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Causes and Remediation of Corrosion Failure of Duplex Stainless Steel Equipment in a PVC Plant

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An existing PVC plant was modernised by the installation of a VCM stripper and two spiral heat exchangers, all made of 2205 duplex stainless steel (S21803). The purpose was to increase production and reduce VCM content of the product. After only nine months of service all equipment items suffered corrosion. After corrosion testing it was decided to replace the heat exchangers, using 6Mo austenitic stainless steel, while the stripper was repaired by welding.

INTRODUCTION

During modifications to an existing polyvinyl chloride (PVC) plant new stripping equipment was installed to increase production and reduce residual vinyl chloride monomer (VCM) in the product. This equipment included two spiral heat exchangers and stripping columns fabricated from type 2205 duplex stainless steel (UNS S31803). The top cones of the columns were 316L (UNS S31603). The duplex stainless steel was selected on the basis of resistance to localized corrosion and followed designs adopted by other PVC producers. After only nine months' operation an inspection revealed corrosion in all the equipment items.

On each of the two production streams, A & B, there is a stripping column with an associated spiral heat exchanger.

The operating conditions are:

Temperatures:
Stripping columns: 95°C in at top, 105°C out at bottom
Spiral exchangers: 105°C hot side 50°C cold side
Process fluid: PVC/VCM/steam
Process conditions:
pH 2.5 – 5
Chlorides >50 ppm
Low oxygen levels, 4 ppm is worst case. (See Figure 1).

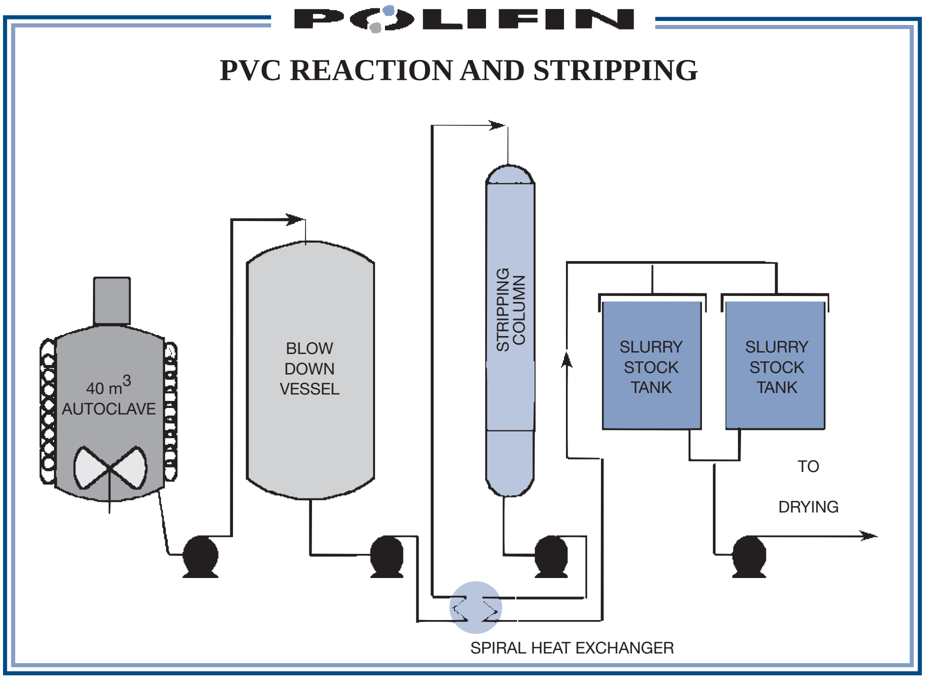

Figure 1.
Schematic diagram of PVC stripping section showing stripper and spiral heat exchanger.

INSPECTION AND REPAIR OF COLUMNS

In column A no cracking or other corrosion was found in the duplex column sections. There was some slight pitting on the 316L top cone. No remedial action was required.

In column B many cracks and pits were observed in the top cone and in the shell sections and bottom cone. The cracking was usually associated with welds. Ultrasonic testing indicated cracks between 4 and 6 mm deep. This column was judged to be repairable. Since there was some danger in making the cracking worse as a result of weld repairs only those cracks considered dangerous to the operation of the column were repaired. The column was repaired using the following procedure:

1. Cracks were ground out to a smooth contour and dye penetrant tested to ensure their complete removal.
2. Ground out areas were thoroughly cleaned and visually inspected.
3. Areas to be repaired were preheated to 200°C and built up to original dimensions using GTAW (Gas Tungsten Arc Welding) followed by SMAW (Shielded Metal Arc Welding).
4. Welded areas were ground flush and polished with a flapper wheel.
5. Repaired areas were shot peened with clean, new glass beads (800 microns), pickled using a proprietary paste and then passivated with nitric acid.
6. The column was pressure tested and put back into service.

INSPECION OF SPIRAL HEAT EXCHANGERS

Visual examination of the two exchangers detected 10 cracks on unit A and 5 cracks on unit B. Numerous pits were also observed on both units and the cracks were often initiated at corrosion pits, welds and locations where weld spatter was present on the surface. All cracking was on the hot side of the exchangers, none on the cold side. Crack length was up to 29 mm on unit A and 20 mm on B. Replicates taken of some of the cracks did not show branching. The spacer pins, which separate adjacent sheets of the exchanger, were also seen to be cracking and corroding. These pins were also 2205 and were attached by CDSW (Capacitor Discharge Stud Welding). It was concluded that neither of the exchangers could be repaired and both should be replaced. A typical crack across a weld is shown in Figure 2.

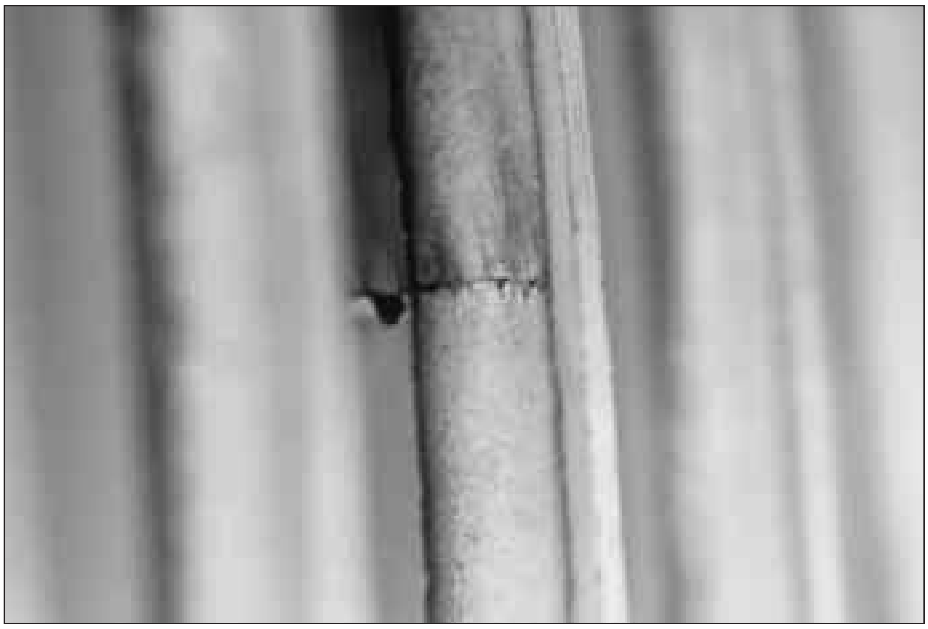

Figure 2.
Crack across weld in spiral heat exchanger.

MECHANISM OF CORROSION ATTACK

Since the equipment was still in operation it was not possible to cut out sections to carry out exhaustive metallurgical examination which could determine the precise corrosion mechanisms operating. However, based on consideration of the process conditions, together with results of the inspection, it is probable that the mechanism was chloride stress corrosion cracking (SCC) combined with chloride pitting.

The replicates taken of cracks were seen to be mainly straight rather than branched. This observation was suggested to be evidence that SCC was not the mechanism. However, in duplex alloys not all stress corrosion cracks are branched. Stress corrosion cracking in duplex alloys often is transgranular in the ferritic phase and intergranular in the austenite-austenite phase and austenite-ferrite grain boundaries. This process can result in brittle, transgranular cracks through the ferrite grains with complete dissolution of the austenite grains in between. The overall effect is a single, straight crack with “fuzzy” edges in regions of corrosion of the austenite, especially in replicates.

The presence of SCC and pitting on the 2205 duplex alloy in these equipment items indicates that its corrosion resistance was marginal under the prevailing operating conditions. Similar cracking in PVC equipment has been reported previously where the association of cracking and welding was also reported and concluded to be due to the anodic polarization effect of the HAZ (Heat Affected Zone) by the weld due to the higher alloy content (1). The association of weld and cracking in this current case is probably due to rapid weld cooling because:

a) Column B had SCC, column A did not. Column B was welded with FCAW (Flux-Cored Arc Welding) and column A with GTAW. Depending on the production rates and heat inputs it is likely that FCAW would produce more rapid cooling and thus unfavourably high ferrite contents.

b) Since the spiral exchangers are constructed of thin plate it is again

likely that rapid cooling would occur locally during welding.
c) The spacer pins on the heat exchangers which were also cracking/corroding were attached using CDSW which uses low heat input and produces rapid cooling.
d) Weld spatter on the hot side of the exchangers also promoted attack. Spot welds, tack welds and weld spatter are detrimental to the corrosion behaviour of duplex alloys because of their rapid cooling and higher ferrite content formed.

INVESTIGATION OF OPTIONS FOR THE EXCHANGERS

Both exchangers needed to be replaced. If the same material were to be used then the operating conditions would need to be altered to make the environment less aggressive to this duplex alloy. If the operating conditions were kept the same then a more resistant material would be required for the replacement exchangers. Both of these approaches were investigated.

Changes in operating conditions

Less aggressive operating conditions would require some combination of lower chloride content, temperatures and tensile stresses or increased oxygen content. The high chlorides are an essential component of the process so can not be reduced. Similarly, both operating temperature and pressures (thus tensile stress) are essentially fixed. The only possible factors that might be changed to reduce attack are pH or oxygen content. The pH would need to be consistently raised to at least 5 to enable 2205 to operate without significant corrosion. The methods available to increase pH are to change the catalyst, which is expensive, and/or lower oxygen level, which creates reaction problems and would increase corrosion. An added complication is that in some product grades high pH causes deposition in the strippers.

Replacement spiral heat exchanger materials

Since the plant could not operate continuously and consistently under conditions that would ensure no appreciable corrosion of 2205 it was decided to upgrade the materials of construction for the replacement heat exchangers.

A number of candidate materials were considered, including SAF 2507, Inconel 625, Incoloy 825, Avesta Sheffield 254 SMO, Krupp VDM 1925 hMo, INCO alloy 25-6MO and Avesta Sheffield 654 SMO. Typical analyses of these materials are given in Table 1. It is probable that any of these alloys would be adequate but based on ease of fabrication and cost a super-austenitic stainless steel containing 6% molybdenum was selected as the primary candidate for further evaluation.

Published information shows that 254 SMO is more resistant than SAF 2205 in standard pitting tests.

Table 2.
Published data on pitting resistance (2).

Alloy	PRE IM	CPT NaCl	CPT 6% FeCl$_3$
316L	26	15	<5
2205	36	50	35
254 SMO	46	>90	75

PRE – pitting resistance equivalent factor based on alloy composition
CPT – lowest temperature at which pitting occurs in these tests
CPT in NaCl – determined by polarization measurements
CPT in FeCl$_3$ – ASTM Standard G48A (3)

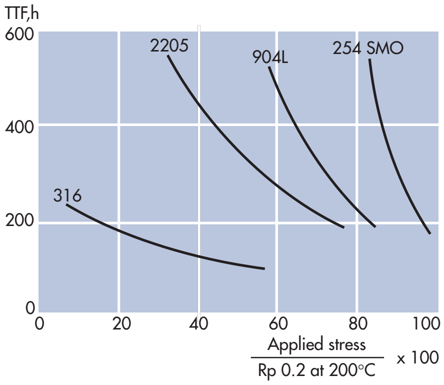

Figure 3.
Comparison of SCC behaviour of 2205 and 254 SMO (3).

An indication of the relative behaviour under SCC conditions is shown in Figure 3 (2). These published data from the NaCl drop evaporation test compare time to failure (TTF) in hours with applied stress levels for various alloys. These data are a bit misleading since the applied stress is related to the proof stress which is

Table 1.
Typical composition of alloys.

Common Name	Werkstoff No.	UNS No.	Cr	Ni	Mo	Cu	N max.	C	Other
316L	1.4404/35	S31603	17	12	2.7	–	–	0.03	
2205	1.4462	S31803	22	5.5	3	–	0.17	0.03	
2507	1.4410	S32750	25	7	4	–	0.27	0.03	
I 625	2.4856	N06625	22	61	9	–	–	0.10	<5Fe,3.6Nb
I 825	2.4858	N08825	21.5	42	3	2.3	–	0.05	0.9Ti
254 SMO®	1.4547	S31254	20	18	6.2	0.7	0.2	0.02	
1925 hMo	1.4529	N08926	20	25	6.2	0.8	0.2	0.02	
I 25-6MO	1.4529	N08925	25	20	6.5	1.2	0.15	0.02	
654 SMO®	1.4652	S32654	24	22	7.3	0.5	0.5	0.01	3Mn

higher for 2205 than for the austenitics. Allowing for this strength factor would reverse the order of 2205 and 904L in this curve but 254 SMO would still have a longer TTF than the other two alloys.

Since the corrosion behaviour of the 6% Mo super austenitic alloys commercially available are not necessarily the same it was decided to test the two principal candidates being considered, viz. 254 SMO and 1925 hMo.

The replacement studs were to be I 625 welded on to the 6% Mo austenitic shell in the production of the replacement spiral exchangers. There was a possibility that this combination might reduce corrosion resistance due to precipitation of alloying elements, particularly molybdenum and chromium, and consequent depletion of these elements in the matrix. Such depletion can lead to a serious reduction in resistance to localized corrosion, i.e. pitting and crevice corrosion. This combination of stud and plate was tested with the alternate shell materials. 2 mm thick test plates were prepared from 254 SMO and 1925 hMo. I 625 studs, 5 mm diameter, were welded on to the plates using production stud welding equipment. All samples were then pickled and passivated.

Corrosion testing

There are a number of standard methods used to determine resistance to localized corrosion including immersion testing in various solutions and electrochemical techniques. Probably the most commonly used standard electrochemical method for this type of testing is ASTM G 61 (4). This standard cyclic potentiodynamic polarization method was used. However, since experience has shown that this standard test is often not severe enough to show differences in behaviour in modern, highly corrosion resistant alloys it was decided to include a more stringent test in addition to the ASTM G 61. This more severe test determines pitting potentials by polarizing samples at 80°C in a 1M NaCl solution, acidified to pH 2.2 with HCl, continuously oxygenated and stirred. Samples are first equilibrated for 1 hour with potential monitoring then scanned from –50 mV below the free corrosion potential at a scan rate of 0.17 mV/sec. The scan rate is reversed once a current density of 1000 µA/cm^2 is reached. Potentials are measured against SCE (Saturated Calomel Electrode).

The equipment used for all test work was an EG&G Model 273 Potentiostat/Galvanostat. SOFTCORR Corrosion Software was used for the potential scans. Duplicate samples were tested using both methods for welded plates using each shell material, i.e. a total of eight tests.

ASTM G 61-86 RESULTS

In all four tests, i.e. for both shell materials, the samples were polarized well into the transpassive zone without exhibiting any signs of pitting. In the terms of this test all samples passed, i.e. were resistant to localized attack.

THE ADVANCED ALLOY TEST RESULTS

254 SMO samples

The pitting potentials measured were:
Sample 1. 680 mV
Sample 2. Transpassive without pitting. Pitted on reverse scan.

1925 hMo samples

The pitting potentials measured were:
Sample 1. 500 mV
Sample 2. 493 mV

Thus, there was good agreement between samples of the same material with the 254 SMO material showing some 200 mV improvement in pitting resistance over the 1925 hMo material in this test.

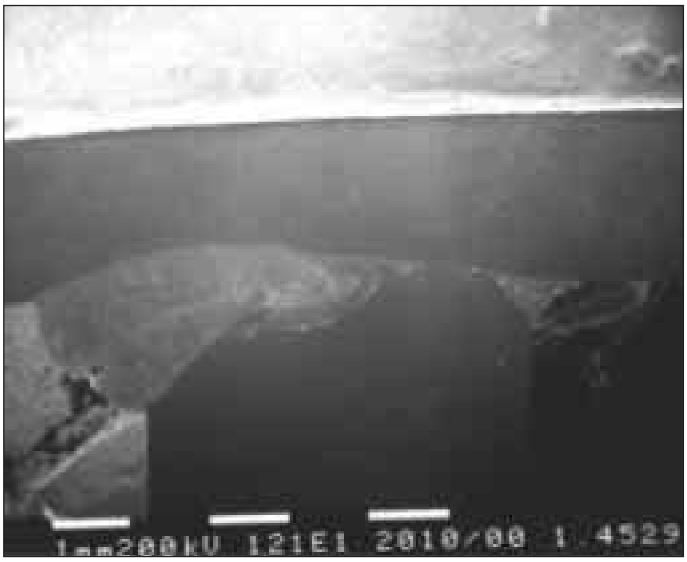

Figure 4.
Section through sample of 1925 hMo plate, weld and I 625 stud.

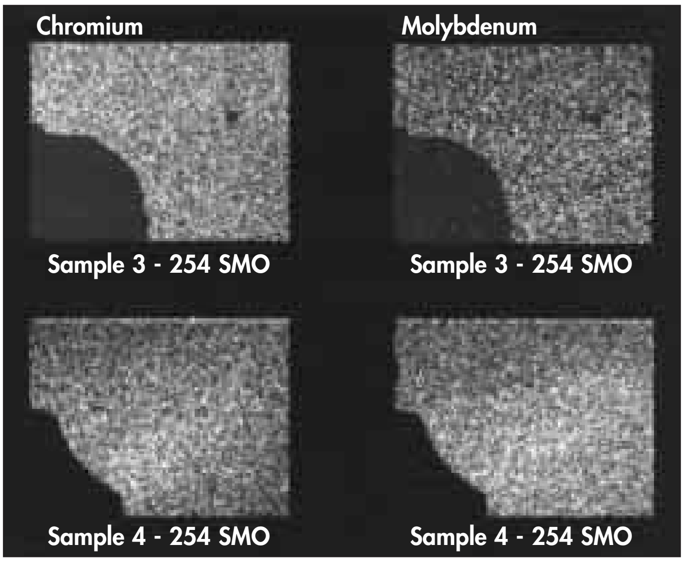

Figure 5.
Digital X-ray map of 254 SMO showing distribution of chromium and molybdenum in 2 samples. The plate material is at the top of each image.

Scanning electron microscopy (SEM) examination

Sections were taken through studs and shell materials and mounted in epoxy resin. These sections were then prepared using standard metallographic techniques. All specimens were carbon coated and examined in a Phillips SEM fitted with Link Analyzer. Sections were examined for uniformity of weld and presence of defects or precipitates.

The weld profiles were irregular in all four samples examined, see for example 1925 hMo in Figure 4. At higher magnification no gross precipitation was evident in the weld area. There was, however, some lack of bonding at the plate-weld interface in some areas. This weld profile variability and lack of bonding was not dependent on the shell material, (see Figure 4).

X-ray analyses were carried out on stud, shell and weld material. Digital X-ray maps were also produced at low magnification to cover all areas of the sectioned joint (Figure 5). These analyses did not detect any areas of depletion or concentration of the key alloying elements in the weld or heat affected zone. No alloy-rich precipitated particles were detected (seeFigure 5).

DISCUSSION OF RESULTS FROM MATERIALS TESTING

The electrochemical investigation has shown that the resistance of these alloys to localized corrosion by chlorides has not been diminished by the stud welding process, which is probably too fast to permit precipitation of alloy-rich particles.

All samples passed the standard ASTM G 61 test and show acceptably high pitting potentials in the more severe test. The results obtained in this test compare well with the body of data generated previously for these alloys and with good service experience.

There were, however, differences between the two shell materials as indicated by the advanced alloy test; the 254 SMO alloy showed higher pitting resistance than the 1925 hMo alloy. The reason for this difference was not investigated but is likely to be caused by the higher nickel content in the 1925 hMo and/or differences in processing the sheet during manufacture.

The SEM examination showed no appreciable segregation of molybdenum or chromium. This correlates well with the pitting resistance behaviour. Lack of fusion at the edge of the stud welds was observed in some of the samples. This seemed to be related to the positioning of the stud over the plate prior to welding. Further evidence for this effect was found in the difference in weld reinforcement from one side of the stud to the other.

Based on these results and prior experience it was recommended that the replacement exchangers should be fabricated from 254 SMO with I 625 spacer pins. In fact, both candidate alloys were used with 254 SMO in the hottest sections and 1925 hMo for the remainder. Quality assurance procedures were improved to eliminate the variability of adhesion and reinforcement found in some of the test pieces. Some changes were also made in the design of the spiral exchangers. The central inlet was modified changed to incorporate a patented design that gives better velocity distribution, eliminates dead spaces, produces less fouling and makes the exchangers easier to clean. One of the replacement exchangers is shown in Figure 6.

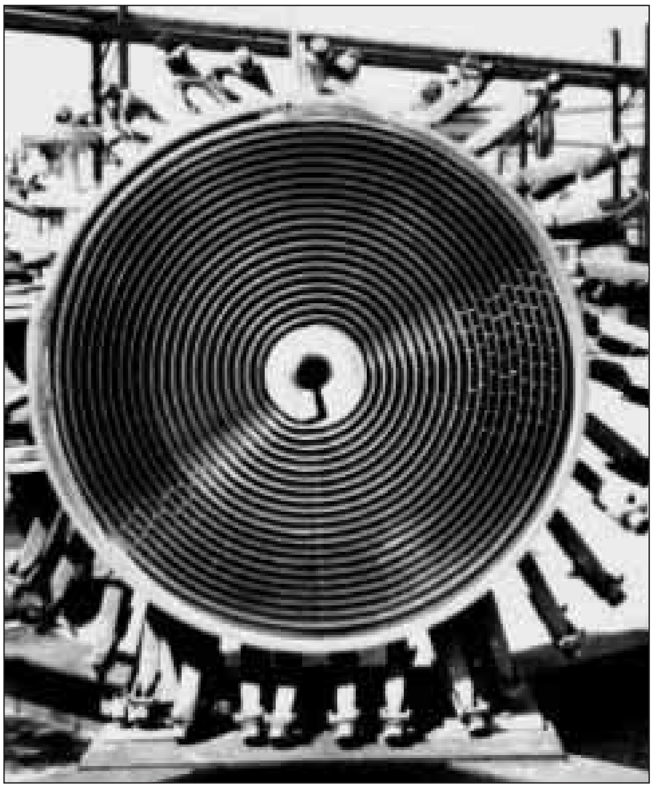

Figure 6.
Replacement spiral heat exchanger in 6% molybdenum austenitic stainless steel.

CONCLUSIONS

The duplex stainless steel 2205 is not suitable for this application in which it is exposed to hot solutions of chloride at low pH and oxygen content. The welding procedures and processes used for some of the fabrication exacerbated the corrosion problem. The corroded stripping column has been repaired under carefully controlled conditions and will be inspected regularly. The spiral heat exchangers could not be repaired so have been replaced using austenitic stainless steels containing 6% molybdenum. Corrosion tests showed that similar 6% Mo alloys do not give identical results. In order to further protect against corrosion in the columns and exchangers the process will be run at as high a pH as possible. In practical terms this means that this part of the plant will operate a pH of between 4 and 7 and preferably between 5 and 6. The oxygen content will be increased to around 35 ppm.

REFERENCES

1. M.J.G. Notten, Stainless Steel Europe, April, pp. 24-31 (1991)
2. Avesta AB Sweden, Avesta Information No. 9063, p. 4
3. ASTM Standard G48, (1997)
4. ASTM Standard G 61, (1986)

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