LOW TEMPERATURE AND HIGH SALT CONCENTRATION EFFECTS ON GENERAL CO₂ CORROSION FOR CARBON STEEL

A thesis presented to

the faculty of

the Russ College of Engineering and Technology of Ohio University

In partial fulfillment

of the requirement for the degree

Master of Science

Haitao Fang

November 2006

This thesis entitled

LOW TEMPERATURE AND HIGH SALT CONCENTRATION EFFECTS ON GENERAL CO₂ CORROSION FOR CARBON STEEL

by

HAITAO FANG

has been approved for

the Department of Chemical and Biomolecular Engineering

and the Russ College of Engineering and Technology by

Srdjan Nesic

Professor of Chemical and Biomolecular Engineering

Dennis Irwin

Dean, Russ College of Engineering and Technology

ABSTRACT

FANG, HAITAO, M.S., November 2006, Chemical and Biomolecular Engineering <u>LOW TEMPERATURE AND HIGH SALT CONCENTRATION EFFECTS ON</u> GENERAL CO₂ CORROSION FOR CARBON STEEL (113 pp.)

Director of Thesis: Srdjan Nesic

In this study, the low temperature and high salt concentration effects on CO₂ corrosion have been investigated using electrochemical techniques and weight loss (WL) measurements. The study started with general CO₂ corrosion experiments at low temperatures (1 – 10°C). It was found that the general CO₂ corrosion rate significantly decreased as the temperature decreased. The general CO₂ corrosion rate was found to be under charge transfer control at low temperatures (1 – 10°C). It was also found that the experimental data were not consistent with the data predicted by the most advanced corrosion prediction model.

A series of experiments were also performed to study high salt concentration effects on general CO_2 corrosion. The corrosion rates of carbon steel were found to be significantly affected by the high content of salt. The corrosion rates decrease significantly and nonlinearly with the increase of salt concentration. It was also found from the potentiodynamic results that the high salt concentration retarded the cathodic reaction, the anodic reaction and the limiting current.

A modification to the well known published electrochemical model was made to account for the low temperature and high salt effects. The modified model agrees well with the experimental data at low temperatures and high salt concentrations. Approved:

Srdjan Nesic

Professor of Chemical Engineering and Biomolecular Engineering

DEDICATION

То

Suocheng Fang, and Fanai Qu (my parents)

Lei Huang (my wife)

Haiyan Fang and Haifeng Fang (my sister and brother)

ACKNOWLEDGEMENTS

I would like to express my great gratitude to Dr. Srdjan Nesic for his generous guidance and support of my research. In addition, I am fortunate to be able to pursue my Ph.D. degree with Dr. Nesic.

I would like to acknowledge my indebtedness to Mr. Bruce Brown, my research group leader for his invaluable advice.

I would also like to thank the technical staff at the Institute for Corrosion and Multiphase Technology, including Mr. Al Schubert and Mr. John Goettge for their assistance in technical matters, and my fellow students: Wei Sun, Jiabin Han, and Yang Yang for providing a wonderful research environment.

I would also like to acknowledge the contribution of the consortium of companies whose continuous financial support and technical guidance made this research possible.

TABLE OF CONTENTS

7

ABSTRACT	3
DEDICATION	5
ACKNOWLEDGEMENTS	6
LIST OF TABLES	9
LIST OF FIGURES	10
CHAPTER 1 INTRODUCTION	15
CHAPTER 2 LITERATURE REVIEW	18
2.1 CO ₂ corrosion	18
2.2 The effect of CO ₂ partial pressure	20
2.3 The effect of temperature	20
2.4 The effect of flow	21
2.5 The effect of pH	
2.6 The corrosion product film	22
CHAPTER 3 RESEARCH OBJECTIVES AND TEST MATRICES	23
3.1 Research objectives	23
3.2 Test matrices	23
CHAPTER 4 EXPERIMENTAL SETUP AND CORROSION MEASUREMENTS	25
4.1 Specimen preparation	25
4.2 Experimental setup	25
4.3 Measurement techniques	28
4.3.1 Electrochemical measurements.	
4.3.2 Weight loss measurements	30
CHAPTER 5 RESULTS AND DISCUSSION OF LOW TEMPERATURE RESEAR	СН
PROGRAM	31
5.1 Flow velocity effects on general CO ₂ corrosion at low temperatures	31
5.2 pH effects on general CO ₂ corrosion at low temperatures	36
5.3 Temperature effect on general CO ₂ corrosion	39

	8
5.4 Corrosion mechanism analysis	40
CHAPTER 6 RESULTS AND DISCUSSION OF HIGH SALT CONCENTRATION	
RESEARCH PROGRAM	42
6.1 pH measurement	42
6.2 Experimental results at 5°C	46
6.2.1 Tests with 3 wt% NaCl	47
6.2.2 Tests with 10 wt% NaCl	49
6.2.3 Tests with 20 wt% NaCl	50
6.2.4 Tests with 25 wt% NaCl	52
6.2.5 Summary of salt effect on corrosion process at 5°C	53
6.3 Experimental results at 20°C	57
6.3.1 Test with 3 wt% NaCl	60
6.3.2 Test with 10 wt% NaCl	62
6.3.3 Test with 20 wt% NaCl	63
6.3.4 Summary of salt effect on corrosion process at 20°C	65
6.3.5 The effect of salt at higher pH	67
CHAPTER 7 ELECTROCHEMICAL MODEL	71
7.1 H^+ reduction	71
$7.2 \text{ H}_2\text{CO}_3$ reduction	73
7.3 Water reduction	
7.4 Iron dissolution	
7.5 Modeling the low temperature effect	
7.6 Modeling the high salt concentration effect.	
7.6.1 Rationale for the salt retardation factors related to charge transfer	
(electrochemical) reactions	94
7.6.2 Salt retardation factors on limiting currents.	96
7.6.3 Comparison between the revised electrochemical model and experimental	
results at different salt concentrations.	98
CHAPTER 8 CONCLUSIONS AND FUTURE WORK	.108
8.1 Conclusions	.108
8.2 Future work	.108
REFERENCES	.110

LIST OF TABLES

9

Table 1.	A water analysis summary for a Texan gas flow well	17
Table 2.	Test matrix for low temperature research program	24
Table 3.	Test matrix for high salt research program	24
Table 4.	Chemical composition of C1018 carbon steel (wt%)	25
Table 5.	Tafel slopes at different temperatures	31
Table 6.	Weight loss corrosion rate in CO ₂ purged solution	36
Table 7.	B value calculations at pH 4, 20°C	58
Table 8.	Activation energy for different reactions at different temperatures	80
Table 9.	Best-fit values of the Frumkin isotherm for the salt inhibition of the anodic	and
cath	nodic reaction	94
Table 10	. Best-fit values of the Frumkin isotherm for the salt inhibition of mass trans	sfer
		97

LIST OF FIGURES

Figure 1. Schematic of a glass cell	. 27
Figure 2. Comparison between the potentiodynamic sweeps with two scan rates in CC) ₂
purged solutions (1000 rpm, 5°C, pH 5, 3 wt% NaCl)	. 30
Figure 3. Flow velocity effect on corrosion rate in CO2 purged solutions as measured	by
LPR (100 – 6000 rpm, pH 4, 3 wt% NaCl, 10°C)	. 32
Figure 4. Flow velocity effect on corrosion rate in CO ₂ purged solutions as measured	by
LPR (100 – 7000 rpm, pH 4, 3 wt% NaCl, 5°C)	. 33
Figure 5. Flow velocity effect on potentiodynamic sweeps in CO ₂ purged solutions (1	00
– 6000 rpm, pH 4, 3 wt% NaCl, 5°C)	. 34
Figure 6. Flow velocity effect on corrosion rate in CO ₂ purged solutions as measured	by
LPR (1000 – 4000 rpm, pH 4, 3 wt% NaCl, 1°C)	. 35
Figure 7. Flow velocity effect on potentiodynamic sweep in CO ₂ purged solutions (10)00
– 4000 rpm, pH 4, 3 wt% NaCl, 1°C)	. 35
Figure 8. LPR corrosion rate in CO_2 purged solutions as measured by LPR (100 – 400	00
rpm, pH 4, pH 5, pH 6, 3 wt% NaCl, 5°C)	. 37
Figure 9. Potentiodynamic sweep in CO_2 purged solutions (100 – 4000rpm, pH 5, 3	
wt% NaCl, 5°C)	. 38
Figure 10. Potentiodynamic sweep in CO_2 purged solutions (100 – 4000 rpm, pH 6, 3	• •
wt% NaCl, 5°C)	. 38
Figure 11. Corrosion rates in CO_2 purged solutions under the condition of pH 4, 1000	~
rpm, 3 wt% NaCl and different temperatures as measured by LPR (1°C, 5°C, 10°C	200
and 25 °C)	. 39
Figure 12. The comparison of LPR corrosion rate, WL corrosion rate and theoretical	41
corrosion rate derived from potentiodynamic sweeps at pH 4, 1°C, 2000 rpm	. 41
Figure 13. The comparison of LPR corrosion rate, WL corrosion rate and theoretical	4.1
corrosion rate derived from potentiodynamic sweeps at pH 4, 5°C, 2000 rpm	. 41
Figure 14. Salt concentration effect on pH measurements in CO_2 purged solution (5°C,	, 3
wt% to 25 wt% NaCl, total pressure 1 bar). (2000)	. 43
Figure 15. Salt concentration effect on pH measurement in CO_2 purged solution (20°C,	, 3
wt% to 20 wt% NaCl, 10tal pressure 1 bar)	. 44 +
Figure 16. Calculated activity coefficient change with salt concentration at 5°C for Na C^{12} U^{+} OU: UCO^{-2} and CO^{-2} at 1 has total supersum	, 11
CI, H, OH, HCO_3 and CO_3 , at I bar total pressure	. 44
Figure 17. Calculated activity coefficient change with salt concentration at 20 C for Na C_{1}^{1} U ⁺ OU ⁻ HCO ⁻ and CO ²⁻ at 1 has total pressure.	a, 15
Eigure 18 Comparison of monoured pll and predicted pll at different celt concentration	. 43 na
Figure 18. Comparison of measured pri and predicted pri at different salt concentration $at 5^{\circ}C_{-1}$ her total pressure	115
Eigure 10. Comparison of monoured pU and predicted pU at different celt concentration	. 43 na
Figure 19. Comparison of measured pri and predicted pri at different salt concentration $at 20^{\circ}C_{-1}$ has total prossure.	115 16
at 20 C, 1 bar total pressure	. 40
rigure 20. Contosion rate as measured by LPK in CO ₂ purged solutions (100 – 6000 rp	лп, ло
рп 4, 5 wt70 INaCl, 5 C)	. 4ð

	11
Figure 21. Potentiodynamic sweep in CO ₂ purged solutions (100 – 6000 rpm, pH 4, 3	40
wt% NaCl, 5°C)	48
Figure 22. LPR corrosion rate in CO ₂ purged solutions (100 – 6000 rpm, pH 4, 10 wt% NaCl, 5°C)	49
Figure 23. Potentiodynamic sweep in CO ₂ purged solutions (100 – 6000 rpm, pH 4, 10	
wt% NaCl. 5°C)	50
Figure 24 LPR corrosion rate in CO_2 purged solutions (100 – 6000 rpm pH 4 20 wt%)	
NaCl 5°C)	51
Figure 25 Potentiodynamic sweep in CO ₂ purged solutions $(100 - 6000 \text{ rpm} \text{ nH } 4 20 $	
wt% NaCl_5°C)	51
Figure 26 LPR correspondence in CO ₂ purged solutions (100 $-$ 6000 rpm pH 4, 25 wt%)	51
NaCl 5°C)	52
Figure 27 Potentiadynamia swaan in CO, purged solutions (100 - 6000 rpm pH 4, 25	52
Figure 27. For introdynamic sweep in CO_2 purged solutions (100 – 0000 rpm, pri 4, 25 wt% NaCl. 5%)	52
Wt/0 NaCl, SC	55
Figure 28. LFR correspondence in CO_2 purged solutions (100 – 0000 fpm, p114, 3 wt/8 tr 25 wt% NaCl 5%)	ј 5 Л
25 wt/o NaCl, 5 C)	54 5
Figure 29. Folentious manne sweep in CO_2 purged solutions (100 fpin, pri 4, 5 wt/6 to 2 wt/9/ NaCl 5%C)	5 55
Figure 20 Potentiadynamia swaan in CO, purged solutions (1000 rpm, pH 4, 2 wt% to	55
Figure 50. For industrating sweep in CO_2 purged solutions (1000 rpm, p114, 5 wt/6 to 25 wt^6 NaCl 5%)	56
Eigure 21 Detentiodynamia sween in CO, purged solutions (6000 rpm, pH 4, 2 wt% to	50
Figure 51. For industrating sweep in CO_2 purged solutions (0000 rpm, p114, 5 wt/6 to 25 wt^6 NaCl 5%)	56
Figure 32 LPR and weight loss corresion rates in CO, purged solutions (20°C, pH 4, 3	50
10 wt^{6} 20 wt 6 NaCl B=12 mV/dec)	58
Figure 33 I PR (corrected B value) and weight loss corrosion rates in CO, purged	50
achieve (20% pH 4.2 wt% 10 wt% 20 wt% NaCl = D=27 mV/dea)	50
Solutions (20 C, pH 4, 5 wt/6, 10 wt/6, 20 wt/6 NaCl; $B=2/100$ / dec)	39
Figure 34. LPR and weight loss corrosion rates in CO_2 purged solutions (20 C, pH 3, 5	<u> </u>
wt%, 10 wt%, 20 wt% NaCl, $B=12 \text{ mv/dec}$ and $B=2/\text{ mv/dec}$)	60
Figure 35. Flow velocity effect on LPR corrosion rate in CO_2 purged solutions (1000 –	<u> </u>
4000 rpm, pH 4, 3 wt% NaCl, 20°C)	b1
Figure 36. Flow velocity effect on potentiodynamic sweep in CO_2 purged solutions (100	JU (1
$-4000 \text{ rpm}, \text{pH 4}, 3 \text{ wt\% NaCl}, 20^{\circ}\text{C}$	61
Figure 37. Flow velocity effect on LPR corrosion rate in CO_2 purged solutions (1000 –	<u> </u>
4000 rpm, pH 4, 10 wt% NaCl, 20°C)	62 20
Figure 38. Flow velocity effect on potentiodynamic sweep in CO_2 purged solutions (100	JU ()
$-4000 \text{ rpm}, \text{pH 4}, 10 \text{ wt% NaCl}, 20^{\circ}\text{C}$	63
Figure 39. Flow velocity effect on LPR corrosion rate in CO_2 purged solutions (1000 –	<i>(</i>)
4000 rpm, pH 4, 20 wt% NaCl, 20°C)	b4
Figure 40. Flow velocity effect on potentiodynamic sweep in CO_2 purged solutions (100 4000 mm mH 4 20 mm/s) NFC1 209C)	JU (1
-4000 rpm, pH 4, 20 Wt% NaCl, 20°C)	04
Figure 41. Sait effect on LKP corrosion rate in CO ₂ purged solutions (1000, 4000 rpm, 114.2 met) ($10 $	<u> </u>
pH 4, 5 wt%, 10 wt% and 20 wt% NaCl, 20° C)	00
Figure 42. Sait effect on potentiodynamic sweep in CO_2 purged solutions (1000 rpm, pF	1
4, 5 Wt%, 10 Wt% and 20 Wt% NaCl, 20°C)	00

12
Figure 43. Salt effect on potentiodynamic sweep in CO ₂ purged solutions (4000 rpm, pH
4, 3 wt%, 10 wt% and 20 wt% NaCl, 20°C)
Figure 44. pH effect on LPR corrosion rate in CO2 purged solutions (1000 rpm, 10 wt%
NaCl, pH 4, pH 5, pH 6, 20°C)
Figure 45. pH effect on LPR corrosion rate in CO ₂ purged solutions (1000 rpm, 20 wt%
NaCl, pH 4, pH 5, pH 6, 20°C)
Figure 46. pH effect on potentiodynamic sweep in CO_2 purged solutions (1000 rpm, 10
Figure 47 pH offset on potentiadynamic sweep in CO, purged solutions (1000 rpm, 20
wt% NaCl, pH 4, pH 5, pH 6, 20°C)
Figure 48. Comparison of LPR and weight loss corrosion rates in CO ₂ purged solutions
(1000 rpm, 10 wt% NaCl, pH 4, pH 5, pH 6, 20°C)70
Figure 49. Comparison between electrochemical model (original) and experimental result
in CO ₂ purged solution (1 to 20°C, 1 bar CO ₂ , 3 wt% NaCl, pH 4, 1000 rpm)77
Figure 50. Comparison between electrochemical model (original) and experimental result
in CO ₂ purged solution (20°C, 1 bar CO ₂ , 3 – 20 wt% NaCl, pH 4, 1000 rpm) 77
Figure 51. Comparison between the experimental sweep and the predicted sweep by
unmodified model (3 wt% NaCl, 5°C, 1 bar CO ₂ , pH 4, 1000 rpm)
Figure 52. Comparison between the experimental sweep and the predicted sweep by
unmodified model (3 wt% NaCl, 1°C, 1 bar CO ₂ , pH 4, 1000 rpm)
Figure 53. The construction of the electrochemical model
Figure 54. Comparison between electrochemical model and experimental result in CO_2
Figure 55 Comparison between electrochemical model and europimental result in CO
Figure 55. Comparison between electrochemical model and experimental result in CO_2
Figure 56 Comparison between electrochemical model and experimental result in CO
right 50. Comparison between electrochemical model and experimental result in CO_2 purged solution (5°C 1 bar CO ₂ 3 wt% NaCl pH 4 2000 rpm) 83
Figure 57 Comparison between electrochemical model and experimental result in CO ₂
nurged solution (5°C 1 bar CO_2 3 wt% NaCl nH 4 3000 rnm) 84
Figure 58 Comparison between electrochemical model and experimental result in CO ₂
nurged solution (5°C 1 bar CO_2 3 wt% NaCl nH 4 4000 rnm) 84
Figure 59 Comparison between electrochemical model and experimental result in CO_2
purged solution (5°C 1 bar CO ₂ 3 wt% NaCl pH 4 5000 rpm) 85
Figure 60 Comparison between electrochemical model and experimental result in CO ₂
purged solution (5°C, 1 bar CO ₂ , 3 wt% NaCl, pH 4, 6000 rpm)
Figure 61. Comparison between electrochemical model and experimental result in CO ₂
purged solution (1°C, 1 bar CO ₂ , 3 wt% NaCl, pH 4, 1000 rpm)
Figure 62. Comparison between electrochemical model and experimental result in CO ₂
purged solution (1°C, 1 bar CO ₂ , 3 wt% NaCl, pH 4, 2000 rpm)
Figure 63. Comparison between electrochemical model and experimental result in CO ₂
purged solution (1°C, 1 bar CO ₂ , 3 wt% NaCl, pH 4, 3000 rpm)
Figure 64. Comparison between electrochemical model and experimental result in CO ₂
purged solution (1°C, 1 bar CO ₂ , 3 wt% NaCl, pH 4, 4000 rpm)

Figure 65. Comparison between predicted (modified and original) and experimental
corrosion rate in CO ₂ purged solution (1 to 20°C, 1 bar CO ₂ , 3 wt% NaCl, pH 4,
1000 rpm)
Figure 66. Salt effect on the viscosity of brines (from the reference model) 89
Figure 67. Salt effect on the density of brines (from the reference model)
Figure 68. Comparison between the experimental and model (without viscosity, density
and ionic strength adjustment) in CO ₂ purged solution (20°C, 1 bar CO ₂ , 3 wt%
NaCl, pH 4, 4000 rpm)91
Figure 69. Comparison between the experimental and model (with viscosity, density and
ionic strength adjustment) in CO ₂ purged solution (20°C, 1 bar CO ₂ , 10 wt% NaCl,
pH 4, 4000 rpm)
Figure 70. Calculating Salt retardation effect on the anodic reaction in CO ₂ purged
solution (5°C, 1 bar CO ₂ , 10 wt% NaCl, pH 4, 100 rpm)
Figure 71. Calculating Salt retardation effect on the cathodic reaction in CO ₂ purged
solution (5°C, 1 bar CO ₂ , 10 wt% NaCl, pH 4, 100 rpm)
Figure 72. Calculating Salt retardation effect on the limiting current in CO ₂ purged
solution (5°C, 1 bar CO ₂ , 10 wt% NaCl, pH 4, 100 rpm)
Figure 73. Anodic factors and fitted trend line as a function of salt concentration
Figure 74. Cathodic factors and fitted trend line as a function of salt concentration 96
Figure 75. Mass transfer factors and fitted trend line as a function of salt concentration 97
Figure 76. Chemical reaction factors vs. salt concentration
Figure 77. Comparison between electrochemical model and experimental result in CO_2
purged solution (3 wt% NaCl, 20°C, 1 bar CO ₂ , pH 4, 1000 rpm)
Figure 78. Comparison between electrochemical model and experimental result in CO_2
purged solution (10 wt% NaCl, 20°C, 1 bar CO ₂ , pH 4, 1000 rpm)
Figure /9. Comparison between electrochemical model and experimental result in CO_2
purged solution (20 wt% NaCl, 20°C, 1 bar CO_2 , pH 4, 1000 rpm)100
Figure 80. Comparison between electrochemical model and experimental result in CO_2
Figure S1 Comparison between electrochemical model and experimental result in CO
Figure 81. Comparison between electrochemical model and experimental result in CO_2 nurged solution (10 yrtl/ NoCl 20°C 1 her CO nH 4 4000 rnm) 101
Figure 82 Comparison between electrochemical model and experimental result in CO
Figure 82. Comparison between electrochemical model and experimental result in CO_2 nurged solution (20 yut% NaCl 20°C 1 har CO, nH 4 4000 rnm) 101
Figure 82 Comparison between experimental and predicted correspondence in CO, purged
solution (20°C 1 bar CO ₂ 3 20 wt% NaCl $nH 4$ 1000 rpm) 102
Figure 84. Comparison between experimental and predicted corrosion rate in CO ₂ , purged
solution (20°C 1 bar CO ₂ 3-20 wt% NaCl nH 4 4000 rpm) 102
Figure 85. Comparison between electrochemical model and experimental result in CO ₂
nurged solution (3 wt% NaCl 5°C 1 bar CO ₂ nH 4 100 rpm) 103
Figure 86. Comparison between electrochemical model and experimental result in CO ₂
nurged solution (3 wt% NaCl 5°C 1 bar CO ₂ nH 4 1000 rpm) 103
Figure 87 Comparison between electrochemical model and experimental result in CO ₂
nurged solution (3 wt% NaCl_5°C_1 bar CO ₂ nH 4 6000 rnm) 104
Figure 88 Comparison between electrochemical model and experimental result in CO ₂
purged solution (10 wt% NaCl. 5°C. 1 bar CO ₂ pH 4 100 rpm) 104
r = 0

CHAPTER 1 INTRODUCTION

A carbon dioxide (CO_2) saturated aqueous system is by far one of the most common corrosive environments encountered in the oil and gas industry. The CO_2 corrosion of carbon steels, also called "sweet corrosion", has been one of the important problems in the oil and gas industry since 1940 because of both high corrosion rates and severe localized corrosion. CO_2 is present as dissolved gas in the water/ brine system that accompanies oil and gas production in high pressure operation environments. In the aqueous phase, CO_2 forms carbonic acid, which has a strong corrosive property towards carbon steel. So it is necessary to understand the mechanism of CO_2 corrosion and then adopt proper methods to prevent the occurrence of corrosion.

 CO_2 corrosion is a complicated process and is affected by many different parameters (for example: temperature, CO_2 partial pressure, pH.), which make it difficult for corrosion prediction models to provide accurate results. A large body of research has been conducted in this field over the last three decades. The first significant CO_2 corrosion model introduced by C. de Waard and Milliams in 1975, identified the combined effect of CO_2 partial pressure and temperature on the corrosion rate as the key parameters in CO_2 corrosion¹. Since then many other parameters have been uncovered such as pH, velocity, etc.²⁻⁷ However, CO_2 corrosion in low temperature and solutions with high salt concentrations, or non-ideal solutions, has not been addressed adequately.

Temperature is known to accelerate most of the chemical and electrochemical processes occurring in the present system⁷, which means that higher temperatures cause higher corrosion rates, lower temperatures cause lower corrosion rates. CO₂ corrosion at higher temperatures (20°C to 80°C) has been successfully modeled. For example, Nesic's

electrochemical model covers the temperature range from 20°C to 80°C⁷, and also can predict the corrosion rate at lower temperatures (1°C to 20°C). However, there are no experimental data to verify the latter results. A new publication by Olsen *et al.*, reports a CO_2 corrosion model that claims to cover the temperature range from 5°C to 150°C⁸ however no details about the model or the test conditions are available in this paper. So general CO_2 corrosion at lower temperature is still unclear, and it is necessary to better understand what really happens with CO_2 corrosion at low temperature conditions.

Salt concentration is another parameter which is seldom mentioned by most of the researchers. Most previous research related to the effect of salt on CO_2 corrosion focused on the effect of chloride ion concentration in localized corrosion. For example, Sun investigated the effect of Cl⁻ on localized corrosion in wet gas pipelines⁹. Ma *et al.* also studied the influence of chloride ions on the corrosion of iron¹⁰. Both investigations concluded that chlorides accelerate localized corrosion. However, the effect of salt content on general CO_2 corrosion was not even mentioned in either paper.

The reality in the field is that dissolved salts with high concentration are present in water recovered from gas wells. For example a water analysis from a Texas gas well is shown in Table 1. Salt content is about 23 wt% by weight, which is typical for this location. It is not uncommon that salt crystals are seen in the production tubing in Texas, meaning salt concentration could be near saturation. So it is important to know if this high content of salt has effects on CO_2 corrosion or not.

Compound	Compound	Concentration	
Compound	(mg/l)	wt.%	
NaCl	131080	13.1	
CaCl ₂ ·2H ₂ O	111510	8.36	
MgCl ₂ ·6H ₂ O	50810	2.39	
TOTAL	293400	23.85	

Table 1. A water analysis summary for a Texan gas flow well

Most CO₂ corrosion research is done at lower salt concentrations typically from 1 wt% to 3 wt% NaCl. No significant effects of salt concentration on general CO₂ corrosion are observed in this range. It was therefore commonly assumed that general CO₂ corrosion of bare steel is not affected by salt concentration. However, this hypothesis is based on the data obtained at relatively low salt concentration. No published information about CO₂ corrosion in solution with high salt concentration (>3 wt%) can be found, so it is necessary to fill this gap by performing general CO₂ corrosion experiments in brines containing up to 25 wt% NaCl which is close to its solubility limit.

CHAPTER 2 LITERATURE REVIEW

2.1 CO₂ corrosion

Carbon dioxide corrosion or "sweet corrosion" of carbon steel is a major problem encountered in the oil and gas industry. Many have dedicated themselves to this field of research for more than three decades. The basic CO₂ corrosion reactions have been well understood and accepted throughout the work done in the past^{1-7, 11-20}. The following reactions describe what happens during the CO₂ corrosion process. First the gas phase carbon dioxide dissolves in the water and undergoes hydration to form carbonic acid:

$$CO_2(g) \Leftrightarrow CO_2(aq)$$

(1)

$$CO_2(aq) + H_2O(l) \Leftrightarrow H_2CO_3(aq)$$

(2)

Carbonic acid then dissociates to bicarbonate and carbonate ions in two steps. Each step generates one hydrogen ion:

$$H_2CO_3(aq) \Leftrightarrow H^+(aq) + HCO_3^-(aq)$$

(3)

$$HCO_3^{-}(aq) \Leftrightarrow H^+(aq) + CO_3^{2-}(aq)$$

(4)

The overall corrosion reaction is an electrochemical reaction given by:

$$Fe(s) + H_2O(l) + CO_2(aq) \Rightarrow FeCO_3(s) + H_2(g)$$

(5)

The overall corrosion reaction can be separated into two types of electrochemical reactions, anodic and cathodic, both of which happen at the metal surface. The anodic reaction is the iron dissolution:

$$Fe(s) \Rightarrow Fe^{2+}(aq) + 2e^{-} \tag{6}$$

This reaction also consists of a number of substeps. According to $Bockris^{21}$, the rate controlling step depends on pH, and the reaction rate decreases with an increase of H^+ concentration.

The cathodic reactions include direct proton reduction and direct carbonic acid reduction and water reduction:

$$2H^+(aq) + 2e^- \Rightarrow H_2(g)$$

(7)

$$2H_2CO_3(aq) + 2e^- \Rightarrow H_2(g) + 2HCO_3(aq)$$

(8)

The two reactions both contribute to the total cathodic current. Which of the two reactions actually prevails at the metal surface depends on the corrosion environment. Normally at lower pH (<4), the hydrogen reduction is the dominant cathodic reaction and at higher pH (>4), the direct carbonic acid reaction is the controlling part. As a rule people take the net cathodic reaction current to be the summation of the current of the two reactions⁵.

There are many complicated environmental parameters affecting general CO₂ corrosion, such as partial pressure of carbon dioxide, temperature, pH, flow velocity, the

formation of the corrosion product scale, etc. These effects will be discussed in the following paragraphs.

2.2 The effect of CO₂ partial pressure

 CO_2 partial pressure is one of the most important factors involved in general CO_2 corrosion. When there is no corrosion film formed on the metal surface during the corrosion process, an increase of CO_2 partial pressure will cause an increase of corrosion rate⁷. With an increase of the CO_2 partial pressure, the direct reduction of carbonic acid reaction will be accelerated due to the increase of carbonic acid concentration. However when the corrosion environment is film formation favorable, an increased CO_2 partial pressure may be helpful to the film formation. At a given high temperature and higher constant pH, an increase of CO_2 partial pressure will cause an increase of $CO_3^{2^2}$ concentration and higher supersaturation of FeCO₃²⁰, thus accelerating the corrosion film formation, and consequently decreasing the corrosion rate.

2.3 The effect of temperature

Temperature affects the corrosion rate of steels in several ways. Temperature accelerates the chemical reaction in the bulk solution and the electrochemical reactions at the metal surface by increasing reaction rates. Temperatures also can speed up the mass transfer process by decreasing the viscosity of the solution. So if there are no protective films formed (especially at low pH), an increase of temperature will increase the general CO_2 corrosion rate. However at higher pH, the increasing temperature will also accelerate the kinetics of precipitation and aid the protective film formation. Normally the corrosion rate reaches a maximum with increasing temperature at around 70 - 90°C²². This is attributed to the formation of a protective corrosion product film, FeCO₃.

2.4 The effect of flow

The flow effect on CO_2 corrosion is mainly about the effect on mass transfer involved in the corrosion process. Higher flow velocity usually means high turbulence and effective mixing in the solution. Increased turbulent flow accelerates the corrosion species both toward and away from the metal surface. This may result in an increase of corrosion rate when the mass transfer is the rate controlling factor and no corrosion film forms at the metal surface. If the corrosion reaction appears to be under activation control, there is no significant effect of liquid flow velocity on CO_2 corrosion.

On the other hand, at higher flow velocity, less protective corrosion film will form at the metal surface²⁰. In some cases with extremely high flow velocity, the flow can even mechanically remove the protective film, resulting in an increase of corrosion rate, sometimes even localized corrosion.

2.5 The effect of pH

The pH is a measure of the acidity or alkalinity of a solution. It is a numerical indication of the concentration in the solution of H^+ . It has been proved that changing the pH of the corrosion environment will significantly change the corrosion rate, *i.e.*, lower pH, higher corrosion rate. The pH also determines which reaction is the rate controlling reaction. At low pH (<4) and low CO₂ partial pressure (<1bar), the flow sensitive proton reduction is the dominant cathodic reaction. At high pH (>5) and high CO₂ partial pressure (>1bar), the controlling cathodic reaction is carbonic acid reduction.

pH can also affect the corrosion product film formation $(FeCO_3)^{20}$. It is easy for a corrosion film to form on the metal surface at a high pH level. At high pH levels, the

solubility of the corrosion film (FeCO₃) will decrease, thus resulting in an increased precipitation rate, faster corrosion film formation rate and a decreased corrosion rate.

2.6 The corrosion product film

The corrosion of carbon steel in CO_2 environments can be classified according to the presence of protective film: corrosion attack without corrosion product films present and attack with films. CO_2 corrosion is strongly dependent on the type of corrosion product film formed on the metal surface during the corrosion process. When there is no film forming at metal surface, most of the corrosion attack is general corrosion. Localized corrosion, which is more severe, normally happens when the corrosion film forms at the metal surface during the corrosion process.

CHAPTER 3 RESEARCH OBJECTIVES AND TEST MATRICES

3.1 Research objectives

Based on the previous research, the principal questions that need to be answered are:

Low temperature research program:

1. What are the main effects of low temperature (1 to 10° C) on the anodic and cathodic reactions present in general CO₂ corrosion?

2. What is the general CO₂ corrosion mechanism at low temperature conditions?

3. How can the experimental data about low temperature effects on general CO_2 corrosion be integrated into a corrosion prediction model?

High salt research program:

1. What are the main effects of high salt concentration (10 wt % to 25 wt %) on the anodic and cathodic reactions present in general CO_2 corrosion?

2. What is the general CO₂ corrosion mechanism under the condition of high salt (NaCl) concentration?

3. How can the experimental data about high salt concentration effects on general CO₂ corrosion be integrated into a corrosion prediction model?

3.2 Test matrices

The following test matrices were defined to answer the above questions.

Parameters	Conditions		
Total Pressure	1bar		
Temperature	1°C, 5°C, 10°C		
Rotation Speed	100, 1000, 2000, 3000, 4000, 5000, 6000 rpm		
Solution	3 wt % NaCl		
pH	4, 5, 6		
Material	C1018		

Table 2. Test matrix for low temperature research program

Table 3. Test matrix for high salt research program

Parameters	Conditions		
Total Pressure	1bar		
Temperature	5°C, 20°C		
Rotation Speed	100, 1000, 6000 rpm		
Solution	3, 10, 20, 25 wt % NaCl		
pH	4, 5, 6		
Material	C1018		

Not all the permutations in the test matrix were performed. For example, for the low temperature research, pH was varied only at 5°C.

It should be mentioned that only general CO_2 corrosion was investigated in this research. Conditions were selected so that no corrosion product films formed during the corrosion process.

4.1 Specimen prepararion

One type of carbon steel (C1018) was used for weight loss, linear polarization resistance (LPR), electrical impedance spectroscopy (EIS) and potentiodynamic sweep analysis. The surface area of the specimen is 5.4 cm². The chemical composition of the carbon steel used in the experiment is shown in Table 4.

Table 4. Chemical composition of C1018 carbon steel (wt%)

С	Si	Р	S	Mn	Al	Fe
0.21	0.38	0.09	0.05	0.05	0.01	balance

The specimen was polished by silicon carbide sand paper before it was tested, and the sand paper grit number was in the following order: 240, 400, 600. After polishing, the specimen was immersed in isopropyl alcohol in an ultrasonic cleaner for 1 to 2 minutes and then air dried.

4.2 Experimental setup

The experiments were performed in a glass cell which is shown in Figure 1 (courtesy of Daniel Mosser). Ag/AgCl (4M KCl) reference electrode was externally connected to the cell *via* a Luggin capillary and a porous Vycor-tip. A counter electrode was made of a concentric platinum ring.

A glass cell was filled with 2 liters of de-ionized water and different concentrations of NaCl. For the low temperature experiment the test cell needed to be put into a refrigerator or water bath until the cell solution reached the desired temperature. Cell temperature was followed by a thermocouple. The solution was deoxygenated by

purging with CO_2 gas. The solution can be deoxygenated in about 40 minutes to 1 hour of purging. When the desired temperature was attained, the pH of the test solution was adjusted from equilibrium pH to the desired pH by adding a deoxygenated sodium bicarbonate solution. Then a working electrode was put into the solution and all electrical connections were made for corrosion rate monitoring. The rotational speed was set and the open circuit potential was monitored for 20 to 60 minutes for a stable signal before all the electrochemical measurements were carried out.



Figure 1. Schematic of a glass cell

- 1. Reference electrode
- 3. Temperature probe
- 5. Rotator
- 7. pH-electrode
- 9. Working electrode

- 2. Gas outlet
- 4. Platinum counter electrode
- 6. Gas inlet
- 8. Luggin capillary
- 10. Hot Plate

4.3 Measurement techniques

There are two main groups of techniques which were used to monitor the corrosion process. They are electrochemical measurement and weight loss measurement.

4.3.1 Electrochemical measurements

The electrochemical measurements were typically conducted in the same order. First, linear polarization resistance (LPR) was performed to measure the corrosion rate, then the solution resistance was measured by conducting electrical impedance spectroscopy (EIS), and last, the potentiodynamic sweep was performed. All electrochemical measurements were made using a Gamry PC4 monitoring system and analyzed using the accompanying software. The electrochemical methods used during the experiments are as follows:

The linear polarization resistance (LPR) technique was used to measure the corrosion rate. The steel sample was polarized at $\pm 5 \text{ mV}$ or $\pm 10 \text{mV}$ (depending on the electrochemical noise) around the open circuit potential during the LPR measurement. The scan rate was 0.125 mV/s. What LPR actually measured was corrosion resistance, not corrosion rate. Corrosion resistance can be converted to rate. From the basic electrochemical theory²³, the corrosion current density *i_{corr}* (A/m²) can be described as:

$$i_{corr} = B \times \frac{1}{R_p} \times \frac{1}{A}$$
⁽⁹⁾

where, R_p is the corrosion resistance measured by LPR. In the real corrosion rate calculation, the solution resistance (R_s) measured by EIS needs to be subtracted from the total corrosion resistance. A is the surface area, which is 5.4 cm². B is the so called 'B value', which can be calculated from the equation below:

$$B = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \tag{10}$$

29

where, β_a and β_c are the anodic and cathodic Tafel slopes, which can be expressed as:

$$\beta_a = \frac{2.303RT}{\alpha_a F} \tag{11}$$

$$\beta_c = \frac{2.303RT}{\alpha_c F} \tag{12}$$

where, *T* is the absolute temperature in K, *R* is the universal gas constant (8.314 J/mol K), α_a and α_c are the symmetry factors for anodic and cathodic reactions. The values of α_a and α_c are typically 1.5 and 0.5, respectively. *F* is Faraday's constant (96,500 coulombs/equivalent).

Corrosion rate in mm/yr is then calculated by the equation below:

$$CR = \frac{m}{At\rho} = \frac{i_{corr}M_w}{\rho nF} = 1.16i_{corr}$$
(13)

where, *m* is the metal loss in kg, t is the time in seconds, ρ is the density of the material in kg/m³, M_w is the molecular weight of iron in kg/mol, *n* is the number of electrons exchanged in the electrochemical reaction.

The potentiodynamic sweep technique was used to investigate the corrosion mechanism. The sweeps were conducted with a scan rate of 0.2 mV/s. Some of the initial experiments were mistakenly conducted by using scan rate of 2 mV/s. To check the scan rate effect on the potentiodynamic sweep, several experiments were done by using two different scan rates (2 mV/s and 0.2 mV/s). Figure 2 shows the comparison between the potentiodynamic sweeps with two scan rates, which does not show a significant

difference. The steel working electrode was polarized over a relatively large potential range (200 mV above to 550 mV below the open circuit potential).



Figure 2. Comparison between the potentiodynamic sweeps with two scan rates in CO₂ purged solutions (1000 rpm, 5°C, pH 5, 3 wt% NaCl)

4.3.2 Weight loss measurements

Weight loss measurement was used to verify the corrosion rate magnitude. At the same test conditions as electrochemical measurements, a pre-weight steel sample was put into the test solution. Typically after 24 hours, the sample was taken out of the test solution, rinsed with isopropyl alcohol and wiped with a cloth to remove any corrosion products, then air dried and weight.

CHAPTER 5 RESULTS AND DISCUSSION OF LOW TEMPERATURE RESEARCH PROGRAM

Three sets of experiments were conducted at temperatures of 10°C, 5°C and 1°C and pH 4. The rotational speeds were varied from 100 rpm to 7000 rpm to observe the flow velocity effect on the corrosion process. In addition, pH was varied from 4 to 6 at 5°C and 1000 rpm to observe the pH effect on the corrosion process.

It was assumed that the corrosion process is under charge transfer control before the experiments were performed. The Tafel slopes used in the LPR corrosion rate calculation were calculated according to Equation (11) and Equation (12). Table 5 shows the calculated Tafel slopes based on temperature.

Temperature °C	20	10	5	1
βc mV/dec	120	114	112	110
βa mV/dec	40	38	37	37
<i>B</i> mV/dec	13	12	12	12

 Table 5. Tafel slopes at different temperatures

5.1 Flow velocity effects on general CO₂ corrosion at low temperatures

The effect of flow velocity on general CO₂ corrosion rate was studied in a 3 wt% sodium chloride solution at pH 4, 1°C to 10°C. Flow velocity was varied from 100 rpm to 6000 rpm. The LPR corrosion rate results with different flow velocities at 10°C are shown in Figure 3. Corrosion rates increased from 0.3 mm/yr to 0.4 mm/yr with the increase of flow velocity from 100 rpm to 6000 rpm *i.e.* a small flow effect on CO₂ corrosion rates was observed. The flow effect on corrosion rate at 10°C is quite different

from the effect at temperatures above 20°C. Previous research results⁷ have shown a significant flow effect on corrosion rates at pH 4 above 20°C, which means that mass transfer has some effect on the corrosion process. But at 10°C, the mass transfer effect decreased. When the temperature decreases from 20°C to 10°C, the corrosion mechanism might change from partial mass transfer control to charge transfer control. The results of the experiment are consistent with the corrosion mechanism assumption made at the beginning.



Figure 3. Flow velocity effect on corrosion rate in CO2 purged solutions as measured by LPR (100 – 6000 rpm, pH 4, 3 wt% NaCl, 10°C)

Figure 4 shows the LPR corrosion rate results at 5°C, pH 4 and different flow velocities. The LPR corrosion rates changed from 0.25 to 0.28 mm/yr with different rotational speeds. There is no significant difference in the corrosion rates measured at the lower rpm and the higher rpm under these conditions. Similar results have been observed at 10°C. Figure 5 shows the potentiodynamic sweeps results at 5°C, pH 4 and different flow velocities. A very clear Tafel area can be seen from this figure. The flow velocity still has an effect on the cathodic limiting current. However, the corrosion rates do not depend on the cathodic limiting current and the open circuit potential does not change with flow velocity. All these observed phenomena are typical features of a corrosion process controlled by charge transfer.



Figure 4. Flow velocity effect on corrosion rate in CO_2 purged solutions as measured by LPR (100 – 7000 rpm, pH 4, 3 wt% NaCl, 5°C)



Figure 5. Flow velocity effect on potentiodynamic sweeps in CO₂ purged solutions (100 – 6000 rpm, pH 4, 3 wt% NaCl, 5°C)

LPR corrosion rate results at 1°C, pH 4 and different flow velocities are shown in Figure 6. Corrosion rates decreased from 0.2 to below 0.1 mm/yr when the flow velocity increased from 1000 rpm to 4000 rpm. The reversed trend of corrosion rate with velocity does not seem reasonable, but the results were repeatable. Weight loss experiments were performed to verify the corrosion rate magnitude. The results are shown in Table 6. The corrosion rate at 1°C, pH 4 and 1000 rpm measured by the weight loss method is 0.1 mm/yr. Potentiodynamic sweep results which are shown in Figure 7 show that the corrosion potential did not change with flow velocity and charge transfer areas in different flow velocities are very close to each other. These phenomena are typical characteristics of the charge transfer controlled process which should not be affected by velocity.



Figure 6. Flow velocity effect on corrosion rate in CO_2 purged solutions as measured by LPR (1000 – 4000 rpm, pH 4, 3 wt% NaCl, 1°C)



Figure 7. Flow velocity effect on potentiodynamic sweep in CO₂ purged solutions (1000 – 4000 rpm, pH 4, 3 wt% NaCl, 1°C)

Initial Weight (g)	8.5512
Final Weight (g)	8.5487
Surface Area (cm ²)	5.4
Time (hour)	48
Corrosion Rate (mm/yr)	0.11

Table 6. Weight loss corrosion rate in CO₂ purged solution (1°C, pH 4, 3 wt% NaCl, 1000 rpm)

So, it can be concluded from the experimental results, at relatively low temperature, that flow does not have a significant effect on general CO_2 corrosion rate.

5.2 pH effects on general CO₂ corrosion at low temperatures

pH effects on general CO₂ corrosion at low temperature were investigated in 3 wt% sodium chloride solution at 5°C, 1000 to 4000 rpm. pH was varied from 4 to 6. Figure 8 shows the LPR corrosion rate results at different pH and velocities. Corrosion rates decrease with an increase of pH, because the concentration of one of the key corrosion species, hydrogen ion, decreases with the increase of pH. The pH effect on corrosion rate at low temperatures is similar to the pH effect at relatively high temperatures, which has been studied before⁷.


Figure 8. LPR corrosion rate in CO_2 purged solutions as measured by LPR (100 – 4000 rpm, pH 4, pH 5, pH 6, 3 wt% NaCl, 5°C)

pH effects on potentiodynamic sweeps were also studied. Figure 5, Figure 9 and Figure 10, show the potentiodynamic sweep results at pH 4, pH 5 and pH 6 with different flow velocities. At pH 4, the limiting currents caused by mass transfer are very clear and significantly affected by flow velocity. At pH 5, the limiting currents are not apparent, because the concentration of hydrogen ion decreased. At pH 6, limiting currents are not observed.



Figure 9. Potentiodynamic sweep in CO_2 purged solutions (100 – 4000rpm, pH 5, 3 wt% NaCl, 5°C)



Figure 10. Potentiodynamic sweep in CO_2 purged solutions (100 – 4000 rpm, pH 6, 3 wt% NaCl, 5°C)

5.3 Temperature effect on general CO₂ corrosion

Figure 11 shows the corrosion rates in CO₂ solutions under the condition of pH 4, 1000 rpm, 3 wt% NaCl and different temperatures (1°C, 5°C, 10°C and 20°C) as measured by LPR. Temperature effects on general CO₂ corrosion at lower temperatures are very apparent. General CO₂ corrosion rates changed from 2 mm/yr at 20°C to 0.1 mm/yr at 1°C. The decrease in temperature significantly decreases the CO₂ corrosion rate. Also at lower temperatures, the corrosion rate is not flow sensitive compared with the corrosion rate at temperatures above 20°C. This indicates that the corrosion rate control mechanism is different at high and low temperatures.



Figure 11. Corrosion rates in CO₂ purged solutions under the condition of pH 4, 1000 rpm, 3 wt% NaCl and different temperatures as measured by LPR (1°C, 5°C, 10°C and 25 °C)

5.4 Corrosion mechanism analysis

All the experimental results above show a charge transfer controlled corrosion mechanism at low temperatures. The Tafel slope analysis is used to analyze the corrosion mechanism. The theoretical cathodic and anodic slopes are calculated according to Equation (11) and Equation (12), and the two Tafel slopes are overlayed with the potentiodynamic sweeps. A theoretical corrosion rate can be obtained, which is based on the assumption of a charge transfer controlled corrosion process. The Tafel corrosion rate is then compared with the experimental LPR corrosion rate. If the corrosion process being under charge transfer control is correct. Figure 12 and Figure 13, respectively, show the comparisons among the theoretical corrosion rate at pH 4, 1°C, 2000 rpm and pH 4, 5°C, 2000 rpm. The corrosion rates from these three different methods were not significantly different, which supports the hypothesized charge transfer controlled corrosion mechanism at low temperatures.



Figure 12. The comparison of LPR corrosion rate, WL corrosion rate and theoretical corrosion rate derived from potentiodynamic sweeps at pH 4, 1°C, 2000 rpm



Figure 13. The comparison of LPR corrosion rate, WL corrosion rate and theoretical corrosion rate derived from potentiodynamic sweeps at pH 4, 5°C, 2000 rpm

CHAPTER 6 RESULTS AND DISCUSSION OF HIGH SALT CONCENTRATION RESEARCH PROGRAM

Two sets of experiments were conducted at 5°C, and 20°C, by using four different weight concentrations of NaCl, 3 wt%, 10 wt%, 20 wt%, 25 wt% at pH 4. The rotational speed was varied from 100 rpm to 6000 rpm to observe the flow velocity effect on the corrosion process. In addition, pH was varied from 4 to 6 at 20°C to observe the pH effect on the corrosion process.

6.1 pH measurement

The determination of the correct pH value in highly saline solutions is an important issue during corrosion studies. Theoretically, it may appear that an increase in salt concentration will cause the pH to increase because less CO₂ can be dissolved and therefore less carbonic acid is formed. However, the measured pH in high salt concentration solutions was lower than the measured pH in low salt concentration solutions (Figure 14 and Figure 15). A water chemistry model²⁴ based on Pitzer's theory, was used to calculate the activity coefficient of each ionic species in solution at different salt concentrations and also to predict the pH. Figure 16 and Figure 17 show the activity coefficient changes for deoxygenated saline solutions at 1 bar total pressure, purged with carbon dioxide. The most notable observation is that the salt concentration has a significant effect on the activity coefficient of the H⁺ ion. In a 20 wt% NaCl solution, the activity coefficient for H⁺ ions is 3 times greater and in 25 wt% NaCl it is 5 times greater than in a solution with 3 wt% NaCl. This can explain the reason why the measured pH decreased with an increase of salt concentration. Figure 18 and Figure 19 show the comparison of measured pH value and predicted pH value at different temperatures

showing some deviation which is more significant at high salt concentrations. Overall, it was concluded that the decrease in pH is due to changes in the activity of the H^+ ion and that the measured value is accurate enough for the purposes of the subsequent corrosion measurements.

In order to clarify the salt effect on the CO_2 corrosion rate, only the concentration of NaCl in solution was varied while the pH was held constant. Therefore before beginning each corrosion experiment, after adding the salt, the pH value was measured and adjusted to the desired pH of 4 in this series of experiments.



Figure 14. Salt concentration effect on pH measurements in CO₂ purged solution (5°C, 3 wt% to 25 wt% NaCl, total pressure 1 bar).



Figure 15. Salt concentration effect on pH measurement in CO₂ purged solution (20°C, 3 wt% to 20 wt% NaCl, Total pressure 1 bar)



Figure 16. Calculated activity coefficient change with salt concentration at 5°C for Na⁺, Cl⁻, H⁺, OH⁻, HCO₃⁻ and CO₃²⁻, at 1 bar total pressure



Figure 17. Calculated activity coefficient change with salt concentration at 20°C for Na⁺, Cl⁻, H⁺, OH⁻, HCO₃⁻ and CO₃²⁻, at 1 bar total pressure



Figure 18. Comparison of measured pH and predicted pH at different salt concentrations at 5°C, 1 bar total pressure



Figure 19. Comparison of measured pH and predicted pH at different salt concentrations at 20°C, 1 bar total pressure

6.2 Experimental results at 5°C

More than 20 glass cell experiments have been conducted at 5°C. Some of the tests were repeated several times to check the reproducibility of the results. Based on previous studies at low temperatures, it is assumed that the corrosion process is under charge transfer control at 5°C. Therefore, the Tafel slopes used in the LPR corrosion rate were calculated for the test temperature according to Equation (11) and (12). The *B* value derived from the Equations (10) was 12 mV/dec.

Three repeated sets of experiments were conducted at each of the four salt concentrations. Each experiment was conducted at a fixed pH 4 and 5°C while the rotational speed was varied from 100 rpm to 6000 rpm to observe the flow velocity effect on the corrosion process.

6.2.1 Tests with 3 wt% NaCl

Figure 20 shows the corrosion rate results measured by LPR at the different rotational speeds for a 3 wt% NaCl solution. The LPR corrosion rate is approximately 0.25-0.3 mm/yr over the whole range of velocities. *i.e.* the corrosion process is velocity insensitive for these conditions. Figure 21 shows the potentiodynamic sweep results at different flow velocities. The cathodic limiting current is flow sensitive which is consistent with a mixed mass transfer / chemical reaction mechanism typical for CO_2 corrosion at pH 4. Even if the flow velocity had an effect on the cathodic limiting current, the corrosion rates did not depend on flow. This clearly suggests that the corrosion process is under charge transfer control which was confirmed by the sweeps, the corrosion current is at least one order of magnitude lower then the limiting current. The clarity of the data along with the reproducibility obtained at this temperature was the reason that the subsequent experiments with high salt concentration were performed at 5°C as well.



Figure 20. Corrosion rate as measured by LPR in CO_2 purged solutions (100 – 6000 rpm, pH 4, 3 wt% NaCl, 5°C)



Figure 21. Potentiodynamic sweep in CO_2 purged solutions (100 – 6000 rpm, pH 4, 3 wt% NaCl, 5°C)

6.2.2 Tests with 10 wt% NaCl

The LPR corrosion rate results for a 10 wt% NaCl solution are shown in Figure 22. The LPR corrosion rate is approximately 0.1 mm/y which is 2-3 times lower than at 3 wt% salt. Clearly, NaCl has a significant retardation effect on the corrosion rate. The corrosion rate at 10 wt% shows no flow sensitivity. In Figure 23 the potentiodynamic sweep results at different rotational speeds are displayed. The cathodic limiting currents did not change from 100 rpm to 1000 rpm but increased significantly at 6000 rpm. Just as at 3 wt %, the corrosion current is at least one order of magnitude lower then the limiting current, explaining the lack of flow sensitivity.



Figure 22. LPR corrosion rate in CO_2 purged solutions (100 – 6000 rpm, pH 4, 10 wt% NaCl, 5°C)



Figure 23. Potentiodynamic sweep in CO_2 purged solutions (100 – 6000 rpm, pH 4, 10 wt% NaCl, 5°C)

6.2.3 Tests with 20 wt% NaCl

Figure 24 shows the LPR corrosion rate results for a 20 wt% NaCl solution. The average corrosion rate (0.05 mm/yr) is further decreased by a factor of 2, when compared with the 10 wt% NaCl solutions. There is no significant flow sensitivity of the corrosion rate, which is similar to the previous results. Figure 25 shows the potentiodynamic sweep results. The flow velocity does not appear to affect either the cathodic or the anodic reaction which clearly explains the lack of flow effect on the corrosion rate. The anodic reaction indicates inhibition at the corrosion potential, which disappears at higher overpotentials.



Figure 24. LPR corrosion rate in CO_2 purged solutions (100 – 6000 rpm, pH 4, 20 wt% NaCl, 5°C)



Figure 25. Potentiodynamic sweep in CO_2 purged solutions (100 – 6000 rpm, pH 4, 20 wt% NaCl, 5°C)

6.2.4 Tests with 25 wt% NaCl

Figure 26 and Figure 27 show the LPR and potentiodynamic sweep results in a 25 wt% NaCl solution. The results are very similar to those measured in a 20 wt% NaCl solution, *i.e.* retardation of all reactions and lack of flow sensitivity.



Figure 26. LPR corrosion rate in CO_2 purged solutions (100 – 6000 rpm, pH 4, 25 wt% NaCl, 5°C)



Figure 27. Potentiodynamic sweep in CO_2 purged solutions (100 – 6000 rpm, pH 4, 25 wt% NaCl, 5°C)

6.2.5 Summary of salt effect on corrosion process at 5°C

Figure 28 shows the NaCl concentration effect on the LPR corrosion rates at 5°C. It is seen that NaCl significantly reduces the CO_2 corrosion rate. Between 3 and 10 wt% NaCl there is a reduction factor of approximately 2 and another reduction factor of 2 occurs between 10 and 20 wt% NaCl. No further decrease in corrosion rate could be measured as the NaCl concentration is increased from 20 wt% to 25 wt%.



Figure 28. LPR corrosion rate in CO_2 purged solutions (100 – 6000 rpm, pH 4, 3 wt% to 25 wt% NaCl, 5°C)

The potentiodynamic sweeps are consistent with the corrosion measurements. In Figure 29, Figure 30 and Figure 31, the sweeps are shown as a function of salt concentration. In all three plots (displaying three different velocities) it is obvious that salt retards both the cathodic and anodic reaction. For the cathodic reaction, the presence of salt decreases the magnitude of the charge transfer reactions (as indicated by the linear sloped portions of the curves) as well as the limiting current which is under mixed mass transfer-chemical reaction control (denoted by the more vertical portions of the curves). On the anodic side, there seems to be a clear retardation of the rate of anodic dissolution of iron which leads to an increase of the corrosion potential. This effect seems to vanish as the applied anodic overpotential and resulting current density increase. *i.e.* as the steel surface is forced to corrode faster, when all the curves come closer together. This behavior is frequently seen with corrosion inhibitors, however typically much larger overpotentials are required to cause the same effect.

The nature of the retardation shown in Figure 28 appears to be consistent with an adsorption controlled mechanism, which is corroborated by the appearance of the potentiodynamic sweeps.



Figure 29. Potentiodynamic sweep in CO_2 purged solutions (100 rpm, pH 4, 3 wt% to 25 wt% NaCl, 5°C)



Figure 30. Potentiodynamic sweep in CO_2 purged solutions (1000 rpm, pH 4, 3 wt% to 25 wt% NaCl, 5°C)



Figure 31. Potentiodynamic sweep in CO_2 purged solutions (6000 rpm, pH 4, 3 wt% to 25 wt% NaCl, 5°C)

6.3 Experimental results at 20°C

Twenty-five glass cell experiments were conducted at 20°C. Some of the tests were repeated several times to check the reproducibility of the results. At the beginning of the experiments, charge transfer control was assumed to be the main corrosion controlling mechanism under these test conditions. Tafel slopes were calculated based on Equations (11) and (12). The *B* value derived from the equations was 12 mV/dec.

Figure 32 shows the corrosion rate results measured by LPR and weight loss under the following conditions: pH 4, 3 wt% to 20 wt% NaCl, 20°C, stagnant and 1000 rpm. It is apparent that the corrosion rates measured by these two different methods are not in agreement. The weight loss results also show some flow effect on the corrosion rates. Therefore, the corrosion mechanism apriori proposed for this set of conditions may be wrong. The corrosion under these conditions is not under pure charge transfer control, rather it is probably under mixed charge/mass transfer control. Therefore, it is difficult to derive Tafel slopes βa and βc from potentiodynamic sweeps for this kind of corrosion mechanism. However, the true *B* values can be calculated by comparing the polarization resistance measured by LPR and corrosion rates measured by weight loss. Table 7 shows the calculated *B* values by using this method. Figure 33 shows the LPR and weight loss corrosion rates after *B* value "correction" *i.e.* when 27 mV/dec is used for all the LPR calculations. As expected the results agree very well.



Figure 32. LPR and weight loss corrosion rates in CO_2 purged solutions (20°C, pH 4, 3 wt%, 10 wt%, 20 wt% NaCl, B=12 mV/dec)

Salt concentration	Weight Loss	Rp	Area	В	Baverage
wt.%	mm/yr	ohms	cm ²	mV/dec	mV/dec
3	2	26.2	5.4	24	
10	1.46	48.9	5.4	33	27
20	0.46	110.8	5.4	24	

Table 7. B value calculations at pH 4, 20°C



Figure 33. LPR(corrected B value) and weight loss corrosion rates in CO₂ purged solutions (20°C, pH 4, 3 wt%, 10 wt%, 20 wt% NaCl, B=27 mV/dec)

Figure 34 shows the corrosion rate results measured by LPR (by using B=12 mV/dec, and B=27 mV/dec) and weight loss under the condition of pH 5, 3 wt% to 20 wt% NaCl, 20°C. LPR corrosion rate at 10 wt% by using B=12 mV/dec matches the weight loss result better than the LPR corrosion by using B=27 mV/dec, which suggests that at pH 5, the corrosion mechanism has changed to charge transfer control. It has also been assumed that the same mechanism is valid at pH 6.

Therefore, for pH 4.0 the B value used in the calculation of LPR corrosion rate is 27 mV/dec. For pH 5 and pH 6, B value used is 12 mV/dec.



Figure 34. LPR and weight loss corrosion rates in CO_2 purged solutions (20°C, pH 5, 3 wt%, 10 wt%, 20 wt% NaCl, B=12 mV/dec and B= 27 mV/dec)

6.3.1 Test with 3 wt% NaCl

Figure 35 shows the corrosion rate results measured by LPR at 20°C, pH 4, 1000 and 4000 rpm for a 3 wt% NaCl solution. The LPR corrosion rate is around 2.2 mm/yr at 1000 rpm, and 3.3 mm/yr at 4000 rpm. There is a significant difference in the corrosion rates measured at the lower rpm and the higher rpm under these conditions. Figure 36 shows the potentiodynamic sweep results at different flow velocities. The corrosion potential increased with the flow velocity because the cathodic corrosion process in this condition is partially under mass transfer control.



Figure 35. Flow velocity effect on LPR corrosion rate in CO_2 purged solutions (1000 – 4000 rpm, pH 4, 3 wt% NaCl, 20°C)



Figure 36. Flow velocity effect on potentiodynamic sweep in CO_2 purged solutions (1000 – 4000 rpm, pH 4, 3 wt% NaCl, 20°C)

6.3.2 Test with 10 wt% NaCl

The LPR corrosion rate results are shown in Figure 37 for a 10 wt% NaCl solution. The LPR corrosion rate is around 1.2 mm/yr at 1000 rpm and 1.6 mm/yr at 4000 rpm. Flow velocity still has an effect on the LPR corrosion rate, but the effect is not significant. A comparison of corrosion rates in 10 wt% NaCl to those in 3 wt% NaCl shows a 50% decrease in the general corrosion rate for all rotational speeds tested, which is similar to the results at 5°C (section 6.2 **Experimental results at 5°C**). Figure 38 shows the potentiodynamic sweep results at different rotational speeds. As was observed at 3 wt%, flow velocity accelerated the corrosion process. But the flow effect seems to be mitigated by adding more salt.



Figure 37. Flow velocity effect on LPR corrosion rate in CO₂ purged solutions (1000 – 4000 rpm, pH 4, 10 wt% NaCl, 20°C)



Figure 38. Flow velocity effect on potentiodynamic sweep in CO₂ purged solutions (1000 – 4000 rpm, pH 4, 10 wt% NaCl, 20°C)

6.3.3 Test with 20 wt% NaCl

Figure 39 shows the LPR corrosion rate results for a 20 wt% NaCl solution. The corrosion rate is further decreased as compared with the data of 3 wt% and 10 wt% NaCl solutions. Flow velocity effect on LPR corrosion rate continues to decrease. Figure 40 shows the potentiodynamic sweep results. The flow velocity effect on the corrosion process is not significant at this saline concentration, which suggests that the corrosion mechanism gradually changes from mixed charge/mass transfer control to pure charge transfer control with the increase of salt concentration.



Figure 39. Flow velocity effect on LPR corrosion rate in CO_2 purged solutions (1000 – 4000 rpm, pH 4, 20 wt% NaCl, 20°C)



Figure 40. Flow velocity effect on potentiodynamic sweep in CO_2 purged solutions (1000 – 4000 rpm, pH 4, 20 wt% NaCl, 20°C)

Figure 41 shows the NaCl concentration effect on the LPR corrosion rates. It is seen that NaCl concentration has a significant effect on the corrosion rates. Corrosion rates are seen to decrease by 50% as NaCl concentration is increased from 3 wt% to 10 wt%, and to decrease further by 50% as the NaCl concentration is increased from 10 wt% to 20 wt%.



Figure 41. Salt effect on LRP corrosion rate in CO₂ purged solutions (1000, 4000 rpm, pH 4, 3 wt%, 10 wt% and 20 wt% NaCl, 20°C)

The fact that corrosion rates decrease with increasing salt concentrations also can be proven by potentiodynamic sweep results. Figure 42 and Figure 43 show the cathodic and anodic curves at different NaCl concentrations at 1000 rpm and 4000 rpm. Independent of the rotational speed, the cathodic curve and the anodic curve show the same trend, both shift left as the NaCl concentration is increased. This means that salt not only retards the cathodic reaction, but also retards the anodic reaction. This phenomena is almost identical to what was observed at 5°C.



Figure 42. Salt effect on potentiodynamic sweep in CO₂ purged solutions (1000 rpm, pH 4, 3 wt%, 10 wt% and 20 wt% NaCl, 20°C)



Figure 43. Salt effect on potentiodynamic sweep in CO_2 purged solutions (4000 rpm, pH 4, 3 wt%, 10 wt% and 20 wt% NaCl, 20°C)

6.3.5 The effect of salt at higher pH

Figure 44 and Figure 45 show the pH effect on LPR corrosion rates at 20°C, 10 wt% and 20 wt% NaCl. It is seen that corrosion rates decrease substantially from pH 4 to pH 5. But when the pH increased from 5 to 6, the corrosion rate increased. Weight loss results, which are shown in Figure 48, show the same pH effect. It is hard to explain these findings, because according to all we know corrosion rate should decrease with the increase of pH.

Potentiodynamic sweeps shown in Figure 46 and Figure 47 are consistent with the LPR results. It can be hypothesized that the higher pH interferes with the salt retardation effect seen in CO_2 corrosion. Further study is needed to clarify this phenomenon.



Figure 44. pH effect on LPR corrosion rate in CO2 purged solutions (1000 rpm, 10 wt% NaCl, pH 4, pH 5, pH 6, 20°C)



Figure 45. pH effect on LPR corrosion rate in CO_2 purged solutions (1000 rpm, 20 wt% NaCl, pH 4, pH 5, pH 6, 20°C)



Figure 46. pH effect on potentiodynamic sweep in CO₂ purged solutions (1000 rpm, 10 wt% NaCl, pH 4, pH 5, pH 6, 20°C)



Figure 47. pH effect on potentiodynamic sweep in CO₂ purged solutions (1000 rpm, 20 wt% NaCl, pH 4, pH 5, pH 6, 20°C)



Figure 48. Comparison of LPR and weight loss corrosion rates in CO_2 purged solutions (1000 rpm, 10 wt% NaCl, pH 4, pH 5, pH 6, 20°C)

CHAPTER 7 ELECTROCHEMICAL MODEL

To build a mechanistic model of CO_2 corrosion, three cathodic reactions (proton reduction, carbonic acid reduction and water reduction) and one anodic reaction (iron dissolution) need to be considered.

7.1 H⁺ reduction

For H^+ reduction, the general rate equation, which can take into account the effect of resistance to charge transfer and mass transfer, is used²⁵:

$$i_{(H^+)} = i_{0(H^+)} \times \left\{ \frac{\left[H^+\right]_s}{\left[H^+\right]_b} \times \exp\left(-\frac{\alpha_c F}{RT}\eta\right) \right\}$$

(14)

where $i_{0(H^+)}$ is the exchange current density in A/m², $[H^+]_s$ and $[H^+]_b$ are the concentration of H⁺ at the metal surface and the bulk solution in mol/m³, α_c is the symmetry factor, and η is the over potential in V, which is equal to the difference between the applied potential and the reversible potential. The reversible potential of hydrogen reduction can be calculated as⁷:

$$E_{rev(H^+)} = -\frac{2.303RT}{F} pH - \frac{2.303RT}{2F} \log P_{H_2}$$
(15)

where the partial pressure of hydrogen normally is assumed to be zero in the experiments. The surface concentration of H^+ can be found from the mass transfer equation:

$$i_{(H^+)} = k_m F \{ [H^+]_b - [H^+]_s \}$$

(16)

Solving the Equations (15) and (16) gives the final current density versus potential relationship equation for H^+ reduction:

$$\frac{1}{i_{(H^+)}} = \frac{1}{i_{\alpha(H^+)}} + \frac{1}{i_{\lim(H^+)}^d}$$
(17)

72

where $i_{\alpha(H^+)}$ is the activation current density (charge transfer) in A/m². $i_{\lim(H^+)}^d$ is the diffusion limiting current density.

The activation current density is given as:

$$i_{\alpha(H^+)} = i_{0(H^+)} \times 10^{-\frac{\eta}{\beta}}$$

(18)

where $i_{0(H^+)}$ is the exchange current density in A/m². The cathodic Tafel slope β_c can be calculated from:

$$\beta_c = \frac{2.303RT}{\alpha_c F} \tag{19}$$

and the temperature dependence of the exchange current density is given as:

$$\frac{\dot{i}_0}{\dot{i}_0^{ref}} = e^{-\frac{\Delta H}{R}(\frac{1}{T} - \frac{1}{T_{ref}})}$$
(20)

where the ΔH is the enthalpy of activation for the H⁺ reduction reaction in kJ/mol and i_0^{ref} is the reference exchange current density at a reference temperature, T_{ref} . From previous experiments, the i_0^{ref} for H⁺ reduction was taken as 0.05 A/m² at 20°C and the enthalpy of activation was taken as 30 kJ/mol⁷. The pH dependence of exchange current density is given as:

$$\frac{\partial \log i_{0(H^+)}}{\partial pH} = -0.5 \tag{21}$$

The diffusion limiting current appearing in Equation (17) is calculated with:
$$i_{\lim(H^+)}^d = k_m F \times \left[H^+\right]_b \tag{22}$$

where k_m is the mass transfer coefficient, which can be calculated from a rotating cylinder correlation of Eisenberg *et al.*²⁶:

$$Sh = \frac{k_m l}{D} = 0.0791 \times R_e^{0.7} \times S_c^{0.356}$$
(23)

The temperature dependence of diffusion coefficient is given as:

$$D = D_{ref} \times \frac{T}{T_{ref}} \times \frac{\mu_{ref}}{\mu}$$
(24)

where D_{ref} is the reference diffusion coefficient at a reference temperature. μ is the water viscosity in kg/m·s and μ_{ref} is the reference viscosity at a reference temperature. D_{ref} was taken as 9.31x10⁻⁹ m²/s²⁷ and μ_{ref} was taken as 1.002 kg/(m·s)²⁸ at 20°C. The temperature dependence of density is given as:

$$\rho = 1152.3 - 0.5116 \times T \tag{25}$$

The water viscosity as a function of temperature is given as:

$$\mu = \mu_{ref} \times 10 \frac{1.3272(20-t) - 0.001053(20-t)^2}{T + 105}$$
(26)

7.2 H₂CO₃ reduction

Modeling of H_2CO_3 reduction is similar to H^+ reduction. The main difference is that the limiting current is caused by a chemical reaction instead of mass transfer. The current versus potential relationship is given as:

$$\frac{1}{i_{(H_2CO_3)}} = \frac{1}{i_{\alpha(H_2CO_3)}} + \frac{1}{i_{\lim(H_2CO_3)}^r}$$
(27)

where $i_{\alpha(H_2CO_3)}$ is the charge transfer current density of H₂CO₃ reduction in A/m² and $i_{\lim(H_2CO_3)}^r$ is the chemical reaction limiting current density in A/m².

The charge transfer current density is given as:

$$i_{\alpha(H_2CO_3)} = i_{0(H_2CO_3)} \times 10^{-\frac{\eta}{\beta_c}}$$
(28)

The cathodic Tafle slope for H_2CO_3 reduction can be calculated using Equation (19). The temperature dependence of exchange current density of H₂CO₃ reduction is modeled the same as H⁺ reduction according to Equation (20). At 20°C, the reference exchange current density of H₂CO₃ reduction, i_0^{ref} was taken as 0.06A/m². The activation enthalpy for H₂CO₃ reduction was taken as 50 kJ/mol²⁹. The correlation among $i_{0(H_2CO_3)}$, H₂CO₃ concentration and pH is given as:

$$i_{0(H_2CO_3)} \propto [H_2CO_3] \times [H^+]^{-0.5}$$

(29)

The CO₂ hydration reaction limiting current density can be calculated using³⁰:

$$i_{\lim(H_2CO_3)}^r = f \times F[CO_2]_b \times (D_{H_2CO_3}K_{hyd}K_{hyd}^f)^{0.5}$$

(30)

where $[CO_2]_b$ is the bulk concentration of dissolved carbon dioxide, which can be obtained from:

$$\left[CO_2\right]_b = k_{CO_2}^d \times P_{CO_2}$$

Henry's constant $k_{CO_2}^d$ as a function of temperature can be calculated using²⁹:

$$k_{CO_2}^d = 14.5/1.00258 \times 10^{-(2.27+5.65\times10^{-3}T_f - 8.06\times10^{-6}T_f + 0.075\times I)}$$
(32)

75

The equilibrium constant for the CO₂ hydration reaction, K_{hyd} , is equal to 2.58 × 10⁻³ and does not change with temperature²⁹. The forward hydration reaction constant (k_{hyd}^{f}) is a function of temperature, which is given as²⁹:

$$k_{hyd}^f = 10^{329.85 - 110.541 \times \log T_k - \frac{17265.4}{T_k}}$$

(33)

7.3 Water reduction

Since there is always a large amount of water at the metal surface, it can be assumed that no limiting current exists and the reduction reaction rate is dominated by charge transfer process. The reaction rate follows the pure Tafel behavior:

$$i_{H_2O} = i_{0(H_2O)} \times 10^{-\frac{\eta}{\beta_c}}$$
(34)

The reversible potential and Tafel slope of water reduction is assumed to be the same as the one for hydrogen reduction. The reference exchange current density was taken as 3×10^{-5} A/m² at 20°C and the activation enthalpy was taken as 30 kJ/mol⁷.

7.4 Iron dissolution

Active iron dissolution at the corrosion potential was assumed to be under charge transfer control. Thus, pure Tafel behavior can be assumed.

$$i_{Fe} = i_{0(Fe)} \times 10^{\frac{\eta}{\beta_a}}$$

(35)

The Tafel slope for anodic iron dissolution is given as:

$$\beta_a = \frac{2.303RT}{\alpha_a F}$$

76

The symmetry coefficient for the anodic reaction of Fe dissolution was taken as 1.5. As indicated by Davies and Burstein³¹ and Videm³², the anodic dissolution of iron is affected by the concentration of CO_2 :

$$i_{0(Fe)} = i_{0(Fe)}^{ref} \left(\frac{C_{CO_2}}{0.0366} \right) \times e^{\frac{-\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right)}$$
(36)

At 25°C, the reference exchange current density of Fe dissolution, $i_{0(Fe)}^{ref}$, was taken as 1 A/m². The activation enthalpy for H₂CO₃ reduction was taken as 37.5 kJ/mol²⁹.

The mechanistic model⁷ described above has successfully predicted the corrosion process at temperatures between 20 and 80°C and salt concentrations between 1 and 3 wt%. However, the corrosion rate is poorly predicted when this model is used at low temperatures and/or high salt concentrations (Figure 49 and Figure 50).



Figure 49. Comparison between electrochemical model (original) and experimental result in CO₂ purged solution (1 to 20°C, 1 bar CO₂, 3 wt% NaCl, pH 4, 1000 rpm)



Figure 50. Comparison between electrochemical model (original) and experimental result in CO₂ purged solution (20°C, 1 bar CO₂, 3 – 20 wt% NaCl, pH 4, 1000 rpm)

7.5 Modeling the low temperature effect

Figure 51 shows the comparison between the experimental sweeps and the sweeps predicted by the original model for 5°C. Figure 52 shows the same comparison for 1°C. It is evident that the model is not in agreement with the experimental sweep at both temperatures. At 5°C, the experimental result shows much slower corrosion reaction rates than the rates predicted by the original model. The iron dissolution, H^+ reduction, H_2CO_3 reduction and H_2O reduction all are slowed down much more than the original model predicted. However, it appears that the limiting current was predicted approximately well, suggesting that the bulk homogenous chemical and mass transfer processes at lower temperatures are accounted for correctly in the original model. Therefore, the main task of model modification for low temperatures seems to be to model the low temperature effect on the rate of electrochemical reactions.



Figure 51. Comparison between the experimental sweep and the predicted sweep by unmodified model (3 wt% NaCl, 5°C, 1 bar CO₂, pH 4, 1000 rpm)



Figure 52. Comparison between the experimental sweep and the predicted sweep by unmodified model (3 wt% NaCl, 1°C, 1 bar CO₂, pH 4, 1000 rpm)

A possible cause for the decrease of reaction rate is that the activation energy of the electrochemical reaction increases with a decrease of temperature below 20°C. This assumption is loosely supported by other researchers' findings. Van de Runstraat proposed that the activation energy for hydroisomerization catalyzed by Pt/mordenite is temperature dependent at low temperatures ($<20^{\circ}C$)³³. Anson also concluded that the activation energy of F-action velocity generated in *Vitro* by skeletal myosin considerably increased with the decrease of temperature at temperatures below 20°C³⁴. But at temperatures above 20°C, his experimental results showed uniform activation energy.

Therefore, to obtain more accurate prediction results at low temperatures, the activation energies for the four different electrochemical reactions need to be reevaluated. The new values for 5°C and 1°C are shown in Table 8.

	80°C>T>20°C	5°C	1°C	
Proton reduction (reaction 7)	30 kJ/mol	100 kJ/mol	140 kJ/mol	
Carbonic acid reduction (reaction 8)	50 kJ/mol	100 kJ/mol	140 kJ/mol	
Iron dissolution (reaction 6)	37.5 kJ/mol	185 kJ/mol	215 kJ/mol	
Water reduction	30 kJ/mol	120 kJ/mol	140 kJ/mol	

Table 8. Activation energy for different reactions at different temperatures

The rationale for the change of activation energies at low temperatures is as follows. All the electrochemical reactions involved in CO_2 corrosion proceed in multiple steps. For the cathodic species, they first need to adsorb onto the metal surface, and then engage in an electron transfer reaction often in multiple steps. The reaction products then need to desorb from the metal surface for the process to complete. For example, for the proton reduction, the proton needs to adsorb on the metal surface first:

$$H^+ \Leftrightarrow H^+_{(ads)} \tag{37}$$

Then the charge transfer reaction occurs:

$$(38)$$

The hydrogen atom needs to react with another atom to form hydrogen molecule:

$$H_{(ads)} + H_{(ads)} \Leftrightarrow H_{2(ads)} \tag{39}$$

Finally, the hydrogen molecule desorbs from the metal surface:

$$H_{2(ads)} \Leftrightarrow H_{2(aq)} \uparrow$$

(40)

When the temperature decreases to, all reaction steps are slowed down. Some steps may be slowed more than others. This can result in a change in the slowest i.e. ratedetermining step, which then leads to a change of activation energy. To prove the exact mechanism, more experiments need to be done.

7.5.1 Comparison between the electrochemical model and experimental results at low temperatures

Figure 53 shows the construction of the electrochemical model with the new constants (three cathodic reactions and one anodic reaction). The comparisons between the results from the revised electrochemical model and the experiments at 5°C and different velocities are shown in Figure 54 - Figure 60. The experimental and predicted sweeps were found to be in very good agreement at different velocities. The model predicted the charge transfer and limiting current regions of the cathodic sweeps very well. The anodic reaction was also predicted very well.

At 1°C, the activation energy for the electrochemical reactions continues to increase. After adjustment, the predicted sweeps and the experimental sweeps were found to be in agreement at different velocities and are shown in Figure 61 - Figure 64.

Figure 65 shows the comparison between the experimental and predicted corrosion rate from 1°C to 20°C. The predicted results by modified model show a good agreement with the experimental results. And the modified model improves the corrosion rate prediction performance greatly compared with the original model.



Figure 53. The construction of the electrochemical model



Figure 54. Comparison between electrochemical model and experimental result in CO₂ purged solution (5°C, 1 bar CO₂, 3 wt% NaCl, pH 4, 100 rpm)



Figure 55. Comparison between electrochemical model and experimental result in CO₂ purged solution (5°C, 1 bar CO₂, 3 wt% NaCl, pH 4, 1000 rpm)



Figure 56. Comparison between electrochemical model and experimental result in CO₂ purged solution (5°C, 1 bar CO₂, 3 wt% NaCl, pH 4, 2000 rpm)



Figure 57. Comparison between electrochemical model and experimental result in CO₂ purged solution (5°C, 1 bar CO₂, 3 wt% NaCl, pH 4, 3000 rpm)



Figure 58. Comparison between electrochemical model and experimental result in CO_2 purged solution (5°C, 1 bar CO_2 , 3 wt% NaCl, pH 4, 4000 rpm)



Figure 59. Comparison between electrochemical model and experimental result in CO₂ purged solution (5°C, 1 bar CO₂, 3 wt% NaCl, pH 4, 5000 rpm)



Figure 60. Comparison between electrochemical model and experimental result in CO₂ purged solution (5°C, 1 bar CO₂, 3 wt% NaCl, pH 4, 6000 rpm)



Figure 61. Comparison between electrochemical model and experimental result in CO₂ purged solution (1°C, 1 bar CO₂, 3 wt% NaCl, pH 4, 1000 rpm)



Figure 62. Comparison between electrochemical model and experimental result in CO₂ purged solution (1°C, 1 bar CO₂, 3 wt% NaCl, pH 4, 2000 rpm)



Figure 63. Comparison between electrochemical model and experimental result in CO₂ purged solution (1°C, 1 bar CO₂, 3 wt% NaCl, pH 4, 3000 rpm)



Figure 64. Comparison between electrochemical model and experimental result in CO_2 purged solution (1°C, 1 bar CO_2 , 3 wt% NaCl, pH 4, 4000 rpm)



Figure 65. Comparison between predicted (modified and original) and experimental corrosion rate in CO₂ purged solution (1 to 20°C, 1 bar CO₂, 3 wt% NaCl, pH 4, 1000 rpm)

7.6 Modeling the high salt concentration effect

Experimental results described in the previous chapter have shown a significant retardation effect of salt on CO_2 general corrosion. From Figure 29 - Figure 31, Figure 42 - Figure 43, it can be observed that high content of salt not only retards the heterogenous charge transfer reactions but also the homogenous chemical reactions and mass transfer reactions.

Salt may affect the mass transfer limiting current by changing the viscosity and density of the corrosion solutions. A model has been adopted for the salt (NaCl) effect on the viscosity and density³⁵, results are shown in Figure 66 and Figure 67. Viscosity and density both increase with the increase of salt concentrations. Therefore, the salt effect on viscosity and density need to be factored into the model.



Figure 66. Salt effect on the viscosity of brines (from the reference model)



Figure 67. Salt effect on the density of brines (from the reference model)

Salt will also affect the homogenous chemical reaction and the heterogenous charge transfer reactions by changing the ionic strength of the corrosion solution. High salt concentration will decrease the solubility of CO_2 in the corrosion solution, which will cause a retardation of charge transfer and chemical reactions. Therefore, the salt effect on ionic strength of the corrosion solution also needs to be considered into the model.

Figure 68 shows the comparison between the experimental results and results predicted by the original model (without any modifications to account for salt effect). Figure 69 shows the comparison between the experimental results and results predicted by the modified model (including salt effect on viscosity, density and ionic strength). The modified model still does not correctly predict the experimental result. Clearly the salt effects on the homogenous mass transfer, chemical reaction and heterogenous charge transfer go beyond the simple viscosity, density and ionic strength change.



Figure 68. Comparison between the experimental and model (without viscosity, density and ionic strength adjustment) in CO₂ purged solution (20°C, 1 bar CO₂, 3 wt% NaCl, pH 4, 4000 rpm)



Figure 69. Comparison between the experimental and model (with viscosity, density and ionic strength adjustment) in CO₂ purged solution (20°C, 1 bar CO₂, 10 wt% NaCl, pH 4, 4000 rpm)

The best way to accurately predict the salt effect on the overall CO_2 corrosion process is by separation of the effects on different reactions involved in the uniform corrosion process. The following paragraph will explain how this can be done.

Figure 70 shows the method by which the salt retardation factors are found for the anodic reaction. First, two Tafel Slope lines were drawn over two anodic curves (experimental and model) at one specific test conditions (5°C, 1 bar CO₂, 10 wt% NaCl, pH 4, 100 rpm). From the current densities derived at any given potential, the retardation factor on the anodic reaction at one salt concentration can be calculated. Figure 71 and Figure 72 respectively show the salt retardation effect on the cathodic charge transfer reaction and for the limiting current. It should be noted that the salt retardation effect on CO₂ corrosion was assumed to be independent of temperature or velocity.



Figure 70. Calculating Salt retardation effect on the anodic reaction in CO₂ purged solution (5°C, 1 bar CO₂, 10 wt% NaCl, pH 4, 100 rpm)



Figure 71. Calculating Salt retardation effect on the cathodic reaction in CO₂ purged solution (5°C, 1 bar CO₂, 10 wt% NaCl, pH 4, 100 rpm)



Figure 72. Calculating Salt retardation effect on the limiting current in CO₂ purged solution (5°C, 1 bar CO₂, 10 wt% NaCl, pH 4, 100 rpm)

7.6.1 Rationale for the salt retardation factors related to charge transfer

(electrochemical) reactions

In some inhibitor research³⁶, chloride ion was found to preferably adsorb on the metal surface and interfere with the reaction occurring at the metal surface. Therefore, the salt retardation effect on the charge transfer reaction can be modeled by using adsorption theory, which is commonly used to model the inhibitor effect.

Figure 73 shows the salt retardation factors on the anodic reaction as determined from the experimental results. Several adsorption isotherms were attempted to explain the experimental data (Langmuir-, Temkin- and Frumkin-type). Only the Frumkin isotherm:

$$K_{a/d}c_{salt} = \left(\frac{\theta}{1-\theta}\right)e^{-f\theta}$$

(41)

successfully captured the relation between the retardation factors and the salt concentration, where c_{salt} is the salt concentration and θ is the chloride surface coverage. The best-fit values of the equilibrium constant for the adsorption/desorption process (K_{a/d}) and the attraction constant (f) are given in Table 9.

 Table 9. Best-fit values of the Frumkin isotherm for the salt inhibition of the anodic and cathodic reaction

Salt retardation effect	K _{a/d}	f
Anodic reaction	2	4
Cathodic reaction	3	1.5

The salt retardation factors should be equal to 1- θ . The modified exchange current density for iron dissolution is given as:

$$i_{0Fe}' = (1 - \theta)i_{0Fe} \tag{42}$$

95

where $i_{0,Fe}$ ' is the modified exchange current density and $i_{0,Fe}$ is the exchange current density without considering the salt effect.



Figure 73. Anodic factors and fitted trend line as a function of salt concentration

Figure 74 shows the salt retardation factors on cathodic reactions. The Frumkin isotherm function is also the best function which can be used to accurately predict the relation between the salt concentration and the retardation factor. The best-fit values of $K_{a/d}$ and f are given in Table 9. The salt retardation factors for all the cathodic reactions are assumed to be the same value. The modified exchange current density for proton reduction and carbonic acid reduction are given as:

$$i_{0,H^+}' = (1 - \theta)i_{0,H^+} \tag{43}$$

$$i_{0,H_2CO_3}' = (1-\theta)i_{0,H_2CO_3}$$

(44)



Figure 74. Cathodic factors and fitted trend line as a function of salt concentration

7.6.2 Salt retardation factors on limiting currents

In CO_2 corrosion systems, the limiting current originates from two sources. One is the slow mass transfer of hydrogen ions, the other being the sluggish chemical reaction (hydration of CO_2):

$$i_{\lim,total} = i_{\lim,mass} + i_{\lim,chemical} \tag{45}$$

Because limiting current originates from two totally different homogenous processes, the salt retardation effect on limiting current should be separated into two parts. Figure 75 shows the salt retardation factors for mass transfer as a function of salt concentration. To best fit the experimental data, the arbitrary function was adopted as no verified theory for this effect could be found in the literature. To make programming simple the same type of equation as used for the adsorption process was employed here, without much physical reasoning. The best-fit values of K and f for mass transfer is given in Table 10. Figure 76 shows the salt retardation factors for chemical reaction versus salt concentration. The salt retardation factors for chemical reaction are almost 1 and do not change with salt concentration. It suggests that the retardation of chemical reaction (hydration of CO_2) is just caused by a decrease of CO_2 solubility which is a result of an increase of ionic strength.

Table 10. Best-fit values of the Frumkin isotherm for the salt inhibition of mass transfer

Salt retardation effect	К	f
Mass transfer	2	3



Figure 75. Mass transfer factors and fitted trend line as a function of salt concentration



Figure 76. Chemical reaction factors vs. salt concentration

7.6.3 Comparison between the revised electrochemical model and experimental results at different salt concentrations

The comparison between the electrochemical model and the experimental results at 20°C are shown in Figure 77 - Figure 82. The agreement between the model and experimental results is good. Figure 83 and Figure 84 show the comparison between the predicted corrosion rate and the experimental corrosion rate at 20°C. They are also in very good agreement.

At low temperature (5°C), the predicted results are also in very good agreement with the experimental data (Figure 85 - Figure 91). The comparison between the predicted and experimental corrosion rates at 5°C shows reasonable agreement (Figure 92 -Figure 94).



Figure 77. Comparison between electrochemical model and experimental result in CO₂ purged solution (3 wt% NaCl, 20°C, 1 bar CO₂, pH 4, 1000 rpm)



Figure 78. Comparison between electrochemical model and experimental result in CO₂ purged solution (10 wt% NaCl, 20°C, 1 bar CO₂, pH 4, 1000 rpm)



Figure 79. Comparison between electrochemical model and experimental result in CO₂ purged solution (20 wt% NaCl, 20°C, 1 bar CO₂, pH 4, 1000 rpm)



Figure 80. Comparison between electrochemical model and experimental result in CO₂ purged solution (3 wt% NaCl, 20°C, 1 bar CO₂, pH 4, 4000 rpm)



Figure 81. Comparison between electrochemical model and experimental result in CO₂ purged solution (10 wt% NaCl, 20°C, 1 bar CO₂, pH 4, 4000 rpm)



Figure 82. Comparison between electrochemical model and experimental result in CO₂ purged solution (20 wt% NaCl, 20°C, 1 bar CO₂, pH 4, 4000 rpm)



Figure 83. Comparison between experimental and predicted corrosion rate in CO₂ purged solution (20°C, 1 bar CO₂, 3-20 wt% NaCl, pH 4, 1000 rpm)



Figure 84. Comparison between experimental and predicted corrosion rate in CO₂ purged solution (20°C, 1 bar CO₂, 3-20 wt% NaCl, pH 4, 4000 rpm)



Figure 85. Comparison between electrochemical model and experimental result in CO₂ purged solution (3 wt% NaCl, 5°C, 1 bar CO₂, pH 4, 100 rpm)



Figure 86. Comparison between electrochemical model and experimental result in CO₂ purged solution (3 wt% NaCl, 5°C, 1 bar CO₂, pH 4, 1000 rpm)



Figure 87. Comparison between electrochemical model and experimental result in CO₂ purged solution (3 wt% NaCl, 5°C, 1 bar CO₂, pH 4, 6000 rpm)



Figure 88. Comparison between electrochemical model and experimental result in CO₂ purged solution (10 wt% NaCl, 5°C, 1 bar CO₂, pH 4, 100 rpm)



Figure 89. Comparison between electrochemical model and experimental result in CO₂ purged solution (10 wt% NaCl, 5°C, 1 bar CO₂, pH 4, 6000 rpm)



Figure 90. Comparison between electrochemical model and experimental result in CO₂ purged solution (20 wt% NaCl, 5°C, 1 bar CO₂, pH 4, 1000 rpm)



Figure 91. Comparison between electrochemical model and experimental result in CO₂ purged solution (25 wt% NaCl, 5°C, 1 bar CO₂, pH 4, 1000 rpm)



Figure 92. Comparison between experimental and predicted corrosion rate in CO₂ purged solution (5°C, 1 bar CO₂, 3-25 wt% NaCl, pH 4, 100 rpm)



Figure 93. Comparison between experimental and predicted corrosion rate in CO₂ purged solution (5°C, 1 bar CO₂, 3-25 wt% NaCl, pH 4, 1000 rpm)



Figure 94. Comparison between experimental and predicted corrosion rate in CO₂ purged solution (5°C, 1 bar CO₂, 3-25 wt% NaCl, pH 4, 6000 rpm)

CHAPTER 8 CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

- The CO₂ corrosion rate of carbon steel at low temperatures (<20°C) significantly decreases with a decrease of temperatures.
- CO₂ corrosion at low temperatures (<20°C) changes from mixed charge transfer/limiting current control to pure charge transfer control mechanism.
- The CO₂ corrosion rate of carbon steel at low temperatures is not sensitive to flow.
- The CO₂ corrosion rate of carbon steel at low temperatures is not sensitive to pH.
- The activation energy of the charge transfer reaction at low temperatures (<20°C) is temperature dependant and increases as freezing point is approached.
- The CO₂ general corrosion rate of carbon steel significantly decreases with the increase of salt concentration.
- At 20°C, corrosion mechanism gradually changes from mixed charge transfer/limiting current control to pure charge transfer control with the increase of salt concentration.
- An increase in salt concentration retards the heterogeneous charge transfer reactions, as well as the homogenous chemical reactions and the mass transfer.

8.2 Future work

The low temperature $(1^{\circ}C > T > 10^{\circ}C)$ effect on general CO₂ corrosion rate has been determined. CO₂ corrosion rate rapidly decreased when the temperature decreased from 20°C to 10°C. This suggests that the corrosion rate determining step may change
when temperature decreases to a low level. However, because there are no experimental data between 10°C and 20°C, more experiments in this range of temperatures need to be done.

The high salt concentration effect on general CO_2 corrosion has also been studied in this project. The pH effect on corrosion process at high salt concentration conditions seems difficult to explain. When pH increased from 5 to 6 at high salt concentration, the corrosion rate increased. It is probably because that the high pH mitigates the salt retardation effect on general CO_2 corrosion. However, to better understand this phenomenon, more experimentation needs to be done.

REFERENCES

1. C. de Waard, D.E. Milliams, "Carbonic Acid Corrosion of Steel", Corrosion, Vol31, Paper no. 5, 1975, p177.

2. C. de Waard and D.E Milliams, "Predictive Model for CO₂ Corrosion Engineering in Wet Natural Gas Pipelines", Paper No.577, CORROSION/91.

3. C. de Waard, U.Lotz, "Prediction of CO₂ Corrosion of Carbon Steel," Corrosion/93, Paper no. 69, NACE International, Houston, Texas, 1993.

4. C. de Waard, U.Lotz, A.Dugstad "Influence of Liquid Flow Velocity on CO₂ Corrosion: A Semi-empirical Model". Corrosion/95, Paper no. 128, NACE International, Houston, Texas, 1995.

5. Linda D.S. Gray, Bruce G. Anderson, Michael J. Danysh, and Peter R. Tremaine, "Mechanisms of Carbon steel Corrosion in Brines Containing Dissolved Carbon Dioxide at pH 4", Corrosion/89, Paper no. 464, NACE International, Houston, Texas, 1989.

6. Linda D.S. Gray, Bruce G. Anderson, Michael J. Danysh, and Peter R. Tremaine, "Effect of pH and Temperature on the Mechanisms of Carbon steel Corrosionby Aqueous Carbon Dioxide", Corrosion/90, Paper no. 40, NACE International, Houston, Texas, 1990.

7. S. Nesic, J. Postlethwaite, and S. Olsen "An Electrochemical Model for Prediction of Corrosion of Mild Steel in Aqueous Carbon Dioxide Solutions", Corrosion 2003, 52, P.280.

8. Stein Olsen, "CO₂ corrosion prediction model – basic principles", Corrosion 2005.

9. Y. Sun, K. Gorge, S. Nesic "The Effect of Cl⁻ and Acetic Acid on Localized CO₂ Corrosion in Wet Gas Flow", Corrosion/2003. Paper no. 03327, NACE International, Houston, Texas, 2003.

10. HY.Ma, C.Yang, G.Y.Li, W.J.Guo, S.H.Chen, J.L.Luo "Influence of nitrate and chloride ions on the corrosion of iron", Corrosion 2003, 59, P.1112.

11. M. R. Bonis, J-L. Crolet, "Basics of the prediction of the risks of CO₂ corrosion in oil and gas wells", CORROSION/89, Paper no. 466, NACE International, Houston, Texas, 1995.

12. B.F.M.Pots "Mechnistic models for the prediction of CO₂ corrosion rates under multi-phase flow conditions". Corrosion/95. Paper no. 137, NACE International, Houston, Texas, 1995.

13. Y.M. Gunaltun. "Combining research and field data for corrosion rate prediction" CORROSION/96, paper no. 27. NACE International, Houston Texas, 1996.

14. C.D. Adams, J.D. Garber, R.K. Singh, "Computer modelling to predict corrosion rates in gas condensate wells containing CO₂", CORROSION/96, Paper no. 31, NACE International, Houston Texas, 1996.

15. R.C. John, K.G. Jordan, S.D. Kapusta, A.L. Young and W.T. Thompson, "SweetCor: An information system for the analysis of corrosion of steels by water and carbon dioxide", CORROSION/98, Paper no.20, NACE International, Houston Texas, 1998.

16. W.P. Jepson, C. Kang, M. Gopal and S. Stitzel, "Model for sweet corrosion in horizontal multiphase slug flow", CORROSION/97, Paper no.11, NACE International, Houston Texas, 1997.

17. R.Zhang, M.Gopal and W.P. Jepson, "Development of a mechanistic model for predicting corrosion rate in multiphase oil/water/gas flows", CORROSION/97 Paper no.601, NACE International, Houston Texas, 1997.

18. B.F.M. Pots, "Mechanistic models for the prediction of CO₂ corrosion rates under multi-phase flow conditions", CORROSION/95, Paper no. 137, NACE International, Houston Texas, 1995.

19. E. Dayalan, F.D. deMoraes, J.R. Shadley, S. A. Shirazi, E. F. Ribicki, "CO2 corrosion prediction in pipe flow under FeCO3 scale-forming conditions", CORROSION/98, Paper no. 51, NACE International, Houston Texas, 1998.

20. S. Nesic and K.J. Lee, "The mechanistic model of iron carbonate film growth and the effect on CO₂ corrosion of mild steel", Paper no.237, CORROSION/02.

21. J.OM. Brockris, Electrochim Acta 4(1961), 325.

22. Arne Dugstad, "The importance of $FeCO_3$ supersaturation on the CO_2 corrosion of carbon steel", CORROSION/92, Paper no. 14, NACE International, Houston Texas, 1995.

23. D. A. Jones, "Principles and Prevention of Corrosion", 2nd Ed. Prentice Hall 1996.

24. ScaleSoftPitzer Version 8.1, Rice University Brine Chemistry Consortium Energy & Environmental Systems Institute Rice University Houston, TX, 77005.

25. J.M. West, "Electrodeposition and Corrosion Processes", Van Nostrand, 1964, p.36.

26. M. Eisenberg, C.W. Tobias, C.R. Wilke, J. Electrochem. Soc. 101(1954): p.306.

27. P.W. Atkins, Physical Chemistry, 2nd Edition (Oxford, England: Oxford University Press, 1982), p.905.

28. Handbook of Chemistry and Physics, 66th Edition (Boca Raton, F1: CRC Press Inc., 1985), p. F-37.

29. M. Nordsveen, S. Nesic, R.Nyborg, A. Stangeland, "A Mechanistic Model for Carbon Dioxide Corrosion of Mild Steel in the Presence of Protective Iron Carbonate Films – Part 1: Theory and Verification" Corrosion/2001, Vol.59, Paper no.5.

30. S. Nesic, B.F.M. Pots, J. Postlethwaite, N. Thevenot, "Superposition of Diffusion and Chemical Reaction Controlled limiting Currents – Application to CO₂ corrosion", Journal of Corrosion Science and Engineering/1995, Vol.1 p.3.

31. H. Davies, G.T. Burstein, Corrosion 36 (1980): p.416.

32. K. Videm, "Fundamental Studies Aimed at Improving Models for Prediction of CO₂ Corrosion", in Progress in the Understanding and Prevention of CO₂ corrosion, Proc. 10th European Corros. Cong., Vol1 (London, U.K.: Institute of Metals, 1993), p.513.

33. A. van de Rustraat, J.van Grondelle, R.A.van Santen, "On the Temperature Dependence of the Arrhenius Activation Energy for Hydroisomerization Catalyzed by Pt/Mordenite", Journal of Catalysis 167, 460-463, 1997.

34. M. Anson, "Temperature Dependence and Arrhenius Activation Energy of F-actin Velocity Generated in Vitro by Skeletal Myosin", J. Mol. Biol. (1992) 224, 1029-1038.

35. Michael Batzle, Zhijing Wang, "Seismic Properties of Pore Fluids", Geophysics, Vol. 57, Paper no. 11 (November 1992); P. 1396-1408.

36. S. Nesic, W. Wilhelmsen, S. Skjerve and S.M. Hesjevik, "Testing of Inhibitors for CO₂ Corrosion Using the Electrochemical Techniques",

Proceedings of the 8th Europe Symposiun on Corrosion Inhibitors (8 SEIC), Ann. Univ. Ferrara, N.S., Sez. V, Suppl. N. 10, 1995.