

## CO<sub>2</sub> corrosion rate calculation model

This NORSOK standard is developed with broad petroleum industry participation by interested parties in the Norwegian petroleum industry and is owned by the Norwegian petroleum industry represented by The Norwegian Oil Industry Association (OLF) and Federation of Norwegian Manufacturing Industries (TBL). Please note that whilst every effort has been made to ensure the accuracy of this NORSOK standard, neither OLF nor TBL or any of their members will assume liability for any use thereof. Standards Norway is responsible for the administration and publication of this NORSOK standard.

Standards Norway  
Strandveien 18, P.O. Box 242  
N-1326 Lysaker  
NORWAY

Telephone: + 47 67 83 86 00  
Fax: + 47 67 83 86 01  
Email: [petroleum@standard.no](mailto:petroleum@standard.no)  
Website: [www.standard.no/petroleum](http://www.standard.no/petroleum)

Copyrights reserved



<b>Foreword</b>	<b>2</b>
<b>Introduction</b>	<b>2</b>
<b>1 Scope</b>	<b>3</b>
<b>2 Normative and informative references</b>	<b>3</b>
2.1 Normative references	3
2.2 Informative references	3
<b>3 Terms, definitions and abbreviations</b>	<b>3</b>
3.1 Terms and definitions	3
3.2 Symbols	3
<b>4 Principles for use of the computer program</b>	<b>4</b>
<b>5 Description of the CO<sub>2</sub> corrosion rate model</b>	<b>5</b>
5.1 General	5
5.2 The corrosion model	5
5.3 The effect of glycol and corrosion inhibitors	6
<b>6 Structure of the computer programme</b>	<b>6</b>
<b>7 Input parameters</b>	<b>7</b>
7.1 Basic input parameters	7
7.2 Other input parameters	7
<b>8 Prediction of some of the input parameters</b>	<b>9</b>
8.1 Fugacity of CO <sub>2</sub>	9
8.2 pH	10
8.3 Humidity	12
8.4 Wall shear stress	12

## Foreword

The NORSOK standards are developed by the Norwegian petroleum industry to ensure adequate safety, value adding and cost effectiveness for petroleum industry developments and operations. Furthermore, NORSOK standards are as far as possible intended to replace oil company specifications and serve as references in the authorities' regulations.

The NORSOK standards are normally based on recognised international standards, adding the provisions deemed necessary to fill the broad needs of the Norwegian petroleum industry. Where relevant, NORSOK standards will be used to provide the Norwegian industry input to the international standardisation process. Subject to development and publication of international standards, the relevant NORSOK standard will be withdrawn.

The NORSOK standards are developed according to the consensus principle generally applicable for most standards work and according to established procedures defined in NORSOK A-001.

The NORSOK standards are prepared and published with support by The Norwegian Oil Industry Association (OLF) and Federation of Norwegian Manufacturing Industries (TBL).

NORSOK standards are administered and published by Standards Norway.

## Introduction

This NORSOK standard contains the following two parts:

1. Clause 4, Clause 5, Clause 6, Clause 7 and Clause 8 act as the user manual for the computer program. A description of the calculation model, the algorithms and the conditions for the corrosion rate calculations are given. In additions, methods and algorithms for calculation of essential input parameters to the corrosion rate calculations are given.
2. The computer program for corrosion rate calculations is available for downloading free of charge from the NORSOK internet website (<http://www.standard.no>) or it may be procured from Standard Norge.

## 1 Scope

This NORSOK standard presents a method for calculation of corrosion rates in hydrocarbon production and process systems where the corrosive agent is CO<sub>2</sub>.

## 2 Normative and informative references

The following standards include provisions and guidelines which, through reference in this text, constitute provisions and guidelines of this NORSOK standard. Latest issue of the references shall be used unless otherwise agreed. Other recognized standards may be used provided it can be shown that they meet or exceed the requirements and guidelines of the standards referenced below.

### 2.1 Normative references

NORSOK standard M-001 "Material Selection".

### 2.2 Informative references

None

## 3 Terms, definitions and abbreviations

For the purposes of this NORSOK standard, the following terms, definitions and abbreviations apply.

### 3.1 Terms and definitions

#### 3.1.1

##### **can**

verbal form used for statements of possibility and capability, whether material, physical or casual

#### 3.1.2

##### **may**

verbal form used to indicate a course of action permissible within the limits of this NORSOK standard

#### 3.1.3

##### **shall**

verbal form used to indicate requirements strictly to be followed in order to conform to this NORSOK standard and from which no deviation is permitted, unless accepted by all involved parties

#### 3.1.4

##### **should**

verbal form used to indicate that among several possibilities one is recommended as particularly suitable, without mentioning or excluding others, or that a certain course of action is preferred but not necessarily required

### 3.2 Symbols

A	is the cross sectional area in m <sup>2</sup>
a	is the fugacity coefficient
CR <sub>t</sub>	is the corrosion rate at temperature t in mm/year
C <sub>(index)</sub>	is the concentration of component
D	is the pipe diameter in mm
F <sub>H<sub>2</sub>O</sub>	is the water mass flow in humidity calculations
F <sub>tot</sub>	is the total mass flow in humidity calculations
f	is the friction factor
f(pH) <sub>t</sub>	is the the pH factor at temperature t
f <sub>CO<sub>2</sub></sub>	is the fugacity of CO <sub>2</sub> in bar
φ	is the watercut
φ <sub>c</sub>	is the watercut at inversion point
I	is the ionic strength given in molar
k	is the pipe roughness in m

$K_{(index)}$	is the equilibrium constant used in pH calculations
$K_{(index)}$	is the constant used in viscosity calculations
$K_{SP}$	is the equilibrium constant of iron carbonate
$K_t$	is the constant for the temperature $t$ used in corrosion rate calculations
$\lambda$	is the liquid fraction
$\mu_o$	is the viscosity of oil in $\text{Ns/m}^2$
$\mu_G$	is the viscosity of gas in $\text{Ns/m}^2$
$\mu_L$	is the viscosity of liquid in $\text{Ns/m}^2$
$\mu_m$	is the mixed viscosity in $\text{Ns/m}^2$
$\mu_{relmax}$	is the maximum relative viscosity (relative to the oil)
$\mu_w$	is the viscosity of water in $\text{Ns/m}^2$
$P$	is the total system pressure in bar
$p_{CO_2}$	is the $\text{CO}_2$ partial pressure in bar
$p_{H_2O}$	is the $\text{H}_2\text{O}$ vapour pressure in bar
$Q_G$	is the volumetric flow of gas in $\text{MSm}^3/\text{d}$
$Q_L$	is the volumetric flow of liquid (i.e. liquid hydrocarbons and water) in $\text{Sm}^3/\text{d}$
$R$	is $\mu_w/\mu_o$
$Re$	is the Reynolds number
$\rho_G$	is the gas density in $\text{kg/m}^3$
$\rho_L$	is the liquid density in $\text{kg/m}^3$
$\rho_m$	is the mixed density in $\text{kg/m}^3$
$\rho_o$	is the oil density in $\text{kg/m}^3$
$\rho_w$	is the water density $\text{kg/m}^3$
$S$	is the wall shear stress in Pa
$t$	is the 20 °C, 40 °C, 60 °C, 80 °C, 90 °C, 120 °C or 150 °C
$T_c$	is the temperature given in °C
$T_f$	is the temperature given in °F
$T$	is the temperature given in Kelvin.
$T_{std}$	is the temperature given in Kelvin at standard conditions (60 °F/15,55 °C)
$u_m$	is the mixed velocity (m/s)
$u_G^S$	is the superficial velocities of gas in m/s
$u_L^S$	is the superficial velocities of liquid in m/s
$Z$	is the compressibility of the gas

#### 4 Principles for use of the computer program

The corrosion rate equations included in this NORSOK standard describe the calculation model which shall apply, while the computer program itself is an optional aid which the users of the model may apply such that they possess an efficient tool to conduct corrosion rate calculations and parameter studies. This computer program is developed based on the corrosion rate model given as equations in this NORSOK standard.

The computer program is an aid in  $\text{CO}_2$  corrosion rate assessments, but the user of the computer program is responsible for the results and the final material selections and piping and equipment design. Therefore the user of the program shall perform a critical evaluation of all results and the applicability of these in each case. Corrosion rate calculation, is only one element in a material selection process. Other essential factors are uncertainty in input data for corrosion rate calculations, construction and commissioning conditions, consideration of normal and upset operating conditions, actual corrosivity of produced fluids, scale, wax, inhibitor efficiency and geometry of corrosion attacks. These and other factors may influence the actual corrosion rates considerably, and be more important than any uncertainty in the corrosion rate calculations.

As the computer program is distributed electronically and may be used on different computers and computer program versions, users of the computer program are sole responsible to verify that the computer calculations are in accordance with the equations in this NORSOK standard.

This NORSOK standard provides an introduction to the corrosion rate computer program. It also gives limitations and requirements to input parameters and results. Instructions for running the program are given in the help functions to the program.

The program covers only calculation of corrosion rates where  $\text{CO}_2$  is the corrosive agent. It does not include additional effects of other constituents which may influence the corrosivity, e.g. contamination's of  $\text{O}_2$ ,  $\text{H}_2\text{S}$

etc. If such constituents are present, which is common in e.g. produced water systems, these effects shall be evaluated separately.

Principles for materials selection is given in NORSOK M-001. The requirements in NORSOK M-001 shall be used when generating input data and when interpreting results from this NORSOK standard. It is important to note that this NORSOK standard and computer program may use or generate data which are outside the limits of NORSOK M-001. One example is corrosion inhibitor efficiency, where NORSOK M-001 provides maximum allowable values, while the computer program accepts all values from 0 % to 100 %. In case of conflict, NORSOK M-001 shall apply when selecting materials.

## 5 Description of the CO<sub>2</sub> corrosion rate model

### 5.1 General

The model is an empirical corrosion rate model for carbon steel in water containing CO<sub>2</sub> at different temperatures, pHs, CO<sub>2</sub> fugacities and wall shear stresses. It is based on flow-loop experiments at temperatures from 5 °C to 160 °C. A large amount of data at various temperatures, CO<sub>2</sub> fugacities, pHs and wall shear stresses are used.

The main bulk of the flow loop tests used in developing the calculation model is taken from research programs at Institute for Energy Technology (IFE) in Norway. The main principles for the testing is described in a paper by Dugstad et. al. /1/. Most of the data directly used in the modelling work has been generated after this paper /1/ was presented.

### 5.2 The corrosion model

The following general equation of the CO<sub>2</sub> corrosion rate for carbon steel at each of the temperatures (t); 20 °C, 40 °C, 60 °C, 80 °C, 90 °C, 120 °C and 150 °C is used:

$$CR_t = K_t \times f_{CO_2,62} \times (S/19)^{0,146 + 0,0324 \log(f_{CO_2})} \times f(pH)_t \quad (\text{mm/year}) \quad (1)$$

The following equation is used at temperature 15 °C:

$$CR_t = K_t \times f_{CO_2,36} \times (S/19)^{0,146 + 0,0324 \log(f_{CO_2})} \times f(pH)_t \quad (\text{mm/year}) \quad (2)$$

The following equation is used at temperature 5 °C:

$$CR_t = K_t \times f_{CO_2,36} \times f(pH)_t \quad (\text{mm/year}) \quad (3)$$

The corrosion rate between temperatures where a constant K<sub>t</sub> has been generated, is found by a linear extrapolation between the calculated corrosion rate at the temperature above and below the desired temperature. The constant K<sub>t</sub> is given in the table below.

**Table 1 - Constant K<sub>t</sub>**

Temperature °C	K <sub>t</sub>
5	0,42
15	1,59
20	4,762
40	8,927
60	10,695
80	9,949
90	6,250
120	7,770
150	5,203

The effect of pH is given in Table 2.

**Table 2 - pH function**

Temperature °C	pH	f(pH)
5 5	$3,5 \leq \text{pH} < 4,6$ $4,6 \leq \text{pH} \leq 6,5$	$f(\text{pH}) = 2,0676 - (0,2309 \times \text{pH})$ $f(\text{pH}) = 4,342 - (1,051 \times \text{pH}) + (0,0708 \times \text{pH}^2)$
15 15	$3,5 \leq \text{pH} < 4,6$ $4,6 \leq \text{pH} \leq 6,5$	$f(\text{pH}) = 2,0676 - (0,2309 \times \text{pH})$ $f(\text{pH}) = 4,986 - (1,191 \times \text{pH}) + (0,0708 \times \text{pH}^2)$
20 20	$3,5 \leq \text{pH} < 4,6$ $4,6 \leq \text{pH} \leq 6,5$	$f(\text{pH}) = 2,0676 - (0,2309 \times \text{pH})$ $f(\text{pH}) = 5,1885 - (1,2353 \times \text{pH}) + (0,0708 \times \text{pH}^2)$
40 40	$3,5 \leq \text{pH} < 4,6$ $4,6 \leq \text{pH} \leq 6,5$	$f(\text{pH}) = 2,0676 - (0,2309 \times \text{pH})$ $f(\text{pH}) = 5,1885 - (1,2353 \times \text{pH}) + (0,0708 \times \text{pH}^2)$
60 60	$3,5 \leq \text{pH} < 4,6$ $4,6 \leq \text{pH} \leq 6,5$	$f(\text{pH}) = 1,836 - (0,1818 \times \text{pH})$ $f(\text{pH}) = 15,444 - (6,1291 \times \text{pH}) + (0,8204 \times \text{pH}^2) - (0,0371 \times \text{pH}^3)$
80 80	$3,5 \leq \text{pH} < 4,6$ $4,6 \leq \text{pH} \leq 6,5$	$f(\text{pH}) = 2,6727 - (0,3636 \times \text{pH})$ $f(\text{pH}) = 331,68 \times e^{(-1,2618 \times \text{pH})}$
90 90 90	$3,5 \leq \text{pH} < 4,57$ $4,57 \leq \text{pH} < 5,62$ $5,62 \leq \text{pH} \leq 6,5$	$f(\text{pH}) = 3,1355 - (0,4673 \times \text{pH})$ $f(\text{pH}) = 21254 \times e^{(-2,1811 \times \text{pH})}$ $f(\text{pH}) = 0,4014 - (0,0538 \times \text{pH})$
120 120 120	$3,5 \leq \text{pH} < 4,3$ $4,3 \leq \text{pH} < 5$ $5 \leq \text{pH} \leq 6,5$	$f(\text{pH}) = 1,5375 - (0,125 \times \text{pH})$ $f(\text{pH}) = 5,9757 - (1,157 \times \text{pH})$ $f(\text{pH}) = 0,546125 - (0,071225 \times \text{pH})$
150 150 150	$3,5 \leq \text{pH} < 3,8$ $3,8 \leq \text{pH} < 5$ $5 \leq \text{pH} \leq 6,5$	$f(\text{pH}) = 1$ $f(\text{pH}) = 17,634 - (7,0945 \times \text{pH}) + (0,715 \times \text{pH}^2)$ $f(\text{pH}) = 0,037$

### 5.3 The effect of glycol and corrosion inhibitors

The effect of glycol on the corrosion rate is calculated as a reduction factor, see /2/, as follows:

- Glycol reduction factor =  $10^{1,6 (\log (100-\text{wt}\% \text{Glycol})-2)}$  for less than 95 weight % glycol.
- For > 95 weight % glycol, the glycol reduction factor is set to 0,008.

The effect of corrosion inhibitors is entered directly as a reduction factor in the computer program.

When both addition of corrosion inhibitors and glycol is entered into the computer program, the one effect giving the greatest corrosion rate reduction factor will be used for calculation of the resulting corrosion rate, i.e. the two effects will not be combined.

## 6 Structure of the computer programme

The computer program has a main dialogue box, denoted as the "Main Menu", where all corrosion rate calculations can be performed. All input parameters can be entered into the program directly at this stage for point calculations.

As options and support functions, it is possible to calculate several of the important parameters by selecting optional dialogue boxes. Such options are

- pH calculations,
- shear stress calculations,



- humidity calculations for gas systems (not an input parameter used in the calculations, but essential in evaluating risk for corrosion in gas systems).

These program options are included in order to generate adequate input data for corrosion rate prediction based on data normally presented in process flow diagrams and design basis documents. The support program options are prepared to give adequate accuracy for corrosion rate calculations, and shall not be used for other purposes, e.g. genuine process, scale or flow calculations.

In the clauses below, the input parameters and the corrosion rate calculation model are explained. Additionally, the support functions for calculation of some of the input parameters are explained.

Other support functions, such as "Parameter study", "Accumulated corrosion", saving of data, print of data etc. are not specifically explained in this NORSOK standard, but are covered by the "Help" function provided in the computer program.

## 7 Input parameters

### 7.1 Basic input parameters

The basic input parameters for the CO<sub>2</sub> corrosion model for carbon steel are given in Table 3. The allowed units and ranges are also given.

**Table 3 - Basic input parameters**

Parameter	Units	Range	Comments
Temperature	°C °F	20 to 150 68 to 302	
Total pressure	bar psi	1 to 1000 14,5 to 14500	
Total mass flow	kmole/h	10 <sup>-3</sup> to 10 <sup>6</sup>	Only relevant when CO <sub>2</sub> is given in kmole/h.
CO <sub>2</sub> fugacity in the gas phase	bar psi mole% kmole/h	0,1 to 10 1,45 to 145 variable variable	The CO <sub>2</sub> partial pressure shall be ≤ the total pressure. The allowed ranges of mole% and kmole/h CO <sub>2</sub> are dependent on the total pressure.
Wall shear stress	Pa	1 to 150	Can be calculated by use of other input parameters, see 7.2.1.
pH		3,5 to 6,5	Can be calculated by use of other input parameters, see 7.2.2.
Glycol concentration	weight%	0 to 100	
Inhibitor efficiency	%	0 to 100	See NORSOK M-001

### 7.2 Other input parameters

#### 7.2.1 Input parameters for wall shear stress calculations

To calculate the wall shear stress, the input parameters given in Table 4, are as a minimum required.

**Table 4 - Input parameters for simplified calculation of wall shear stress**

Parameter	Units	Range	Comments
Temperature	°C °F	5 to 150 41 to 302	
Total pressure	bar psi	1 to 1000 14,5 to 14500	
Superficial liquid velocity/ Liquid flow	m/s Sm <sup>3</sup> /d	0 to 20 (depends on internal pipe diameter)	Requirement: turbulent flow, i.e. Re > 2300
Superficial gas velocity/ Gas flow	m/s MSm <sup>3</sup> /d	0 to 40 (depends on internal pipe diameter)	Requirement: turbulent flow, i.e. Re > 2300
Watercut, $\Phi$	%	0 to- 100	
Internal pipe diameter	mm	0 to $\infty$	Requirement: turbulent flow, i.e. Re > 2300

For more accurate wall shear stress calculations, the input parameters given in Table 5 should also be used.

**Table 5 - Input parameters for accurate calculation of wall shear stress**

Parameter	Units	Range	Default value
Roughness	$\mu\text{m}$	0 to 100	50
Compressibility		0,8 to 1	0,9
Specific gravity of gas relative to air		0,5 to 1	0,8
Water density, $\rho_w$	kg/m <sup>3</sup>	995 to 1050	1024
Oil density, $\rho_o$	kg/m <sup>3</sup>	600 to 1100	850
Gas density, $\rho_g$	kg/m <sup>3</sup>	1 to 1700	calculated
Water viscosity, $\mu_w$	cp N s/m <sup>2</sup>	0,17 to 1,1 0,00017 to 0,0011	calculated
Oil viscosity, $\mu_o$	cp N s/m <sup>2</sup>	0,2 to 200 0,0002 to 0,2	1,1
Gas viscosity, $\mu_g$	cp N s/m <sup>2</sup>	0,02 to 0,06 0,00002 to 0,00006	0,03
Water cut at inversion point, $\phi_c$		0,3 to 0,9	0,5
Maximum relative liquid viscosity, $\mu_{relmax}$		1 to 100	7,06

### 7.2.2 Input parameters for pH calculations

To predict the pH in the condensed water or formation water, the parameters given in Table 6 are needed.

**Table 6 - Input parameters for pH calculations**

Parameter	Unit	Range	Default values	Comments
Temperature	°C °F	5 to 150 41 to 302		
Total pressure	bar psi	1 to 1000 14,5 to 14500		
Total mass flow	kmole/h	10 <sup>-3</sup> to 106		Only relevant when CO <sub>2</sub> is given in kmole/h.
CO <sub>2</sub> fugacity	bar psi mole% kmole/h	0 to 10 0 to 145 variable variable		The CO <sub>2</sub> partial pressure shall be < the total pressure. The allowed ranges of mole% and kmole/h CO <sub>2</sub> are dependent on the total pressure.
Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	mg/l mM	0 to 20000 0 to 327	0	Default values for formation water.
Ionic strength/salinity	g/l M	0 to 175 0 to 3	50	Default values for formation water.

### 7.2.3 Humidity calculations

**Table 7. Input parameters for humidity calculation**

Parameter	Unit	Range	Comments
Temperature	°C °F	-16 to 200 3,2 to 392	
Total pressure	bar psi	1 to 1000 14,5 to 14500	
Water mass flow	kmole/h	10 <sup>-3</sup> to 10 <sup>6</sup>	
Total mass flow	kmole/h	10 <sup>-3</sup> to 10 <sup>6</sup>	The water mass flow shall be < the total mass flow.

## 8 Prediction of some of the input parameters

### 8.1 Fugacity of CO<sub>2</sub>

Gases are not ideal at high pressures. To compensate for this, the partial pressure of a gas is multiplied by a fugacity constant. The real CO<sub>2</sub> pressure can then be expressed as:

$$f_{\text{CO}_2} = a \times p_{\text{CO}_2} \quad (4)$$

The CO<sub>2</sub> partial pressure is found by one of the following expressions:

$$p_{\text{CO}_2} = (\text{mole\% CO}_2 \text{ in the gas phase} / 100 \%) \times P \quad (5)$$

or

$$p_{\text{CO}_2} = \frac{\text{mass flow of CO}_2 \text{ in the gas phase (kmole/h)}}{\text{total mass flow in the gas phase (kmole/h)}} \times P \quad (6)$$

The fugacity coefficient is given as (see /2/):

$$a = 10^{P \times (0,0031 - 1,4/T)} \quad \text{for } P \leq 250 \text{ bar} \quad (7)$$

$$a = 10^{250 \times (0,0031 - 1,4/T)} \quad \text{for } P > 250 \text{ bar} \quad (8)$$

The total pressure is set to 250 bar in the fugacity constant for all pressures above 250 bar.

## 8.2 pH

### 8.2.1 General considerations

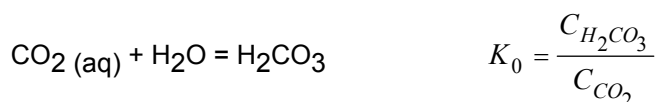
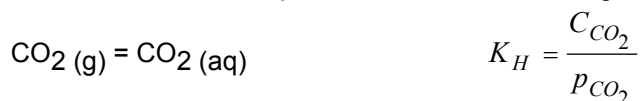
The program contains a pH calculation module. The pH in both condensed water and formation water can be calculated. Some essential general considerations relevant for pH assessment is given below.

The reported pH in water analyses is usually measured after depressurisation and atmospheric exposure of the sample. Such pHs give no information about the in situ pH which is a requisite for the corrosion rate evaluation. The in situ pH has to be determined by calculations which take into account the three controlling buffer systems  $\text{CO}_2/\text{HCO}_3^-$ ,  $\text{H}_2\text{S}/\text{HS}^-$  and  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ . The buffer system  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$  can be extended to include all the other organic acids that may influence the pH determination as these acids have similar dissociation constants.

The bicarbonate concentration, which is used for pH calculation, is routinely determined by titration and the reported value is set equal to the alkalinity. This is correct as long as the  $\text{H}_2\text{S}$  concentration is low and the system does not contain acetic acid. For waters containing significant amount of organic acids, the reported bicarbonate concentration requires correction because organic acids contributes to the measured value of total alkalinity. The correction will be 2/3 of the organic acid concentration assuming that the end point pH of the titration is 4.3. Lower pH requires a higher fraction. More details about the interpretation of the water analysis and the determination of pH can be found in the European Federation of Corrosion (EFC) publication number 16 /3/.

### 8.2.2 Calculation of pH

The routine for calculation of pH is based on the following chemical reactions and equilibrium constants:



The system has to be electro-neutral, which can be described by the following equation:

$$C_{\text{Na}^+} + C_{\text{H}^+} = C_{\text{HCO}_3^-} + 2C_{\text{CO}_3^{2-}} + C_{\text{OH}^-} + C_{\text{Cl}^-} \quad (9)$$

It is assumed that bicarbonate is added as sodium bicarbonate ( $\text{NaHCO}_3$ ). It is also assumed that no other salts than sodium bicarbonate and sodium chloride ( $\text{NaCl}$ ) are present in the solution. These salts will dissolve as follows:





Based on these assumptions, the amount of sodium bicarbonate equals the difference in the concentrations of sodium and chloride as shown below. The mass balance for bicarbonate will therefore be as follows:

$$C_{0,Bicarb} = C_{\text{Na}^+} - C_{\text{Cl}^-} \quad (10)$$

$C_{0,Bicarb}$  equals the initial amount of sodium bicarbonate.

By combining the equations for the equilibrium constants with the required electro-neutrality and the mass balance for bicarbonate one get the following expression for the concentration of the hydrogen cation:

$$C_{\text{H}^+}^3 + C_{0,Bicarb} C_{\text{H}^+}^2 - (K_H K_0 K_1 p_{\text{CO}_2} + K_W) C_{\text{H}^+} - 2K_H K_0 K_1 K_2 p_{\text{CO}_2} = 0 \quad (11)$$

This equation is solved by using the Newton's method.

The pH in a condensed water system saturated with iron carbonate can also be calculated. Based on a similar deduction as above, the equation becomes:

$$\left( \frac{2K_{SP}}{K_H K_0 K_1 K_2 p_{\text{CO}_2}} \right) C_{\text{H}^+}^4 + C_{\text{H}^+}^3 + C_{0,Bicarb} C_{\text{H}^+}^2 - (K_H K_0 K_1 p_{\text{CO}_2} + K_W) C_{\text{H}^+} - 2K_H K_0 K_1 K_2 p_{\text{CO}_2} = 0 \quad (12)$$

### 8.2.3 Equilibrium constants

The equilibrium constant for iron carbonate was taken from The International Union of Pure and Applied Chemistry (IUPAC) with Institute for Energy Technology (IFE) ionic strength dependence, see /5/:

$$K_{sp} = 10^{-(10.13+0.0182T_c-2.44T_c^{0.5}+0.72I)} \text{ molal}^2 \quad (13)$$

NOTE The other equilibrium constants have various origin. Crovetto has made an extensive compilation of data for the solubility of CO<sub>2</sub> in water as function of temperature and based on that found an equation which is valid from 0 °C to the critical point of water /6/. This equation is used as the basis for the Henry's law equation. The pressure dependence as given by Oddo and Tomson has been added together with an Institute for Energy Technology (IFE) expression for the ionic strength dependence /7/. The IFE equation is fitted to data by Cramer /8/. This Henry's law equation requires CO<sub>2</sub> fugacities as given by the equations given in 8.1.

0 °C – 80 °C:

$$K_H = 55.5084 \cdot e^{-\left(4.8 + \frac{3934.4}{T_K} - \frac{941290.2}{T_K^2}\right)} \cdot 10^{-(1.790 \cdot 10^{-4} \cdot P + 0.1071)} \text{ molar / bar} \quad (14)$$

80 °C – 200 °C:

$$K_H = 55.5084 \cdot e^{-\left(\frac{1713.53 \cdot \left(1 - \frac{T_K}{647}\right)^{\frac{1}{3}}}{T_K} + 3.875 + \frac{3680.09}{T_K} - \frac{1198506.1}{T_K^2}\right)} \cdot 10^{-(1.790 \cdot 10^{-4} \cdot P + 0.1071)} \text{ molar / bar} \quad (15)$$

The dissociation constants for carbonic acid when the concentration of H<sub>2</sub>CO<sub>3</sub> is set to the sum of dissolved CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub>, are based on equations given by Atkinson /9/ and Oddo and Tomson /7/:

$$K_1 = 10^{-\left(356.3094 + 0.06091964 T_K - \frac{21834.37}{T_K} - 126.8339 \cdot \text{Log}_{10}(T_K) + \frac{168491.5}{T_K^2} - 2.564 \cdot 10^{-5} \cdot P - 0.491 T_c^{0.5} + 0.379 T_c - 0.06506 T_c^{1.5} - 1.458 \cdot 10^{-3} \cdot T_c \cdot T_f\right)} \quad (16)$$

$$K_2 = 10^{-\left(107.8871 + 0.03252849 \cdot T_K - \frac{2151.79}{T_K} - 38.92561 \cdot \text{Log}_{10}(T_K) + \frac{563713.9}{T_K^2} - 2.118 \cdot 10^{-5} \cdot P - 1.255 \cdot 10^{-5} + 0.867 T_c - 0.174 T_c^{1.5} - 1.588 \cdot 10^{-3} \cdot T_c \cdot T_f\right)} \quad (17)$$

where P is the pressure given in psi.

The equation for the equilibrium constant for the dissociation of water was based on data given by Delahay/10/:

$$K_w = 10^{-(29.3868 - 0.0737549T + 7.47881 \cdot 10^{-5} T^2)} \text{ molar}^2 \quad (18)$$

### 8.3 Humidity

A prerequisite for corrosion to occur is that there is liquid water present in the system. In gas systems, an essential assessment is to determine if the presence of condensed water is possible. The program therefore includes a support function to calculate humidity in pure water /11/, i.e. in systems without glycol.

$$\text{Humidity (\%)} = 100 \times (P \times F_{H_2O}) / (p_{H_2O} \times F_{tot}) \quad (19)$$

The dew point temperature ( $T_{dew}$ ) equals the temperature where the humidity is 100 %.

### 8.4 Wall shear stress

Wall shear stress is one of the parameters needed for calculation of corrosion rate. In the model, the mean wall shear stress in straight pipe sections is used.

Obstacles and other geometrical changes in the flow will give rise to higher shear stresses than calculated by this program. Further, different flow regimes and geometrical obstacles may generate shear stress fluctuations where the shear stress peaks may be considerably higher than the average shear stress.

High shear stress may cause mesa attacks, with corrosion rates significantly higher than what is estimated by this computer program.

It is not the objective of this computer program to cover all such eventualities, and the user of the program shall evaluate the flow effect in each system/part of a system based on expertise and available experience and documentation.

The mean wall shear on the wall at medium to high superficial velocities of one or both of the liquid and gas velocities:

$$S = 0,5 \times \rho_m \times f \times u_m^2 \quad (\text{Pa}) \quad (20)$$

where the friction factor,  $f$ , can be expressed as:

$$f = 0,001375 \left[ 1 + \left( 20000 \frac{k}{D} + 10^6 \frac{\mu_m}{\rho_m u_m D} \right)^{0,33} \right] \quad (21)$$

Mixture density, velocity and viscosity is expressed as:

$$\begin{aligned} \rho_m &= \rho_L \lambda + \rho_G (1 - \lambda) \\ \rho_L &= \phi \rho_w + \rho_o (1 - \lambda) \\ \rho_G &= 2,7 \ 14,5 \ 16,018 \ P \ \text{specific gravity} / (Z (460 + T_f)) \end{aligned}$$

$$u_m = u_L^s + u_G^s$$

$$\begin{aligned} \text{The liquid is considered incompressible:} \quad u_L^s &= Q_L / A \\ \text{The gas superficial velocity is:} \quad u_G^s &= (Q_G / A) Z (T / T_{std}) \end{aligned}$$

$$\mu_m = \mu_L \times \lambda + \mu_G \times (1 - \lambda)$$

$$\lambda = \frac{Q_L}{Q_L + Q_G}$$

This model (see /12/) is verified for medium/high flow rates by tests.

If water is present the viscosity of the liquid is found as follows:

The effective viscosity of a kinetically stable oil/water mixture depends on the watercut /13/. Preferably the maximum magnitude of viscosity and the corresponding watercut should be known. The viscosity of the oil wet region, i.e. below the inversion point in a dispersed flow, can be represented as:

$$\mu_L = \mu_o \left( 1 + \frac{\frac{\phi}{K_0}}{1,187 - \frac{\phi}{K_0}} \right)^{2,5} \quad (\text{Ns/m}^2) \quad (22)$$

The value of  $K_0$  for the maximum relative viscosity  $\mu_{rel\max}$  (relative to the oil) and corresponding watercut at the inversion point,  $\phi_c$ , is equal to:

$$K_0 = \frac{\phi_c}{1,187 \left( 1 - \left( \frac{1}{\mu_{rel\max}} \right)^{0,4} \right)}$$

If not known, data for a medium viscosity oil/water dispersion will be used. This dispersion exhibits a maximum value of relative viscosity = 7,06 at a watercut of 0,5. The oil viscosity is equal to 0,0011 Ns/m<sup>2</sup> at 60 °C and the water viscosity is equal to 0,00046 Ns/m<sup>2</sup>.

Above the inversion point, the viscosity of any dispersion is given as:

$$\mu_L = \mu_w \left( 1 + \frac{\frac{1-\phi}{K_w}}{1,187 - \frac{1-\phi}{K_w}} \right)^{2,5} \quad (\text{Ns/m}^2) \quad (23)$$

where

$$K_w = \frac{1 - \phi_c}{1,187 \left( 1 - \left( \frac{R}{\mu_{rel\max}} \right)^{0,4} \right)}$$

The viscosity of water is as default given as function of temperature,  $T_c$ , given in °C /11/:

0 °C - 20 °C:

$$\mu_w = 10^{1301/(998,333+8,1855(T_c-20)+0,00585(T_c-20)^2)-1,30233} \cdot 10^{-3} \quad (\text{Ns/m}^2) \quad (24)$$

20 °C - 150 °C (the formula is strictly only valid up to 100 °C, but used up to 150 °C in this context):

$$\mu_w = 1,002 \left( 10^{\frac{(1,3272(20-T_c)-0,001053(T_c-20)^2)}{(T+105)}} \right) 10^{-3} \quad (\text{Ns/m}^2) \quad (25)$$

For the medium viscosity oil at 60 °C , R is equal to 0,42.

## Bibliography

- /1/ A. Dugstad, L. Lunde, K.Videm "Parametric study of CO<sub>2</sub> corrosion of carbon steel" NACE-Corrosion-94 paper No 14.
- /2/ C. de Waard, U. Lotz, D.E.Milliams "Predictive model for CO<sub>2</sub> Corrosion engineering in wet natural gas pipelines", Corrosion December 1991 pp. 976
- /3/ Guidelines on materials requirement for carbon and low alloy steels for H<sub>2</sub>S-containing environments in oil and gas production, European Federation of corrosion publication number 16, the Institute of Materials, 1995
- /4/ D. A. Palmer and R. V. Eldik, Chem. Rev., Vol. 83, p. 651, 1983.
- /5/ IUPAC: Chemical Data Series No 21. Stability constants of Metal-Ion Complexes. Par A: Inorganic ligands. Pergamon Press.
- /6/ R. Crovetto, J. Phys. Chem. Data, 20 (3), 1999.
- /7/ J. E. Oddo and M. B. Tomson, "Simplified Calculation of CaCO<sub>3</sub> Saturation at High Temperatures and Pressures in Brine Solutions". SPE of AIME, pp. 1583, 1982.
- /8/ S.D. Cramer, "The Solubility of Methane, Carbon Dioxide, and Oxygen in Brines from 0 to 300 °C", Bureau of Mines Report of Investigations, RI 8706, 1982.
- /9/ G. Atkinson, Oilfield Scale Symposium, 27.-28. January, Aberdeen Scotland, 1999.
- /10/ P. Delahay, "Implication of the Kinetics of Ionic Dissociation with regard to some Electrochemical Process-application to Polarography." I.Am.Chem.Sic, 74, 1952 pp 3497.
- /11/ D. R. Lide, "CRC Handbook of Chemistry and Physics" 66<sup>th</sup> edition, CRC Press Inc. 1985-1986
- /12/ A. E. Dukler, M. Wicks III, R.G. Cleveland, Frictional pressure drop in two phase flow. An approach through similarity analysis, A.I.Ch.E. Journal, Vol. 10, No 1, January 1964
- /13/ H. Kvandal, T. Sørtvedt, Frictional pressure loss for stable oil-water emulsions in pipeflow. Symposium on two phase flow modelling and experimentation, Rome 1995.





