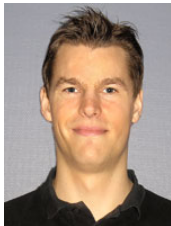


CORROSION IN DISTILLATION UNITS FOR THE RECOVERY OF ETHANOL, A REVIEW

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ABSTRACT

The recovery of ethanol is a well-known process in the chemical and pharmaceutical industries. The distillation technology has been used for many years, but changes to the operating conditions are constantly being effected in order to optimise the process and meet new demands. The corrosivity of the medium is related to the media from which the ethanol is recovered where a number of more or less aggressive species may be present. Especially the content of aggressive elements in the media and the operating temperature have been increasing, leading to corrosion and equipment failure if the application limits of the production equipment are not being observed.

20-30 years ago the distillation equipment was often made from AISI 316 stainless steel grades. The increasing demand for efficient production has, however, led to corrosion and upgrading of the construction material to e.g. SAF2205. Over time the operating conditions have been tightened even more, and it has been necessary to upgrade more parts of the process equipment; even to nickel alloys such as Hastelloy C22.

The most common corrosion failures in evaporator units for the recovery of ethanol are pitting corrosion and crevice corrosion, but problems with stress corrosion cracking have also been observed. Especially stress corrosion cracking may lead to abrupt failures, production shutdowns and huge costs. Failure examples from industrial cases during the last 20-30 years are given.

Attention is drawn to key issues such as the application limits of the construction materials. To consider these limits is important - not only when new plants are being constructed but also continuously during service. Finally the paper discusses what can be done operationally in order to reduce the risk of corrosion.

INTRODUCTION

The recovery of ethanol is a well-known process in the chemical and pharmaceutical industries. The plants usually consist of a distillation column with appurtenant reboiler. The feeds are preheated in heat exchangers, e.g. tube type or crossflow. The temperature in the different units depends on the actual service conditions; both usual service conditions and upset situations.

The recovery proceeds as distillation, where the ethanol is separated to the top of the column and the water fraction containing a number of more or less aggressive species including salts such as chloride concentrates at the bottom. The reboiler handles the residue from the distillation column and thus the saline water fraction from the ethanol waste from the production. Depending on which product is produced, the composition of the feeds varies accordingly. Thus the conditions in the reboiler as well as other areas with elevated temperatures become the most critical areas.

Even though the equipment for the recovery of ethanol is not a direct part of the actual production equipment it is nevertheless a crucial part of the production cycle. The equipment handles the alcohol waste and is necessary in order to sustain production. The availability of the equipment must therefore be just as high as that of the rest of the plant.

The distillation technology has been used for many years, but changes to the operating conditions are constantly being effected in order to optimise the process and meet new demands. Especially the content of aggressive elements in the media and the operating temperature have been increasing, leading to corrosion and equipment failure if the application limits of the production equipment are not being observed. The most common corrosion failures are pitting corrosion and crevice corrosion, but problems with stress corrosion cracking have also occurred.

Up to the 1970's the distillation equipment was often made from AISI 316 stainless steel grades. The increasing demand for efficient production has, however, led to problems with stress corrosion cracking, for which reason the construction material was upgraded to e.g. EN 1.4462 (SAF2205). Over time the operating conditions have been tightened even more, and in recent years it has been necessary to upgrade more parts of the process equipment; even to nickel alloys such as Hastelloy C22.

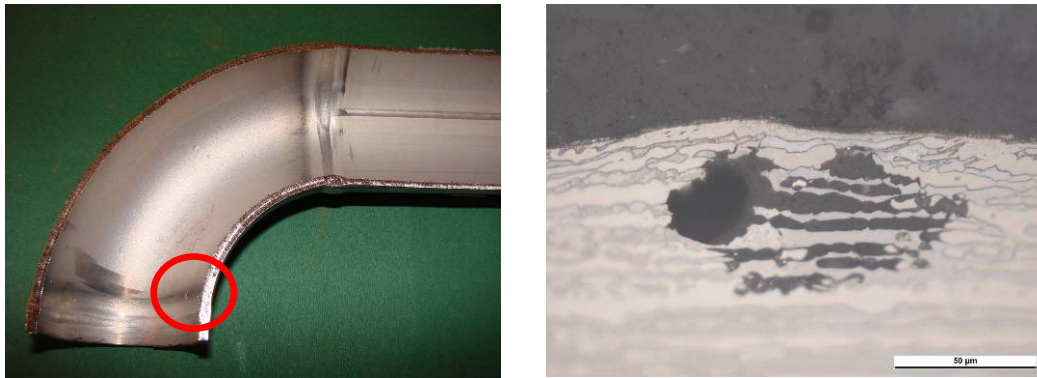
FORCE Technology undertakes failure analysis in a wide range of industrial systems, including the chemical and pharmaceutical industries. During the last 20-30 years we have been involved in numerous cases of corrosion in distillation columns ranging from minor to more severe proportions.

The intention of this paper is to present and discuss typical cases as well as means of preventing corrosion.

Case 1 – Pitting corrosion in a column inlet pipe

A feeding pipe, grade EN 1.4462, containing alcohol waste had been in service for approximately 6 years when a leakage was discovered. The pipe, which fed the column, contained 15-35 % ethanol at a pH of 5.5-7.0. The temperature was approximately 95 °C and the chloride content had been kept below 0.3 %. However approximately six months prior to the leakage was discovered an increased chloride content of up to 0.6 % had unintentionally been present for a period of 2-3 months.

The leakage was detected as a corrosion pit in the heat affected zone (HAZ) of one of the bendings, Figure 1a. Apart from the penetrating corrosion pit, no other apparent corrosion attacks were observed at the inner surface of the pipe section when examined visually in stereo microscope. Cross section of the pipe close to the penetrating pit showed no structural defects or microstructural inconsistencies, but a few very minor corrosion attacks were discovered, Figure 1b.



a.
FIGURE 1 – a) The penetrating corrosion pit was located in the heat affected zone (at circle). b) Very minor corrosion attack at the inner surface of the pipe.

Whether the critical pitting temperature (CPT) of the material had been exceeded depends on several factors such as the actual corrosion potential, local defects as well as the precise temperature and chloride concentration.

We expect a corrosion potential of maximum 200 mV vs. SCE. Data from *Bernhardsson* [1], FIGURE 2, show that the CPT for EN 1.4462 (SAF2205) at this potential can be expected around 95 °C at 0.6 % chloride.

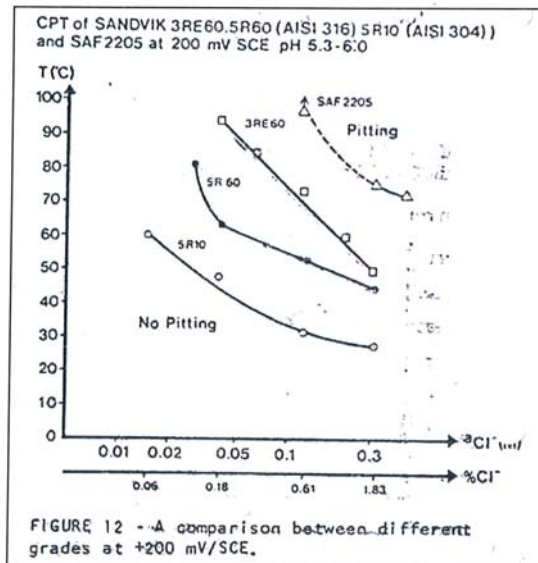


FIGURE 2 – CPT data from *Bernhardsson* [1].

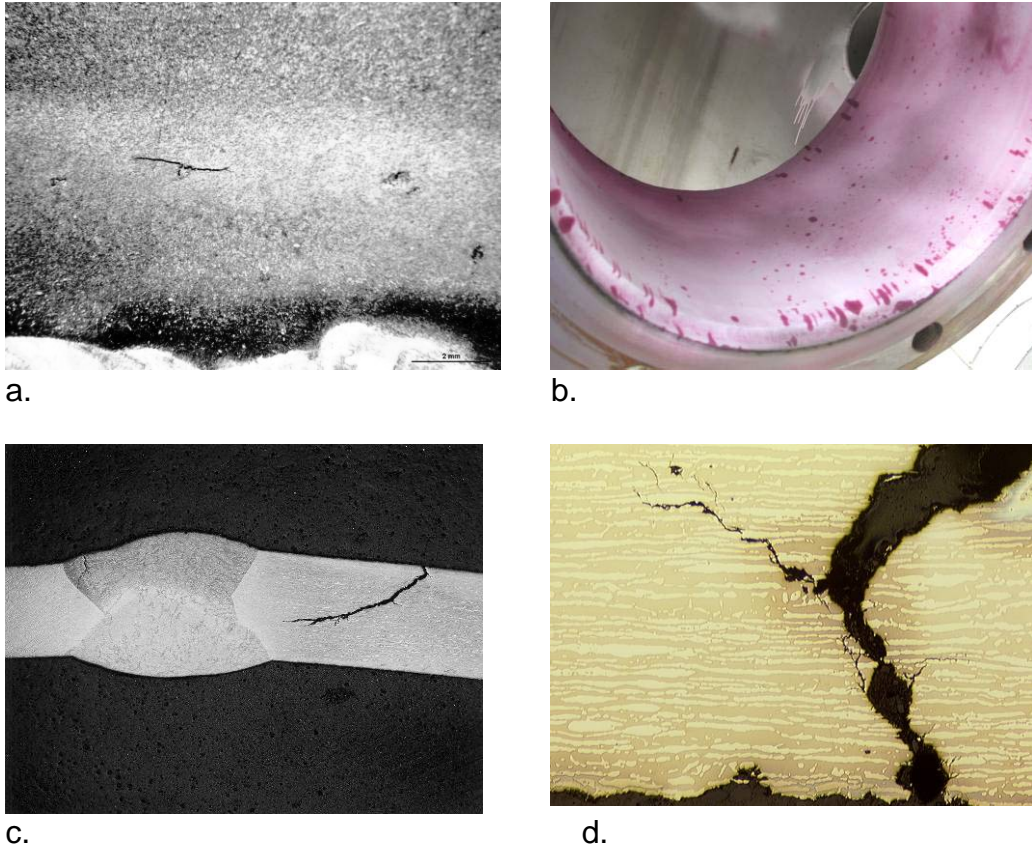
We find it probable that the increased chloride content prior to the failure has led to the CPT of the material being slightly exceeded, which is supported by the presence of the very minor corrosion attacks in the inner surface of the pipe as seen in Figure 1b. The penetrating pit is located in the HAZ (Heat Affected Zone) and we assess that the attack has developed as a consequence of a local defect. Furthermore it cannot be ruled out that other pitting attacks might be developing elsewhere in the system, even though the chloride content again is below 0.3 %. If a pit has initiated the local environment inside the pit will change and further corrosion will be controlled by the local environment and no longer by the bulk environment.

Subsequently video endoscopy of the HAZ's in the system was performed in order to investigate if there were other pits in the system. Experience shows that if corrosion is present it is most likely to have initiated in areas with slightly reduced corrosion resistance as the HAZ's. The investigating did not show any signs of pitting corrosion, but it must be taken into consideration that video endoscopy is not a fool-proof method to search for pits. Only pits above a certain size may be discovered and it takes experience to assess whether observed irregularities are pits or other phenomena. However the investigation significantly increases the probability of finding other severe pits in the pipe system.

Case 2 – Stress corrosion cracking in reboiler

Repeated repairs of cracks in reboiler and piping system led to a thorough investigation of the root cause of the cracking. The system was manufactured in EN 1.4462 for all equipment in contact with the products. The plant had been constructed to handle a maximum chloride concentration of 1 %. The temperature was strictly controlled to 160 °C.

Visual examinations revealed widespread stress corrosion cracking (SCC) especially in the end plates of the column and reboiler; example shown in Figure 3a. Furthermore dye penetrant testing showed that the extent of cracking was very far-reaching, Figure 3b.



c. d.
FIGURE 3 – a) Pitting corrosion and micro cracks in the HAZ of one of the repairs. b) Dye penetrant testing of end plate flange showed extensive cracking. c) Cross section showed cracking in weld as well as base material. d) Branched cracks in base material.

Selected cracks examined in cross sections showed that the cracking had occurred as chloride-induced stress corrosion cracking, Figures 3c and d.

Since the temperature had been strictly controlled and was well documented, focus was set on the chloride content in the feeds as well as the pH. Subsequently it was discovered that the chloride content and the pH of the feeds had been out of control prior to the damages. The feeds came from a number of different sources, and single feeds with a chloride content of up to 17 % might have been processed in the plant significantly exceeding the limits for initiating SCC in EN 1.4462. The pH of the feeds had been lowered down to approximately pH 3 as well.

In this case the reboiler had to be upgraded to a much more corrosion resistant alloy such as Hastelloy C-276 or C-22.

CASE 3 – Localised corrosion in reboiler tubes

Corrosion was observed at the top of reboiler tubes. Several tubes were plugged due to penetrating corrosion and an investigation of the root cause was undertaken.

The reboiler was manufactured in EN 1.4462 while sleeves in the reboiler top were of Hastelloy C22. Several feeds with varying chloride content were possible in the system. The maximum chloride content in these feeds was given to 0.9 %.

The temperature at the bottom of the column was given to 135 °C, however on the basis of pressure calculations the steam inflow might happen at a temperature of 170-180 °C. Since the inflow was close to the top of the reboiler the temperature here might be close to the steam inflow temperature.

Furthermore in order to avoid deposits, pH adjustments to pH 3-3.5 had been conducted during the last year prior to the incident. The adjustment was conducted manually in the beginning which might have led to lower pH values down to pH 2 or even lower.

The corrosion was located at the top of the reboiler tubes, Figure 4a. On the inside of the tubes corrosion and deposits were seen as well, Figure 4b. On the majority of the sleeves corrosion was observed in local areas as general corrosion leading to a rougher surface, Figure 4c. The attacks on the sleeves were apparently a smooth etching and by closer examination it could be established that the attacks followed the grain boundaries as intercrystalline corrosion, Figure 4d.

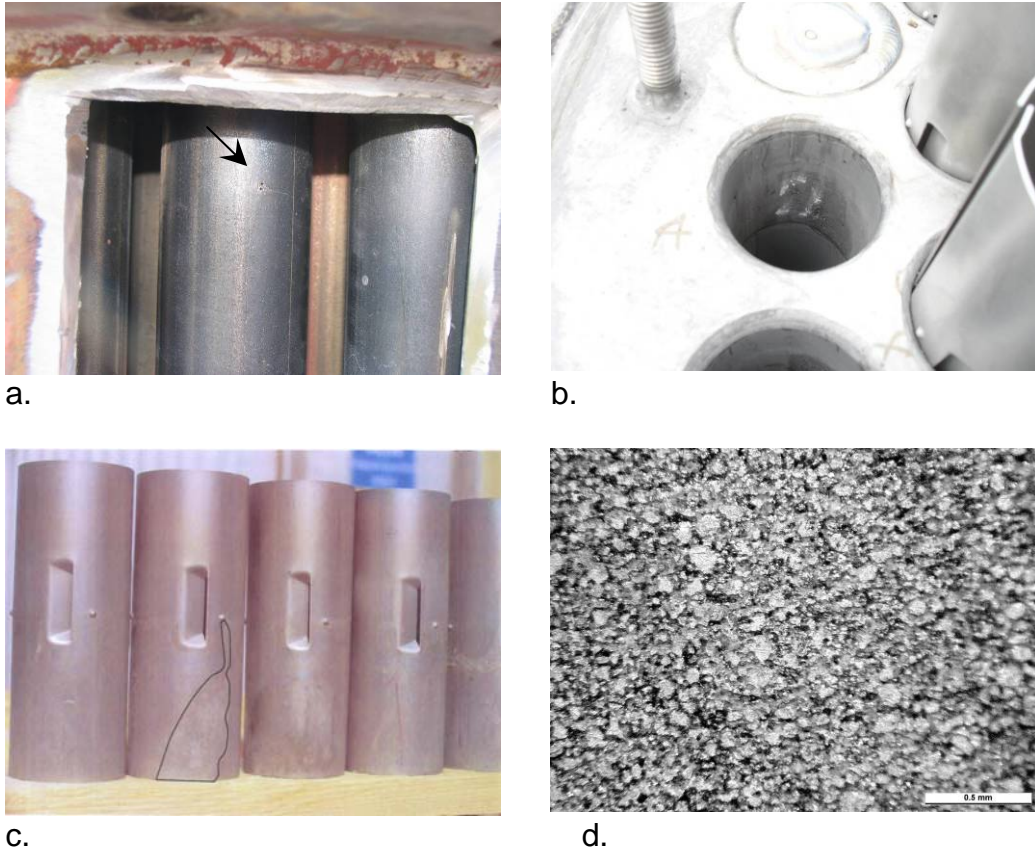


FIGURE 4 – a) Top of reboiler with two small penetrating pits. b) Top of reboiler tubes with corrosion and deposits. c) Sleeves with corroded areas. d) Corrosion attacks on sleeves seen at high magnification.

The given service conditions are close to the limits at which stress corrosion cracking (SCC) may occur in EN 1.4462 but SCC is not the problem. The troubles are caused by a more localised corrosion phenomenon between the sleeves and the boiler tubes.

Since residue may seep into the tight crevice between the sleeve and the tube, the fluid may start to boil before it has travelled through the crevice. Hereby the chloride concentration as well as the acid concentration will increase leading to a more corrosive environment locally compared to the bulk environment. The corrosion will in this case be controlled by a micro galvanic element primarily dependent on the chemistry of the solution in the crevice.

The addition of acid has furthermore supplied a driving force to the corrosion consisting of hydrogen development as supplementary cathodic process. The corrosion may hereby proceed even under deaerated conditions. Thus the acidic conditions together with the increased chloride concentration in the crevice might be the combination causing the corrosion.

Case 4 – Pitting and stress corrosion cracking in distillation column

In the 1990's FORCE Technology investigated the root cause of severe corrosion in a distillation column in the pharmaceutical industry. The relevant column had been in service for more than 10 years when problems with pitting and crack formations were discovered. The parts for the column were manufactured in stainless steel type EN 1.4436 or AISI 316. The temperature was given to 78 °C at the inflow and to 102 °C at the bottom of the column. The alcohol fraction was around 22 %.

For a period of 2 years prior to the appearance of the damages, a chloride concentration of approximately 0.5 % had been present in the feeds. This had at the time of the investigation been corrected, so that feeds did not contain more than 0.1 % chloride as originally desired.

The investigation revealed pitting corrosion localised around the welds in the column. No corrosion was observed at the free surfaces. Some pits had penetrated the endplate and led to leakage of the media into the insulation. On this background the insulation had become wet resulting in severe concentration of chloride on the outer surfaces due to alternating moistening and drying-up of the steel surface. Subsequently severe stress corrosion cracking had occurred from the outside surface of the column.

Since the effect of increased chloride content is most distinct on the risk of pitting and crevice corrosion compared to stress corrosion cracking, it is likely that the increased chloride content of 0.5 % had led to initiation of pitting corrosion which eventually had penetrated the endplate. The stress corrosion cracking may subsequently have developed even though the chloride content was again below 0.1 %, since the corrosion then was controlled by concentration of chloride on the outside surface.

In order to reduce the risk of corrosion in the future it was suggested to upgrade the material to for instance EN 1.4462 or EN 1.4539.

DISCUSSION

The presented cases demonstrate that continuous focus on the environmental conditions is essential when dealing with distillation columns used for the recovery of ethanol.

When projecting a plant, careful considerations should be made in order to establish the worst case environmental conditions. Especially the temperature, the chloride concentration as well as the pH of the feeds should be considered, since these factors are the most important parameters with respect to the risk of corrosion.

Oftentimes the material suppliers are capable of supplying relevant corrosion data regarding the material choice. However the chemical composition of the media may not always be precisely defined or test data may be scarce. In these cases relevant tests in the actual environment or careful assessment of available data may be the best way forward in order to make a sound material selection.

As mentioned the most common corrosion failures in evaporator units for the recovery of ethanol are pitting corrosion, crevice corrosion as well as stress corrosion cracking. Stress corrosion cracking (SCC) must be considered the most severe corrosion form. As presented in the cases, the corrosion form may lead to abrupt and extensive damages.

For high alloyed austenitic materials the risk of SCC may be evaluated according to tests such as boiling magnesium chloride, ASTM G36 or U-bend tests, ASTM G30.

For duplex materials such as EN 1.4462 data produced by Slow Strain Rate Testing (SSRT), ASTM G129 may be used, for example from *J. Charles* [3], FIGURE 5. However SSRT testing must be considered a tough test in the actual environment in which it is performed and the results must therefore be considered as conservative.

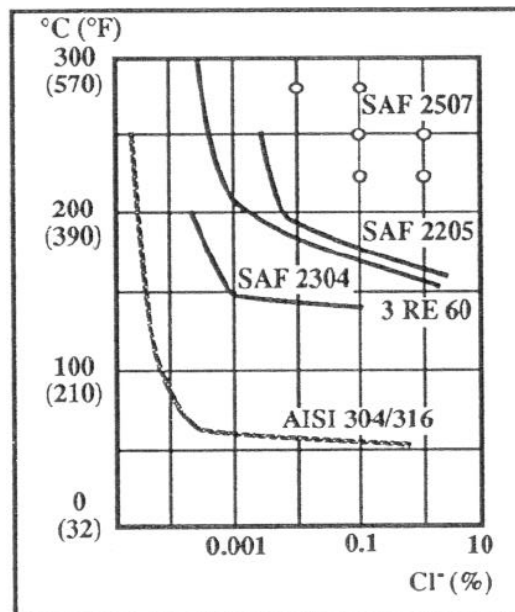


FIGURE 5 – SCC data from *J. Charles* [3] based on SSRT.

The high alloyed nickel materials such as Hastelloy C-276 and C-22 are considered immune towards SCC in chloride containing neutral environments [2].

The relative risk of crevice and pitting corrosion may be roughly assessed on the basis of the composition according to the pitting resistant equivalent (PRE). For the relevant fluids at neutral pH values, the degree of aeration plays a decisive role regarding pitting and crevice corrosion, since this

controls the conditions for the corrosion potential. In distillation columns the environment at the bottom of the column must be presumed deaerated, since the air will leave the column at the top with the ethanol. Therefore if it is known that a material is resistant at aerated conditions at a certain chloride content, one should be on the safe side.

The risk of crevice corrosion in austenitic, duplex as well as high alloyed nickel materials may be evaluated on the basis of standard ferrichloride test, ASTM G48. However this test must be considered tough since it is performed under strong oxidising conditions. Limits may instead be assessed by careful extrapolation of the data.

For the exposed surfaces without crevices pitting corrosion will be the limiting factor. Austenitic and duplex stainless steels may be evaluated according to standard CPT tests given in ASTM G48. For high alloyed nickel materials the risk of pitting may furthermore be evaluated according to tests such as oxidising NaCl-HCl solution ("yellow death"-solution). Since the test solution is oxidising careful extrapolation of data will be necessary here as well.

The presented cases clearly show that the operating conditions have been tightened significantly during the years. Even though the tightened operating conditions lead to increased efficiency there is a limit for the temperature increase and for how much water can be saved cost-effectively, since at some point one has to upgrade the equipment to even more corrosion resistant alloys significantly increasing the construction cost.

In some of our cases we have observed that the bottom temperature of the column has been around 130 °C. Although a higher temperature in the reboiler must be expected, a temperature of 160 °C seems rather high. It has to be emphasised, that the higher the temperature, the more the chloride content has to be limited in order to be within the limits of corrosion resistance of the reboiler material. This means again that higher temperature means an earlier demand for upgrading the reboiler material.

The presented cases also show a considerable increase of the level of impurities - first of all the chloride content - during the years. Not only has the general level been increasing, but with chloride coming from a number of sources with chloride concentration varying widely, very high peak values may be observed from some sources as the afore mentioned 17 %.

A high-risk scenario which may initiate severe corrosion in the equipment occurs when high chloride feeds are transferred directly to the columns. Therefore, in order to stay on the safe side, the chloride content should be carefully monitored and steps taken if the limits are exceeded. One way to prevent these extraordinary high chloride levels from being processed directly in the columns could be to install buffer tanks, thereby levelling out possible peaks in the chloride content.

Another important area which should receive focus is the pH. In order to control deposits producers may adjust the pH. However as demonstrated in

case no. 3 this may lead to unintentional problems with corrosion, since the acidic conditions not only supply a driving force to the corrosion in the form of hydrogen development but also increase the chemical attack on the protecting oxide. Therefore it is not without consequences when the conditions are tightened so much that considerable acidic operating conditions are necessary.

All in all it is advisable to establish a clear policy regarding the operating conditions. Especially limits regarding the operating temperature and the chloride content in the feeds are of utmost importance. One should be aware of the precise maximum permissible levels of impurities in the feeds at all time. On-line surveillance of the temperature, chloride content, pH and, if necessary, the corrosion potential may be helpful in this connection as a supplement to conventional calculations.

In summary the presented cases and our experience in general show that when changes to the service- and environmental conditions are being considered in order to save energy or water, one must assess the possible consequences with respect to corrosion in the process equipment.

At last it is important to continuously get an accurate picture whether corrosion is developing in the equipment. In order to investigate pitting and crevice corrosion, visual examinations will often be the best option. Had visual examinations been conducted frequently in the presented case no. 4, the corrosion had probably been discovered in time. However as even visual inspection is intrusive it must be added that the intervals between inspections may be longer if the composition of the feed is well controlled.

In order to investigate for stress corrosion cracks visual examinations are very difficult to conduct and dye penetrant examinations may be preferable. However one should have in mind that SCC often develops so rapidly that it may be very difficult to discover cracks at an early stage why good control of composition of the feed becomes crucial here as well.

CONCLUSIONS

The presented examples demonstrate that good control of the composition of the feeds processed in the equipment for the recovery of ethanol is crucial in order to avoid problems with corrosion and costly shutdowns. When the limits for initiating corrosion are being exceeded, expensive damages due to pitting, crevice and stress corrosion cracking have occurred in the industry during the last 20-30 years. The most important parameters to watch are the temperature, the chloride content as well as the pH.

If changes of the process conditions are being considered in order to save energy or water one must be aware of the consequences with respect to corrosion as well as the economical impact of the changes. During the years the process conditions in the industry have continuously been tightened

eventually leading to upgrading of construction material from AISI 316 types to EN 1.4462 and latest Hastelloy C22.

When new plants are being projected it is of utmost importance that the corrosion resistance of the process equipment match the service conditions. In this connection data from well-known standard tests as well as tailored test series may be applicable depending on the actual conditions.

REFERENCES

1. Bernhardsson, S. Mellström, R. and Brox, B., Corrosion80, Paper 85, 1980.
2. Hastelloy Alloy C-276, Data sheet, Haynes International, 1987.
3. J. Charles: Super duplex stainless steels: Structure and properties. Duplex Stainless Steels '91, vol. 1.