Electrochemical screening of several alloys for use in a flue-gas desulphurisation prescrubber

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Abstract

The spray-nozzle fasteners in the prescrubber of a flue-gas desulphurisation plant were damaged by corrosion: the materials used - stainless steel and later titanium also - had corroded in the acidic scrubbing water.
The behavior of stainless steels, nickel alloys and titanium, which can be applied for the nozzles, was studied by means of electrochemical measurements in a laboratory measuring cell. The measurements showed that, that under corrosive conditions, most stainless steels exhibit pitting and crevice corrosion. Some nickel alloys, especially Hastelloy-C22, appear more suitable for use. The measurements also showed that the $TiO2$ layer dissolves at pH = 0.7 under reducing conditions. Titanium also corrodes severely at pH < 0.7 under oxidizing conditions. The laboratory measurements were consistent with the field test results for most materials.

Introduction

The spray manifold in flue-gas desulphurisers (FGD) consists of a central supply header and branches with ceramic spray nozzles at the end. The nozzles are necessary for spraying the circulating wash water. Internal parts in contact with the scrubbing water are rubberlined.

The spray nozzles on the tubes were mounted, in the FDG involved in the present project, using bolting with a stainless steel 904L. After a year of unsatisfactory performance of this stainless steel, it was decided to use grade-12 titanium as construction material for the bolting. After another year of operation had elapsed, the grade-12 titanium also appeared to suffer from severe corrosion, as shown by the extended bolting in Figure 1.

Electrochemical examination of various stainless steels, nickel alloys and titanium was therefore carried out in order to screen for suitable materials for an acidic environment, and to compare the results of laboratory tests with the results of field tests. Polarization curves and corrosion potentials were measured for the purpose in prescrubbing water in the laboratory measuring cell.

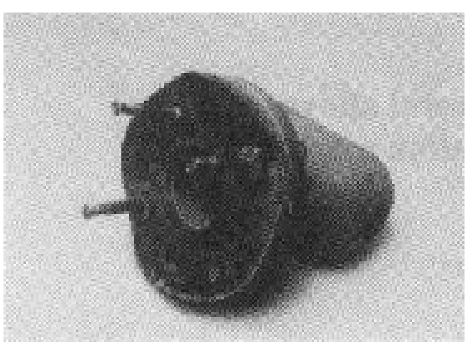

Fig. 1 Spray nozzle with titanium bolting after operation.

In addition, a few other materials were exposed to the same conditions in the prescrubber.

Some of the relevant literature was studied, especially findings about corrosion behavior of materials used for outlet ducts of wet scrubbers in electricity-generating plants (Dene, 1985/1986). Locations of the scrubber where corrosion occurs mostly, had been investigated earlier (Whitaker, 1987).
In the present study, the polarization curves were examined to ascertain that the following criteria were fulfilled:
(1) no hysteresis,
(2) no active peak behavior, (3) passive behavior,
(4) no reactivation at lower potentials.

A computer-controlled potentiostat was used for testing the various alloys.

Materials

Several available candidate materials, considered potentially appropriate for this environment, were tested. The nominal compositions are given in Table 1. Various heats were tested with some of the materials. Special treatment was applied to the test specimens, which is noted in column 4 of Table 1.

For the laboratory test, the stainless steels were deburred and sanded. They were then etched for thirty minutes in 15% HN03 + 5% NH4HF2 (by weight) and passivated in 21 % HN03 (by volume) at room temperature. The Monel and Inconel test specimens were deburred and sanded. The Hastelloy specimens had been slightly sanded then immersed for some time in the prescrubbing water before testing. The titanium alloys were used without any preparation (they were not deburred). A platinum measuring wire was spot-welded to some test specimens. The spot-welds and part of the circumference were sealed off with a Colturite-TCN coating. To facilitate measurement of test tubes in one piece, a so-called flag was cut from the sample pipe material in such a way that the surface area was approximately 20 cm2.

For the field tests, the test plates were sanded at grit 400, etched in a HN03/HF bath then passivated in a HN03 bath for thirty minutes at 338 K.

Test procedures

This section describes the procedures as followed in: (1) the laboratory tests,
(2) on-site exposure tests.

Laboratory tests

The operating conditions occurring in the FDG were simulated in a laboratory cell. The mean flue-gas temperature under operating conditions was 318-323 K. The pH value varied between 0.8 and 1.2. The concentrations during operation fluctuated between 6 and 9 g/l for chloride, between 0.05 and 0.2 g/l for fluoride and between 1 and 3 g/l for sulfate.
The liquid was turbid due to the presence of fly-ash. Pre-scrubbing water is drained from the FDG after scrubbing flue gas in counterflow. All measurements were carried out in unfiltered pre-scrubbing water. In practice both aerated and de-aerated conditions may occur.
Sodium sulfite dosing preceding the laboratory test led to the formation of a reducing environment roughly comparable to the presence of sulfur dioxide under actual conditions. The counter electrode was surrounded by a glass tube with a porous filter. The solution was agitated.

Polarization curves on passive material

Polarization curves on passive material were measured at a low potential scanning rate (3 mV per minute). Scanning was carried out from the electrochemical corrosion potential (ECP) up to the pitting potential and back again. This method is usually applied to test the susceptibility of stainless steel to pitting corrosion (ASTM, 1982). In the present study, the occurrence of hysteresis was specially investigated.

Polarization curves on slightly sanded samples

Polarization curves at a high potential scanning rate (60 mV per minute) were measured on samples slightly sanded in advance (800 grit paper). Scanning was first carried out from the ECP in the direction of the cathode until hydrogen developed. Each scan was done up to a maximum current density of 60 mA - cm2. Scanning was then reversed at the same rate, up to the pitting potential or at most until oxygen was formed, after which scanning was again carried out in the direction of ECP. This test procedure was used for the nickel alloys and titanium. Special attention was paid to the occurrence of an active peak and passive behavior of the nickel alloys. The titanium was screened for reactivation at lower potentials. Electrochemical measurements on platinum were performed to obtain some idea about the presence of oxidisable and reducible substances in the test environment.

Table 1
Materials tested in the laboratory and preparation method applied.

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Materials tested in the laboratory and preparation method applied.

common name of alloy	heat no.	DIN composition	preparation
stainless steels			
316L		x2CrNiMo 18 10	passivated
2RK65		x2NiCrMoCu 25 20 5	passivated
904L/1.4539		x2NiCrMoCu 25 20 5	passivated
Sanicro28		x1NiCrMoCu 31 27 4	passivated
Noridur		x2NiCrMoN 22 5	as received
254SMO		x2NiCrMoCu 20 18 6	passivated
VEW A965		x2NiCrMoCu 20 18 6	passivated
Monit 2502		x2CrNiMo 25 4 4	passivated
Al 29-4C	1	x2CrMo 29 4	passivated
Al 29-4C	2		passivated
nickel alloys			
Monel 400		NiCu 30 Fe	sanded
Inconel 600		NiCr 15 Fe	sanded
Inconel 625		NiCr 22 Mo 9 Nb	passivated
Incoloy 825		NiCr 21 Mo	passivated
Hastelloy-C	1	NiMo 16 Cr	sanded
Hastelloy-C	2		sanded
Hastelloy-C4		NiMo 16 Cr	sanded
Hastelloy-C276	1	NiCr 20 Mo 15	sanded/passivated
Hastelloy-C276	2		sanded
Hastelloy-C21		NiCr 22 Mo 6 Cu	sanded
Hastelloy-C33			sanded
Hastelloy-C30			sanded
Hastelloy-C3			sanded/passivated
Hastelloy-C22		NiCr 21 Mo 13	passivated
titanium			
grade-12 Ti		Ti Ni.6-.8 Mo .2-.4	as received/passivated
grade-7 Ti		Ti Pd.2 Fe .068	as received/passivated
grade-2 Ti		Ti	as received/passivated
platinum		Pt	as received

Potential measurements on titanium
The test environment was changed during these measurements, the changes having an impact on the behavior of the material to be tested. Particular attention was paid to the behavior of titanium in acidic prescrubbing water under reducing and oxidizing conditions. Several test specimens were exposed simultaneously.

On-site exposure tests

The dimensions of the test plates were 120x180 mm. Figure 2 shows an example of a block with test plates. A 60-mm slot was cut in the middle. This slot was welded with additives appropriate for the various materials. The welds were applied by means of the TIG process.

A crevice-corrosion test was also performed on the test plates by means of teflon discs with slots which had been screwed on, as described in the ASTM test (ASTM, 1983).

Strips, 1 mm, from various test materials were sawn off and bent in a U-shape, according to ASTM (1979). These strips served to perform the test on stress-corrosion sensitivity.

Fig. 2
Block with test plates.

Results

This section covers the results obtained for:
(1) the laboratory tests,
(2) the on-site exposure tests.

Table 2
Results of the laboratory tests.

alloy	heat no.	figure	NH	NA	P	NR	F
stainless steels							
316L							− −
2RK65		3-A	−				
904L/1.4539							−
Sanicro28		3-B	−				−
Noridur		(3-B)	−				
254SMO		3-C	−				−
VEW A965		3-D	+				−
Monit 2502		3-E	−				
Al 29-4C	1	(3-E)	−				
Al 29-4C	2	3-D	+				
nickel alloys							
Monel 400		4-A		−			
Inconel 600		(4-A)		−			
Inconel 625							−
Incoloy 825							−
Hastelloy-C	1	4-B		+			
Hastelloy-C	2	4-C		−	−		
Hastelloy-C4		4-D		−	+		
Hastelloy-C276	1	(4-B)		+			−
Hastelloy-C276	2	(4-B)		+			
Hastelloy-C21		(4-B)		+			−
Hastelloy-C33		(4-B)		+			
Hastelloy-C30		(4-B)		+			
Hastelloy-C3		(4-B)		+			−
Hastelloy-C22							+
titanium							
grade-12 Ti		5-A			+	−	− −
grade-7 Ti		5-B/C			−	−	− −
grade-2 Ti							− −
platinum		4-E					

NH = no hysteresis in polarization curve.
NA = no active peak behaviour.
P = passive behaviour.
NR = no reactivation at lower potentials.
F = summarised behaviour in the field of Table 3.
− − = bad; − = average; + = good.

Laboratory tests

It seems useful to distinguish between the various types of materials tested in the laboratory. These are:

(1) stainless steel,
(2) nickel alloys
(3) titanium.

The main results of the laboratory tests are presented in Table 2.

Stainless steel

The polarization curves recorded from stainless steels are given in Figure 3. Stainless steel of type 2RK65 (Fig. 3-A) showed a somewhat fluctuating current and hysteresis during the reversed scan, which suggests pitting corrosion. The Sanicro28 material (Fig. 3-B) showed delayed hysteresis during the reversed scan. The steel types 254SM0 (Fig. 3-C) and VE WA965 (Fig. 3-D) have almost identical compositions. Hysteresis is seen in Figure 3-C. Figure 3-D shows an example of suitable behavior. The polarization curve recorded for the duplex material, Noridus, a casting alloy for pumps, is identical to that shown in Figure 3-B.

Among the ferritic steels, the commercial alloys Monit 2502 and A1 29-4C were tested. Monit showed a transpassive peak (Fig. 3-E). The results of the measurement of Al 294C gave the same results. Testing of a second batch of A1 29-4C yielded results comparable to those of the measurements for VE WA965 (Fig. 3-D).

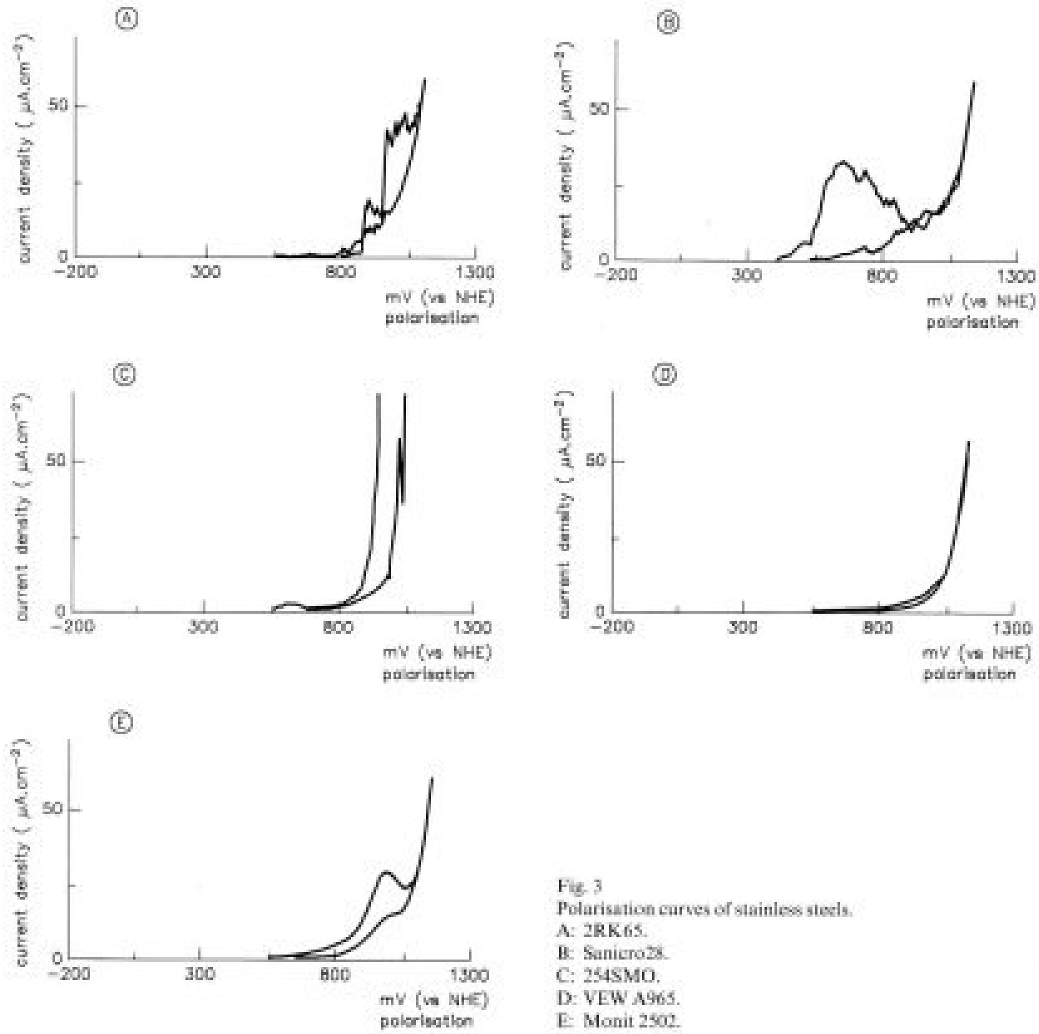


Fig. 3
Polarisation curves of stainless steels.
A: 2RK65.
B: Sanicro28.
C: 254SMO.
D: VEW A965.
E: Monit 2502.

Nickel alloys

Testing of nickel alloys showed that the Mone1400 alloy has an active peak behavior (Fig. 4-A). The same behavior was observed for the Inconel 600 alloy. Figure 4-B shows the curve for Hastelloy-C, with a very broad passive range. Figure 4-C, with the test of a second heat of Hastelloy-C, shows that a passive peak did not develop after the primary passive peak: the current remained high.

Measurement of two Hastelloy-C4 batches gave curves with large passive ranges, developing a primary passive peak during one of the tests (Fig. 4-D). The two Hastelloy-C276 batches exhibited a large passive range during all the measurements (Fig. 4-B). The polarization curve recorded from platinum was used as a reference measurement. The total available oxidisable and reducible substances in the solution could be derived from the measurement (Fig. 4-E).

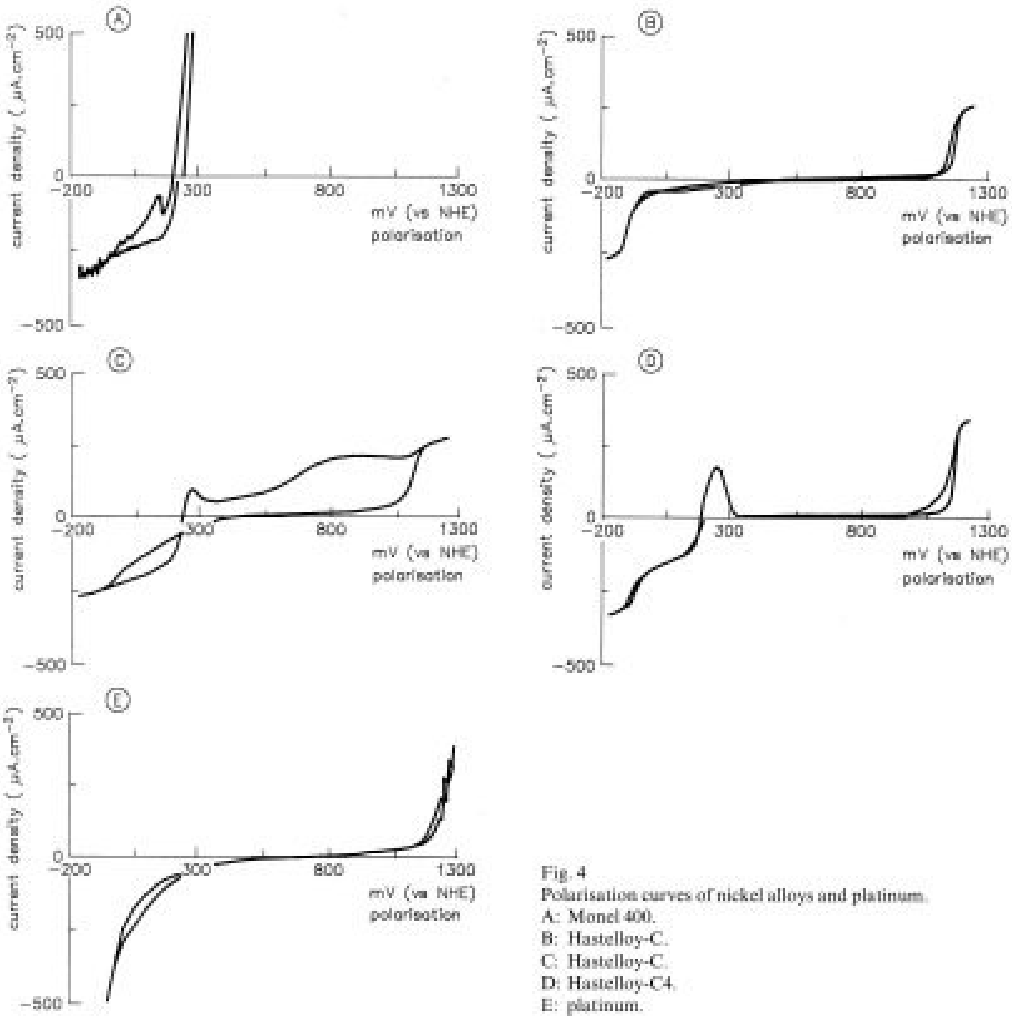


Fig. 4
Polarisation curves of nickel alloys and platinum.
A: Monel 400.
B: Hastelloy-C.
C: Hastelloy-C.
D: Hastelloy-C4.
E: platinum.

Titanium

Figure 5-A gives an example of a polarization curve measured for grade-12 titanium. Oxygen formation was detected during scanning towards high positive potentials. The measurements for the titanium/ palladium alloy presented a similar picture.

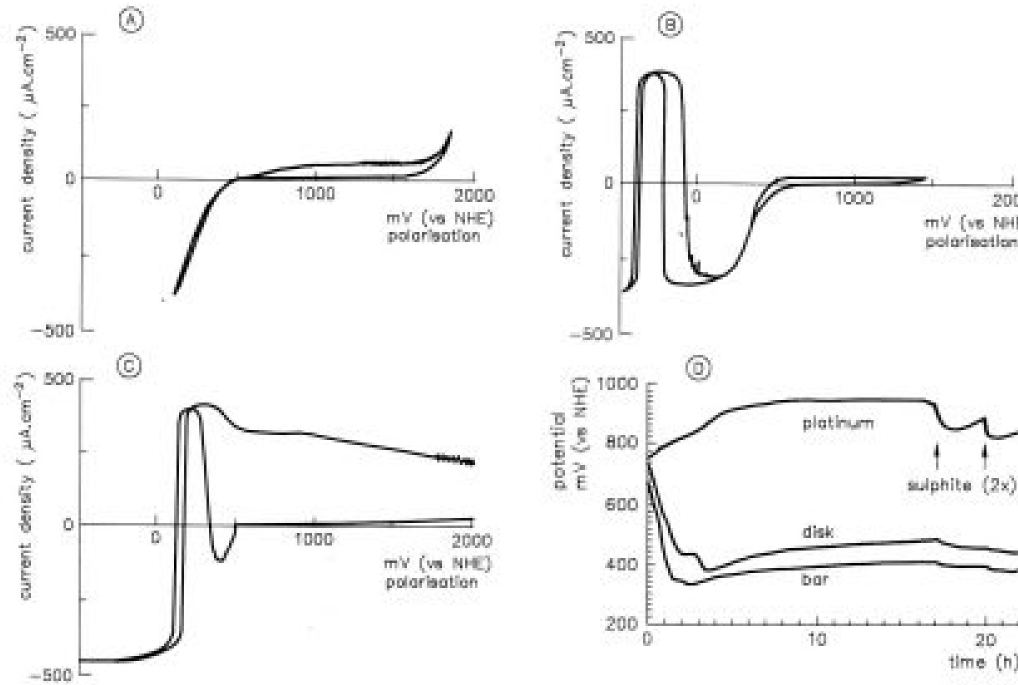
A special phenomenon occurred during the measurement of grade-7 titanium. Figure 5-B shows that, when potentials lower than -100 mV were scanned, the current suddenly - and surprisingly - became positive between approximately -100 and -400 mV. The active range, however, had shifted towards approximately 300 mV with regard to SHE. Measurements made after the addition of sodium sulphite revealed that even the primary passive peak was not detected. A large active range developed instead (see Fig. 5-C). This phenomenon was measured for grade-7 and for grade-12 titanium.

Measurements of the corrosion potential for (passive) titanium in prescrubbing water at pH = 0.7 under reducing conditions showed that the potential was still in the passive range, even after tens of hours. The addition of sodium sulphite to the test solution had resulted in a slight reduction of the potential but not to within the active range (Fig. 5-D). Acidifying the prescrubbing water with hydrochloric acid to below pH = 0.7, however, showed that the corrosion potential of the titanium test specimen fell sharply to -300 V - (Fig. 5-E). Severe corrosion was found on the titanium test specimens after completion (Fig. 5-F) of the test. The platinum redox potential curve is also presented in Figure 5-E. It gives a clear indication of the changing oxidising capacity of the solution during the test.

When air was led through instead of nitrogen, the grade-12 titanium plate showed a tendency towards passivation after some time. Repeating this procedure caused a potential fluctuation on platinum. NaOH addition to pH = 0.31ed to the test specimens becoming passive. The platinum redox potential measured had returned to its initial level.

On-site exposure tests

Blocks of several materials were placed on the lower spray manifold, where conditions are expected to be the most corrosive. The results are shown in Table 3. The number of minus signs indicates the degree of corrosion. A score of five minus signs indicates that the entire specimen had dissolved. Pitting corrosion was found in material 904L. After three months' exposure, the various titanium alloys (grades 2, 7 and 12) were all so severely corroded (due to crevice and general corrosion) that they had entirely disappeared. The behavior of Hastelloy-C22 proved satisfactory.



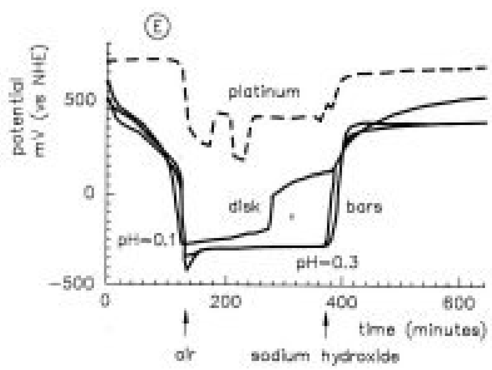


Fig. 5
Polarisation curves and potential measurements of titanium and platinum.
A: grade-12 Ti.
B: grade-7 Ti.
C: grade-7 Ti.
D: titanium and platinum.
E: titanium and platinum.

Discussion and conclusions

The right-hand part of Table 2 gives the aggregate results from the polarization curves and the behavior during field testing of the relative materials. The serviceability of the material in the FGD prescrubbing water was assessed on the basis of the four criteria and of the summarized behavior in the field test.

Problems can be expected for most stainless steels in this strongly acidic environment if the measurements evidence hysteresis. 2RK65 as well as Noridus will present these corrosion problems when exposed in the prescrubber. Stainless steel, Sanicro28, is probably also unsuitable, due to its delayed hysteresis. 254SM0 and VEW A965 may be satisfactory in practice, although 254SM0 shows a small degree of hysteresis. Monit 2502 and Al 294C exhibit a transpassive peak as hysteresis.

Table 3
Results from the on-site tests.

alloy corrosion	crevice corro-sion	pitting corro-sion	general corro-sion	stress corro-sion
316L	— — —	— —	+	— — — — —
904L/1.4539	— —	+	+	+
Sanicro28	— —	—	—	+
254SMO	— —	—	+	+
Inconel 625	— —	—	—	+
Incoloy 825	— —	+	— — — —	+
Hastelloy-C276	—	—	—	—
Hastelloy-C3	— —	+	+	+
Hastelloy-C22	+	+	+	+
grade-12 Ti			— — — — —	
grade-7 Ti			— — — — —	
grade-2 Ti			— — — — —	

There is therefore some uncertainty touching the use of these ferritic steels in this environment. It is quite conceivable that the pH value decreases sharply in crevices. Whenever hysteresis is observed, this appears to coincide with average to unsatisfactory behavior in practice.
Mone1400 and Incone1600 are also active in this environment. The use of Hastelloys was assessed with regard to the presence of active peaks and rate of passivation. Application of several heats to the alloy C-276, -G types and of one heat of alloy-C showed that no problems whatsoever are to be expected. The conclusion is therefore justified that the absence of an active peak is no guarantee of satisfactory behavior in practice. Only the Hastelloy-C22 shows no attack whatsoever and is the best material for this environment.
Titanium proved highly susceptible to corrosion in acidic prescrubbing water, because of the reactivation at lower potentials. The protective Ti02 layer on the titanium is not stable in the strong acidic scrubbing water at pH < 0.7. Titanium is not passive in stronger acidic scrubber water. Under field conditions, the available sulfite will also cause a reduction of the redoxpotential, so that passivation of active titanium will become even more difficult. Titanium is passivated again under less acidic conditions. The presence of fluoride can activate the titanium, but fly-ash seems to inhibit corrosion of titanium when the pH exceeds a value of 0.7. The effect of chlorides and fluorides on titanium alloys in simulated scrubber environments was studied by Thomas & Bomberger (1983). There is good agreement between the absence of reactivation behavior and behavior in practice.

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