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APPLICATION OF REGRESSION MODELS ON THE PREDICTION OF CORROSION DEGRADATION OF A CRUDE OIL DISTILLATION UNIT

ABSTRACT

The crude distillation unit is the most critical elements in the refining process. Moreover, most of the equipment in the distillation unit are made of general carbon steels. Data analysis models, machine learning techniques can predict corrosion degradation rates. We used Pearson's correlation coefficient and multiple linear regression, to predict the impact of process parameters. Altogether, we have analysed 84 channels of technological parameters, and 22 different types of crude oils. Among the corrosion agents, the chloride content strongly affected the weight loss of coupons, where the highest coefficient was 0.68. The most influential parameter is found to be the pH value. Thus, an estimation method of the pH value is set up to predict the corrosion degradation rate. The regression correlation for estimating the pH value is 0.53 if the corrosion agents are not used, which can be improved to 0.76 if the corrosion agents are also used in the regression analysis.

Keywords: *regression analysis; corrosion prediction; predictive maintenance; carbon steel*

INTRODUCTION

Different specific degradation methods can occur in the refinery and power industry [1–4]. Among the degradation mechanisms, corrosion processes can lead to significant damages, and thus to the risk of safe operation [5–8].

The crude distillation unit (CDU) is one of the most critical elements in the refining process [9–11]. The CDU is the first processing unit, where the crude oil is distilled into various fraction products according to their boiling ranges. The products are then further processed in other refining units. As the CDU is the first main unit in the refining process, most corrosion agents appear, severely affecting the static equipment's degradation.

According to the API 571 standard (Damage Mechanisms Affecting Fixed Equipment in the Refining Industry) [12] 19 different degradation mechanisms can occur in the CDU. One of the most affected equipment groups is the overhead system of the preflash, atmospheric, and vacuum towers. Thus, monitoring the amount and concentration of the corrosion agents is critical. Loto [13] compared different stainless steel grades for the application in the crude distillation unit. He has found that, the higher alloyed duplex stainless steel grade is showing better corrosion resistance in chloride-bearing medium, which is one of the most significant factors in crude distillation overhead systems. Ahmed also showed that in the overhead unit of the distillation facility hydrochloric acid and ammonium chloride have been those that have acted in the operational context [14]. Fadhil et al. [15] showed that, the presence of sulfur components in crude oil can be considered as the main reason for the corrosion of the distillation column.

Data analysis models and machine learning techniques can predict corrosion degradation rates and investigate and rank the effects of different technological parameters on corrosion mechanisms. Machine learning-based approaches can be successfully used for the corrosion assessment of oil and gas pipelines [16]. In their comprehensive review, Soomro et al. [17] demonstrating their importance in corroded oil and gas pipeline integrity assessment. Ossai [18] developed and tested different machine-learning methods to predict corrosion rates on grade X52 pipelines. The research results showed that with the developed principal component analysis model, the prediction accuracy is up to five times higher than the conventional models, which helped compute the corrosion risks using the failure probabilities at different asset lifecycle phases. Yang et al. [19] used the multi-source data-driven method to predict corrosion rates in a refinery's atmospheric tower unit. The developed prediction models are based on the equipment process parameters, medium components, and data from monitoring and detection. With the help of their model, the most critical parameters have been realised (temperature, flow rate, pressure, ammonium, and iron ion concentration), and the corrosion rate can be predicted with a good correlation. Alqarni et al. [20] used the isotonic regression model for the corrosion rate prediction of oil and gas pipelines in the refining industry. The isotonic regression model was a promising solution to overcome the complexity associated with the properties of different corrosion processes. Suo et al. [21] have used combined neural network-based models to predict corrosion growth in a refinery's circulating water units. The established model predicts the corrosion rate with less than 9 % error, which provides sufficient information on corrosion assessment without the problem of long-term corrosion state identification. Also, Mohammad Zubir et al. [22] successfully used the artificial neural network-based model to evaluate CO_2 corrosion, specifically. In their paper, a few areas are also highlighted for further development, such as testing a wider range of parameters and using real industry datasets. Mohammed et al. [23] have compared different techniques for the prediction of pipe wall thicknesses. In their research, it was found that the long short-term memory method showed the best correlation to the actual wall thicknesses, and thus this method has been recommended for further evaluation. Yang et al. [24] used the particle swarm optimisation method to improve further the accuracy of a random forest model used for equipment corrosion diagnosis in the oil refining industry. The optimisation improves the practicability of corrosion diagnosis, which is beneficial for investigating hidden dangers in the degradation of different equipment.

In the investigated oil refinery distillation unit the material type of the investigated equipment is mostly carbon steel. The material grade of the 122 overhead drum (Figure 1.) is KL3-type carbon steel (equivalent to P295GH). The connected pipeline is made of A35K carbon steel (equivalent to 1.0305). The material grade of the 102 distillation column head section is St20K (equivalent to 1.1151), cladded with X6Cr13 ferritic stainless steel. The

corrosion coupons are made of general structural carbon steels. According to API 571 Damage Mechanisms Affecting Fixed Equipment in the Refining Industry recommended practice, ammonium chloride, and HCl corrosion are expected in the distillation column head. Besides, in the overhead drum wet H_2S and erosion corrosion can be expected.

In our research, we used different regression methods, namely Pearson's correlation coefficient and multiple linear regression, to predict the effects of process parameters and crude oil composition on the corrosion degradation of the overheads of the crude oil distillation unit.

METHODS AND MODELS

Data and pre-processing

Initially, 84 channels were collected. Four were removed due to being double or containing irrelevant data. Table 1 contains some general information about the measured signals, such as sampling time or the number of data points. 22 different crude oil are processed and measured individually, and the sum is also considered.

Table 1. *Basic data of the analyzed channels*

ID	Type	Number of signals	Sampling time	Number of data
CDU3	CDU3 crude oil	22+1	daily	1542
CC	Corrosion coupon	4	~monthly	26
CA	Corrosion agents	7	~twice a week	250-300
TP	Technological parameters	14	daily	1112
CI	Corrosion inhibitors	8	daily	1113

For better understanding of the technological system under investigation, Figure 1. shows the simplified process flow diagram (PFD) of the crude distillation unit. The process chemicals used for mitigating the corrosion, the location of the weight-loss corrosion coupons (WLC) and the sampling points of streams utilized for determining the key corrosion influencing parameters are also depicted on the PFD. The corrosion coupons are made of general structural carbon steel. The main difference between the weight loss corrosion coupons is their location, which is designed to measure specific corrosion processes. CC1 and CC4 monitor the corrosion degradation in the overhead drum bottom product. CC1 is located in the effluent water pipeline, and CC4 is in the heavy naphtha pipeline. CC2 and CC3 monitor the corrosion degradation of the head product of the distillation columns. CC2 measures in the atmospheric columns, while CC3 is in the vacuum tower.

There is information about the corrosion at four different locations with coupon measurement, and seven indicators are measured, such as iron content and pH value of bootwaters. Moreover, there are 14 technological parameters (e.g. pressures, temperature) and the quantity of 8 different process chemicals applied in the unit including neutralizer, corrosion inhibitor (filming amine), caustic, emulsion breaker etc.

To find correlation between the corrosion degradation rate and the influencing chemical and physical parameters weight-loss coupon (WLC) corrosion measurement method was used where the mass loss of coupons is determined by measuring the weight difference before and after the coupon is immersed in the corrosive medium for a specified amount of time.

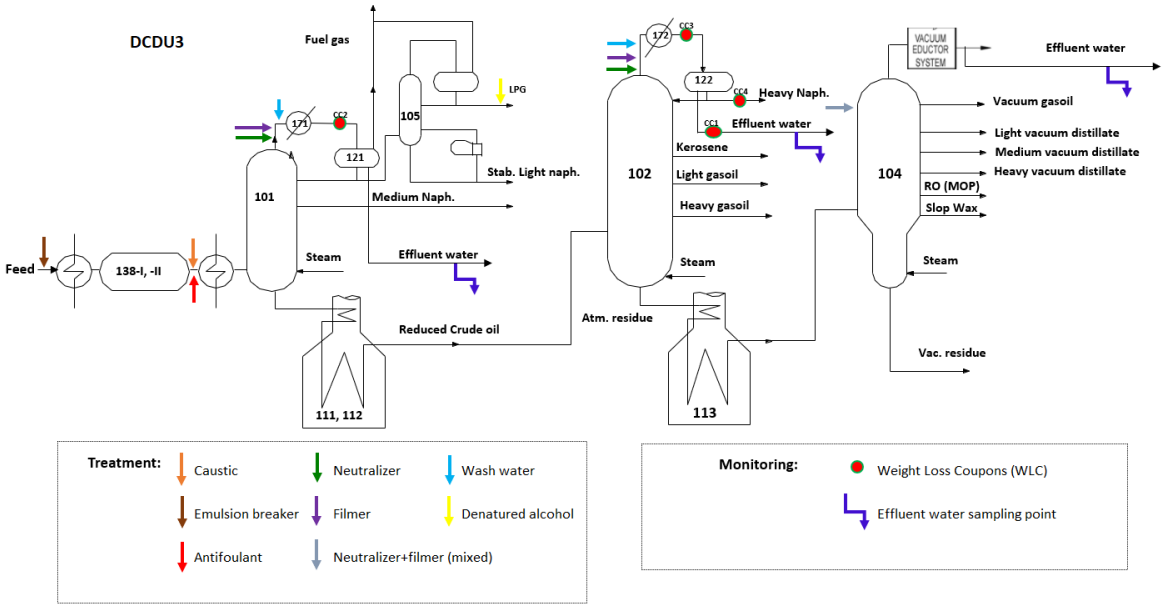


Fig. 1. Process Flow Diagram of the Crude Distillation Unit considered

This is a simple to apply and well-established standardized method to quantify the corrosion rate, however it has some important limitations. It provides average corrosion rate based on the exposure duration (in our cases 1-month-long), however the key corrosion influencing parameters can vary more frequently (hourly or daily). It does not provide information about the corrosion mechanisms, however many mechanisms can be in place and can interact with each other. In case of localized corrosion (such as pitting) it underestimate the true corrosion rate, if the weight losses are used for the assessment. For the further study in the future we are considering the application of on-line, real-time corrosion measurement technologies like ER of LPR probes.

Corrosion damage mechanisms at the overhead of the distillation unit

In our study the overhead systems were investigated that includes the upper section of the distillation towers (in our cases preflash-, main fractionator and vacuum tower), the vapor lines, coolers, reflux drums and the interconnected pipelines. In these areas of concern many corrosion degradation mechanisms can occur. The primary mechanism of concern is the acidic attack due to mainly the presence of hydrochloric acid deriving from the inadequate desalter operation and in lesser extend to the presence of other acidic components such as volatile organic acids. All prevalent corrosion damage mechanisms are aqueous and low-temperature ones. Other corrosion and operational concerns include under-deposit corrosion, and fouling resulting from the improper neutralization, wash water addition and inefficient desalting.

According to the API RP571 (Damage Mechanisms Affecting Fixed Equipment in the Refining Industry) the following damage mechanisms should be a primary consideration:

- HCl corrosion
- Aqueous organic acid corrosion
- Ammonium chloride and amine hydrochloride corrosion
- Wet H_2S Damage (Blistering/HIC/SOHIC/SSC)

Chemical treatment approach at the distillation unit

The basic causes of overhead corrosion are the acidic components which are either produced by salt hydrolysis or derive from light organic acids like formic and acetic acids. Also, the improper neutralizer application can cause serious corrosion issues.

To mitigate the corrosion the first line defense is said to be the proper desalter operation where emulsion braker is added to the raw crude in order to reduce hydrolysable salt carryover to the distillation towers. As desalters are not 100% efficient, there is always residual salts entering the crude hot preheat train. To further reduce these salts caustic is injected downstream the desalter.

At the overhead of the distillation towers in general neutralizer, filming corrosion inhibitor and wash water are dosed to the vapor line. The aim of proper neutralizer addition is to set the pH close to neutral (5,5-6,5), while the film forming corrosion inhibitor protects the overhead equipment and pipelines from corrosion by preventing the corrodents from contacting with the metal surfaces. Wash water is also injected in order to avoid salt deposition on the dry area and to force the condensation to happen on the right place.

Mathematical models

Pearson's correlation coefficient is a traditional, widespread tool to quantify the relationship between two independent variables. Its value takes place between -1 and 1. While 1 represents the two quantities in a perfect linear relationship with a positive slope, -1 means the slope is negative. The closer the coefficient gets to 0, the weaker the linear relation. Pearson's correlation coefficient can only detect the linearity, not the actual general function. For example, a sinusoidal function would lead to a 0 coefficient.

Multiple linear regression can build a relationship between two or more input variables and an output quantity. The output is approximated by

$$\beta_0 + \beta_1 x_1(t) + \beta_2 x_2(t) + \cdots + \beta_n x_n(t) \tag{1}$$

linear relationship, where xi are the inputs and βi the weights, β0 represents a zeroth order term. The least-squares method can find the weights to achieve the best To find the best approximation of the output. Since the inputs typically have multiple different units, and their range is different, the ratio of βi values represents which input variable influences the results the most; the inputs are standardized first between zero and one to keep them comparable. The standardized inputs use the minimum and maximum values, i.e.,

$$\tilde{x}_i(t_j) = \frac{x_i(t_j) - \min(x_i)}{\max(x_i) - \min(x_i)}, \tag{2}$$

also the standardized output

$$\tilde{y}_{app}(t) = \tilde{\beta}_0 + \tilde{\beta}_1 \tilde{x}_1(t) + \tilde{\beta}_2 \tilde{x}_2(t) + \cdots + \tilde{\beta}_n \tilde{x}_n(t). \tag{3}$$

Finally, the approximated output is non-standardized

$$y_{app}(t) = \tilde{y}_{app}(t)(\max(y_i) - \min(y_i)) + \min(y_i) \tag{4}$$

The goodness of the fit is characterised by Pearson's correlation coefficient between the original output and the approximated one.

RESULTS AND DISCUSSION

To reduce the collected data's complexity, Pearson's correlation matrix was evaluated. The matrix can be seen in Figure 2, where the value ±1 represents a perfect linear correlation between the variables. For input, the crude oil types (CDU), the amount of corrosion agents (CA), the distillation technological parameters (TP, such as temperature, pressure and volumetric flow rate), and the amount of corrosion preventing additives (CI, such as caustic, neutralizer, filming corrosion inhibitor, emulsion breaker, antifoulant, denatured alcohol) were taken into account. The output is the wall thickness (mm/year corrosion rate) loss of the four different corrosion coupons (CC) in the atmospheric distillation unit.

From the correlation matrix in Figure 2, the following conclusions can be drawn. The addition of corrosion inhibitors has seemingly weak effect on the corrosion rates of the four coupons. During the evaluation of the results, the effects of corrosion preventing additives were not taken into account. The reason for this is that, the corrosion rates were low in all of the cases, which indicates that the additives exerted their influence on the different corrosion mechanisms.

In the evaluation period, different crude oil types were distilled in the crude distillation unit CDU3. In unit CDU3, 10 different crude oil types were used. The types of crude oil were also found to have a relatively weak correlation with the corrosion rates of the four coupons. In general, Pearson's correlation numbers remained under 0.4. The exceptions are CDU3 2, CDU3 3, and CDU3 6 crude oil types, which had stronger relation to the corrosion coupons CC2 and CC3. These types of crude oils' additions must be further monitored during the distillation process. Monitoring systems are found to be a useful tool to follow the effects of different corrosion processes during the crude oil distillation [25]. However, as the sampling rate between the crude oil type (daily) and the corrosion rate (monthly) is very different in the evaluation period, the crude oil types were not further evaluated.

The technological parameters (TP) of the distillation have a modest influence on the corrosion rates. The salt content of the crude oil (TP3) correlates to all four corrosion rates between 0.2 and 0.5. The desalination feedwater flow rate (TP5) also correlates with at least 0.5. However, only to the nearest corrosion coupon in the technological order (CC2). The corrosion agents (CA) significantly influence the corrosion coupon rate among all the input data. In this case, multiple agents correlate on a corrosion coupon above 0.5 (in absolute value). CA2, referring to the crude oil's acetate content, has a coefficient of 0.55 on the corrosion rate of the CC3 coupon. CA4, chloride content, showing high coefficients with the corrosion rates CC1 and CC4, located in the technological order of the distillation process. Corrosion agent CA7, iron content, showing very high coefficients to the corrosion coupons CC1 (0.87) and CC4 (0.94). However, the linear correlation between the iron content and the coupon corrosion rate can be interpreted as the iron content originating from the mass loss of the coupons. Thus, not the iron content that is the cause of the high corrosion rates, but vice versa. The pH value seems to have high correlations to coupons CC1, CC3 and CC4, where the coefficients are ~0.6, 0.65, and 0.68, respectively. Thus, from the linear correlation matrix, the pH value strongly influences the corrosion rates in the atmospheric distillation process.

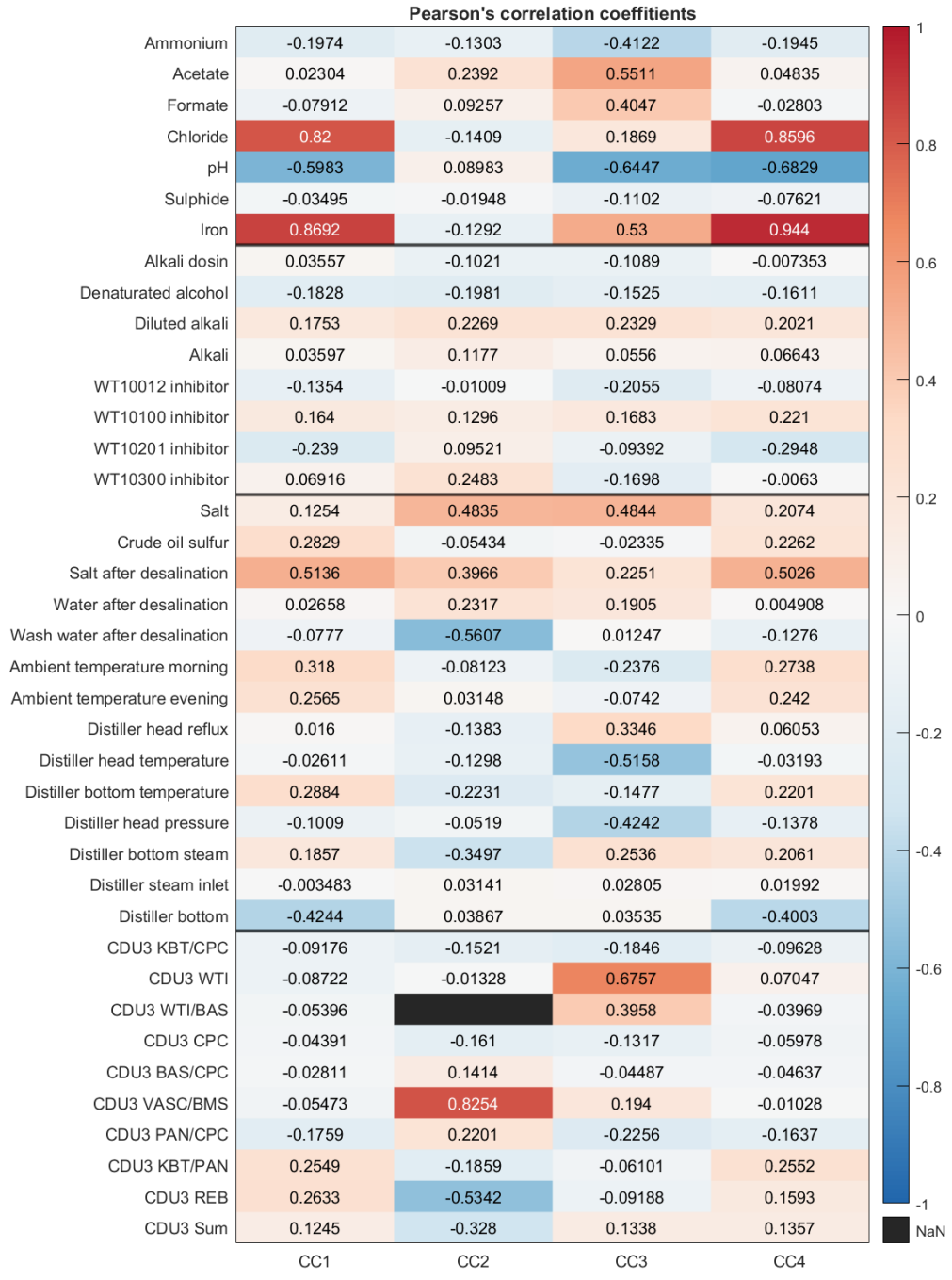


Fig. 2. Pearson's correlation matrix of the analysed data and the corrosion rate of the coupons (CC)

Figure 3. shows the result of the multiple linear regression analysis of the input data and the corrosion rate of the four corrosion coupons. In Figure 4. the linear regression analyses were supplemented with the effects of corrosion agents, which are the most influential parameters, according to Pearson's correlation matrix. In all cases, the first 5 parameters (with the most significant effects according to the correlation matrix) were selected and represented on the graphs. The "r" values show Pearson's correlation of the linear regression to the measured corrosion rates, marked with black crosses. Higher "r" values represent a higher correlation to the measured corrosion coupon wall losses. The most influential parameters were selected according to their relative improvement effect on the correlation to reduce the number of parameters. The selected parameters are highlighted with continuous lines in the graphs and represented in Table 2.

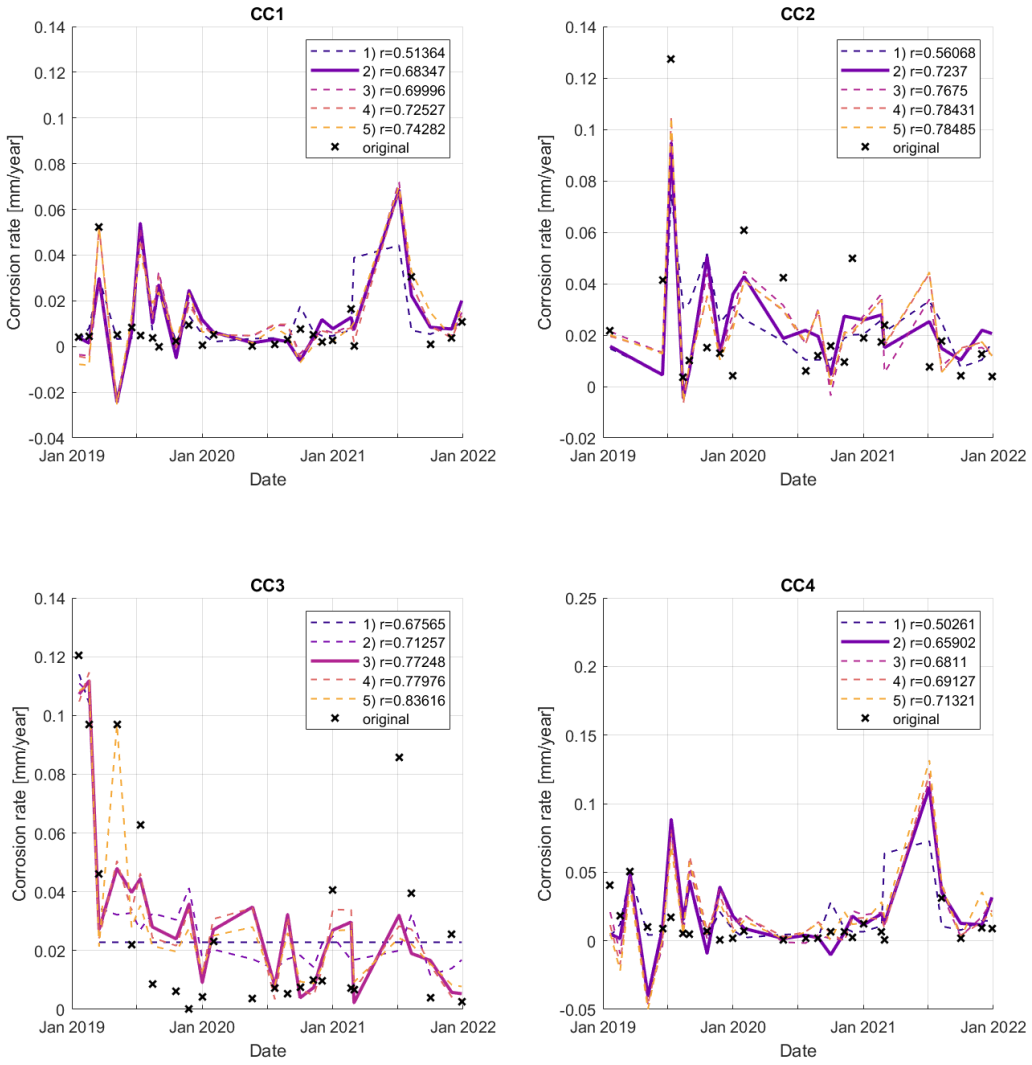


Fig. 3. The result of the multiple linear regression analysis of the input data and the corrosion rate of the four corrosion coupons

For the corrosion rate of CC1, the technological parameters were the strongest influence, not considering the corrosion agents. The selected parameter was crude oil salt content after the desalination process (TP3), which improved the correlation to 0.68. The three further parameters only had a lower influence on the linear regression. Considering the corrosion agents, the first (most influential) parameter, which is the chloride content (CA4), already increased the correlation to the measured values to 0.82. Thus, the corrosion rate of coupon CC1 is mostly influenced by the chloride content, while the rest of the parameters only have a negligible effect.

For the corrosion rate of CC2, the corrosion agents had no evincible effect. The first two parameters were selected as the most influential, where the second parameter is the type of crude oil. Thus, it can be said, for the corrosion rate of the coupon, the crude oil type had the most significant effect, with a correlation of 0.72.

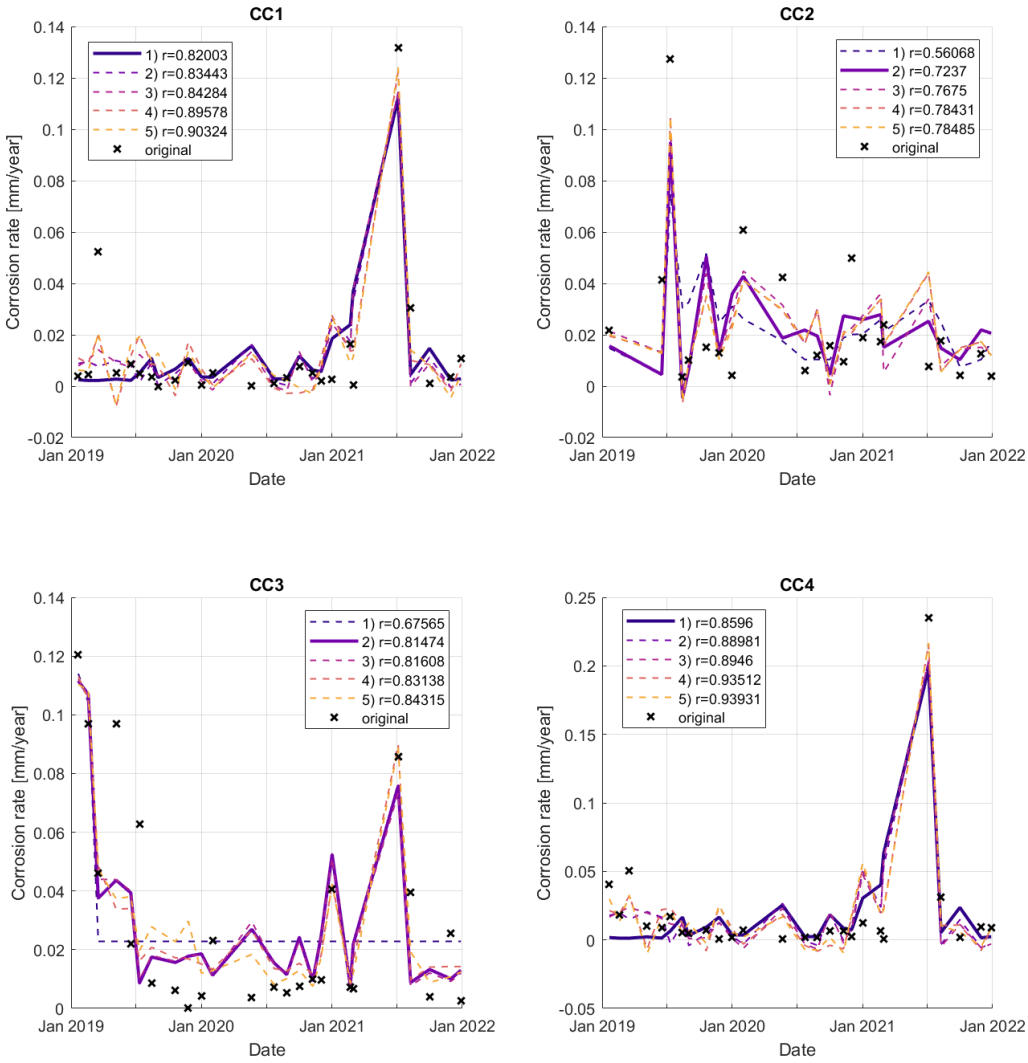


Fig. 4. The multiple linear regression analysis by using the effects of corrosion agents too

In the case of the corrosion rate of the coupon CC3, three parameters were taken into attention without the corrosion agents. The most influential parameters were the crude oil type (CDU3 2), crude oil salt content (TP1) and distiller head temperature (TP9). The weighting considering these three parameters resulted in r = 0.77. The additional parameters have not had a significant influence on the corrosion rates. Considering the corrosion agents, the weighting on the regression was improved to 0.81, using only two parameters. The most influential parameters were the crude oil type (CDU3 2) and pH value (CA5). Thus, the corrosion rate of coupon CC3 is mainly influenced by the crude oil type and the pH value, and the technological parameters only have a minor influence.

The technological parameters mostly influence the corrosion rate of coupon CC4 if the corrosion agents are not taken into consideration. The most influential parameters are crude oil processing rate (TP14) and crude oil salt content after the desalination process (TP3). These two parameters resulted in a 0.66 correlation. The correlation of the regression is highly increased to 0.86 value by the first, most influential, corrosion agent, which is the chloride content of the crude oil (CA4). Considering the effects of all parameters, the corrosion rate of the corrosion coupons CC1 and CC4 mostly depends on the same variables.

Table 2. *The most influential parameters and their correlation to the corrosion rate of the coupons*

	without CA		with CA	
CC1	-0.419	Distiller bottom	0.8343	Chloride
	0.3837	Salt after desalination	0.0169	Constant
	0.1851	Constant		
CC2	0.7355	Constant	0.7355	Constant
	-0.4970	Wash water after desalination	-0.4970	Wash water before main fractionator condenser
	-0.4840	CDU3 REB	-0.4840	CDU3 REB
CC3	0.5568	CDU3 WTI	0.6287	Constant
	0.2788	Salt	0.5895	CDU3 WTI
	-0.2080	Distiller head temperature	-0.5680	pH
	0.1884	Constant		
CC4	-0.3800	Distiller bottom	0.8379	Chloride
	0.3592	Salt after desalination	0.0037	Constant
	0.1611	Constant		

From the results of the linear regressions, it can be stated that the corrosion agents have more significant effect on the corrosion rates compared to the technological parameters. Among the corrosion agents, the chloride content (CA4) strongly affected the weight loss of coupons CC1 and CC4 and the pH value (CA5) on coupons CC1, CC3 and CC4. This correlates to the results of other researchers [11], [14], who also showed that the chloride content has a significant effect on the corrosion rate of the CDU. Thus, for further evaluation, the pH value was selected. The change in pH value within the period under review can be seen in Figure 5. For the prediction of the pH value, input parameters without and with the corrosion agents were used. As in the case of the corrosion rates, the corrosion agents have a stronger influence on the pH value. The correlation of the regression without the agents is 0.53 and 0.76 with the agents.

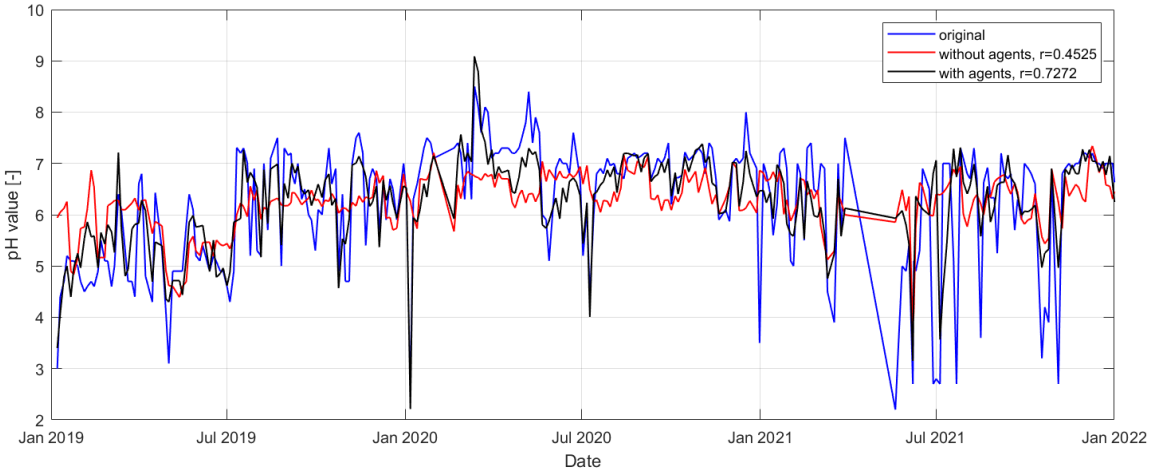


Fig. 5. The change in pH value within the period under review

Among all of the corrosion agents the chloride content is found to be the most influential on the corrosion rate of the investigated coupons. This result corresponds to the findings of Subramanian [26], where he also showed the importance of chloride management in the

distillation column overhead corrosion. Schempp et al. [27] also showed that chloride is one of the most important corrosion agent in the crude distillation unit overhead line, thus they suggested a chloride limit for the overhead system.

The comparisons of the measured and the estimated pH values can be seen in Figure 6. If the corrosion agents are not presented in the regression, then the lower pH values are usually overestimated. On the contrary, the higher pH values (pH > 6.0) are typically underestimated if the corrosion agents are not considered. The regression correlation for estimating the pH value is 0.53 if the corrosion agents are not used, which can be improved to 0.76 if the corrosion agents are also used in the regression analysis.

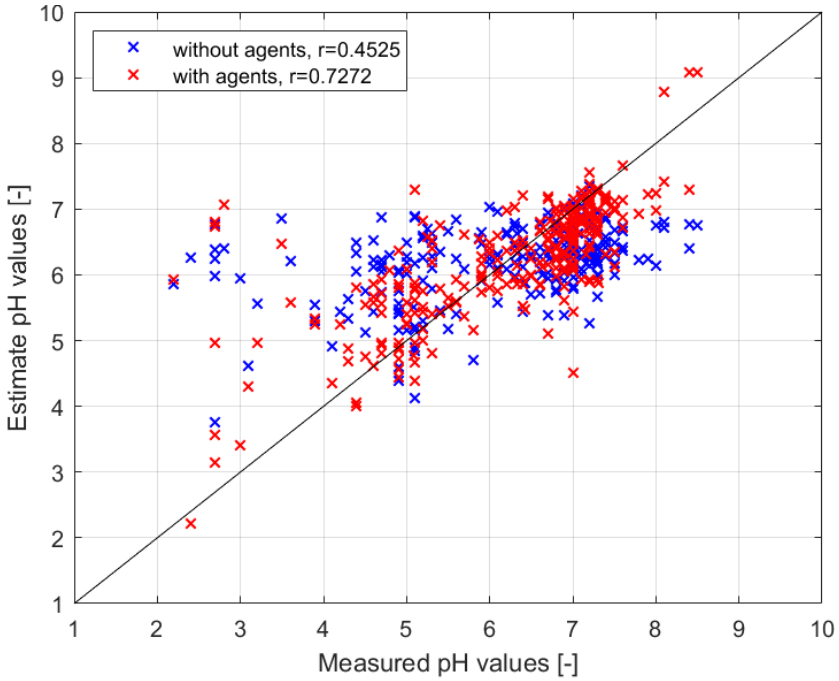


Fig. 6. The comparison of the measured and the estimated pH values

In Table 3. the correlations to the pH value of the most influential parameters can be seen. The table represents the distilled crude oil under the examined period, where the pH value was measured. The correlation values show that the crude oil type has the most influence on the pH value, as all of the correlations are over 0.85.

Table 3. *Regression coefficients of the pH value for the most influential parameters*

without CA		with CA	
-0.5336	Diluted alkali	-0.5663	Chloride
-0.3346	CDU3 WTI/BAS	-0.5423	Acetate
-0.2322	CDU3 WTI	0.3167	Sulphide
-0.2122	CDU3 PAN/CPC	-0.3053	Diluted alkali
-0.2036	Alkali dosin	-0.2901	CDU3 WTI/BAS
0.1945	CDU3 IRL	-0.1445	CDU3 BAS/CPC
-0.1817	CDU3 BAS/CPC	-0.1268	CDU3 Basrah
-0.1500	CDU3 Basrah	-0.1040	CDU3 PAN/CPC
-0.1395	CDU3 VASC/BMS	0.0865	Formate
-0.1015	CDU3 CPC	-0.0814	CDU3 VASC/BMS

CONCLUSIONS

In our research, we have used different regression models to predict the corrosion degradation of the atmospheric distillation tower and overhead drum in a crude distillation unit. In the analysis, we evaluated the effects of 84 channels of technological parameters and 22 different types of crude oils. From our results, the following conclusions can be drawn:

- The distillation's technological parameters (TP) have a modest influence on the corrosion rates. The salt content of the crude oil (TP3) correlates to all four corrosion rates between 0.2 and 0.5. The desalination feedwater flow rate (TP5) also correlates with at least 0.5.
- The corrosion agents (CA) significantly influence the corrosion coupon rate. Among the corrosion agents, the chloride content (CA4) strongly affected the weight loss of coupons CC1 and CC4 and the pH value (CA5) on coupons CC1, CC3, and CC4, where the coefficients are ~0.6, 0.65, and 0.68, respectively.
- From the evaluated data and period, a model has been set up to predict the pH value. The regression correlation for estimating the pH value is 0.53 if the corrosion agents are not used, which can be improved to 0.76 if the corrosion agents are also used in the regression analysis.
- Our results confirmed that our models are suitable for accurately describe the relationship between the technological parameters, such as distiller head and bottom temperatures and pressures, in the crude distillation unit and the corrosion rates of the main distillation tower. Future work should investigate whether more frequent, possibly online, measurement of corrosion agents can improve corrosion protection.

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Conflicts of Interest

The authors declare that they have no competing financial interests or personal relationships that could have seem to influence the study reported in this paper.

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