

**NPL REPORT
DEPC MPE 013**

**Impact of Water Chemistry
Transients on Pitting and
Stress Corrosion Cracking of
a Steam Turbine Disc Steel**

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NOT RESTRICTED

May 2005

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ABSTRACT

The impact of environmental transients on pitting and stress corrosion cracking of a steam turbine disc steel has been evaluated. The testing represents an attempt to simulate the water chemistry aspects of two-shifting in power plant but with the specimens held under constant stress. With aerated pure water off-load and deaerated 300 ppb Cl^- + 300 ppb SO_4^{2-} solution on-load, enhanced pit and stress corrosion crack development compared with continuous on-load or off-load exposure was observed. The key factor is considered to be sustainment of an electrochemical driving force for pitting and stress corrosion cracking on-load despite the absence of oxygen.

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ISSN 1744-0262

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We gratefully acknowledge the financial support of the UK Department of
Trade and Industry (National Measurement System Policy Unit)

Approved on behalf of the Managing Director, NPL,
by Dr M G Gee, Knowledge Leader, Materials Performance Team
authorised by Director, Engineering and Process Control Division

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INTRODUCTION

For economic reasons, the UK power industry is now operating its 500 MW coal-fired plants on a two-shift cycle in which the turbines are on-load for 16 hours per day and off-load overnight and at weekends. The concern with ‘two-shifting’ is the impact on environment assisted cracking of the associated transients in stress, water chemistry and temperature¹. On-load, with well-controlled water chemistry, the condensate on the low-pressure turbines will be free of oxygen with chloride and sulphate levels both up to about 300 ppb. The temperature below which condensation occurs will be about 90 °C. Off-load, the condensate would essentially be pure water but aerated unless there is nitrogen blanketing. The temperature would be about 70 °C but falling to 20 °C for a weekend shut down. The stress off-load would be zero.

Ideally, to fully simulate two-shifting in laboratory testing, the combined influence of transient stress and water chemistry would be evaluated but there are technical difficulties in synchronising the changes in the stress, temperature, oxygen and anion (chloride and sulphate) concentrations. Hence, a separate study was undertaken of the effect of transient stress under constant environmental exposure conditions using fracture mechanics specimens². Here, we have focused on assessing the impact of environmental transients for plain tensile specimens under constant load.

EXPERIMENTAL

Material

The material used in this work was a disc steel (3% NiCrMoV), cut from an ex-service steam turbine disc supplied by PowerGen. The chemical composition is listed in Table 1.

Table 1. Chemical composition of the 3% NiCrMoV disc steel (mass %)

C	Si	Mn	P	S	Cr	Mo	Ni	V	N	Fe
0.30	0.28	0.45	0.017	0.013	0.69	0.27	2.89	0.091	0.21	bal

Specimens

Self-loaded cylindrical specimens of the disc steel were manufactured according to ASTM E8³ with the longitudinal axis perpendicular to the radius of the turbine disc. The overall length was 100.0 mm, the shoulder diameter 16.0 mm, the gauge length 25.4 mm and the diameter 6.4 mm. The specimen and the loading frame are described in detail elsewhere⁴. To avoid galvanic corrosion, the loading frames and the nuts were also made of the disc steel. The specimen surface was dry ground using P2400 grinding paper (1200 SiC grit finish). The surface profile⁴ was measured using a laser profilometer. Measurements were made at twenty locations on two specimens. The length of profile for each individual measurement was 5 mm. The arithmetical mean deviation of the assessed profile, R_a , was $0.12 \pm 0.02 \mu\text{m}$. The corresponding maximum height of the

profile, R_z , was $0.66 \pm 0.10 \mu\text{m}$. The final grinding direction, and hence any grinding marks, were parallel to the length of the specimen.

16 specimens self-loaded to 50%, 70% and 90% $\sigma_{0.2}$ were tested.

Stress relief

To avoid an uncontrolled influence of residual stress resulting from machining or from grinding, all specimens, after final grinding, were stress-relieved in vacuum for 2 hours at 625 °C. The mechanical properties at ambient temperature and at the test temperature are listed in Table 2. The data were the average of three tests under each condition.

Table 2. Mechanical properties of the disc steel (mass %)

Condition	T /°C	E /GPa	$\sigma_{0.2}$ /MPa	UTS /MPa	Elongation /%
As received	23	208 ± 2	747 ± 9	882 ± 5	23 ± 1
Stress relieved	23	206 ± 1	734 ± 4	870 ± 2	20 ± 0
Stress relieved	90	210 ± 4	705 ± 4	827 ± 13	20 ± 0

It can be seen that the stress relief had no effect on the mechanical properties. Since the specimens were cut from an ex-service disc, there was a concern that the mechanical properties might vary at the different locations of the disc. Therefore, the hardness of the steel was measured on ten randomly selected specimens. There was no significant variation in the hardness measured; the average value being 28.5 (Rockwell C), with a standard deviation of 1.5.

Water chemistry

Daily changes of water chemistry and temperature required a level of resource and/or instrumentation that was untenable. For this reason, we have explored the effect of environmental transients by maintaining the solution chemistry under simulated on-load conditions during weekdays and switched to off-load conditions over the weekend. This was not ideal but will provide insight as to the impact of excursions.

Thus the exposure conditions were as follows:

On-load: Deaerated 300 ppb Cl^- + 300 ppb SO_4^{2-} solutions at 90 °C for 104 hours

Off-load: Aerated pure water at 70°C for 64 hours

The transition from on-load to off-load conditions was achieved by pumping aerated pure water through the four test cells at a flow rate of 11 litre/hour. The temperature was gradually reduced from 90 °C to 70 °C over 2 hours. The oxygen concentration and the solution conductivity were monitored during the transition and indicated that the conductivity reached 0.9 $\mu\text{S}/\text{cm}$ (the value for aerated water) in 2 hours. The oxygen concentration also reached the equilibrium concentration (3.6 ppm) within 2 hours.

To reverse the process back to on-load conditions, the pure water in the test cells was deaerated with N_2 at a rate of 200 ml/min for one hour before pre-deaerated 300 ppb Cl^- + 300 ppb SO_4^{2-} solutions from a reservoir was passed through at a flow rate of 11 litre/hour. This was necessary to minimise an uncontrolled combination of oxygen and anion-containing solution. Typically the oxygen concentration was below 30 ppb in 3 hours, 10 ppb in 7 hours and 1 ppb after 14 hours (see below). The temperature increased gradually to 90 °C in about 30 minutes after the introduction of the deaerated solution to the cell.

The test set up in Figure 1 gives an indication of this cell arrangement though not all features are shown. A magnetic stirrer is located in each cell and essentially determines the local flow rate at the specimens.

In a separate set of tests, measurements were made using a very similar arrangement with specimens stressed up to 90% $\sigma_{0.2}$ but in a constant environment of deaerated 300 ppb Cl^- + 300 ppb SO_4^{2-} solutions at 90 °C.



Figure 1. Arrangement of four test cells for cyclic water chemistry; the reservoir with deaerated 300 ppb Cl^- + 300 ppb SO_4^{2-} is out of shot.

RESULTS AND DISCUSSION

Corrosion potential

The four cells containing the specimens were arranged in series and there was some concern that the later cells might exhibit a different response. In practice, the flow rate

was such that no difference in the corrosion potential for the different cells could be identified as indicated in Figure 2, showing the transition from off-load to on-load conditions. This was true also for the transition from on-load to off-load water chemistry.

A key observation was that the rate of the change in the corrosion potential decreased with the number of cycles, despite similar rates of change of the oxygen concentration in each cycle, taking more than 60 hours to restore the original value after 17 excursion cycles (Figure 3).

This slow change reflects formation of a film off-load in aerated solution which is only slowly dissolved. Also, cathodic reduction of the film will provide some stimulus for a higher potential. This slow change in potential may be accentuated by daily cycling of the solution chemistry, more typical of service conditions.

The change in the corrosion potential and the oxygen concentration during the transition from on-load to off-load is shown in Figure 4. It can be seen that the oxygen and the corrosion potential reached a stable value relatively quickly. In contrast to the impact of the number of water chemistry cycles on the transition from off-load to on-load, there is little sensitivity when the reverse situation is considered as shown in Figure 5.

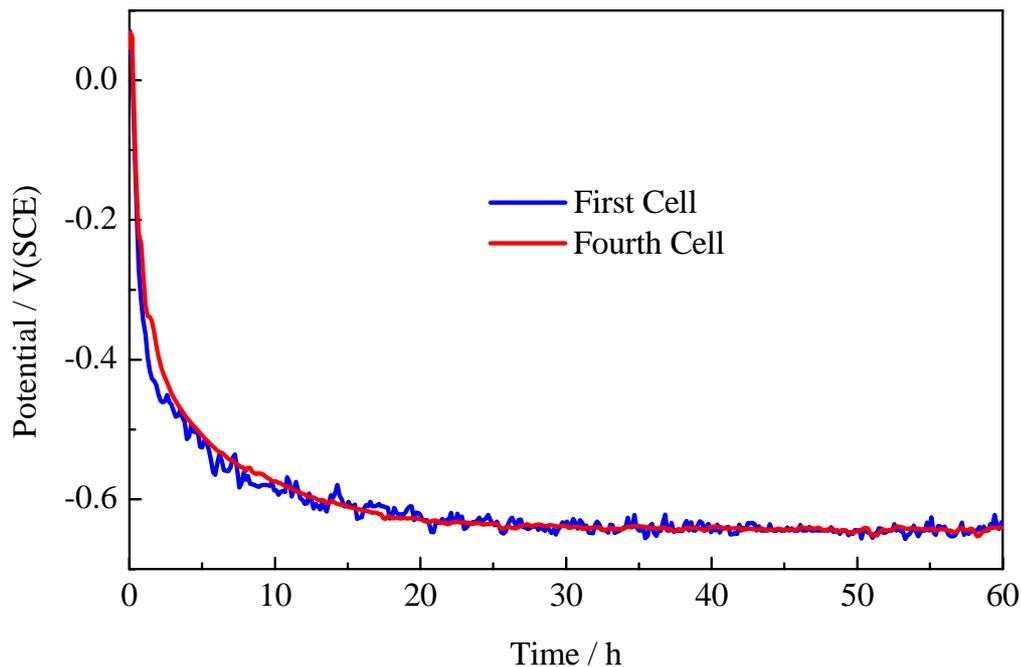


Figure 2. Change in the corrosion potential of the turbine disc steel during the transition from off-load to on-load environmental conditions, showing that the cell position in the circulation line does not have a significant effect on the corrosion potential.

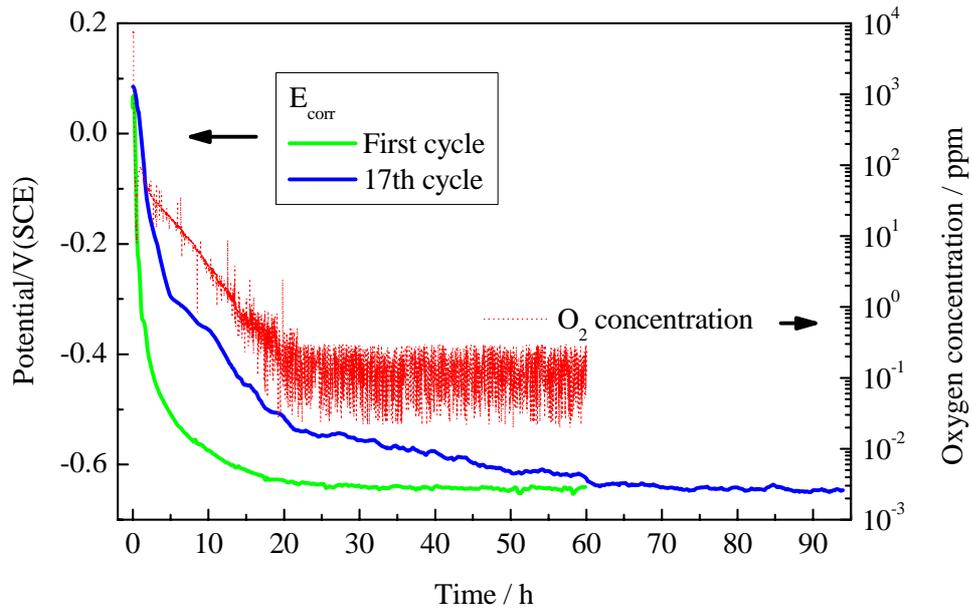


Figure 3. Effect of the number of water chemistry cycles on the rate of corrosion potential change during the transition from off-load to on-load water chemistry.

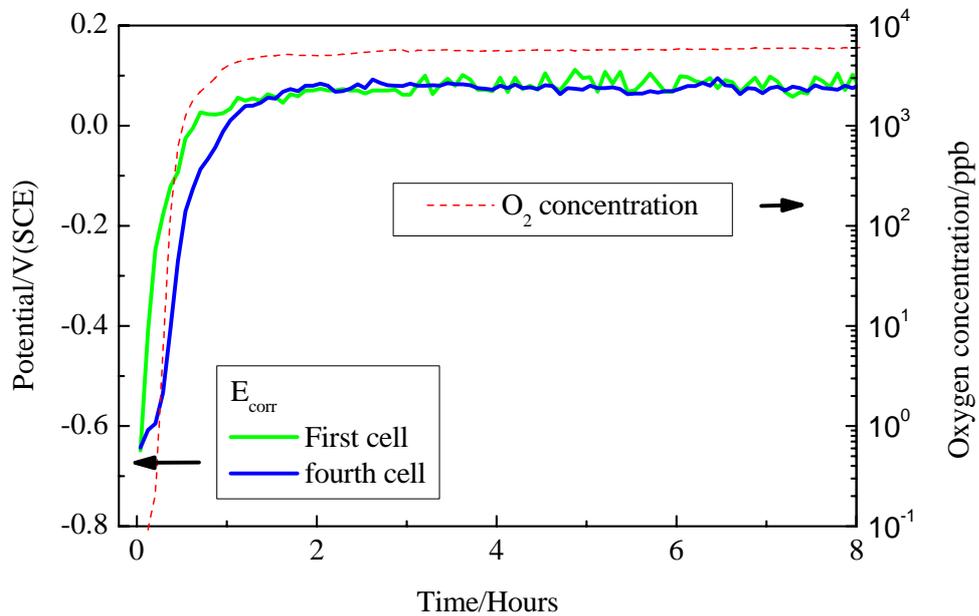


Figure 4. Time dependence of the corrosion potential during the transition from on-load to off-load, also showing that the cell position in the circulation line does not have a significant effect on the corrosion potential.

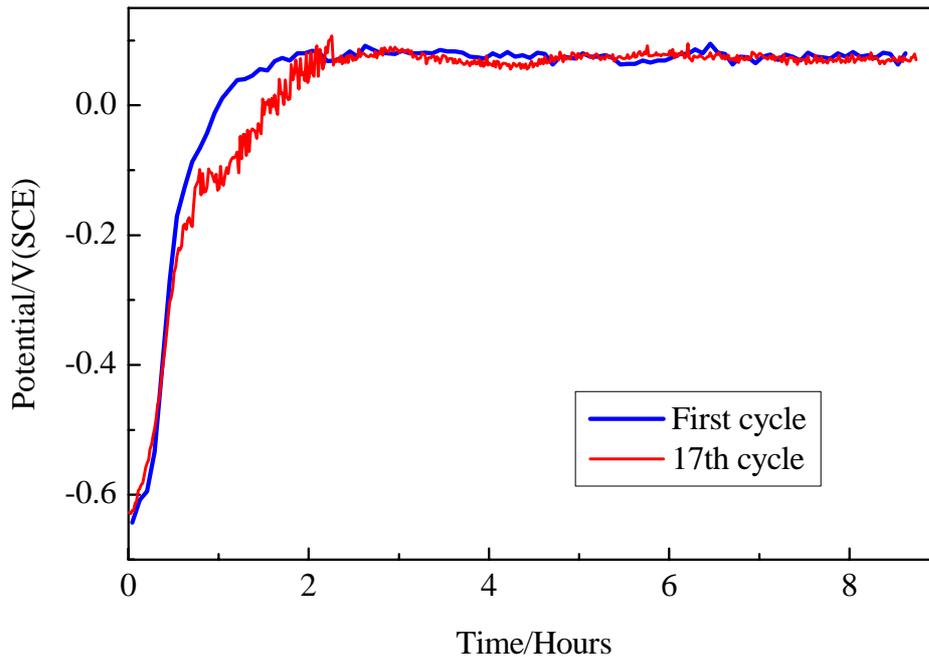


Figure 5. Effect of the number of water chemistry cycles on the rate of corrosion potential change during the transition from on-load to off-load water chemistry.

Pit and crack evaluation

Two specimens were removed from the first and fourth cell after testing for 3575 hours to check for sensitivity of pitting to the particular cell in the flow line. The results showed that there was no significant effect of the cell positions in the flow line on either the pit depth or the pit distribution.

The depth and aspect ratio of pits in the specimens removed at different times were measured using a travelling microscope on a computer controlled XYZ stage and the results are summarised in Table 3. Longer-term testing is still on-going with other specimens. There are unusual features of these data. The density decreases with exposure time. This is in contrast to the behaviour in aerated solution, with or without chloride. At the shortest exposure time in the chloride and sulphate solution, individual pits were clearly observed, consistent with previous work. However, at longer times, there were a number of patchy areas of corrosion as well as individual pits. This local metal loss is probably associated with coalescence of pits to the extent that the pit features become lost as the corrosion spreads laterally. The extent of this patchy corrosion extends with exposure time and thus the pit density decreases. Linking of pits was observed with aerated 1.5 ppm chloride but the pit-like features were still discernible.

In the separate set of tests in a constant environment of deaerated 300 ppb Cl^- + 300 ppb SO_4^{2-} solutions at 90 °C, no pitting was detected even up to 8368 h exposure (nearly 1 year). In contrast, in previously reported work⁵, pitting had been observed in deaerated pure water after 22 months but with no evidence of cracking. There is a need to rationalise these varied observations.

For the constant environment tests, the absence of pitting in 300 ppb Cl^- + 300 ppb SO_4^{2-} solution compared with deaerated pure water is not due to differences in oxygen concentration, which was less than 0.7 ppb in the pure water tests, too low to have an effect on corrosion potential. There was a difference in flow rate, 11 litre/hour in the present work, compared to a previously used flow rate of 0.9 litre/hour but this would seem unimportant as the magnetic stirrer dominates the hydrodynamics. The absence of pitting most likely reflects the lower corrosion potential, -0.65 V SCE compared with -0.61 V SCE previously (it is envisaged to be associated with the anions influencing film stability).

Table 3. Summary of measurements on self-loaded cylindrical tensile specimens.

Test time (Hour)	Cycles	Specimen No	Stress (% $\sigma_{0.2}$)	Pit density ^a (cm^{-2})	Average aspect ratio	Average depth of 10 deepest pits (μm)	Cracking (Yes/no)
1687	10	11	90	239	0.40	176	No
		25	90	/	/	/	/
3575	21	1	90	193	0.35	328	Yes
		5	90	/	/	/	/
		26	50	171	0.38	178	No
		28	50	/	/	/	/
5562	33	13	90	/	/	/	/
		37	90	125	0.39	208	Yes
7098	42	14	70	/	/	/	/
		15	70	/	/	/	/
		16	90	103	0.37	208	Yes
		45	90	/	/	/	/

It is no surprise that the transient oxygen exposure enhances pitting. However, it is notable that when compared with aerated pure water under constant exposure conditions⁵, the average depth of the deepest pits is greater and more importantly, stress corrosion cracks initiate after a relatively short exposure time, <5 months compared with >13 months for aerated pure water. The experiments do not allow us to assess the relative extent of pit growth under on-load (oxygen-free) vs off-load conditions. Once pitting has initiated, there may be retention of anions in the pit during the aerated off-load period because of the potential gradient counteracting concentration-driven diffusion from the pit. It is feasible that the damage is developing most significantly during that period. Tests varying the relative times are proposed to resolve this as it is an important issue since here we are maintaining the stress in the off-load environment, whereas in service the stress will be near zero. However, our on-load period is long compared with service and the most important feature may be the slow decay of potential after coming on-load (Figure 3). Thus, there is a cathodic driving force for a significant period when the steel is exposed to chloride and sulphate, which will be accentuated with the reduced on-load period (16 hours) in normal weekday service operation.

However one assesses the fine details, the indication is that the transient water chemistry is a relative severe environmental exposure condition that will lead more readily to pitting and cracking in service. With transient stress, pit initiation and early development will be easier because of the impact of the loading on interfacial separation of MnS inclusions from the matrix. Furthermore, crack evolution from pits will be expected to be accelerated and work in parallel² indicates a high cyclic crack growth rate.

CONCLUSIONS

Cycling of the water chemistry to simulate two-shifting of a steam turbine leads to enhanced pit and crack development compared with continuous on-load or off-load exposure. Indeed, in the former with deaerated 300 ppb Cl⁻ + 300 ppb SO₄²⁻, no pits developed although pitting in deaerated pure water occurred.

A key observation was the slow recovery of corrosion potential in transferring from off-load aerated pure water to on-load 300 ppb Cl⁻ + 300 ppb SO₄²⁻ solution, even though the oxygen level was very low. The associated cathodic reaction, perhaps reduction of higher oxidation states of iron in the oxide, is likely to play the key role in inducing stress corrosion cracking during two shifting when the turbine disc is stressed on-load.

ACKNOWLEDGEMENTS

This work was conducted as part of the “Life Performance of Materials” programme, a joint venture between the United Kingdom Department of Trade and Industry and an Industrial Group comprising Douglas Gass (Siemens), Sarah Harris (BNFL Magnox), Stuart Holdsworth (Alstom), Paul McIntyre (IOMMM), Paul Mulvihill (Powergen), Terry Parsons (BNFL Magnox), Geoff Spinks (Innogy) and Mike Tookey (British Energy).

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