

**Assessment of the Role of  
the Acetic Acid/Acetate  
Buffer in Corrosion/Stress  
Corrosion Testing of  
Modified 13 Cr Stainless  
Steels and Carbon Steels**

**A Griffiths and A Turnbull**

**January 2003**

© Crown copyright 2003  
Reproduced by permission of the Controller of HMSO

ISSN 1473 2734

National Physical Laboratory  
Teddington, Middlesex, UK, TW11 0LW

Extracts from this report may be reproduced provided  
that the source is acknowledged

Approved on behalf of Managing Director,  
NPL, by Dr C Lea, Head, NPL Materials Centre

**CONTENTS**

SUMMARY .....	1
1 INTRODUCTION .....	1
2 SOLUTION CHEMISTRY .....	2
3 RECENT LITERATURE .....	2
3.1 13 Cr steels.....	2
3.1.1 Amaya and Ueda.....	2
3.1.2 Turnbull and Griffiths .....	3
3.2 C-steels.....	4
3.2.1 Crolet et al.....	5
3.2.2 Hedges and McVeigh.....	8
4 CONCLUSIONS.....	9
5 ACKNOWLEDGEMENTS .....	9
6 REFERENCES .....	9



**ASSESSMENT OF THE ROLE OF THE ACETIC ACID/ACETATE  
BUFFER IN CORROSION/STRESS CORROSION TESTING OF  
MODIFIED 13 Cr STAINLESS STEELS AND CARBON STEELS**

Aeronwen Griffiths and Alan Turnbull  
Materials Centre  
National Physical Laboratory  
Teddington, Middlesex TW11 0LW, UK

**SUMMARY**

Acetic acid and acetate anions are present in oil production fluids and are also used as a buffer system in laboratory testing in simulated produced waters. In the latter case, there has been controversy as to the possible direct effect of this buffer on the stability of the passive film on modified 13 Cr martensitic stainless steel outwith its role in maintaining constancy of pH. Also, there have been investigations into the role of this buffer in the corrosion of carbon steel with the intention of better reflecting its known enhancement of corrosion rates in service. The most recent literature has been evaluated.

For the modified 13 Cr martensitic stainless steel, the initial indication that the buffer can have a direct detrimental effect on the stability of the passive film when testing in NaCl solutions at pH 3.5 (with 1% H<sub>2</sub>S/bal. CO<sub>2</sub>) at 20 °C was not supported by a later more controlled study. In view of the later findings, the reduction in acetate concentration by a factor of 10 from the previously used value of 4 g/L, incorporated into the most recent EFC17 guidelines<sup>1</sup>, may not have been prudent. Maintenance of the solution pH in acidified H<sub>2</sub>S-containing environments at ambient temperature, when this steel is in the active state, may then become a problem.

In relation to the role of this buffer system in corrosion of carbon steel the indication from rotating cylinder testing at ambient temperature is that the acetic acid/acetate buffer can act as a weak anodic inhibitor when testing in a relatively innocuous environment (0.2 M NaClO<sub>4</sub>). In more relevant laboratory testing at 50 °C or 60 °C with bubbling CO<sub>2</sub>, bicarbonate and chloride, the presence of this buffer enhanced the corrosion rate. The enhancement was not related to the bulk solution. pH. The most likely explanation is that dissociation of acetic acid is the predominant process in buffering the rise in pH at the cathodic regions. Provided the supply of acetic acid to the surface is sustained, then, correspondingly, the dissociation of CO<sub>2</sub> or bicarbonate, the alternate buffering mechanisms, would be much reduced. This would then limit the formation of bicarbonate and carbonate respectively, thus limiting the formation of protective deposits. In addition, acetic acid causes dissolution of existing iron carbonate films. Technically, a problem for simulated service testing is sustaining the acetic acid concentration without the need for regular refreshment. A gas mixture comprising CO<sub>2</sub> with acetic acid vapour is proposed but recirculation through the test cell from a large reservoir would seem to be required also for more direct relevance to service.

The contrasting effects of the acetic acid/acetate buffer on the modified 13 Cr steel in the active state at pH 3.5 at 20 °C and on the carbon steel in the bicarbonate solutions at 50 °C is due to the fact that in the former the acid conditions and lower temperature constrain the formation of protective carbonate films.



## 1 INTRODUCTION

The corrosion behaviour and hence the cracking resistance of martensitic stainless steels are strongly dependent on the pH of the environment. The pH of formation and condensate waters is determined generally by the pressure of CO<sub>2</sub> and the concentration of bicarbonate ions. In laboratory tests designed to select materials for specific applications the CO<sub>2</sub> pressure and concentration of bicarbonate ions are simulated. However, for general ranking tests at ambient temperature artificial buffers are often used to control the pH, enabling tests to be conducted at atmospheric pressure.

The critical pH affecting corrosion behaviour is not the bulk pH but the pH at the metal-solution interface, which will tend to rise in unbuffered solutions under freely corroding conditions. The increase in pH may be significant when the steel is in the active state with a high corrosion rate. In the passive state, with a relatively low dissolution rate, the elevation in pH at the surface would tend to be more modest but would depend on the magnitude of the passive current density.

In well-stirred solutions, mixing encourages maintenance of the bulk chemistry at the metal surface whether in service or in the laboratory. The problem for laboratory testing is often that tests are carried out for pragmatic reasons under stagnant flow conditions without refreshment and with no forced convection or with flow conditions that are not related to service conditions. Under these conditions, a strong buffering agent may be required to maintain the pH at the metal surface at the same value as the bulk solution.

The contentious issue for buffering is not the maintenance of the pH per se, as its significance there is clear, but whether the particular buffer agent alters the stability of the passive film directly. A buffering solution should control the pH but in no other way influence the electrochemistry. Confusion has arisen because of mixed reports of the role of the acetic acid/acetate buffer system in the corrosion behaviour of modified 13 Cr martensitic stainless steel but also perhaps because of perceptions based on its role in the corrosion of carbon steels. The objective of this short report is to highlight the findings of some recent papers and to provide a clear guidance with respect to laboratory testing.

## 2 SOLUTION CHEMISTRY

Reaction	K (25 °C) (equil. const. or solubility constant)	K (50 °C) (equil. const. or solubility constant)	Reference
$\text{CH}_3\text{COOH}(\text{aq}) = \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$	$1.64 \times 10^{-5}$	$1.54 \times 10^{-5}$	x
$\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq})$	$3.42 \times 10^{-2}$	$1.98 \times 10^{-2}$	y
$\text{H}_2\text{O}(\text{aq}) + \text{CO}_2(\text{aq}) = \text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq})$	$4.43 \times 10^{-7}$	$5.20 \times 10^{-7}$	y
$\text{HCO}_3^-(\text{aq}) = \text{CO}_3^{2-}(\text{aq}) + \text{H}^+(\text{aq})$	$4.71 \times 10^{-11}$	$6.81 \times 10^{-11}$	y
$\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) = \text{CaCO}_3(\text{c})$	$5.02 \times 10^{-9}$	$3.00 \times 10^{-9}$	y+z
$\text{Ca} + 2\text{HCO}_3^{2-} = \text{Ca}(\text{HCO}_3)_2(\text{c})$	Data not available		
$\text{Fe}^{2+} + 2\text{HCO}_3^- = \text{Fe}(\text{HCO}_3)_2(\text{c})$	Data not available		
$\text{Fe}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) = \text{FeCO}_3(\text{c})$	$5.30 \times 10^{-9}$	$1.98 \times 10^{-9}$	x+z
$\text{Fe}^{2+} + 2\text{CH}_3\text{COO}^- = \text{Fe}(\text{CH}_3\text{COO})_2(\text{c})$	Data not available		

c – crystalline

x) MTDATA implementation of the Supercrit98 database (MTSPCRT), version 1.3

y) NPL Aqueous database (MTAQ), version 2.0

z) SGTE Substance Database, version 10.0

## 3 RECENT LITERATURE

### 3.1 13 Cr STEELS

#### 3.1.1 Amaya and Ueda

Amaya and Ueda<sup>2</sup> evaluated the effect of acetate concentration on the corrosion of a super 13 Cr steel. The environment was 5% NaCl with 0.4 or 4.0 g/L CH<sub>3</sub>COONa (equivalent to  $4.9 \times 10^{-3}$  or  $4.9 \times 10^{-2}$  M). The pH was adjusted to 3.5 using acetic acid. On deaeration, the corrosion potential was about -0.365 V (SCE) at both levels of acetate (Figure 1). When CO<sub>2</sub> containing 1% H<sub>2</sub>S was bubbled through the solution the potential remained relatively unchanged and the surface remained shiny in the solution containing 0.4 g/L CH<sub>3</sub>COONa. However, in the solution containing 4.0 g/L CH<sub>3</sub>COONa the potential decreased rapidly to -0.590 V (SCE) and the specimen surface appeared dark indicating that the specimen had become active. Amaya and Ueda concluded that acetate at the higher concentration was affecting the stability of the passive film.

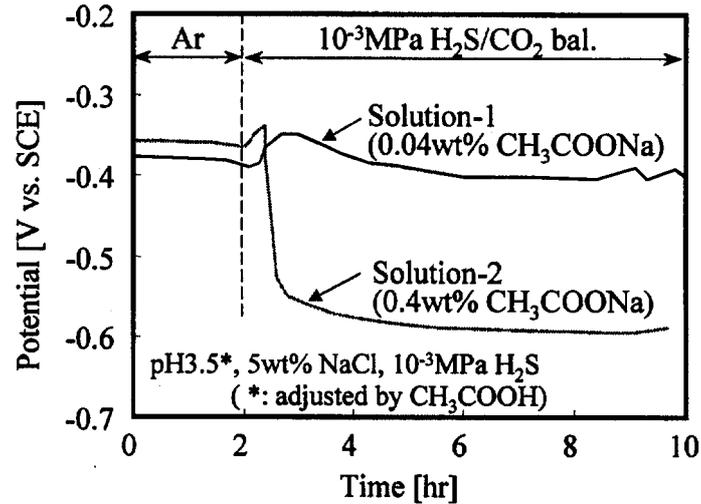


Figure 1. Corrosion potential of super 13 Cr steel as a function of time (pH 3.5, 5 wt% NaCl, 0.001 MPa H<sub>2</sub>S, 25 °C)

### 3.1.2 Turnbull and Griffiths

As the results reported by Amaya and Ueda had initiated a major reconsideration of proposed solutions for testing in EFC 17 guidelines, Turnbull and Griffiths<sup>3</sup> attempted to validate their work. Tests were conducted using a super 13 Cr steel in 5% NaCl with 0.4 or 4.0 g/L CH<sub>3</sub>COONa (equivalent to  $4.9 \times 10^{-3}$  or  $4.9 \times 10^{-2}$  M). The pH was adjusted to 3.5 using either acetic acid or HCl. Tests were conducted under quasi-stagnant (only gas bubbling) and in vigorously stirred (magnetic stirrer) conditions. When the environment was deaerated, the corrosion potential was about -0.450 V (SCE) (Figure 2). This was not affected by the concentration of acetate, the extent of stirring or whether HCl or acetic acid was used to acidify the solution. On bubbling of 1% H<sub>2</sub>S/bal. CO<sub>2</sub> through the solution the potential decreased rapidly to -0.600 V (SCE) and the specimen surface appeared dark, indicating that the material was actively corroding, as confirmed by anodic polarisation tests. This behaviour occurred at both levels of acetate and with solution acidified by HCl or by acetic acid. There was no evidence that the concentration of acetate affected the stability of the passive film. Some effect of acetate/acetic concentration on the anodic polarisation behaviour was noted in unstirred solutions with the current in the 'quasi-passive' region being higher at the lower concentration of acetate. During anodic polarisation tests the pH at the specimen surface tends to decrease due to hydrolysis of chromium ions. At the lower acetate concentration the buffering capacity is not sufficient to constrain this change in pH.

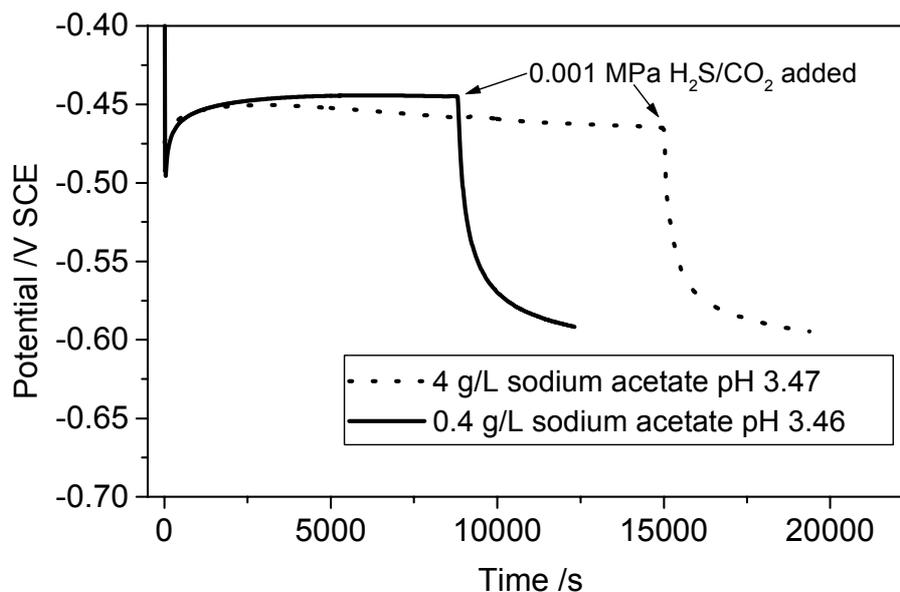


Figure 2. Corrosion potential time behaviour for super 13 Cr steel in 5 wt% NaCl with acetate and with acetic acid added to achieve acid pH. The solution was quasi-stagnant.

It is not clear why these results are different from those of Amaya and Ueda but is most likely related to the details of the test procedure since the steel composition and surface preparation were broadly similar. A possible significant factor is that Turnbull and Griffiths measured a more negative corrosion potential than Amaya and Ueda in the deaerated solution prior to the addition of  $\text{CO}_2/\text{H}_2\text{S}$  gas mix. A corrosion potential similar to that reported by Amaya and Ueda was measured on one occasion when there was accidental oxygen ingress in one test via diffusion through a PTFE connecting tube.

The effect of the work of Amaya and Ueda combined with general misunderstanding of the dependence of surface pH on flow and buffer capacity<sup>4</sup> led to a reappraisal of the EFC 17 guidelines and a recommendation for the use of 0.4 g/L for supermartensitic stainless steels instead of the previous value of 4 g/L. The revision of NACE TM0177-96 currently being balloted also includes this revision. That does not mean that it is inherently a bad move but the reduced buffer capacity may pose a problem in sustaining pH through the period of a test in acidified  $\text{H}_2\text{S}$ -containing environments at ambient temperature when the steel is in the active state. Since it is very difficult to adjust the pH during the test without letting in oxygen, it may not be an ideal choice of buffer concentration. Unless there is convincing evidence to the contrary, 4g/L may still be the best bet.

### 3.2 C-STEELS

There have been two key studies<sup>5,6</sup> of the role of the acetic acid/acetate buffer in the corrosion of C-steels prompted by the known detrimental effect in service and inconsistency of laboratory testing in that context.

### 3.2.1 Crolet et al

Crolet et al<sup>5</sup> set out to establish why acetic acid is perceived to enhance corrosion rates in service but often testing in the laboratory shows variable results. Two sets of test were carried out, viz. anodic polarisation and corrosion rate measurements at ambient temperature; corrosion rate measurements at 50 °C.

#### 3.2.1.1 Anodic dissolution at ambient temperature

The authors evaluated the effect of acetic acid on anodic dissolution using carbon steel rotating cylinder electrodes but in a relatively simple solution with acetic acid/acetate as the primary buffer system. A base solution of 0.2 M NaClO<sub>4</sub> was used as it is 'inert'. Tests were conducted at 22 °C. Acetic acid was added in the range 0.001 to 1 M and the pH was adjusted to the required value by adding HClO<sub>4</sub> or NaOH. Anodic polarisation scans were conducted in solution of pH 5 with either N<sub>2</sub> or CO<sub>2</sub> bubbled through the solution. Under 1 bar CO<sub>2</sub> (or in N<sub>2</sub>) at a constant pH of 5, increasing the concentration of acetic acid from 0.001 M to 1 M (equivalent to increasing the acetate concentration at constant pH of 5) moved the corrosion potential to more positive values and generally decreased the magnitude of the anodic current; i.e. the presence of acetic acid/acetate is inhibiting the dissolution process (Figure 3). An explanation based on the buffer solution constraining a decrease in pH at the surface due to hydrolysis of ferrous ions is feasible but the authors would argue that with a rotating cylinder at 4000 rpm that is very unlikely. Also, any pH decrease at the steel surface in this solution is limited and would not get below pH 4 (the limiting value for saturated ferrous chloride). Since an inhibition effect was observed in corrosion rate studies at pH 4 also (Figure 4), this would confirm the anodic inhibitive effect of the acetic acid/acetate buffer.

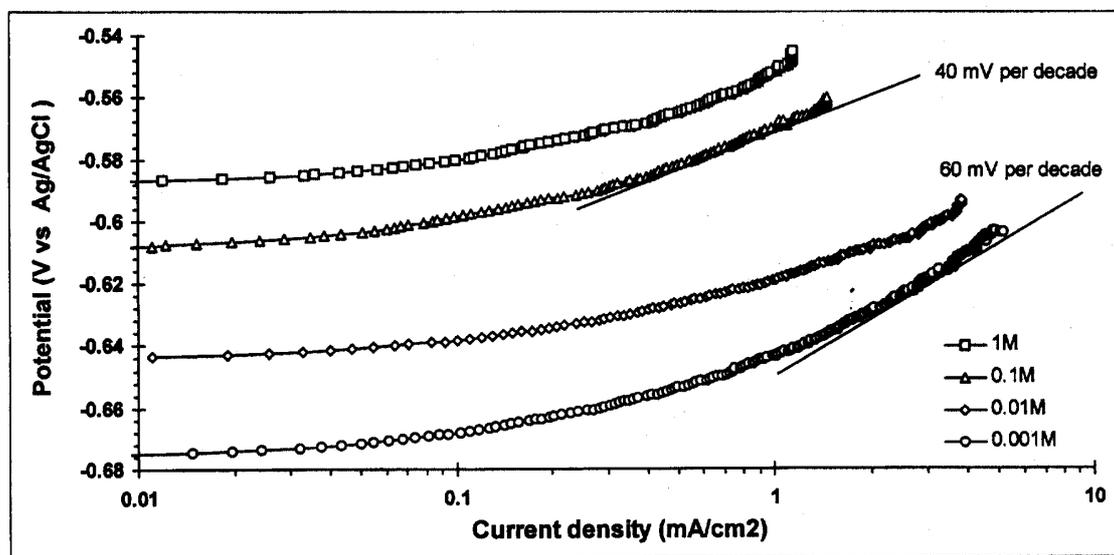


Figure 3. Anodic polarisation curves in 1 bar CO<sub>2</sub>, pH 5, CH<sub>3</sub>COOH = 0.001 to 1 M, NaClO<sub>4</sub> = 0.2 M, T = 22 °C, 400 rpm, steel X65.

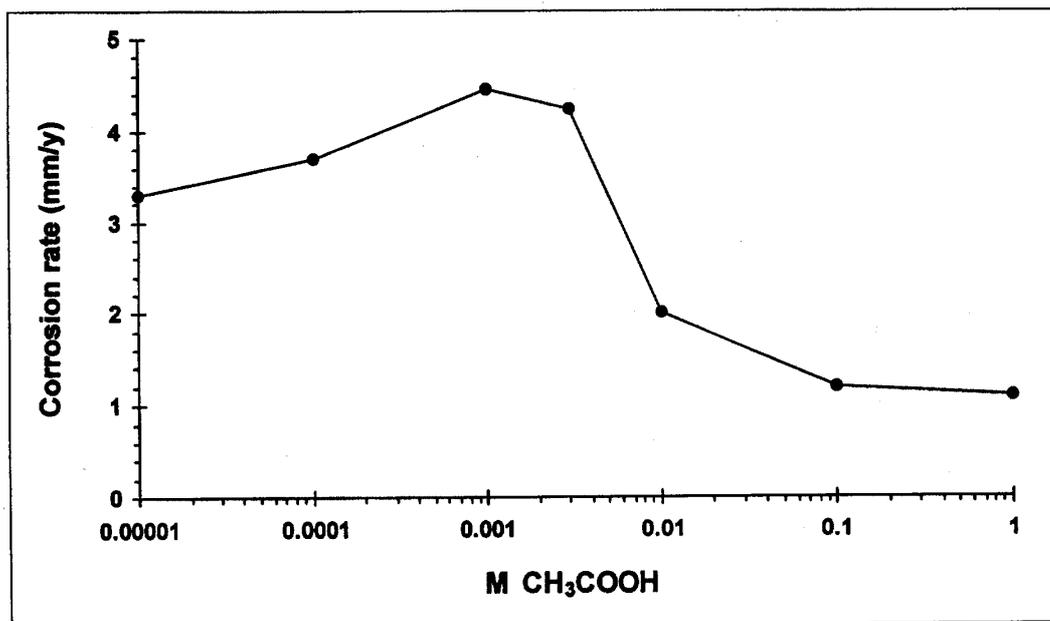


Figure 4. Corrosion rates as a function of acetic acid concentration, at pH = 4, 1 bar CO<sub>2</sub>, 4000 rpm, T = 22 °C, NaClO<sub>4</sub> = 0.2 M.

However, it should be emphasised that the supporting electrolyte was chosen to examine the direct effect of the acetate on the anodic dissolution in the absence of an aggressive anion like chloride, which would probably swamp the weak inhibiting influence of the acetate. Unfortunately, complementary tests in chloride were not conducted to confirm this perspective. No data were provided to assess the impact of the acetic acid/acetate mixture on the cathodic reactions but Crolet et al stated, without reference, that the acetate/acetic acid buffer had no effect on the cathodic reaction kinetics.

### 3.2.1.2 Corrosion tests at 50 °C

In contrast to the ambient temperature tests, the measurement at 50 °C were conducted in a cell with little solution agitation except by bubbling of 1 bar CO<sub>2</sub> gas. The corrosion rate of carbon steel was measured over 7 days using LPR in a base solution usually of 1M NaCl (CaCl<sub>2</sub> is the exception) at pH 5.18. The essential results are summarised in Figure 5. The solution contained 3 mM NaHCO<sub>3</sub> with the exception of the 0.5 M CaCl<sub>2</sub> solution, which contained 4 mM NaHCO<sub>3</sub>. The initial concentration of sodium acetate was 10 mM. The low current density at the high level of CaCl<sub>2</sub> is simply related to formation of calcium carbonates, which can block both the anodic and cathodic process.

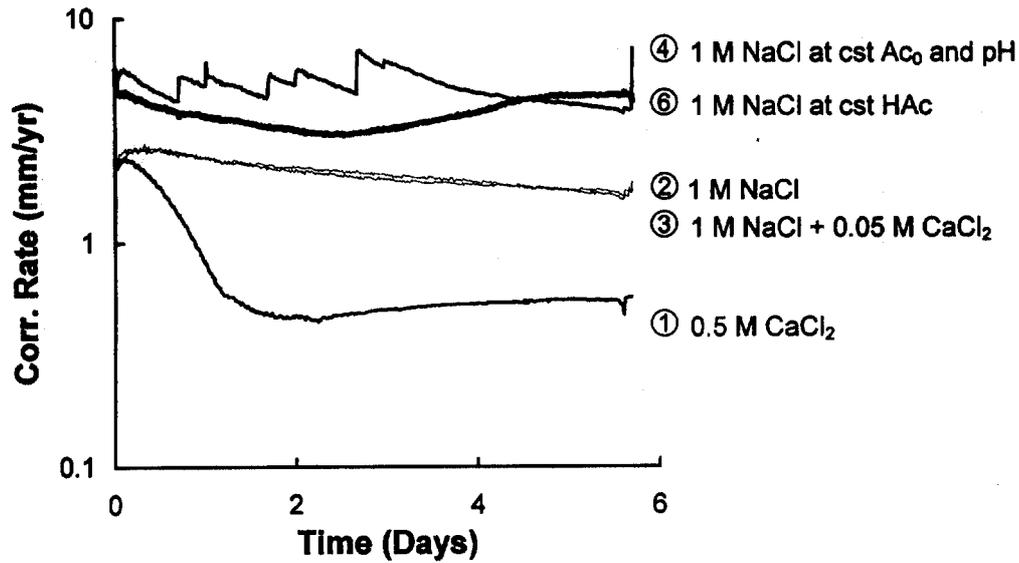


Figure 5. Variation of corrosion rate with time (1 bar  $\text{CO}_2$ , 50 °C, pH  $\approx$  5.2).

When acetate was present the corrosion rate was higher than the equivalent acetate-free solution by a factor of 2-3. In Test 4 the corrosion rate decreased as the acetic acid was depleted and then increased rapidly when it was replenished. In Test 6 the higher corrosion rate was sustained by using a  $\text{CO}_2$ /acetic acid vapour gas mixture. The essential role of the acetic acid is to constrain the pH increase at the cathodic region of the steel surface. By virtue of being the stronger acid, this tends to dominate over the  $\text{CO}_2$  and  $\text{HCO}_3^-$  buffers. As a consequence, there is less  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  formed and a reduced level of protective precipitation products on the surface. The fact that addition of acetic acid in Test 4 increased the corrosion rate demonstrates that acetic acid caused dissolution of iron carbonate.

The issue is the availability of the acetic acid at the metal surface. This will depend on local transport kinetics and the bulk concentration. Since acetic acid is depleted in converting to the acetate it is necessary to refresh the bulk solution. Crolet et al propose the use of a gas mixture containing a partial pressure of acetic acid vapour, as that would then provide a fix for the bulk acetic acid concentration. However, this does not deal adequately with the problem of accumulation of products in poorly agitated solutions of constrained volume. To maintain the bulk solution constant, recirculation from a sufficiently large reservoir is required.

There remains still the issue of local mass transport at the surface. Where this is constrained and precipitation products start to develop, replenishment of HAC may be poor and bicarbonate and carbonate may begin to dominate the anion chemistry (relative to acetate). Thus protective layers build up still. In acidified environment, it is harder to generate the protective layers as the bicarbonate concentration is low and local mass transport constraints to acetic acid replenishment due to layers no longer exist.

Crolet et al argue that the presence of acetic acid will help to stabilise localised corrosion by maintaining the efficiency of the cathodic reaction for the reasons indicated whilst there is little change in environment at the anode. This is probably true once pits have developed but

the presence of acetate anions may constrain the initial development by constraining local acidification.

### 3.2.2 Hedges and McVeigh

Hedges and McVeigh<sup>6</sup> also investigated the effect of acetate on the corrosion of carbon steels, a factor thought to have contributed to a service corrosion failure at Wytch Farm.

Tests were conducted on carbon steel specimens in a glass cell with a magnetic stirrer. The corrosion rates were measured using LPR. Tests were conducted at 60 °C, 1 bar CO<sub>2</sub>, in 3 environments: 3% NaCl, synthetic seawater (0.20 g/L NaHCO<sub>3</sub>), and synthetic brine (0.067 g/L NaHCO<sub>3</sub>).

Addition of acetate (as acetic acid) in the range 25 –5000 ppm acetate (equivalent to  $3.0 \times 10^{-4}$  to 0.06 M) to 3% NaCl increased the corrosion rate by up to a factor of more than 5. In this study, the initial pH would decrease as the concentration of acetate increased. The corrosion rate increased with exposure time initially but consumption of acetic acid with time resulted in a corrosion rate that eventually decayed to that in the absence of acetic acid, as confirmed by addition of more acetic acid. By measuring the pH with time, comparison of corrosion rates for equivalent pH values suggested a distinct effect of acetic acid on the corrosion rate, which the authors attributed to the distinct role of the acetate anion.

The tests were repeated with varying concentrations of CH<sub>3</sub>COONa (25 ppm – 5000 ppm acetate, equivalent to  $3.0 \times 10^{-4}$  to 0.06 M), rather than acetic acid, in 3% NaCl. The corrosion rate was found to increase with acetate concentration despite the higher pH. Note the contrast with the weak inhibitive effect observed by Crolet et al in 0.2 M NaClO<sub>4</sub> at ambient temperature.

The reported variation with time in corrosion rate in 3% NaCl (no acetate) was not consistent, with one test indicating a small increase, another showing little change and one showing a decrease. A decrease might have been expected due to the elevation of pH from about 4 to 5.8.

For the simulated Wytch Farm solution and the seawater solution, acetate was also found to increase the initial corrosion rate.

Polarisation studies in 3 % NaCl (1 bar CO<sub>2</sub> and 60 °C) with either acetate or acetic acid suggest an increased cathodic reduction rate in both cases, even in the higher pH sodium acetate solution. It is not clear that the initial surface condition was comparable in all the tests and it appears that acetate was added to the solution after the scan in the absence of acetate had been conducted. The authors postulate an effect due to iron carbonate formation in the absence of acetate; the iron is presumed to come from initial dissolution at open circuit for 1 hour prior to cathodic polarisation. This film limits hydrogen ion transport in contrast to the thinner or film-free surface in the sodium acetate or acetic acid solutions. The role of acetate, they consider to be due to ‘solubilising of the ferrous ions’, the acetate being a chelating ion for ferrous ions, so that they remain in solution. The explanation of Crolet et al of the acetate in the form of acetic acid constraining the pH increase due to cathodic reaction would seem a

more tenable explanation. In this case, the ferrous ions remain in solution because there is less carbonate formed.

Hedges and McVeigh also go on to note the possibility of errors in bicarbonate concentration measurement due to acetate, which can lead to an overestimation of its value.

#### **4 CONCLUSIONS**

Whilst further work would be of value, the latest results do not support an effect of acetate concentration on the corrosion behaviour of modified 13 Cr martensitic stainless steel in solution of pH 3.5 with 1% H<sub>2</sub>S/bal. CO<sub>2</sub> at ambient temperature.

The tenfold decrease in acetate concentration in the revised EFC17 guidelines and in the proposed revision of TM0177-96 may pose problems in maintaining the pH constant during testing in solutions for which the alloy is in the active state.

For carbon steels, tests at 50 °C to 60 °C indicate that the acetate/acetic acid buffer system can enhance the corrosion rate, primarily by virtue of restraining the pH increase at cathodic areas and the build up of the bicarbonate and carbonate concentrations sufficient to form protective layers in the presence of ferrous ion in excess of the solubility limit. In addition, acetic acid causes dissolution of existing iron carbonate films.

There are no specific data for the acidic environments associated with Test Solution A and B for TM0177-96 but in view of the low pH of these solutions, the low concentration of bicarbonate ions and the lower temperature it might be envisaged that an effect of acetate would not be apparent.

#### **5 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 BP, Shell Exploration, Halliburton KBR, ConocoPhillips, HSE and ChevronTexaco.

#### **6 REFERENCES**

1. Corrosion Resistant Alloys for Oil and Gas Production: Guidance on General Requirements and Test Methods for H<sub>2</sub>S Service’, 2<sup>nd</sup> edition, European Federation of Corrosion, Publication Number 17, Institute of Materials, 2002.
2. H. Amaya and M. Ueda, Corrosion 99, Paper No. 585, NACE Int., Houston, 1999.
3. A. Turnbull and A. J. Griffiths, ‘An evaluation of the effect of artificial buffers on the corrosion and electrochemistry of super 13 Cr steel’ Paper no. 010, Supermartensitics 2002, KCI Publishing BV, 2002.
4. A. Turnbull and A. J. Griffiths, ‘Corrosion and Cracking of Weldable 13 Cr Martensitic Stainless Steels – A Review’, NPL Report MATC(A)108, 2002.

5. J.L. Crolet, N. Thevenot and A. Dugstad, 'Role of free acetic acid on the CO<sub>2</sub> corrosion of steels', Corrosion 99, Paper No.24, NACE Int., Houston, 1999.
6. W. Hedges and L. McVeigh, The role of acetate in CO<sub>2</sub> corrosion: the double whammy', Corrosion 99, Paper no. 21, NACE Int., Houston, 1999.