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CORROSION IN WAIRAKEI STEAM PIPELINES

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SUMMARY – The erosion corrosion of carbon steel steam pipelines at Wairakei steam field and power station, first observed in the 1970's has been attributed to a reduction in separated water carry-over from steam/water separators being present in the steam lines. This led to improvement in steam condensate quality and erosion corrosion rates of up to 0.5 mm/year that seriously threatened to diminish the life of pipelines expected to last in excess of 20 years. Initiation of corrosion can be attributed to wet shutdown conditions leading to acid dissolution of the normally protective magnetite (Fe_3O_4) film and dislodging of the film from condensate flow/impact under operating conditions or to slow dissolution of magnetite in high purity water. Injection of separated geothexmal water into each steam pipeline has proven effective in controlling the corrosion by stabilising magnetite films and allowing the formation of new films on the previously corroding patch-like areas. Dissolved silica has been identified as the principal corrosion inhibitor, although the mechanism for the corrosion control remains elusive. Steam turbine silica scaling and the potential for chloride induced corrosion are controlled by ensuring that the chemical and thermodynamic conditions which exist within steam pipelines, the header and turbine inlets are such that concentrating mechanisms are avoided. Erosion in power station headers, where the steam quality is controlled, for protection of the turbines, remains as a maintenance problem.

1. INTRODUCTION

The "discovery" of erosion corrosion in the Wairakei steam pipelines during an annual inspection in 1977 (Page, 1977, Braithwaite, 1977) was followed by efforts to characterise the extent of corrosion damage (Page and Marshall, 1978, Braithwaite, 1978, 1980, Stacey and Thain, 1983) and later to quantify the rate of attack (Stacey, 1978, Stacey and Cryus, 1978, Stacey, 1979) and the mechanism of corrosion (Braithwaite, 1978, 1980, Giggenbach, 1979, McAdam, 1980). Testing of corrosion control options (Soylemezoglu et al., 1980, Stacey, 1981, Thain et al., 1981, McAdam et al., 1981, Wilson and Lichti, 1982, Wilson, 1984, Bacon and Stacey, 1984) resulted in the installation of a preferred corrosion control method (Stacey and Thain, 1983, Bacon and Stacey, 1984). The mechanism of corrosion control was further elucidated by Inman, (1994).

Figure 1 – Distribution of patch-like erosion corrosion areas in the 30" J-line as seen after a wet shutdown (Braithwaite, 1978).

This paper aims to summarise the available engineering knowledge describing the extent of the problem and the scientific knowledge of the corrosion mechanism in order to promote understanding of the corrosion control options.

2. STEAM PIPELINE CORROSION OBSERVATIONS

Engineering observations of the corrosion revealed:

- foxmation of distinct patch-like patterns of corrosion areas along the floor and lower side walls of the pipelines (Page, 1977, Braithwaite, 1977, 1978) Figure 1.
  - corrosion patch spacing from <0.5 to several meters (Page and Marshall, 1978)
  - corrosion occurred independent of pipeline steam pressure and independent of steam pipeline size (clown to 20" diameter) but was only observed in pipelines carrying wet steam (Bacon and Stacey, 1984)
  - erosion patches occurred primarily in the pipelines close to the power station with the

depth of attack increasing on approach to the station, reaching a maximum of 5mm (in a 10 year period) (Stacey, 1980,1981)

- erosion patches were not observed in steam water separators or in pipelines close to steam separators (Thain et al, 1981, Bacon and Stacey, 1984)
- corrosion patches were characterised by a central area of freely corroding bare steel and a *tail* of precipitating corrosion products, Figure 2 (eg Braithwaite, 1980).

Initial scientific investigations of the corrosion indicated

- magnetite, Fe_3O_4 (up to 3 mm thick) was the predominant corrosion product formed within the Wairakei geothermal steam pipelines, Figure 3 (Braithwaite, 1980)
- the iron sulfide, pyrite, FeS_2 was observed within the magnetite scale in distinct patterns associated with interruptions in magnetite growth, possibly associated with upset conditions during shutdown and at startup (Braithwaite, 1978, 1980)
- predictive thermodynamic models of corrosion product stability correlated with the observed occurrence of magnetite and iron sulfides, Figure 4 (Braithwaite, 1980, Wilson and Lichti, 1982, Inman, 1994,)
- under *dry* shutdown conditions the bare steel areas of the corrosion patches remained clean, being bright or dull in appearance (Figure 2) whereas under wet shutdown conditions sulfuric acid formed and the bare areas had localised pitting corrosion and "rusty" red coloured deposits (Wilson and Lichti, 1982)
- there was a pattern of silicon distribution (presumed to be as silica) within the magnetite scale, Table 1 (McAdam, 1980, Stacey, 1980)
- there was a pattern of silica concentration in the steam condensate in the pipelines as seen from analysis of condensate discharged from catchpots, Table 1 (Thain et al., 1981, McAdam, 1980)
- the long term corrosion penetration appeared to be inversely related to the sampled levels of silica discharged from catchpots and silica present in magnetite scales, Table 1.

3. THE CORROSION REACTIONS

Erosion corrosion is defined by NACE International as:

"A corrosion reaction accelerated by the relative movement of the corrosive fluid and the metal surface".

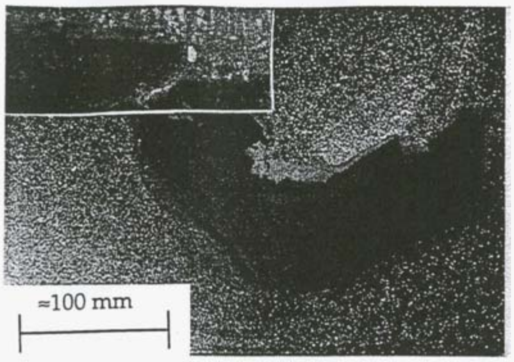

Figure 2 – Typical erosion patch-like area seen after a *dry* steam pipeline shutdown.

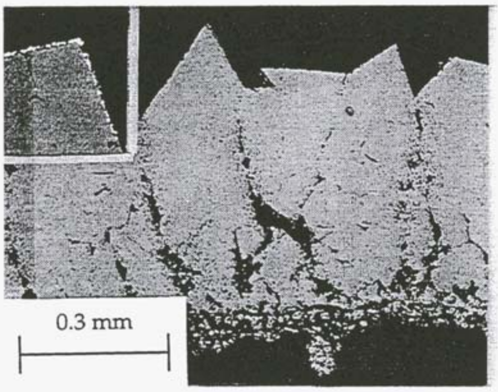

Figure 3 – Cross section of magnetite removed from J-line (Braithwaite, 1980).

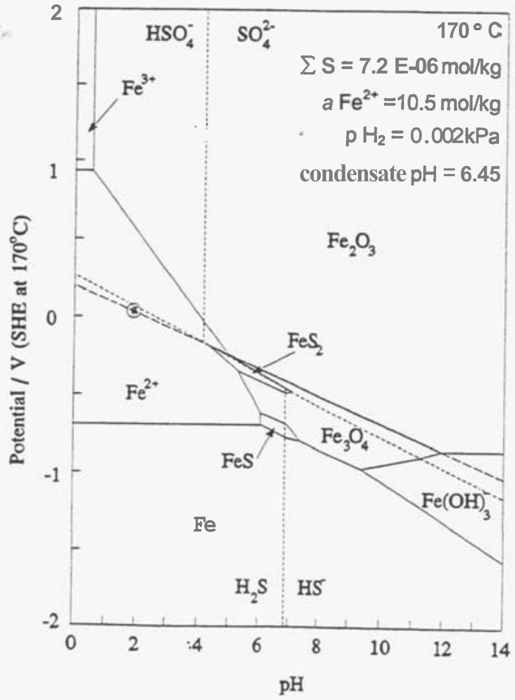

Figure 4 – Potential-pH 'Pourbaix' phase stability diagram for Wairakei steam pipeline (Inman, 1994).

Table 1 – Silica concentrations in catchPOT drains and MAGnetite scales removed from upstream sections of pipeline and corrosion PENetration observed in the pipelines (Stacey, **1980,** McAdam, **1980, Thain** et al., **1981).** Thain et al., **(1981)** indicated **no** continuing corrosion penetration **was** observed below the line, at the time when the silica discharges in the catchpot drains were measured.

Location	Pipe Lines											
	L			J			K			G		
	POT mg/kg	MAG wt?!	PEN mm	POT mg/kg	MAG wt%	PEN Mm	POT mg/kg	MAG wt%	PEN mm	POT mg/kg	MAG wt%	PEN mm
A1		**0.15**	**5.7**	**0.2**	**0.13**	**5.8**	**0.2**	-	**4.7**	**2**	-	
A2	**0.3**	**0.32**	**4.4**	**0.2**	**0.17**	**5.0**	**0.1**	**0.21**	**4.0**	**2**	**0.43**	-
A3	**0.2**	**0.17**	**4.5**	**0.5**	**0.26**	**3.9**	**0.2**	-	**2.9**		-	
A4	**0.1**	**0.11**	**4.0**	**0.4**	**0.27**	**4.2**	**0.2**	-	-	**5**		
A5	**0.1**	-	**3.0**	**2.8**	-	**4.6**	**3.7**	-	-	**13**		
A6	**0.1**	-		**1.7**	-	**2.1**	**29**	-	-	**66**		
A7	**0.1**	-		**6.8**	-	**2.3**	**0.6**	.		**47**		

The corrosion reaction in this case is the dissolution of iron by the reactions (Braithwaite, **1979, 1980):**

$$Fe + 2\,H_2O = Fe(OH)_2 + 2\,H_2 \qquad (1)$$

$$3\,Fe(OH)_2 = Fe_3O_4 + 2\,H_2O + 2\,H_2 \qquad (2)$$

which gives an overall reaction:

$$3\,Fe + 4\,H_2O = Fe_3O_4 + 8\,H_2 \qquad (3)$$

Under static or low flow conditions the reaction goes to completion in the vicinity of the corroding iron and magnetite is precipitated on the metal surface thereby blocking the metal from the corrosive condensate. Under flowing conditions the iron may go into solution and be precipitated downstream of the corroding location. The precipitation may be sufficiently uniform even under flowing conditions to protect the entire pipeline. Soylemezoglu et al. **(1980)** demonstrated increasing erosion rates with increasing condensate turbulence using externally located Corrosometer probes.

In the presence of a catalyst such a H_2S, the hydrogen generated from the reaction may be absorbed by the metal and **diffuse** through the metal to the outside of the pipe (McAdam et al, **1981).** The collection of hydrogen on the outside of corroding plant is an effective method of measuring corrosion rate.

Braithwaite **(1980)** argued that the magnetite **stability** depended on shutdown conditions. He proposed that under wet shutdown conditions when condensed steam containing dissolved sulfur species are exposed to air, an acid condensate containing $SO_4^=$ is formed and this readily attacks the iron at the magnetite-to-steel interface. Braithwaite, **(1979)** proposed that once the pipelines are returned to service the dissolution of iron at the magnetite-to-steel interface resulted in detachment **of** “patch” areas at locations of local flashing or condensate impingement.

The formation of acid condensates at wet shutdowns would also affect the stability of formed magnetite (Bohnsack, **1987)** and it can be argued that many of the magnetite films exhibit evidence **of** dissolution at the grain boundaries (see for example Figure **3).**

Braithwaite (**1980**) also observed that corroding patches moved upstream as the magnetite and pipe wall at the lip of the patch were corroded in the flowing condensate. Dissolved iron from corrosion of the base steel and from “reductive dissolution” of the upstream magnetite, then precipitated at the downstream edge of the patch and downstream **of** the patch.

Magnetite scales removed from upstream of actively corroding patch-like areas did have high porosity, however this high porosity could also have occurred by dissolution in clean condensate that was low in Fe^{++}. Figure **5** illustrates the dependence of magnetite solubility on pH in condensate formed in conventional boiler systems at high temperature **(McAdam** et al., **1981)**

Giggenbach **(1979)** proposed a model of variation in condensate chemistry and Fe” across and beyond the corroding patch-like areas under operating conditions. This model also suggests the limited size of the corroding patch-like areas is due to iron concentration levels being low at the upstream side of the patch and at saturation at the downstream side where deposition of magnetite tails is observed, Figure **2.**

The influence of silica distriiution was well documented (Table 1), but is not well understood The above observations, however led to a consensus that erosion corrosion in the lower sections of the pipeline was due to a change in the chemistry of the steam condensate due to steam scrubbing and removal of dissolved solids in catchpots distributed along the pipelines. Condensate removal lowered the level of silica, which was the intention of steam scrubbing originally advocated and in place to prevent silica and chloride, carried over from the steam/water separators that could enter and deposit on the steam turbines (McDowell, 1975). The onset of erosion in specific pipelines was correlated with removal of these dissolved solids, namely silica, by changes to steam field design which effectively increased the length of pipeline to which no steam separator carry-over was added. Although the mechanism of inhibition was not fully understood the re-introduction of separated geothermal water was advocated as a viable means of corrosion control provided turbines could be adequately protected.

4. ON-LINE EVALUATION OF CORROSION INHIBITORS

Proposals to control erosion corrosion by re-introduction of dissolved silica or separated water containing dissolved silica were debated because of the presumed risk to the steam turbines. Altemative proposals based on conventional, clean steam and recirculated condensate power station corrosion control methods were advocated to avoid steam turbine damage. Application of coatings was also proposed.

Two conventional thermal power station corrosion inhibitors (Stacey, 1979, Soylemezoglu et al, 1980, Thain et al., 1981) and separated water injection (McAdam et al., 1981, Thain et al., 1981, Bacon and Stacey, 1984) at a rate intended to simulate steam/water separator carryover, were trialled with varying effects:

- Octodacylamine – This filming amine required high levels of inhibitor to effect condensate corrosion rates (Thain et al., 1981). Finger type Corrosometer probe results (Soylemezoglu et al, 1980) and measurements of remaining wall thickness before and after the tests showed continuing corrosion (Stacey, 1979).
- Tri-sodium phosphate – Injection of this inhibitor resulted in a change in condensate pH from 6.5 to 8. Corrosometer probe corrosion rates decreased from over 125 µm/year to less than 10 µm/year within 5 days of commencement of injection (Soylemezoglu et al, 1981). A primary effect of the injection was that the magnetite film was totally stripped from the pipe walls (McAdam et al., 1981). Figure 5 gives a reason for this as the solubility of magnetite increases as pH is increased. The inhibiting effect is presumed to have been due to the formation of an iron phosphate film on the pipe walls (Bohnsack, 1976). The inhibition effect continued for 1 or 2 days after injection was stopped.
- Separated water (as a carrier of silica) – hydrogen evolution patches placed opposite previously corroding patches indicated a rapid decrease in evolved hydrogen and hence corrosion rate (Figure 6), corroding patches were successfully passivated through the formation of magnetite scales (Figure 7), (McAdam et al, 1981). The inhibiting effect again continued after injection was stopped.

Application of a coal tar epoxy after normal preparation by blasting, also prevented the onset of localised erosion corrosion (Stacey, 1981). This method of control was not continued because of the time (and cost) required for surface preparation and application of the coating and the known temporary nature of coal tar epoxy in geothermal steam, typically one to two years in geothermal steam turbine casing applications.

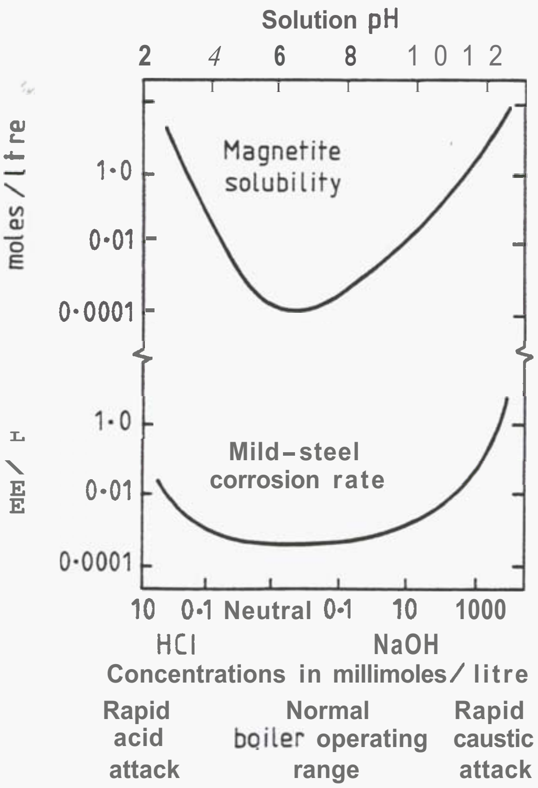

Figure 5 – Magnetite solubility in conventional boiler condensate environments at 300°C (reproduced from McAdam et al., 1981, Mann, 1976).

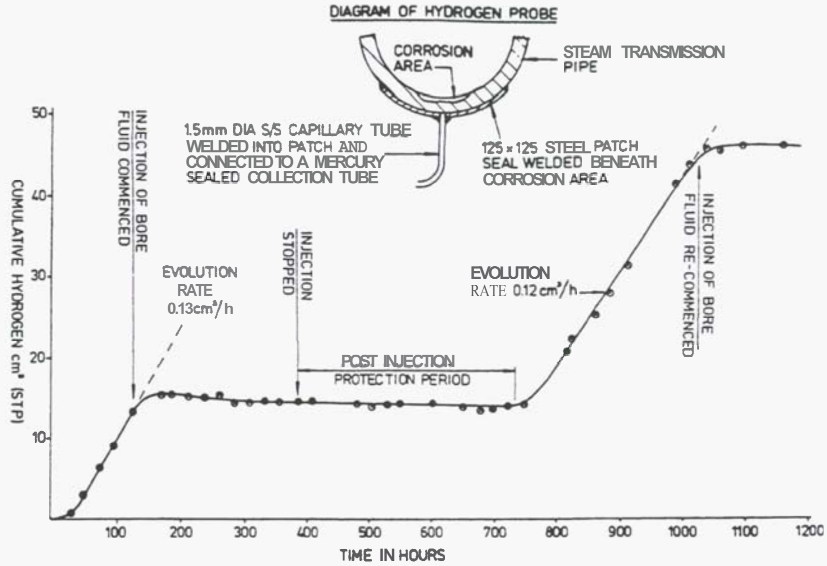

Figure 6 – Hydrogen evolution curves from a hydrogen patch probe located opposite an area of erosion corrosion (McAdam et al., 1981).

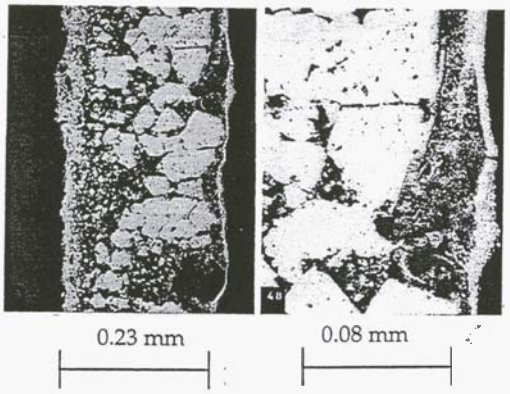

Figure 7 - Newly formed magnetite removed from passivated area opposite the hydrogen patch probe (McAdam et al., 1981). The metal was in contact with the film at the right of the figures. (Note the thin coherent layer of magnetite next to the metal which provides the protection.)

5. CORROSION CONTROL AND MONITORING

The cost of continuing application of tri-sodium phosphate was significant, in comparison with the use of separated water, because of the once through nature of the energy production process. A condition imposed by the desired use of separated water, as a corrosion inhibitor, was the presumed need to minimise unacceptable levels of silica and chloride entering the turbine. Maximum acceptable silica and chloride levels were set based on results of previous operating experience. A mathematical model was developed which simulated the scrubbing mechanism that occurs in saturated steam lines of different diameters allowing for differences in steam velocity, condensate production rate and catchpot efficiency (Stacey et al., 1981, Lee, 1982). The model calculated steam and condensate, silica and chloride levels at any point downstream of the injection point and provided sufficient confidence to trial the injection of separated water into all pipelines in 1984. The pump was installed at a point about 1500 metres upstream from the power station and has run almost continuously since that time. (Bacon and Stacey, 1984).

A condensate silica concentration greater than 1 to 2 mg/kg measured at catchpot drains has been demonstrated to be effective in controlling the corrosion in the majority of steam pipelines. A level of 1 mg/kg at the catchpots just before the power station was selected to avoid turbine contamination. Some erosion of deep corrosion patches continues in lines carrying excess condensate and in the steam headers.

Continued monitoring of hydrogen evolution patch type probes and by visual inspection has confirmed the efficiency of this method of corrosion control (Wilson, 1984).

6. EXPERIENCE WITH TURBINE CONTAMINANT LEVELS

The main concerns in this area relate to silica scaling and the potential for chloride induced stress corrosion cracking (SCC) of steam turbine rotors and corrosion fatigue of turbine blades. In general however no significant problems have resulted from the injection of separated water, although the low strength levels of turbine components at Wairakei may contribute to this good performance. It is also recognised that thermodynamic conditions have a significant effect on both scaling and SCC, perhaps greater than that of steam quality. Hence, where and when possible, the management of the steam supply system requires the avoidance of operating procedures which would otherwise produce superheat and conditions for concentrating dissolved solids. Specifically this requires limitations on the use of turbine throttle valves, pressure reducing valves and pipeline steam flows and pressures.

7. THE MECHANISM OF CORROSION CONTROL

The mechanism of the inhibition effect of silica on corrosion of carbon steel in the $Fe\text{-}S\text{-}H_2O$ systems of Wairakei and Ohaaki / Broadlands steam condensates has been further defined by Inman, (1994):

- In laboratory simulations of the Wairakei steam system, having low Total S ($H_2S + HS^- = 7.18x10^{-6}$ molkg) magnetite, Fe_3O_4 stability only was observed. Addition of dissolved SiO_2 to S fiee $Fe\text{-}H_2O$ systems and low S systems where magnetite was formed resulted in significant uptake if silicon (as SiO_2) that blocked the pores in the formed *film,* thereby limiting the corrosion rate.
- In simulations of the Ohaaki/Broadlands steam, having Total S ($H_2S+HS^- = 10^{-4}$ to 10^{-5} mol/kg) a duplex film of iron sulfides over magnetite was observed. Addition of dissolved SiO_2 to the higher S containing $Fe\text{-}S\text{-}H_2O$ system resulted in lesser amounts of entrained silicon, that was attributed to lesser amounts of silica being taken up by the sulfide films and silica not reaching the magnetite film at all. It was proposed that if erosion corrosion occurred in high S steam pipelines then addition of silica would not provide inhibition and that altemative corrosion inhibition methods would be required.
- Inspections of Ohaaki/Broadlands steam pipelines, where the duplex iron sulfide over magnetite scales are formed, have not revealed any incidence of patch-like erosion corrosion.

One reason for the apparent resistance of pipelines scaled with the duplex films may be that the sulfide scales are less susceptible to local breakdown in acid condensates and can readily precipitate at lower pH levels even under turbulent flow conditions (Tewari et al., 1979).

8. PARAMETERS OF INFLUENCE

Stability of magnetite scales was the predominant factor influencing the onset of erosion corrosion.

Moisture is required, erosion corrosion ceased in dry steam lines and was rare on the ceiling areas of wet steam pipelines.

Solution pH determines the solubility of magnetite, both at shutdown and while on-line, local variations can be present.

Temperature did not appear to influence the occurrence of erosion as it was observed in all pipelines at some time or other, insufficient data was obtained to relate penetration rates to temperature.

Flow path, geometry and velocity appeared to be significant factors in determining the initiation, distribution and severity of the erosion corrosion.

Condensate purity, primarily silica content strongly influenced the erosion corrosion, by providing inhibition through stabilisation of magnetite.

9. CONCLUSIONS

The successful use of carbon steel for geothermal steam pipelines at Wairakei depends on the formation of magnetite as a protective corrosion product. Localised breakdown of this corrosion product scale and erosion corrosion was first detected in 1977. The severity of the erosion was correlated with silica content of condensate in the saturated steam pipelines and with the level of silica (detected as silicon) in magnetite scales. Steam scrubbing by removal of condensate in catchpot drains distributed along the Wairakei steam pipelines was done to ensure silica and chloride present in steam entering the steam turbines were low; however, the levels reached produced a neutral pH condensate of high corrosivity. Two models for initiation of erosion corrosion have been proposed. One is the degradation of magnetite scales, particularly at the magnetite-to-metal interface in acidic fluids formed at wet pipeline shutdowns. Subsequent operation of the pipelines with high purity condensate fails to precipitate magnetite in the immediate vicinity of the corroding surface resulting in erosion. The second is the dissolution of magnetite under on-line conditions when condensate quality is high and Fe^{++} levels are extremely low. Both of these initiation mechanisms would lead to periodic patch-like erosion corrosion areas as the level of Fe* cycles fiom low levels at the upstream edge of the corroding areas to magnetite saturation levels at the downstream edge and back to low levels as magnetite is precipitated.

A controlled re-introduction of separated water as a carrier of silica was demonstrated as a viable method for inhibiting erosion corrosion and has been used in all steam pipelines for over 10 years. The inhibition effect has been shown to be due to blocking of pores which prevents fluid access to the underlying steel and helps to stabilise protective magnetite films.

10. ACKNOWLEDGMENTS

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