings.

However, the heat exchangers under consideration cannot be internally coated or cladded. For this reason, it is important to measure the actual wall thickness at different elapsed times to determine the corrosion rate. The corrosion rate is important for estimating the remaining life of a heat exchanger and establishing an adequate maintenance program. Furthermore, more accurate estimation of the remaining life of a heat exchanger can reduce human fatalities, environmental damage and unscheduled oil refinery shutdowns.

The main problem that motivates this research was that no one else has paid any attention before to the application of Short-Term and Long-Term Corrosion Rate (STCR & LTCR) in the remaining useful life estimation of pressure vessels. Sometimes the result of using STCR or LTCR can have a great impact in the decision to replace more vessels unnecessarily, questioning to renovation or not a refinery plant because it could provoke an unuseful investment. To produce ULSD, Pemex needed to have an approximation of the cost of improvement the existing the middle-distillate plants, to approximate more accurately it was necessary to know which corrosion rate can be applied, encouraging the purpose of this work.

On the other hand, corrosion data are frequently published with the purpose to provide enough information for the maintenance or design engineers. An example, it is the reference [7] that published data of the pipeline corrosion in soil. For this reason, this paper also provides information about corrosion rate in heat exchangers in hydrotreating units for designers and people that works repairing this kind of vessels.

2. APPLICATION IN THE ULSD PROJECT IN MEXICO

In almost all of the developed countries of the world, the specifications for the upper limits of sulfur content in diesel are approximately 15 ppm [2]. Reducing sulfur has benefits such as reduced SOx emissions to the atmosphere, acid rain reduction and promotion of energy-efficient diesel vehicle use. Particularly for Mexico, which has registered a gasoline deficit in recent years [8], diesel could be an option to change the fuel model applied in the country, where gasoline is the predominant fuel in automobiles. In this context, the Mexican government has decided to place restrictions on sulfur content for diesel [3]. Additionally, PEMEX has launched a clean fuel project for producing ULSD. Improvement existing facilities for desulphurization of middle distillates has been shown to be economically and technically feasible by A Stanislaus and coworkers in 2010 [2]. Accordingly, PEMEX decided to improvement 17 hydrotreating plants across the country. Improvement plants requires a mechanical integrity analysis of the pressure vessels to determine which vessels will be modified by the change of the process technology and which vessels will be replaced or repaired because of limited remaining life.

In all of the existing diesel facilities operated by PEMEX, the vessels that suffer the fastest deterioration by corrosion are the heat exchangers that preheat the stream that feed the reactor using the effluent stream from the same reactor. The working temperature and pressure in the hottest heat exchangers are approximately 350°C and 5883 KPa (60 kg/cm^2) gauge, respectively. Within the shell and tube heat exchangers, the effluent flows through the tubes while the feed (primary diesel) flows through the shell, which is usually manufactured from low alloyed steel.

3. CORROSION RATE ESTIMATION

Usually the two most popular threats to the heat exchanger integrity are both the corrosion-erosion [9] and the pitting corrosion attack [10]. The hydrotreating reactors are used to remove the undesirable sulfur and nitrogen that come from the sour naphta, sour diesel or other intermediate distillates. The heat exchangers in the hydrotreating units that are responsible of decreasing the temperature of the stream that flows out from reactors cool down the byproducts, including ammonia (NH_3) and hydrogen sulfide (H_2S). The product of these two gases forms a salt, ammonium bisulfide (NH_4HS) [11,12], that provokes a kind of degradation named Ammonium Bisulfide Corrosion or Alkaline Sour Water Corrosion [13]. The Alkaline Sour Water Corrosion is influenced mainly by the fluid velocity, temperature and H_2S partial pressure. In 2006, a study lead by Horvath et al. [14] indicates that in the last 25 years there have been several major incidents where NH_4HS corrosion caused loss of containment in hydroprocessing units that resulted in damage/lost production on the order of 50 million dollars. This fact makes an important point in the study of this kind of corrosion.

Pemex has already developed some criteria for assessing the integrity of a heat exchanger [15]. First, it is necessary to determine how many observations are required to estimate the remaining life of a heat exchanger. The experiment in this research consists mainly in making a sampling inspection plan for reliable estimates of the remaining life of the vessel because to measure the wall thickness across the entire vessel, it is necessary to entirely remove the external coating.

The wall thickness measurement was determined using conventional ultrasonic thickness gages, similar to the described by Bray [16] and according to the ASME Section V, Articles 4,5 and 23 [17].

In the heat exchangers that preheat the feed to the reactor, between 30 and 40 observations were carried out. To determine the corrosion rate (metal loss rate), the wall thickness was first measured at designated locations at different times. The API-510 standard method [18] ("Pressure Vessel Inspection Code: In-Service Inspection, Rating, Repair and Alteration") named these locations as condition monitoring locations (CLMs). The corrosion rate (metal loss rate) can be determined by the difference in thickness measurements at two different times divided by the time interval between readings. The API-510 standard also establishes that either the long-term corrosion rate (LTCR) or the short-term corrosion rate (STCR) must be chosen according to the inspector's experience [18].

The LTCR can be computed by Equation (1):

$$\mathrm{LTCR} = \frac{t_i - t_a}{\Delta Tl} \quad (1)$$

where t_i is the initial thickness measurement at a CML,.
t_a is the current thickness at the same CML measured at the most recent inspection, and
ΔTl is the time between thickness measurements.

The STCR can be computed by Equation (2):

$$\mathrm{STCR} = \frac{t_p - t_a}{\Delta Ts} \quad (2)$$

where t_p is the thickness measured at a previous measurement, and .ΔTs is the time between the previous measurement and the current one.

After computing both the LTCR and the STCR, typically the inspector then predicts the remaining life of the vessel; however, the following question may emerge. When or under which condition is it more appropriate to apply: LTCR or STCR? A wrong decision could result in unnecessary repair or, even worse, a possible rupture. This research aims to help provide more information for answering this question.

4. DATA ANALYSIS

To study the corrosion rate behavior, two heat exchangers seriously affected by temperature in an oil refinery in the South of Mexico were selected. The wall thicknesses measurements were collected using ultrasonic tests; however, for data analysis, the wall thicknesses were converted to metal loss by subtracting the wall thickness at a particular time from the initial wall thickness. For each heat exchanger, more than 30 metal loss observations were conducted, and then a fitting of the metal loss histogram with a theoretical distribution model was also carried out in this research.

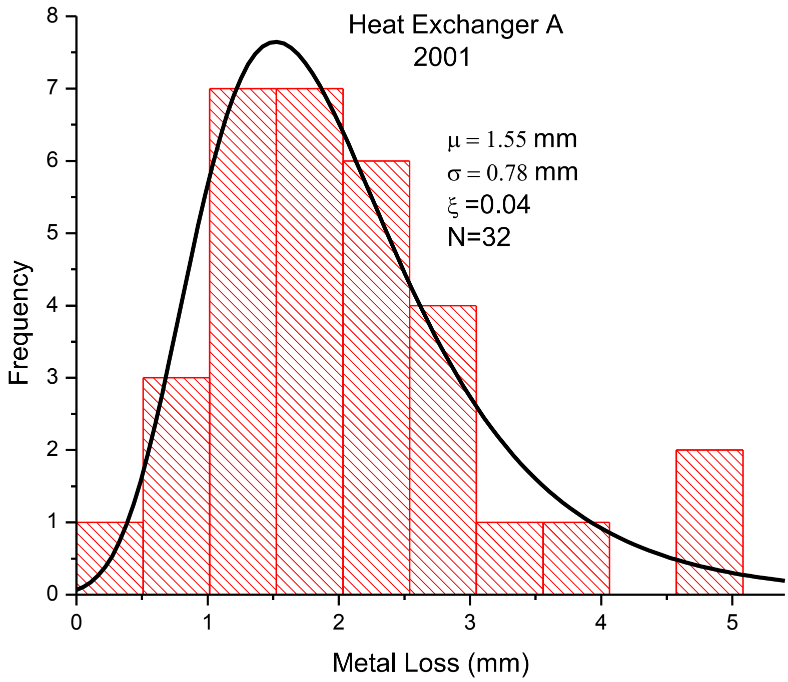

Figure 1. Metal loss histogram for Heat Exchanger "A" in 2001 and its corresponding fitting curve.

The theoretical distribution selected is the generalized extreme value distribution (GEVD) as its application to the corrosion analysis is well established [19-22]. Equation (3) represents the probability density function (PDF) for a GEVD.

$$f(x) = \frac{1}{\sigma}\left[1 + \xi\left(\frac{x-\mu}{\sigma}\right)\right]^{\left(-\frac{1}{\xi}\right)-1} exp\left\{-\left[1 + \xi\left(\frac{x-\mu}{\sigma}\right)\right]^{-1/\xi}\right\} \quad (3)$$

where μ is the location parameter, σ is the scale parameter and ξ is the shape parameter.

To assess that this distribution was selected correctly, the Kolmogorov-Smirnov (K-S) and chi-square tests were applied. The metal loss histogram was fitted for each inspection performed at three different times. Figure 1 shows the histogram for metal loss in millimeters and its corresponding fitting data.

In addition to fitting the metal loss histogram, it was also useful to fit the metal loss rate histogram. Fitting the metal loss rate (corrosion rate) histogram is not only beneficial for plant maintenance personnel, corrosion engineers and safety engineers but also for plant operation personnel, process engineers and project engineers. This is because it is possible to plan shutdowns, make better estimations of equipment life in the design stage and to plan more accurately project execution.

The same procedure, i.e., the use of GEVD fitting and K-S and chi-square tests, was used for the LTCR. Figure 2 illustrates the LTCR histogram for Heat Exchanger "A" and its corresponding fitting data.

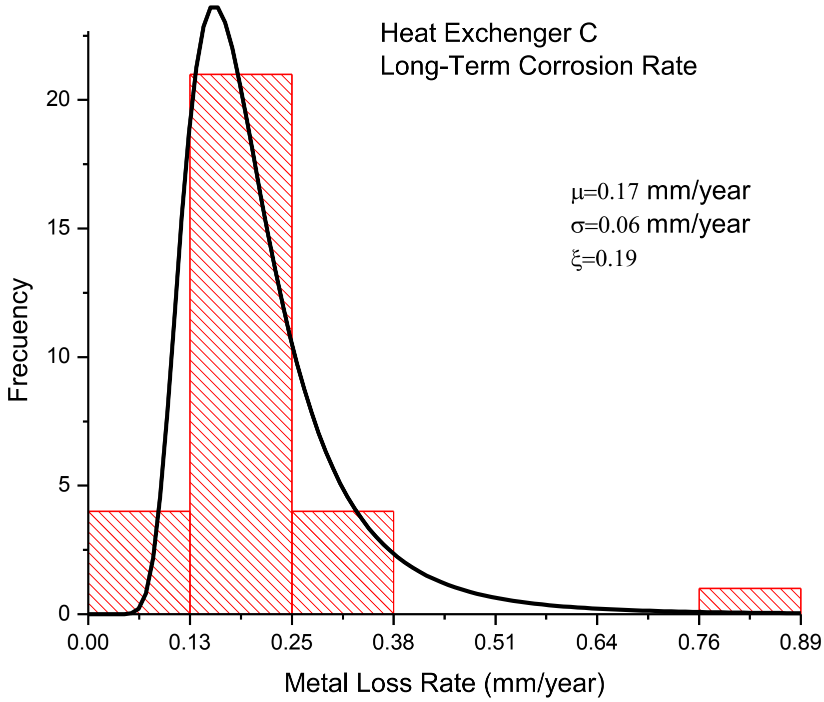

Figure 2. Long-term metal loss rate for Heat Exchanger "C" and its corresponding fitting curve.

Table 1. Fitting to the GEVD of the metal loss histograms at two periods.

Heat Exchanger	Year	GEVD PARAMETER			p-value (Kolmogorv-Smirnov test)	p-value (Chi squared test)
		μ	σ	ξ		
A	2001	1.55	0.78	0.04	0.95	0.96
	2006	2.22	1.33	-0.06	0.42	0.36
B	2001	0.86	0.59	-0.05	0.86	0.37
	2006	1.97	1.32	-0.10	0.96	0.97
C	2001	1.68	1.52	-0.03	0.98	0.86
	2008	3.11	1.81	-0.25	0.79	0.15
D	2001	2.10	1.41	0.04	0.94	0.86
	2008	2.19	1.37	0.05	0.96	0.76

Table 2. Fitting to GEVD of the LTCR and STCR histograms.

Heat Exchanger	Corrosion Rate	GEVD PARAMETER			p-value (Kolmogorv.Smirnov test)	p-value (Chi squared)
		μ	σ	ξ		
A	LTCR	0.46	0.27	-0.06	0.86	0.91
	STCR	0.23	0.12	-0.08	0.82	0.93
B	LTCR	0.27	0.19	0.46	0.33	0.62
	STCR	0.33	0.24	-0.16	0.98	0.74
C	LTCR	0.17	0.06	0.19	0.33	0.89
	STCR	0.06	0.04	0.44	0.83	0.60
D	LTCR	0.16	0.07	0.28	0.82	0.77
	STCR	0.07	0.06	0.45	0.71	0.69

Figure 3 schematizes the STCR distribution. The GEV distribution was also selected to fit the observations. Tables 1 and 2 show the results obtained in the fitting of metal loss histograms at different times and LTCR and STCR histograms.

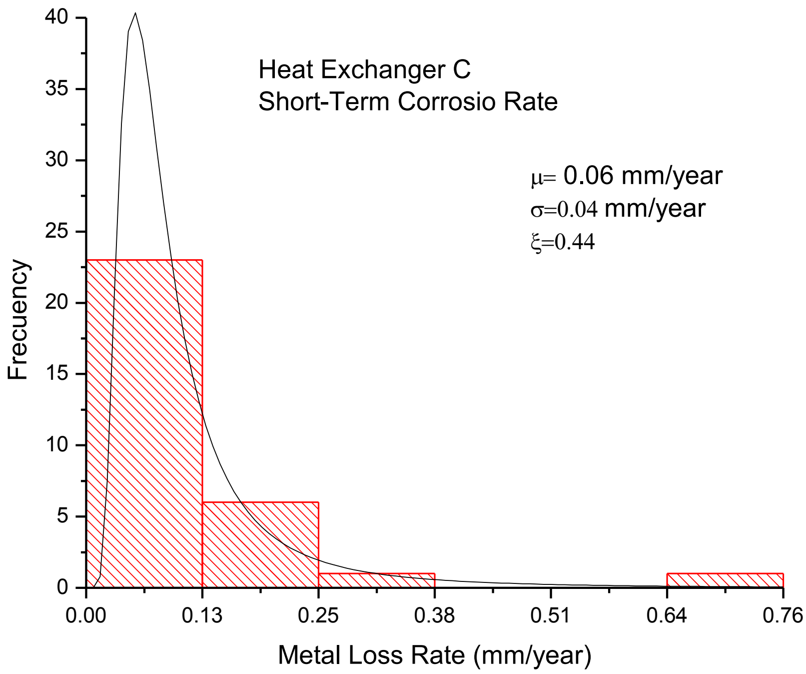

Figure 3. Short-term metal loss rate for Heat Exchanger "C" and its corresponding fitting curve

Figure 4 represents the metal loss histogram evolutions for Heat Exchanger "A". Evolution of the mean and the variance can also be observed, the values for which can be computed from the parameters shown in Table 1.

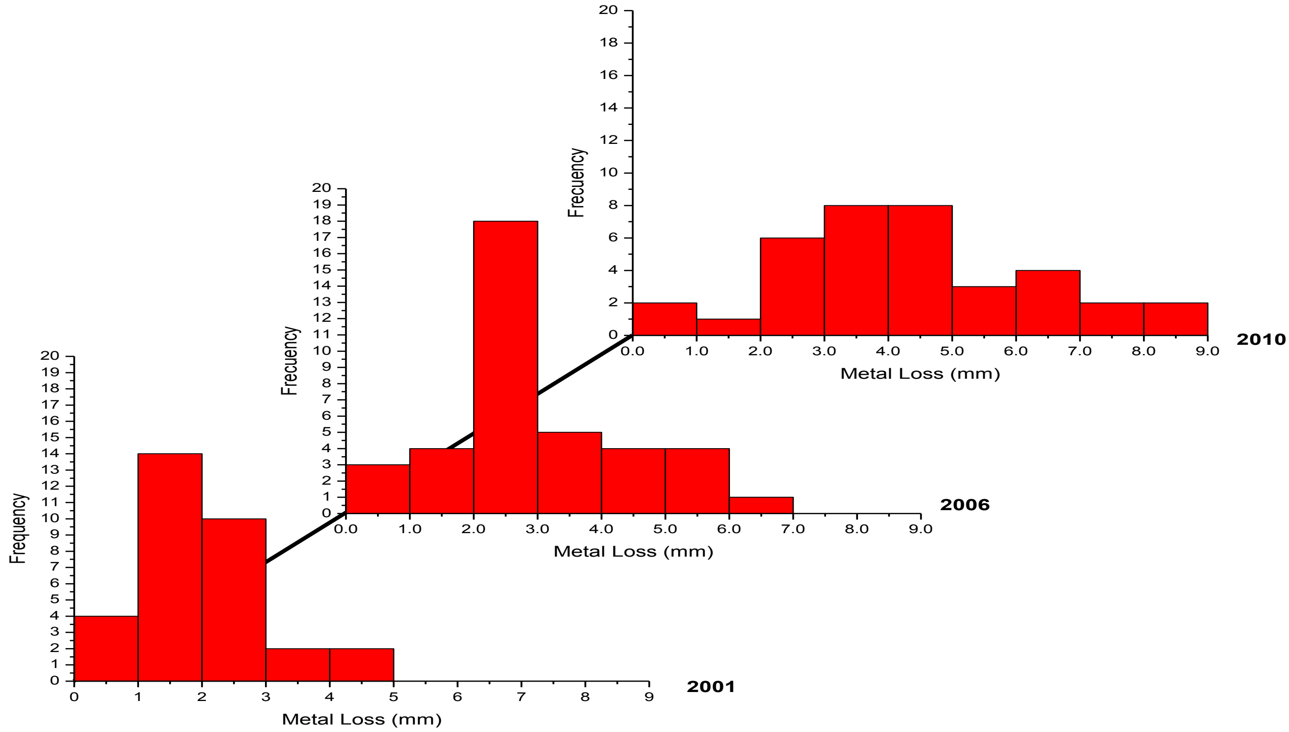

Figure 4. Evolution of the metal loss in Heat Exchanger "A".

5. RESULTS OF THE FUTURE METAL LOSS ESTIMATION

Once the corrosion rate and the metal loss PDFs are determined, it is feasible to estimate a future metal loss PDF. To do this, it is necessary to convolve the metal loss PDF and the corrosion rate PDF. Equation 4 represents the convolution of these PDFs. This convolution was already applied in corrosion problems; References [23] and [25] that represent some of the applications, assuming that the metal loss and corrosion rates are random variables.

$$f(x2) = \int_0^\infty g(v) f(x1 - v\delta) dv dx1 \quad (4)$$

where $g(v)$ is the corrosion rate PDF, $f(x1)$ is the metal loss PDF in time t1, $f(x2)$ is the metal loss PDF estimated for time t2 and δ is the difference between t2 and t1.

To demonstrate the application of Equation 4, the metal loss PDF fitted for measurements for Heat Exchangers A, B, C and D (see Table 1) were used to predict a future metal loss PDF. This prediction was carried out by applying the LTCR PDF and the STCR PDF in Equation (4) to estimate the future metal loss distribution. Figure 5 illustrates this application for Heat Exchanger "A" using the STCR PDF with the parameters shown in Table 2 from 2006. It may be observed that the estimated PDF and the observed histogram are quite similar. The p-value for the K-S test was 0.45 indicating excellent applicability for estimation of future observations.

Because the API 510 standard establishes two possible options for estimating the corrosion rate in a vessel (Equations 1 and 2), Equation 4 was used to estimate the future PDF for metal loss using both STCR and LTCR information and for different time periods (see Table 2). Table 3 shows both the non-parametric mean and non-parametric standard deviation for the observed metal losses in 2010 and 2012 for the heat exchangers studied. Additionally, Table 4 summarizes the results obtained including the estimated GEVD parameters for different time periods and different metal loss PDFs at time t1 for both types of corrosion rates. All of this information was obtained from Tables 1 and 2. In the last column of Table 4, it is possible to observe the p-value that results from the K-S test when one compare the observed heat exchanger metal loss and the theoretical probability distribution.

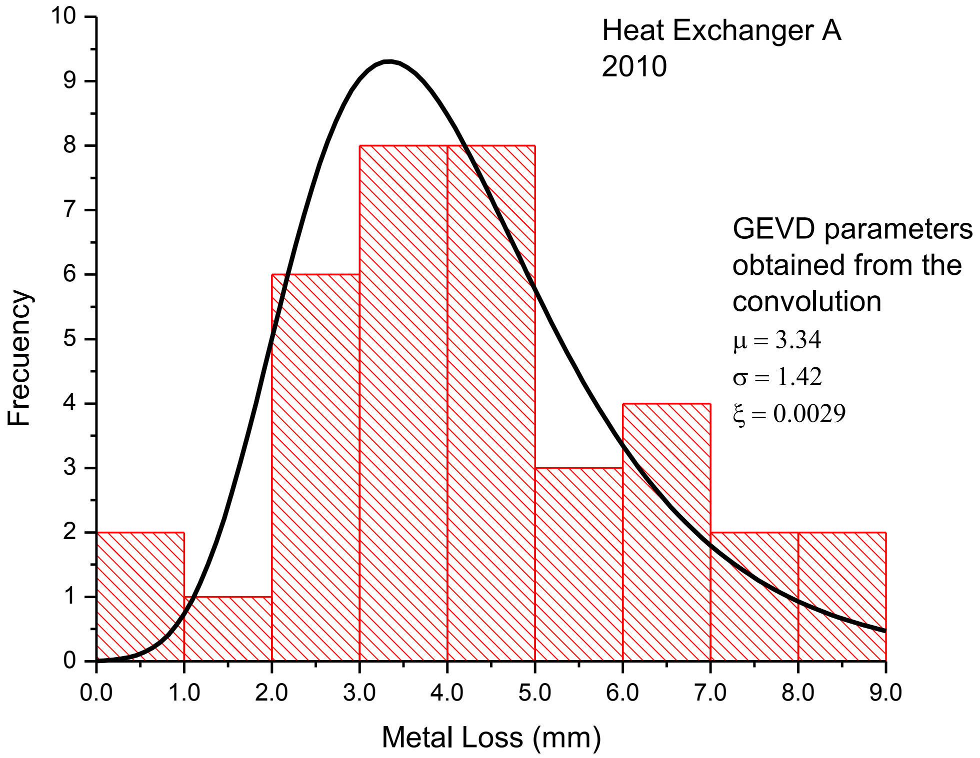

Figure 5. Metal loss histogram for Heat Exchanger “A” in 2010 and the GEVD curve estimated from convolution of the STCR probability density function and observations in 2006.

Table 3. Observed metal loss non-parametric means and non-parametric standard deviations for the heat exchangers.

Heat Exchanger	Year of the last measurements	Metal loss non-parametric mean (mm)	Metal loss non-parametric standard deviation (mm)
A	2010	4.29	2.00
B	2010	3.79	2.10
C	2012	4.07	2.59
D	2012	4.22	2.01

Table 4. GEVD parameters and p-value resulting from Equation 4.

Heat Exchanger	Year for t1	Year for t2	GEVD Parameters for predicted PDF in t2			Corrosion Rate	p-value For K-S test
			μ (mm)	σ (mm)	ξ		
A	2006	2010	3.34	1.42	0.0029	STCR	**0.45**
	2001		4.07	1.83	0.0036	LTCR	< 0.01
	2001		3.94	1.44	-0.0031	STCR	0.02
	2006		5.23	2.57	0.0101	LTCR	< 0.01
B	2006	2010	3.72	1.70	0.0124	STCR	**0.051**
	2001		3.80	2.31	0.0027	LTCR	0.02
	2001		4.16	2.13	-0.0039	STCR	< 0.01
	2006		3.54	1.85	-0.0021	LTCR	**0.12**
C	2008	2012	3.59	1.80	-0.1582	STCR	**0.06**
	2001		3.91	1.76	-0.0073	LTCR	< 0.01
	2001		3.98	1.79	-0.2044	STCR	<0.01
	2008		2.81	1.81	0.0053	LTCR	**0.65**
D	2008	2012	3.14	1.75	-0.0058	STCR	**0.52**
	2001		4.37	1.81	0.0198	LTCR	< 0.01
	2001		3.69	2.03	0.0056	STCR	< 0.01
	2008		3.06	1.44	0.0020	LTCR	**0.25**

According to the literature [24] regarding the p-value, the general rule is that 0.05 is used as the level where reasonable doubt begins. Something happening with probability less than or equal to 0.05 is thus viewed as being exceptional. In other words, if a p-value of less than or equal to 0.05 is calculated, there is a greater probability of errors when that option is chosen. In this research, the results obtained from the convolution are compared with the most recent metal loss histograms: 2010 measurements for Heat Exchangers A and B and 2012 measurements for Heat Exchangers C and D. According to the information shown in Table 3, to convolve the STCR PDF and the PDF resulting from the fitting of the last observations provided the best results, obtaining p-values higher than 0.5 in all cases. This can be explained by the fact that in general, the LTCR has much larger variance. F. Caleyo et al. showed that the variance of the corrosion rate tends to increase in time [25]; in this sense, it is feasible to affirm that the use of the STCR PDF could provide more confidence in the estimation of metal loss by corrosion in the future.

This result suggests that in case of having enough Short-Term Corrosion Rate data, it is more convenient to use them than the Long-Term Corrosion Rate data. For instance, in the ULSD project in Mexico, this result contributed to decide the suitability of improvement the hydrotreating units, avoiding making unnecessary repairs, alterations and vessels replacement. Valor et al. [26] also indicated that the use of Long-Term Corrosion data can provoke an underestimation of the remaining life in oil and gas pipelines. These authors explained this situation because of LTCR takes into consideration the rapid corrosion rate that occurs at the beginning of any corrosion process. So, including LTCR in the remaining life estimation of any structure could carry over in a lack of accuracy. The use of LTCR can be justified only by the fact of not having enough STCR data.

6. CONCLUSIONS

The main conclusions in this research are as follows.

- In heat exchangers, the metal loss observed can be fitted to a GEVD model with a high level of confidence (See Table 1). This can help to predict the future evolution of the metal loss in the vessels, as shown in the literature [23,25,26]. It is expected that these data can be fit to a GEVD because the CLM points are located at sites most susceptible to metal loss.
- Both the STCRs and LTCRs observed in heat exchangers can also be fit to a GEVD with high level of confidence as is shown in Table 2 and Figure 2. Also, it is important to mention that the mean and variance tend to increase with respect to the time, as has been reported in other types of corrosion phenomena (i.e. localized corrosion in References [25-26]).
- The results of the convolution of the fittings of the metal loss and the metal loss rate can also be fitted to a GEVD.
- After convolving and fitting the data and distributions for the four heat exchangers studied, it was shown that the STCR provides superior estimation to LTCR for future metal loss. Use of STCR rather than LTCR may then provide benefits of increasing reliability of remaining life estimates for heat exchangers in hydrotreating units, avoiding unnecessary repairs, reducing sudden shutdowns and reducing the probability of failure. The details of this result is shown in Table 3, it can be observed that in all the results obtained the use of STCR method can lead in a better estimation of the wall thickness, in which p-value is higher in almost all cases.

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