Master Thesis

Corrosion Monitoring Concept for Oil Wells

Supervised by: Univ.-Prof. Dipl.-Ing. Dr.mont. Herbert Hofstätter Ao. Univ.-Prof. Dipl.-Ing. Dr.mont. Gregor Mori

AFFIDAVIT

I declare in lieu of oath, that I wrote this thesis and performed the associated research myself, using only literature cited in this volume.

Place, date Signature

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Abstract

This "Master of Science" thesis deals with the creation of a corrosion monitoring concept of oil wells. In the end, the reader should have a deeper understanding regarding important parameters affecting corrosion, parameters to be measured in terms of corrosion surveillance and the connected prevention of metal deterioration. At the beginning, a theoretical background is provided to create an overview on corrosion issues. As a second step, a field data analysis of oil wells in Austria is being performed, where critical parameters are screened and checked for validity. Field data investigations do not show a good match according to literature and so reliable outputs, like an optimum dose of inhibitors to be injected downhole, can not be published by means of field data investigations only. That is why autoclave experiments, with respect to selected field data parameters, have been performed and results, indicating clear trends towards critical questions, are being published at the experimental section in this work. At the end of this work, guidelines for a measurement concept are recommended to achieve a reliable feedback by means of routine measurements

This project has been carried out in close cooperation between an austrian oil company and University of Leoben. Departments of petroleum production and corrosion of both institutions have been involved. The employed software was Microsoft Excel 2010 and Origin 8.5. Valuable input came from several industry experts, while further information was taken from books, papers and journals. All used sources were stated using ISO 690 convention for citation, in order to honour the authors and to make sure that continuative research can start from this work's final stage of knowledge.

1 Introduction

Corrosion is a dominant problem in the oil and gas industry. About 10 % of the price for crude oil serves for maintenance costs due to corrosion and approximately 4 % of the gross national product is lost in industrial countries due to corrosion processes.¹⁹ As may be expected, controlling corrosion is a target very difficult to be reached and set- ups, granting 100 % reliability, have not be found so far.

Of course also oil companies in Austria are familiar with corrosion problems. In fields of Austria, with over 50 years of oil and gas production history, watercuts of approximately 90 % are being faced. Basically, inhibitors are injected to keep the corrosion rate below the threshold- limit of 0.05 mm/a. The corrosion rates are being measured via coupons placed either downhole, or at surface installations, where fluid streams are in contact with coupons' surface.

As a matter of fact, bigger variations concerning corrosion rate measurement- outputs and actual tubing replacements have been experienced in the past. Wells, with corrosion rates lower than 0.05 mm/a, still show larger traces of corrosion on tubing walls than expected. Those corrosion rates are to be analysed intensively, in order to understand backgrounds and the reason for deviations of corrosion measurements and actual corrosion failures. Secondly, inhibition doses have been adjusted independently in the past, because no guideline was created regarding measurement and inhibitor concentration. Focus is set on an optimum concentration of inhibitors, whereas the corrosion measurement- methods and inhibitor doses injected so far have to be verified and controlled for correct application. To achieve a level of comparison between field data and laboratory experience, several autoclave experiments will be done. In connection to the correct inhibitor dose, optimum coupons measurement adjustments regarding location, duration and frequency need to be evaluated to maintain control and overview on field's corrosion status.

Before analyses of field data is conducted, a theoretical backup of corrosion principles and influences is presented.

This thesis should provide a major guideline in corrosion management, to achieve a reduction of corrosion problems and failures.

2 Theory of CO₂ Corrosion

One of the most common corrosion types in oil and gas production is Carbon Dioxide $(CO₂)$ corrosion.^{1, 2} In order to understand $CO₂$ corrosion, basic equations and important side effects of this corrosion process have to be demonstrated. As a matter of fact, this process is a function of many influences in production environments³.

2.1 Basic Reactions

Generally $CO₂$ dissolves in water and results in carbonic acid, a weak acid compared to mineral acids but still able to deteriorate the surface condition of carbon steel.

$$
CO2(g) + H2O(l) \leftrightarrow H2CO3(aq)
$$

Four equations, following up, summarize the corrosion process and demonstrate three cathodic and one anodic reaction.¹

In connection to $Fe²⁺$ ions the following reaction products are precipitating:

$$
Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3
$$
 Equation 6

 $Fe^{2+} + 2HCO_3^- \rightarrow Fe(HCO_3)_2$ Equation 7

$$
Fe(HCO3)2 \rightarrow FeCO3 + CO2 + H2O
$$
Equation 8

As a consequence of reactions illustrated above, produced iron carbonate (FeCO₃) can be important in protection of metal surfaces and preventing advanced corrosion. 4

2.2 Effect of Key Parameters on $CO₂$ Corrosion

In the following subchapter, relevant parameters regarding oilfield corrosion are being elaborated. Other parameters affecting $CO₂$ corrosion have not been considered.

2.2.1 Fluid Characteristics, Contents and Watercut

Oil

Crude oils are not corrosive at typical oil and gas production temperatures and can provide a barrier for water and prevent corrosion processes on the metal surface because of that.^{3, 5, 14}

Basically, hydrocarbons can, because of their complex composition, be classified with respect to their geochemical history.⁶ Types are based on their maturity and Kerogen type, which is defined as the organic fraction within the sedimentary rock. By determination of the amount of aromatics and paraffins and their geochemical history, three types 6 of Kerogen can be defined.

- Kerogen I: Crude oils derived from algal matter, contain mainly paraffinic chains and is poor in aromatics
- Kerogen II: Consists of both paraffinic and aromatic structures from marine organic substrates

Kerogen III: Mostly aromatic chains derived from terrestrial plants

It has to be mentioned that crude oil, which contains organic acids, supports corrosion via decrease of pH- value.^{7, 8, 9} Nevertheless, influences of organic acids are not presented in this work.

Wettability

Generally oil is not considered to be corrosive^{3, 5, 14}; corrosion only takes place if water wets metal surface. According to Kermani², there are two concepts of water wetting relevant to corrosion modelling, one in connection to electrochemistry and surface physics, the other one related to $CO₂$ corrosion, that are to be mentioned shortly in this section.

"Electrochemistry and surface physics wetting" concept relates to simple contact of liquid to metal surface. This concept delivers high support in modeling of water wetting. $CO₂$ corrosion related concept is based on liquid soaked porous films holding water, even if temporarily media in contact with the film has no carrying traces of water. Behavior of corrosion processes within that concept can be different regarding scales of protective layers and can occur in connection to shut down periods of wells or slug flow velocities. This is the reason why watercuts' impacts on corrosion rates should be analyzed in connection with the flow velocity and the two associated concepts of water wetting.²

In order to model wetting phases of particular fluids, De Waard and Smith postulated wettability relations to oil, water and steel with help of interfacial tension (γ liquid-steel), where a lower value indicates better wetting. As a matter of fact, γ oil-steel varies with different crude oils, which is not expected to be the case at γ water-steel.³

$$
\gamma_{\text{water }-oil} = \gamma_{\text{oil }-steel} - \gamma_{\text{water }-steel}
$$

Equation 9 implies, under consideration of improved water wetting characteristics of iron carbonate films on steel surfaces³, interfacial tension between oil and steel to be bigger. This assumption seems reasonable, since generally water tends to wet metal surfaces more easily. Depending on crude oil gravity, different amounts of water can be carried before separation into two phases. That means lighter oils are less effective in forming water- oil emulsions, increasing water wetting tendencies and thus the corrosion potential.³ Additional information is being found in chapter "2.3.1 Corrosion Models- De Waard- Milliams- Smith".

Watercut

Water is the basis of every corrosion process, even though pure water does not show corrosive tendencies up to boiling temperatures.¹⁰ With addition of corrosive gases like oxygen, $CO₂$ or H_2S , corrosion is able to attack metal surfaces.^{10, 19, 21} Whereas oxygen influence is considered to be excludable in oil reservoirs and its upstream installations², CO₂ is able to create an acid and consequently attacks subsurface installations like demonstrated within Equation 1 and its theoretical background, presented below in "2.2.2 $CO₂$ partial pressure" section.

The watercut (WC) simply describes the percentage [%] of water that is being produced in an oil and gas production flow stream. That is why corrosion basically is a function of water content in "local crude oil/ produced water" mixtures for constant environmental conditions.¹¹ Produced waters are strongly linked to the corresponding oil and its tendency to form water- oil emulsions. This leads to a threshold- watercut, where corrosion commences. Investigations of Carew et al.^{11, 12} showed a threshold watercut of 30 to 40 % within their experiments with different crude oils, where no significant corrosion processes were evident. Below this value water is completely dispersed in oil, above, water is wetting metal surfaces. Higher this volume, both localized as well as uniform corrosion was found. Results additionally showed sharper slopes concerning corrosion rates at watercuts of 50 to 70 % than within 70 % to 100 %,¹² indicating a level, where water is fully covering the metal surface. This leads to an increased electrochemical activity at the steel surface, making corrosion rates rise.

pH and $Fe²⁺$ Content

To refresh one's memory, pH, ranges from 1 to 14, whereas 7 stands for neutral state. It describes the concentration of dissolved hydronium ions in solutions. The higher the pH, the lower is its H_3O^+ concentration;

$$
pH = -\log(H^+)
$$

Equation 10

Major impacts on corrosion rates of oil wells that produce water to a certain extent, are linked to the pH value.^{13, 17, 18} Equation 5 describes theoretically the anodic dissolution rate, when no additional solid reaction is formed, with its ability to proceed intermediates that involve hydroxyl ions (OH) and thus decreasing its rate with decreasing pH. 13 As a matter of fact, this effect is expected rarely in practice because of control of cathodic reaction, illustrated under deaerated conditions by Equation 4. A higher pH affects primarily the cathodic reaction, making the reduction of H⁺ ions slower and so the anodic dissolution of iron as well.²⁵ The increase in rate of cathodic reaction with decreasing pH more than offsets pH dependence of the intermediate reaction of anodic Equation 5. The net effect is that corrosion rates increase with decreasing $pH.¹³$ In H₂S – CO₂ mixed environments in- situ pH is based²¹ on

- \bullet HCO₃ via Equation 1
- HS⁻ via Equation 13

Calculations for pH evaluations in $CO₂$ corrosion prediction models are principally based on measured bicarbonate concentrations, $CO₂$ solubilities and carbonic acid dissociation constants.³

Figure 1 – Example of Buildup of dissolved Iron Concentration on pH and Corrosion Rate at 20 °C, 100 bar System Pressure and 1 % $CO₂$ at 1 m/s¹⁴

The increase of corrosion rates with decreasing pH is also shown in connection to Fe^{2+} concentrations in solutions affecting the already mentioned protective $FeCO₃$ films. Iron contents are depending on anodic reaction mechanisms¹⁵ and solubility varies with $CO₂$ concentrations, temperature, pH and concentration of other ions.² Equation 8 describes the creation of supersaturation, where the concentration of $Fe²⁺$ is higher than the solubility limit of FeCO₃, increasing the pH and reducing corrosion rates.^{4, 16} Figure 1 illustrates an example,

where a solution with variations in Fe^{2+} saturations is being plotted. It can be seen that corrosion rates decrease with Fe^{2+} saturation (and pH increase).¹⁴ In natural environments, fluids very often are saturated or even supersaturated with iron carbonate explaining the high iron carbonate scale frequency.¹⁴

2.2.2 CO2 and H2S Partial Pressures

CO₂

It is a widely used simplification that systems' total pressure is the sum of corresponding partial pressures of ideal gases. Still assuming ideal conditions, partial pressures are calculated by

$$
x_i = \frac{P_i}{P} = \frac{n_i}{n}
$$
 Equation 11

where P_i is the partial pressure, x_i mole fraction and n_i the amount of moles of an individual gas. P and n are total values of corresponding parameters.

CO₂ partial pressures are in direct relationship to pH and its calculations, explained by Equation 1. De Waard¹⁷ postulated via Equation 12, Henry's law and knowing that concentration of carbonic acid is proportional to $CO₂$ partial pressure

$$
pH = -\frac{1}{2} \cdot \log(P_{CO_2}) + const
$$
 Equation 12

where P_{CO_2} describes the CO_2 partial pressure and the constant implies the dissociation constant (K) and Henry's constant, both depending on temperature.

In literature, often partial pressures are related to corrosion rates^{2, 17} via their impacts on pH and the connected changes of corrosion rates.

Describing non- ideal gases in connection to partial pressures of $CO₂$ is an issue. That is why very often $CO₂$ fugacity is added for exact calculations and investigations on corrosion rate impacts.^{3, 18} Even more problematic is the relation of non- ideal gas phase at high rate gas wells to the water phase, where an activity coefficient should be introduced for homogeneity. Due to weak availability of activity coefficients for water phases out of Pressure – Volume – Temperature (PVT) data, predictions of corrosion behaviour very often are limited to fugacities.²

Figure 2 – Corrosion Rates of Steel St52 at 90 °C as a Function Partial Pressures of CO₂ for flow rates of 20 m/s and differing pH¹⁶

Figure 2 demonstrates the influence of $CO₂$ partial pressure on steel. As can be seen, experiments with Fe^{2+} saturated electrolytes show once more lower corrosion rates at 90 °C, compared to the ones that are connected to fluids with low amounts of iron ions. In Literature, often slopes of the partial pressure curves are decreasing with increasing partial pressure of CO_2 . ^{16, 19}

 $H₂S$

Dihydrogen Sulphide (H₂S) containing wells, also known as "sour" wells, have increased steadily in recent years, as by production of only "sweet" reservoirs (not containing H_2S) demand can not be met nowadays.²⁰

Basically H_2S corrosion follows reactions, depending on parameters fluid chemistry, organic acids, flow velocity and presence of elemental sulphur. 21

The anion HS splits further up to H⁺ and S²⁻. S²⁻ results via Fe²⁺ in FeS, a commonly found corrosion product. Those iron sulfide scales act under certain conditions highly protective against corrosion.²¹ In mixed CO₂ and H₂S environments, corrosion causes are not easier to be found. Ignoring the metal cracking effects of H_2S sour services, low levels of hydrogen sulfide can influence corrosion in different ways. H₂S either supports $CO₂$ corrosion by accelerating anodic dissolution- reaction of Equation 5 through sulfide adsorption, or it decreases "sweet" corrosion of CO_2 by formation of an iron sulfide layer^{20, 21, 22, 23, 24}, that, contrary to insulating effects of iron carbonate layers, exhibit electronic conductivity.²⁵ Due to the fact that H₂S relation

to $CO₂$ corrosion is not fully understood, available equations or models for corrosion prediction must be handled with care. However, Pots et al.²⁶ postulated in 2002 via CO₂ and H₂S ratios three different domains for corrosion management:

- P_{CO_2} / P_{H_2S} < 20
	- \circ Corrosion dominated by H₂S
		- FeS as the main corrosion product
- 20 < P_{CO_2} / P_{H_2S} < 500
	- \circ Mixed by CO₂/H₂S corrosion dominance
		- A mixture of FeS and $FeCO₃$ as the main corrosion products
- P_{CO_2} / P_{H_2S} > 500
	- \circ CO₂ corrosion dominates
		- $FeCO₃$ as the main corrosion product

Details are found at Background Data 1 and Background Data 2 in Appendix section.

Other experimental flow- loop investigations²¹ on low H_2S partial pressures showed same tendencies. Via H₂S partial pressures of 1.5*10⁻³, 1.5*10⁻² and 1.5*10⁻¹ psi, (0.0001, 0.001 and 0.01 bar) with $H₂S$ concentrations of 100, 1000 and 10000 ppm in gas phase, tests were carried out on X65 steel at 30, 50 and 75 °C in presence of 14.7 psi (1 bar) $CO₂$. Environmental details are illustrated in Background Data 1. Out of those tests low corrosion rates in connection to low H₂S concentrations can be concluded.²¹ Results indicate that low levels of H₂S, defined to be below limits of SSC occurrence of 0.05 psi, can reduce $CO₂$ corrosion by a factor of 3 to 4. 21

Brown et al.²¹ concluded that small amounts of H₂S (10 ppm) can reduce $CO₂$ corrosion rates, without presence of protective iron carbonate and sulphide layers. Protective adherent films were formed at 60 °C with 25 ppm H_2S at pressures of 114.6 psi (7.9 bar) and a pH of 6.

In cases where FeS breakdown occurs the corrosion rate can be an order of magnitude higher than the corresponding rate for pure $CO₂$. This high corrosion rate in the presence of H₂S is a result of drop in the pH due to the reduction of the dissolved iron ions that occurs with FeS precipitation and galvanic couple formed between the steel and corrosion scale.¹⁴ This phenomenon is called "Pitting" and its probability of occurrence increases with increasing H_2S partial pressure, like Figure 3 demonstrates.^{2, 14, 19, 21, 22}

Figure 3 – Example of Effect of H2S Concentration at 100 bar, 50 °C, 1 % CO $_2$, 1 m/s, supersaturated in FeCO $_3{}^{14}$

It has to be kept in mind, that reactions published so far are strongly connected to anaerobic conditions. Especially speaking about iron carbonates, stability of scales is affected and reduced significantly when oxygen is present.¹ Like already mentioned, presence of oxygen is unlikely in oil reservoirs and its upstream installations², but the small chance, that a finite amount of oxygen migrates into installations, exists.¹

Oxygen contamination is recognized as a main difficulty studying corrosion influences in laboratory experiments. 27

A simple comparison of dominant gases in hydrocarbon production, $CO₂$ and H₂S, and oxygen is shown by Jones²¹ in Figure 4. This plot is based on data gained by exposing clean carbon steel samples to water solutions containing various conditions of each gas at 25 °C. Of course, this plot is not considering synergistic effects of corresponding gas mixtures and is for example material selection not applicable. Nevertheless, it gives an idea about corrosion tendency as well as aggression concerning metal deterioration of those three gases. As can be seen, oxygen is due to its ability to mutate Fe^{2+} ions into ferric ions of Fe^{3+} and its ability to accelerate cathodic reactions^{1, 27} the most aggressive gas regarding corrosion.

Figure 4 – Comparative Corrosiveness of 3 common Gases in water solutions (25 °C, 5-7 days exposure, 2-5 g/l NaCl, HCO₃ alkilinity <50 mg/l- computed from several data sources) 21

2.2.3 Fluid Velocity

The effect of velocities on corrosion tendency is not fully understood today as well. 2 However, it is not only the fluid content that needs to be verified in corrosion predictive modelling; flow regimes have to be analyzed as well, even though they are difficult being determined. Key factors can be presented with oil- water ratios, emulsion tendencies and stabilities, as well as with gas- oil ratios (GOR).² For many crude oils, watercuts, higher than 30 %, lead to water wetting tendency and thus to potential corrosion risk.^{2, 11, 12} Also with increasing GORs, continuous water wetting by condensed water can be expected. 2

Figure 5 below illustrates main flow regimes possible in two phase flow. One major problem dealing with velocities is the property of removal of protective layers.^{16, 28, 29} In flow loop experiments of Nesic et al. 28 protective films formed, generally were resistive to severe flow conditions. At lower temperatures, within pH values of 5.1 and 6.8, precipitation of iron carbonate films were not permanently the case even if $FeCO₃$ concentration exceeded the saturation limit; at higher pH values only the very thin $Fe₃C$ film was strengthened as the only protective layer. Fe3C films did not show any protective tendencies in those experiments and contribute to even higher corrosion rates contrary to $FeCO₃$ films, formed with increasing temperatures more easily. It was found that slug flow, with high fluctuating wall forces, causes higher damage to these films compared to single phase flow. In most cases, highest corrosion rates were found in vicinity of flow disturbance. Similar results with coupons exposed to flow streams are gained by Heuer.²⁹ Again, evident changes in protective film thickness are noticed changing from full pipe flow to slug flow. Additionally, with slug flow, streaked corrosion films

became less common and were replaced by rougher films, allowing the enhanced transport of reacting materials to the metal surface. Furthermore, flow impacts can change basic temperature influences on corrosion processes; in slug flow conditions, thinner corrosion films and no $FeCO₃$ crystals are found on metal surfaces and films remained constant over temperature variations between 40 °C to 80 °C. Showing no maximum within that ranges of temperatures contrary to full pipe flow, evidence suggested flow impacts on temperature influences, in that case.

Figure 5 – Baker Diagram showing Flow Behaviour depending on Gas and Liquid Velocity (D= 1", 3% NaCl Brine, CO₂ Partial Pressure =150 psg, Temperature= 160 °F or 71 °C)¹⁹

For corrosion rate prediction, the common primary parameter for velocity consideration is the wall shear stress between liquid and pipe walls.¹⁸ But not only slug flow, causing maximum wall shear stress, is considered to be a crucial velocity parameter. The removal of oil films or damage of FeCO₃ films, covering metal surfaces protecting against corrosive influences, can be removed by higher velocities of conventional full pipe flow as well.^{11, 28, 29} Of course the oilremoval tendency is governed by the velocity itself and the watercut. The higher the watercut, the thinner is the oil film on metals and the less resistant it is against turbulent velocities.^{11, 12}

Even more problems occur if velocity is connected to transport of particles. No industry guidelines concerning that topic have been published.² Often used API RP- 14E² is as well not considering particulates as such and refers to the formula:

$$
=\frac{C}{\sqrt{\rho_m}}
$$
 Equation 15

where v_e is the mixed velocity, ρ_m the mixed fluid density and C is supposed to be a material constant.

e v

2.2.4 Temperature

Temperature is one important parameter talking about iron carbonate films. At temperatures below 60 $^{\circ}$ C solubility of FeCO₃ is of higher dimensions and protective layers are not formed unless pH is increased compared to reference pH of 60 °C. In lower temperature ranges, to approximately 60-80 $^{\circ}$ C (depending on pH), corrosion rate is proportional to temperature increase, since diffusion and reaction speeds are being stimulated, until temperature values higher than 80 °C make the precipitation of iron carbonate possible, resulting in a reduction of corrosion rates. $1, 2, 25, 46$ Figure 6 below gives an example where iron carbonate precipitates cause a corrosion rate reduction with a temperature of approximately 80 $^{\circ}$ C.³⁰

Figure 6 – Corrosion Rate of X65 Steel as a function of temperature (408 hours with Partial Pressure CO₂ of 0.8 MPa and 1 m/s)³⁰

Summarizing, precipitation of iron carbonate is not only influenced by temperature, but also by pH and $CO₂$ partial pressure, since $CO₂$ is being transformed to carbonic acid, which is the primary source for carbonates and thus the basis for protective layers (Equation 2 & 3). At pH values of for example 6.5, carbonate films can be formed at room temperature.²⁵

In combination with hydrogen sulfide, corrosion behavior with respect to temperature can be found differently, as Valdes et al.³¹ concluded. In Autoclave Weight Loss Experiments within temperatures of 50, 100 and 150 °C and $CO₂$ pressures of 450 psi with additions of 10, 20, 30 and 40 ppm of H_2S , the corresponding corrosion rates were examined. The test solution was 5 % NaCl during 96 120 hours test procedures. Results indicate an acceleration of corrosion rates in presence of very low amounts of H_2S at temperatures lower than 50 °C.

Figure 7 – Corrosion Rate of A516 Steel in 450 psi of CO₂ at different temperatures and Concentrations of H₂S³¹

As can be seen in Figure 7, as temperatures increase the corrosion rate as well as the influence of H2S decrease. Here, a critical value of approximately 10 ppm can be obtained, before protective layers are formed and corrosion rate are reduced.³¹ Temperature has major impacts on H₂S solubility and stability of corrosion products.³¹

2.2.5 Inhibitors

In the oil and gas industry, chemicals, usually on an amine basis, are used to reduce corrosion rates. With concentrations in dimensions of [ppm] levels, fine layers are formed on metal surfaces, inhibiting electric conductivity.¹⁹

For a general overview, the following types³² of inhibitors can be classified:

- Amides and imidazolines
- Salts of nitrogenous molecules with carboxylic acids (fatty acids, naphthenic acids)
- Nitrogen Quaternaries
- Polyoxylated Amines
- Nitrogen heterocyclics

Application in the Fields

Laboratory screening should be performed in order to find best inhibitors for corresponding reservoirs and their corrosive environments.

In daily operations, continuous inhibition is preferred to batch inhibition procedures, since permanent availability of corrosion restricting amines on surfaces of steels is being realized.³³ Direct downhole injection via annulus has the great advantage of protection of lower casing parts as well as tubing surfaces. 33

Batch inhibitor treatment is carried out by squeezing inhibitors into formation, with respect to reservoir compatibility of the chemicals with the formation, to produce the inhibitor with the expected reservoir fluids.³³

Inhibitor Performance

Very often inhibitor concentrations are plotted versus the corresponding corrosion rates in order to see the overall performance of the inhibitor. $34, 35, 38, 45$ Below an example is given, where out of flow loop experiments, a threshold value for that particular case of 10 ppm was concluded.⁴⁵

Figure 8 – Illustration of a 10 ppm Threshold Concentration in the Performance Curve of a Corrosion Inhibitor;5 liter Flow Loop, Forties Brine, 50 °C, 1 bar CO₂⁴⁵

Inhibitor performance is based on three elements 36 describing main procedures of chemical inhibition. Additionally influences of sand and flow are being mentioned.

Partitioning

Corrosion Inhibitors partition between oil and water phases according to their partition coefficient; it describes the relative concentrations of the inhibitor in the water phase, C_w [ppm], to the relative concentration in the oil phase, C_0 [ppm], assuming the solutions to be dilute. It is assumed that corrosion inhibitors are not affecting the miscibility of the two fluids and that molecular state of the corrosion inhibitor is unchanged between the two phases.³⁶

$$
P_{wo} = \frac{C_w}{C_o}
$$
 Equation 16

The amount of inhibitor partitioning into the aqueous phase is strongly related to the volume fraction of oil in the system. 38

To realize the complexity of the partitioning effect, laboratory tests of Josten 37 et al. with an inhibitor in connection to watercuts are given as an example:

 It was found that partitioning between oil and water varied by several orders of magnitude depending on the watercut (or volume fraction of oil). In the lower watercut region (< 20 %), the inhibitor preferentially partitioned into the water phase (P_{wo} = 17), whereas with decreased contents of oil (< 20 %) the partitioning coefficient was evaluated to be around 0.5. This trend was seen at ambient and elevated temperatures, as well with differing concentrations. Partitioning does not follow any concepts of solubility 37 within that example. In the petroleum industry, very often one single partitioning coefficient is assumed for calculations, which has to be treated with a lot of caution, like investigations³⁷ have shown. Josten recommended further investigations on the corrosion inhibitor to determine whether this case is unusual or not, but still underlining that various inhibitors are known showing that tendency.

However, the partition coefficient depends, besides the watercut, on the relative contribution of the molecules' hydrophilic and hydrophobic properties and the tendency of formation of microemulsions, as a consequence.³⁸ Additionally, temperature, brine salinity, pH and nature of the oil phase are influential. Inhibitor partitioning coefficients are needed very often to fully understand inhibitor performance. 39 For many products, like inhibitors that are being faced in this work later on, this information is not available.

Dissociation

Before the corrosion inhibitor can be adsorbed on a surface it is has to be dissociated in the aqueous phase. 36 The dissociation process is assumed from a non- ionic to an ionic state, whereas the ionized form is able adsorb on the pipe wall and creates a surface film, inhibiting electron flow of the corrosion process. The dissociation constant:

$$
K_d = \frac{[C_w^{+/-}]^2}{C_w}
$$
 Equation 17

Adsorption

Like already mentioned, corrosion inhibition mechanisms are assumed as a protective layer, created by adsorption on the metal surface.^{19, 36} Because of that, the inhibitor can occupy a certain area or volume on the surface valued via the surface coverage (θ). Langmuir's isotherm connects the adsorption to the desorption phenomena within the inhibition process and reflects only mono- atomic adsorption onto surface, showing adequate results:

$$
\theta = \frac{K_L \cdot C_w^{+/-}}{[1 + K_L \cdot C_w^{+/-}]}
$$
 Equation 18

where K_L is supposed to be the Langmuir's Constant, $C_w^{\star\prime}$ the ionic concentration.³⁶

The higher θ is, the higher is the rate of adsorption.³⁶ Increasing the efficiency of the corrosion inhibitor surface coverage has to be maximized and dissociation has to be in equilibrium with the adhesion process. Corrosion inhibitors that preferentially partition into the oil phase, decrease corrosion inhibitor concentration in the water phase and thus corrosion rates are increased. 36 That is why generally water soluble inhibitors should be preferred to oil soluble inhibitors.

Figure 9 – Schematic of Adsorption of an Inhibitor¹⁹

The formation of a fine inhibitor- layer on the metal surface, which prevents the electrons from passing through it, is shown in Figure 9.

Flow Influences

Basically, critical flow intensities can cause a limitation of corrosion inhibitor efficiencies and thus be a reason for flow induced localized corrosion. A number of studies performed in the past did not show up any significant inhibition deterioration of state-of-the-art inhibitors up to flow velocities of 9-20 m/s or 1400 Pa wall shear stress.^{40, 41, 42} Secondary flow effects, like high gas liquid interfaces resulting in foam conditions or liquid- liquid interfaces can cause adsorption $\cos^{40, 43, 45}$ Figure 5 shows different flow regimes possible in a pipe. During slug flow, gas bubbles can be entrained into the liquid hitting the bottom of the pipe during horizontal flow and collapse, removing an inhibitive film.^{40, 43, 45}

It is to be mentioned, that produced sediments like clay, sands or various types of carbonates can influence inhibitor performances negatively by adsorption or erosion of the inhibitor's fluid films. $44, 45$

2.3 CO₂ Corrosion Models

Controlling corrosion means full understanding of corrosion processes and predicting future performance of corrosive cases as a consequence. In order to have future outlooks, numerous models on $CO₂$ corrosion are published and three of them, that are considered to be most important, are presented in following subchapters. All equations and variables are presented and prepared for application in oil fields. Points, especially relevant for pipeline engineering e.g., like presence of glycol, were excluded in corresponding models.

2.3.1 De Waard-Milliams-Smith

De Waard- Milliams

In 1975 C. De Waard and D. E. Milliams published one of the most famous and still applicable CO₂ corrosion models so far. With help of weight loss, polarization resistance measurements, relations of carbonic acids and $CO₂$ partial pressures corrosion rates can be predicted. The gained values are considered to be worst case scenarios (especially at temperatures higher than 40 °C, since $FeCO₃$ precipitation was not considered).¹⁷

In the same year De Waard and Milliams published an alternate form containing the critical parameters in "The first International Conference on Internal and External Protection of Pipes", emphasized on wet natural gas.⁴⁶ Generally corrosion rates do not differ significantly and also assume worst case scenario corrosion rates⁴⁶, but are applicable more easily. Additional factors are introduced, including protective scales decreasing corrosion.

$$
\log(V_{nomo}) = 5.8 - \frac{1710}{T} + 0.67 \cdot \log(f_{CO_2})
$$
 Equation 19

This equation shows the relations of the "nomogram corrosion rate" (V_{nom}) to temperature and fugacities (or partial pressures), which can be elaborated with straight lines as well in relevant nomograms illustrated in Background Data 5. Here, fugacities instead of partial pressures, applied in the first publication of 1975, are chosen for more reliable investigations, since with increasing pressure non- ideal behaviour of gases play a bigger role. Like above, pressures and temperatures are valid as [bar] and [Kelvin].⁴⁶

$$
f_{CO_2} = a \cdot P_{CO_2}
$$
 Equation 20

A chart providing basic fugacity constants (a) is provided in Background Data 6, valid for the binary $CO₂$ - CH₄ system.

Formation of protective films is also being included by an additional scaling factor (F_{Scale}) gained by division of observed corrosion rates with nomogram corrosion rates at temperatures above 60 °C and finding best fit to 1/T and log(f_{CO_2}) by multidimensional regression analysis.

$$
\log(F_{scale}) = 2400 \cdot (\frac{1}{T} - \frac{1}{T_{Scale}})
$$
Equation 21

T > T_{scale}, otherwise F_{scale} is chosen as maximum (=1).⁴⁶ T_{Scale} [Kelvin] is defined as the temperature with maximum corrosion rates possible.

$$
T_{Scale} = \frac{2400}{6.7 + 0.6 \cdot \log(f_{CO_2})}
$$
 Equation 22

In order to include pH and $Fe²⁺$ content, the pH factor is introduced. First of all, pH is defined as a result of $CO₂$ and water only. During experiments with constant volumes of water at constant pressures of $CO₂$, the Fe²⁺ concentration will increase while the H⁺ concentrations decrease until solution saturation. That precipitation of FeCO₃ and Fe₃O₄ does not necessarily mean formation of protective films, meaning corrosion still can take place in a saturated solution.⁴⁶

$$
pH = 3.71 + 0.00417 \cdot T_{Celsius} - 0.5 \cdot \log(T_{CO_2})
$$

This equation, with T_{Celsius} as temperature [°C] and f_{CO_2} again as fugacity of CO₂, is also available as a nomogram in Background Data 7. Indeed, the pH factor is governed by the actual and saturated pH values of the solution.

$$
log(F_{pH}) = 0.32 \cdot (pH_{sat} - pH_{act})
$$

for pH_{sat} > pH_{act} . When actual pH values are greater than the saturated values due to alkaline substances, the following equation is recommended:

$$
\log(F_{pH}) = -0.32 \cdot (pH_{act} - pH_{sat})^{1.6}
$$

It has to be understood, that application of both, pH and scale factors is not valid. The corrosion rate of scale covered steel is more likely to be under pH and Fe^{++} concentration control, resulting from a local saturation of $FeCO₃$ and $Fe₃O₄$ at corresponding surfaces. Because of that, F_{pH} is set to 1 if F_{scale} < 1.⁴⁶

Calculations regarding the saturated pH additionally have to be treated with caution. Equation 19 refers to steady state corrosion rate readings with necessary $Fe²⁺$ concentrations needed for FeCO₃ and Fe₃O₄ saturations in 10 % NaCl.⁴⁶ The results can be approximated by

$$
pH_{sat} = 1.36 + \frac{1307}{T_{Celsius} + 273} - 0.17 \cdot \log(f_{CO_2})
$$

Equation 26

which is connected to $Fe₃O₄$. Equation 27 on the other hand, is for $FeCO₃$. The smaller the pH_{sat} value, the more stable and earlier the corresponding corrosion product is being formed. 46 Investigations of Dunlop et al. confirm $Fe₃O₄$ to be the primary corrosion product compared to $\mathsf{FeCO_3.}^{46}$

$$
pH_{sat} = 5.4 - 0.66 \cdot \log(f_{CO_2})
$$
 \tEquation 27

Application of pH factors is valid within a temperature range of 20-80 $^{\circ}$ C.

Talking about hydrocarbon inhibiting effect, oil factors with respect to water content and crude velocity are also presented within this model. After Lotz et al.⁴⁶ at least 30 % of water can be accommodated before creating a water wetting state, making $F_{\text{oil}} = 0$ at WC < 30 % and crude velocities > 1 m/s. If velocities are lower than 1 m/s in horizontal flow lines, separation of oil and water can take place and dispersion of water is not the case. If those two laws are violated, F_{oil} is assumed to be 1. In that situation it is important to know, that those threshold values were elaborated for pipeline flow conditions.

The effect of an inhibitor decreasing the corrosion rates can be included by a simple multiplication of corrosion rates with an inhibitor efficiency factor.

However, a major issue concerning De Waard Milliams relationship is the absence of velocity in calculations, making this model of limiting application in oilfields.¹³

De Waard-Smith

L. Smith and C. De Waard published another model^{3, 14} especially for oil field application. Here, a special focus was set on the already mentioned wettability (Equation 9). A semi empirical model with bases of reaction kinetics V_r and rate of mass transport, divided into carbonic acid and acetic acids can be presented. Below, the model for SI units is elaborated.

$$
\frac{1}{V_{Cor}} = \frac{1}{V_r} + \frac{1}{V_{m_{H_2CO_3}} + V_{m_{HAc}}}
$$

Equation 28

Every term is treated separately below

$$
log(V_r) = 4.84 - \frac{1119}{T_{Celsius} + 273} + 0.58 \cdot log(f_{CO_2}) - 0.34 \cdot (pH_{actual} - pH_{CO_2})
$$
 Equation 29

 pH_{actual} and pH_{CO_2} are the actual pH and the pH of pure water at given partial pressure $CO₂$, respectively.

The calculations were based on measured bicarbonate concentrations, $CO₂$ solubilities, carbonic acid dissociation constants and on best fit equations for their temperature dependence.³ So, if the actual pH is increased by supersaturation of Fe²⁺ e.g., corrosion rate is lowered. In those calculations, pH_{CO_2} is chosen as a reference pH value.

Again, fugacities can be calculated via Equation 20³, but also with the following update¹⁴:

$$
\log(f_{CO_2}) = \log(P_{CO_2}) + (0.0031 - \frac{1.4}{T + 273}) \cdot P
$$
 Equation 30

Like already mentioned, the mass transfer rate [mm/a] is split up and below the following equations are found. Of course, if acetic acids are not present in the system, the term can be neglected.

$$
V_{m_{H_2CO_3}} = 2.8 \cdot \frac{u_L^{0.8}}{D^{0.2}} \cdot f_{CO_2}
$$
 Equation 31

$$
V_{m_{HAC}} = k_m \cdot [HAC]_{undiss}
$$
 Equation 32

 k_m is the mass transfer rate of HAc, containing of diffusion coefficient D_{HAC} of HAc in water, the kinematic viscosity ν [m²/s] and already presented variables velocity [m/s] and inner diameter [m]. [HAc]_{undiss} refers to the bulk concentration of undissociated HAc [mol/l], K to dissociation constant [mol/l] and H^+ the concentration of hydrogen ions $[mol/l]$. D is connected to pipe inner tubing diameter $[m]$ and u_l to liquid flow velocity $[m/s]$.¹⁴

$$
[HAc]_{undiss} = \frac{[HAc]_{total}}{1 + \frac{K_{diss}}{H^+}}
$$

$$
k_m = \frac{D_{HAc}^{0.7}}{v^{0.5}} \cdot \frac{u_L^{0.8}}{D^{0.2}}
$$
 Equations 33

Compared to de Waard- Milliams models, de Waard- Smith is emphasizing on inhibiting factors of oil, flow velocity and FeS film formation. Besides the scaling factor, also other factors are published additionally.

$$
\log(F_{Scale}) = \frac{2400}{T_{Celsius} + 273} - 0.6 \cdot \log(f_{CO_2}) - 6.7
$$
 Equation 34

Also the influence of crude oils concerning wetting of steel in relation to watercuts and oil gravity has been investigated more closely via data analysis of two fields with oil gravities of 49 °API and 38 °API. With definition of W_{break} , implying how much water can be dispersed before separation into water and water- in- crude- oil emulsions and including W_{break} into the oil factor equation, makes the factor valid for multiple oil gravities, which are presented within Background Data 15. 3 As can be seen, lighter oils have lower water entrainment tendencies than heavier ones.

$$
W_{break} = -0.0166 \cdot API + 0.83 \quad For \ 50 > ^{\circ}API > 20
$$
\nEquation 35\n
$$
F_{oil} = 0.059 \cdot \frac{W}{W_{break}} \cdot U_{liq} + \frac{1.1 \cdot 10^{-4}}{W_{break}^2} \cdot \frac{\alpha}{90} + 0.059 \cdot \frac{W}{W_{break}} \cdot U_{liq} \cdot \frac{\alpha}{90}
$$
\nEquation 36\nEquation 36

 $\frac{V_{oil}}{W_{break}} \cdot U_{liq} + \frac{W_{break}}{W_{break}} \cdot \frac{W}{90} + 0.059 \cdot \frac{W}{W_{break}} \cdot U_{liq}$

W

 $\frac{V}{W_{break}} \cdot U$

where α is the angle of deviation Ide are e^{α} from vertical and W is supposed to be the Watercut measured at wellhead.

Theoretically, a watercut of 74 % is the maximum possible to be carried in an emulsion, after Ostwald. Since the corrosion inhibiting effects of oil is expected to be very low in that situation, the oil factor is conservatively assumed to be 1 with Watercuts >80 %.³

To account the presence of iron sulphide films, a factor with respect to partial pressures of H₂S and $CO₂$ is introduced. It has to be mentioned, that scaling factors, both concerning FeCO₃ and FeS films, are in a speculative relation to reality. Both layers can reduce corrosion rates significantly but creation is primarily not guaranteed or can suffer breakdown with time.

$$
F_{H_2S} = \frac{1}{1 + 1800 \cdot \frac{P_{H_2S}}{P_{CO_2}}}
$$
 Equation 37

For calculations, a "Partial Pressure $CO₂$ / Partial Pressure H₂S" ratio of 200 would decrease the corrosion rate by 90 %. The standard deviation of corrosion rate prediction increases with 5 % to overall 30 % compared to lean $CO₂$ corrosion forecasting.

2.3.2 NORSOK

This model is based on empirical investigations for carbon steel corrosion in water containing $CO₂$ at different temperatures, pHs, $CO₂$ fugacities and wall shear stresses (S) via flow loop installations. Temperature ranges from 5 °C to 160 °C. It does not include H_2S impacts.

$$
CR_{t} = K_{t} \cdot f_{CO_{2}}^{0.62} \cdot \left(\frac{S}{19}\right)^{0.146 + 0.0324 \cdot \log(f_{CO_{2}})} \cdot f(pH)_{t}
$$
 Equation 38

 K_{t} is found via linear extrapolation between the calculated corrosion rate above and below the desired temperature (Background Data 8). The function of pH is illustrated in Background Data 10. All input parameter ranges and requirements for oil well upstream calculations are attached in the appendix section starting from Background Data 8 to Background Data 14. The pH calculations are based on Equation 1 to Equation 5 reactions, as well as sodium bicarbonate and sodium chloride to be only present salts in solutions.¹⁸

$$
K_H = \frac{C_{CO_2}}{P_{CO_2}} \qquad \qquad \text{for} \qquad \qquad CO_{2(g)} \to CO_{2(aq)}
$$

$$
K_0 = \frac{C_{H_2CO_3}}{C_{CO_2}}
$$
 for Equation 1

$$
K_1 = \frac{C_{HCO_3^-} \cdot C_{H^+}}{C_{H_2CO_3}}
$$
 for Equation 2

$$
K_2 = \frac{C_{CO_3^{2-}} \cdot C_{H^+}}{C_{HCO_3^-}}
$$
 for Equation 3

 $K_W = C_{H^+} \cdot C_{OH^-}$ for $H_2O \rightarrow H^+ + OH^-$ Equations 39

Above, the routine calculation of pH is based on equations presented on the right hand side and results in chemical equilibrium constants (K) , respectively.¹⁸

Combining constants from above with the assumption of electro neutrality, the following equation¹⁸ for formation waters' $H⁺$ concentration can be gained:

$$
C_{H^{+}}^{3} + C_{0, Bicarb} \cdot C_{H^{+}}^{2} - (K_{H} \cdot K_{0} \cdot K_{1} \cdot P_{CO_{2}} + K_{W}) \cdot C_{H^{+}} - 2 \cdot K_{H} \cdot K_{0} \cdot K_{1} \cdot K_{2} \cdot P_{CO_{2}} = 0
$$

Equation 40

This equation is to be solved by using Newton's method.¹⁸ $C_{0 Bicarb}$ equals the initial concentration of bicarbonate, $\,C_{H^+}\,$ the concentration of hydrogen ions in the system.

Fugacities are calculated via same principle performed in Equation 20.

Wall shear stresses S [Pa] are also an important parameter for corrosion rate prediction including flow velocity in calculations. As can be seen in Background Data tables, many parameters like watercuts, oil- gas- water viscosities or compressibility are inserted. It has to be kept in mind, that within that model, only average shear stresses are assumed and calculated. If for example obstacles are influencing flow streams, fluctuations of shear stresses could be

obtained, where peak shear stresses might exceed the average limit in higher dimensions and, because of that, even higher corrosion rates are faced than those calculated by the model.¹⁸

The mean wall shear stress at medium or high velocities for liquids:

$$
S = 0.5 \cdot \rho_m \cdot f_{friction} \cdot u_m^2
$$

where

$$
f_{friction} = 0.001375 \cdot \left[1 + \left(20000 \cdot \frac{k}{D} + 10^6 \cdot \frac{\mu_m}{\rho_m \cdot u_m \cdot D} \right)^{0.33} \right]
$$
Equation 42

with ρ_m , u_m describing the mixed density [kg/m³] and velocity [m/s], k for the pipe roughness [m] and D for the pipe inner diameter [mm]. µ stands for viscosities [Pas], Q for flowrates [Sm³/day] for liquids and [MSm³/day] for gas and the subindices L, G,O and W account for liquid, gas, oil and water. Remaining equations for proper application of the model are found below.

$$
\rho_m = \rho_L \cdot \lambda \cdot \rho_G \cdot (1 - \lambda)
$$

\n
$$
\rho_L = \varphi \cdot \rho_w + \rho_o \cdot (1 - \lambda)
$$

\n
$$
\rho_G = 2, 7 \cdot 14, 5 \cdot 16, 018 \cdot P \cdot spec.gravity / Z \cdot (460 + T_f)
$$

\n
$$
u_m = u_L^S + u_G^S
$$

\n
$$
\mu_m = \mu_L \cdot \lambda \cdot \mu_G \cdot (1 - \lambda)
$$

\n
$$
\lambda = \frac{Q_L}{Q_L + Q_G}
$$
 Equations 43

Z for the compressibility of gas, s for superficial and variables P and T_f stand for total system pressure [bar] and temperature [°F].

Also flow effects are determined empirically, which does not allow determining any critical velocities via NORSOK.⁴⁷

The viscosity of the water wet region, that means above the inversion point of dispersed flow, the viscosity of any dispersion is given as^{18} .

$$
\mu_L = \mu_w \cdot \left(1 + \frac{\frac{1 - \phi}{B_w}}{1.187 - \frac{1 - \phi}{B_w}} \right)^{2.5}
$$

Equation 44

where B_w :

$$
B_w = \frac{1 - \phi_c}{1.187 \cdot \left(1 - \left(\frac{R_\mu}{\mu_{rel/max}}\right)^{0.4}\right)}
$$
Equation 45

If corresponding data for upper equations are not available, medium viscosity of oil/water dispersion is being used. For 60 °C, a maximum relative viscosity to oil, $\mu_{rel/max}$, of 7.06 is assumed at watercuts, ϕ , of 0.5 with water viscosities of 0.00046 Pas and R_u, μ_w/μ_o , equal to 0.42^{18}

For 20 °C to 150 °C:

$$
\mu_{w} = 1,002 \cdot \left(10 \frac{(1,3272 \cdot (20 - T_{c}) - 0,001053 \cdot (T_{c} - 29)^{2})}{T + 105} \right) \cdot 10^{-3}
$$
 Equation 46

Units can be converted with support of conversion tables in the Appendix, which is to be found at "10 Literature".

Concluding from literature the following parameters result in trends given below:

- Increase of Partial Pressure $CO₂$, which decreases pH, raises corrosion rates.
- Increase of Partial Pressure H_2S reduces corrosion rates (to a certain extent). The "partial pressure CO_2 " to "partial pressure H_2S " ratio is of importance in terms of protective FeS film dropout.
- Increase of Flow Velocity is considered to increase corrosion rates.
- At temperatures of 80°C a corrosion peak is experienced, so exceeding that temperature value, protective $FeCO₃$ films are formed reducing corrosion rate.
- Correct inhibitor injection and application result in corrosion rate reduction.

3 Field Data

Data is provided by an oil company (O.C.), in order to have a clear picture on the corrosion situation of austrian oilfields. Coupons have been installed on surface within a three phases measurement cycle, where three coupons were installed one after another at wellhead region for 69 days each (average). After each phase, adjustments concerning inhibition could have been set. Pictures to understand coupons installation are provided within Background Data 17 and Background Data 18. Downhole investigations have been performed as well prior to surface measurements, where coupons have been installed below the sucker rod pumps inside the tailpipe (Background Data 18). Of course downhole coupons were exposed to corrosive environments for a longer period of time (888 days average), since workover and thus undesired production stop is required to extract the samples.

For evaluation of influential parameters (except inhibitor performance), only uninhibited wells were chosen as reference. The first installed coupons of surface measurements include the greatest amount of uninhibited wells as well as the shortest time gap between downhole and surface measurements.

3.1 Fluid Characteristics and Watercut

 pH and $Fe²⁺$

pH values measured in austrian oilfields range from 6.5 minimum to 7, according to the oil company's laboratory experiments.⁴⁸ Still it has to be kept in mind, that those pH values of water- samples are being measured under atmospheric laboratory conditions, where influences of pressures are decreased dramatically. That is why, for example at dealing with $FeCO₃$ and its precipitation temperature, the correct assumption of pH is an issue.

Like already mentioned in the theoretical part, with pH values of 6.5, FeCO₃ is able to precipitate at room temperature already.²⁵ Downhole measurement tools are often applied to measure the pH of formation waters downhole under relevant conditions in the oil and gas industry.^{49, 50} To include the partial pressure $CO₂$ in pH analysis, two corrosion prediction models are used. Calculating the pH values, based on representative surface- and downhole oilfield data, by means of NORSOK, the following values can be gained:

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Formulas are to be found in the NORSOK sector. As shown in the table above, bicarbonates are not considered and ionic strength values were set to the NORSOK default value for formation waters and constant.

Calculating the pH via de Waard- Milliams approach (Equation 23), implying a diffusion factor of 1, a partial pressure of $CO₂$ of 0.1 bar and a temperature estimate of 20 °C, a result of approximately 4.3 can be gained as well. Further investigations can be done easily by means of Background Data 7- nomogram and Background Data 9, which shows graphically the distribution and the influence of partial pressure $CO₂$ and bicarbonates. This shows that laboratory pH measurement results can not be used within this work, whereas it has to be understood, that those pH calculations are approximations and have to be treated with caution as well, since a number of parameters $(H_2S,$ chlorides, acetic acids etc.) were not considered. Formation waters are considered to be Fe^{2+} saturated.¹⁴

Watercut

The percentage of water produced in oil and gas production is represented by the watercut. Water supports corrosion by serving as an electrolyte and creating acids in combination with corrosive gases. $1, 2, 10, 19, 21$

Below uninhibited wells' surface and downhole corrosion rates are plotted with respect to its watercuts and are sorted after decreasing surface watercuts. In this situation it is important to know, that oilfields of Austria are faced with an average watercut of approximately 90 %. Considering that value, inhibiting support of oil- water emulsions can not be expected after Smith. $^{3, 14}$ Below 80 % of water content in the fluid stream, an inhibitive factor for the oil phase, is applied within that corrosion prediction model (Chapter "2.3.1 De Waard- Milliams- Smith). 3 As can be seen, higher amounts of wells show watercuts below 80 %, which of course needs to be analyzed more deeply, because of the strong deviation from the fields' average. Since there are bigger time gaps between some surface and downhole measurements, the watercuts are being presented separately.

Figure 10 shows low corrosion rates at wells with watercuts lower than 80 %. Especially by following the surface watercut decrease, the impact of the oil can be seen.

Figure 10 – Numbered Downhole and "Surface 1. Installation" Watercuts versus corresponding Corrosion Rates⁵¹

But still there are low corrosion rates at higher watercuts that can not be explained by inhibiting effects of oil (Number 19, e.g.). This is why other parameters are expected to influence measurements and their results.

Like already mentioned, low watercuts like illustrated in Figure 10 are not distinctive for fields in that region. That is why the corresponding velocity is being screened and a correlation between the watercut can be found. The reason for the low water content is the connected low velocity. During measurement interval, pump and flow velocity as a consequence, were being reduced for some reason not to be identified anymore. With increasing velocity, a higher amount of water is being sucked into the borehole and creating a higher watercut because of that. On the other hand, with a lower velocity, oil can accumulate and separate downhole more easily and decrease watercut and corrosion rate.

Figure 11 as well as Figure 12 show clearly the dependence of the watercut on velocity already described above. Here it can be seen that watercut increases with velocity. With the lower limit of approximately 0.1 m/s, a threshold value of velocity could be found additionally to the watercut limit of 80 %. Details regarding velocity calculations and closer description of the velocity distribution and its corrosive limits are elaborated in the next subchapter "3.2 Velocity".

Figure 11 – "Surface 1. Installation" Corrosion Rates versus Watercut and Wellhead Velocity⁵⁶

The 3D diagrams are created with Origin® 8.5; in order to fit an appropriate surface on the data points, the "Kriging" correlation was selected. The "Kriging" correlation uses a weighted average interpolation, minimizing the variance of a certain point with help of the weighted average of surrounding points. The weighted average is evaluated via the correlation structure connected to the corresponding area of the original data points.⁵² A 20 x 20 matrix, with a radius of investigation of 2, a minimum- maximum point window from 10 to 100 and a smoothening grade of 1 was created. Smoothening the plane simply creates a better picture for the reader. Whereas 0 does not influence the diagram and its plane, a too high smoothening grade can lead to a misleading output. The investigation radius defines the number of data points next to the newly created data point, chosen as calculation basis.⁵² As can be seen, the z- values of the plane are calculated via x - and y axis' values. To see the real background distribution, "raw" data points, marked as white squares, from the plotted measurement are included in 3D diagrams. To have a more precise look on relevant issues, highest corrosion rates can not be seen sometimes in the plots. Figure 10 can be used for total corrosion rate inspection and connecting relevant corrosion data to the well number and so to the full data background of every well in the Appendix Section. A major problem with "Kriging" correlations can be seen at Figure 11 and Figure 12 for the first time. If the number of data points of one sector is low, high values create extraordinarily high peaks. This could lead to a misinterpretation of tendencies and would be even more dangerous if "raw" data was not inserted in 3D figures. There is one

value exceeding 0.05 mm/a at Figure 12 at a watercut of 76 % creating such a peak (Corrosion rate 0.12 mm/a), whereas all other measurements stay below the threshold- limit of 0.05 mm/a. Nevertheless create those 3D plots a good overview about interaction of parameters and are applied whenever necessary throughout this work.

Figure 12 – Downhole Corrosion Rates versus Watercut and Wellhead Velocity⁵⁶

Lower watercuts could be explained via low velocities and disappear as soon as velocity exceeds a velocity lower limit. In order to "lift" the measurements to a comparable stage, watercut limits are applied in further steps to make sure that other external forces and influences on corrosion are identified more clearly.

3.2 Fluid Velocity

Velocity calculations are based on the average flowrates produced within the measurement time interval and the diameter of the pipe, where the coupons have been installed and liquid streams were able to interact with coupons' metal surfaces. The production of gas and multiphase flows as a consequence was not considered in analysis.

$$
v = \frac{2 \cdot Q}{\left(\frac{D^2 \pi}{4}\right) \cdot 24 \cdot 3600}
$$
Equation 47

where Q stands for the flowrate in $[m^3/day]$, D for the inner diameter of the coupon location [m], 24 and 3600 conversion factors to achieve a velocity in [m/s]. The factor 2 accounts for the creation of upstream velocity only at the upstroke of the sucker rod pump.

Generally it has to be understood, that only with upstroke movement of the sucker rod pumps, fluid is passing by the coupons. For this calculation, a uniform constant flow with the corresponding upstroke fluid velocity is assumed as an approximation.

As already mentioned in previous chapters, velocity can contribute highest support for corrosion and metal deterioration. High fluid velocity streams, independent of particle or solid content, is able to remove protective layers, like $FeCO₃$, FeC or conventional oil films, increasing corrosion processes.^{10, 11, 28, 29} With increasing velocity, higher wall shear stresses are created and impacts of liquid streams on metal surfaces are higher.¹⁸ Generally, there should be a threshold velocity. Below that limit, no impacts of velocity on metal structures can be determined or they are of lower importance.

Figure 13 and Figure 14 sketch the velocity distribution illustrated in Figure 11 and Figure 12 in a more precise manner to have a better overview on the distribution. As can be seen, "Surface 1. Installation" velocities are higher to a certain degree, explained by the smaller (inner) exposure diameter of 2", compared to the possible downhole tubing diameters of 2 7/8" and 3.5" (Inner Diameters of 2.441" and 2.992"). Like already described, for calculations the inner diameters of tubings were chosen. Additionally a velocity lower limit of both, surface and downhole, can be gained and applied to future investigations to make the operation with most relevant data possible.

Table 2 – Lower Limits of "Surface 1. Installation" and Downhole Velocity⁵¹

Calculation of Reynolds numbers with respect to threshold velocity limits:

$$
N_{\text{Re}} = \frac{\rho v D}{\mu}
$$
 Equation 48

by inserting the inner diameter of the largest tubing with 2.992" or 0.076 m (of 3.5" tubing), the velocity of 0.11 m/s, the dynamic viscosity (μ) and density (ρ) of water, a Reynolds number of 8360 can be obtained.

In full pipe flow, turbulent flow occurs with N_{Re} > 4000.⁵³ Practically spoken, even conservatively calculated, flow is considered to be turbulent, which is critical to conservation of protective layers.^{10, 11, 28, 29}

Most low velocity values deal with low watercuts (Figure 14). In one example, with well number 24,(Background Data 20) the low velocity of approximately 0.07 m/s includes a higher watercut of 84 %. But that value is not being considered regarding the velocity limit and assumed to be controlled, since the surface value of the first coupon installed are far below the limit and comparable velocities do not show corrosive tendencies.

Secondly, with increasing velocities, a large number of low corrosion rates in surface (Figure 13) as well as in downhole measurements (Figure 14) is found. This decrease in corrosion rates under advanced velocity was already visualized within 3D- plots of Figure 11 and Figure 12. Those low values could be explained by certain flow anomalies created with increasing flow velocities, which can not be proven reasonably in this situation. With progressing investigations on corresponding data within this work, explanations need to be found in order to understand those velocity distributions.

Figure 13 – "Surface 1. Installation" Corrosion Rate versus Wellhead Velocity⁵¹

Figure 14 – Downhole Corrosion Rate versus Tubing Velocity⁵¹

To connect the sketched data from above to corresponding well names and other data, alternative illustrations, sorted after decreasing velocities are attached within Background Data 19 and Background Data 20. The term "Tubing Velocity" accounts for the velocity in the tailpipe, the lowest part of the tubing string, where the coupons are installed internally.

The threshold values of the velocities as well as concerning the watercut are used in future parts of this work to create an equal level for interpretations.

3.3 $CO₂$ and H₂S Partial Pressure

Oxygen is not present in the system and can be excluded.⁵⁴

Partial pressures (Equation 11) are calculated on the basis of coupons position. Downhole partial pressures are calculated via dynamic fluid levels of the corresponding sucker rod pump. The hydrostatic column of this fluid level to the tailpipe entrance, where the coupons are located, was chosen as system's total pressure.

 $P_{\text{Downhole}} = \rho \cdot g \cdot h_{\text{Fluid Analysis}} + P_{\text{Casine}}$ $\qquad \qquad$ Equation 49

Surface partial pressures are based on wellhead pressures chosen to be the total system pressure in that situation.

CO₂ partial pressures dominate corrosion processes over creation of carbonic acid and reduction of pH because of that. With decrease of pH, the reduction of H^+ ions is accelerated and so the whole corrosion process.¹³ Basically, the corrosion rate in $CO₂$ corrosion processes can be considered as proportional to the CO₂ partial pressure.^{19, 21}

In Figure 15 and Figure 16, input gained from literature can not be strengthened. As a matter of fact, in both surface and downhole measurements, there is a high amount of measurements resulting in low corrosion rates at relatively high partial pressures of $CO₂$. Partial Pressure $CO₂$ and the corresponding corrosion rates are not to be correlated in a proper manner within those data points and so no outcome or theses can be published.

Figure 15 – "Surface 1. Installation" Corrosion Rates versus CO₂ Partial Pressures for Watercuts > 80 % and Velocities > 0.15 m/s⁵¹

Figure 16 – Downhole Corrosion Rates versus CO2 Partial Pressures Watercuts > 80 % and Velocities > 0.11 m/s ⁵¹

Of course downhole pressures are, due to the dynamic fluid column, higher compared to the wellhead pressured samples on surface. To have again the possibility to compare freely various wells in the Appendix and also to have an alternative view on the data, Background Data 21 and Background Data 22 are provided.

For those partial pressure- investigations, velocity and watercut restraints, presented in previous sectors, were applied to filter low corrosion rates caused by those parameters.

To find an explanation for the low corrosion rates and the corresponding distribution, other parameters have to be screened. Focussing on protective films, which possibly could lead to a reduction of coupons' corrosion rate, FeS is the first that is considered. Screening the H_2S contents in affected wells, using the same system pressures, new outputs are possible to be found.

Iron sulphide layers can be created also in lower temperature regions and can accumulate at the metal surface in a dynamic or in a static system.²¹

Below, figures on page 35 show H_2S partial pressures in connection to CO_2 partial pressures versus corrosion rates. Again, "Surface 1. Installation" and Downhole values are split into two diagrams; for a better picture on the impact of $H₂S$ partial pressures, 3D diagrams with help of "Kriging" correlations and same adjustments like in watercut investigations, are applied. As can be seen in Figure 17 and Figure 18, corrosion rates decrease with increasing partial pressure of H2S. This is not only valid for downhole values; also for "Surface 1. Installation" measurements, where partial pressures are lower, it can be accounted. In the past, flow loop investigations proved the creation of protective iron sulphide films with pressures lower than 0.0001 bar partial pressure H_2S^{21}

Again, the weaknesses of the "Kriging" Correlation can be seen. Especially Figure 17 creates a peak due to one single data point at approximately 1.2 bar $CO₂$ pressure. That can be explained by a lack of data in the radius of investigation of the correlation. Changing the radius is also not changing that problem, since data points are not distributed equally and may result in a misleading picture at regions, where higher amounts of data is present.

Looking on the provided data and considering Figure 19 and Figure 20, where the necessary numbered H2S wells are presented, the formation of protective films could be expected. Still, there are wells not showing low corrosion rates in connection to its hydrogen sulphide partial pressures. Well number 4, 8 and 11 from "Surface Measurements" or for example 18, 43 and 16 at downhole measurements show raised corrosion rates.

 Nevertheless, those charts show in average much higher corrosion rates on the right hand side, where no partial pressure of H_2S is registered, compared to the ones where H_2S was measured.

Figure 17 – "Surface 1. Installation" Corrosion Rates with Respect to Partial Pressures CO₂ and H₂S for Watercuts > 80 % and Velocities > 0.15 m/s 51

Figure 18 – Downhole Corrosion Rates with Respect to Partial Pressures CO₂ and H₂S for Watercuts > 80 % and Velocities > 0.11 m/s⁵¹

Figure 19 – "Surface 1. Installation" Corrosion Rates versus numbered Partial Pressures of H2S for Watercuts > 80% and Velocities > 0.15 m/s 5

Figure 20 – Downhole Corrosion Rates versus numbered Partial Pressures of H₂S for Watercuts > 80% and Velocities > 0.11 m/s ⁵¹

To have an additional view on the data, a diagram based on $Pots^{26}$ et al. theory, concerning the partial pressure ratios of $CO₂$ and H₂S is created.(Figure 21, Figure 22). Basically, between 20 and 500 (P_{CO_2} / P_{H_2S}) a mixed corrosion process of CO₂ and H₂S takes place. That means, besides FeCO₃, also iron sulphide (FeS) is able to precipitate. As can be seen in relevant figures, most H₂S wells screened are located in the mixed corrosion region. Above 500, the formation of iron sulphide films is unlikely and $CO₂$ corrosion could attack freely. As seen in

previous charts, a possible sulphide layer created, would not be that efficient downhole compared to "Surface 1. Installation".

In downhole measurements, again 18, 43 and 16 do not fit to other results. This could be explained by a possible removal of iron sulphide film and localized corrosion or also called "Pitting" tendency of the material. The pitting probability increases with increasing H_2S partial pressure.¹⁴ Also in surface analysis, the corrosion rates of coupons exposed to the corrosive fluid stream can not be connected 100 % to the formation of FeS layers. Of course the pressure ratios are the same surface and downhole, since there is no variation of $CO₂$ and H₂S contents. But still, the surface and downhole conditions are differing in temperature and fluid velocity (only parameters mentioned, that are considered in this work).

Especially temperature influence is important talking about $FeCO₃$ precipitation and its formation as a protective layer. Compared to FeS films, temperatures as well as pH are more critical in FeCO₃ precipitation.^{21, 25, 26, 31, 55} In the subchapter "3.4 Temperature" discussion of temperatureinfluence on $FeCO₃$ scales is emphasized.

Figure 21 -Partial Pressure CO₂ and H₂S Ratio versus "Surface1. Installation" Corrosion Rates connected to corresponding Well Number for Watercuts > 80 % and Velocities > 0.15 m/s after Pots⁵¹

All wells were included in Figure 21 and Figure 22 to keep track which wells contain H₂S. Only corrosion rates (and pressure ratios), measured at H_2S wells, are illustrated.

Figure 22 – Partial Pressure CO2 and H2S Ratio versus Downhole Corrosion Rates connected to corresponding Well Number for Watercuts > 80 % and Velocities > 0.15 m/s after Pots ⁵¹

Parameters without H2S Wells

To obtain relevant well numbers and deeper information from Appendix the reader is advised to consult previous figures with numbers, containing $H₂S$ wells, or look up the numbered distributions without H₂S wells in the Background Data section. In this subchapter same figures like published before with the main parameters, except temperature, which is presented separately, are shown without the possibly influential H_2S measurements. Since all H_2S partial pressures are theoretically able to form protective films²¹, all H₂S containing wells have been excluded to have an alternative perspective on respective parameters.

Velocity

Velocity was the first parameter, where no generic output was proposed in previous investigations. Very low corrosion rates with increasing velocity could not be explained. Low corrosion rates may to be reasoned by FeS layers on installed coupons, preventing impacts of velocities and its shear stresses.

Figure 23 - "Surface 1. Installation" Corrosion Rate versus Wellhead Velocity without H₂S Wells⁵¹

The modified velocity distributions, Figure 23 as well as Figure 24 show a weak correlation related to the literature output. Here, the velocity constraints were not considered, since the figure needs to demonstrate an overall picture on velocities. Nevertheless it can be seen in both figures, that high amounts of low corrosion rates, compared to Figure 13 and Figure 14, have disappeared by extraction of H_2S wells. That makes the influence of velocity according to literature more obvious and shows weakly, that with increasing velocity the corrosion rate increases.

It still has to be kept in mind that also a small amount of high corrosion rates are lost in the H₂S data extraction process. Once more, those corrosion rates could be referred to pitting.^{2, 14, 19, 21, 22} But still there are low corrosion rates in advanced velocity regions. In surface installations, well measurement numbers 23, 12, 17, 14 and 42 and downhole well measurement numbers 13, 2 and 42 (from highest to lowest velocities; Background Data 23 and Background Data 24) are below the corrosion limit.

The main issue with FeS layers is the possibility to prove it in that situation. Since relevant coupons are not available for visual inspection, the provided velocity output can not be verified regarding a protective sulphide layer, even though partial pressures, faced in the oil fields of Austria, are experienced to create FeS precipitation according to cited literature.^{2, 14, 19, 21}

So, the extraction of H₂S wells and the resulting trend of downhole and surface velocity to the corrosion rates is speculative and can only be seen as a strong indicator.

Figure 24 – Downhole Corrosion Rate versus Tubing Velocity without H₂S Wells 51

CO2 Partial Pressure

The same procedure performed with velocities has been applied also to surface and downhole partial pressures to demonstrate that parameter without H_2S influence.

Comparing critical well numbers 23, 12 and 17 (Figure 23), with the surface partial pressures of $CO₂$, it can be concluded that those values have the lowest partial pressure $CO₂$ values of all H2S free uninhibited wells with watercuts higher than 80 % and wellhead velocities higher than 0.15 m/s (Background Data 25). Well number 42 ranges in average partial pressure region and 14 even is calculated as a maximum.

Screening the partial pressure distribution of "Surface 1. Installation" and Downhole measurements, again, like in the modified velocity distribution, only a weak proportional relation to corrosion rate can be seen. (Figure 25 and Figure 26)

Downhole well number 13, 42 and 2 are, with progressing partial pressure, below the critical corrosion rate limit of 0.05 mm/a. Explaining other wells with comparable partial pressures of $CO₂$ (compared to well 13, 42 and 2) and still equipped with higher corrosion rates than number 13, 42 and 2 via higher velocities, is not possible. As can be seen in Background Data 24 and Background Data 26, this is not the case. Numbers 13 and 42 are linked to low tubing velocities, but well number 23 or 5 have comparable values and still show higher corrosion rates.

To summarize, not all anomalies of modified partial pressures and velocity plots can be explained via corresponding velocity or partial pressure distributions.

It has to be underlined, that Figure 25 as well as Figure 26 show increased corrosion rates with increased partial pressures by application of a linear interpolation trendline, but from an engineering point of view, the trendline could be seen as parallel to the y- axis. That is why the "partial pressure $CO₂$ to corrosion rate"- correlation is considered to be very weak.

The reader is free to control or deepen investigations via Background Data 23 to Background Data 26 and corresponding data sheets in the Appendix section.

Figure 25 – Downhole Corrosion Rate versus Partial Pressure CO₂ without H₂S Wells for Watercuts > 80 % and Velocities > 0.11 m/s⁵¹

Figure 26 – "Surface 1. Installation" Corrosion Rate versus Partial Pressure CO2 without H2S Wells for Watercuts > 80 % and Velocities > 0.11 m/s 51

Contrary to previous investigations, the application of 3D diagrams was decided not to be meaningful, since the number of data points is too small.

For definition of a minimum $CO₂$ partial pressure, Figure 26 is most important, since lower pressures are being faced. Downhole as well as surface measurements show a corrosion rate increase at very low $CO₂$ partial pressures. Considering the low partial pressures and the first violation of corrosion- limits with approximately 0.05 bar partial pressure $CO₂$ in Figure 26, a lower limit is not to be found in this situation, since only one data point exists lower that 0.05 bar. Estimation of an independent downhole value is not performed, due to the equal problem. Downhole, the lowest partial pressure- value immediately violates threshold corrosion- rate.

3.4 Temperature

Temperature is another very important parameter influencing corrosion. Its main role is referred to the dependency of $FeCO₃$ to precipitate and being able to form protective layers to reduce corrosion with increasing temperature. $21, 25, 28$

The pH was calculated to approximately 4.3 previously.

Focussing once more on Figure 21, high surface corrosion rates of well numbers 4, 8 and 11 in the lean $CO₂$ corrosion process after Pots are visualized. FeCO₃ dropout and the formation of a protective layer is unlikely under surface conditions and temperatures of 20 °C, facing a pH value of approximately 4.3. 21,25,28 The lack of a protective FeCO₃ layer could be an explanation for the high corrosion rates in Figure 21.

Of course $FeCO₃$ layers are, like FeS layers, not to be proven in that situation without the analysis of the coupons' surfaces.

Since surface temperature is assumed to be constant, only downhole values are plotted versus temperature. To have a more detailed look on the gained data, threshold values of watercut and downhole velocity are applied, decreasing the number of wells to be investigated. It has to be mentioned, that temperature values are calculated by means of "3.3 °C/100 m" gradient.

Figure 27 – Numbered Downhole Corrosion Rates with Respect to Temperature at Coupon setting Depth for Watercuts > 80 % and Velocities > 0.11 m/s⁵¹

Figure 27 makes the distribution of downhole- temperature related to corrosion rates visible. The majority of those values range below 45 °C and nor on this chart, neither in Figure 28, where trends usually can be seen more easily, a correlation according to literature investigations could be found. Also downhole, pH is, besides temperature, an important parameter talking about FeCO₃ precipitation. In both relevant figures corrosion rate variation is very high not allowing any conclusions. Basically, the corrosion rates are expected to increase to a certain threshold temperature, where the corrosion rate finally decreases due to the formation of protective iron carbonate films. 21 Additionally, there is the possibility of FeS layers of H₂S wells, which are precipitating out of solutions more easily compared to FeCO₃, misleading the interpretation of both plots. Extraction of H₂S wells was performed because of that one more time.

Figure 28 – Downhole Temperatures versus Downhole Corrosion Rates for Watercuts > 80 % and Velocities > 0.11 m/s⁵¹

Temperature without H₂S Wells

Figure 29 shows the distribution of temperature without H_2S influence. Wells below corrosionlimit are again the same demonstrated in figures before, 42, 2 and 13, whereas 42 is exposed to highest and 13 to lowest temperature of those three measurements.

As a matter of fact, trends of temperature influence according to literature can not be seen. Again, low corrosion rates of 42, 13 and 2, that could not be explained by lower tubing velocities compared to others, can also not be reasoned by the impact of temperature.

Furthermore, due to the removal of H_2S containing wells, a grand amount of low corrosion rates disappeared, but a redesigned distribution, supporting temperature impacts, is not created because of that. Indeed it is possible, that temperature influences can not be concluded due to the low deviation of temperatures.

If the iron- sulphide- precipitates- thesis is true, iron sulphide precipitations are independent of temperature ranges from approximately 40 °C to 55 °C as a consequence. A graph equipped with well numbers is found at Background Data 27.

Temperature as well as partial pressure distributions are influenced by lots of factors downhole as well as on surface not to be included in data analysis within this work. That is why especially partial pressure $CO₂$ and temperature correlations do not show a sufficient match to literature publications and may create a misleading picture of dominance of those factors.

Figure 29 – Downhole Corrosion Rate versus Downhole Temperature without H₂S for Watercuts > 80 % and Velocities > 0.11 m/s⁵¹

3.5 Inhibitor Performance

For evaluation of inhibitor performances in austrian oilfields, only surface coupons measurements are available. Basically, two types of inhibitor are injected continuously via the annulus into the borehole. FS1 and the newly acquired FS2 have shown within several laboratory experiments and field analyses their positive effects regarding metal conservation and corrosion prevention. Nevertheless, a general guideline in inhibitor application as well as optimum doses was not elaborated by responsibles. To screen the inhibitor performance, corrosion rates versus the respective inhibitor dose, injected during coupons exposure, was plotted. Inhibitor concentrations [ppm] are based on the brutto production of treated wells. The assumption that water soluble inhibitors, like FS1 and FS2, remain only in the water phase is not valid, obviously.^{36, 37} Deeper investigations on partitioning of both inhibitors are not possible, since partitioning coefficients are unknown. Influences of low watercuts and low velocities are excluded to achieve an optimum picture of the inhibitor efficiency. Compositions and trade names of inhibitors are illustrated within Background Data 28.

FS1 Evaluation

FS1 was screened via conventional coupons surface measurements, whereas a separation of data sets between "1- 3 installation" (measurements by O.C.'s corrosion department) and an alternative screening, called "List green Inhibitors"⁵⁷, where 17 wells were measured, has been performed. That separation makes an exact comparison of FS2 and FS1 corrosion rates in future parts of this work possible. "List green Inhibitors" was not supportive in prior parameter evaluations, since uninhibited measurements have not been performed within this report.

Surface Installation 1-3

Looking at FS1- inhibitor performance chart of first installed coupons, a corrosion rate decrease related to the inhibitor dose increase can be seen. Highest corrosion rates are already inhibited with approximately 30 ppm, showing a high deviation between the corrosion rates.

Figure 30 – Inhibitor FS1 versus Surface Corrosion Rates of 1st Installation- Coupons for Watercuts > 80 % and Velocities > 0.15 m/s ⁵⁶

Especially to be mentioned are very low corrosion rates, even though no inhibition was applied within the measurement time interval. This leads to the assumption, that there are wells that have no corrosive tendency.

The average of all corrosion rates decrease with further installation measurements, illustrated within Figure 31 and Figure 32, where the final maximum corrosion rate of the third installation is approximately 1.2 mm/a. Possible environmental differences, like acidizing stimulations, which often are responsible for elevated corrosion rates, between those measurements could not be found. "Surface Installation" figures indicate again the problems of corresponding field measurements. Various influential parameters are creating high deviations of corrosion rates not to be explained 100 % within this work. This can be reasoned once more by the lack of measurement coupons and the maturity of the data itself, respectively.

Below in Table 3, 7 example- corrosion rates are presented, where a high deviation of the corrosion rates is illustrated.

Inhibitor	Corr. Rate	Inhibitor	Corr. Rate	Inhibitor	Corr. Rate
1.Installation	1.Installation	2.Installation	2.Installation	3. Installation	3. Installation
[ppm]	[mm/a]	[ppm]	[mm/a]	[ppm]	[mm/a]
21.8	3.6	21.8	0.6	26.5	0.004
23.1	3.2	36	0.003	38	0.002
64	2.4	66	0.2	67	0.4
28.1	2.2	28.1	0.4	37.9	0.02
0	2.1	15	0.2	7	0.02
18	1.2	90	0.8	100	0.2
74	1.1	35	0.9	37	0.1

Table 3 –Corrosion Rate Curriculum of highest "Surface 1. Installation" Corrosion Rates⁵⁶

Corrosion rate points 3.6, 2.2 and 2.4 mm/a change at second phase to corrosion rates of 0.6 mm/a, 0.4 and 0.2 mm/a with no change of inhibitor dose at points 3.6 and 2.2 and a low raise of inhibition of 2 ppm at point 2.4. The fourth point chosen to be a presented additionally is 3.2 mm/a, where after a raise of inhibitor concentration of 13 ppm corrosion rate decreases to 0.003 mm/a in second evaluation process.

To keep in mind, all surface coupons measurements have been performed chronologically for 69 days average. After each coupons measurement, the following coupon was installed immediately for the same amount of time.

Indeed it has to be understood, that with progressing measurements and after the first results have been gained, more and more wells needed to be inhibited in order to decrease their corrosion rates. That leads to elevated corrosion rates in connection to higher inhibitor doses, since often the optimum amount was not injected, only decreasing the corrosion rates to a certain degree. Practically spoken, if for example corrosion rates already inhibited with 20 ppm of FS1 is exceeding 0.05 mm/a and after injection of 80 ppm still exceed that limit (but with a lower corrosion rate), inhibition performance plots could give a wrong impression.

Exactly this is the reason, why at first installed measurements the optimum dose of inhibition is, read off at Figure 30, roughly at 80 \pm 20 ppm, 90 \pm 10 ppm at Figure 31 and 100 \pm 10 ppm at Figure 32.

Figure 31 – FS1 versus Surface Corrosion Rates of 2nd Installation- Coupons for Watercuts > 80 % and Velocities > 0.15 m/s ⁵⁶

Figure 32 – FS1 versus Surface Corrosion Rates of 3rd Installation-Coupons for Watercuts > 80 % and Velocities > 0.15 m/s ⁵⁶

It has to be mentioned that there are corrosion rates exceeding corrosion limit within multiple measurements and have not been inhibited throughout the coupons evaluation phases. A reason for that can not be given.

List green Inhibitors

20 Wells are screened regarding corrosion behaviour in contact with FS1 and FS2 to realize a reliable comparison of inhibitors' field performance. As a matter of fact, coupons are installed in wellhead regions under same circumstances like Surface Installation 1- 3 data measurements. All wells are related to watercuts higher than 80 % and velocities higher than 0.15 m/s, so no filter was applied.

Figure 33 – Inhibitor FS1 versus Corrosion Rates of "List Green Inhibitors" 56, 57

Three wells were not qualified due to stimulations, damage of sucker rod pump or injection pump failure during measurement period. (well numbers 198, 196 and 206)

High corrosion rates of well- measurement number 193 with approximately 1.64 mm/a, well numbers 197, 199 and 203, with the lowest corrosion rate of approximately 0.7 mm/a, require special consideration and possibly raised amounts of inhibitor doses to decrease their corrosion rates.

Again, corrosion reducing impacts of FS1 can be expected. It has to be considered, that wells have been chosen specifically for that investigation and more care regarding data and coupons evaluation has been applied compared to "Surface Installation 1-3" measurements, e.g..

Comparing third Installation evaluation plot, Figure 32, with Figure 33 from above, indeed similarities are visuable. Maximum concentrations are located in approximately 100 ppm regions and concentration minimum values, neglecting uninhibited wells, of around 20 ppm are seen in both charts as well. An optimum dose of inhibition is expected roughly at 80 \pm 30 ppm.

Inhibitor FS2 Evaluation

FS2 is the latest introduction of inhibitors in austrian oilfields. Here availability of data is more limited compared to FS1 performances. Investigations concerning FS2 are performed once more by internal report "List green Inhibitors"⁵⁷ with same wells like in FS1 measurements.

Figure 34 - Inhibitor FS2 versus Corrosion Rates of "List Green Inhibitors"56, 57

For FS2 evaluations same 20 wells were being chosen; fortunately no problems occurred in evaluation process making all 20 measurements valid. Same conditions during coupons measurements concerning duration, exposure area and coupons- material are found to have levels of comparison. Well- measurement number 206, responsible for maximum corrosion rate in Figure 34 of 0.373, not able being evaluated in FS1 evaluations due to stimulations, could require also a higher concentration of inhibition for corrosion rate reduction. Two other wells not considered in FS1 plot (Figure 33), number 196 and 206, show low corrosion tendencies of 0.003 and 0.028 mm/a with advanced FS2 inhibitor doses of 54 and 61 ppm. Number 193, with approximately 1.64 mm/a (Figure 33), shows, with a dose of 22 ppm FS2, a surprisingly low corrosion rate of 0.038 mm/a in Figure 34. Well number 197, 199 and 203 on the other hand still maintain the corrosive tendency already illustrated in FS1 Internal Report investigations and exceed corrosion limit of 0.05 mm/a.

The optimum dose via Figure 34 is determined as roughly 60 \pm 10 ppm.

Comparison FS1 with FS2

58 wells were treated with FS2 by September 2010, most of them starting with September 2007, whereas only in 20 wells a coupon measurement for FS2 evaluation (List green Inhibitors) was performed. Report "List green Inhibitors"⁵⁷ processes performance of both inhibitors (FS1 and FS2) in the field and targets for strengthening the performed laboratory tests, published in report "COR20050025"⁵⁸, where FS2 succeeded already.

Figure 35 below shows both inhibitors in comparison, where immediately higher corrosion rates in FS1 inhibited wells are noted.

Figure 35 – Inhibitors FS1 and FS2 versus corresponding Corrosion Rates of "List Green Inhibitors"56, 57

A closer look on differences of FS1 and FS2 inhibition has already been taken in the "FS2 Field Evaluation" chapter before. Additionally the changes of inhibition of relevant wells need to be screened, since basically, after gaining the results of FS1 investigations, adjustments of inhibitor FS2 (and a better result as a consequence), are possible. FS1 measurements have been performed approximately 6 months before FS2 measurements. Looking on average inhibitor doses of all Internal Report wells^{56, 57} equal doses of both approximately 42 ppm can be calculated. But considering the extremely high dose of well number 195, illustrated at Table 4, reasoned by the unexpected low production rate of 14.8 m^3 /day leading to a lower wellhead velocity of 0.17 m/s and excluding that value from the average, a difference of 6 ppm can be found.

Generally, slight deviations due to the flow rates are being faced. Nevertheless, FS2 corrosion rates are lower in average compared to FS1 treated coupons with respect to comparable inhibitor doses, since those deviations are, first of all, not to be prevented and, secondly, not considered as relevant.

Corrosion Monitoring Concept for Oil Wells

Table 4 – Deviations of Concentrations between FS1 and FS2 Inhibitors of FS1 Wells exceeding Corrosion Limit56, 57

In order to have an alternative view on both inhibitors and their ability to reduce metal deterioration, the rate of Workover was selected as a parameter. The parameter "WO per year" is not valid to be correlated to corrosion processes as such, since not all failures, registered in databanks, are described explicitly whether corrosion was involved or not; however, differences regarding maintenance operations of FS1 and FS2 still have to be explored because of a direct relationship to runtime and costs.

Table 5 – Comparison of Inhibitors FS1 and FS2 via alternative Parameters^{56, 59}

Parameter	Inhibitor FS2	Inhibitor FS1
WO/year	0,433	0,481

Table 5 shows clearly a positive impact of FS2 regarding Workover. In that analysis, additionally a time factor needs to be considered. Whereas earliest FS2 applications were started in 2007, a lot of FS1 treatments have been performed in the 1990s in some wells for the first time. For FS1 investigations, a lower time limit of January 1999 has been set. For wells, where inhibition took place after 1999, the date of first injection has been taken. Within that time interval, relevant changes in well or reservoir conditions have been taken care of and time interval was adjusted, if necessary. So the average time interval of investigation of FS2 inhibition is 991 days (2.7 years) and for FS1 2040 days (5.5 years).

4 Experimental

Reliable conclusions, supported alone by field data investigations, can not be drawn due to their deviation to literature outputs of certain parameters. The maturity of field data definitely is an issue; the latest measurements have been performed approximately 10 years ago and recreating equivalent measurement- environments to corresponding evaluation dates is of limited reliability, obviously. Missing coupons to prove created theses, is another problem not to be solved in that scenario. That is why an experimental investigation was added to have an extra perspective on critical data that was not providing a satisfying match to the literature. The following experiments were emphasized on partial pressures of $CO₂$, temperatures and inhibitor performance of FS1 with help of Autoclave Pressure Cells. To obtain comparisons between FS1 and FS2, FS2 was tested at 80 °C with variations in partial pressures.

4.1 Materials

The material used as specimen was an API- $L80^{60}$ sucker rod with a diameter of 1 1/8". Before it was cut by saw to a sample- cylinder of 10 mm height, the bar was turned to remove irregularities from its surface. 24 hours before installation into the pressure cell, samples were grinded wet at all planes and edges by three types of sandpaper with grain sizes of 120, 220 and finally 320. After each type, the samples were degreased with ethanol and dried. After the last sandpaper interval, the samples were stored in an oven at 120 °C (for 24 hours). Before installation, the samples' weight, height and diameter was determined. The chemical composition and mechanical properties of used steel is shown at Table 6 and Table 7.

Table 6 – L80 Steel Composition^{61, 62}

Table 7 - L80 Steel mechanical Properties^{61, 62}

Dimensions and an image of a sample and its microstructure are shown from Background Data 29 to Background Data 31. Dimensions vary due to treatments like turning and sandpapering. All samples were equipped with specific numbers to prevent confusion.

4.2 Autoclave Testing

Three pressure cells with an inner diameter of 6.7 cm, a height of 67 cm and an inner volume of 2362 cm³ were filled with 1.5 I of electrolyte each. The electrolyte contained of distilled water with 27 g/l NaCl content. Exceeding 3 weight% of NaCl at room temperature, corrosion rate is finally expected to decrease within aerated conditions, since oxygen solubility is being decreased.⁶³ The dose of NaCl creates a worst case scenario regarding chlorides, since same behaviour regarding solubility of $CO₂$ is assumed. In the field, an average of approximately 12000 ppm of chloride concentration is calculated, since all fields are being injected with water containing that specific chloride concentration.⁵¹ Closed autoclaves were purged with $CO₂$ with 1 l/min (1 bar) for 5 hours, to evacuate oxygen. Afterwards, samples were installed in a glass specimen holder, preventing metal to metal contact of sample and autoclave (or sample to samples) and then dropped into the electrolyte, creating permanent exposure and full coverage of the metal by the liquid. If necessary, inhibitor doses were injected by means of a pipette and stirred, before specimens were installed into the autoclave. The experiments were performed under static conditions and thus samples were always covered in liquid. Autoclaves were finally closed for the corrosion measurement and purged with $CO₂$ again for 1 hour to remove again freshly migrated oxygen. After purging, the cell was pressurized and put into a heating oven, if higher temperatures were required for evaluations. A leak detection spray (Herbert Torrey) was used in order to check valve and autoclave tightness. Testing time was set to 6 days (144 hours). At the end of the testing time, the samples were extracted from the autoclave and immediately cleaned with ethanol and dried. After the second weighing procedure, samples were exposed to a staining agent⁶⁴ (Background Data 32) for 5 minutes, neutralized with water and then again purged with ethanol. At the end, they were brushed with a rubber brush to remove possible residuals on the surface, once more purged with ethanol, dried and weighed for the third and final time. All samples were stored in a desiccator. The testing conditions, the samples are exposed to, are illustrated in Table 8.

4.3 Evaluation

The weight difference between weighing procedure 1 and weighing procedure 3 has been computed and was used as a basis for calculation of corrosion rates. The scale used is only valid up to unit [mg], which was rounded to the hundredth digit after computation of the uniform mass loss.

Three specimens were installed into one autoclave per experiment. The following formula was applied to calculate the mean corrosion rate CR [mm/a] of each sample.

$$
CR = \frac{365 \cdot \Delta m}{\rho_{Fe} \cdot t \cdot A}
$$

Equation 50

where Δ m describes the mass loss [g], ρ_{Fe} the density of the iron [g/mm³], t for the elapsed time [days] and A represents the surface area of the samples [mm²].

For each experiment, the arithmetic mean was calculated, creating a single value for every investigation.

5 Experimental Results

5.1 Repeatability

Like already mentioned before, three samples were assembled inside the autoclave for achievement of reliable results.

All results need to be able to be repeated for validity. That is why the standard deviation is calculated for every measurement and inserted as "error bars" into respective plots, to see how widely values are dispersed from the average value. If no error bar is visible at certain data points, error bars are smaller than data points' plotting area.

The formula used for standard deviation based on a sample is shown at Equation 51:

$$
\sigma_s = \sqrt{\frac{\sum (x - \overline{x})^2}{(n-1)}}
$$

Equation 51

where x is the sample value, \bar{x} refers to the mean of all samples and n to the total amount of samples.

5.2 Partial Pressure CO₂

Figure 36 shows the corrosion rate as a function of partial pressure of $CO₂$ at varying temperatures. Basically it shows that with increasing partial pressure, corrosion rates increase. The corrosion rate can not be connected to the partial pressure in a linear manner, but more in a logarithmic manner. That logarithmic distribution was already visualized in Figure 2, within "2 Theory of $CO₂$ Corrosion" and can be explained by de Waard's Equation 12, connecting the pH value logarithmically to partial pressure CO₂. The pH value, accelerating the cathodic reaction if lowered, is not changing significantly between 3 and 10 bar, whereas variations of 1 to 3 bar are more effective in pH decrease.

The standard deviation of 20 °C experiments is high compared to other results and ranges from approximately 0.21 (relative standard deviation of 51 %) at 3 bar to 0.27 (relative standard deviation of 54 %) at 10 bar.

Additionally, logarithmic distributions are independent of temperatures. Deeper analysis of temperature influences are found in chapter 5.3.

Figure 36 – Partial Pressure CO₂ Distribution with Variations in Temperature from Autoclave Experiments

5.3 Temperature

Figure 37 – Temperature Distribution with Variations in Partial Pressure CO₂ from Autoclave Experiments

As already stated above, corrosion rates are proportional to partial pressure of $CO₂$. Looking at temperature distribution within Figure 37, also a correlation according to literature outputs, like shown within Figure 6, can be seen. Precipitation of FeCO₃, acting as a protective film, leads to a reduced corrosion rate at 120 °C. Background Data 34 illustrates the mentioned black $FeCO₃$ layer, which was found on all samples exposed to maximum temperature. In maximum

temperature region, corrosion rates of 3 bar is slightly higher than corrosion rates of 10 bar. This can be referred to measurement inconsistencies, considering high relative standard deviations of 1 and 3 bar of both approximately 35 %. The maximum corrosion rate is illustrated at 80 °C. Again, highest standard deviations are under room temperature at 3 and 10 bar.

5.4 Inhibitor Performance

Figure 38, Figure 39 and Figure 40 illustrate the Inhibitor FS1 performance under 20, 80 and 120 $^{\circ}$ C at different partial pressures of CO₂. At room temperature, corrosion rate decreases significantly by addition of FS1. Nevertheless, corrosion rate reduction, not violating 0.05 mm/a threshold, is not feasible by means of 30 ppm doses, independent of created laboratory conditions. With increasing concentration of inhibitor up to 100 and 300 ppm, corrosion rates decrease below the corrosion limit, showing up the measurement limits of 0.01 mm/a, since the applied scale is only valid up to unit [mg] and rounded, which was already mentioned before. As can be seen in Background Data 33, difference of 100 ppm inhibitor dose at 1 and 3 bar still is significant, even though difference is only 0.01 mm/a. 300 ppm creates maximum protection compared to the other concentrations at corresponding partial pressures. At room temperature, standard deviations decrease with increasing doses of inhibitor.

Figure 38 – Inhibitor FS1 Performance with Variations in Partial Pressures at Roomtemperature

Efficiency of FS1 is reduced at 80 °C, like Figure 39 or Background Data 35 shows. No injected concentration is able to keep corrosion rates below the corrosion limit. 30 ppm show low protection- tendencies at 3 and 10 bar and also at 1 bar corrosion rates are of higher dimensions. Comparing 100 ppm results with others, it can be seen that corrosion rates are being reduced significantly at 1 and 3 bar and do not change significantly at a raise to 300 ppm.

Additionally, with concentrations of 300 ppm, results of 10 bar can be "shifted" to the same corrosion rate level than already realized with 100 ppm at 1 and 3 bar.

Figure 39 – FS1 Performance with Variations in Partial Pressures at 80 °C

Figure 40 – FS1 Performance with Variations in Partial Pressures at 120 °C

At 120 °C results (Figure 40), inhibitor does, independent of partial pressures, not reduce corrosion rates significantly. At 100 ppm, a slight reduction can be seen, but facing error bars and its standard deviation, the slight reduction can be considered as measurement-variation. As already mentioned, the reason for lower corrosion rates compared to 80 °C can be connected to the precipitation of $FeCO₃$ and the connected creation of a protective film. However, Figure 40 shows slightly lowered corrosion rates at uninhibited measurements compared to measurements with injected inhibitor FS1. Inhibitors can influence homogeneity of siderite (FeCO₃) layers significantly⁶⁵ and thus deteriorate the protection potential of respective films. During evaluation procedures, $FeCO₃$ layers of inhibited samples were removed much easier than $FeCO₃$ layers of uninhibited samples.

FS2

To continue comparison between inhibitor FS1 and FS2, like performed in the "Field Data" sector, an additional experiment screening FS2 and its performance under 80 °C with variations in partial pressures has been made. Comparing inhibitors' performances under same autoclave conditions, FS2 evidences once more the improved performance regarding corrosion inhibition.

Figure 41 – Comparison FS1 to FS2 with Variations in Inhibitor Doses of FS1 at 80 °C

FS2 is, independent of exposed partial pressures, lowering corrosion rates more efficiently than inhibitor FS1. As a matter of fact, results of 100 ppm FS2 and 300 ppm of FS1 can be considered as equal. This shows additionally an improved performance under highest pressure.

6 Discussion

After gaining the experimental results, literature and field data are to be discussed and verified for proper outputs.

6.1 Watercut

Watercut investigations by means of field data show corrosion- inhibitive properties of oil at watercuts lower than 80 %. This result reflects investigations of Smith et al.¹⁴ and shows that in fields of Austria, generally no inhibition support of oil can be expected, since the average watercut is near 90 %.

 Furthermore, watercuts measured in wells can be influenced by its flow rate or velocity. That means, with increasing production rates more water is sucked into the borehole and oil is not able to accumulate and segregate downhole, which would lead to an artificial decrease of watercut.

6.2 Fluid Velocity

The dependency of the watercut on the velocity makes the identification of the net-influence of velocity an issue. Furthermore, only by removal of H_2S containing wells a weak correlation according to literature could be found. Basically, corrosion rates are considered to increase with increasing velocity. $11, 28, 29$ The analysis of velocity influence additionally was simplified by exclusion of gas and linked slug flow. Knowing all that and keeping in mind that the presence of FeS films and the connected extraction of wells is highly speculative, reliable outputs (except the dependency of watercut) regarding fluid velocity can not be made. Nevertheless, velocity thresholds, also with respect to watercut, can be presented. At wellhead velocities lower than 0.15 m/s and tubing velocities lower than 0.11 m/s corrosion rates stay below "0.05 mm/a- limit".

6.3 CO₂ and H₂S Partial Pressure

Like already mentioned in experimental introduction, partial pressures $CO₂$, gained via field analysis, are not to be correlated to literature outputs. That is why experimental investigations have been added in order to verify field data. Basically, literature outputs of partial pressures $CO₂$ can be repeated and prove a misleading picture of field analysis. But field analysis still is helpful talking about classification of partial pressure relevance. Whereas 1 and 3 bar partial pressures are common in lower tubing areas (Figure 16), 10 bar is not registered in corresponding oil wells' analysis. Knowing that most $CO₂$ partial pressures are lower than 3 bar, further steps regarding well management need to be taken with respect to that threshold value.

H₂S partial pressures as well as analyzed " P_{CO_2} / P_{H_2S} " ratios show, according to numerous literature citations, a strong indication of FeS precipitation.^{20, 21, 22, 23, 24, 26}

Additionally, by analysis of H_2S wells, a lot of low corrosion rates could be explained under advanced velocities and higher $CO₂$ partial pressures. Removing H₂S wells, weak correlations of those parameters according to literature were found (Figure 23 to Figure 26). Like mentioned several times already, installed coupons are not available to prove that hypothesis, which makes assumptions still highly speculative. Whatsoever, H₂S influence needs to be considered in future, since FeS on coupons' surface can falsify measurement results. FeS is not supportive in corrosion prevention and needs to be taken seriously. It increases pitting probability, since FeS layers are not always homogeneous and H_2S as such is referred to cause Sulfide Stress Cracking (SSC).^{14, 19}

6.4 Temperature

Temperature was another parameter to be explored separately by means of laboratory experiments. Surface temperatures were considered to be constant, whereas downhole temperatures were calculated on basis of common "3.3 °C/100 m" gradient in oilfields. No connections of field data to literature were found. With help of experiments, temperature can be considered as proportional to corrosion rates until 80 °C, where peak corrosion rates are experienced. With further increase, corrosion rates finally decrease due to $FeCO₃$ formation. This has also been experienced in numerous scientific articles. ^{1, 2, 25, 30, 46} Again, field data is supportive regarding qualification of temperature. That means that temperatures of 120 °C are not found at lowest tubing location; highest temperatures are calculated to approximately 60 °C (Figure 27 and Figure 28).

Once more, the appearance of protective scales can not be guaranteed in oil fields, since a lot of parameters, like velocity or pH, can influence protectiveness negatively.

6.5 Inhibitor Performance

The last point to be discussed is the inhibitor performance of FS1 and FS2. Starting with FS1, clear trends regarding an optimum dose of respective inhibitor could not be found via provided data of austrian fields (Figure 30 to Figure 33). Emphasizing on laboratory results and considering harshest conditions present downhole, 100 ppm of FS1 show optimum efficiency regarding corrosion rate reduction. At room temperature, as well as at elevated temperatures of 80 °C, 100 ppm shows satisfying results at 1 and 3 bar. As already mentioned in chapter "5 Experimental Results", under higher partial pressures of 10 bar, concentrations of 300 ppm show better performance than lower concentrations. Focussing on tubing protection, 10 bar of partial pressure $CO₂$ is excludable, like field investigations have shown. With temperatures of 120 °C, inhibitor performance breaks down showing no metal protection tendencies. Additionally, the inhibitor seems to decrease capabilities of protection of the $FeCO₃$ scale within the created laboratory conditions. This could be explained via adsorption of the inhibitor on $FeCO₃$ particles, leading to a decrease of grip of $FeCO₃$ on metal surfaces, explaining the easy removal of $FeCO₃$ films at inhibited samples within the evaluation phase. Furthermore, with increasing amounts of $FeCO₃$ particles, surfaces that need to be covered by the inhibitor is
increased, decreasing available inhibitor amounts to protect the metal surface. Like already mentioned, inhibitors are able to change $FeCO₃$ layers' porosity as well as other physical parameters.⁶⁵

Focussing now on FS2, an improved reduction of corrosion rates can be evidenced from field investigations, by means of "List Green Inhibitors", as well as from laboratory analyses. Especially at 10 bar $CO₂$ partial pressure and 80 °C, FS2 is able to halve the accomplished corrosion rate of FS1. To obtain more reliable properties of the inhibitor FS2, further investigations accordingly are necessary. Once more, description of differing compounds of respective inhibitor is being found at Background Data 28.

7 Conclusions

With field analyses alone only few reliable outputs were gained. With support of autoclave experiments, the following reliable results and findings can be published in order to understand critical parameters.

- Coupon measurements with watercuts lower than 80 % show significantly lower corrosion rates compared to the ones with higher watercuts. Knowing the average watercut of 90 % of Austrian oilfields, large inhibitive support from oil can not be expected.
- Velocity threshold values of 0.15 m/s for surface and 0.11 m/s for downhole are being defined. Below those threshold values corrosion is not proven and expected, since also watercuts depend on velocity.
- The precipitation of FeS can not be proven, due to missing coupons. Nevertheless, there are strong indicators from literature, underlining a high probability of FeS presence on relevant coupons.
- Field data analyses show insufficient trends and correlations with respect to partial pressure $CO₂$ and $H₂S$, velocity and temperature.
- Temperature and partial pressure $CO₂$ autoclave experiments show outputs according to literature.
- 30 ppm of FS1 inhibition is not sufficient in terms of optimum protection against corrosion, like experiments have shown.
- For most efficient protection of production tubings, 100 ppm of FS1 can be recommended. Dealing with higher $CO₂$ partial pressures of 10 bar and raised temperatures of 80 °C, an increase to 300 ppm improves metal conservation.
- At 120 °C, inhibitor FS1 is not efficient.
- Inhibitor FS2 performs better under 80 °C within autoclave experiments than FS1 and strengthens the results gained in field analyses.

8 Recommendations & Future Work

To achieve a higher reliability of field data, an independent record related to corrosion management is recommended. With an unified program, problems as well as benefits can be identified with less efforts.

8.1 Measurement Concept

Monitoring the corrosion rate alone does not provide the full overview on corrosive problems. The influence of wear by coupling of pumps e.g., can provide a synergism increasing the conventional corrosion rate, which can not be computed via coupons measurements. $66, 67$ That is why the additional implementation of "meantime between failure" (MBF) to corrosion analysis is strongly recommended. By inclusion of MBF or "Workover per Year", also mechanical forces like abrasion or possible erosion can be considered and weaknesses in corrosion operations can be discovered more easily.

8.1.1 Start

All wells need to be screened and adjustments on inhibition need to be performed. For that, a three phase coupons- measurement cycle, each with a duration of one month minimum, like "surface measurements 1 3", for evaluating inhibitor doses, is recommended. Minimum doses of inhibition were already concluded previously. After that, an optimum treatment of the corrosion processes as such is expected. Coupons surface measurements are preferred to downhole measurements, since results can be achieved faster with fewer efforts.

8.1.2 Frequency

MBF

The limit for workover was set to 0.33 WO/a providing also a good basis for evaluation frequency. This value was determined with respect to the average MBF of Table 5. That is why every third year, all wells are to be screened for workover linked to corrosion damage and are to be compared to previous years.

Surface Coupons Measurement Cycle

After every workover, where signs of corrosion were being observed, surface coupons measurement cycles should be performed additionally to check for inhibitor efficiency. Furthermore, unplanned coupons- measurement cycles and inhibitor adjustments should be performed, if new conditions in the borehole, like perforation of new horizons, have been conducted. Basically, a well is recommended to be screened once in three years.

8.1.3 Documentation

To make sure that corresponding treatments can be justified via environmental background and to understand basic behaviour of a corrosive situation, important parameters have to be conserved.

MBF

In order to evaluate workover caused by corrosion, exact documentation of workover data has to be done. That means, even if a workover is conducted due to a stuck pump e.g. and tubings as well as other downhole equipment is replaced due to signs of corrosion on that occasion, it needs to be documented and the key word "Corrosion Replacement" needs to be registered in workover reports.

- What type of damage
- Where is that damage located (Measured Depth)
- Pump type and setting depth
- Depth of perforation and perforated horizon
- $CO₂$ and H₂S content as well as pH of formation water
- Watercut and chloride average until last workover
- Average inhibitor concentration and type until last workover
- Average pump rate and production rate (liquid and gas) until last workover
- Average sediment production until last workover
- Surface Measurement Cycle
	- Depth of perforation and perforated horizon
	- $CO₂$, H₂S content and pH value before start of first measurement cycle
	- Chlorides before first measurement cycle
	- Watercut average during each surface measurement cycle
	- Average inhibitor concentration and type during each surface measurement phase
	- Average pump rate and production rate (liquid and gas) during each surface measurement phase

All coupons installed need to be isolated to prevent corrosion and attached to corresponding measurement records. Of course, weight before and after installation needs to be recorded.

In addition, screening of sediment production must be conducted at least once a year for every well during conventional production, in order to evaluate the possibility of erosion or three body abrasion.

8.2 Future Work

8.2.1 FS2 Analysis

 The inhibitor FS2 needs to be exposed to all conditions inhibitor FS1 has been exposed to within autoclave experiments in this work; that creates the optimum chance for comparison and provides the best level which one of the inhibitors performs better. Additionally, a field test like "List Green Inhibitors" needs to be performed with both inhibitors. Only the amount of treated wells needs to be increased to approximately 50 wells, compared to "List Green Inhibitors" test. Coupons need to be installed on surface for 1 month after corresponding well- system was saturated with respective inhibitor. There should be at least a time gap of 1 month between injections of different inhibitors.

8.2.2 FS1 and FS2 Performance connected to Sediments

Very often sediments tend to adhere inhibitors and reduce the accumulated amount on the metal surface, which causes a reduced protection. Inhibitors need to be screened for corresponding properties. For that, experiments, where autoclaves are being rotated, with variations of inhibitor doses and sediments representative of Austrian oilfields are recommended.

8.2.3 Proving protective Layers on Measurement Coupons in Wells

The existence of both $FeCO₃$ and FeS layers needs to be proven. Both layers can influence measurements and could lead to misinterpretations of well corrosivity as a consequence. Especially FeS layers at H₂S wells are to be treated with a lot of caution, like mentioned several times within this work. If layers are evident, proper consideration is of primary importance. Layers are not always homogeneous and can be removed by external forces. Critical areas in production streams need to be highlighted as well as layer integrity has to be determined along the production system. As a matter of fact, inhibitor performances in connection to FeS particles would be another step to be investigated.

8.2.4 Implementation and Verification of Measurement Concept

The recommendations suggested within 8.1 needs to be implemented and checked for applicability and validity. Especially the start requires maximum consistency and one single person in charge for surveillance. For that, a record form, containing all suggested parameters and considerations, needs to be created and every measurement needs to be controlled and recorded according to invented guidelines. Furthermore, problems, criticism and other concerns during the evaluation phase have to be registered and, as a result, innovations can be introduced. The monitoring concept should be a dynamic corpus that has to be maintained over decades with maximum consistency to lower corrosion rates in a standardized manner.

9 Appendix

9.1 Background Data

Background Data 1- Environments created at Investigations^{21, 26}

H₂S-CO₂ Corrosion Dominance and Prediction Guides (A Rule of Thumb)

Background Data 2- Pots' Rule of Thumb for CO₂- H₂S Corrosion Prediction^{21, 26}

Background Data 3 – Influence of CO₂ Partial Pressure on Corrosion Rates¹⁷
CORROSION RATE AT _PM = 4, mm/yr

Background Data 4 – Arrhenius Plot of Corrosion Rates normalized to pH = 4 (grit blasted samples)¹⁷

Background Data $5 -$ Nomogram for $CO₂$ Corrosion⁴⁶

Background Data 6 – Fugacity Coefficient for CO₂ in Methane for Gas Mixtures less than 5 mol % CO₂⁴⁶

Background Data 7 – Nomogram for pH of Water and CO₂ as a function of CO₂ Pressure (Fugacity) and Temperature⁴⁶

Background Data 8 – Constant K_t of NORSOK¹⁸

Background Data 9 – The pH of condensed Water (wet Gas) or Formation Waters containing Bicarbonate (undersaturated in CACO3) under CO₂ and H₂S Pressure⁶⁸

Background Data 10 – pH Function of NORSOK18

Backgound Data 11 – Basic Input Parameters of NORSOK¹⁸

Background Data 12 – Input Parameters for simplified Calculation of Wall Shear Stress of NORSOK¹⁸

Background Data 13 – Input Parameters for accurate Calculation of Wall Shear Stress of NORSOK¹⁸

Background Data 14 – Input Parameters for pH Calculations of NORSOK¹⁸

Background Data 15 – Watercut Readings in Emulsions at the Point where at least 10% of the total Water has seperated from Oil Water Emulsions³

Background Data 16 – Dimensions and Content of an original C1020 Coupon⁶⁹

Background Data 17 – Example Picture of Surface/ Wellhead Coupons Installation of Prottes 109

Background Data 18 – Example Picture of Downhole Coupons Installation in Tailpipe

Background Data 19 – Numbered "Surface 1. Installation" Corrosion Rate versus Wellhead Velocity⁵¹

Background Data 20 – Numbered Downhole Corrosion Rate versus Tubing Velocity⁵¹

Background Data 21 - "Surface 1. Installation" Corrosion Rates versus numbered CO₂ Partial Pressures for Watercuts > 80 % and Velocities > 0.15 m/s⁵¹

Background Data 22 – Downhole Corrosion Rates versus numbered CO₂ Partial Pressures for Watercuts > 80 % and Velocities > 0.11 m/s 51

Background Data 23 – Wellhead Velocity versus numbered "Surface 1. Installation" Corrosion Rate without H₂S Wells⁵¹

Background Data 24 – Tubing Velocity versus numbered Downhole Corrosion Rates without H₂S Wells⁵¹

Background Data 25 – Partial Pressure CO₂ versus numbered "Surface 1. Installation" Corrosion Rate for Watercuts > 80 % and Velocity > 0.15 m/s without H_2S Wells⁵¹

Background Data 26 – Partial Pressure CO2 versus numbered Downhole Corrosion Rate for Watercuts > 80 % and Velocity > 0.11 m/s without H₂S Wells⁵¹

Background Data 27 – Temperature versus numbered Downhole Corrosion Rate for Watercuts > 80% and Tubing Velocities > 0.11 m/s without H₂S Wells⁵¹

Background Data 28 – Composition of Inhibitors FS1 and FS2⁷⁰

Background Data 29 – Sample for Autoclave Experiments

Background Data 30 – Dimensions of Specimen for Autoclave Experiments

Background Data 31 – Microstructure of L80 Steel

Background Data 32 - Staining Agent (Bühler GmbH, Düsseldorf, Germany) for Autoclave Tests⁶⁴

Background Data 33 – Corrosion Rates at Room Temperature versus Inhibitor Dose with Variations in Partial Pressure CO² (log-scale)

Background Data 34 – FeCO₃ layered Sample represantative for all Samples after Exposure to 120 °C Environment

Background Data 35 – Efficiency of Inhibitor FS1 within Autoclave Experiments

9.2 Spreadsheets

Data 1st Installation

Data 2nd Installation

Data 3rd Installation

Data Downhole Measurement and Deviations

Data Watercuts, Chloride Content, Velocities, Tubing Sizes

Data Watercuts CO2 & H2S Contents, Surface (Partial4) Pressures, Pump setting Depth, Casing Pressure

Data Watercuts Partial Pressures Downhole, Pco2/P_{H2S} Ratio, Temperature

List Green Inhibitors Content CO2 & H2S, Velocity,

Partial Pressure CO²

List Green Inhibitors Partial Pressure H2S, Chloride Content, additional Info

10 Literature

List of Symbols and Abbreviations

Conversion into metric Units

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