
Master thesis

Behavior and interaction of oil field additives
in the surface equipment
of RAG

Rudolf Pirker

Submitted to the Department of Petroleum Engineering at the
Mining University of Leoben (Austria)

INDEX

INDEX OF FIGURES.....	1
INDEX OF CHARTS.....	1
INDEX OF PICTURES.....	2
ABSTRACT.....	1
LIST OF ABBREVIATIONS.....	1
1 INTRODUCTION TO SCALE, PARAFFIN AND CORROSION.....	1
1.1 SCALE.....	2
1.1.1 GENERAL INFORMATION ABOUT SCALE GENERATION AND PRECIPITATION.....	2
1.1.2 CARBONATE SCALE.....	3
1.1.3 SULFATE SCALE.....	5
1.1.3.1 Calcium sulfate.....	5
1.1.3.2 Barium sulfate.....	6
1.1.3.3 Strontium sulfate.....	7
1.1.4 SULFIDE SCALE.....	7
1.1.5 FURTHER TYPES OF INORGANIC SCALE.....	8
1.1.6 PROBLEMS ARISING FROM SCALE PRECIPITATION.....	8
1.2 PARAFFIN.....	9
1.2.1 INTRODUCTION AND BACKGROUND.....	9
1.2.2 FORMATION OF PARAFFINS.....	10
1.2.3 PARAMETERS CAUSING AND/OR INFLUENCING PARAFFIN DEPOSITION.....	10
1.2.4 CRUDE OIL COMPOSITION.....	11
1.2.5 TEMPERATURE.....	11
1.2.6 PRESSURE.....	12
1.2.7 FLOW REGIME.....	12
1.2.8 COOLING RATE.....	12
1.2.9 SURFACE ROUGHNESS.....	13
1.2.10 PROBLEMS DUE TO PARAFFIN PRECIPITATION.....	13
1.2.10.1 Problems in the reservoir and wellbore.....	13
1.2.10.2 Problems in the tubing string.....	14
1.2.10.3 Problems in surface installations.....	14
1.3 CORROSION.....	14
1.3.1 STRUCTURE OF THE ELEMENT EXPOSED TO CORROSION.....	15
1.3.2 MATERIAL.....	15
1.3.3 MEDIUM.....	16
1.3.4 PROBLEMS RESULTING FROM CORROSION.....	17
1.4 TREATING METHODS.....	17
1.4.1 TREATING METHODS OF PARAFFINS.....	17
1.4.1.1 Mechanical methods of treating paraffins.....	18
1.4.1.2 Thermal methods of treating paraffins.....	18
1.4.1.3 Biological methods of treating paraffins.....	18
1.4.1.4 Chemical methods of treating paraffins.....	18
1.4.2 TREATING METHODS OF SCALE.....	19
1.4.3 TREATING METHODS OF CORROSION.....	20

2	<u>CURRENTLY APPLIED CHEMICALS</u>	22
2.1	GENERAL INFORMATION	22
2.2	COMBINED CORROSION/PARAFFIN INHIBITOR CHAMPION TECHNOLOGIES FLOTRO CW511	22
2.3	CORROSION INHIBITOR M-I SWACO KI-350	24
2.4	SCALE INHIBITOR M-I SWACO SI-4041	24
3	<u>SYSTEM ANALYSIS</u>	26
3.1	GENERAL INFORMATION	26
3.1.1	WELL INFORMATION	28
3.1.1.1	Logging data	28
3.1.1.2	Production well data	30
3.2	PIPELINE SYSTEM	32
3.3	PRODUCERS	36
3.3.1	INTENTION AND BACKGROUND INFORMATION	36
3.3.2	RESULTS OF THE CHEMICAL ANALYSES	37
3.4	SETTLING TANK	39
3.4.1	BACKGROUND AND INFORMATION	39
3.4.2	PHYSICAL PARAMETERS – HAZE, TEMPERATURE, PH VALUE, REDOX POTENTIAL, CONDUCTIVITY, SOLIDS AND WBF	40
3.4.3	CHEMICAL PARAMETERS – ROC, IRON, TOTAL HARDNESS, CALCIUM AND MAGNESIUM CONTENT	44
4	<u>CORROSION COUPONS - EVALUATION</u>	49
4.1	BACKGROUND AND OVERVIEW	49
4.2	CORROSION COUPONS INSTALLED IN THE FIELD NETWORK VOITSDORF	49
4.2.1	GENERAL INFORMATION AND PROCEDURE	49
4.2.2	PRODUCER WELLS	50
4.2.3	INJECTOR WELLS	51
4.2.4	STATIONS	51
4.3	CORROSIVENESS OF THE THREE INHIBITOR TYPES	51
4.3.1	BACKGROUND INFORMATION AND SET-UP	51
4.3.2	DOCUMENTATION	52
4.3.2.1	KI-350 in open jar	52
4.3.2.2	CW511 in open jar	52
4.3.2.3	SI-4041 in open jar	53
4.3.2.4	KI-350 in sealed glass	53
4.3.2.5	CW511 in sealed glass	54
4.3.2.6	SI-4041 in sealed glass	54
4.3.3	COUPON WEIGHING	55
4.3.3.1	Procedure description	55
4.3.3.2	Weights and results	55
5	<u>SCALE COUPONS INSTALLED AT PREDETERMINED LOCATIONS</u>	56
5.1	BACKGROUND AND INFORMATION	56
5.2	EVALUATION OF INSTALLED SCALE-COUPONS	57
5.2.1	FIRST EXAMINATION AFTER 15 DAYS	57
5.2.2	SECOND EXAMINATION AFTER 50 DAYS	59
5.3	RESULTS OF THE EXAMINATION	59

6	<u>CHEMICAL INHIBITION AT RAG</u>	<u>60</u>
6.1	GENERAL INFORMATION	60
6.2	DE-FACTO DOSAGE	60
6.2.1	AVERAGE PARAFFIN/CORROSION INHIBITOR DOSAGE – CHAMPION TECHNOLOGIES FLOTRON CW511	61
6.2.2	AVERAGE SCALE INHIBITOR DOSAGE – MI-SWACO SI-4041	61
6.2.3	AVERAGE CORROSION INHIBITOR DOSAGE – MI-SWACO KI-350	62
6.3	LABORATORY TESTING OF INHIBITOR MIXTURES	62
6.3.1	BACKGROUND INFORMATION AND INTENTION	62
6.3.2	DOSAGE SELECTION FOR THE INHIBITOR MIXTURES	63
6.3.3	PREPARATION OF THE INHIBITOR MIXTURES	63
6.3.4	OPTICAL EVALUATION OF THE SEVERITY OF MIXTURE EFFECTS	63
6.3.4.1	Clear	64
6.3.4.2	Weak haze	64
6.3.4.3	Strong haze	65
6.3.4.4	Streaks	65
6.3.4.5	Precipitations	66
6.3.4.6	Mixing of concentrated inhibitor liquids	66
6.3.4.7	Rating	67
6.3.5	INJECTIVITY EVALUATION – THEORY FOR WBF	70
6.3.6	EXPERIMENTAL SET-UP AND PROCEDURE	71
6.3.7	RESULTS OF THE EXPERIMENTS	72
6.4	ELECTROPHYSICAL SCALE TREATMENT WITH WEATHERFORD CLEARWELL	74
6.4.1	BACKGROUND INFORMATION	74
6.4.2	PRINCIPLE OF WORK	75
6.4.3	SELECTION OF WELLS	75
7	<u>CONCLUSION</u>	<u>77</u>
	<u>REFERENCES</u>	<u>1</u>

Index of figures

Figure 1: Solubility of calcite over temperature in °C and °F at 1atm partial pressure of carbon dioxide ..	4
Figure 2: Solubility of the several forms of calcium sulfate over temperature.....	6
Figure 3: Effect of temperature and salinity on barium sulfate solubility at atmospheric pressure	7
Figure 4: Iron sulfide stability diagram (Smith 1994); (c) NACE International 1994	8
Figure 5: Crude oil components.....	9
Figure 6: structures of n- and iso-paraffins	10
Figure 7: structure of a cyclo-paraffin	10
Figure 8: Heat transfer from crude oil to surrounding formations.....	12
Figure 9: Effect of pH on the corrosion rate of iron in water	16
Figure 10: Function of a film-forming corrosion inhibitor	21
Figure 11: Western part of the producers and injectors of the Voitsdorf field	32
Figure 12: Eastern part of the producers and injectors of the Voitsdorf field	33
Figure 13: Producers and injectors of field Sattledt	35
Figure 14: Schematic of crude oil upstream and processing.....	39
Figure 15: Distribution of measured haze values [NTU]	40
Figure 16: Distribution of measured temperature values [°C]	41
Figure 17: Distribution of measured pH values [-].....	41
Figure 18: Distribution of measured redox potential values [mV]	42
Figure 19: Distribution of measured conductivity values [mS/cm]	42
Figure 20: Distribution of measured HCl-acidizable solids [mg/l]	43
Figure 21: Distribution of the measured ROC values [ppmv]	44
Figure 22: Sketch of a scale coupon; for dimensions see Chart 24	56
Figure 23: Flow behavior of an installed scale coupon	56
Figure 24: Sketch of the blocked scale coupon from V-033 after 50 days.....	59
Figure 25: Inhibitor dosage schematic at RAG	60
Figure 26: Example for WBF evaluation	70
Figure 27: Sketch of the experimental set-up	71
Figure 28: Filtration curves for the chosen inhibitor mixtures and blind samples	73
Figure 29: Comparison between measured WBFs and check sum from evaluation.....	74
Figure 30: Sketch of ClearWell's signal transfer	75

Index of charts

Chart 1: Solubility of alkaline earth salts (Becker 1998).....	5
Chart 2: EU stainless steel prices 2010 (per ton).....	15
Chart 3: EU carbon steel prices 2010 (per ton)	15
Chart 4: Flotron CW511's structures of known effective components	23
Chart 5: Chemical structure of the KI-350's known effective component.....	24
Chart 6: Chemical structure of the component AMPASS.....	25
Chart 7: Overview of the oil producing wells dealt with in this diploma thesis, their collector stations and production method	26
Chart 8: Overview of the oil producing wells for this diploma thesis and their inhibition	27
Chart 9: Producers and their producing layers	30
Chart 10: Producer wells and their production test data	31
Chart 11: Pipeline lengths, producers and injectors in field Voitsdorf.....	34
Chart 12: Pipeline lengths, producers and injectors in field Sattledt.....	36
Chart 13: Main water producers to be treated at VZ station	37
Chart 14: Chemical analyses of the wells from Chart 13	37
Chart 15: Daily contribution of analyzed components to system (in kg)	38
Chart 16: Measured values of the WBF [-].....	43
Chart 17: Comparison of measured WBFs with filtratable material and contents of iron, calcium and magnesium	43
Chart 18: Base line parameters for haze, temperature, pH value, redox potential, conductivity and HCl-acidizable solids	44
Chart 19: Measured values of ROC and ROC ranges compared with oil and condensate deliveries	45
Chart 20: Distribution of cracked iron values [mg/l].....	46
Chart 21: Distribution of total hardness' values	47
Chart 22: Values for calcium and magnesium concentration based on the values from Chart 21	47

Chart 23: Base line parameters for ROC, cracked iron, total hardness, calcium and magnesium values/ranges	48
Chart 24: Coupon surface data of the coupons used in the field network Voitsdorf	49
Chart 25: Corrosion rates of the producer wells in the field network Voitsdorf	50
Chart 26: Corrosion rates of the injector wells in the field network Voitsdorf	51
Chart 27: Corrosion rates of the stations in the field network Voitsdorf	51
Chart 28: Weights of the single coupons after different treatment steps	55
Chart 29: Weight loss, residues weight and calculated annual corrosion rate with the surface from Chart 24	55
Chart 30: Temperature and locations for occurrence of potential interactions and their effects	62
Chart 31: Result prioritization of "hot-sets" - pt. 1 of 2	68
Chart 32: Result prioritization of "hot-sets" - pt. 2 of 2	69
Chart 33: Determined WBFs and filtrate weights	72

Index of pictures

Picture 1: The petroleum system - overview	1
Picture 2: Open glass with corrosion coupon	52
Picture 3: Dried coupon	52
Picture 4: Open glass with corrosion coupon in CW511	52
Picture 5: Dried coupon	52
Picture 6: Open glass with corrosion coupon in SI-4041	53
Picture 7: Dried coupon	53
Picture 8: Sealed glasses with corrosion coupons in pure CW511, SI-4041 and KI-350	53
Picture 9: Dried coupon from the sealed jar with KI-350	54
Picture 10: Dried coupon from the sealed jar with CW511	54
Picture 11: Dried coupon from the sealed jar with SI-4041	54
Picture 12: Residues from the corrosion process chipping off the sealed SI-4041 coupon	54
Picture 13: Scale coupon holder installation at VW-009 (pre-pressurization module)	57
Picture 14: Scale coupon of producer V-033 15 days after installation	58
Picture 15: Scale coupon of pre-pressurization module VW-009 15 days after installation	58
Picture 16: Scale coupon of VZ exit 15 days after installation (wiped clean with woven felt)	59
Picture 17: Clear liquid (KI-350: 200ppmv, CW511: 0ppmv, SI-4041: 20ppmv)	64
Picture 18: Weak haze (KI-350: 100ppmv, CW511: 500ppmv, SI-4041: 100ppmv)	64
Picture 19: Strong haze (KI-350: 200ppmv, CW511: 300ppmv, SI-4041: 0ppmv)	65
Picture 20: streaks (KI-350: 100ppmv, CW511: 300ppmv, SI-4041: 20ppmv)	65
Picture 21: Precipitations (KI-350: 200ppmv, CW511: 150ppmv, SI-4041: 200ppmv)	66
Picture 22: Mixture of concentrated inhibitor liquids (KI-350, CW511 and SI-4041)	66

Abstract

This master thesis deals with the application of oil field chemicals in the producer network of RAG. Herein included are also the upstreams of the fields Hiersdorf, Sattledt, Eberstanzell and Mayersdorf as well as partially Kematen and Engenfeld; the research is dated to October 28th 2010. Excluding Kematen and Engenfeld, the oil producer network lies within an approximate radius of 7.5km around the station VZ (“Voitsdorf Zentrale”; Address: RAG Kremsmünster, Kriß 50, A-4550 Kremsmünster) in the vicinity of the town Kremsmünster in Oberösterreich.

A part of this master thesis deals with the analysis of the existing producer system and their respective upstreams – in detail with their co-produced formation water. Furthermore depositions of scale and paraffin are formed in the producers as well as in the subsequent piping system and surface installations due to i.e. pressure drops, temperature alterations, different flowing velocities etc. Additionally corrosion affects all parts of the system susceptible to it. The severity of scale precipitation and the corrosion rate at the single measuring sites was captured within the scope of possibilities. A part of the consequences of scale and paraffin deposits and corrosion effects resp. their avoidance is treated by constant addition of chemicals (“inhibition”).

The investigated chemicals – from all those which are applied – are inhibitors for the treatment of corrosion, scale and paraffin problems, whereas chemicals with the purpose of separation and processing of the crude oil and formation water (de-emulsification, biocides) were not dealt with. Also not taken into consideration were residues of different stimulation methods (EDTA-treatments, acidizing workovers etc) and external influences (tailings pond). The investigation’s main focus was on a possible mutual interference of the investigated chemicals and an accordingly impact on the flood water quality. As reference as rating parameters served the injectivity (composite parameter of the flood water quality), the hardness with calcium and magnesium content as well as the sulphate, the iron and residual oil content.

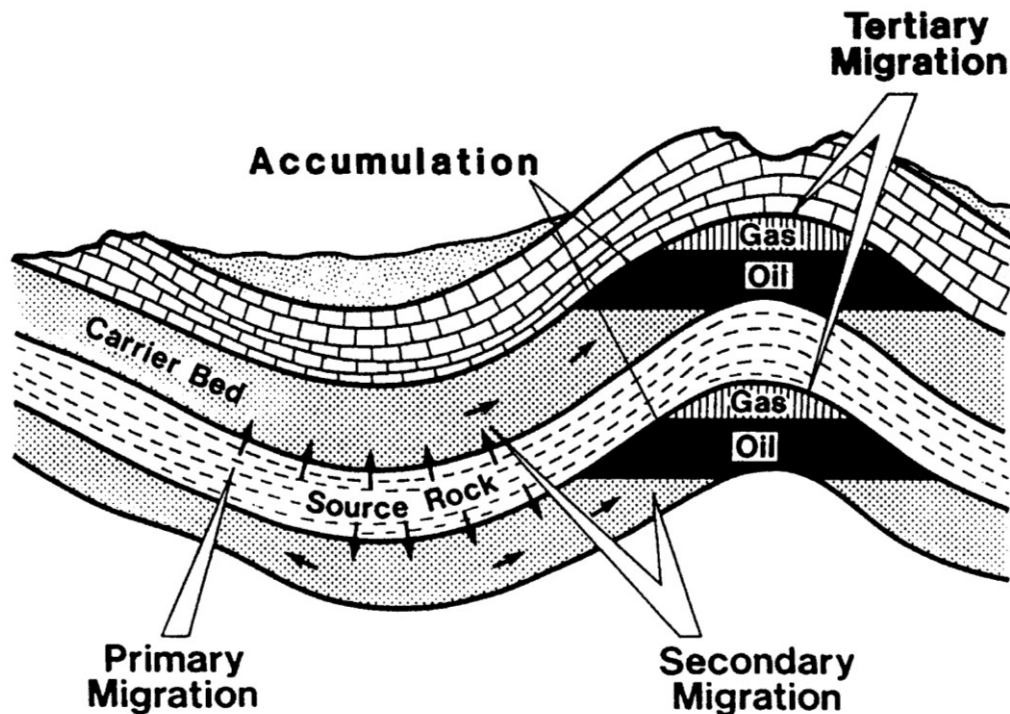
Eventually it was thought about an alternative to chemical well inhibition and treatment and its implementation was initiated.

List of abbreviations

Well codes:	BH-002	BAD HALL 2
	BH-003	BAD HALL 3
	BH-004	BAD HALL 4
	BH-009	BAD HALL 9
	BH-N-001	BAD HALL NORD 1
	EB-006	EBERSTALZELL 6
	EB-007	EBERSTALZELL 7
	EN-005-A	ENGENFELD 5A
	EN-006-A	ENGENFELD 6A
	HIER-001	HIERSDORF 1
	HIER-002-A	HIERSDORF 2A
	HIER-004	HIERSDORF 4
	KE-001	KEMATEN 1
	MDF-001-A	MAYERSDORF 1A
	OB-001	OBERAUSTAL 1
	RA-002	RAPPERSDORF 2
	SAT-002	SATTL EDT 2
	SAT-006	SATTL EDT 6
	SAT-007	SATTL EDT 7
	SAT-008	SATTL EDT 8
	SAT-010	SATTL EDT 10
	SAT-023	SATTL EDT 23
	STHS-006	STEINHAUS 6
	V-001	VOITSDORF 1
	V-007	VOITSDORF 7
	V-011	VOITSDORF 11
	V-013-A	VOITSDORF 13A
	V-015-C	VOITSDORF 15C
	V-016	VOITSDORF 16
	V-019	VOITSDORF 19
	V-021	VOITSDORF 21
	V-023	VOITSDORF 23
	V-030	VOITSDORF 30
	V-033	VOITSDORF 33
V-039	VOITSDORF 39	
V-041	VOITSDORF 41	
V-043	VOITSDORF 43	
Station codes:	S-III	Sattledt III
	S-V	Sattledt V
	Sat-SAT	Sattledt SATELLIT
	VZ	Voitsdorf Zentrale
Production of well:	E	eruptive
	IMP	impeller
	SR	sucker rod
Material:	GFC	glass fiber carbon
	PE	polyethylene
Other:	EDTA	ethylene diamine tetra acetic acid
	ROC	residual oil content
	ppmv	parts per million by volume

1 Introduction to scale, paraffin and corrosion

Petroleum is no homogenous liquid, but consists of a mixture of water, hydrocarbons of different lengths – liquid and gaseous – and solids. This mixture, which is mostly referred to as “crude” or “crude oil”, is located in the reservoir. Before it can be produced from there, it has to be generated as described in the petroleum system.



Picture 1: The petroleum system - overview¹

In the source rock, frequently also titled “oil kitchen”, the crude is generated at adequate conditions concerning temperature, time and pressure. The pressure and partially the temperature, too, are exerted by the overburden rock. Through one or several migration paths the petroleum reaches the reservoir rock, which has to be covered by a sealing formation in order to stop migration. After the oil’s migration is stopped and it is trapped below the seal rock, it usually covered a significant distance through several rock layers and structures. Therefore, it consists not anymore of its original composition from the source rock, but came in contact with i.e. additional water, dissolved minerals, potential other hydrocarbon migration streams etc., before the crude oil is stored under reservoir conditions.

During the production of crude oil, its flow regime and as a consequence its composition is altered again by changes of its temperature and pressure regime. These alterations cannot be avoided, since they occur through effects like e.g. pressure relieves when increasing pipe diameter or cooling off according to the temperature gradient of the well’s upstream.

In fact, already the drilling and completion of a well changes the behavior of a reservoir, where all components like oil, gas, solution gas, formation water, solids, minerals etc. are dissolved and dispersed in equilibrium. The penetration of the reservoir formation already creates a change in the pressure regime

If these alterations in the flow regime are strong enough to shift the petrochemical equilibrium, they can lead to the precipitation of solids. These solids usually origin from the formations flown through and can occur in several forms: scales, paraffins/waxes, asphaltenes and solids from the formation itself. Their effects on the well and its installations are numerous, such as

wellbore damage, increased material wear in the downhole equipment, reduced diameter, often followed by total blockage etc.

1.1 Scale

1.1.1 General information about scale generation and precipitation

Scale is understood as non-organic mineral precipitation of solids originally dissolved in a fluid, eventually forming accumulations on a surface. In petroleum business, it is usually produced from the reservoir together with the crude oil and precipitates on the inner surfaces of upstream equipment, such as tubings, pipelines, heat exchangers and separators. Nevertheless it can also precipitate anywhere in the wellbore where appropriate conditions bring forward scale precipitation and deposition. The most troublesome place for its deposition is in the downhole equipment – such as pump inserts and liners – since there the presence of scale can only be determined for sure by conducting a workover trip.

The precipitation conditions afore mentioned depend upon the following properties of the produced fluid:

- Composition
- Scale-forming ions' concentration
- pH-value
- Temperature
- Pressure
- Further properties

Usually, scales are composed by anions and cations, ligated via ionic bindings. The anions and cations usually are confined in an aqueous equilibrium in the formation fluid, where the chemical equilibrium is balanced towards the unbound single components. The formation minerals usually provide the cations; the anionic species is provided in form of ionic brines which are part of the total formation fluid amount. The composition relates to the formation the crude oil is produced from. The most common scale variants are: carbonates, silicates and sulfates, named after their anionic part.

Whereas the composition determines the type of the scales, other properties – especially the scale-forming ions' concentration – specify the consequences of the dissolved scales on the upstream equipment. The total amount of scale precipitation that will occur in the upstream equipment depends onto the concentration of the ions both in the formations and the brines.

The pH-value is a vital parameter, since it is a trigger for ionic binding reactions, which are highly dependent on it. A pH-value below 7 (low) or above 7 (high) means an acidic or caustic environment, which can promote the precipitation of scale. The pH-value can also be influenced by workover and stimulation jobs, such as i.e. acidizing. The removal of scale in downhole equipment is usually conducted by acid flushing; as a matter of fact, these treatments may dissolve scale but generate corrosion problems (see also Figure 9).

Temperature and pressure are the two parameters of the production fluid which influence and shift its chemical equilibrium – a quantifying parameter for the reaction is the solubility product. The lower the solubility product of a dissolving reaction is, the smaller will be the amount of solids that can be in solution in the respective liquid. Since the anionic and cationic species' in crude oil usually are in equilibrium, the precipitation of scale is caused by changes

in temperature and pressure. This usually happens in the wellbore region, but can also occur in the production string and the surface installations.

Temperature changes occur gradually in the tubing string. The velocity of the pumped fluid usually drags the scales along to accumulate somewhere after the point of precipitation.

Pressure depends not only on the environment, but is also dependent on the temperature via thermodynamic interaction. Pressure changes mostly occur more rapidly than temperature changes due to the installed equipment, like at a liner or pump intake. Flow control installations such as chokes and valves are a very common place for scale to precipitate and amass.

“Further properties” refers to characteristics and contents of the crude oil which are not necessary to be contained, but also can cause or promote scale precipitation: For example, the presence of sand was proven to be a reason for scale accumulation.

If a production fluid is seen in the matters of thermodynamic energy, it consists of the two main parts “heat” and “work”. The thermodynamic energy of a system cannot be altered; it only can shift the ratio between heat and work. Since the solidification of a before dissolved part of the fluid requires a change in the fluid’s thermodynamic energy distribution, the system will still try to achieve this change with as little energetically effort as possible. This means that the precipitation will rather occur on the sand grain than in the middle of the water, since the energy necessary to bond with an already existing surface is less than the one to form a completely new surface. In short, the sand grains can act as a core – called “nucleus” – for the scale, which will skip the phase of nucleation and directly start with the phase of growth by adhering to the generated nucleus.

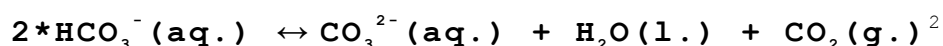
Another property is the salinity of the water. This property is different for each of the various scale types and its effect on the precipitations can vary strongly according to the salt concentration. Therefore it has to be watched for every scale type differently.

The properties “composition” and “concentration” depend on the formation’s lithology; pressure and temperature characteristics can be derived from the well’s installation plan and trajectory.

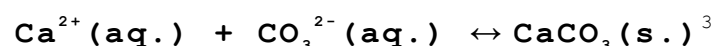
Frequently also scale predicting software is applied to determine the most probable location of scale precipitation by generating a software model of the upstream installations.

1.1.2 Carbonate Scale

Carbonate scale is the most common precipitation in the oil industry, formed from hydrogen carbonate. Its origin is shown below using the example of calcium carbonate:



The hydrogen carbonate is broken up into hydrogen, water and carbon dioxide when due to a pressure drop the equilibrium of the upper equation is shifted to the right in order to balance out the drop by liberating gaseous CO_2 . The liberated gas is usually produced through the well, so the pressure dropping continues. The gas liberation also creates a caustic environment with increasing pH-value. At sufficient amount and concentration, the chemical base CO_3^{2-} then can dissolve the calcium ions from the formation. The reaction equation shows that Ca^{2+} -ions together with the carbonate ions will form the solid CaCO_3 .



CaCO_3 is a white, fine powder which even in clean water can hardly be dissolved and exists in its mineral forms calcite, aragonite and vaterite. Its low solubility originates from the chelate ligation between the Ca^{2+} -cation and the CO_3^{2-} -anion, which form a very stable $\frac{2}{3}$ -bond. For dissolving in water, the addition of carbon dioxide into the solution highly increases the solubility of calcium carbonate.

The influence of temperature on the formation of calcite can be seen in Figure 1.

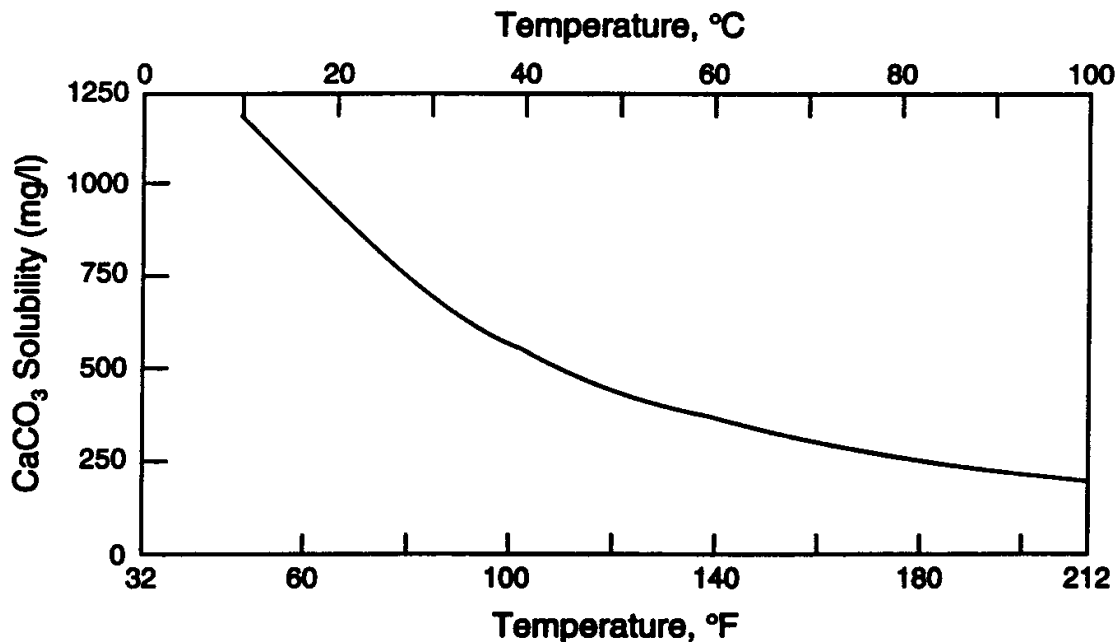


Figure 1: Solubility of calcite over temperature in °C and °F at 1atm partial pressure of carbon dioxide⁴

The fact that the solubility of calcium carbonate is indirectly proportional to the temperature explains why often injector wells are blocked, since the precipitation occurs because water heats up during its way down to the formation.

The pressure in the system influences the formation of calcite in two ways: in thermodynamic ways (PVT relation of a two- or three-phase system) and by the partial pressure of the dissolved carbon dioxide. The higher the overall pressure, the higher the partial one due to the coherence

$$\text{Partial pressure of CO}_2 = (\text{mole fraction of CO}_2 \text{ in gas}) \times (\text{total pressure})^5$$

Due to the facts that calcium carbonate does not only accumulate in the upstream equipment, but also can block the perforations and the formation, removal is necessary. In order to remove calcium carbonate precipitation, usually acidizing jobs are performed. These acidizing jobs usually are known factors: comparably cheap, organized and carried out relatively fast, with known manpower and financial efforts, known downtime and therefore easy financial loss calculation etc. The disadvantage of these acidizing or souring jobs lies in the fact that the acid not only dissolves the scale, but also can damage the formation during the acidizing while being pressed in through the perforations. The acid also can affect the completion and downhole equipment itself and damage the tubing by causing and/or supporting corrosion.

Similar forms of carbonate scale can be found when other cations bonding with the carbonate anion, such as magnesium and iron(II). In case of magnesium, the mineral formed is called

“magnesite” with the chemical formula MgCO_3 , whereas the iron complex is called “ion-carbonate siderite” with the chemical formula Fe (II) CO_3 . Another possible form is called “dolomite”, which commonly originates from calcite and is converted into the chemical form $\text{CaMg (CO}_3)_2$ with time, pressure and chemical environment.

What species of carbonate scale is generated depends basically on the chemistry of the formations getting in contact with in formation water dissolved carbon dioxide. The main factor deciding which scale is formed is again the solubility:

SOLUBILITY OF ALKALINE EARTH SALTS (BECKER 1998)					
M^{2+}	Radius (10^{-8} cm)	Fluorides	Hydroxides	Carbonates	Sulfates
Mg	0.31	very soluble	1.2×10^{-11}	1.2×10^{-3}	2.4
Ca	0.65	2×10^{-4}	2.1×10^{-2}	1.5×10^{-4}	1.5×10^{-2}
Sr	1.13	1×10^{-3}	6.5×10^{-2}	7.0×10^{-4}	5.0×10^{-3}
Ba	1.35	1×10^{-2}	2.8×10^{-1}	1.0×10^{-4}	1.0×10^{-5}

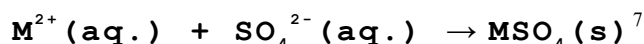
Moles per 1,000 g water at 1 atm and saturated with CO_2 for carbonates

Chart 1: Solubility of alkaline earth salts (Becker 1998)⁶

In the presence of acids the solubility of carbonate minerals also increases. This complicates the process of scale prediction since H_2S and CO_2 provide sufficient acidity under the well’s high pressure. When dissolved in formation waters, these gases’ acidic influence on carbonate formations favors the dissolution and keeps it in equilibrium until the formation is drilled and/or produced from. Furthermore, they complicate the precipitation process by boosting the accumulation of scales on corrosion sites and particles.

1.1.3 Sulfate scale

Group II metal ions, except magnesium, can all form sparingly soluble sulfate scales by mixing of sulfate ions and metal ions as given below:⁷

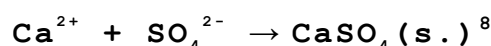


These metal ions, also called alkaline earth metals, form through their chelate ligation a very stable and hard-to-break bond with the sulfate anion. The strength of the bond increases downwards the main group of group II in the PSE¹. Whereas calcium sulfate, also known as Anhydrite or gypsum is relatively easy to dissolve in water and in many chelate solvers, heavier molecules like i.e. barium sulfate are very difficult to deal with.

1.1.3.1 Calcium sulfate

Three forms of calcium sulfate are known to precipitate in the oil field: gypsum with the chemical structure formula $\text{CaSO}_4 \cdot 2 \cdot \text{H}_2\text{O}$, hemi-hydrate with $\text{CaSO}_4 \cdot \frac{1}{2} \cdot \text{H}_2\text{O}$ and anhydrite in the form of CaSO_4 .

The basic reaction equation states:



At temperatures up to 80°C usually gypsum forms; from ~80°C to 121°C all three of the above mentioned species can form. From 121°C and above the most expectable form of calcium

¹ periodic system of elements

sulfate is anhydrite; hemi-hydrate is also found in the 80-to-120°C-temperature range at non-turbulent flow conditions with high ionic strengths.⁸

The solubility of the calcium sulfate depends strongly on the temperature, but behaves differently than calcium carbonate.

A special property is the anomaly of gypsum, which reaches its solubility peak at 38°C.

The solubility of calcium sulfate in pure water is given in Figure 2.

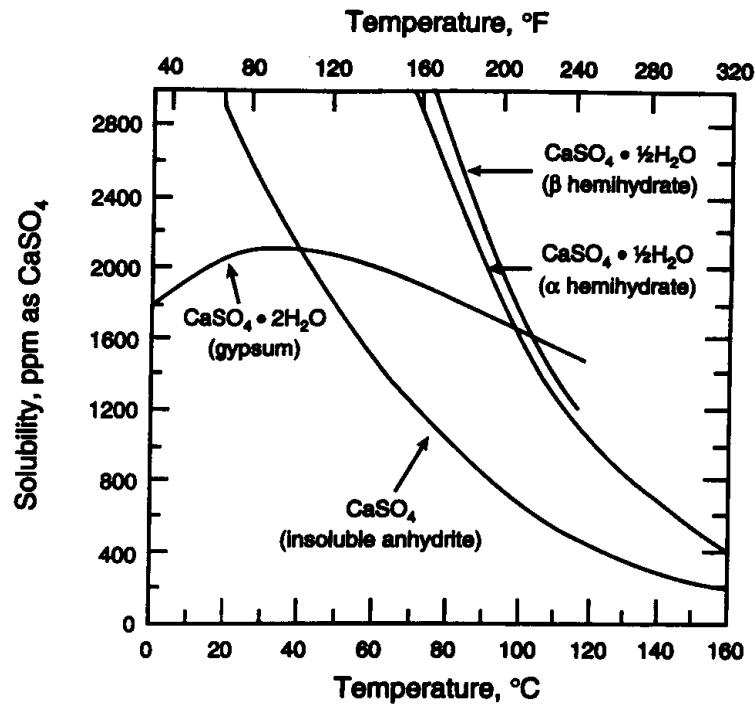


Figure 2: Solubility of the several forms of calcium sulfate over temperature

As a matter of fact, the actual form of calcium sulfate that precipitates is very difficult to predict, because it is not only temperature dependent. Also other factors such as pressure, salinity, flow conditions and the speed of the precipitation itself determine the type of carbonate sulfate which is formed.

The presence of dissolved salts as potassium chloride increases the solubility of carbon sulfate with increasing salinity up to about 150,000 mg/liter. Above and below this concentration the solubility decreases, which usually means precipitation of CaSO_4 .

The system pressure exerts its influence in thermodynamic ways in form of increasing solubility with increasing pressure. If calcium sulfate is dissolved in the co-produced water, it will come out of solution at pressure drops. These pressure drops and the responding precipitations are usually observed at similar places like calcium carbonate scale.

1.1.3.2 Barium sulfate

Due to its high molecular weight and the resulting strong bonding forces, barium sulfate is sparingly soluble in water with a solubility of 2.3mg/l. The solubility increases up to temperatures of 95°C and starts to decrease from temperatures of 100°C and above with 50,000 pm of total dissolved salts. Furthermore the amount of total dissolved salts has a very high influence, as shown in Figure 3.

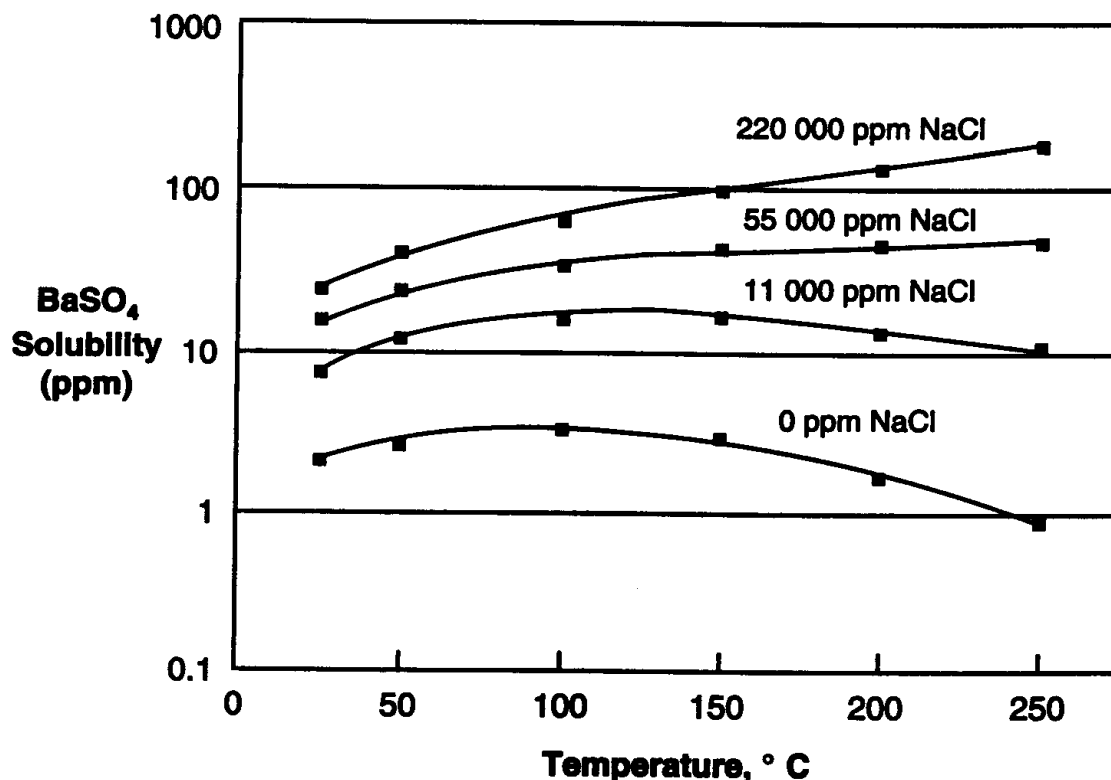


Figure 3: Effect of temperature and salinity on barium sulfate solubility at atmospheric pressure

While a change in the pH-value has little or no influence on the solubility, the pressure behavior is regular: an increase/decrease of the pressure increases/decreases the solubility of barium sulfate when maintaining constant other parameters.

1.1.3.3 Strontium sulfate

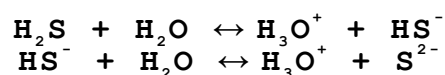
Strontium sulfate is more soluble than barium sulfate; its solubility decreases with increasing temperature. Way more significant is the influence of the amount of total dissolved salts, which peaks at approximately 175,000 mg/l. Further increase of dissolved salt leads to a decrease in the solubility of strontium sulfate.

Strontium sulfate solubility in NaCl brines increases with pressure. However, solubility data measured by Jacques and Borland shows that the increase is small up to 3,000 psig.⁹

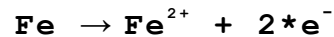
Most occurrences of strontium sulfates go together with barium sulfate.

1.1.4 Sulfide scale

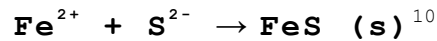
Sulfide scale is not as common as the two afore mentioned types of scale. Yet it can show up in production systems – especially when corrosion is to be dealt with, forming iron sulfide. One of the most common causes for the formation of sulfide scale is the existence of sulfate-reducing bacteria, which reduce sulfate to hydrogen sulfide (H_2S). When the equilibrium is shifted to the right, the conversion of water and hydrogen sulfide states as follows:



In the corrosion process, iron from the downhole or upstream equipment is reduced to iron (II)-ions according to



As given in the partial reaction below, the sulfide anion then ligates with the Fe^{2+} -ions and forms iron sulfide, the most common sulfide scale form. Instead of iron(II), also metals with (II)-electron configuration such as lead and zinc can bond with the sulfide.



The show-up up iron sulfide can clearly be observed, since it blackens the color of the water with thin, adherent scale. Black suspension in the injection respectively formation water usually is induced by the transportation of iron sulfide. In which forms the precipitation of iron sulfide actually occurs depends on the temperature, the H_2S activity and partially on the pH-value as well (Figure 4).

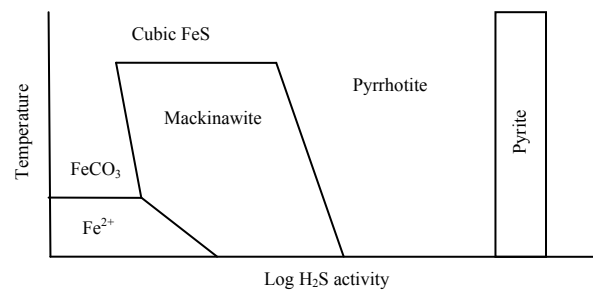


Figure 4: Iron sulfide stability diagram (Smith 1994); (c) NACE International 1994¹¹

The origin of sulfide is not always necessarily a single well. It can also occur by mixing the production streams of i.e. an iron-containing producer with a sulfide-saturated production fluid. Such situations can occur in manifolds, where i.e. field lines are merged into collector pipelines.

1.1.5 Further types of inorganic scale

The types of scale exceeding the before mentioned most common variations are numerous, i.e. iron oxides such in the various forms of the Fe_2O_3 compounds as for example $\alpha\text{-Fe}_2\text{O}_3$ (*hematite*)¹² and $\gamma\text{-Fe}_2\text{O}_3$ (*maghemite*)¹³, silica (SiO_2) and silica hydrate scales ($\text{SiO}_2 \cdot \text{H}_2\text{O}$) or salts which are found usually in and on surface equipment, halite resp. salt (NaCl) from high water-cut oil and/or gas wells and copper depositions from galvanic corrosion.

Since these scales open a wide field of research and possibilities to conduct analyses, they will not be part of this thesis, which was intended from RAG to be an “introduction study” for the scale problematic at the Voitsdorf station.

1.1.6 Problems arising from scale precipitation

The presence of scale precipitation usually means a severe constraint of equipment functionality. Scale precipitation can occur anywhere in the well where the conditions fulfill the requirements given in 1.1.1.

In a pipeline scale causes by its amassment a reduction in diameter. This means that a higher pumping pressure is required to keep the amount of pumped fluid constant. Increasing pump pressure at the beginning of the pipeline can cause several problems, such as extended wear of the pump and the blockage of mounted installations.

Scale precipitation in the downhole string can cause the blockage of downhole installations such as liners, the wreckage of pump inserts, the sticking of rods from sucker rod pumps and usually causes massive costs for workover trips and replacement of defect equipment. When occurring in treatment equipment, it can lower the overall efficiency of i.e. heaters, block filters and fill up sedimentation vessels such as separators, causing down-time of the equipment, cleaning and replacement costs.

1.2 Paraffin

1.2.1 Introduction and background

The term “paraffins” defines hydrocarbons composed as a chain in several forms. They mostly consist of pure hydrocarbons – both saturated and non-saturated hydrocarbons, furthermore asphaltenes and gas - but also may contain NSO-components (nitrogen, sulfur and oxygen). A detailed figurative overview of the several compounds of crude oil can be seen in Figure 5.

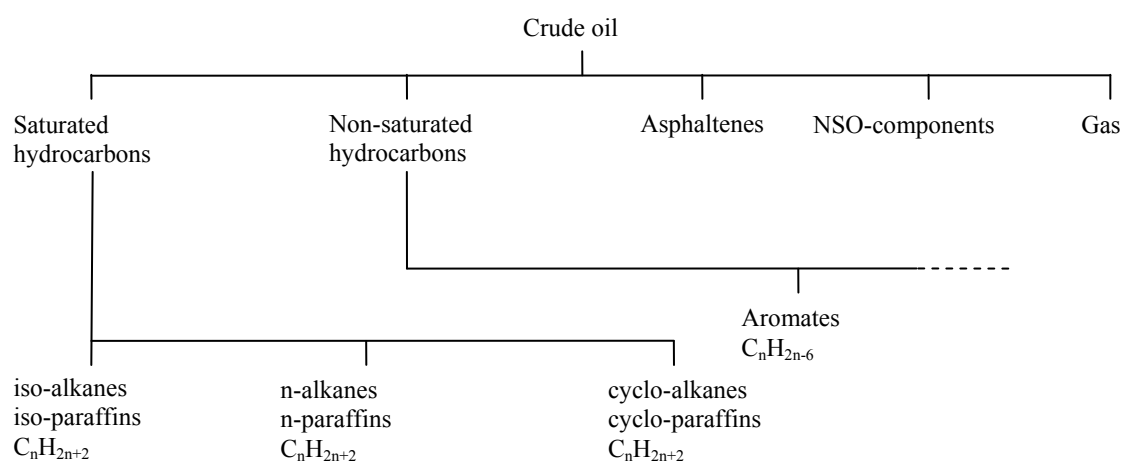


Figure 5: Crude oil components

As visible, paraffins belong to the group of saturated hydrocarbons, which are split into three sub-groups: n-, iso- and cyclo-paraffins.

N-paraffins refer to straight chain molecules, iso-paraffins to branched chain molecules and cyclo-paraffins form a ring with their C-atoms (Figure 6 and Figure 7). Furthermore, deposits from long-chained paraffins ($C_{15} \dots C_{75+}$) in the reservoir or its installations are also often named “waxes” due to their wax-like appearance and consistency.

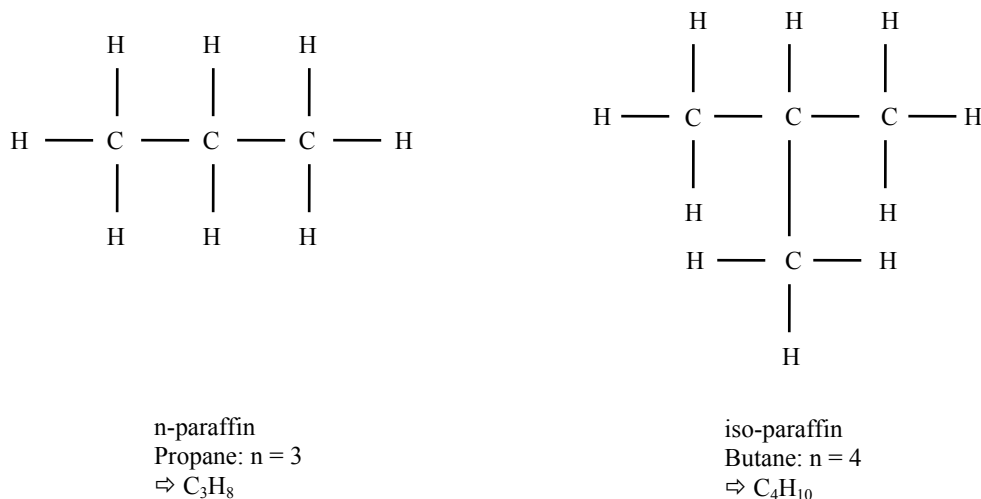


Figure 6: structures of n- and iso-paraffins

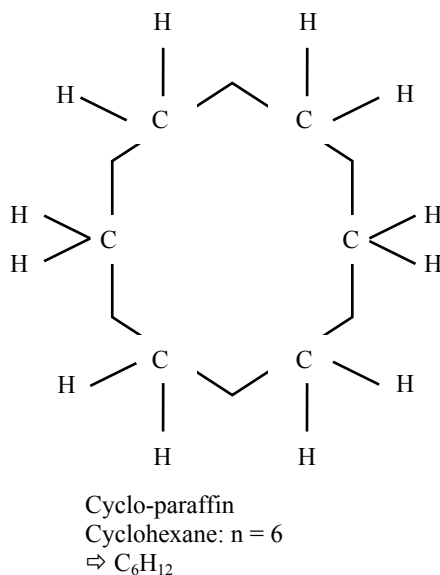


Figure 7: structure of a cyclo-paraffin

1.2.2 Formation of paraffins

Paraffin formation takes place in two stages: nucleation and growth. When nucleation happens, the first paraffin molecules precipitate out of solution due to a change of the parameters mentioned in the following paragraph, forming a tiny solid – the nucleus. It can already be seen from the surrounding crude by high-resolution microscopy.

The phase of growth follows the nucleation, when additional molecules precipitate out of the crude oil and interconnect with the already existing nucleus. This causes a mass propagation of paraffins and the formation of the well known “waxes”.

1.2.3 Parameters causing and/or influencing paraffin deposition

The main parameters that influence paraffin precipitation are:

- Crude oil composition
- Temperature
- Pressure
- Flow regime
- Cooling rate
- Surface roughness

1.2.4 Crude oil composition

Usually, the major part of crude oil consists of n- and iso-paraffins, aromates and NSO-components. The longer the molecules' chains, the higher the probability of forming a cluster and precipitate out of the solution as a waxy solid.

Aromates are known as very good solvents for paraffinic waxes and cyclo-paraffins have also a negative effect on paraffin precipitation. These components tend to disturb and disrupt the wax nucleation process, but even when nucleation has occurred they continue having negative contribution to wax deposition in hindering the growth process.

Beside nucleation caused from precipitation of paraffins – especially the long-chained heavy ones - it is also possible that impurities from the reservoir alter the composition of the crude oil and cause the formation of nuclei. The process of nucleation is one of the interconnection between paraffins and asphaltenes, since the latter often serve as nucleus for the formation of waxes. Usually it can be observed that the precipitation of paraffins is caused by a disturbance between the amounts of light solvents and the heavy molecules within the lighter fraction. But also sand particles and fines are potential nucleus sources.

Nevertheless, the main part of waxes consists of n-paraffins forming needle-shaped crystals as nuclei (approx. 50%) with a part of asphaltenes of about 5%. The rest consists of several other impurities, crude oil and water. The range for the carbon atoms in the precipitates starts at C_{15} and reaches up to C_{160} .

1.2.5 Temperature

Temperature has a major influence on the formation of paraffin deposits in all locations of the production chain (reservoir, production string, surface installations, storage and piping). The most vital parameter is the so-called “wax appearance temperature” (WAT); a temperature drop to or below wax appearance temperature causes a stop of the molecular motion, leading to an agglomeration of the crude's components. At this point the chaotic phase of the liquid or gaseous liquid starts to transform in the orderly structured state of the solid phase. Therefore, it can be stated that the lower the WAT the lesser the chances for paraffin deposits to precipitate. For liquids the cloud point is the most important one, where the former randomly spread molecules start to cluster together. When these clusters reach sufficient size a nucleus is formed. The difference to regular nucleation is that this one is temperature-dependent and will not occur at temperatures above cloud point. The agglomeration of paraffins is principally reversible, meaning that already precipitated waxes can revert into their liquid state provided their exposure to temperatures below WAT for sufficient time to re-melt them again. Usually, this is made more difficult due to the fact that waxes tend to bond with asphaltenes, impurities and fines, which usually leads to more complicated bindings and forms clumps very difficult to dissolve by temperature alteration.

A possible chance for temperature drops may result from several factors. One f.e. is the change due to the formation temperature gradient, causing the production string to cool off and therefore reduce the produced fluid's temperature within as well. Another possibility is the heat exchange between the formation fluid and a completion fluid – since metal pipes are excellent conductors for heat transfer, the warmth of the formation fluid dissipates into the completion fluid. The problem lies within the uncertainty of the location where the first solids form. Therefore, paraffin deposition can only be found when pulling out the production string or carrying out extensive and expensive logging, measuring and control activities to detect the precipitation of solids.

Another vital property with regards to temperature is the pour point, which defines where due to the temperature drop the flow of the crude is stopped and it keeps stuck. This effect is comparable to a large nucleus with a massive growth causing a vast prop of deposits, which

are usually non-removable without taking apart the blocked part of the facilities and/or thorough mechanical cleaning.

Both cloud point and wax appearance temperature is usually evaluated under laboratory conditions using stock tank oil (also referred to as “dead oil”). When conducting experiments with such oils, a profound knowledge of the well history, trajectory and the thermal history of the crude is necessary due to its sensitivity.

1.2.6 Pressure

The influence of pressure on paraffin precipitation is small compared to the effects of temperature changes. However, it exists.

Light fractions in the crude oil keep the wax appearance temperature low, so nucleation is inhibited. As soon as the pressure drops, these fractions become liberated and the WAT of the crude increases leading to a sooner precipitation of paraffins. This can occur already in the production zone due to the pressure drop in the wellbore.

1.2.7 Flow regime

The flow environment has clear influence on the deposition of paraffins. High-speed flow regimes reaching turbulent states with Reynolds numbers exceeding the value of 3,200 prevent the single molecules of hydrocarbons to align together and therefore reduce or prevent nucleation. On the other hand, the comparable slow and smooth laminar flow regimes with Reynolds number below 2,000 do only little or not at all disrupt the congregation process. This would allow paraffin precipitations to deposit. The flow rate yet has another effect on the crude oil: The smaller the flow rate the longer the crude stays in the wellbore respectively in the downhole string after leaving the formation. This increases the cooling period and therefore diminishing the temperature which aids nucleation and growth.

1.2.8 Cooling rate

With otherwise constant system parameters a high flow rate leads to a lower cooling rate since the exposure time to the cooling effect will be reduced. The cooling rate increases with the temperature difference between the flowing fluid and the surrounding cold medium, as f.e. the production string inside a well (Figure 8). When precipitation due to rapid cooling occurs, not only many nuclei are formed, but they also tend to cluster together forming a weak porous structure with cavities full of oil due to crystallization.

Since the formed waxes have gel forming tendencies, a change of viscosity has to be taken into consideration. Therefore often rheological studies have to be carried out in order to find the viscosity behavior of the crude and its dependence on temperature.

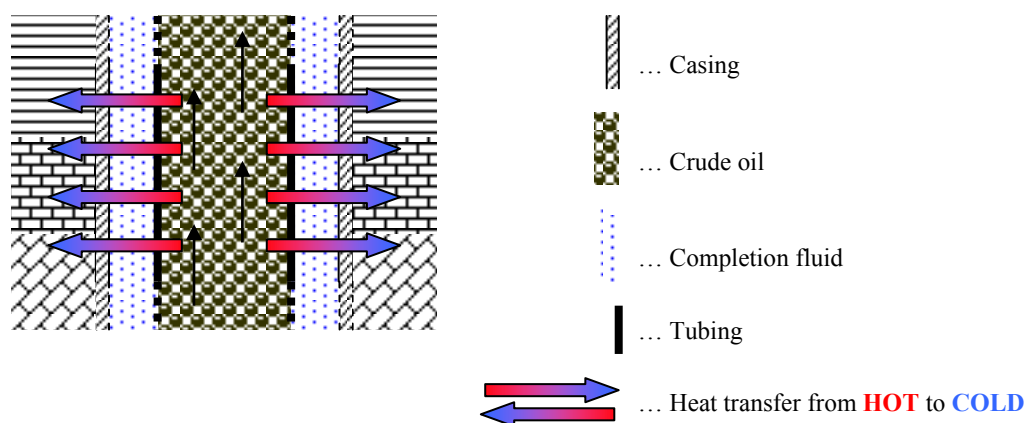


Figure 8: Heat transfer from crude oil to surrounding formations

1.2.9 Surface roughness

Basically, a water-wet environment diminishes the risk of paraffin deposition, whereas an oil-wet environment favors it. As a matter of fact, oil-wet conditions adhere better to rough than to smooth surfaces. Therefore it can be stated that paraffin depositions tend to precipitate on rough surfaces.

The reasons are adsorption forces which are a function of surface area. Since rough surfaces own a larger area, these forces are bigger and therefore paraffins stick stronger to it respectively are more likely to adhere to the rougher surfaces. But not only increases the amount of paraffins proportional to the roughness of the surface, but also the strength of the adhesion, the hardness, and the molecular weight of the deposits. The weight also depends on the carbon number which is the amount of C-atoms in the paraffin molecules. As a consequence of that, rough surfaces adhere longer and/or more branched paraffin molecules. Due to their length parts of them pointing into the fluid again interconnect with other molecules causing a chain reaction of paraffin agglomeration.

Another effect is corrosion. Although it does not directly affect paraffin precipitation, it roughs up the surface of the corroded equipment and therefore indirectly supports the deposition.

On the other hand, too smooth pipes as well can cause paraffin troubles to the well. When paraffin deposits precipitate without any possibility to adhere to the pipe surface, the effect of “paraffin sliding” occurs, where either gravitational force causes the precipitations to slide down the well or up due to the flow forces of the fluid.

A temporary problem with surface roughness is that originally smooth pipes can have their surface altered due to fines and sand production. The production of these abrasive particles then leads to removal or destruction of the smooth surface and roughening it up, worsening the paraffin problems.

1.2.10 Problems due to paraffin precipitation

Precipitations can occur anywhere in the production system: From the reservoir over the wellbore and its perforations, the tubing string with the connected surface installations and the pipeline to the separator and tank. The troubles caused differ due to the location, but also have to be treated individually.

1.2.10.1 Problems in the reservoir and wellbore

Precipitation in the reservoir can lead to pore plugging and a reduction of permeability, thus affecting the quality of the productive formation(s). Here the two main reasons are temperature and pressure drops in the wellbore and the near-wellbore area.

The temperature drops mostly result from contact with cold fluids, either originating from injections from the surface, such as washing, solvents, well killing fluids from workovers, acidizing jobs, fracturing jobs a.s.o. But they also can occur from other contact with cold fluids, like f.e. water flooding from injection wells.

Exposing the crude oil to pressure drops below the bubble point of the higher volatile fractions can cause their evaporation and a precipitation of the dispersed asphaltenes, leading to nucleation and paraffin aggregation.

Another effect that can occur is the oil-wetting of the formation through the precipitation of wax, reducing the relative permeability to oil. This can cause a loss in production through a higher water cut.

1.2.10.2 Problems in the tubing string

Depositions in the tubing string can cause several different problems, depending on the installed equipment.

In systems with sucker rod pumps, the “first contact” can occur when running the pump down the hole, where cool temperatures can cause precipitation and agglomeration at the pump. This can cause problems producing from the well. Another effect is the blocking of the sucker rod due to the deposition of paraffins, which can be read off the dynamometer card in the field. In case of not paying attention, the rods can bend or in case of serious problems even break, requesting to kill the well and repair or replace the rod.

Bent rods can also deviate from their regular up-and-down movement and damage the well tubing string. Another risk is the risk of partially or completely plugged tubings due to paraffin deposition. In case of completely plugged tubings, a workover trip has to be conducted in order to replace the tubing.

In gas lift wells paraffin depositions can occur due to the Joule-Thompson effect of gas cooling because of expansion and the usually lower temperature of the lift gas. Usually, this happens in the distance of a few centimeters upstream of the gas valve, causing the paraffin deposition process to begin even deeper than a comparable f.e. sucker rod well, since the cooling of the produced crude oil starts already deeper down the well.

1.2.10.3 Problems in surface installations

The main problems in surface installations and the pipeline system are caused by plugging of pipes and armatures, such as valves and chokes. In this case the especially unpleasant effect of “restarting pressure” appears where the established gel strength in a pipe is necessary to be overcome and re-establish a flow regime despite the depositions and agglomerations.

The “advantage” of paraffin depositions in surface installations lies within the fact that in almost all cases the treatment is eased by the clearly greater accessibility of these than the wellbore or downhole equipment.

1.3 Corrosion

Corrosion is the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties.¹⁴

In oilfield terms, it usually refers to the deterioration and consequently destruction of installations and equipment, caused by the production fluid, co-produced gas or one of its components.

The following elements and their respective components affect the equipment’s type and severity of corrosion:

- Structure of the element exposed to corrosion
 - Geometry
 - Mechanical load
- Material
 - Chemical composition
 - Mechanical properties
 - Grain structure
 - Surface
- Medium
 - Oxygen
 - Sand
 - Carbon dioxide
 - Bacteria
 - Hydrogen sulfide
 - Velocity
 - pH-value
 - Flow pattern
 - Composition

1.3.1 Structure of the element exposed to corrosion

The influence of the structure usually goes hand in hand with erosive processes. This erosion occurs due to the composition of the fluid: in crude oil can be found corroded pieces of equipment, sand grains and pieces of scale depositions, in gas there can be hydrates and also corrosion products, and in injection water there is the possibility of deposits from the water treatment system, corrosion products and scale depositions.

The structural component is especially distinctive in elements causing changes of the flow pattern, such as elbows, branch connections and cross-over pieces.

Since the structure is usually pre-determined by the technical specifications of the equipment, it would require high efforts in terms of costs and personnel to achieve a reduction of corrosion by structural measures.

1.3.2 Material

The usual choice of oilfield industry is different variations of mild steel, since raw or “pig” iron is too brittle and generally not resistant enough against physical and chemical influences. Its insufficiency originates from pig iron’s impurities: 3-5% carbon, and lower percentages of silicon, phosphorus and sulfur.¹⁵ Because of those, mild steel is usually chosen as main material, since it provides sufficient physical and medium chemical resistivity for the oil industry’s needs, achieved through the treating process in the blast furnace. Nevertheless, the assignment of high alloy steel would be desirable, but usually is unaffordable due to the high material price. A comparison of prices for mild and high alloy steel is given in Chart 2 and Chart 3.

EU stainless steel prices 2010 (per ton) ¹¹								
Month	Hot rolled coil (304)	Hot rolled coil (316)	Hot rolled plate (304)	Hot rolled plate (316)	Cold rolled coil (304)	Cold rolled coil (316)	Drawn bar (304)	Drawn bar (316)
Jan	€ 1.852	€ 2.738	€ 2.208	€ 3.065	€ 1.987	€ 2.880	€ 2.177	€ 3.218
Feb	€ 2.054	€ 3.113	€ 2.419	€ 3.448	€ 2.190	€ 3.256	€ 2.481	€ 3.742
Mar	€ 2.137	€ 3.262	€ 2.503	€ 3.599	€ 2.274	€ 3.402	€ 2.567	€ 3.964
Apr	€ 2.449	€ 3.763	€ 2.817	€ 4.102	€ 2.587	€ 3.903	€ 3.080	€ 4.708
May	€ 2.805	€ 4.196	€ 3.198	€ 4.558	€ 2.943	€ 4.342	€ 3.530	€ 5.243
Jun	€ 2.845	€ 4.261	€ 3.240	€ 4.624	€ 2.984	€ 4.407	€ 3.638	€ 5.400
Jul	€ 2.618	€ 3.924	€ 3.035	€ 4.308	€ 2.757	€ 4.070	€ 3.361	€ 4.961

Chart 2: EU stainless steel prices 2010 (per ton)¹⁶

EU carbon steel prices 2010 (per ton)							
Month	Hot rolled coil	Hot rolled plate	Cold rolled coil	Hot dipped galv. coil	Wire rod (mesh)	Structural sections and beams	Rebar
Jan	€ 409	€ 435	€ 476	€ 515	€ 380	€ 513	€ 372
Feb	€ 438	€ 455	€ 505	€ 550	€ 386	€ 503	€ 381
Mar	€ 469	€ 497	€ 535	€ 597	€ 402	€ 529	€ 383
Apr	€ 561	€ 601	€ 610	€ 667	€ 525	€ 611	€ 515
May	€ 612	€ 672	€ 685	€ 738	€ 580	€ 706	€ 556
Jun	€ 613	€ 704	€ 686	€ 746	€ 555	€ 691	€ 529
Jul	€ 588	€ 662	€ 667	€ 726	€ 454	€ 657	€ 438

Chart 3: EU carbon steel prices 2010 (per ton)¹⁷

¹¹ The numbers 304 and 316 are SAE (Society of Automotive Engineers) steel grades. SAE 304 equals X5CrNi18-10 in the EN-standard; SAE 316 equals X5CrNiMo17-12-2.

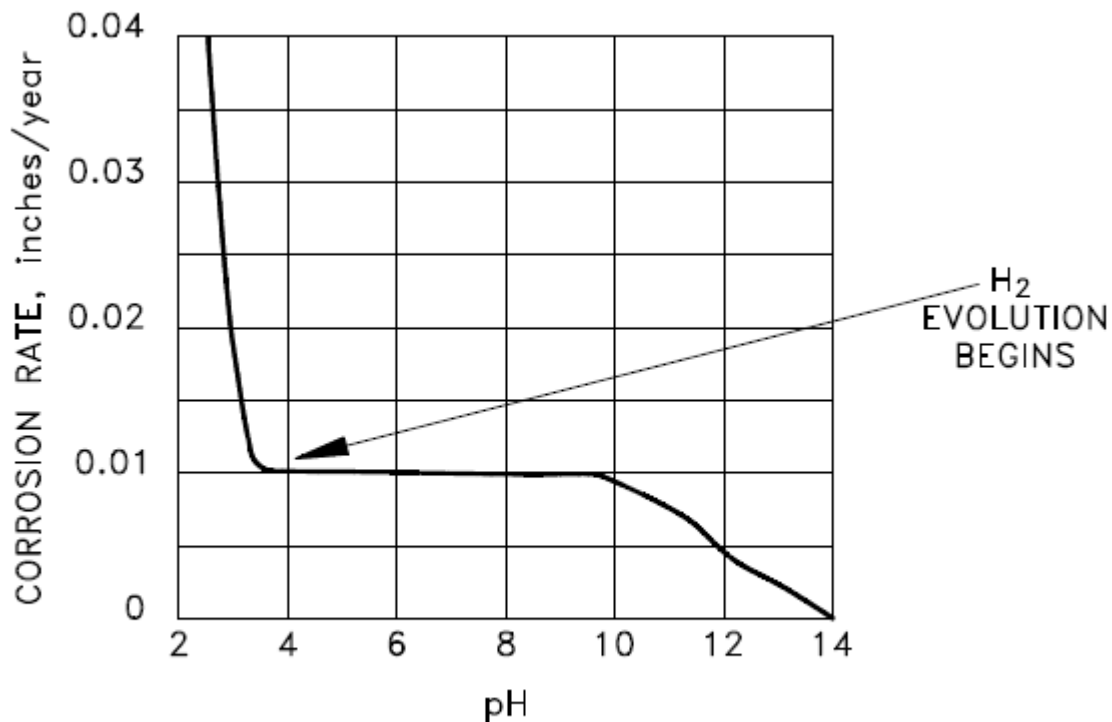
1.3.3 Medium

- Oxygen
- Carbon dioxide
- Hydrogen sulfide
- pH-value
- Composition
- Sand
- Bacteria
- Velocity
- Flow pattern

The main medium factors influencing corrosion are of chemical nature. Pure petroleum does not attack non-alloy steel at normal temperature. However, already small amounts of water cause corrosion by sulphur compounds, carbon dioxide, salts and oxygen.¹⁸

In both cases of producing crude oil with certain water cut and injecting formation water after the separation in the settling-tank, the pH value is a vital parameter helping to determine the corrosiveness of the fluid. It also helps providing information about the quality of if so installed or operated anti-corrosion systems.

The pH value is used to represent the acidity of a solution. First, consider the exposure of iron to aerated water at room temperature (aerated water will contain dissolved oxygen). The corrosion rate for iron as a function of pH is illustrated in Figure 9.¹⁹



EFFECT OF pH ON THE CORROSION OF IRON EXPOSED TO AERATED WATER AT ROOM TEMPERATURE

Figure 9: Effect of pH on the corrosion rate of iron in water

In the range of pH 4 to pH 10, the corrosion rate of iron is relatively independent of the pH of the solution. In this pH range, the corrosion rate is governed largely by the rate at which oxygen reacts with absorbed atomic hydrogen, thereby depolarizing the surface and allowing the reduction reaction to continue.¹⁹

With regards to the corrosion rate, it would be recommendable to keep the pH value as high as possible, in the ideal case at pH 14. Since this is not or only possible with a vast chemical

effort, it is highly recommended to keep the pH value in the range of 4 to 10 for a largely constant affection of the system's corrosion rate. Another unwelcome side effect is the increased tendency for scale precipitation, since the divergence from pH 7 (and therefore from the pH-neutral state) of the medium will shift its chemical equilibrium. In terms of oilfield fluids this means an increased probability for scale molecules to form and precipitate (see also Seite 2).

1.3.4 Problems resulting from corrosion

Corrosion causes problems directly by the gradual reduction of the affected equipment itself: directly resulting in leaks in or weakening of the respective structural element, such as pipes, pipelines, valves, but also larger structures like separators and tanks. Indirectly corrosion can affect the resistivity of structural elements against mechanical loads and weaken them, causing an earlier failure or collapse in comparison to the design values.

Another possibility of damage is its infliction through the corrosion products during the regular operation of the system. This includes depositions of and abrasive processes through particles originating from the various corrosion processes. Especially corrosion products such as iron(III) hydroxide ($\text{Fe}(\text{OH})_3$), composing from the tubing steel and i.e. Kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$] or Glauconite [frequently found as sandstone component, chemical formula $(\text{K}, \text{Na})(\text{Fe}^{3+}, \text{Al}, \text{Mg})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2$] dissolution out of formation) and iron sulfide (FeS , from i.e. anaerobic bacterial corrosion) can serve as “grinders” everywhere with suitable flow regime.

Another problem is the accumulation and deposition tendency of such particles. This can affect the system both in short, middle and long terms. In short terms it means blocking of filters and meshes, in middle terms it can cause wear and/or failure of equipment such as pipes, elbows and valves, and in long term a massive cleaning effort for removal of depositions caused by corrosion or a complete replacement of equipment.

1.4 Treating methods

Whereas mechanical and chemical treatments are in service in the oilfield industry already for decades, thermal and biological treatments are still stuck in the research or prototype stadium or still have to prove their efficiency or profitability. Nevertheless, a full description of all available methods would exceed the boundaries of this thesis; therefore the main focus will lie on the chemical treatment/inhibition.

1.4.1 Treating methods of paraffins

Generally spoken, the treatment methods for paraffins can be subdivided into five groups:

- mechanical
- thermal
- chemical
- biological
- combined

Contrary to the other three groups, mechanical methods can be used only after the deposition of paraffins occurred, whereas chemical and thermal methods can be used not only as treatments of already existing problems, but also frequently as precaution for risk minimization.

1.4.1.1 Mechanical methods of treating paraffins

The mechanical removal of paraffin depositions is the most traditional approach. In general, it means scraping of tubings and pigging of pipes.

Mechanical treatment of paraffins in oil wells not only makes it necessary to scrape the paraffins, but also to remove them after the scraping from the well. This usually is accomplished by pumping them to the surface either through tubing or annulus – in both cases exerting out pressure to the formation is necessary. Plus, an extra treatment with chemical solvents can be necessary to aid transportation and avoid re-deposition of the paraffins.

Another inconvenient aspect is the workover costs for such jobs, since the rod string and the pump have to be removed prior to the actual scraping job.

1.4.1.2 Thermal methods of treating paraffins

This category includes all methods where heat is added to the system in order to increase the deposits' temperature and re-liquefy them. In case of surface installations also the application of heating elements as f.e. electrical heating mats is possible.

Down in the wellbore the only possibility to transfer heat to is pumping hot liquids down the wellbore via the tubing-casing annulus, where the heat transfer via the tubing string restores the thermal conditions prior the precipitation and causes the paraffins to be dissolved again. The chosen liquids either are water or oil, depending on the well planning, the location of the deposits and the completion. A major risk in hot watering is the possibility of a water block – this especially valid for wells with a high water cut.

For wells with open completions with paraffin deposition in the wellbore, the most common method is “hot oiling”. This means that stock tank oil is pumped after heating up down the wellbore to bring the required amount of heat to the paraffin deposits. Since the use of water would cause an unwanted wettability change of the formation, usually hot oil from the stock tank bottom is used. What sounds basically like a good idea, arises the following problems:

The oil at the stock tank bottom is usually the heaviest part of the crude, which has already lost part of its volatile components. Therefore it is similar to the crude oil, but not alike (“dead oil”).

An alternative possibility is the application of chemicals generating heat down the tubing string or the well – either in capsular form or as solvent acting when getting in contact with the formation fluids. Since these methods still are not widely enough tested in the industry, their possible side effects are yet widely unknown and not well documented.

1.4.1.3 Biological methods of treating paraffins

Several types of hydrocarbons can be metabolized by bacteria and microbial species; as a rule the longer chained hydrocarbons are more easily “digested” than the short chained ones. With increasing length of the hydrocarbon also increases the variety of microbial organisms that can be utilized for biological paraffin degradation.

The treatment shows its effect by release of small particles of paraffin deposits, usually of half an inch size. To guarantee optimal performance, biological degradation methods are best combined with other methods for best performance and optimum effects.

1.4.1.4 Chemical methods of treating paraffins

Since every well and therefore its paraffin problems are unique, the most tailor-made method of paraffin removal is chemical treatment. To achieve maximum success, test samples should be taken from the well and examined carefully in order to develop the best-fitting treatment.

Downhole samples are preferred, but usually hard to obtain because of the tight space. Therefore, sufficient sample acquisition often requires a roundtrip of the used production string or the use of coiled tubing.

After the sample has been taken and examined, the appropriate chemical is to be determined. Whereas it of course is possible only to perform only remedial operations by applying solvents, a more provident approach is the chemical inhibition. Generally spoken, this means constant dosage of chemicals to the crude oil already at the producer in sufficient amount to diminish or suppress the formation and/or precipitation of paraffins, waxes, asphaltenes, scales and corrosion deposits.

Of course, the sooner the inhibitor is added to the production fluid, the better the inhibition effect will be. Therefore, the best spot for the chemicals to be added to the crude oil is the downhole area, where the inhibitors can mix with the production fluid coming straight from the formation. This either can be achieved by regular washings – similar to a stimulation job – or by constant addition of the inhibitor into the crude oil. The advantage of the last variant lies in a reduced down-time of the well, since the theoretical intention is to maintain a constant production without shut-downs for workover jobs.

1.4.2 Treating methods of scale

Scale treating can be carried out similar to paraffin control. Here as well, it is possible to remove the scale mechanically by grinding, cutting or pigging. Nevertheless, the more efficient method is chemical removal. The type of chemical varies according to the scale type precipitating in the well. A short overview is given below:

- Carbonate scales such as calcium carbonate or calcite [CaCO_3] can be readily dissolved with hydrochloric acid [HCl] at temperatures less than 250oF [121oC]. Sulfate scales such as gypsum [$\text{CaSO}_4 \cdot 2 \cdot \text{H}_2\text{O}$] or anhydrite [CaSO_4] can be readily dissolved using ethylenediamine tetra acetic acid (EDTA). The dissolution of barytine [BaSO_4] or strontianite [SrSO_4] is much more difficult.
- Chloride scales such as sodium chloride [NaCl] are easily dissolved with fresh water or weak acidic solutions, including HCl or acetic acid.
- Iron scales such as iron sulfide [FeS] or iron oxide [Fe_2O_3] can be dissolved using HCl with sequestering or reducing agents to avoid precipitation of by-products, for example iron hydroxides and elemental sulfur.
- Silica scales such as crystallized deposits of chalcedony or amorphous opal normally associated with steam flood projects can be dissolved with hydrofluoric acid [HF].²⁰

To avoid scale precipitation, here also the method of scale inhibition usually is chosen over scale treatment. Scale treatments are generally performed by the application of acids, usually hydrochloric or hydrofluoric acid. Despite their efficiency, these acids alter the chemical equilibrium in the well and are responsible for corrosive damages downhole when repeated frequently. Another unwanted side effect is the shut-down and the accordingly production loss. Finally, also the costs for the workover itself need to be taken into consideration. Scale inhibitors, on the other hand, are chemically designed to keep the single ions in solution in the formation water and keep them from accumulating or agglomerating at the surface of downhole equipment and pipes. By preventing scale-forming ions to bond and precipitate, controlled inhibition is accredited as the preferred method of managing scale problems.

Since the formation of scale precipitation resembles the formation phases of paraffins – nucleation and growth – scale inhibition works similarly to paraffin inhibition.

As a broad generalization, polymers are good nucleation inhibitors and dispersants.²¹ Studies have shown that only 3-5% of the surface of a carbonate or sulfate scale crystal needs to be covered by some polymeric inhibitors for complete inhibition.²²

Since a detailed overview of all inhibitor liquids would clearly exceed the range of this thesis, below only a brief excursion is to be found of the main basic ions which frequently are polymerized and mixed according to the customers' of inhibitors needs and specifications:

- phosphate ions ($-\text{OPO}_3\text{H}^-$)
- phosphonate ions ($-\text{PO}_3\text{H}^-$)
- phosphinate ions ($-\text{PO}_2\text{H}^-$)
- carboxylate ions ($-\text{COO}^-$)
- sulfonate ions ($-\text{SO}_3^-$)
- salts of iron(II), zinc and lead(II) ions
- nitrilotriacetic acid (NTAA)
- aminocarboxylates
- aminophosphonates (see Chart 6)

All the ions show strong ligation tendencies with the cations from the scale complexes, forming connections due to their electronegativity and making the cations unavailable for binding with the anions. The polymer structure of the ions given above aids keeping the formed complexes in solution in the production fluid. The more complex compounds are classified as "chelates" and exist in various forms such as the above mentioned NTAA or EDTA.

An electrophysical treatment also was chosen for a test run (see 6.4).

1.4.3 Treating methods of corrosion

Beside the mechanical removal of corrosion with grinding, steel-brushing and replacing, also here the use of corrosion inhibitors is highly recommended. Another possibility is cathodic protection, since corrosion always is a process between an electron donor and an electron acceptor. The equipment to be protected is seen as a cathode and equipped with sacrificial anodes, i.e. aluminum or zinc, and powered with electric current to provide electron flow. In dependence of amperage, material surface, material combination, medium and environment the sacrificial anodes need to be exchanged in shorter or longer intervals.

Chemical inhibition can be distinguished as follows:

- passivating (anodic)
- cathodic
- vapor-phase or volatile
- film-forming

Passivating inhibition means that the use of the inhibitor chemical leads to the formation of a thin non-reactive layer on the metal that prevents the access of corrosive chemicals. The species of passivating inhibitors can be subdivided into two groups: inhibitors which requires the presence of oxygen for their functioning – such as phosphate ($-\text{PO}_4^{3-}$), polyphosphate, tungstate (WO_4^{2-}) and silicate (SiO_3^{2-}) – and inhibitors which do not require oxygen, such as chromate (CrO_4^{2-}), nitrite (NO_2^-), molybdate (MoO_4^{2-}) and meta-, ortho- and pyrovanadates (NaVO_3 , Na_3VO_4 and $\text{Na}_4\text{V}_2\text{O}_7$).

Cathodic inhibitors are mostly used in drilling fluids. An example for a cathodic inhibitor is zinc(II) ions in zinc oxide.

Vapor phase corrosion inhibitors are volatile organic molecules with sufficient vapor pressure under ambient conditions to travel through the surface of the metal to be protected and be adsorbed. When getting in contact with water, these molecules become polarized and form a

protective layer on the metal. This layer consists of cations adsorbing to the metal and anions forming a hydrophobic film attracting non-aqueous parts of the liquid. The difference to film-forming inhibitors lies in the fact that vapor phase corrosion inhibitors penetrate the surface of the metal.

Film forming corrosion inhibitors form a protective coating on the surface of the material to be protected. Contrary to vapor phase corrosion inhibitors they do not penetrate the metal's surface, but consist of a polar head group and a hydrophobic tail. The head group bonds with the metal ions of the i.e. pipe's lattice, whereas the hydrophobic tail attracts non-aqueous parts of the corrosive fluid (see Figure 10).

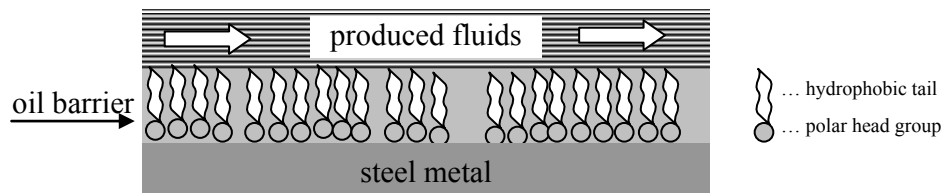


Figure 10: Function of a film-forming corrosion inhibitor²³

Typical classes of film-forming corrosion inhibitors are phosphate esters, various nitrogen compounds – i.e. amine salts of (poly)carboxylic acids (see 2.3, p. 24, Chart 5), quaternary ammonium salts and betaines (zwitterionics), amidoamines and imidazolines – and non-homogenous sulfur compounds containing i.e. nitrogen in their lattice. Also amines and polyamines with fatty tails have been claimed to show effect as a film-forming corrosion inhibitor.

Similarly to all types of chemicals, there are many articles and conference papers describing the results and efforts of newly introduced corrosion inhibitors. However, their chemical structure and fabrication are rarely described.

2 Currently applied chemicals

2.1 General information

The information in 2.2, 2.3 and 2.4 refers to the inhibitors applied in the Voitsdorf field and its producer network. In the tables describing the components found in the safety data sheets, the name outside the brackets is the one provided by the chemicals' supplier. This can very often be a synonym for the name inside the brackets, which is the most common chemical nomenclature leading to an entry when searched in chemical databases. The main disadvantage lies in the fact that the safety data sheet only must contain the hazardous chemicals, but is not a list of contents like in food. Therefore many components not reported as hazardous, dangerous or otherwise harmful to people and environment do not need to be listed in the safety data sheet.

Since this information is usually classified as "company internal", it was not available until by the day 2011-02-17 then the data in here as written.

2.2 Combined corrosion/paraffin inhibitor Champion Technologies Flotron CW511

This inhibitor is currently applied at 18 producer wells in order to prevent both corrosion and the precipitation of paraffins. According to the product bulletin, it works in two ways: a) by forming a film on the surface of the tubing respectively the pipe to protect it against sweet corrosion and paraffin deposition and b) by keeping the paraffin crystals in dispersion by reducing the cohesive forces between them. The recommended dosage lies (based on the total production volume) between 50 and 300ppmv according to the product bulletin.

The well's inhibition usually is achieved by letting the corrosion/paraffin inhibitor drip down the annulus, where it reaches the surface of the well's dynamic level. Due to the inhibitor's density of 1,030 kg/m³ (for comparison: water has ~1,000 kg/m³, crude oil has approx. 800...900 kg/m³), it crosses the surface oil-layer and reaches the formation water, in which the inhibitor dissipates. From the well's bottom, the inhibitor will be part of the production fluid and start to form the desired protective coating in the tubing and piping system.

Chart 4 gives the components listed in the safety data sheet of the inhibitor, giving a little hint about its principle of work.

2. Benzenesulphonic acid sodium salt is an organic salt of the benzenesulphonic acid; the acid's purpose is the ligation of cationic components in the production fluid before their reaction with the anionic brine. This is achieved by a separation of the sodium atom from the rest of the molecule, providing a vacant electron to form an ionic binding. The application in its salt form provides its solubility in water.
3. 2-butoxy-ethanol is a very common inexpensive hydrocarbon solvent and frequently used as a dispersant as well. It works by loosing the hydroxyl-part of its chainlike structure; the remnants adhere to the paraffin depositions and dissolve them by breaking the inter-paraffinic ligations.
4. Ethandiol disrupts hydrogen ligations when dissolved in water. It also works as an anti-freeze agent; since the inhibitor tanks at the dosage station are neither cooled in summer nor heated during winter, it prevents the liquid inhibitor from freezing.
5. 2,2'-Oxydiethanol has similar properties like ethandiol, varying mainly in viscosity, freezing and boiling point.

2.3 Corrosion inhibitor M-I SWACO KI-350

Contrary to the corrosion/paraffin combined inhibitor, the corrosion inhibitor is applied where only corrosion problems need to be avoided. For this chemical a dosage between 20 and 50ppmv based on the produced water volume is recommended.

The currently applied inhibitor is water soluble; according to the product bulletin, it works by forming a film on the surface of the tubing respectively the pipe to protect it against corrosion both originating from H_2S and CO_2 . This is usually achieved by letting the corrosion inhibitor drip down the annulus, where it reaches the surface of the well's dynamic level. Due to the inhibitor's density of 1,030 to 1,070 kg/m³, it crosses the surface oil-layer and reaches the formation water, in which the inhibitor dissipates. From the well's bottom, the inhibitor will be part of the production system and start to form the desired protective coating in the tubing and piping system.

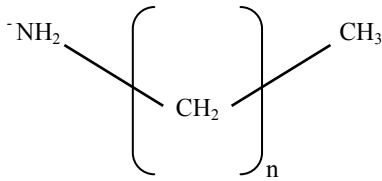
Component	Percentage
Alkyl amine salts 	1-10%

Chart 5: Chemical structure of the KI-350's known effective component

The alkyl amine component is modified into salts by bonding with elements from the first row of the periodic system. In aqueous solution, these salts dissolve and the alkylamine group is supposed to form a bond with the aggressive H_2S and CO_2 gases to prevent them from contact with the iron of the tubing or pipes.

2.4 Scale inhibitor M-I SWACO SI-4041

According to the product bulletin, the currently applied scale inhibitor is based on phosphonates and especially suitable for calcium carbonates and calcium sulfates. Depending on the severity of the problem, a dosage between 5 and 50ppmv, based on the amount of produced water, is recommended by the product bulletin.

Here again, the inhibitor drips down the annulus, where it reaches the surface of the well's dynamic level. The relatively seen very high density of 1,125 kg/m³ ensures a quick crossing of the dynamic level and mixing with the production fluid and maybe the perforation area. From there on, it will be part of the production upstream and is intended to protect the tubing and piping system.

The main component is aminomethylphosphonic acid sodium salt; its structure is depicted in Chart 6.

Component	Percentage
<p style="text-align: center;">Aminomethylphosphonic acid sodium salt (AMPASS)</p> $ \begin{array}{c} \text{OH} \\ \\ \text{O} = \text{P} - \text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{Na} \end{array} $	30-60%

Chart 6: Chemical structure of the component AMPASS

Phosphonic acid is a very common chemical consisting basically of a PO(OH)₂ structure from the phosphoric acid. Through the salification it is soluble in water, where it loses its sodium atom and forms an aqueous negatively charged solution, intended to bond the positively charged ions which usually originate from the formation, as i.e. Ca²⁺-ions. From the water-soluble property of the acid and the cation-bonding property of the amine molecule results the ability of the aminomethylphosphonic complex to keep scale-causing cations in solution and hinder them from forming precipitations.

3 System analysis

3.1 General information

Since the whole system is permanently changed, under workover, shut-in/shut-down, put back on stream etc, the reference day for the system overview is dated as October 28th 2010 (if not stated otherwise).

Well code	Well name	Oil field	Collecting station ^{III}	Production method ^{IV}
BH-002	BAD HALL 2	BAD HALL NORD II	VZ	SR
BH-003	BAD HALL 3	BAD HALL NORD I	VZ	SR
BH-004	BAD HALL 4	BAD HALL NORD II	VZ	E
BH-009	BAD HALL 9	VOITSDORF X	VZ	SR
BH-N-001	BAD HALL NORD 1	BAD HALL NORD I	VZ	SR
EB-006	EBERSTALZELL 6	EBERSTALZELL II	S-V	SR
EB-007	EBERSTALZELL 7	EBERSTALZELL III	S-V	SR
EN-005-A	ENGENFELD 5A	ENGENFELD I	Engenfeld	SR
EN-006-A	ENGENFELD 6A	ENGENFELD I	Engenfeld	SR
HIER-001	HIERSDORF 1	HIERSDORF I	S-III	SR
HIER-002-A	HIERSDORF 2A	HIERSDORF I	S-III	SR
HIER-004	HIERSDORF 4	HIERSDORF I	S-III	SR
KE-001	KEMATEN 1	KEMATEN I	Kematen	SR
MDF-001-A	MAYERSDORF 1A	MAYERSDORF I	S-V	SR
OB-001	OBERAUSTALL 1	EBERSTALZELL III	Sat-SAT	SR
RA-002	RAPPERSDORF 2	SATTLIEDT VIII	Sat-SAT	SR
SAT-002	SATTLIEDT 2	SATTLIEDT I	Sat-SAT	SR
SAT-006	SATTLIEDT 6	SATTLIEDT II	Sat-SAT	SR
SAT-007	SATTLIEDT 7	SATTLIEDT IV	Sat-SAT	SR
SAT-008	SATTLIEDT 8	SATTLIEDT I	Sat-SAT	SR
SAT-010	SATTLIEDT 10	SATTLIEDT II	Sat-SAT	SR
SAT-023	SATTLIEDT 23	SATTLIEDT I	Sat-SAT	SR
STHS-006	STEINHAUS 6	SATTLIEDT V	Sat-SAT	SR
V-001	VOITSDORF 1	VOITSDORF I	S-II	SR
V-007	VOITSDORF 7	VOITSDORF III	S-V	SR
V-011	VOITSDORF 11	VOITSDORF IV	VZ	SR
V-013-A	VOITSDORF 13A	VOITSDORF V	S-V	SR
V-015-C	VOITSDORF 15C	VOITSDORF III	S-III	IMP
V-016	VOITSDORF 16	VOITSDORF I	S-II	SR
V-019	VOITSDORF 19	VOITSDORF V	S-V	SR
V-021	VOITSDORF 21	VOITSDORF I	S-III	SR
V-023	VOITSDORF 23	VOITSDORF IV	VZ	SR
V-030	VOITSDORF 30	VOITSDORF III	S-III	IMP
V-033	VOITSDORF 33	VOITSDORF I	S-II	IMP
V-039	VOITSDORF 39	VOITSDORF V	S-V	SR
V-041	VOITSDORF 41	VOITSDORF IV	VZ	SR
V-043	VOITSDORF 43	VOITSDORF X	VZ	SR

Chart 7: Overview of the oil producing wells dealt with in this diploma thesis, their collector stations and production method

^{III} VZ: Voitsdorf Zentrale, S-V: Sattledt V, S-III: Sattledt III, Sat-SAT: Sattledt SATELLIT, S-II: Sattledt II

^{IV} SR: Sucker rod pump, E: Eruptive, IMP: Impeller pump

Well code	Well name	Oil field	Inhibitor 1	Inhibitor 2
BH-002	BAD HALL 2	BAD HALL NORD II	Flotron CW 511 ^V	
BH-003	BAD HALL 3	BAD HALL NORD I	Flotron CW 511	
BH-004	BAD HALL 4	BAD HALL NORD II	Flotron CW 511	
BH-009	BAD HALL 9	VOITSDORF X	Flotron CW 511	
BH-N-001	BAD HALL NORD 1	BAD HALL NORD I	Flotron CW 511	
EB-006	EBERSTALZELL 6	EBERSTALZELL II	Flotron CW 511	
EB-007	EBERSTALZELL 7	EBERSTALZELL III	Flotron CW 511	
EN-005-A	ENGENFELD 5A	ENGENFELD I	Flotron CW 511	
EN-006-A	ENGENFELD 6A	ENGENFELD I	Flotron CW 511	
HIER-001	HIERSDORF 1	HIERSDORF I	Flotron CW 511	
HIER-002-A	HIERSDORF 2A	HIERSDORF I	Flotron CW 511	
HIER-004	HIERSDORF 4	HIERSDORF I	Flotron CW 511	
KE-001	KEMATEN 1	KEMATEN I	Flotron CW 511	
MDF-001-A	MAYERSDORF 1A	MAYERSDORF I	Flotron CW 511	
OB-001	OBERAUSTALL 1	EBERSTALZELL III	SI-4041	KI-350
RA-002	RAPPERSDORF 2	SATTLEDT VIII	Flotron CW 511	
SAT-002	SATTLEDT 2	SATTLEDT I	Flotron CW 511	
SAT-006	SATTLEDT 6	SATTLEDT II	SI-4041 ^{VI}	KI-350 ^{VII}
SAT-007	SATTLEDT 7	SATTLEDT IV	Flotron CW 511	
SAT-008	SATTLEDT 8	SATTLEDT I	SI-4041	KI-350
SAT-010	SATTLEDT 10	SATTLEDT II	SI-4041	KI-350
SAT-023	SATTLEDT 23	SATTLEDT I	KI-350	
STHS-006	STEINHAUS 6	SATTLEDT V	SI-4041	KI-350
V-001	VOITSDORF 1	VOITSDORF I	SI-4041	KI-350
V-007	VOITSDORF 7	VOITSDORF III	KI-350	
V-011	VOITSDORF 11	VOITSDORF IV	SI-4041	KI-350
V-013-A	VOITSDORF 13A	VOITSDORF V	SI-4041	KI-350
V-015-C	VOITSDORF 15C	VOITSDORF III	SI-4041	KI-350
V-016	VOITSDORF 16	VOITSDORF I	KI-350	
V-019	VOITSDORF 19	VOITSDORF V	SI-4041	KI-350
V-021	VOITSDORF 21	VOITSDORF I	Flotron CW 511	
V-023	VOITSDORF 23	VOITSDORF IV	SI-4041	KI-350
V-030	VOITSDORF 30	VOITSDORF III	SI-4041	KI-350
V-033	VOITSDORF 33	VOITSDORF I	SI-4041	KI-350
V-039	VOITSDORF 39	VOITSDORF V	KI-350	
V-041	VOITSDORF 41	VOITSDORF IV	KI-350	
V-043	VOITSDORF 43	VOITSDORF X	Flotron CW 511	

Chart 8: Overview of the oil producing wells for this diploma thesis and their inhibition

Chart 7 provides an overview of the thirty-seven overall wells whose crude oil is collected directly or indirectly via other stations and finally partially treated in Voitsdorf. Chart 8 also provides an overview which inhibitors are applied to which well in order to maintain a steady flow and high production rates.

^V Champion Technologies Flotron CW 511, see also 2.2

^{VI} MI-SWACO SI-4041, see also 2.4

^{VII} MI-SWACO KI-350, see also 2.3

3.1.1 Well information

3.1.1.1 Logging data

Well code	Well name	Production interval	Net thickness [m]	Formation name
BH-002	BAD HALL 2	2080.5 - 2086.5 m	6.0	Cenomanium
BH-003	BAD HALL 3	2083.2 - 2085.0 m	1.8	Eocene
		2087.0 - 2088.6 m	1.6	Eocene
		2093.2 - 2094.0 m	0.8	Eocene
		2095.1 - 2100.8 m	5.7	Eocene
		2102.1 - 2103.7 m	1.6	Eocene
		2110.4 - 2111.8 m	1.4	Eocene
		2119.8 - 2120.9 m	1.1	Eocene
BH-004	BAD HALL 4	2137.5 - 2141.0 m	3.5	Eocene
		2134.2 - 2135.6 m	1.4	Eocene
		2138.9 - 2140.6 m	1.7	Eocene
		2143.5 - 2145.2 m	2.7	Eocene
		2154.5 - 2157.0 m	2.5	Eocene
BH-009	BAD HALL 9	2166.0 - 2176.5 m	10.5	Eocene
		2074.2 - 2075.2 m	1.0	Eocene
		2078.8 - 2079.8 m	1.0	Eocene
		2082.0 - 2083.0 m	1.0	Eocene
		2084.0 - 2086.0 m	2.0	Eocene
BH-N-001	BAD HALL N 1	2177.4 - 2179.7 m	2.3	Eocene
		2026.0 - 2028.5 m	2.5	Cenomanium
		2031.7 - 2039.0 m	7.3	Cenomanium
EB-006	EBERSTALZELL 6	2043.0 - 2046.5 m	3.5	Basement
		2059.5 - 2065.0 m	5.5	Eocene
EB-007	EBERSTALZELL 7	2038.2 - 2044.5 m	6.3	Eocene
		2047.6 - 2049.7 m	2.1	Eocene
EN-005-A	ENGENFELD 5A	1141.8 - 1150.1 m	8.3	Eocene
EN-006-A	ENGENFELD 6A	1047.5 - 1050.8 m	3.3	Eocene
HIER-001	HIERSDORF 1	2463.2 - 2464.7m	1.5	Eocene
		2465.4 - 2466.6m	1.2	Eocene
		2474.9 - 2478.9m	4.0	Eocene
		2483.1 - 2484.8m	1.7	Eocene
		2486.8 - 2489.3 m	2.5	Eocene
		2491.3 - 2510.0 m	18.7	Eocene
HIER-002-A	HIERSDORF 2A	2512.0 - 2519.0 m	7.0	Eocene
		2526.2 - 2530.4 m	4.2	Eocene
		2531.6 - 2533.1 m	1.5	Eocene
		2535.4 - 2537.8 m	2.4	Eocene
		2540.5 - 2543.5 m	3.0	Eocene
HIER-004	HIERSDORF 4	2544.8 - 2554.0 m	9.2	Eocene
		2468.0 - 2472.0 m	4.0	Eocene
		2474.9 - 2481.2 m	6.3	Eocene
		2486.0 - 2488.2 m	2.2	Eocene
		2489.6 - 2491.4 m	1.8	Eocene
		2494.3 - 2505.8 m	11.5	Eocene
KE-001	KEMATEN 1	2506.7 - 2513.6 m	6.9	Eocene
		1151.0 - 1153.0 m	2.0	Eocene

Well code	Well name	Production interval	Net thickness [m]	Formation name
MDF-001-A	MAYERSDORF 1A	2360.5 - 2366.5 m	6.0	Jurassic
		2368.0 - 2377.0 m	9.0	Jurassic
OB-001	OBERAUSTALL 1	1837.0 - 1841.0 m	4.0	Eocene
		1968.0 - 1970.0 m	2.0	Cenomanium
RA-002	RAPPERSDORF 2	1620.0 - 1623.5 m	3.5	Eocene
		1625.0 - 1625.5 m	0.5	Eocene
SAT-002	SATTLEDT 2	1700.8 - 1703.5 m	2.7	Eocene
		1705.8 - 1706.5 m	0.7	Eocene
		1708.4 - 1710.2 m	1.8	Eocene
SAT-006	SATTLEDT 6	1745.2 - 1749.2 m	4.0	Eocene
		1750.0 - 1751.0 m	1.0	Eocene
		1751.5 - 1754.5 m	3.0	Eocene
SAT-007	SATTLEDT 7	1752.1 - 1755.8 m	3.7	Eocene
		1756.4 - 1759.1 m	2.7	Eocene
		1759.8 - 1761.1 m	1.3	Eocene
		1764.4 - 1765.1 m	0.7	Eocene
SAT-008	SATTLEDT 8	1683.7 - 1689.7 m	6.0	Eocene
		1692.3 - 1694.6 m	2.3	Eocene
SAT-010	SATTLEDT 10	1694.6 - 1700.1 m	5.5	Eocene
		1701.9 - 1702.7 m	0.8	Eocene
SAT-023	SATTLEDT 23	1761.0 - 1763.5 m	2.5	Eocene
		1764.0 - 1766.5 m	2.5	Eocene
STHS-006	STEINHAUS 6	1579.9 - 1583.4 m	3.5	Eocene
V-001	VOITSDORF 1	2072.0 - 2074.5 m	2.5	Eocene
		2075.0 - 2082.5 m	7.5	Eocene
		2085.0 - 2088.0 m	3.0	Eocene
V-007	VOITSDORF 7	2118.0 - 2121.0 m	3.0	Eocene
		2131.0 - 2133.5 m	2.5	Eocene
		2170.5 - 2179.0 m	8.5	Cenomanium
V-011	VOITSDORF 11	2087.6 - 2091.8 m	4.2	Eocene
		2091.8 - 2120.1 m	28.3	Eocene
		2120.1 - 2127.2 m	7.1	Eocene
V-013-A	VOITSDORF 13A	2063.5 - 2072.5 m	9.0	Eocene
V-015-C	VOITSDORF 15C	2187.6 - 2193.0 m	5.4	Cenomanium
		2195.0 - 2196.5 m	1.5	Cenomanium
		2204.0 - 2227.5 m	23.5	Cenomanium
V-019	VOITSDORF 19	2067.5 - 2068.5 m	1.0	Eocene
		2071.5 - 2074.5 m	3.0	Eocene
		2076.0 - 2078.0 m	2.0	Eocene
		2079.8 - 2084.3 m	4.5	Eocene
		2091.3 - 2093.0 m	1.7	Eocene
V-021	VOITSDORF 21	2106.0 - 2111.0 m	5.0	Eocene
		2113.0 - 2114.5 m	1.5	Eocene
		2116.4 - 2119.4 m	3.0	Eocene

Well code	Well name	Production interval	Net thickness [m]	Formation name
V-023	VOITSDORF 23	2085.3 - 2086.3 m	1.0	Eocene
		2089.2 - 2090.0 m	0.8	Eocene
		2093.7 - 2095.3 m	1.6	Eocene
		2105.0 - 2106.0 m	1.0	Eocene
		2108.3 - 2109.8 m	1.5	Eocene
		2115.0 - 2116.5 m	1.5	Eocene
		2125.0 - 2128.0 m	3.0	Eocene
V-030	VOITSDORF 30	2010.0 - 2018.5 m	8.5	Cenomanium
		2022.5 - 2024.5 m	2.0	Jurassic
		2026.0 - 2028.0 m	2.0	Jurassic
V-033	VOITSDORF 33	2097.0 - 2104.0 m	7.0	Cenomanium
V-039	VOITSDORF 39	2052.5 - 2055.0 m	2.8	Eocene
		2058.0 - 2059.0 m	1.0	Eocene
V-041	VOITSDORF 41	2193.5 - 2196.5 m	3.0	Eocene
		2199.0 - 2202.0 m	3.0	Eocene
		2211.5 - 2213.0 m	1.5	Eocene
		2214.5 - 2218.5 m	4.0	Eocene
V-043	VOITSDORF 43	2062.6 - 2064.0 m	1.4	Eocene
		2066.1 - 2066.8 m	0.7	Eocene
		2069.8 - 2070.7 m	0.9	Eocene
		2072.4 - 2073.6 m	1.2	Eocene
		2075.0 - 2077.0 m	2	Eocene
		2092.3 - 2095.5 m	3.3	Eocene
		2098.0 - 2100.2 m	2.2	Eocene
		2101.7 - 2102.7 m	1	Eocene
		2108.0 - 2119.5 m	11.5	Eocene
		2274.0 - 2275.0 m	1	Cenomanium
		2275.9 - 2277.4 m	1.5	Cenomanium

Chart 9: Producers and their producing layers

3.1.1.2 Production well data

Here a rough overview of the wells and stations dealt with is given. The figures on p. 32, p. 33 and p. 35 give an approximate idea in what position the single wells are located in comparison to VZ station. Additionally they help to visualize the coalescing of the single upstreams on their way to VZ station – especially the fact that the upstream from Sat-SAT arrives at VZ station via Sat-II (see Figure 13). As an addendum, the production data was taken from the reporting system respectively from the most recent known tests.^{VIII}

^{VIII} As at September 16th 2010

Well name	Collector station	Transport	Test date	Total prod. fluid [m³/d]	Oil net [m³/d]	Water [m³/d]	Water cut [%]	Gas [std m³/d]
BAD HALL 2	VZ	Pipeline	2010-06-01	3.0	2.6	0.5	15.0	120
BAD HALL 3	VZ	Pipeline	2010-08-11	22.0	12.3	9.7	44.0	550
BAD HALL 4	VZ	Pipeline	2010-08-26	43.0	42.9	0.1	0.2	17,764
BAD HALL 9	VZ	Pipeline	2010-08-13	2.2	2.2	0.0	0.1	340
BAD HALL N 1	VZ	Pipeline	2010-09-06	5.0	4.9	0.1	2.0	2,000
EBERSTALZELL 6	S-V	Pipeline	2010-08-20	10.7	2.8	7.9	74.0	479
EBERSTALZELL 7	S-V	Pipeline	2010-08-09	11.0	0.1	10.9	99.0	0
ENGENFELD 5A	Engenfeld	Truck	currently shut-in					
ENGENFELD 6A	Engenfeld	Truck	currently shut-in					
HIERSDORF 1	S-III	Pipeline	2010-06-01	72.1	48.7	23.4	32.5	2,300
HIERSDORF 2A	S-III	Pipeline	2010-06-28	34.1	33.9	0.1	0.3	1,000
HIERSDORF 4	S-III	Pipeline	2010-09-02	65.0	39.0	26.0	40.0	2,000
KEMATEN 1	Kematen	Truck	2010-08-01	9.1	1.7	7.4	81.6	15
MAYERSDORF 1A	S-V	Pipeline	2009-10-14	2.1	2.1	0.0	1.2	9
OBERAUSTALL 1	Sat-SAT	Pipeline	2010-05-17	53.2	2.5	50.7	95.3	20
RAPPERSDORF 2	Sat-SAT	Pipeline	2009-10-15	0.8	0.8	0.0	1.4	60
SATTLEDT 2	Sat-SAT	Pipeline	2010-09-02	5.9	5.4	0.5	8.5	400
SATTLEDT 6	Sat-SAT	Pipeline	2010-01-14	35.8	2.7	33.1	92.4	60
SATTLEDT 7	Sat-SAT	Pipeline	2010-01-28	3.9	1.3	2.6	66.0	40
SATTLEDT 8	Sat-SAT	Pipeline	2010-08-19	12.6	0.5	12.1	96.0	400
SATTLEDT 10	Sat-SAT	Pipeline	2010-08-23	3.6	0.8	2.8	77.0	135
SATTLEDT 23	Sat-SAT	Pipeline	2010-01-21	37.2	3.0	34.2	91.9	70
STEINHAUS 6	Sat-SAT	Pipeline	2010-08-19	19.7	1.6	18.1	92.0	476
VOITSDORF 1	S-II	Pipeline	2010-05-09	1.8	1.8	0.0	0.1	682
VOITSDORF 7	S-V	Pipeline	2010-05-14	7.8	0.5	7.3	94.0	2,250
VOITSDORF 11	VZ	Pipeline	2010-03-26	15.8	1.6	14.2	89.6	1,070
VOITSDORF 13A	S-V	Pipeline	2010-06-10	29.8	7.3	22.5	75.5	1,410
VOITSDORF 15C	S-III	Pipeline	2010-03-18	231.0	8.5	222.5	96.3	850
VOITSDORF 19	S-V	Pipeline	2010-02-11	2.2	1.1	1.1	49.0	1,280
VOITSDORF 21	S-III	Pipeline	2010-01-22	3.7	1.8	1.9	50.4	340
VOITSDORF 23	VZ	Pipeline	2010-09-02	5.8	3.4	2.5	42.0	7,520
VOITSDORF 30	S-III	Pipeline	2010-09-04	135.0	3.4	131.6	97.5	950
VOITSDORF 33	S-II	Pipeline	2010-07-19	210.0	3.6	206.4	98.3	620
VOITSDORF 39	S-V	Pipeline	2009-09-07	0.8	0.8	0.1	8.0	850
VOITSDORF 41	VZ	Pipeline	2010-01-27	0.1	0.1	0.0	2.0	20
VOITSDORF 43	VZ	Pipeline	2010-08-12	7.2	6.2	1.0	14.0	9,500

Chart 10: Producer wells and their production test data

The charts above indicate that the crude oil mixture which is collected, treated and stored at VZ station is produced from many different formations and layers, resulting in a high precipitation probability due to the different compositions of each crude oil.

3.2 Pipeline system

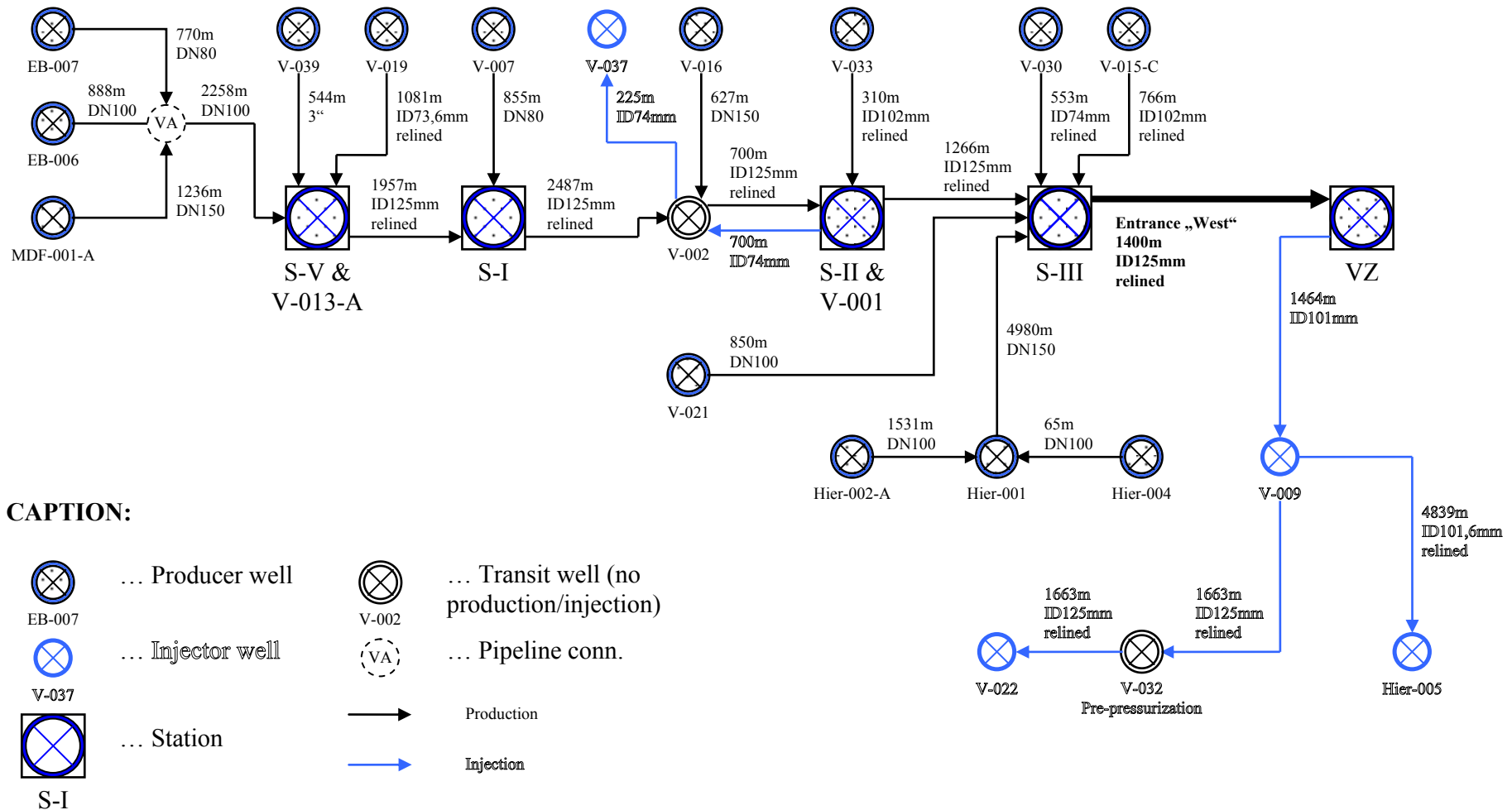
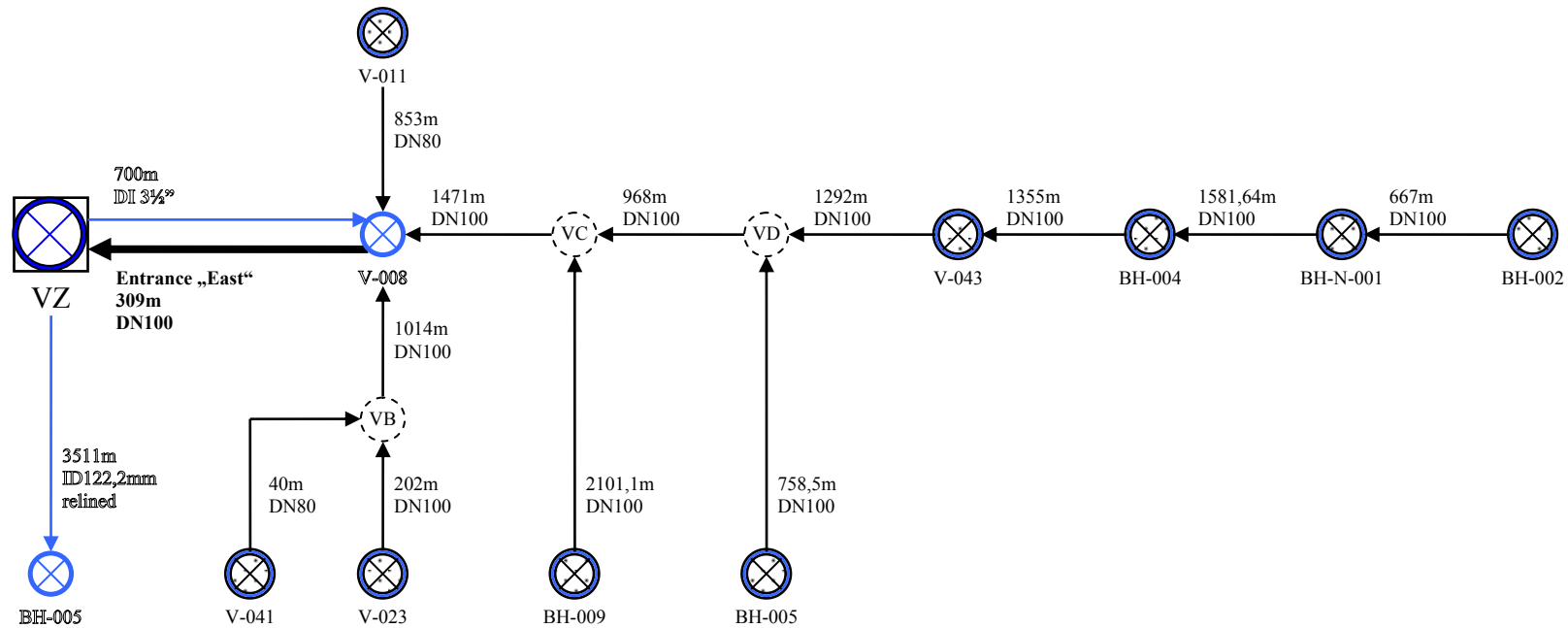


Figure 11: Western part of the producers and injectors of the Voitsdorf field^{IX}

^{IX} As at October 28th 2010



CAPTION:

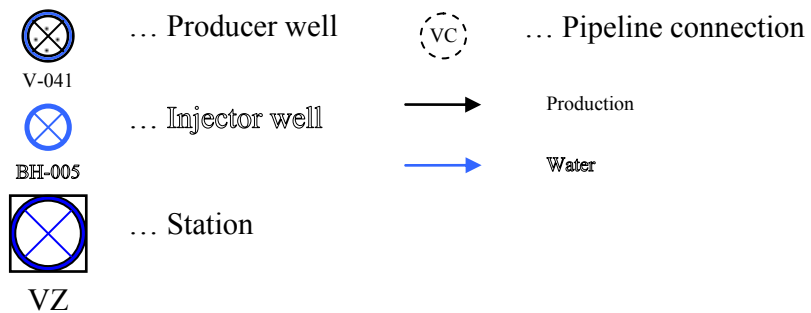


Figure 12: Eastern part of the producers and injectors of the Voitsdorf field^X

^X As at October 28th 2010

For better readability in tabular form:

Entrance	#	Origin	End	Mat.	Length	DI _{pipe}	#	Origin	End	Mat.	Length	DI _{pipe}	
East	1	BH-002	BH-N-001	Steel	667m	0.100m	1	VZ	V-008	Steel	700m	0.089m	
	2	BH-N-001	BH-004	Steel	1581m	0.100m	2	VZ	VW9 ²	PE	1464m	0.102m	
	3	BH-004	V-043	Steel	1355m	0.100m	3	VW9 ²	Hier-005	PE	4839m	0.102m	
	4	V-043	(VD)	Steel	1292m	0.100m	4	VW9 ²	VW32	PE	1663m	0.091m	
	5	BH-005	(VD)	Steel	759m	0.100m	5	VW32	V22	GFC	1539m	0.080m	
	6	(VD)	(VC)	Steel	968m	0.100m							
	7	BH-009	(VC)	Steel	2101m	0.100m							
	8	(VC)	V-008	Steel	1471m	0.100m							
	9	V-011	V-008	Steel	805m	0.080m							
	10	V-023	(VB)	Steel	202m	0.100m							
	11	V-041	(VB)	Steel	10m	0.080m							
	12	(VB)	V-008	Steel	1014m	0.100m							
	13	V-008	VZ	Steel	309m	0.100m							
West	14	EB-007	(VA)	Steel	770m	0.080m							
	15	MDF-001A	(VA)	Steel	1236m	0.150m							
	16	EB-006	(VA)	Steel	888m	0.100m							
	17	(VA)	S-V	Steel	2258m	0.100m							
	18	V-039	S-V	Steel	544m	0.076m							
	19	V-019	S-V	Steel	1081m	0.074m							
	20	SV	SI	Steel	1957m	0.125m							
	21	V-007	S-I	Steel	855m	0.080m							
	22	S-I	V-002 ¹	Steel	2487m	0.125m							
	23	V-016	V-002 ¹	Steel	627m	0.150m							
	24	V-002 ¹	S-II	PE	700m	0.125m							
	25	V-033	S-II	Steel	310m	0.102m	6	S-II	V-002	PE	700m	0.064m	
	26	S-II	S-III	Steel	1266m	0.125m	7	V-002	V-037	GFC	225m	0.064m	
	27	V-030	S-III	Steel	553m	0.074m							
	28	V-015C	S-III	PE	766m	0.102m							
	29	V-021	S-III	Steel	850m	0.100m							
	30	HIER-002A	HIER-001	Steel	1531m	0.100m							
	31	HIER-004	HIER-001	Steel	65m	0.100m							
	32	HIER-001	S-III	Steel	4980m	0.150m							
	33	S-III	VZ	Steel	1400m	0.125m							

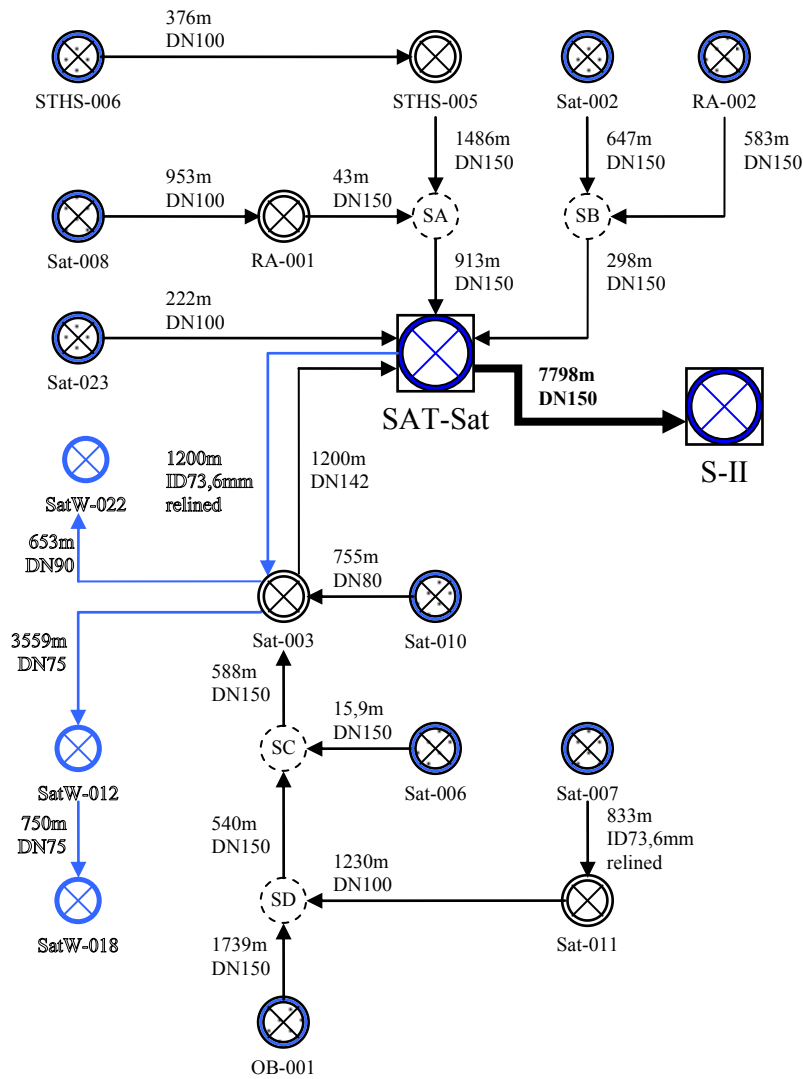
¹ ... only transit station. no production

² ... only transit station. no injection

- (VA): connection to pipe EB-006 → S-V
- (VB): connection to pipe V-023 → V-008
- (VC): connection to pipe (VD) → V-008
- (VD): connection to pipe V-043 → (VC)

Chart 11: Pipeline lengths, producers and injectors in field Voitsdorf^{XI}

^{XI} The injector BH-005 was not listed due to the insignificance of injected water amount (as for October 28th 2010)



CAPTION:

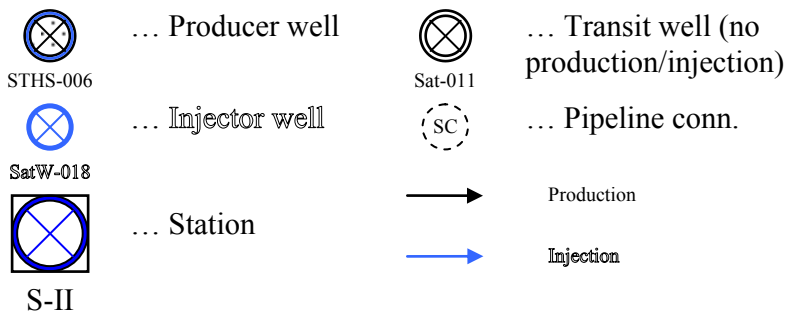


Figure 13: Producers and injectors of field SattledtXII

For better readability in tabular form, including more detailed information:

PRODUCER NETWORK						INJECTOR NETWORK					
#	Origin	End	Length	Mat.	DI _{pipe}	#	Origin	End	Length	Mat.	DI _{pipe}
1	STHS-006	STHS-005 ¹	376m	Steel	0.100m	1	Sat-SAT	Sat-003 ¹	1200m	PE	0.074m
	STHS-005 ¹	(SA)	1486m	Steel	0.150m		Sat-SAT → Sat-0031				
	(SA)	Sat-SAT	913m	Steel	0.150m	2	Sat-003 ¹	SatW-022	653m	PE	0.080m
	STHS-006 → Sat-SAT						Sat-0031 → SatW-022				
2	Sat-008	RA-0011	953m	Steel	0.100m	3	Sat-003 ¹	SatW-012	3559m	PE	0.070m
	RA-0011	(SA)	43m	Steel	0.150m		Sat-003¹ → SatW-012				
	Sat-008 → (SA)					4	SatW-012	SatW-018	750m	GFC	0.075m
3	Sat-023	Sat-SAT	222m	Steel	0.150m		SatW-012 → SatW-018				
	Sat-023 → Sat-SAT										
4	Sat-002	(SB)	647m	Steel	0.150m						
	(SB)	Sat-SAT	298m	Steel	0.150m						
	Sat-002 → Sat-SAT										
5	RA-002	(SB)	583m	Steel	0.150m						
	RA-002 → (SB)										
6	Sat-010	Sat-003 ¹	755m	Steel	0.080m						
	Sat-010 → Sat-0031										
7	Sat-007	Sat-011 ¹	833m	Relined	0.074m						
	Sat-011 ¹	(SD)	1230m	Steel	0.100m						
	Sat-007 → (SD)										
8	OB-001	(SD)	1739m	Steel	0.150m						
	(SD)	(SC)	540m	Steel	0.150m						
	(SC)	Sat-003 ¹	588m	Steel	0.150m						
	OB-001 → Sat-0031										
9	Sat-006	(SC)	16m	Steel	0.150m						
	Sat-006 → Sat-003¹										
10	Sat-003 ¹	Sat-SAT	1200m	Steel	0.142m						
	Sat-003¹ → Sat-SAT										

1 ... derived from well test data base

2 ... only transit station. no production

(SA): connection to pipe STHS-006 → Sat-SAT

(SB): connection to pipe Sat-002 → Sat-SAT

(SC): connection to pipe OB-001 → Sat-006

(SD): connection to pipe OB-001 → Sat-006

Chart 12: Pipeline lengths, producers and injectors in field Sattledt

3.3 Producers

3.3.1 Intention and background information

The knowledge of the components contained in the formation water of the single producers is a vital piece of information concerning the planning of the inhibition. It also can be used for further analyses with the intention to determine the connection between the formation from which is produced and the expectable solids. Since formation data is provided already in 3.1.1.1, this chapter's item of the thesis is to provide an analysis of the production water from the wells with water streams incoming to VZ station.

Since for some producers the water cut is relatively small, only producers with water production equal or above 5m³ per day and water cut equal or above 10% were selected for the analysis. Additionally, the production from the wells OB-001, RA-002, SAT-002, SAT-006, SAT-007, SAT-008, SAT-010, SAT-023 and STHS-006 is collected at the station SAT-Sat. From there on, a part of the water stream is injected already in the injectors of the Sattledt field, and only a surplus average merged inflow of 25 to 30m³ of water per day is incoming at VZ station via Sat-II station. Thus the production water stream from SAT-Sat is treated as one producer coming in at VZ station.

3.3.2 Results of the chemical analyses

delivery via	station	well code	testing day	production [m ³ /d]			WC ^{xiii} [%]	water inflow share to VZ
				total	net oil	water		
Pipeline	S-III	V-030	10-09-10	328.0	8.2	319.8	97.5%	31,94%
Pipeline	S-III	V-015	09-01-10	231.0	8.5	222.5	96.3%	22,22%
Pipeline	S-II	V-033	07-19-10	210.0	3.6	206.4	98.3%	20,62%
Pipeline	S-III	HIER-004	10-22-10	62.1	32.0	30.1	48.5%	3,01%
Pipeline	Sat-SAT	Sat-SAT		25.0 ...		30.0	0.0%	3.00%
Pipeline	S-III	HIER-001	09-20-10	72.1	44.3	27.8	38.5%	2.77%
Pipeline	S-V	V-013	06-10-10	29.8	7.3	22.5	75.5%	2.25%
Pipeline	VZ	V-011	09-09-10	12.1	1.3	10.8	89.0%	1.08%
Pipeline	VZ	BH-003	08-11-10	22.0	12.3	9.7	44.0%	0.97%
Pipeline	S-V	V-007	05-14-10	7.8	0.5	7.3	94.0%	0.73%
Pipeline	S-V	EB-006	09-09-10	6.8	1.8	5.0	74.0%	0.50%
permanent inflow to VZ [m³/d]:				1288.7	287.6	1001.1		

Chart 13: Main water producers to be treated at VZ station

Overall the producers given in Chart 13 were selected according to the criterions from p.36 and provide 89.09% of all the water inflow to VZ station. Therefore, they were the most interesting wells for the chemical analyses of the incoming production water (Chart 14 and Chart 15).

well code	Fe ²⁺ _{cracked} [mg/l]		Mn ⁺ [mg/l]	Cl ⁻ [mg/l]	SO ₄ ²⁻ [mg/l]		hardness [°dH]		Ca ²⁺ [mg/l]		Mg ²⁺ [mg/l]	
	total	<0.45µ			total	<0.45µ	total	<0.45µ	total	<0.45µ	total	<0.45µ
V-030	0.47	0.21	1.01	2600	54	32	68	62	442	361	51	24
V-015	0.16	0.08	0.39	7600	85	81	72	72	476	478	24	21
V-033	2.43	1.52	1.45	8200	115	98	80	78	519	513	30	27
HIER-004	0.00	0.00	2618	8200	93	46	51	51	338	340	18	16
Sat-SAT	1.48	0.28	0.30	9600	141	132	77	77	459	465	57	52
HIER-001	0.00	0.00	2686	7500	100	61	57	53	362	346	28	18
V-013	1.42	1.08	2.83	9200	84	84	53	44	297	253	50	37
V-011	4.94	2.25	1.29	9900			50	50	276	279	51	48
BH-003	0.73	0.45	0.32	9300								
V-007	1.25	0.88	1.36	4400	44	31	28	24	107	133	58	23
EB-006	1.36	1.12	16.14	6600	161	157	60	21	191	61	145	55

Chart 14: Chemical analyses of the wells from Chart 13

^{xiii} Water cut

For the wells V-011 and BH-003 the test kits were not available due to numerous delays in the delivery of laboratory equipment. Nevertheless, V-011 is expected to be corresponding with V-013, since they are both producing from similar formations.

The cracked iron (Fe^{2+}) alone provides information about the iron content of the production water. Since this iron concentration can origin from corrosion and the formation water, the second parameter necessary to be watched is the manganese concentration (Mn^{+}). A both high manganese and iron concentration can be an indicator for corrosion, since the corrosion process destroys the crystal lattice from the steel, which is also alloy containing manganese. Plus, information about the H_2S content is a factor, since sulfur hydrogen causes a corrosive environment. With these regards, especially the wells HIER-001, HIER-004, V-033 and V-011 are to be watched. Since the hereby found values for the producers HIER-001 and HIER-004 is extremely high, the test for manganese was repeated twice, but with corresponding results.

The chloride content (Cl^{-}) was found useful for the staff from the geological and reservoir engineering department and therefore analyzed as extra work. Its purpose is to show alterations in the water front moving from the injectors towards the producers. An alteration means that a change in the water front occurred.

The sulfate content (SO_4^{2-}) was supposed to help find out the nature of the scale. Its purpose is to show whether there exists sulfate scale or not – and if yes, in what concentration.

Hitherto the main assumption was that the majority of scale problems results from carbonate compounds. As written in 1.1.2 these scale forms usually are formed by compounds from carbonate with calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions. As assumed, such compounds were found in all cases. Especially the three high water-cut wells V-015, V-030 and V-033 with the impeller pumps installed were predestined for such scales. As visible from Chart 14 the only “producer” which could keep up with the three impeller wells is the line from the SAT-Sat station, where the transferred liquid origins from different wells, is transported over very long distances and is exhibited to numerous changes in temperature, pressure and environment.

To further illustrate the importance of scale precipitations respectively their appearance in the single water streams, Chart 15 provides an overview how much of the various ions is pumped daily from each producer.

well code	water rate [m ³ /d]	Daily contribution into system [kg]									
		Fe ²⁺ _{cracked}		Mn ⁺	Cl ⁻	SO ₄ ²⁻		Ca ²⁺		Mg ²⁺	
		total	<0.45µm	<0.45µm	<0.45µm	total	<0.45µm	total	<0.45µm	total	<0.45µm
V-030	319.8	0.15	0.07	0.32	831	17.27	10.23	141.51	115.36	16.16	7.77
V-015	222.5	0.04	0.02	0.09	1691	18.91	18.02	105.92	106.28	5.41	4.76
V-033	206.4	0.50	0.31	0.30	1693	23.74	20.23	107.23	105.90	6.22	5.62
HIER-004	30.1	0.00	0.00	78.85	247	2.80	1.39	10.19	10.24	0.53	0.47
Sat-SAT	30.0	0.04	0.01	0.01	288	4.23	3.96	13.76	13.95	1.72	1.55
HIER-001	27.8	0.00	0.00	74.56	208	2.78	1.69	10.06	9.61	0.78	0.51
V-013	22.5	0.03	0.02	0.06	207	1.89	1.89	6.67	5.70	1.12	0.83
V-011	10.8	0.05	0.02	0.01	107			2.97	3.00	0.54	0.51
BH-003	9.7	0.01	0.00	0.00	90						
V-007	7.3	0.01	0.01	0.01	32	0.32	0.23	0.79	0.98	0.43	0.17
EB-006	5.0	0.01	0.01	0.08	33	0.81	0.79	0.96	0.31	0.73	0.28

Chart 15: Daily contribution of analyzed components to system (in kg)

From the data presented in Chart 13, Chart 14 and Chart 15 it will be definitely necessary to keep an eye on proper scale inhibition for the wells with high water cuts and high production rates. In terms of corrosion although the value for the producers from Hiersdorf is exorbitant high it is anyway recommended to keep up proper inhibition and monitoring with the corrosion coupons installed all over the network.

3.4 Settling tank

3.4.1 Background and information

This part of the thesis refers to the chemical composition of the water after its production as well as separation and collecting in the settling tank (see Figure 14).

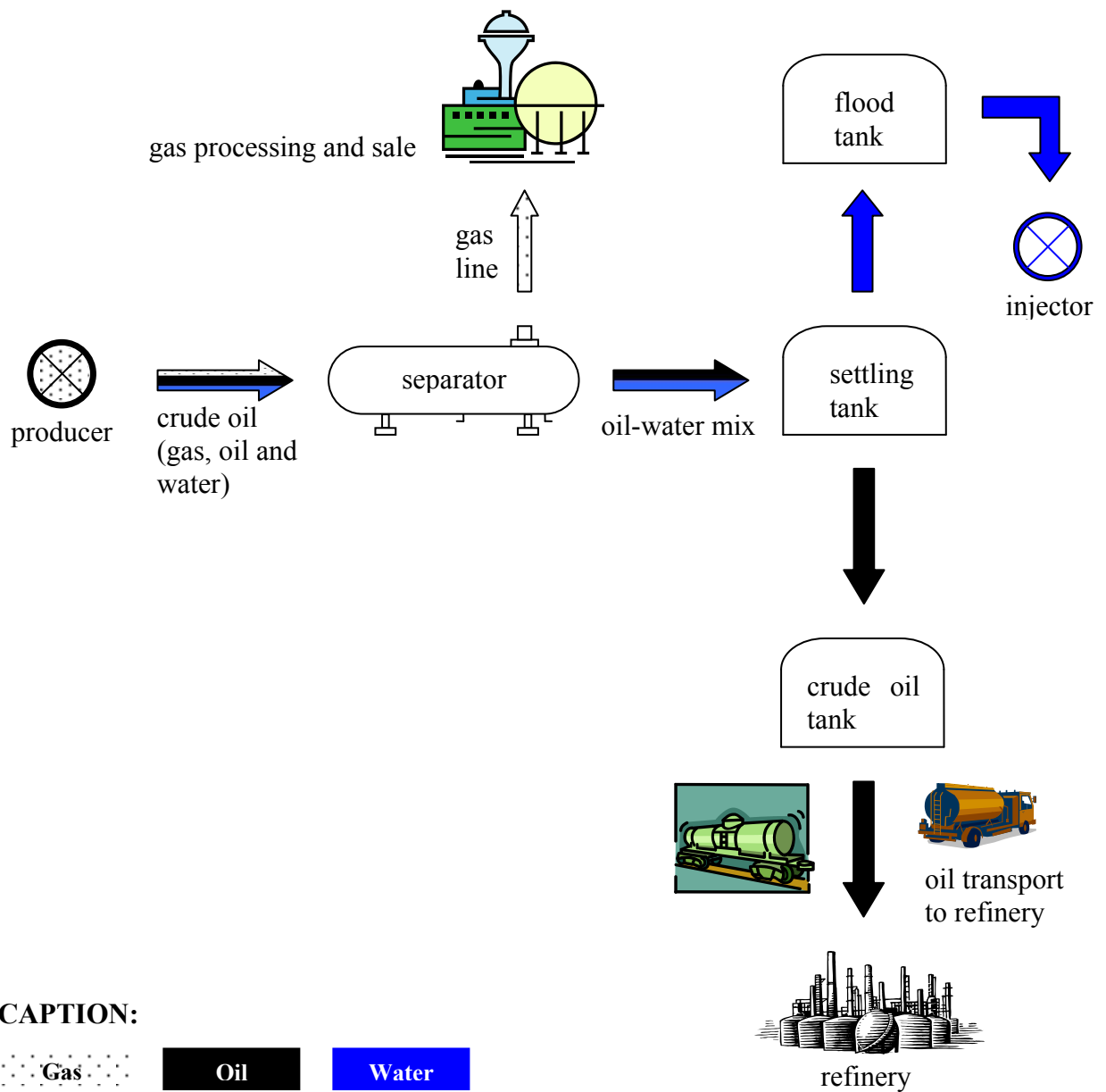


Figure 14: Schematic of crude oil upstream and processing^{XIV}

^{XIV} In the element “crude oil tank” also the crude oil processing at VZ station is included.

The purpose of this task was to define a “base line” for the values of:

- haze in [NTU]
- temperature [°C]
- pH value [-]
- redox potential [mV]
- conductivity [mS/cm]
- oxygen O₂ [mg/l]
- H₂S [ppmv]
- residual oil content (ROC) [ppmv]
- water blocking factor WBF [-]
- HCl acidible material [mg/l]
- total (“cracked”) iron content (unfiltered, 3µm-filtered and 0.45µm-filtered) [mg/l]
- total hardness (unfiltered, 3µm-filtered and 0.45µm-filtered) [°dH]
- calcium content (unfiltered, 3µm-filtered and 0.45µm-filtered) [mg/l]
- magnesium content (unfiltered, 3µm-filtered and 0.45µm-filtered) [mg/l]

This was performed because of a planned “standard” operation period at VZ station without any major reconstruction operations and highly influencing workover tasks. Although altogether 37 samples of the settling tank water were taken and analyzed, not all of them were evaluated the same way – purposefully and by accident. The following restrictions were given:

- By dropping the oxygen probe of the multimeter the sensor cap on the probe’s top broke. Since delivery of a new cap took a while, only a few measurements were taken.
- The hydrogen sulfide (H₂S) measurements were stopped after it turned out after the first measurements that it was always 0 (“Zero”) – as expectable after sufficient time for separation and de-gassing of the crude oil in both the separators and the settling tank itself.
- The recording of the water blocking factor (WBF) started comparatively late, since it took a while for the suppliers to deliver all the ordered equipment and/or fulfill the necessary changes in the planning and set-up in 6.3.6.
- Several measurements of iron, total hardness, calcium and magnesium were carried out according to the current requests from engineering department and availability of test kits.

3.4.2 Physical parameters – haze, temperature, pH value, redox potential, conductivity, solids and WBF

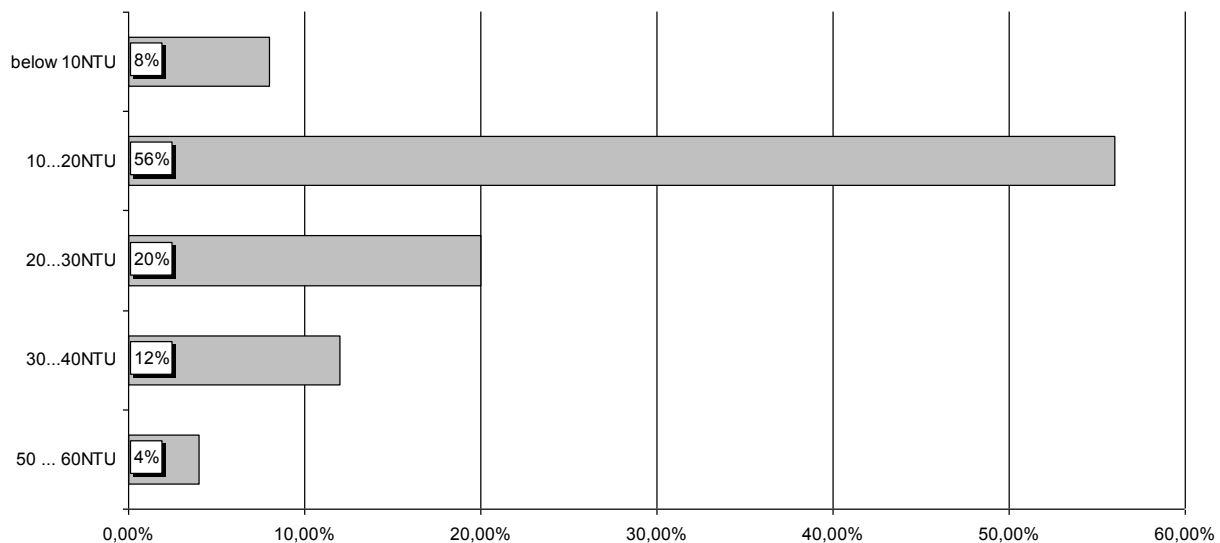


Figure 15: Distribution of measured haze values [NTU] in the settling tank

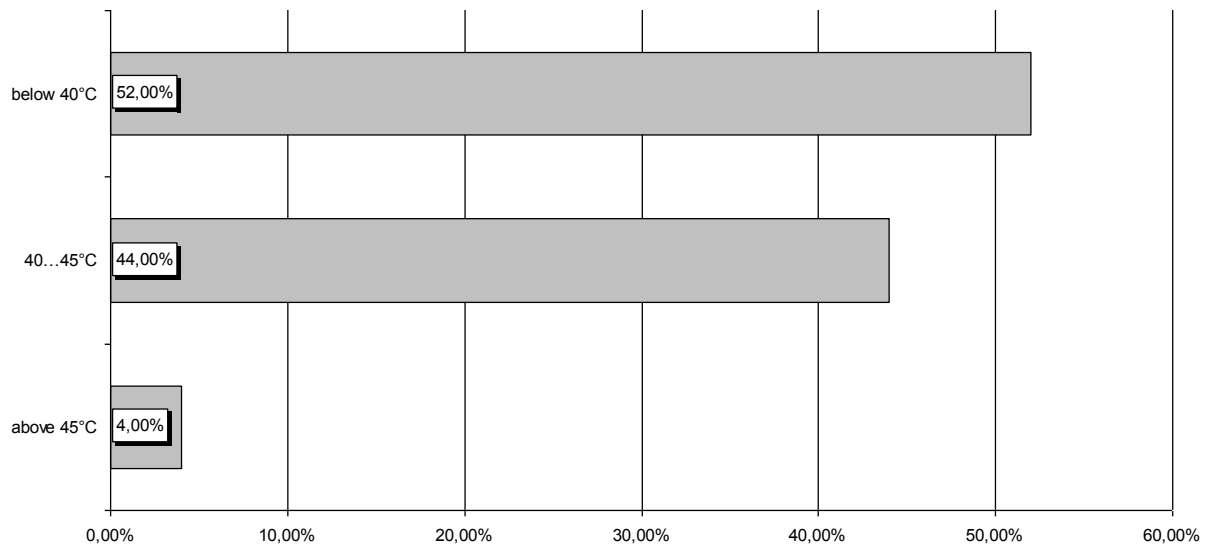


Figure 16: Distribution of measured temperature values [°C] in the settling tank

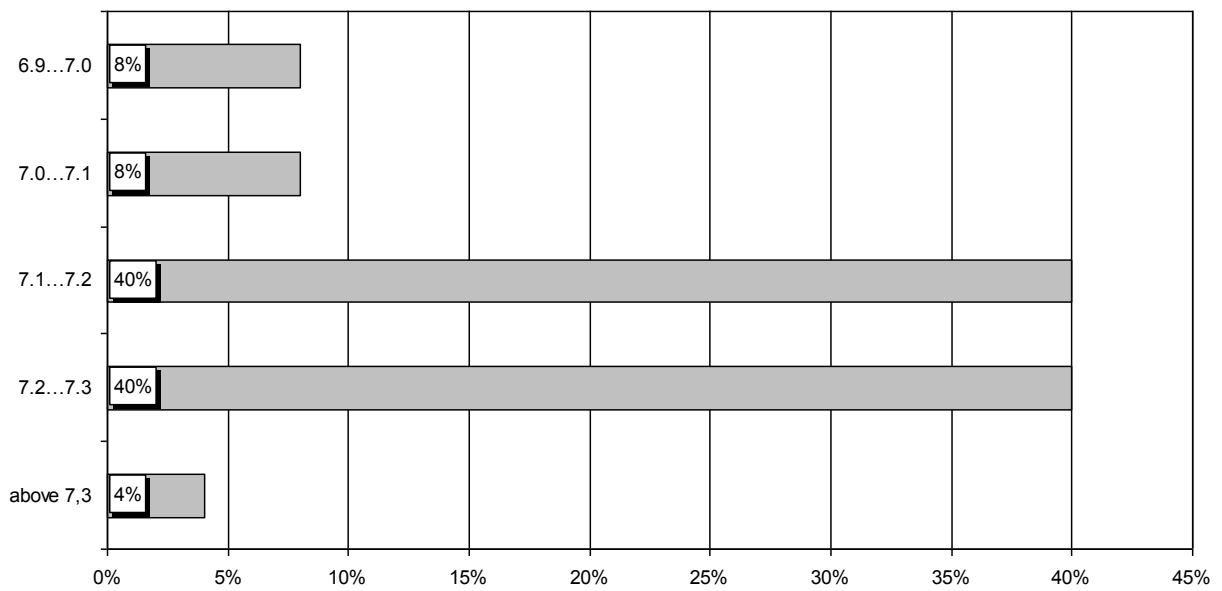


Figure 17: Distribution of measured pH values [-] in the settling tank

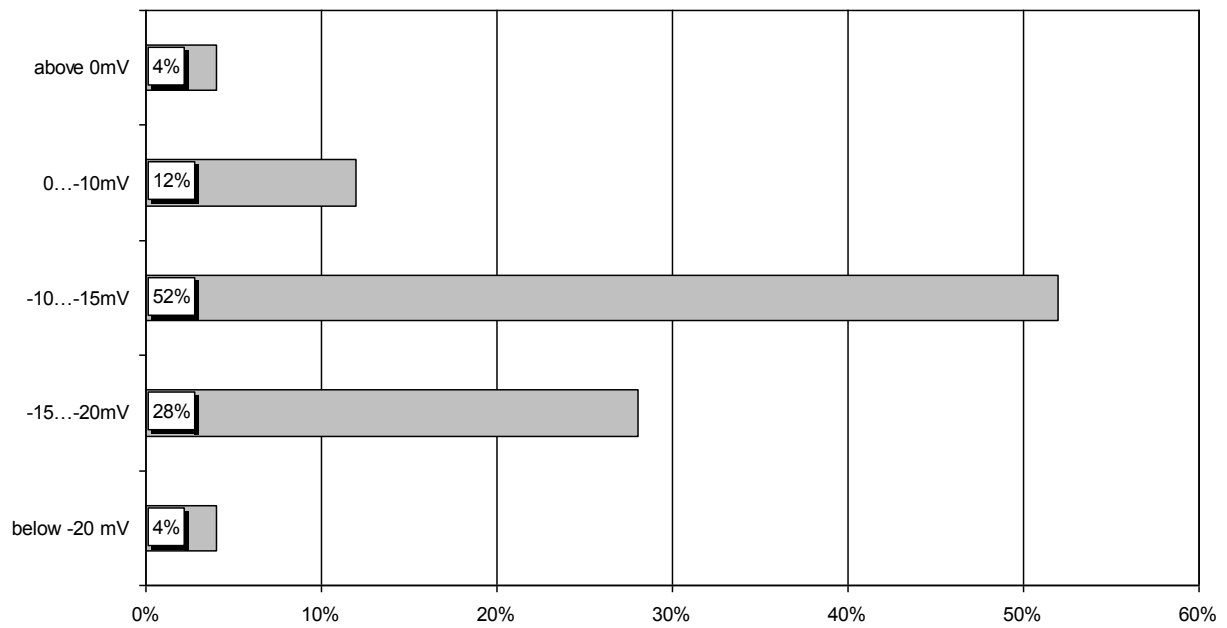


Figure 18: Distribution of measured redox potential values [mV] in the settling tank

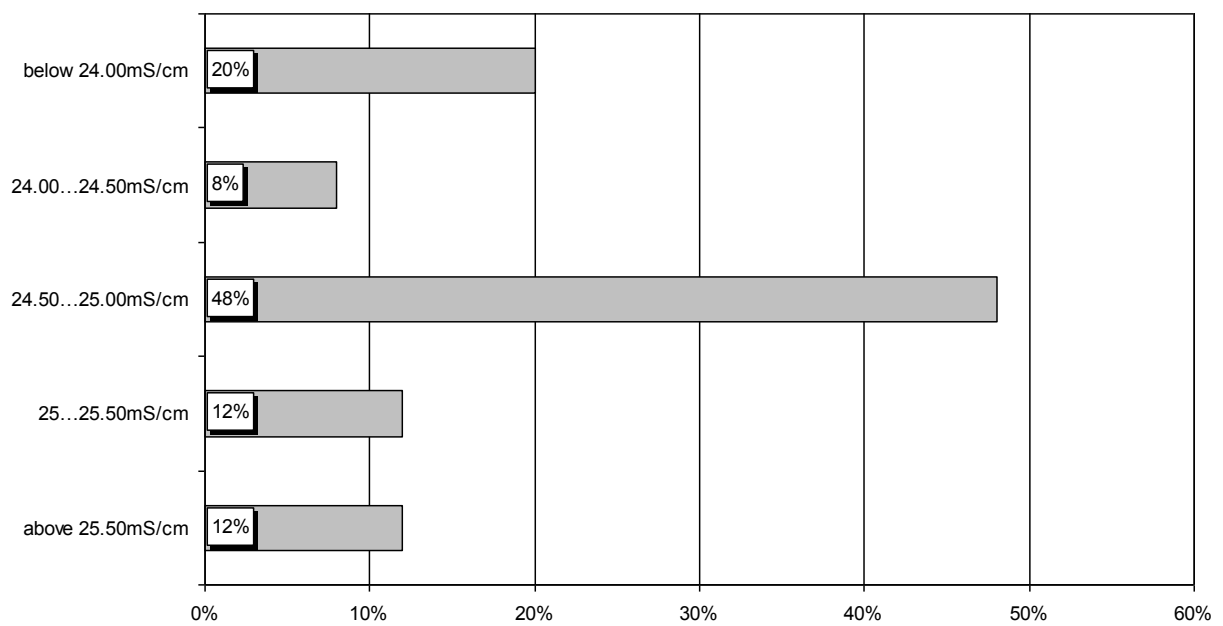


Figure 19: Distribution of measured conductivity values [mS/cm] in the settling tank

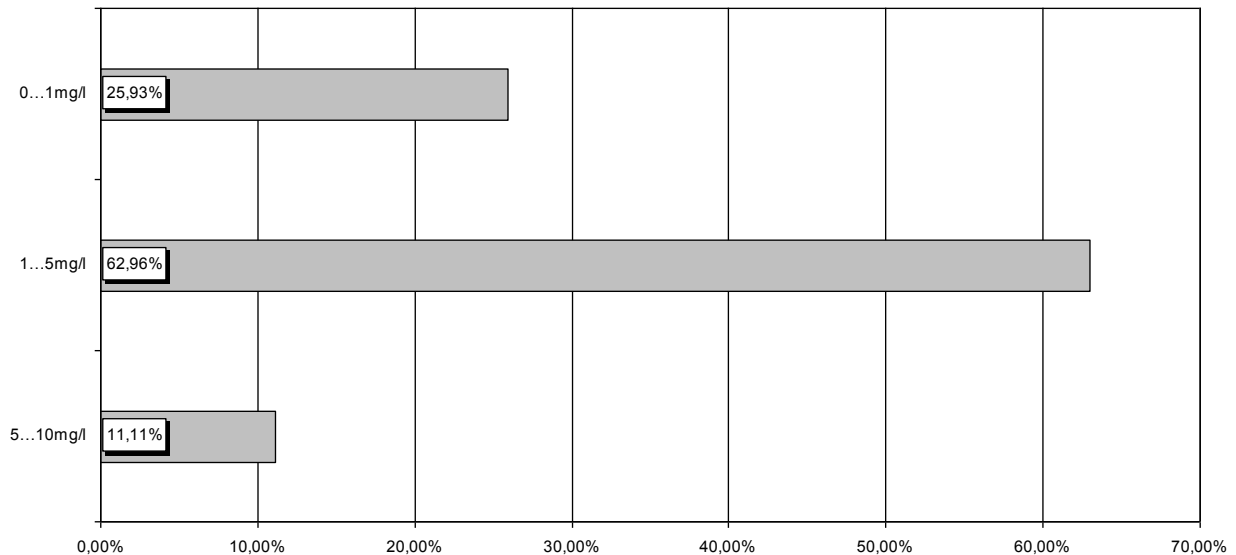


Figure 20: Distribution of measured HCl-acidizable solids [mg/l] in the settling tank

sample #	date	time	sample location	WBF [-]
62	10-20-10	13:08	VZ exit	5,98
64	10-21-10	08:40	VZ exit	14,59
69	10-27-10	09:54	VZ exit	8,89
76	10-28-10	14:30	VZ exit	3,46
78	11-02-10	11:29	VZ exit	9,06
79	11-08-10	10:02	VZ exit	11,66

Chart 16: Measured values of the WBF [-]

Since the delivery of the adjustable manometer was delayed for several weeks, only a relatively small amount of WBFs was measured. Nevertheless further filtrations and research are necessary, since the changes in the measured WBFs (yet) cannot be linked with the filterable materials or the contents of iron, calcium and magnesium.

#	WBF [-]	filtratable material			cracked iron [mg/l]			calcium [mg/l]			magnesium [mg/l]		
		1)	2)	3)	not filtered	filtratable		not filtered	filtratable		not filtered	filtratable	
						3µ	0.45µ		3µ	0.45µ		3µ	0.45µ
62	5.98	10.20	8.79	1.41									
64	14.59	6.10	4.57	1.52	1.41	0.83	1.00	421.6	14.4288	22.4448	35.96	13.6080	14.5800
69	8.89	2.16	1.68	0.48	0.82	0.34	0.48	410.4	12.8256	14.4288	23.33	0	1.9440
76	3.46	8.27	5.44	2.82	0.86	0.54	0.61						
78	9.06	5.51	4.08	1.43	3.43	0.58	1.40	444.1	12.8256	11.2224	38.88	0.9720	8.7480
79	11.66	6.62	5.89	0.74	2.22	1.16	1.96	575.1	16.0320	16.0320	35.24	3.6450	8.5050

- 1) de-oiled, 3µm-filtered [mg/l]
- 2) de-oiled and acidized, 3µm-filtered [mg/l]
- 3) = 1) – 2); acidizable with HCl, 3µm-filtered [mg/l]

Chart 17: Comparison of measured WBFs with filtratable material and contents of iron, calcium and magnesium

From the measured values of the settling tank's physical parameters, the following base line – except for the WBF – can be drawn:

haze [NTU]	temperature [°C]	pH value [-]	redox potential [mV]	conductivity [mS/cm]	HCl-acidizable solids [mg/l]
10 ... 20	< 40	7.1 ... 7.3	-10 ... -15	24.50 ... 25.00	1 ... 5

Chart 18: Base line parameters for haze, temperature, pH value, redox potential, conductivity and HCl-acidizable solids

3.4.3 Chemical parameters – ROC, iron, total hardness, calcium and magnesium content

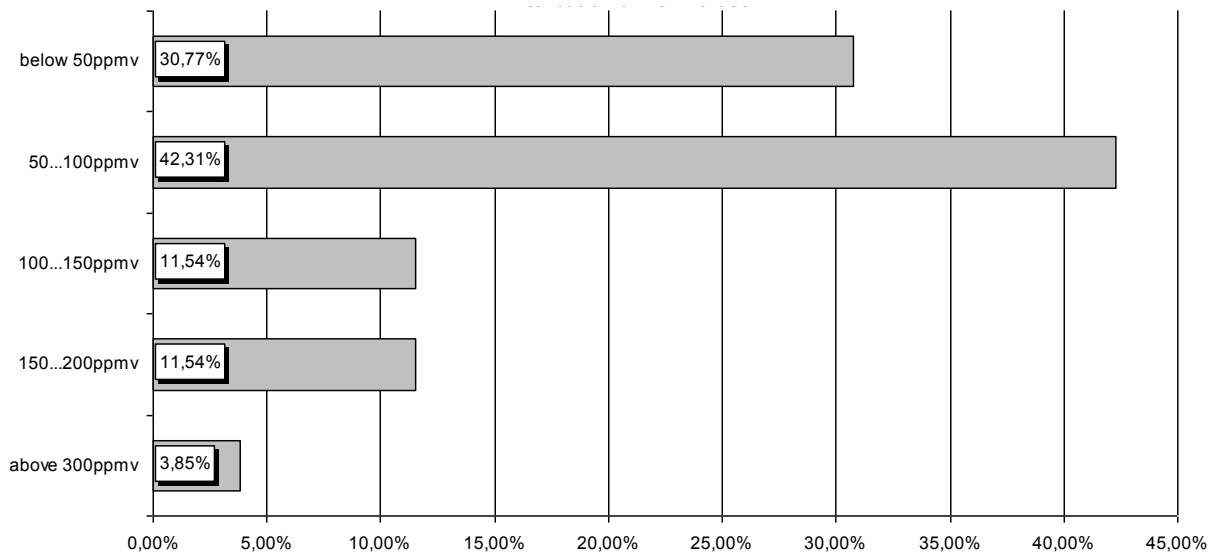


Figure 21: Distribution of the measured ROC values [ppmv]

The residual oil content ROC in Figure 21 gives a distribution of the measured values for the total amount of hydrocarbons in the settling tank water in ppmv. Since it was assumed that the ROC is proportional to the oil and condensate delivered to VZ station the previous days, these deliveries over the last three days were taken from the report system and compared among each other regarding the measured ROC (see Chart 19). A clearly recognizable interconnection between the ROC and the hydrocarbon deliveries is yet to be found, since in the observed period different amounts and types of hydrocarbons were delivered to and pumped from VZ station.

#	sample data			ROC [ppmv]	ROC range [ppmv]	OIL AND CONDENSATE DELIVERIES THREE DAYS BEFORE						
	date	time	location			total [m ³]	date	volume [m ³]	date	volume [m ³]	date	volume [m ³]
48	18-Oct	10:35	VZ exit	342	above 300	229	17-Oct	63.7	16-Oct	63.43	15-Oct	101.47
62	20-Oct	13:08	VZ exit	196	150...200	154	19-Oct	0	18-Oct	90.16	17-Oct	63.7
55	19-Oct	08:53	VZ exit	165	150...200	217	18-Oct	90.16	17-Oct	63.7	16-Oct	63.43
76	28-Oct	14:30	VZ exit	153	150...200	254	27-Oct	102.95	26-Oct	25.12	25-Oct	125.67
46	15-Oct	09:45	VZ exit	132	100...150	119	14-Oct	28.37	13-Oct	60.44	12-Oct	30.28
9	30-Sep	13:42	VZ exit	122	100...150	280	29-Sep	82.49	28-Sep	72.82	27-Sep	124.21
79	8-Nov	10:02	VZ exit	100	100...150	213	7-Nov	93.28	6-Nov	60.58	5-Nov	59.27
7	30-Sep	08:30	VZ exit	93	50...100	280	29-Sep	82.49	28-Sep	72.82	27-Sep	124.21
78	2-Nov	11:29	VZ exit	85	50...100	125	1-Nov	62.69	31-Oct	31.06	30-Oct	30.78
10	1-Oct	08:18	VZ exit	70	50...100	227	30-Sep	71.81	29-Sep	82.49	28-Sep	72.82
24	6-Oct	15:42	VZ exit	68	50...100	243	5-Oct	54.94	4-Oct	99.73	3-Oct	88.58
64	21-Oct	08:40	VZ exit	64	50...100	181	20-Oct	90.36	19-Oct	0	18-Oct	90.16
30	8-Oct	07:30	VZ exit	62	50...100	221	7-Oct	42.47	6-Oct	123.44	5-Oct	55.03
32	11-Oct	11:27	VZ exit	58	50...100	185	10-Oct	26.27	9-Oct	66.91	8-Oct	91.75
18	5-Oct	13:45	VZ exit	57	50...100	199	4-Oct	99.73	3-Oct	88.58	2-Oct	11.14
28	7-Oct	14:24	VZ exit	56	50...100	278	6-Oct	123.44	5-Oct	55.03	4-Oct	99.73
34	11-Oct	16:27	VZ exit	53	50...100	185	10-Oct	26.27	9-Oct	66.91	8-Oct	91.75
36	12-Oct	07:46	VZ exit	52	50...100	199	11-Oct	105.72	10-Oct	26.27	9-Oct	66.91
26	7-Oct	10:40	VZ exit	44	below 50	278	6-Oct	123.44	5-Oct	55.03	4-Oct	99.73
38	13-Oct	09:44	VZ exit	43	below 50	162	12-Oct	30.28	11-Oct	105.72	10-Oct	26.27
69	27-Oct	09:54	VZ exit	39	below 50	180	26-Oct	25.12	25-Oct	125.67	24-Oct	29.25
12	4-Oct	11:00	VZ exit	39	below 50	167	3-Oct	88.58	2-Oct	11.14	1-Oct	67.47
16	5-Oct	11:08	VZ exit	38	below 50	199	4-Oct	99.73	3-Oct	88.58	2-Oct	11.14
22	6-Oct	13:27	VZ exit	37	below 50	243	5-Oct	54.94	4-Oct	99.73	3-Oct	88.58
14	4-Oct	15:50	VZ exit	36	below 50	167	3-Oct	88.58	2-Oct	11.14	1-Oct	67.47
20	6-Oct	09:53	VZ exit	23	below 50	243	5-Oct	54.94	4-Oct	99.73	3-Oct	88.58

Chart 19: Measured values of ROC and ROC ranges compared with oil and condensate deliveries

Several sample combinations from Chart 19 oben – sorted by ROC respectively ROC range – show that the measured ROC does NOT depend on the amount of oil and condensate delivered of the respective last three days. For example, sample #48 showed up a value of 342ppmv ROC at 229m³ of oil and condensate delivered the three days before, whereas sample #10 showed up a completely different value of 70ppmv ROC with a similar amount of 227m³ of oil and condensate delivered. Another sample combination supporting this theory is #26 and #38: Although their ROC is almost equal, the previously delivered amounts of oil and condensate are completely different with 278ppmv respectively 162ppmv.

#	sample data			cracked iron values [mg/l]			cracked iron value range(s) [mg/l]		
	date	time	location	unfiltered	3 μ filtered	0.45 μ filtratable	unfiltered	3 μ filtered	0.45 μ filtratable
4	27-Sep	11:51	VZ exit	2.23			above 3.5mg/l		
5	27-Sep	15:21	VZ exit	1.72			3...3.5mg/l		
6	29-Jun	11:25	VZ exit	3.71		2.33	3...3.5mg/l		above 2.0mg/l
78	2-Nov	11:29	VZ exit	3.43	0.58	1.40	2.5...3mg/l	0.5...1.0mg/l	1.0...1.5mg/l
79	8-Nov	10:02	VZ exit	2.22	1.16	1.96	2.0...2.5mg/l	1.0...1.5mg/l	1.5...2.0mg/l
9	30-Sep	13:42	VZ exit	3.02		1.77	2.0...2.5mg/l		1.5...2.0mg/l
10	1-Oct	08:18	VZ exit	2.52		1.48	2.0...2.5mg/l		1.0...1.5mg/l
8	30-Sep	11:24	VZ exit	2.10		0.31	1.5...2.0mg/l		below 0.5mg/l
55	19-Oct	08:53	VZ exit	1.71	1.35	1.06	1.5...2.0mg/l	1.0...1.5mg/l	1.0...1.5mg/l
62	20-Oct	13:08	VZ exit	1.54	0.88	1.22	1.5...2.0mg/l	0.5...1.0mg/l	1.0...1.5mg/l
48	18-Oct	10:35	VZ exit	1.99	0.68	1.14	1.5...2.0mg/l	0.5...1.0mg/l	1.0...1.5mg/l
64	21-Oct	08:40	VZ exit	1.41	0.83	1.00	1.0...1.5mg/l	0.5...1.0mg/l	1.0...1.5mg/l
42	14-Oct	09:10	VZ exit	1.23	0.83	0.95	1.0...1.5mg/l	0.5...1.0mg/l	0.5...1.0mg/l
32	11-Oct	11:27	VZ exit	1.01	0.39	0.46	1.0...1.5mg/l	below 0.5mg/l	below 0.5mg/l
24	6-Oct	15:42	VZ exit	0.91	0.65	0.68	0.5...1.0mg/l	0.5...1.0mg/l	0.5...1.0mg/l
76	28-Oct	14:30	VZ exit	0.86	0.54	0.61	0.5...1.0mg/l	0.5...1.0mg/l	0.5...1.0mg/l
22	6-Oct	13:27	VZ exit	0.76	0.50	0.55	0.5...1.0mg/l	0.5...1.0mg/l	0.5...1.0mg/l
30	8-Oct	07:30	VZ exit	0.78	0.48	0.59	0.5...1.0mg/l	below 0.5mg/l	0.5...1.0mg/l
46	15-Oct	09:45	VZ exit	0.84	0.40	0.54	0.5...1.0mg/l	below 0.5mg/l	0.5...1.0mg/l
26	7-Oct	10:40	VZ exit	0.75	0.46	0.53	0.5...1.0mg/l	below 0.5mg/l	0.5...1.0mg/l
69	27-Oct	09:54	VZ exit	0.82	0.34	0.48	0.5...1.0mg/l	below 0.5mg/l	below 0.5mg/l
20	6-Oct	09:53	VZ exit	0.70	0.41	0.47	0.5...1.0mg/l	below 0.5mg/l	below 0.5mg/l
36	12-Oct	07:46	VZ exit	0.96	0.18	0.47	0.5...1.0mg/l	below 0.5mg/l	below 0.5mg/l
28	7-Oct	14:24	VZ exit	0.74	0.37	0.41	0.5...1.0mg/l	below 0.5mg/l	below 0.5mg/l
18	5-Oct	13:45	VZ exit	0.63	0.36	0.40	0.5...1.0mg/l	below 0.5mg/l	below 0.5mg/l
38	13-Oct	09:44	VZ exit	0.58	0.27	0.34	0.5...1.0mg/l	below 0.5mg/l	below 0.5mg/l
34	11-Oct	16:27	VZ exit	0.88	0.20	0.32	0.5...1.0mg/l	below 0.5mg/l	below 0.5mg/l
14	4-Oct	15:50	VZ exit	0.70	0.20	0.26	0.5...1.0mg/l	below 0.5mg/l	below 0.5mg/l
12	4-Oct	11:00	VZ exit	0.75	0.33	0.25	0.5...1.0mg/l	below 0.5mg/l	below 0.5mg/l
16	5-Oct	11:08	VZ exit	0.56	0.26	0.24	0.5...1.0mg/l	below 0.5mg/l	below 0.5mg/l

Chart 20: Distribution of cracked iron values [mg/l]

From Chart 20 oben it can be read that the most common cracked iron value ranges combination is “unfiltered – 0.5...1.0mg/l; 3 μ filtered – below 0.5mg/l; 0.45 μ filtratable – below 0.5mg/l” with a 33% percentage of all measured values (shaded grey). The cells left empty origin in lack of equipment to perform a 3 μ m filtration.

sample data				total hardness			total hardness range(s)		
#	date	time	location	unfiltered [°dH] ^{xv}	3µ filtered [mg/l]	0.45µ filtratable [mg/l]	unfiltered [°dH] ^{xv}	3µ filtered [mg/l]	0.45µ filtratable [mg/l]
30	8-Oct	07:30	VZ exit	91.78			90...100°dH		
79	8-Nov	10:02	VZ exit	88.64	3.09	4.21	80...90°dH	1...5mg/l	1...5mg/l
62	20-Oct	13:08	VZ exit	70.69	6.51	7.85	70...80°dH	above 5mg/l	above 5mg/l
48	18-Oct	10:35	VZ exit	75.17	1.80	3.14	70...80°dH	1...5mg/l	1...5mg/l
78	2-Nov	11:29	VZ exit	71.13	2.02	3.59	70...80°dH	1...5mg/l	1...5mg/l
64	21-Oct	08:40	VZ exit	67.32	5.16	6.51	60...70°dH	above 5mg/l	above 5mg/l
36	12-Oct	07:46	VZ exit	67.77	3.81	7.41	60...70°dH	1...5mg/l	above 5mg/l
42	14-Oct	09:10	VZ exit	68.89	3.37	4.04	60...70°dH	1...5mg/l	1...5mg/l
16	5-Oct	11:08	VZ exit	65.08	2.52	3.65	60...70°dH	1...5mg/l	1...5mg/l
38	13-Oct	09:44	VZ exit	66.65	4.94	3.37	60...70°dH	1...5mg/l	1...5mg/l
69	27-Oct	09:54	VZ exit	62.83	1.80	2.47	60...70°dH	1...5mg/l	1...5mg/l
32	11-Oct	11:27	VZ exit	62.38	2.02	1.68	60...70°dH	1...5mg/l	1...5mg/l
14	4-Oct	15:50	VZ exit	61.71	0.90	1.40	60...70°dH	below 1mg/l	1...5mg/l
46	15-Oct	09:45	VZ exit	69.56	0.28	2.52	60...70°dH	below 1mg/l	1...5mg/l
4	27-Sep	11:51	VZ exit	65.36		2.52	60...70°dH		1...5mg/l
6	29-Jun	11:25	VZ exit	61.15		2.24	60...70°dH		1...5mg/l
28	7-Oct	14:24	VZ exit	59.13	2.36	3.59	50...60°dH	1...5mg/l	1...5mg/l
26	7-Oct	10:40	VZ exit	56.66	2.24	2.47	50...60°dH	1...5mg/l	1...5mg/l
24	6-Oct	15:42	VZ exit	54.98	1.57	1.46	50...60°dH	1...5mg/l	1...5mg/l
22	6-Oct	13:27	VZ exit	54.98	0.56	0.11	50...60°dH	below 1mg/l	below 1mg/l
5	27-Sep	15:21	VZ exit	56.10		2.81	50...60°dH		1...5mg/l

Chart 21: Distribution of total hardness' values

From Chart 21 it can be read that the most common total hardness value ranges combination is “unfiltered – 60...70°dH; 3µ filtered – 1...5mg/l; 0.45µ filtratable – 1...5mg/l” with a 23,81% percentage of all measured values (shaded grey).

sample data				calcium [mg/l]			magnesium [mg/l]		
#	date	time	location	unfiltered	3µ filtered	0.45µ filtratable	unfiltered	3µ filtered	0.45µ filtratable
16	5-Oct	11:08	VZ exit	424,85	6,01	14,03	24,30	7,29	7,29
38	13-Oct	09:44	VZ exit	429,66	27,25	14,43	28,19	4,86	5,83
69	27-Oct	09:54	VZ exit	410,42	12,83	14,43	23,33	0,00	1,94
median				421,64	15,36	14,30	25,27	4,05	5,02

Chart 22: Values for calcium and magnesium concentration based on the values from Chart 21

The values for calcium and magnesium concentration in Chart 22 were derived from the values of Chart 21. Two values were deleted, since the measuring inaccuracy of the photometer in combination with the dilution ratio of 1:4 (sample volume in distilled water) turned out negative “3µ filtered” and “0.45µ filtratable” values for the calcium concentration.

^{xv} German degrees of hardness (“Deutsche Härte”)

From the measured values of the settling tank's chemical parameters, the following base line can be drawn:

ROC range [ppm]	cracked iron value ranges			total hardness value ranges		
	unfiltered [mg/l]	3 μ filtered [mg/l]	0.45 μ filtratable [mg/l]	unfiltered [mg/l]	3 μ filtered [mg/l]	0.45 μ filtratable [mg/l]
50...100	0.5...1.0	below 0.5	below 0.5	60...70°dH	1...5mg/l	1...5mg/l
calcium			magnesium			
unfiltered [mg/l]	3 μ filtered [mg/l]	0.45 μ filtratable [mg/l]	unfiltered [mg/l]	3 μ filtered [mg/l]	0.45 μ filtratable [mg/l]	
421.64	15.36	14.30	25.27	4.05	5.02	

Chart 23: Base line parameters for ROC, cracked iron, total hardness, calcium and magnesium values/ranges

4 Corrosion coupons - evaluation

4.1 Background and overview

Corrosion coupons are a widely spread method to determine the corrosion rate of a fluid stream. They consist of a highly corrosive alloy and are mounted into the pipe usually with the help of coupon fittings. Before installing the coupons, each of them is activated, weighted and registered by its serial number. After a predetermined period they are dismantled from their installment spot, cleaned and weighted again. Since their original measurements are known (see Chart 24), the loss of weight is used to determine an annual corrosion rate in i.e. [mm/yr].

coupon measurements and surface	
length [cm]	12.7
width [cm]	1.6
net surface [cm ²]	41

Chart 24: Coupon surface data of the coupons used in the field network Voitsdorf

4.2 Corrosion coupons installed in the field network Voitsdorf

4.2.1 General information and procedure

This chapter's purpose is to overview the actual^{XVI} corrosion rates in the field network Voitsdorf in the following three sub-chapters. The installed corrosion coupons were dismantled from their coupon holder, brought to the laboratory and cleaned and weighted according to the 13-point procedure listed below:

1. activate and weigh a non-installed ("maiden") coupon
2. soak the coupons for a day in gasoline
3. wipe the coupons clean with woven felt
4. spray the coupons with acetone for cleaning and quick drying
5. weigh the coupons
6. mix approximately 500ml of 80% hydrochloric acid with 5ml 1% Cronox242 liquid (acid inhibitor)
7. immerse the coupons for five minutes into the Cronox 242-acid mixture
8. stir the mixture somewhat
9. take the coupons out and put them in a jar with water to stop the acidizing process
10. immerse the coupons in a jar with acetone for cleaning and quick drying
11. weigh the coupons
12. heat the Cronox 242-acid mixture from 6. to 50°C and restart the procedure at 7.
13. repeat the steps 7. to 12. until no significant weight difference between the weight loss from the maiden coupon and the sunk coupon can be detected

The annual corrosion rates were not always measured according to schedule, which led to unavailability of data. Sometimes it was also decided to dismantle a corrosion holder from its installation spot and install it in another place – especially when the corrosion rate had reached an acceptable level. This was decided either individually or by the rule that a corrosion rate of 0.004...0.007mm/yr was acceptable and below 0.003mm/yr was decided to be excellent. The corrosion coupons of the wells in Chart 25, Chart 26 and Chart 27 with their well code written in bold letters are planned to be dismantled and evaluated in round 9. Grey shaded cells

^{XVI} Based on data available on February 10, 2011

indicate that the corrosion rate is still too high, meaning that the corrosion inhibition and management still requires improvement.

4.2.2 Producer wells

Well code	corrosion rate in [mm/yr]			
	round 6 8-Nov-09	round 7 3-Apr-10	round 8 4-Jul-10	round 9 ^{xvii}
BH-002	0.001			
BH-003		0.001		
BH-004				
BH-009				
EB-006	0.002			0.002
EB-007	0.006			0.002
EN-005				
EN-006				
HIER-001	0.002			
HIER-002	0.001			
HIER-004	0.001			
KE-001				
MDF-001				
OB-001			0.001	0.001
RA-002	0.008			0.001
SAT-002	0.005			0.001
SAT-006	0.001			
SAT-007	0.002			0.001
SAT-008	0.001			0.001
SAT-010	0.010			0.001
SAT-023				0.001
STHS-006	0.001			0.001
V-001	0.006	0.002		
V-0011	0.001			
V-013	0.003			0.002
V-015				
V-016	0.003			
V-019				0.003
V-021	0.006			
V-023	0.010			
V-030				
V-033	0.009	0.011		
V-039	0.004			
V-041	0.002			
V-043	0.001			

Chart 25: Corrosion rates of the producer wells in the field network Voitsdorf

^{xvii} Contrary to the previous rounds, the actual round is not carried out anymore on a certain date, but as and when required due to manpower reasons.

4.2.3 Injector wells

Well code	corrosion rate in [mm/yr]			
	round 6	round 7	round 8	round 9
	8-Nov-09	3-Apr-10	4-Jul-10	
SAT-W12				0.003
V-037	0.007			
V-009	0.034	0.004	0.009	0.022
BH-005				
HIER-005			0.003	

Chart 26: Corrosion rates of the injector wells in the field network Voitsdorf

4.2.4 Stations

Station code	corrosion rate in [mm/yr]			
	round 6	round 7	round 8	round 9
	8-Nov-09	3-Apr-10	4-Jul-10	
Sat SAT				
S-II	0.731	0.370		
VZ	0.023	0.004		0.004
BH ST				

Chart 27: Corrosion rates of the stations in the field network Voitsdorf

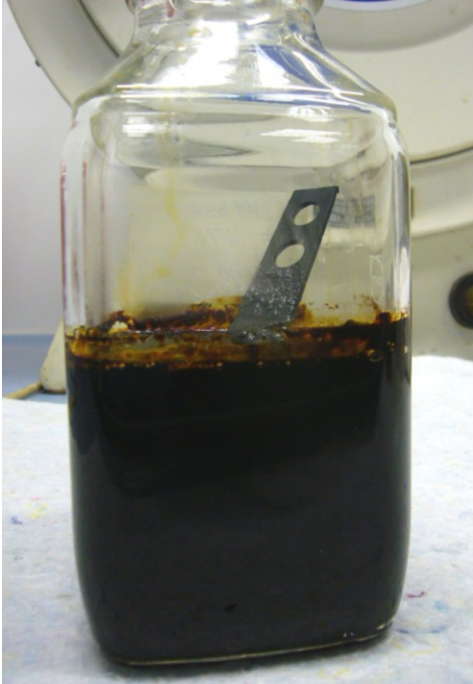
4.3 Corrosiveness of the three inhibitor types

4.3.1 Background information and set-up

To evaluate whether there might be a chance that the three researched inhibitors contribute to the overall corrosion in the well, a laboratory simulation was conducted for the three inhibitors. For this purpose into every pure inhibitor liquid a weighted and activated corrosion coupon was sunk and stored at 70°C in an oven. To keep the possible corrosion constant and the coupon covered in inhibitor all the time, the level of fluid was daily checked and refilled if necessary. The corrosiveness experiment was conducted in order to get an impression whether the inhibitor on its way down the tubing outside could cause corrosion during letting it drip down. Additionally, this experiment was carried out for every inhibitor in glasses both hermetically sealed and open. After one month (exact periods given in 4.3.3.2), they were taken out from the oven, cleaned and weighed again (see unterhalb).

4.3.2 Documentation

4.3.2.1 KI-350 in open jar



Picture 2: Open glass with corrosion coupon in KI-350^{XVIII}



Picture 3: Dried coupon

Description

As it can be seen in Picture 3, the top material layer of the coupon is corroded and chips off. Below unharmed material was visible.

4.3.2.2 CW511 in open jar



Picture 4: Open glass with corrosion coupon in CW511



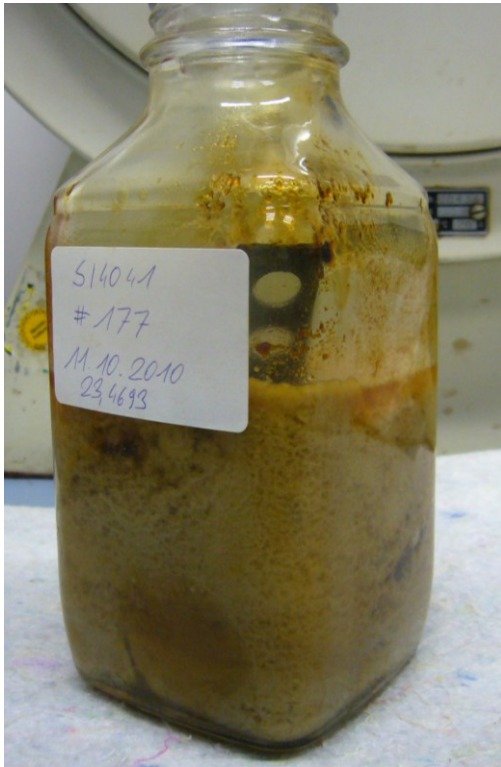
Picture 5: Dried coupon

Description

As visible in Picture 5 the surface appears to be unharmed and the coupon still has its original grey color. No significant corrosion is visible, although there are residues visible resembling mineral depositions.

^{XVIII} Inhibitor liquid partially emptied from glass for better visibility

4.3.2.3 SI-4041 in open jar



Picture 6: Open glass with corrosion coupon in SI-4041^{XIX}



Picture 7: Dried coupon

Description

Whereas Picture 7 shows minimal local corrosion (similar to „pitting“), massive residues of inhibitor can be found on the coupon. Below these the surface is mostly intact and unharmed.

During the jar's stand time in the oven small bubbles were permanently rising from the coupon's surface.

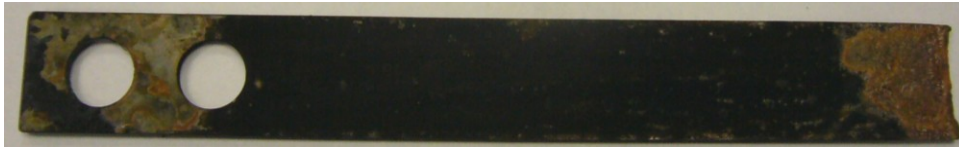
4.3.2.4 KI-350 in sealed glass



Picture 8: Sealed glasses with corrosion coupons in pure CW511, SI-4041 and KI-350

^{XIX} Partially empty due to vaporization in spite of frequent re-filling

Since all inhibitor liquids in their sealed jars became too much clouded, no pictures of the single coupons in their respective jars were taken.



Picture 9: Dried coupon from the sealed jar with KI-350

Description: The surface layer of the coupon is corroded and partially chips off, whereas the metal below seems unharmed and intact. Partially oxygen corrosion is visible, assumedly from the air in the jar when sinking the coupon into the inhibitor liquid. At the right hole-less end of the coupon also material reduction due to corrosion is visible.

4.3.2.5 CW511 in sealed glass



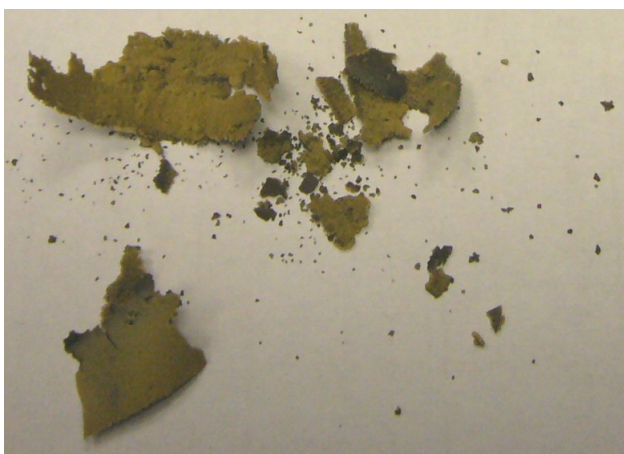
Picture 10: Dried coupon from the sealed jar with CW511

Description: Contrary to the other coupons here no visible corrosion occurred. The only effect the coupon showed after its bath in the inhibitor liquid was that the grey of the coupon surface became a little darker than originally. The surface itself was covered in a greasy film consisting of dried droplets of approximately 0.5mm diameter.

4.3.2.6 SI-4041 in sealed glass



Picture 11: Dried coupon from the sealed jar with SI-4041



Picture 12: Residues from the corrosion process chipping off the sealed SI-4041 coupon

Description: The top layer of the coupon's surface is lamellar corroded and can be peeled off in stripes (see Picture 12, left half of the picture). Whereas the flake side facing the coupon has the coupon-typical grey color, the other coupon-averted side's color changes between olive and khaki.

4.3.3 Coupon weighing

4.3.3.1 Procedure description

The weighting procedure followed the same rules as described in 4.2.1. This allowed comparing the results from the laboratory testing with those from the coupons installed in the field.

4.3.3.2 Weights and results

#	inhibitor	open or sealed	date of		period [days]	weight [g]		
			beginning	ending		new	dried	cleaned
0176	KI-350	Open	10.11.2010	11.11.2010	31	23.3953	22.8372	22.5330
0178	KI-350	Sealed	10.15.2010	11.11.2010	27	23.3453	22.2649	22.0564
0200	CW511	Open	10.11.2010	11.11.2010	31	23.7661	24.9960	23.5965
0180	CW511	Sealed	10.15.2010	11.11.2010	27	23.5895	23.8870	23.5439
0177	SI-4041	Open	10.11.2010	11.11.2010	31	23.4693	22.1559	21.0150
0179	SI-4041	Sealed	10.15.2010	11.11.2010	27	23.4515	22.8527	22.0278

Chart 28: Weights of the single coupons after different treatment steps

#	inhibitor	open or sealed	period [days]	weight loss [g]	weight of residues and corrosion [g]	corrosion rate [mm/yr]
0176	KI-350	Open	31	0.8623	0.3042	0.2476
0178	KI-350	Sealed	27	1.2889	0.2085	0.4250
0200	CW511	Open	31	0.1696	1.3995	0.0487
0180	CW511	Sealed	27	0.0456	0.3431	0.0150
0177	SI-4041	Open	31	2.4543	1.1409	0.7048
0179	SI-4041	Sealed	27	1.4237	0.8249	0.4694

Chart 29: Weight loss, residues weight and calculated annual corrosion rate with the surface from Chart 24

The corrosion rate is calculated from the loss of weight multiplied with the density of the steel divided by the coupon's net surface from Chart 24 to get an equivalent length reduction. This value then is divided through the number of days where the coupons were exposed to the chemical, which gives the corrosion rate per day. Finally, the daily corrosion rate is multiplied with 365 to convert it into the annual corrosion rate (see also formula below).

$$\text{annual corrosion rate} = \frac{\text{weight loss} \times \rho_{\text{steel}} \times 365}{\text{coupon net surface} \times \text{exposure period}} \text{ in [mmy/yr]}$$

The calculation of the corrosion rate clearly shows that the scale inhibitor is the most corrosive of the three liquids. Therefore corrosion processes and consequences will be very likely in places where the SI-4041 can accumulate. Also, the corrosiveness of the KI-350 – already known at RAG – was confirmed with this experiment.

Also the weight of residues and corrosion of the CW511 inhibitor stored under air access is remarkable. Therefore, a sealed storage for as long as possible is recommended.

5 Scale coupons installed at predetermined locations

5.1 Background and information

Since the surveillance program at RAG was decided to be improved by the installation of scale coupons, three of them were installed at the following places of the water injection system: VZ exit, at the pre-pressurization module VW-009 and at the high water-cut producer V-033. To play it safe, corrosion coupons were converted into basic scale coupons with two series of seven holes drilled into. Every series starts with a diameter of 1mm, increasing each time for 1mm until it reaches the maximum diameter of 7mm (see Figure 22).

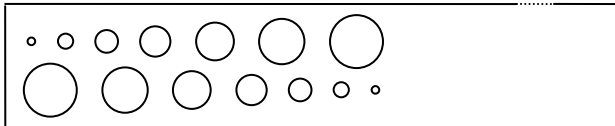


Figure 22: Sketch of a scale coupon; for dimensions see Chart 24

Scale is most likely to form in cavities, and therefore forms most readily in the smallest size hole (due to pressure drop). If a pipeline medium has a tendency to form scale, the strength of this tendency can be determined by the largest hole that has accumulated scale. The greater the concentration of scaling compounds, the larger the hole size that is likely to accumulate scale.²⁴

Based on this principle, the scale coupons were mounted crosswise to the flow direction into the places given oben with the pressure drop causing the precipitation and agglomeration of scale in the holes (see also Figure 23). This effect shows in the smallest of all holes first. An example for a scale coupon holder installation can be seen in Picture 13 unterhalb.

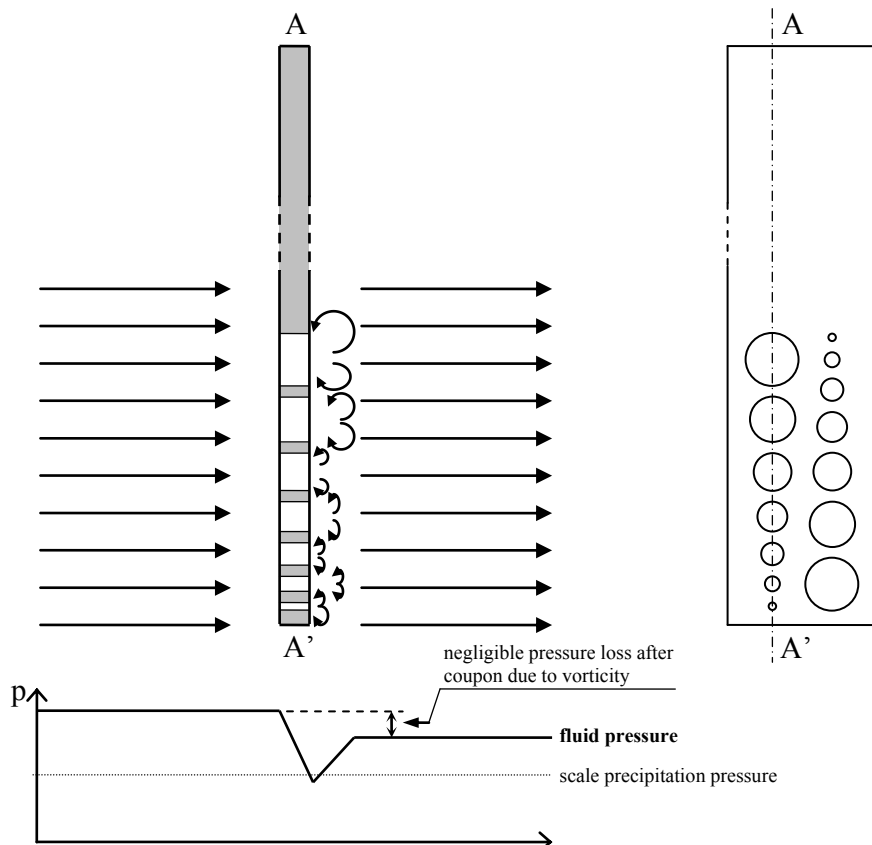
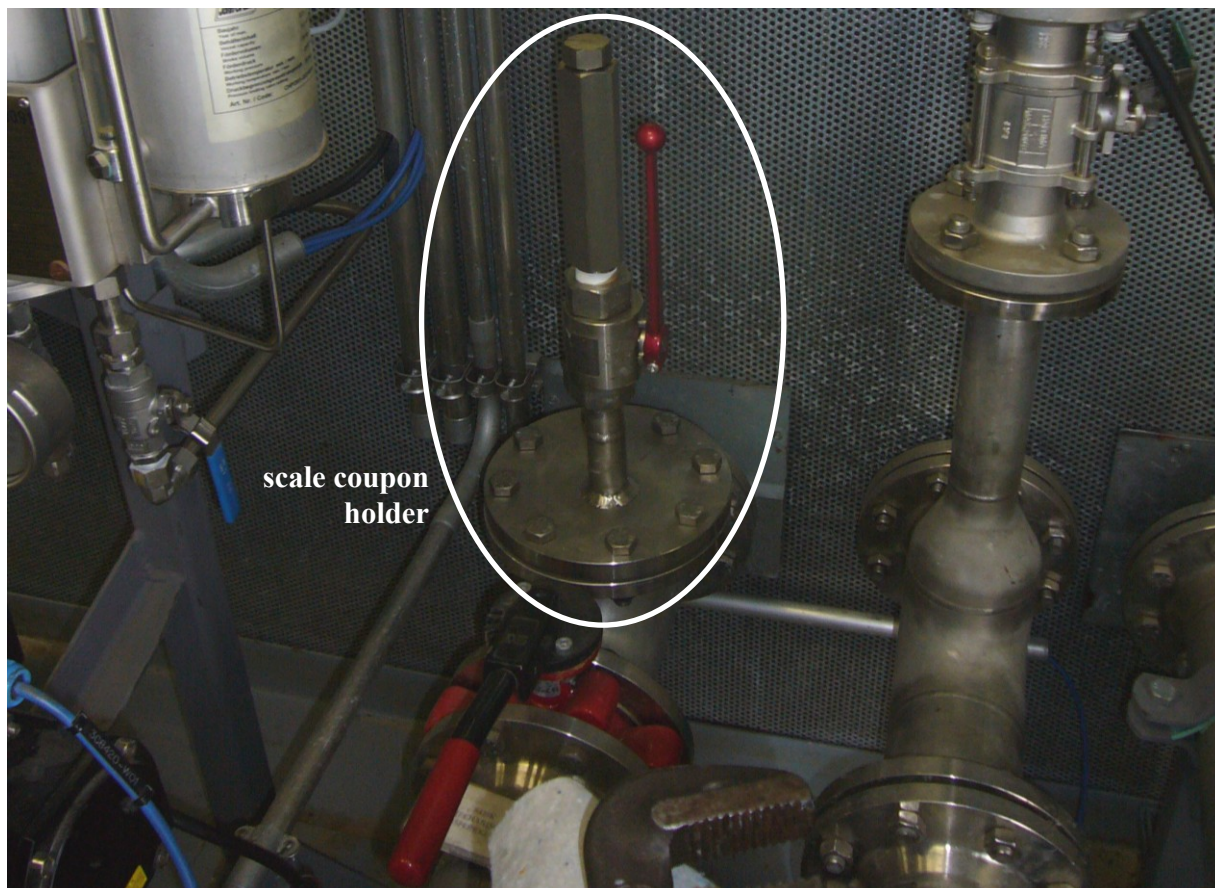


Figure 23: Flow behavior of an installed scale coupon



Picture 13: Scale coupon holder installation at VW-009 (pre-pressurization module)

5.2 Evaluation of installed scale-coupons

5.2.1 First examination after 15 days

The scale coupons were activated and built-in on the 8th of September 2010. A first check was carried out on September 23rd. The optical examination of the three coupons showed no results, since none of the holes of any coupon was blocked by scale precipitations (see Picture 14, Picture 15 and Picture 16).



Picture 14: Scale coupon of producer V-033 15 days after installation



Picture 15: Scale coupon of pre-pressurization module VW-009 15 days after installation

Although the coupon in Picture 15 shows no scale precipitations in any of its holes, the residual oil content of the water seems to be very high.



Picture 16: Scale coupon of VZ exit 15 days after installation (wiped clean with woven felt)

5.2.2 Second examination after 50 days

After a period of fifty days, on October 28th, the scale coupons were demounted again and checked visually for their second time. The only effect was that the top left hole of the V-033 coupon was blocked (sketch see Figure 24).

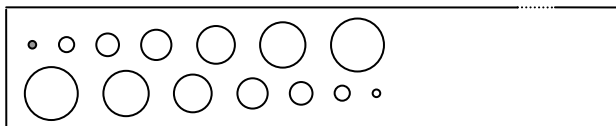


Figure 24: Sketch of the blocked scale coupon from V-033 after 50 days

5.3 Results of the examination

The examination of the built-in scale coupons proved that such short-time surveillance periods are insufficient for representative results. Nevertheless it is shown that scale precipitation occurs at V-033 despite the conducted scale inhibition. Together with the knowledge that this producer still needs workovers, to be acidized and treated with EDTA every half year, a reconsideration of the inhibition plans seems to be necessary.

Further evidence would require a longer and more detailed surveillance in terms of pressure and temperature at the single installation spots.

6 Chemical inhibition at RAG

6.1 General information

Currently, the inhibitor is added through the annulus by letting it drip down the outside of the tubing until it reaches the dynamic level of the well (see Figure 25). There, it is supposed to mix with the water of fluid after travelling through the top oil layer (compare 2.2, 2.3 and 2.4).

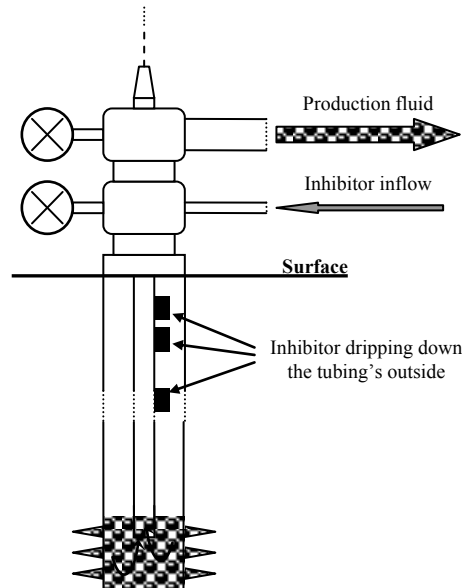


Figure 25: Inhibitor dosage schematic at RAG

6.2 De-facto dosage

Since there were problems determined in the Voitsdorf field, a dosage calculation was carried out based on the weekly chemicals' refilling reports of the field supervisors. For this purpose, the reported level change in the inhibitor containers at the producers was converted into liters and dispersed across the days between two checks. After consulting with the chief of staff, this calculation was carried out for the chemical application rate of seven weeks (calendar week 27 to 34), representing the warm ("summer") period of the year. After this, the data was adjusted by removing the values from those weeks, where the chemicals container was refilled or found empty. The removal was necessary due to the fact that it is not possible to determine for how many days the container was empty before it was refilled or its emptiness was detected by the field supervisor.

The average dosages are shown in 6.2.1, 6.2.2 and 6.2.3. Although it may spring to one's mind that in certain cases the dosage is way too high compared to the specifications in the product bulletins, it is necessary to keep in mind that this dosage has to be suited to the total flow rate for the Flotron CW511 (6.2.1) respectively the water production rate for the KI-350 corrosion inhibitor (6.2.3) and the SI-4041 scale inhibitor (6.2.2). Additionally it depends on the adjustability of the dosing pumps at the single producers. Since fine adjustable pumps are assessed with prices between €8,000 and €15,000 (depending on manufacturer, type, desired pump volume, rate and other technical specifications), they are definitely too expensive to be set up at oil wells with a total production of only a few cubic meters per day. Therefore pumps already available at RAG were installed, which could not pump such small amounts of inhibitor liquid.

Therefore, for certain producer-inhibitor-combinations it may seem that the inhibition is kept overdosed, but a change would be non-profitable. Plus, due to the small total amount of pumped inhibitor the loss from over-dosage seems negligible.

6.2.1 Average paraffin/corrosion inhibitor dosage – Champion Technologies Flotron CW511

Well code	Average q_{Total} [m ³ /d]	Average dosage [ppmv]	Average dosage [l/d]
BH-002	3.0	774.3	2.3
BH-003	23.5	201.7	4.7
BH-004	44.3	173.9	7.7
V-043		shut-down ^{xx}	
BH-N-001	5.0	553.3	2.8
EB-006	13.3	54.0	0.7
EB-007	5.3	314.7	1.7
EN-005A	47.0	156.7	7.4
EN-006-A	2.9	209.3	0.6
HIER-001	72.1	225.4	16.3
HIER-002A	34.1	418.7	14.3
HIER-004	66.1	224.8	14.9
MDF-001-A	2.1	458.0	1.0
RA-002	0.8	600.4	0.5
SAT-002	6.5	507.3	3.3
SAT-007	3.9	533.8	2.1
V-021	3.7	155.5	0.6

Although the dosage of the paraffin/corrosion inhibitor is exceeding the upper threshold of 300ppmv in several cases, in terms of total daily injected volume it is negligible. Only the producer HIER-002A is both exceeding the threshold and consuming more than a few liters per day. Due to the fact that the well is producing 33.9m³/d pure oil – total production 34.1m³/d with a water cut 0.3%²⁵ – this high dosage is well accepted as necessary by RAG.

According to the manufacturer, there are no records showing that over-inhibition shows any negative side effects concerning the properties of the fluid with the inhibitor added.

6.2.2 Average scale inhibitor dosage – MI-SWACO SI-4041

Well code	Average q_{Water} [m ³ /d]	Average dosage [ppmv]	Average dosage [l/d]
OB-001	50.7	20.3	1.0
SAT-006	33.1	18.4	0.6
SAT-008	12.0	49.9	0.6
SAT-010	2.1	389.5	0.8
STHS-006	17.8	24.7	0.4
V-011	14.2	36.7	0.5
V-013-A	22.5	24.0	0.5
V-015-C	222.5	15.0	3.3
V-019	1.1	121.8	0.1
V-030	235.2	16.3	3.8
V-033	202.8	17.0	3.4

Although the scale inhibitor in use is sensitive of over-dosage, here as well the total average dosage has to be kept in mind. Although a critical exceeding of the maximum dosage of

^{xx} Due to expansion and work-over of producers in the Bad Hall area i.e. BH-004 and BH-010

50ppmv can cause a reverse effect – formation of depositions instead of their inhibition – the effective over-dosage is so small that it can be considered negligible.

6.2.3 Average corrosion inhibitor dosage – MI-SWACO KI-350

Well code	Average q_{Water} [m ³ /d]	Average dosage [ppmv]	Average dosage [l/d]
OB-001	50.7	91.9	4.7
SAT-006	33.1	72.7	2.4
SAT-008	12.0	136.6	1.6
SAT-010	2.1	950.5	2.0
SAT-023	34.2	44.2	1.5
STHS-006	17.8	47.7	0.9
V-011	14.2	45.6	0.6
V-013-A	22.5	83.1	1.9
V-015-C	190.7	44.7	8.5
V-016		shut-down ^{XXI}	
V-019	1.1	241.6	0.3
V-030	163.1	49.3	8.0
V-033	202.8	28.3	5.7

According to the manufacturer, there are no records showing that over-inhibition of the KI-350 shows any negative side effects concerning the properties of the fluid where the inhibitor is added.

6.3 Laboratory testing of inhibitor mixtures

6.3.1 Background information and intention

Since the main issue of this thesis is the behavior and mutual influence of the three types of inhibitors, their potential precipitation behavior was investigated at different temperatures. For this, different mixing simulations were carried out in the laboratory with the intention not only to determine whether there exists an interaction of the three inhibitors, but also mapping the temperature ranges where these interactions could accrue (see Chart 30).

Temperature	Location
5°C	during underground transport
20°C	when mixing in the manifold, production or water treatment system
90°C	downhole in a stopped producer with the injection system still operating

Chart 30: Temperature and locations for occurrence of potential interactions and their effects

An initial testing period of 96 hours at each respective temperature was designated for every temperature. This period was chosen after due consideration with the aim

- to be long enough for potential interactions and/or precipitation to form out with sufficient severity,
- to be still short enough to be completed without distorting effects possibly showing up from i.e. possible impurities or other laboratory users and
- to keep the experiments short enough for the used test jars to withstand the temperatures.

If any of the initial mixture sets would show any optically recognizable signs of interaction, such as i.e. solids precipitation, it was the plan to repeat this test for redundancy purposes.

^{XXI} Shut-down at federal mining authority's disposition

6.3.2 Dosage selection for the inhibitor mixtures

The following dosages were prepared based on the de-facto dosages in 6.2:

- Flotron CW511
 - 0 ppmv,
 - 50ppmv (for lower threshold resp. under-dosage),
 - 150 and 300ppmv (both representing the recommended manufacturer range respectively the currently applied dosage) and
 - 500ppmv (exemplary for over-dosage)
- SI-4041
 - 0ppmv,
 - 20ppmv (lying within the recommended manufacturer range),
 - 100 and 200 ppmv (representing two different over-dosages occurring in the field)
- KI-350
 - 0ppmv,
 - 50ppmv (representing the recommended dosage),
 - 100ppmv (representing a higher range, frequently found in the field),
 - 200ppmv (overdose)

Under-dosage can occur when the waters of different production streams mix in the manifold or later, i.e. in the water treatment system, especially when mixing with not or insufficient inhibited water streams. Effects of over-dosage (see p. 61) are also possible when the chemicals leave their containers and are pumped towards the well-head, since they share the injection line at the producer, or when production streams from different wells and/or manifolds merge in the separator of a station.

6.3.3 Preparation of the inhibitor mixtures

For each temperature, a large batch of salt water with a salinity of 15,000mg pure sodium chloride per liter was prepared. From this salt water reservoir small sub-batches of an approximate volume of one liter were prepared with the concentrations given in 6.3.2 oben. Since every inhibitor mixture would be diluted with the water from the other two inhibitor mixtures, every dosage was necessarily tripled to compensate the dilution caused by the other two ingredients. The available sample jars consisted of a transparent body with a white screw-on lid (compare 6.3.4.1, 6.3.4.3, 6.3.4.4 and 6.3.4.5). In each jar 10ml of every mixture were pipetted – if one inhibitor’s dosage was zero, 10ml of pure salt water from the original large batch were added. After this, all jars were screwed tight, well shaken on the laboratory shaking device – 200 times per minute for a period of ten minutes – and then stored at the corresponding temperatures. To avoid separation of the inhibitor mixtures due to their different densities they were repeatedly shaken throughout the day. After the experiment’s period of 96 hours, the samples were checked for the various degrees of haze (see 6.3.4).

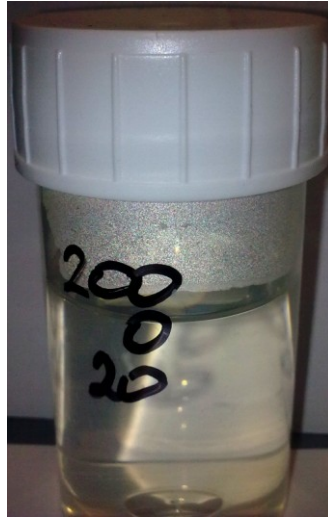
6.3.4 Optical evaluation of the severity of mixture effects

The initial mixture sets stored at 5°C and 20°C for 96 hours showed no effects and remained clear, whereas the mixtures at 90°C showed already hazes and precipitations in the first run. Therefore two more sets very prepared and the experiment was repeated. All three “hot-sets” were compared according to their haze and the worst concentration combinations were evaluated by a weighing system. Samples for each optical classification and their respective description are given in the following sub-chapters. On every jar in the pictures Picture 17, Picture 18, Picture 19, Picture 20 and Picture 21, the upper number is the concentration of KI-350, the middle number is the concentration of Flotron CW511 and the lower number gives

the concentration of SI-4041. If any of these numbers equals Zero, this part of the mixture was replaced with pure salt water.

6.3.4.1 Clear

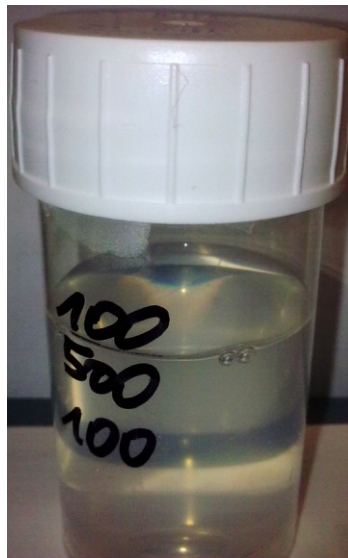
The majority of all inhibitor mixtures did not show any haze or precipitation. For comparison there is also a picture given below (Picture 17).



Picture 17: Clear liquid (KI-350: 200ppmv, CW511: 0ppmv, SI-4041: 20ppmv)

6.3.4.2 Weak haze

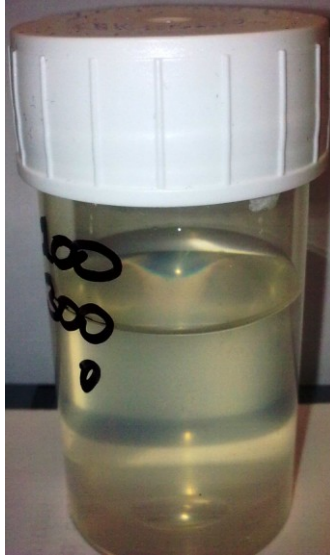
In this case, it is still possible to look through the sample jar, but the liquid inside is blurred. Nevertheless, contours of objects behind the sample in the transparent sample jar still appear recognizable.



Picture 18: Weak haze (KI-350: 100ppmv, CW511: 500ppmv, SI-4041: 100ppmv)

6.3.4.3 Strong haze

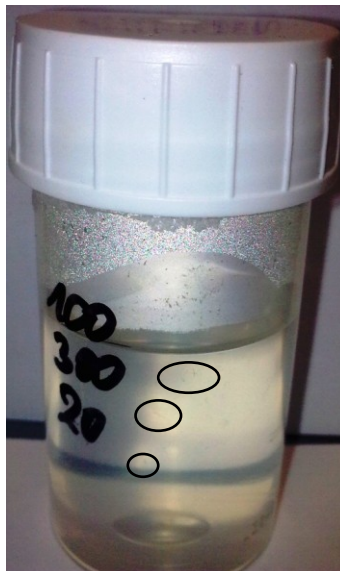
Here it is not possible anymore to look through the fluid. The mixture's haze inside the sample jar makes objects behind the sample appear not anymore clearly visible (note the black stripe below the number "0" in Picture 19 and compare its visibility with the one behind the number "100" in Picture 18).



Picture 19: Strong haze (KI-350: 200ppmv, CW511: 300ppmv, SI-4041: 0ppmv)

6.3.4.4 Streaks

These looked like small amounts of gasoline floating in water and are therefore very difficult to be photographed. Their occurrence is marked with black ellipses in Picture 20 unterhalb.



Picture 20: streaks (KI-350: 100ppmv, CW511: 300ppmv, SI-4041: 20ppmv)

6.3.4.5 Precipitations

Precipitations occurred mostly in the shape of very fine, almost transparent fibers of approximately 1-2mm length, going together with a very strong haze of the sample's liquid.



Picture 21: Precipitations (KI-350: 200ppmv, CW511: 150ppmv, SI-4041: 200ppmv)

6.3.4.6 Mixing of concentrated inhibitor liquids

The only effect seen in this experiment was that the paraffin/corrosion combination CW511 and the corrosion-only inhibitor KI-350 mix very well with each other due to their similar density. When scale inhibitor SI-4041 was added, a phase separation was visible. The lower part (see Picture 22) originates presumably in the heavier components of the scale inhibitor, whereas the upper part comes from the scale inhibitor's more volatile parts and the other two inhibitors. Due to the crack in the top section of the lid, a part of the volatile components evaporated. This crack occurred during the jar's stand-time in the oven. Nevertheless, no mixing problems were encountered when looking at the mixtures of pure inhibitor liquids.



Picture 22: Mixture of concentrated inhibitor liquids (KI-350, CW511 and SI-4041)

6.3.4.7 Rating

Since the sets exposed to 5°C and 20°C showed no effects, Chart 31 and Chart 32 shows only the effects from three “hot-sets” exposed to 90°C.

All three runs were evaluated and categorized. For better assessability each severity was assigned a certain value. These values were:

- 0: Equals CLEAR (see 6.3.4.1, for better readability left blank in the tables below)
- 1: Equals WEAK HAZE (see 6.3.4.2)
- 2: Equals STRONG HAZE (see 6.3.4.3)
- 3: Equals STREAKS (see 6.3.4.4)
- 4: Equals PRECIPITATIONS (see 6.3.4.5)

In the columns “check sum” in Chart 31 and Chart 32 the sums of the values converted from the three runs’ results were calculated. These check sums were intended as “total” parameters for the results of all three runs. The main intention was to find concentration combinations with sufficient effect severity. For the later filtration experiments (see 6.3.6 unterhalb) the initially predefined criterion was whether the severities of any of the inhibitor mixtures would reach a check sum equal to 9 or above. This would mean according to the ranking oben that the mixture showed problems equaling at least three times the severity of STREAKS.

Since this was never the case, the prioritization was carried out based on the check sum and its single factors.

This meant that

- the check sum of all three test series was equal or higher than 7 or
- the mixture showed once PRECIPITATIONS (value of 4) with a check sum equal or larger than 6 or
- at least two times STREAKS (value of 3) with a check sum equal or larger than 6.

An optical re-evaluation of the jars after their according-to-plan stay in the oven showed that the mixing effects were reversible independent of their severity degree. This effect was noticed for every “hot-set”, therefore it was decided that the following filtration experiments for determining the WBF of the worst mixtures could be carried out at room temperature, equaling roughly the temperature inside a separator at the collecting station.

KI-350 [ppmv]	CW 511 [ppmv]	SI-4041 [ppmv]	1 st run	2 nd run	3 rd run	check sum	priority
0	0	0					
0	0	20					
0	0	100					
0	0	200					
0	50	0					
0	50	20					
0	50	100					
0	50	200					
0	150	0	1		2	3	
0	150	20	1	1		2	
0	150	100	2	2		4	
0	150	200	2	1	1	4	
0	300	0					
0	300	20					
0	300	100					
0	300	200		1	1	2	
0	500	0	1	1		2	
0	500	20		1		1	
0	500	100		2		2	
0	500	200	4	2		6	4c
50	0	0					
50	0	20					
50	0	100					
50	0	200					
50	50	0	3	3		6	
50	50	20	4		3	7	2
50	50	100					
50	50	200			3	3	
50	150	0	4		1	5	5
50	150	20	3	3		6	6
50	150	100	2	1	1	4	
50	150	200	2	1	1	4	
50	300	0					
50	300	20			2	2	
50	300	100	2	2	2	6	
50	300	200	2	1	2	5	
50	500	0					
50	500	20		1		1	
50	500	100					
50	500	200			2	2	

Chart 31: Result prioritization of "hot-sets" - pt. 1 of 2

KI-350 [ppmv]	CW 511 [ppmv]	SI-4041 [ppmv]	1 st run	2 nd run	3 rd run	check sum	priority
100	0	0					
100	0	20					
100	0	100			1	1	
100	0	200	1		1	2	
100	50	0	3		3	6	
100	50	20	3	1		4	
100	50	100	1	1		2	
100	50	200	1			1	
100	150	0	4	1	1	6	4a
100	150	20	1	2	1	4	
100	150	100	4	2		6	4b
100	150	200	1	1	1	3	
100	300	0			2	2	
100	300	20		1	2	3	
100	300	100	2	2	2	6	
100	300	200	2	2	2	6	
100	500	0			2	2	
100	500	20			1	1	
100	500	100		1	2	3	
100	500	200	2	2	2	6	
200	0	0	1	1		2	
200	0	20					
200	0	100	1		1	2	
200	0	200	4		1	5	
200	50	0	1	1		2	
200	50	20	1	1		2	
200	50	100	1		1	2	
200	50	200	1			1	
200	150	0	3	2	1	6	
200	150	20	4	2	1	7	1
200	150	100	1	2	1	4	
200	150	200	1	2	1	4	
200	300	0		4	2	6	7
200	300	20		1	2	3	
200	300	100	2	3	2	7	3
200	300	200	2	2	2	6	
200	500	0		3	2	5	
200	500	20			2	2	
200	500	100	1		2	3	
200	500	200	2	2	2	6	

Chart 32: Result prioritization of "hot-sets" - pt. 2 of 2

6.3.5 Injectivity evaluation – theory for WBF

Generally, the injectivity is given as a relation between flow rate and pressure through a medium (the “injectivity index” $\Pi=q/\Delta p_0$).

In the laboratory, this medium was a filter paper with a mesh size of $3\mu\text{m}$. Since in the laboratory the change in flow rate occurs very quickly, but the pressure was decided to be kept constant at 1.4bara, another characteristic was necessary to be introduced in order to compare different filtration abilities. This characteristic refers to the already filtered water amount over time in comparison to the maximum water amount, is called the “water blocking factor (WBF)” and was adopted from the laboratory of OMV²⁶.

$$V_{iw}(t[\text{min.}]) = \frac{2813*(1-e^{-\text{WBF}/t[\text{min.}]})}{\text{WBF}}, \text{ where}$$

- t[*min.*] ... time in minutes
- $V_{iw}(t)$... injected water volume at time t in [ml]
- 2813 ... empirically determined correction factor
- WBF ... water blocking factor.

The WBF is evaluated via the Microsoft Excel Solver through the “method of least squares”²⁷ and is the sum of the differences between the data points representing the already filtered water amount and the total filtered water amount. Both curves are also compared graphically with each other for equal area between their intersection and beginning resp. end (for example see Figure 26).

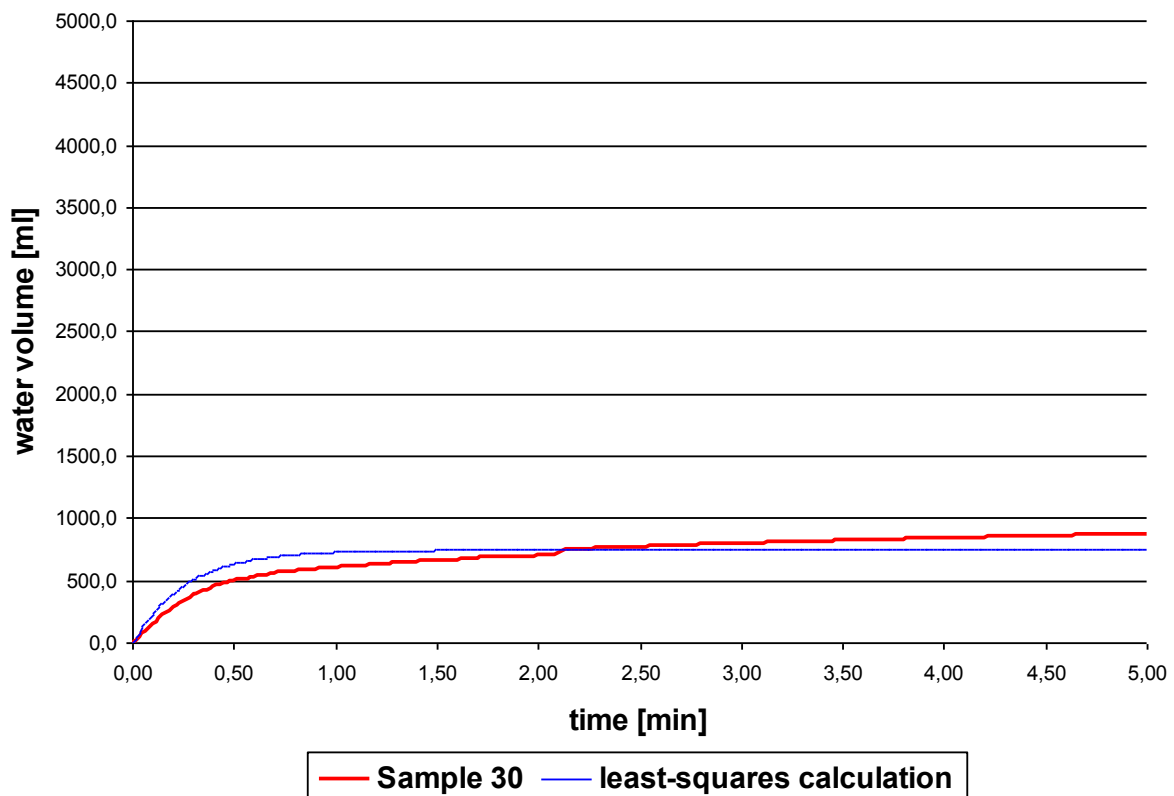
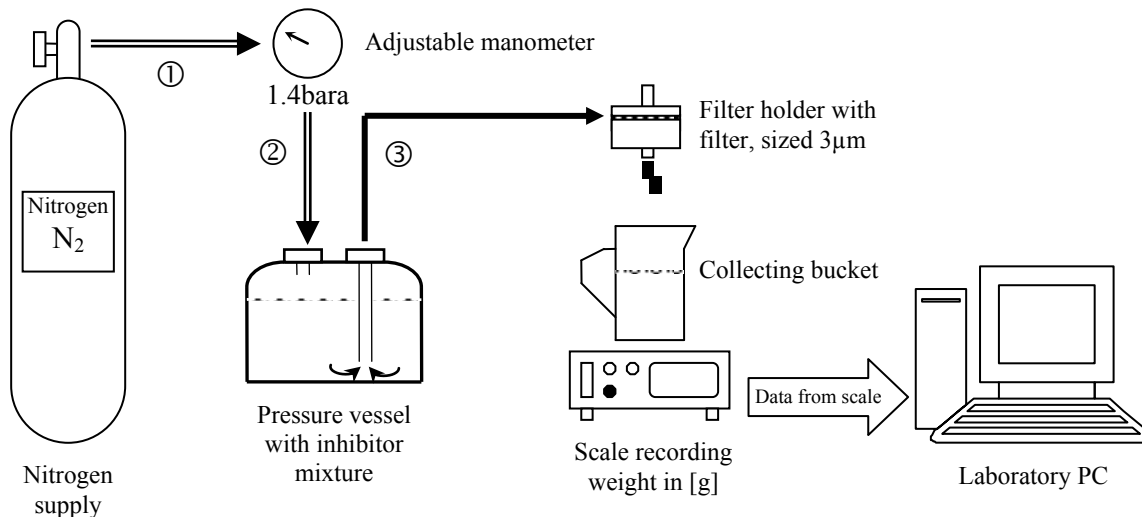


Figure 26: Example for WBF evaluation^{XXII}

^{XXII} Data source: sample #30, 2010-10-08 at 7:30 a.m., VZ exit

6.3.6 Experimental set-up and procedure

To provide comparable results for the measurements, the following experimental set-up was used:



- ①... Permanent nitrogen supply line from nitrogen bottle outside the laboratory to manometer inside the laboratory
- ②... 1.4bar nitrogen line from manometer to pressure vessel (entrance valve labelled “ENTRANCE”)
- ③... Inhibitor mixture line from pressure vessel to filter holder (exit valve labelled “EXIT”)

Figure 27: Sketch of the experimental set-up

All valves of the pressure vessel start in closed position. The vessel is weighted empty, filled almost to the brim with distilled water and weighted again. Then the vessel is equipped with a stir bar and put on a magnetic stirrer. Next, enough sodium chloride is added to achieve a salinity of 15,000mg/l to simulate the properties of formation water. Into this solution the appropriate amount of inhibitor is pipetted under constant stirring to attain the desired inhibitor concentration. Then line ② from the manometer is connected to the pressure vessel which has to be closed with its air-tight lid before opening the manometer and the entrance valve. After a few seconds, the pressure in the vessel should have reached 1.4bara, as set and displayed on the manometer. In the next step a cleaned, weighted and dried 3µm-filter is mounted into its holder and connected to the pressure vessel via line ③. The filter needs to be fit into the holder under water to avoid air bubbles falsifying the result or hindering the filtration.

After connecting the filter holder with the vessel, the scale data transfer software OHAUS is started and a continuous data transfer from the scale to the laboratory PC is established with one value per second transferred.

When all lines are connected and the data transfer from the scale to the PC is established and running, then a countdown for five minutes is set and the exit valve of the pressure vessel is opened.

The water-inhibitor mixture is now pressed through the 3µm-filter; the scale is measuring the weight^{xxiii} and transferring it once per second to the PC, where it is recorded.

^{xxiii} Assumed to be proportional to the filtered volume (1ml≈1mg)

Two possibilities exist to end the experiment: a) The five minutes expire or b) more than 5liters from the pressure vessel are pressed through the filter.

After the filtration, the filter holder is dismounted and the filter is dried and weighted again. The water volume data is after its recording manipulated and copied into the draft MS Excel spreadsheet in order to determine the WBF. Then the Excel solver function is run and the WBF is sought.

6.3.7 Results of the experiments

The filtration was carried out according to the prioritization list acquired from Chart 31 and Chart 32. Additionally, two blind samples were prepared in order to have reference values for the WBF. The determined WBFs and the results from the filter weighting are given in Chart 33, the filtration curves are given in Figure 28 Seite 73.

priority	water [ml]	salt added [g]	inhibitor concentration [ppmv]			inhibitor volume added [µl]			WBF
			KI-350	CW-511	SI-4041	KI-350	CW-511	SI-4041	
0	6199.1	92.99	1 st blind sample			0	0	0	0.25
1	6105.6	91.58	200	150	20	1221	916	122	0.31
2	6231.2	93.47	50	50	20	312	312	125	0.32
3	6238.1	93.57	200	300	100	1248	1871	624	0.27
4a	6123.6	91.85	100	150	0	612	919	0	0.40
4b	6111.0	91.67	100	150	100	611	917	611	0.22
4c	6208.9	93.13	0	500	200	0	3104	1242	0.41
5	6157.2	92.36	50	150	0	308	924	0	0.32
6	6198.7	92.98	50	150	20	310	930	124	0.37
7	6150.9	92.26	200	300	0	1230	1845	0	0.34
8	6137.9	92.07	2 nd blind sample			0	0	0	0.35
priority	weight of filter and glass before/after filtration		mass difference [mg]	filtration volume [l]	filtrate [mg/l]				
	before [mg]	after [mg]							
0	13,018.64	13,021.58	2.94	5.5925	0.526				
1	13,012.57	13,015.82	3.25	5.3632	0.606				
2	13,012.97	13,016.48	3.51	5.2936	0.663				
3	13,001.77	13,004.05	2.28	5.5859	0.408				
4a	12,987.27	12,990.31	3.04	5.5240	0.550				
4b	13,008.85	13,012.70	3.85	5.4364	0.708				
4c	13,032.44	13,037.16	4.72	5.3980	0.874				
5	13,013.92	13,016.78	2.86	5.3729	0.532				
6	13,011.25	13,013.36	2.11	5.4020	0.391				
7	13,013.21	13,016.49	3.28	5.7011	0.575				
8	13,012.15	13,014.85	2.70	5.5629	0.485				

Chart 33: Determined WBFs and filtrate weights

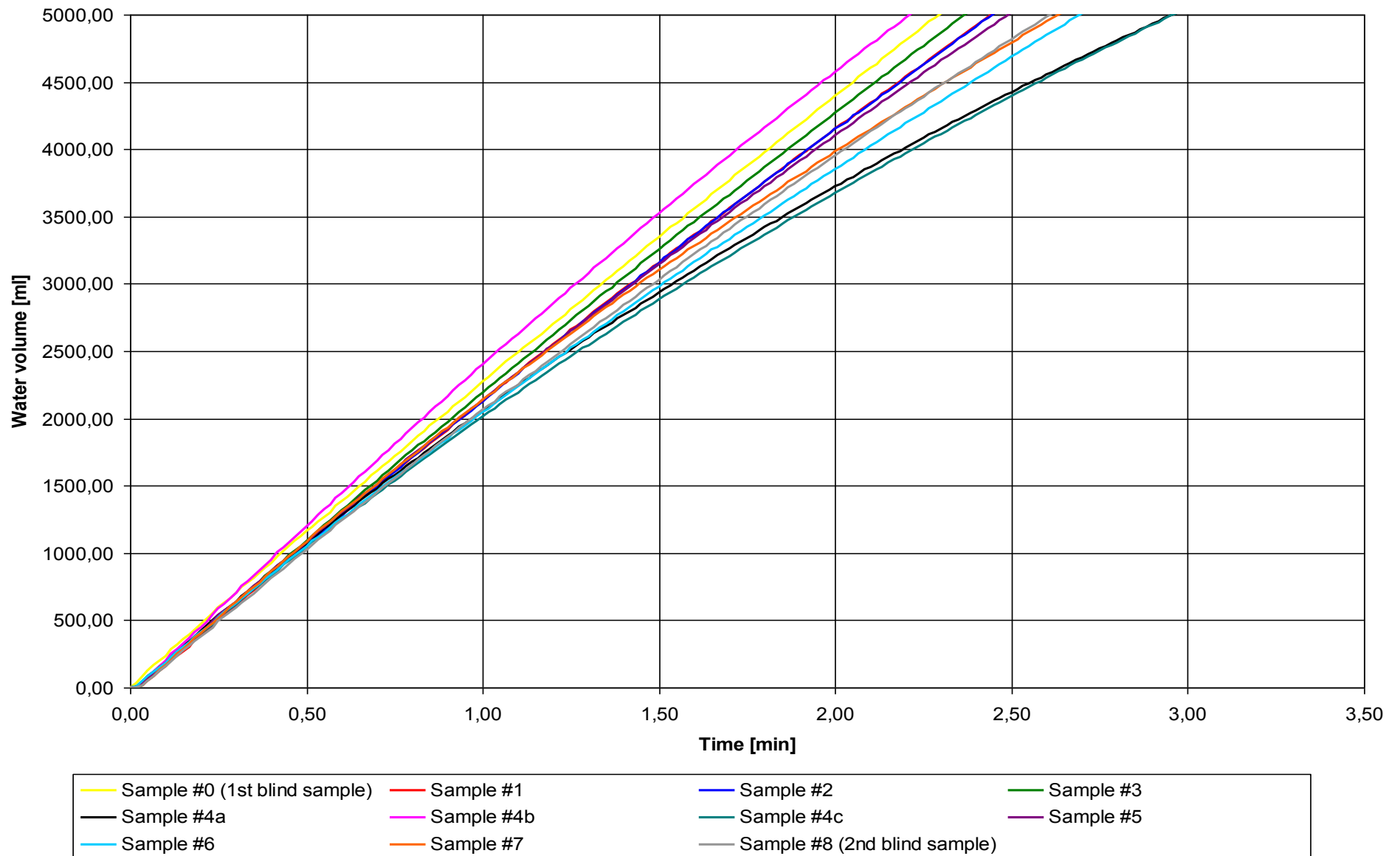


Figure 28: Filtration curves for the chosen inhibitor mixtures and blind samples

As visible from Figure 28 and Chart 33 oben, the WBF range and the filtration curves are very similar. ^{XXIV} Although the inhibitor mixture curves differ slightly from each other and the sample curves, their spread is acceptable small.

If the WBF values of the inhibitor mixtures are compared with the WBF values from the settling tank samples, these are differing from those at least by factor 8.4. Plus the inhibitor mixture WBFs from the experiments do not correspond with the severity according to the optical evaluation from 6.3.4.7 (see Figure 29), because in this case the WBF of the measured samples would increase with increasing sample number – except for sample #8, where it should drop to its initial value (example drawn as thick black solid line in Figure 29).

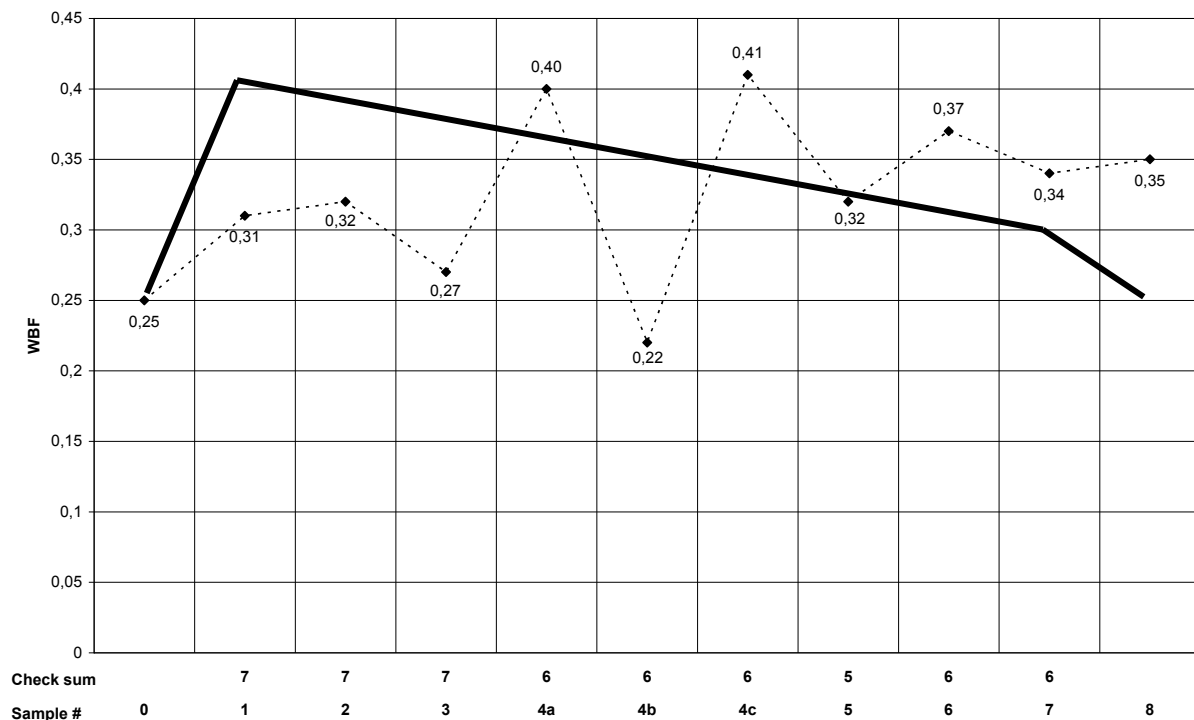


Figure 29: Comparison^{XXV} between measured WBFs and check sum from evaluation^{XXVI}

The combination of the facts above indicates that the mixing of inhibitors has a negligibly small share in the WBF and therefore the injectivity behavior of the flood water.

6.4 Electrophysical scale treatment with Weatherford ClearWell

6.4.1 Background information

Due to the especially unsatisfying results of the current scale inhibition at the wells STHS-006, V-013, V-015, V-030 and V-033, the companies MI-SWACO, Champion Technologies, Baker Hughes and Weatherford were contacted. Whereas MI SWACO, Champion Technologies and Baker Hughes suggested the continuation of the chemical inhibition, Weatherford came up with their developed device ClearWell, which intends to avoid the precipitation of scale on an electrophysical base.

^{XXIV} The WBF lines (as the one in Figure 26 on page 70) were not added in Figure 28 for reasons of better readability.

^{XXV} Sample 0: 1st blind sample, sample 8: 2nd blind sample

^{XXVI} Compare Chart 31 and Chart 32 on p. 68 and 69

6.4.2 Principle of work

The basic principle behind this device is very simple, already known for a while and adapted from household de-scaling devices. An alternating electric field with a frequency of 120 kHz is applied to a piece of metal reaching into the wellbore (usually the tubing, see Figure 30). Since the electric field disrupts the balance of the cations and anions in solution in the wellbore, they tend to form a compound amongst each other, causing scale to precipitate (“nucleation”, see also p. 3).

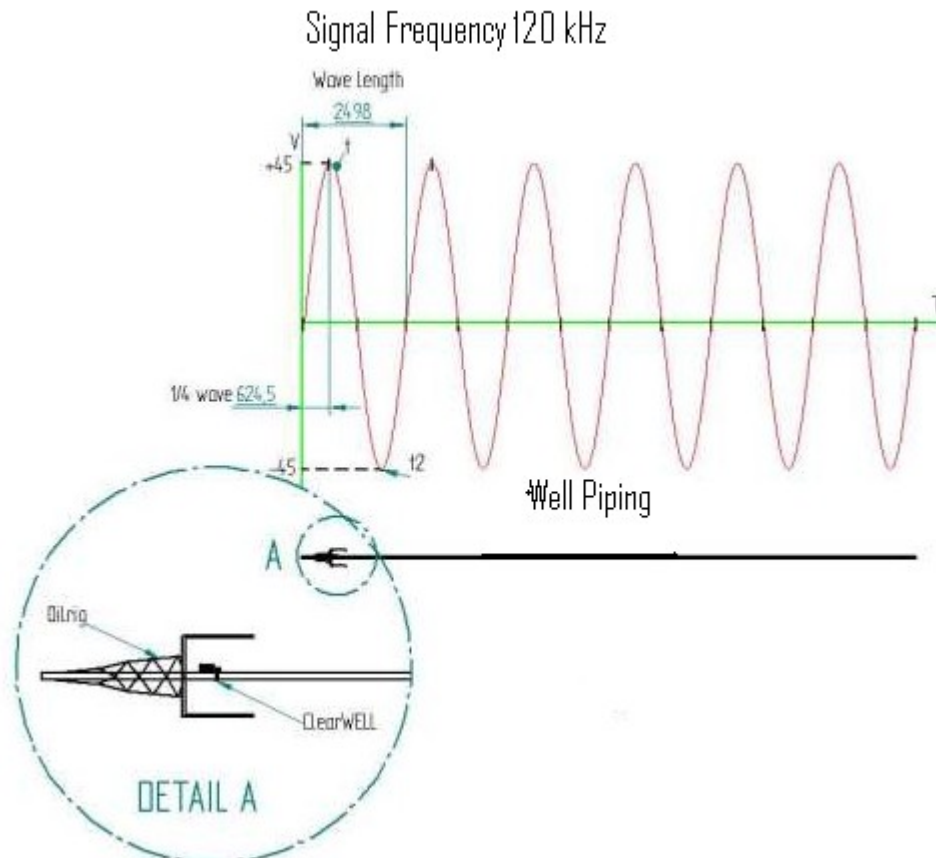


Figure 30: Sketch of ClearWell's signal transfer²⁸

The device is designed to extend an electric field in and around the tubing. In simple terms the electric field creates seed crystals held in suspension in the aqueous phase. These crystallites act as sites for other crystallites and ions to attach and grow rather than seeking nucleation sites on the tubing walls and creating a severe operating issue. In an oil or gas well using the PWT device, the scale is carried out with the produced fluids.²⁹

The advantage lies in the fact that the nucleation processes take place already downhole – small enough to be kept in suspension and to be transported to the top of the well – and the almost total ionic neutralization of the involved ions. This means that the ionic charge of the formed molecule is so low that it will experience no or only a very little growth phase. Plus it is less likely to attach to polar surfaces in the well, such as i.e. the tubing's inside surface, resulting in considerably less scale adhesion to the downhole installations.

6.4.3 Selection of wells

After a detailed consideration of the five most troublesome wells concerning scale precipitation, the two impeller producers V-030 and V-033 were selected. The main criterions were the total production rate and water cut, sufficient production data and surveillance

possibilities via RAG's process control system, and the clear advantage of impeller pump installations that the power cable of the downhole pump can be used for the transfer of the 120-kHz-signal without any losses due to i.e. tubing anchors, but protected by the cable's isolating coating.

As surveillance parameters the wellhead pressures and the intervals of the necessity of acidizing jobs with RAG acid mixture #4 and EDTA were chosen.

Since the results of these devices' installation are expected to be recognizable after at least six months, waiting for them to show their effects would have exceeded the planned duration of this thesis. Therefore herein only the function principle and reasons for the decision are given without the results.

7 Conclusion

The conclusions and recommendations listed below are the statements of the author based on the time spent at and around Voitsdorf central and the work carried out in this period. The selection and realization of these suggestions is solely the business of RAG.

The upstream of oil and gas is exposed to various changes of its physical parameters (i.e. temperature, pressure, velocity etc.) and chemical composition. Especially the treatment with the various oil field chemicals – intended for improving the producing conditions and solving potential problems – can cause side effects which shift the problems to a different level rather than solve them. Additionally workover jobs and stimulations add chemicals and residues to the upstream network which can also interact with the regularly applied oilfield chemicals.

Regarding the injectivity the conducted experiments showed that the inhibitor mixtures do not worsen the WBFs and therefore affect the injectivity behavior compared to the blind samples (see 6.3.7). Since the filtration behavior of the examined mixtures and samples was almost equal, it is suggested to be very unlikely that the mixture of inhibitor fluids causes negative effects in the later-on injection water (see Chart 33 on p. 72). However, the experiments were conducted in a very simplified way and without considering all influences due to the system's complexity. Here especially irregular, unpredictable or very difficultly includible influences such as i.e. pH value, temperature changes throughout the year, H_2S content, condensate deliveries or water from the tailings pond make an absolutely judging statement impossible. Nevertheless it is recommended to continue the measurements and analyzes of the water and a cross-linking with the registration of delivered fluids. To avoid further “contaminations” of the water injection system it is recommended to work out a solution to improve the waste water management.

To ensure the orderly arrival of the inhibitors pumped in at the well head, their transportation to the dynamic level needs to be improved. This could be achieved i.e. by refitting the currently applied dosage installations with capillary strings down to the wellbore or via flushing the chemicals down with a part of the already produced fluid. Also the forming of so-called “hot spots” – places where chemicals (both pure and diluted) can accumulate in a high-temperature environment – should be avoided in order to prevent mixing effects (see 6.3.4 ff). This would not only ensure that the applied inhibitors reach the wellbore, but also hinder the concentrated inhibitor of direct contact with the tubing's outside. Precipitations in these aforementioned “hot spots” could also serve as nuclei for paraffin, asphaltene or scale precipitations. These steps would serve as a countermeasure to the precipitation of deposits and/or potential corrosion effects caused from long-term contact of pure inhibitor liquid with steel (see 4.3 ff.).

A special eye has to be kept on the three wells V-015, V-030 and V-033 with their high water cut and production. Such producers usually are responsible for the major part of scale problems by contributing large amounts of scale-forming ions to the overall water system. The wells V-015, V-030 and V-033 also contribute the largest part of iron ions to the system (see Chart 14 and Chart 15). Since – contrary to the hitherto belief – the analyzed production water also contains a severe fraction of sulfate ions, the hypothesis that carbonate scale is responsible for the scale problems is hereby refuted. The evidence of the sulfate's existence is only a first step on the corresponding track: water analyzes on a regular basis for every well with a sufficient water cut. Based on these analyzes' results a diligent inhibitor selection is recommended specifically fitted to the well's scaling tendency. To monitor the efficiency of

the newly selected inhibitors, the producers should be equipped with scale coupons and long-term records regarding the scaling tendency should be kept. Also an eye should be kept on alternatives to chemical scale inhibition like i.e. devices like the Weatherford ClearWell in 6.4, which are intended to provide not only scale deposition, but also help to avoid side effects as the “hot spots” (Seite 77 oben). For wells with high scale tendency and therefore high inhibitor consumption it is recommended not to let the monitoring of the inhibition interrupt in order to ensure constant supply with chemicals. This could be achieved i.e. by checking the inhibitor liquid level in the storage containers at the well twice a week instead of only once and pre-calculating the remaining time before the storage container at the well site is emptied.

Since several times an incident with a quality reduction of the delivered inhibitors was reported, it is suggested to test both the incoming inhibitor deliveries as well as the concentration of inhibitor in the co-produced formation water. This test should also be suitable to provide information about the residual concentration of inhibitor liquid in other waters, such as i.e. the water of the settling tank or at the injector well. The intention would be to answer the question “Does the inhibition sustain throughout the whole system from the producer to the injector with sufficient dosage?” This would require a business cooperation between RAG and the several inhibitor suppliers after the well-by-well selection of the optimal inhibitor.

References

- ¹ L.B. Magoon and W.G. Dow, “The Petroleum System – from Source to Trap”, AAPG Memoir 60, Tulsa, OK, USA; 655pp.
- ² Malcolm A. Kelland, “Production chemicals for the oil and gas industry”, CRC Press Taylor & Francis Group, ISBN 978-1-4200-5 (Hardback), p. 54
- ³ See 2, p. 54
- ⁴ Dr. Charles C. Patton, president of C.C. Patton & Associates, Inc., “Applied water technology”, Campbell Petroleum Services, ISBN , p. 57
- ⁵ See 4, p. 54
- ⁶ Wayne W. Frenier and Murtaza Ziauddin, “Formation, Removal and Inhibition of Inorganic Scale in the Oilfield Environment”, SPE Society of Petroleum Engineers, ISBN 978-1-55563-140-6, p. 28
- ⁷ See 2, p. 55
- ⁸ See 4, p. 58
- ⁹ See 4, p. 64
- ¹⁰ See 2, p. 56
- ¹¹ See 6, p. 39
- ¹² See 5, p. 40
- ¹³ <http://webmineral.com/data/Maghemite.shtml>
- ¹⁴ DI Dr. Markus Oberndorfer, „Metallurgy and corrosion for petroleum engineers” lecture script (summer term 2010), Chair in General and Analytical Chemistry MU Leoben, course number 120.023, p. 46
- ¹⁵ J.R. Becker. “Corrosion and Scale Handbook”, PennWell Corporation, ISBN 0-87814-749-7, p. 58
- ¹⁶ <http://www.meps.co.uk/Stainless%20Price-eu.htm> (Date of check: 23rd of November 2010)
- ¹⁷ <http://www.meps.co.uk/EU%20price.htm> (Date of check: 23rd of November 2010)
- ¹⁸ Klaer Ralph-Harry and Mönning Wolfgang (Editors), “Praxis-Handbuch Industriearmaturen 2003”, Vulkan Verlag GmbH, ISBN 3-8027-2729-0, 2003, p. 151 (Translation from German into English by myself)
- ¹⁹ U.S. Department of Energy, “DOE FUNDAMENTALS HANDBOOK CHEMISTRY Module 2 Corrosion”, DOE-HDBK-1015/1-93, 1993, p. 15
- ²⁰ <http://www.glossary.oilfield.slb.com/Display.cfm?Term=scale%20removal>
- ²¹ See 2, p. 59
- ²² See 2, p. 59
- ²³ See 2, p. 201
- ²⁴ Caproco International Corrosion Monitoring Specialists “Special purpose coupons & coupon holder assemblies”, <http://www.caproco.com/catalog/pdf/Coupons-Holders/Corrosion-Coupons/Special-Purpose-Coupons-Holder-Assemblies.pdf>, p. 1
- ²⁵ RAG well test, 2010-06-08
- ²⁶ Erich Panzer, „09-09-10 VZ-Ausgang_Injektivität Eigenschaften.xls“, OMV Aktiengesellschaft, generated Wednesday, March 09, 2005
- ²⁷ Ao. Univ.-Prof. Mag. et Dr.rer.nat Clemens Brand, “Computing in technics” lecture script (summer term 2004), Chair of Applied Mathematics MU Leoben, course number 170.151, p. 55
- ²⁸ Lawrence Rzeznik and Michael Juenke, Weatherford International; Daniel Stefanini, Hydropath Holdings; and Martin Clark and Paolo Lauretti, MSL Oilfield Services, “Two Year Results of a Breakthrough Physical Water Treating System for the Control of Scale in Oilfield Applications”, SPE International, SPE 114072See 29, p. 7
- ²⁹ See 28, p. 2