Master Thesis

Solving Scale Problems in Oil- and Gas Industry

T. Huong Pham

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

Affidavit

Herewith I declare in the lieu of oath that this master thesis is entirely of my own work using only literature cited at the end of this volume

(T. Huong Pham)

Vienna, September 2007

Dedication

To Azizam mane

Acknowledgements

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Table of Contents

List of Figures

List of Tables

Kurzfassung

Scale übersetzt bedeutet Kesselstein und ist im Prinzip nichts anderes als eine Kalkablagerung. Diese Ablagerungen entstehen wenn hartes Wasser verdunstet oder erhitzt wird. Dabei entweicht Kohlendioxid und das gelöste Kalziumhydrogenkarbonat wandelt sich in das unlösliche Kalziumkarbonat (=Kalk). In einem normalen Haushalt können diese Ausfällungen meistens mit Essig oder verdünnter Zitronensäure erfolgreich entfernt werden.

In der Erdölindustrie verursacht dieses Problem Jahr für Jahr Verluste im Wert von mehreren Billionen von U$ Dollars. Scale ist insofern ein Thema, da es bei der Produktion von Kohlenwasserstoffen zu einer Reihe von Temperatur- und Druckänderungen kommt, die die Bildung von Scale bewirken und/bzw. verstärken können. Durch Scale verursachte Ablagerungen führen zu einem Produktionsverlust, da Leitungen und Separatorenzu- und ausgänge innerhalb kürzester Zeit zuwachsen können und somit den Durchfluss nicht mehr gewährleisten können.

Scale kann auf zweierlei Arten entfernt werden: mechanisch oder chemisch. Oft ist auch eine Kombination der beiden Methoden notwendig. Welche Methode schlussendlich angewendet wird, hängt hauptsächlich von der Scaleart ab.

Diese Arbeit soll dem Leser einen Einblick in die Scaleproblematik und möglichen Behandlungsmethoden geben. Teil der Arbeit ist es auch durch ein Screeningverfahren verschiedene Scale Inhibitoren aus dem Global Tender der OMV die besten und effizientesten Produkte zu identifizieren, die auch bei verschiedenen Bedingungen einsetzbar sind. Getestet wird mit Wasserproben aus Libyen, Österreich und Rumänien.

Im Anschluss an die dynamischen Tests sollen mit einem Scale Vorhersagemodell, bzw. Computer Programm, mögliche Ausfällungen berechnet werden, um die Endresultate vergleichen zu können.

Abstract

Limescale is a well-known term, since it occurs everywhere, where water is processed, i.e. water is heated up or evaporated. It precipitates out of hard water, whereas carbon dioxide outgases leading to formation of insoluble calciumcarbonate. In a normal household, these precipitations can be easily removed by using vinegar or diluted citric acid.

In oilfield industry, the problems with precipitations cause a loss of billions of US dollars every year. Scale is a problem, since the production of hydrocarbons is connected with a series of temperature and pressure changes, which can initiate and/or aggravate the formation of scale. Precipitations can lead to a production loss, since the effective line diameter in general and also those from and to the separators is reduced and thus reducing the production rate.

Removing of scale is based on two methods: mechanical and chemical. Often there is combination of these two methods necessary. However, which one of the method is taken, depends in the end mainly on the type of scale occurring.

The purpose of this work is to introduce the reader into the scale problem and its handling. Another part of this work is to do a screening of scale inhibitors, taken out of the Global Tender from OMV. Aim of the screening is to find out the best and most efficient scale inhibitors, which can be used under different conditions. The screening should be done with water samples from Libya, Austria and Romania.

Subsequent to the dynamic tests, predictions of possible precipitations should be done with a scale prediction software. In doing so, the results achieved from the tests can be compared with those from the calculations.

1 Introduction

Crude oil production is not just a simple matter of drilling a hole in the earth's crust, tapping a pool of oil and gas, and allowing the gas pressure to push up the oil. [1]

Often the intervals of interest consist of highly compressed and dense reservoir rock sandwiched between rocks of even greater density, thus making the whole process a little bit complicated.

Crude oil or also called petroleum comes from the Greeks and is split into two words, whereas *petro* means rock and *oleum* means oil. So, it's no wondering that in its strictest sense, petroleum includes only crude oil, but however, petroleum includes both crude oil and natural gas. [2]

Petroleum was found several thousand years ago when it came to the surface due to its light density. In Mesopotamia, people used petroleum, which came to the surface as sealing for their boats by mixing with other materials. Petroleum was also used for lightening or as weapon in wars. Even the walls and towers of Babylon were constructed by using petroleum as asphalt.

It was only a matter of time when the first oil well was drilling. This happened in China in the 4th century or even earlier. These wells had depths of about 800 ft and were drilled using bits attached to bamboo poles, which in fact was based on the principle of percussion. The first modern oil well was drilled in 1848 in Baku, the capital of Azerbaijan.

Significant oilfields had been discovered in Canada (1910), the Dutch East Indies (1885, Sumatra), Iran (1908), Peru, Venezuela and Mexico. The currently top three oil-producing countries are Saudi Arabia, Russia and the United States, whereas about 80% of the accessible reserves are located in the Middle East.

However, this thesis will give a detailed insight into problems in producing and refining petroleum, especially scale problems.

This thesis will focus on the carbonate scale problem since it is the most common type of scale in the fields operated by OMV. Nevertheless, other scale types will also be shortly explained and described.

1.1 Problem Definition

Water plays an important role in every stage of oilfield life. This starts with evaluating the oil-water contact for determining the oil-in-place and goes through development, production and abandonment.

When considering the worldwide daily water production that goes hand in hand with the oil production, on the first sight it seems that some oil companies are water companies. According to an article from the year 2000 the relationship between the daily produced oil and accompanying water is roughly 1:3, i.e. production of one barrel oil goes hand in hand with three barrels of water. Speaking worldwide, this would mean that about 225 million barrels of water are produced for every 75 million barrels of oil. When considering the costs of water treatment - about 5 to 50 cents per barrels of water – the treatment of 210 million barrels water per day every year would give an average cost of about 22.6 Billion $/year. Besides, this high water cut can cause serious problems concerning every stage of oil production. [3]

Production of petroleum hydrocarbons from underground formations accompanies the production of varying amounts of formation or connate water. The ratio of this produced water to produced hydrocarbon changes over the lifetime of a well. Very often, the oil well production fluids are composed of 90% or more of water and only 10% or less of crude oil. Oilfield produced water contains a diverse mixture of compounds that varies from formation to formation. [3]

Everyone has experience with scale, either as white layer in water kettles or as depositions that clog the washing machine. Therefore, it is clear, that these depositions will hinder the flow of whatever. Moreover, it is the job of a petroleum engineer to avoid or reduce such depositions by mechanical or chemical treatment.

The present thesis will give a detailed insight into the process of scale formation and how it can be prevented and removed. The focus will be on chemical inhibition, since it is part of the work to do an inhibitor screening to find out the most favorable one.

1.2 Objective Target

The target of this thesis is to find the appropriate scale inhibitors for selected problem wells from OMV. This should be done through laboratory dynamic screening tests with 23 scale inhibitors selected from the Global Tendering. The scale inhibitors are tested concerning their ability to inhibit scale formation in the test tube and should be then accordingly ranked.

The tests should be carried out with the same scale apparatus as used for the previous screening tests a few years ago. Afterwards, a new scale apparatus should be tested and the results with each other compared.

Screening tests should be done with brine samples from the well Matzen 172 and with brine samples from Romanian wells.

Furthermore, three inhibitors should be tested concerning to their efficiency with Libyan brine samples. One of the inhibitors is used in Libya, but it does not show the desired effect, thus the reason should be evaluated.

Another part of this thesis is to confirm the results of the dynamic tests with the results from a scale prediction software, called MultiScale®.

2 General Basics

2.1 Definition of Crude Oil

“Crude oil is a mixture of hydrocarbons - from almost solid to gaseous. These were produced when tiny plants and animals decayed under layers of sand and mud millions of years ago.” [4]

According to the above definition crude oil is therefore a mixture of organic material that is compressed and heated up over geological time. This organic matter consists of tiny aquatic animals and plants that lived in ancient seas, which sank to the bottom after they died. Afterwards they are buried with sand and mud, forming an organic rich layer. This process is repeated layer over layer. Then with time, over millions of years, the seas withdrew. When the formed sedimentary rock did not contain enough oxygen to completely decompose the organic material bacteria will break down the residue into substances rich in hydrogen and carbon. Crude oil and natural gas are then transformed with help of increased pressure and heat from the weight of the layers above.

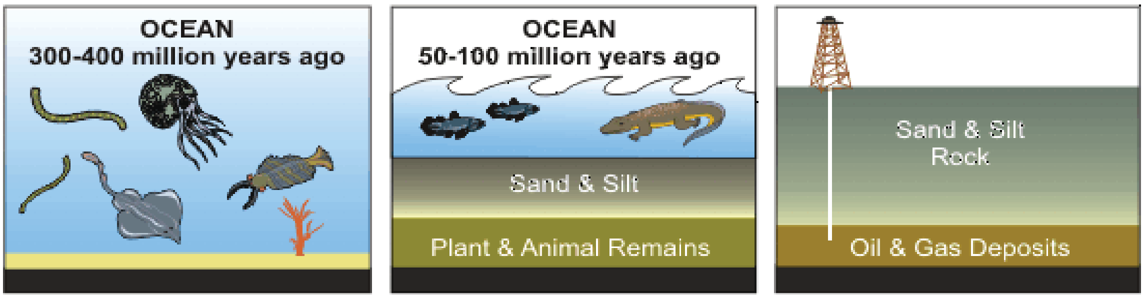

Figure 1: Formation of Petroleum and Natural Gas [5]

Depending on the levels of heat and pressure, different products will result. In the first stage kerogen, which is a waxy material and found in various oil shales will develop in a process known as metamorphose. In the next step, the catagenesis, where higher temperatures and pressures dominate, this kerogen is transferred into liquid and gaseous hydrocarbons. These hydrocarbons are then trapped in reservoirs, which are porous rocks within impermeable rocks.

When looking on the chemistry of petroleum one can see that the main components are molecules made of hydrogen and carbon atoms. These hydrocarbons can have different configurations, where the carbon atoms may be linked in a ring or a chain, each with a full or partial complement of hydrogen atoms. Some of them can be easily combined with other materials and some not. The approximate length range is C_5H_{12} to $C_{18}H_{38}$. Any shorter hydrocarbons are considered natural gas or natural gas liquids, while longer hydrocarbon chains are more viscous, whereas the longest chains are paraffin wax. Naturally, it may contain other nonmetallic elements such as sulfur, oxygen, and nitrogen. The appearance of crude oil varies with its composition, but usually it is black or dark brown.

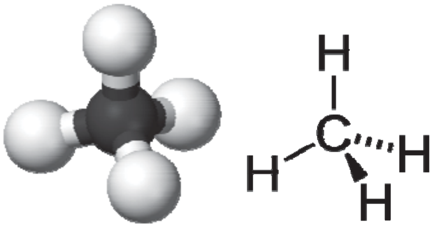

Figure 2: Methane molecules – different models

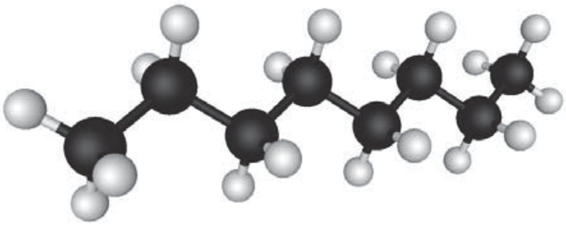

Figure 3: Octane molecule - black spheres are carbon, white spheres are hydrogen

Hydrocarbons can be separated by distillation at an oil refinery to produce gasoline, jet fuel, kerosene, and other hydrocarbons. The general formula for these alkanes, i.e. atoms that are linked together by single bonds, is C_nH_{2n+2}. The simplest hydrocarbon is methane, which is besides the major component of natural gas.

When burning methane CO_2, water and heat are the results. This is an example of a complete combustion.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + Heat \tag{2-1}$$

An incomplete combustion of petroleum however results in emission of poisonous gases such as carbon monoxide and/or nitric oxide. Below there is an example of an incomplete combustion of 2,2,4-Trimethylpentane, better known as isooctane, which is widely used in gasoline.

$$C_8H_{18} + 12.5O_2 + N_2 \rightarrow 6CO_2 + 2CO + 2NO + 9H_2O + Heat \tag{2-2}$$

The number of carbon atoms is an important measure for the oil's relative weight or density. Gases generally have one to four carbon atoms, while heavy oils and waxes may have 50, and asphalts some 100s. Hydrocarbons not only differentiate in configuration but also in boiling temperatures that are important in separating the different components of crude oil by weight and boiling point. Gases, for example, are the lightest hydrocarbons and they boil below atmospheric temperature, whereas crude oil components for gasoline boil in the range of 13°C – 204°C, those for jet fuel boil in the range of 149°C – 260°C and those for diesel at about 370°C.

The most important characteristics of crude oil are summed up in the table below.

API Gravity	6° – 50°
Viscosity	0.005 – 90 Pas
Color	Brown, green, black, yellow

Table 1: Characteristics of Crude Oil

Carbon	82 - 87%
Hydrogen	12 - 15%
Sulfur	0.1 - 5.5%
Nitrogen	0.1 - 1.5%
Oxygen	0.1 - 4.5%

Table 2: Chemical Composition of average Crude Oil

For a crude oil field to be developed there are some preconditions that have to be fulfilled [6]:

- Firstly, there must be a source rock. As the name already indicates this is a rock rich in organic matter, which, if heated sufficiently, will allow the formation of oil or gas. Usually shales or limestones are typical source rocks. They contain about 1% organic matter. Generally, rocks of marine origin tend to be oil-prone and terrestrial source rocks, e.g. coal, tend to be gas-prone.
- Secondly, migration of hydrocarbons from their source rock to a reservoir rock with enough thickness and porosity to be capable of a sizeable accumulation of hydrocarbons. Sedimentary rocks usually have sufficient porosity and permeability to store and transmit fluids and they are the most common reservoir rocks.
- Primary migration is the movement of hydrocarbons out of their source rock into a reservoir rock. The further movement into a reservoir rock in a trap or other area of accumulation is called secondary migration. Generally, migration occurs from a structurally lower area to a higher one due to the relatively buoyancy of hydrocarbons compared to the surrounding rock. Migration is essential for the formation of a commercially producible petroleum system.
- Thirdly, entrapment. The movement of hydrocarbons is stopped by traps where the hydrocarbons then accumulate. Traps are created by irregular geologic structures through both sudden and gradual movements – earthquakes, volcanic eruptions and erosion. There are two types of traps, which are structural traps and stratigraphic traps.
- Structural traps are simply deformed strata, such as faults or folds. Stratigraphic traps, however, are results of rock type changes, such as unconformities, pinch-outs and reefs. These traps act as receptacles for the moving hydrocarbons.

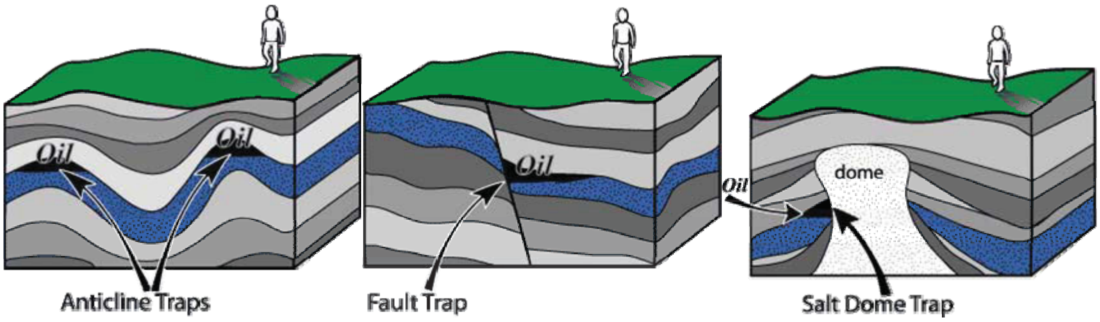

Figure 4: Examples of structural traps [6]

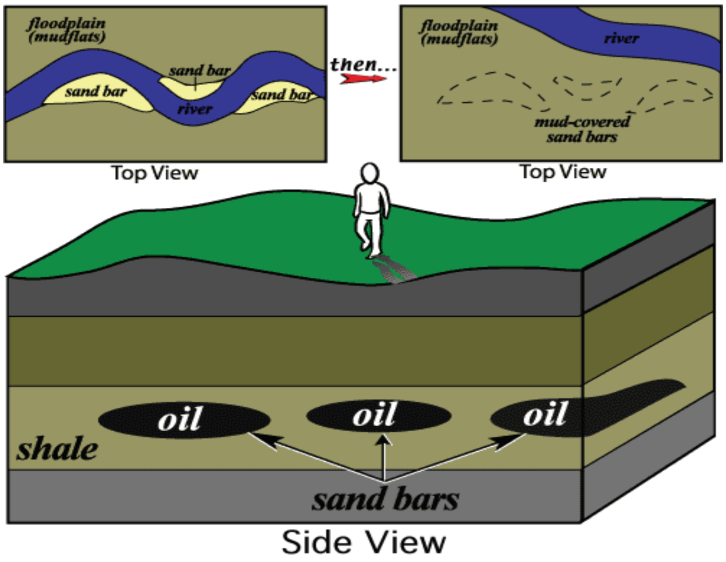

Figure 5: Example of a stratigraphic trap [6]

When having an accumulation of hydrocarbons there should be an impermeable rock overlying the trap to seal the migrating hydrocarbons in the structure.

Analysis stated that the oldest oil-bearing rocks date back more than 600 million years, whereas the youngest are only about 1 million years old.

The process of oil creation is influenced by many factors. The greatest impact on this process is the temperature. Temperature increases with increasing depth. Most hydrocarbons form in a temperature range of 107°C – 149°C. At temperatures above 127°C hydrocarbons are carbonized and destroyed, i.e. the hydrocarbons are solidified.

Another important factor influencing crude oil composition and characteristics is its geologic history. Crude oil formed from non-marine sources has a similar composition, e.g. crude oil from the Far East generally is waxy, black or brown and low in sulphur, which is very similar to crude oil from central Africa. Crudes from similar marine deposits are also similar, like crude oil from Louisiana and Nigeria. In the United States, many kinds of crudes can be found due to the great diversity in the geologic history of its different regions. The oil industry classifies crudes by its origin, e.g. Brent, West Texas Intermediate WTI, Dubai, Minas, etc.

Since 1965 we have used about 860 thousand million barrels of oil according to the BP Statistical Review of World Energy 2004. [3]

In addition, there are still 1,148 billion barrels of proven reserves left.

Analysis done by the Centre for Global Energy Studies show that we use about 29 thousand million barrels per year, this means a consumption of 79 million a day. With this rate the known reserves will suffice for approximately 40 years.

According to OPEC, world's demand will rise to 90 million barrels of oil per day by 2010 and 107 million barrels per day by 2020. This of course would shorten the time of the remaining oil.

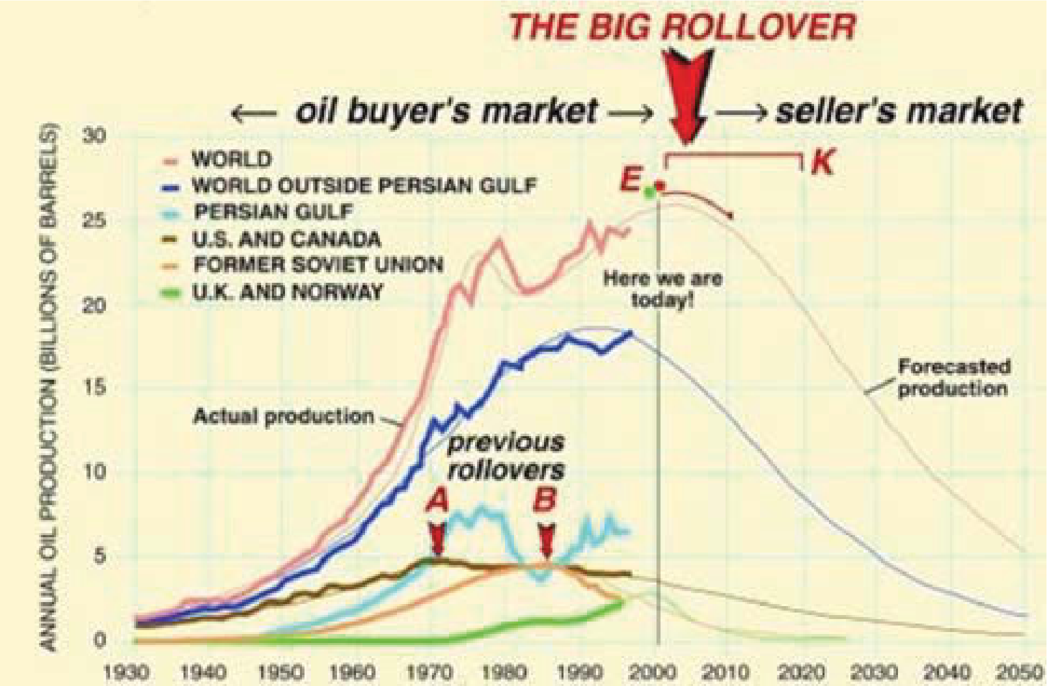

Figure 6: The big rollover [3]

Concerning gas, we have used about 60 trillion cubic meters of gas since 1980 and there are still 176 trillion cubic meters left, according to BP's review. In 2000, we were using about 2,442 million cubic meters. When staying at this rate gas will last 70 years, but demand is increasing and more reserves will be found. Due to that the IGU predict that by 2030 we will be using 4,381 million cubic meters. Figure 6 shows the actual and forecasted production. At a certain point, the production cannot be increased anymore. After this peak, called "the big rollover", the production will decline and fall behind the demand. At this point we are not running out of oil but the production can not be assured for the daily consumption.

Since oil consumption and oil price are constantly rising, it becomes economical to produce oil from small oilfields or to extract more oil from old fields using Enhanced Oil Recovery methods.

Production from known reserves including heavy oil, tar sands, bitumen and shale oil will also become more interesting. Normally production from these reserves is expensive but when the oil price is high enough this will become economical.

2.2 Definition of Formation Water

The term formation or interstitial water is a quite young term, i.e. it was not recognized until 1938. Although Colonel Edwin Drake drilled the famous oil well near Titusville in the manner of salt well drillers, early oil producers did not realize the significance of the oil and saline waters occurring together. Nevertheless, core tests showed that there existed immobile water that could not be produced by conventional pumping methods.

Munn was then the first who recognized that underground water might be the primary reason for migrating and accumulation of oil and gas. However, it took its time to use this water for the recovery of hydrocarbons.

There exist many terms describing water, which initially occurs in the pores of the rocks. It is not unusual that people mix them up thinking they all mean the same. Some of them are listed below with a short definition.

Formation water: or also called interstitial water occurs naturally within the rock pores where it coexists with the oil prior to exploitation.

Connate water: water that is trapped within the pores during its formation, i.e. water in place as the rock was formed.

Groundwater: water that is subsurface below the water table. This water is held in the pores of rocks and can be connate, from meteoric sources or associated with igneous intrusions.

Meteoric water: water that has come from the atmosphere as rain or condensation and deposited in the ground, rather than forming chemically underground

Brine: water containing more dissolved inorganic salt than typical seawater. Brine is commonly produced along with oil.

Fresh water: water that is low in dissolved salt, < 2000 ppm.

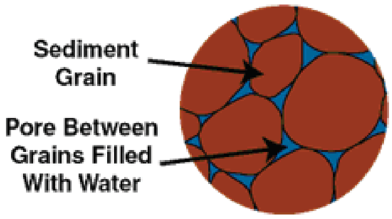

Figure 7: Idealized microscopic cross section of a sediment. In three-dimensions all of the pore spaces are connected (Not to scale) [7]

Water that is captured in the pore space of rocks is in equilibrium with hydrostatic and capillary forces. This water has a fixed composition and the quantity depends on the hydrostatic forces present in any multiple phase system. Any introduction of an external force will disturb this equilibrium and lead to a change in the interstitial water. External forces can be the raising and lowering of the water table or the migration of oil into a water-filled formation.

When produced along with oil water, either formation water or connate water, or both of them, can lead to a number of problems in producing and refining the oil. On its way up to the surface, the water undergoes additional pressure and temperature drops that aggravate these problems. The problems will be discussed in this thesis.

In the early days of petroleum production water that was produced along with oil was considered as waste and was disposed. These waters were dumped on the ground where it seeped below the land surface. Until 1930, it was usual practice to dispose the oilfield waters into local drainage, where it could kill fish and even surface vegetation. After that, the water was evaporated in earthen pits to remove all oil and basic sediment from the waters before pumping them into injection wells to prevent clogging of the pore spaces in the formation receiving the wastewater. [9]

The intention behind injection of these waters was and still is to produce additional petroleum, to utilize a potential pollutant and to control land subsidence in some areas. Of course, it is important to check and ensure the chemical compatibility of wastewater and host aquifer water.

2.1.3 Sampling of Oilfield Water

The composition of any subsurface water changes with depth and laterally in the same aquifer. The reasons for composition changes can be the intrusion of other waters and/or discharge from and recharge to an aquifer. Therefore, it is quite difficult to get a representative water sample. The composition of oilfield waters also varies with the position within a geologic structure from which it is obtained.

Furthermore, the samples will change with time. To be precisely, gases will come out of solution or supersaturated solutions will approach saturation.

Samples can be taken by drill stem tests, or immediately after completing the well. However, the best formation water sample, which is most truly representative, is usually taken after the oil well has produced for a period of time and where all extraneous fluids adjacent to the well bore have been flushed out.

There are several procedures for taking water samples depending on the information desired, e.g. information concerning dissolved gas or hydrocarbons in the water or the reduced species present, such as ferrous or manganous compounds.

The water samples taken for this thesis were obtained at the flowline and at the wellhead.

Table 3 shows a comparison of two water sample analysis, whereby one sample contained formation water and the other sample sea water.

Concentrations [mg/l]		
Ion	**Formation water**	**Sea water**
Na^+	8,442	10,680
K^+	159	396
Mg^{2+}	25	1,279
Ca^{2+}	671	409
Sr^{2+}	150	8
Ba^{2+}	11	0
Fe^{2+}	0	0
Cl^-	14,245	19,221
Br^-	0	0
SO_4^{2-}	4	2,689
Total organic acid	0	0
Total alkalinity	517	141

Table 3: Example showing the composition of two different waters [10]

Seawater has a quite high sulphate concentration, usually about 2,500 mg/l. Formation water however may have large concentrations of calcium, barium and strontium, as it can be seen from the example in the above table. Mixing of these different waters will therefore lead to massive precipitation of sulphates. Since the solubility of sulphates is more or less independent of pH and concentrations of carbonate/sulphate species, sulphate scales are easy to evaluate.

3 Scale – What is it?

When talking about scale, everyone thinks about the off-white chalky deposits found in kettles for tea water, water heaters or on faucets. These solids are the results of precipitation of minerals from hard water, i.e. this water has a high calcium and magnesium carbonate content. The consequences of occurring scales can be very bad, e.g. if scale in washing machines leads to flooding.

Scales always occur where water is processed and they can clog water heaters, pipes, coat the inside of tea and coffee pots, and therefore lead to energy loss.

Scales in homes are mainly limescales, which are precipitations caused by changes in temperature and pressure. As mentioned above hard water contains far more metal ions, mainly calcium and magnesium in forms of carbonates than soft water. Limescales are less soluble in hot water and precipitate at a temperature higher than 50°C on heating rods, e.g. of washing machines. They act like insulators and therefore increase energy consumption. Cold water however evaporates and leaves white stains as it can be seen on faucets. The reason why scale often precipitate on heat transfer surface is that some scale constituents, $CaCO_3$, $Mg(OH)_2$, and $CaSO_4$, have solubilities, which diminish with temperature and therefore, solutions in contact with heat transfer surface have the lowest equilibrium solubility.

Removal of these deposits in homes can be done with weak acids, like citric acid or vinegar. In machines or flowlines where scale has lasted a few years, only mechanical methods, like blasting or knocking off the scale, are efficient.

This thesis is focused only on those scales most common in oil and gas production.

In oilfield industry, water is an essential part of producing and refining oil and gas. Therefore, it is nearly impossible to avoid scale formation in the oilfield industry. Furthermore, there exists not only $CaCO_3$ but also $CaSO_4 * 2H_2O$, $CaSO_4$, $SrSO_4$ and $BaSO_4$. Other scales, which are occasionally encountered, are $FeCO_3$, Fe_2O_3, SiO_2 and CaF_2.

Therefore, we can distinguish between carbonate scales, sulphate scales and a small number of other scales. Carbonate scales primarily form due to pressure changes in wellbore and topsides and precipitate due to self-scaling of formation water. Sulphate scales however are a result of mixing of incompatible brines, i.e. injection and formation water. Nevertheless, the conditions for the formation are for sulphate and carbonate scales the same.

Those scales consist of inorganic crystalline deposits. These deposits can occur along all water paths and clog them. Calcium carbonate is the most common one among the various minerals precipitating from formation water. This $CaCO_3$, as other scales too, can decrease the permeability in the formation; adhere to the inside of the production tubing, and clog valves and other equipment. The logical consequence will be loss of production and time consuming removal operations.

As mentioned before, the main causes of scale are pressure and temperature drops, when producing hydrocarbons and water from the reservoir to the surface. Furthermore, mixing of two incompatible waters, the produced water can get oversaturated with scale components and thus leading to scale deposits. Mixing of incompatible waters leads to other scales than $CaCO_3$, such as $BaSO_4$ and $SrSO_4$, which are more difficult to remove.

Removal of scale involves both mechanical and chemical methods, whereas, $CaCO_3$ can be dissolved by acid like limescales in teakettles. $BaSO_4$, however, which is extremely resistant to both removal methods, requires a thoroughful planning of removal and prevention.

3.1 Sources of Scale

Scale only occurs when water is present. Therefore, the oil industry has a high potential of getting in contact with scale deposition problems.

Oilfield scales form because of precipitation of solids from brines, which are present in the reservoir and production flow system. Changes in the ionic composition, pH, pressure and temperature induce and enhance the process of precipitation.

Scale types vary depending on the physical and chemical condition of the production environment and on the chemical composition of the produced water. [1]

Thus, it can be said that oilfield scales reflect the geologic composition of the formation from which the oil is taken.

Fact is that water is a good solvent for many minerals and that it contains dissolved components acquired through contact with mineral phases from its environment. Therefore, waters in different depths differ from each other. Ground water, for example, differs from deep subsurface water in that way, that ground water is often dilute and chemically different. Seawater, however, has complex fluids rich in ions, which are by-products of marine life and water evaporation.

Fluids from sandstone formation for example often contain barium and strontium cations whereas water in carbonate and calcite-cemented sandstone reservoirs usually contains divalent calcium and magnesium cations. To sum up, it is to say that the composition of the fluids has a complex dependence on mineral diagenesis and other types of alteration encountered as formation fluids flow and mix over geological time. [14]

The trigger for scale formation is a change of the equilibrium state of the natural fluid such that the solubility limit for one or more components is exceeded. This solubility limit itself is a function of temperature and pressure. Usually the water solubility increases as the temperature increases because more ions are then dissolved. A decrease in pressure causes a decrease of the solubilities. Other consequences of this perturbation can be chemical reactions, which can lead to a change in composition of the solution or chemical reactions with a surface.

When surveying the water problem one is bound to say that water is the main culprit of production related damage. There are many reasons for this claim. One fact is that water is heavier than oil and thus robs the production systems of energy. Water produced along with hydrocarbons to the surface is difficult and expensive to dispose. Moreover, water causes corrosion, hydrates, emulsions and scale formation.

3.2 Effects of Precipitation Products on Production

Generally, it has to be said that any depositions will cause a reduced production and thus a delay or even reduction in NPV.

During production, inorganic or organic products may be deposited in surface facilities, in the tubing, in the perforations and in the formation. Precipitations in surface flowlines and facilities are problematic but not of great concern because facilities can be cleared and/or removed. The same counts for precipitations in the tubing, where they affect the tubing performance by reducing the tubing ID. In the formation surrounding the wellbore and in the perforations however, they reduce the productivity by increasing the pressure losses in the near wellbore region. Often there is a combination of different kinds of depositions in the completion equipment.

In following the two groups of deposition, inorganic and organic, will be described and explained.

3.2.1 Organic Deposits

Asphaltene and paraffin are deposits of organic origin.

Paraffin is a common name for a group of alkane hydrocarbons with the general formula C_nH_{2n+2}. The simplest paraffin molecule is that of methane, CH_4, a gas at room temperature. Heavier members of the series, such as e.g. octane C_8H_{18}, appear as liquids at room temperature. The solid forms of paraffin, called *paraffin wax*, are from the heaviest molecules. [12]

Paraffin deposits are primarily caused due to temperature drops and the tendency of paraffin deposition is crude specific. Temperature drops happen in tubing, flowlines and surface facilities. Although paraffin does not form in the formation, it can be carried into it by perforations and anything else bull-headed into the formation. Another possibility for paraffin in the formation would be gas breakout and expansion, which can cause a temperature drop too. Usually paraffin deposition in the formation is rare. Prevention of paraffin is normally not possible but it can be removed by injecting aromatic solvents, heating the tubing, e.g. hot washes, and wireline cutter.

Asphaltenes are high molecular weight substances held in the oil by polar compounds. The trigger for asphaltene formation is a pressure close to bubble point pressure. As with paraffin, asphaltenes are crude specific. Asphaltenes are not as easy to remove as paraffin. They are insoluble in non-aromatic solvents and can be slowly removed by aromatic solvents. However, care has to be taken when using asphaltene solvents, because some of them can destroy elastomers in packers, seals and other production equipment.

3.2.2 Inorganic Deposits

Scale is an inorganic and solid material that precipitates in the reservoir, near the wellbore or in surface equipment during oil/gas production or related operations.

As mentioned earlier, there are three main reasons when scale forms:

- A pressure decline, causing release of CO_2
- A change in temperature or pressure, causing the solubility to drop
- Mixing of two incompatible fluids

Once a well is put on production, it is then only a matter of time when scale forms. Therefore, it is necessary to make a detailed chemical and thermodynamic study at the outset to predict scale formation so that plans can be made to minimise the cause and the effect. For that purpose, computer programs were developed to assist in scale precipitation studies.

When scale has formed in the reservoir, it reduces the porosity and permeability and thus increasing the skin.

3.2.2.1 Carbonate Scales

The most common inorganic scales occurring in the oilfield are carbonate scales and among them calcium carbonate, $CaCO_3$. Since many rocks contain calcite, formation brine is saturated with $CaCO_3$. CO_2 is dissolved in the formation water due to pressure drop around the wellbore during production or due to gas breakout from the oil. This CO_2 then enters the gas phase and leads to $CaCO_3$ precipitation. The following equation shows the process of dissolved CO_2.

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_{3solid} + CO_{2gas} + H_2O \qquad (3\text{-}1)$$

Pressure alone can cause precipitation too. This is typically the case in regions of sudden pressure drops, e.g. the downstream end of a subsurface safety valve.

In the formation, scale reduces the PI and increases the pressure drops for the same production rate. Furthermore, scale depositions cause an additional skin.

Nevertheless, hydrochloric or acetic acid or ethylenediamenetetraacetic acid (EDTA) chelating chemicals can easily remove carbonate scale.

This thesis will deal with $CaCO_3$ scale since it is the main scale occurring in OMV fields.

3.2.2.2 Sulphate Scales

The most common sulphate scales are calcium sulphate, barium sulphate and strontium sulphate scale. $BaSO_4$ and $SrSO_4$ often appear together, forming a mineral with a composition intermediate between $BaSO_4$ and $SrSO_4$.

Generally, sulphate scales form when incompatible waters are mixed together. This is because formation waters often have a high concentration of Ca^{2+}, Ba^{2+} and Sr^{2+}, whereas seawaters generally have a high concentration of SO_4^{2-}.

Figure 8 shows important information about $BaSO_4$. [13]

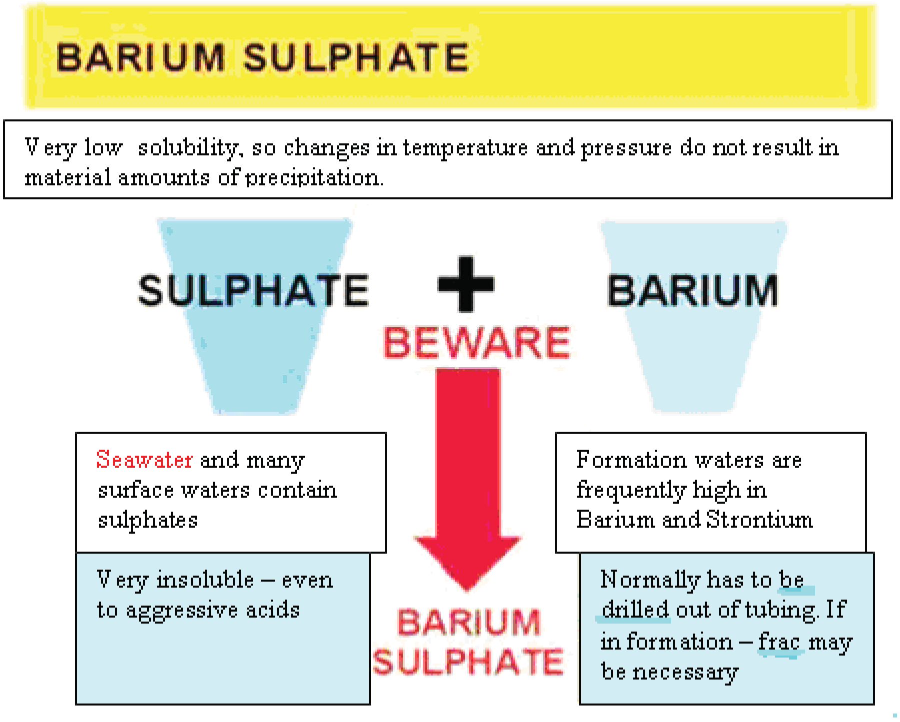

Figure 8: How $BaSO_4$ forms [13]

$CaSO_4$ on the contrary depends on pressure, temperature and water chemistry. At low temperatures it is more likely that gypsum will form, whereas at higher temperatures (>100°C) and pressures anhydrite will form. Thus, the different crystal forms of $CaSO_4$ will have different solubilities at given conditions.

Removing sulphate scales is often difficult because they are quite insoluble and cannot be removed by HCl acid directly. In most cases, $BaSO_4$ can only be removed by mechanical means, i.e. drilling out the $BaSO_4$. Chelating agents can also be used, like the well-proven EDTA, but this is expensive, slow and ineffective if the scale is oil coated.

3.3 Costs caused by Deposits

Any deposits, regardless of composition and origin, cause a reduction of the permeability of the adjacent reservoir rock and effective diameter of tubings. In case of oilfield scales, the costs are very high due to drastic oil and gas production decline, frequently pulling of downhole equipment for replacement, re-perforation of the producing intervals, remaining re-drilling of the plugged oil wells, stimulation of the plugged intervals, and other remedial workovers. [14]

3.3.1 Reduced Production Rate

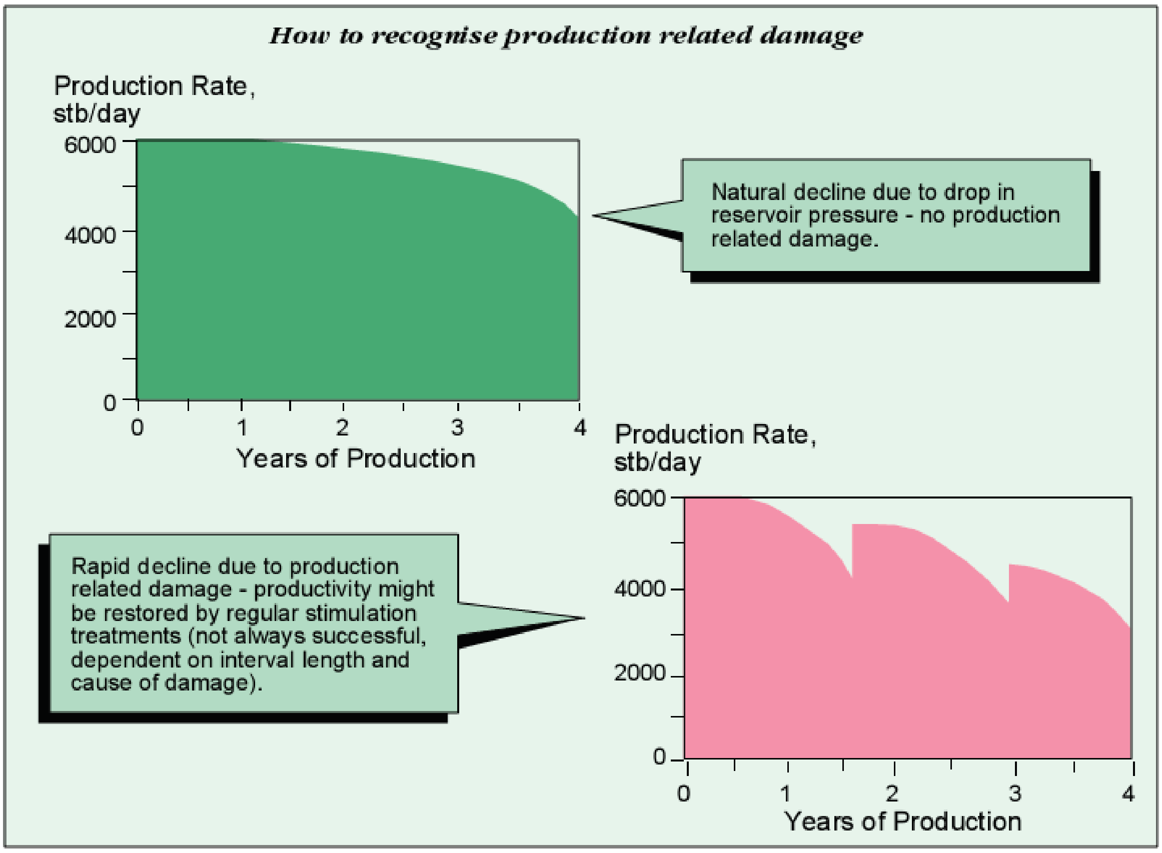

Figure 9: How to recognize production related damage [13]

In case of reduced production rate, there is a chance that this rate will be produced later or in the worst case this rate is already seen as lost rate. However, if the rate is seen as lost the costs would be the same as the income, i.e. there is no benefit at all, whereas if the reduced rate will be produced later the costs will be equal to the loss of interest.

3.3.2 Tripping of Equipment

For gas injection wells deposits in the tubing lead to higher injection gas consumption due to a reduced tubing diameter. Downhole pumps will have a shorter lifetime because the friction increases and thus in turn will increase the energy consumption. Topside equipment, like heaters cannot work properly due to deposits, which inhibit the heat transfer. These are the most common problems concerning depositions; of course, there are much more possible scenarios of equipment malfunction. All these malfunctions will result in an increased Capital Expenditure (CAPEX).

3.3.3 Chemicals

Chemicals are used to remove or to prevent depositions. The costs depend on the chemical itself and on its dosage. Depending on the situation, the usage of chemicals to remove deposits can be cheaper than the prevention.

3.3.4 Equipment to remove the Deposits

Additional equipment will be necessary to remove the deposits even if chemicals are used. Sometimes it is better to change the tubing than cleaning it.

3.3.5 Safety

Deposits can block safety valves so that they cannot be operated anymore. The well has then to be shut down to remove the deposits. This of course leads to production losses. Not only downhole safety equipment is endangered but also topside equipment. For example, measurement equipment will not work properly and can therefore lead to hazardous situations.

3.3.6 Time

All remedial works are time and of course cost consuming. Additional personnel are needed to carry out these works. As it is well known that time is money, any delay in production is lost money.

3.4 Conditions for Scale Formation

As scale deposits are inorganic minerals precipitated from brine, crystallization and nucleation are the processes of these deposits. Therefore, it may be necessary to explain some terms for overall understanding before going further.

3.4.1 Crystallization [15]

Crystallization is a process in which solid crystals form from a solution. Thus, crystallization is a chemical solid-liquid separation technique, which has been used for centuries. This process can be either natural or artificial and consists generally of two events, namely nucleation and crystal growth.

The condition for crystallization is a supersaturated solution, which contains more dissolved ions or molecules than it would under its equilibrium. Natural supersaturation occurs as a result of chemical reactions or pH changing. Processes like solution cooling, addition of a second solvent to reduce the solubility of the solute or solvent evaporation are used to induce an artificial crystallization. [16]

Examples for natural crystallization would be mineral crystal growth, snowflakes formation, honey crystallization, etc. where crystallization is a result of spontaneous chemical reactions.

For the industry crystallization is an important method to produce particulate materials, which are used in many applications.

3.4.2 Nucleation

Nucleation is an incident during the crystallization process and is nothing else than the start of a phase transition. Common examples for this phase transition are the formation of bubbles, e.g. in a soft drink, or crystals, or also the formation of liquid droplets in a saturated vapour. The process of nucleation proceeds relatively slow because the initial crystal components must jump into each other in the correct orientation and placement for them to adhere and form the crystal.

The process occurs at nucleation sites on surfaces containing the liquid or vapour. One can distinguish between heterogeneous and homogeneous nucleation. Heterogeneous nucleation happens when suspended particles or tiny bubbles provide nucleation sites. This kind of nucleation proceeds more quickly because the foreign particles act as a framework for the crystal to grow on. Homogeneous nucleation, on the contrary, occurs spontaneous and random without preferential nucleation sites and without the influence of foreign particles.

3.4.2.1 Homogeneous Nucleation

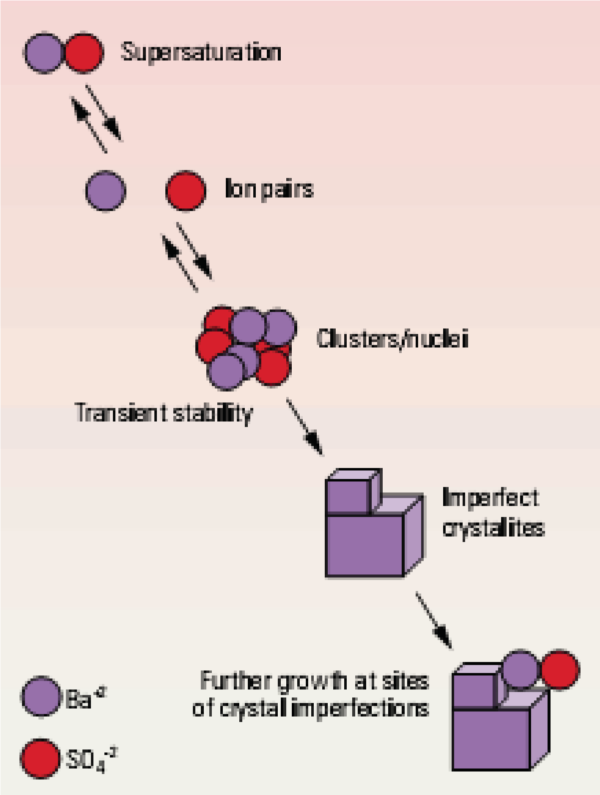

Figure 10: Homogeneous nucleation [11]

Figure 10 shows the process of a homogeneous nucleation. First, unstable clusters of atoms are formed in a saturated fluid. These atom clusters themselves form small crystals after local fluctuations caused a change in the equilibrium ion concentration in supersaturated solutions. Imperfections on the crystal interfaces enhance the growth of the seed crystals by adsorbing on them. Thus, the crystal size is extended. After a critical radius is exceeded the surface free energy of the crystal decreases rapidly with increasing radius and this is the driving energy for seed crystal growth. This means that if a crystal is too small, there is not enough energy to create its surface because the energy released by forming its volume is too less and nucleation does not proceed. In this case the crystals may re-dissolve. Another implication is that large crystals favor continuing crystal growth.

When there is a large enough degree of supersaturation, any seed crystals will encourage an increase in the growth of scale deposits. Thus, a seed crystal is a catalyst for scale formation.

3.4.2.2 Heterogeneous Nucleation

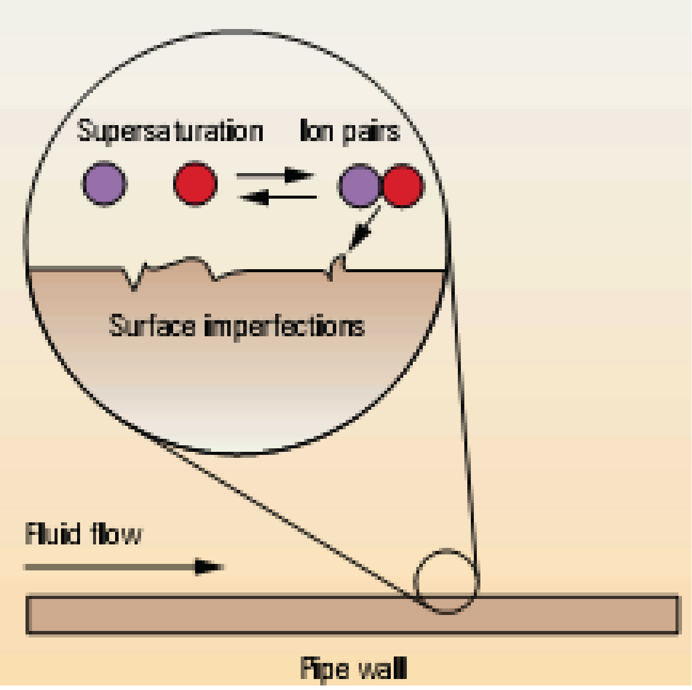

Figure 11: Heterogeneous nucleation [11]

Heterogeneous nucleation occurs on surface defects such as pipe surface roughness or perforations in production liners, or also on joints and seams in tubing and pipelines. An additional trigger could be a high degree of turbulence. This means that scale depositions can occur at the position of the bubblepoint pressure in the flowing system, thus, scale deposits rapidly build on downhole completion equipment.

3.4.3 Scale Formation

The composition of formation water can vary a lot within a small area. Each of the many waters accompanying the oil production has a certain chemistry, which changes as the equilibrium is changed. This means that under certain situations, the low solubility compounds of the waters may precipitate out and scale can form.

A simplification of $CaCO_3$ formation is following: a sudden pressure drop causes dissolved CO_2 to go out of solution, which in turn causes aqueous bicarbonate, HCO_3^- to be converted to insoluble CO_3^{2-}, and thus forming $CaCO_3$.

The formula below demonstrates the process of calcium carbonate scale formation, which is the most common scale in oilfield. The successful precipitation of $CaCO_3$ depends upon the equilibrium [1]:

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + H_2O \qquad (3\text{-}2)$$

$K_{SP} = 10^{-8}$ mole/liter at 20°C

When a solution contains a gas phase, which in turn contains some CO_2 then the carbonate distribution between the water and the gas is calculated following:

$$CO_2(g) \rightarrow CO_2(aq) \tag{3-3}$$

$$CO_2(aq) + H_2O \rightarrow H^+ + HCO_3^- \tag{3-4}$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \tag{3-5}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s) \tag{3-6}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(aq) \tag{3-7}$$

The main conditions for scale to form are a temperature or pressure change, pH shift, outgassing, or mixing of incompatible waters. Nevertheless, for a scale to form it must grow out from a saturated solution.

Supersaturation is a condition a fluid will reach when the solution contains more ions than is thermodynamic possible. This means, that eventually a salt will precipitate. Although the supersaturation does not tell anything about the amount of salt that can precipitate it is a good indication whether the possibility for salt precipitation is high or not. Relating to this the kinetics of reaction will give information about how fast the precipitation reaction will be.

Nucleation and crystal growth rates are a function of the mineral saturation ratio or the logarithm of the saturation ratio, which is called the saturation index SI. There are several definitions for the saturation ratio, which are saturation level or saturation index. Sometimes people use the logarithm of the saturation ratio, taking either *ln* or *log* of the ratio in Eq.(3-8). The time from creation of supersaturation until formation of critical nuclei for crystal growth is defined as retention time. The measured induction time is longer because the nuclei have to grow to a detectable size.

The saturation ratio for a salt MX is defined as following:

$$\text{SR(MX)} = \frac{a_{M^+} a_{X^-}}{K^0{}_{SP}(MX)} = \frac{m_{M^+} m_{X^-}}{K_{SP}(MX)} \tag{3-8}$$

With K_{SP} as the stoichiometric solubility product which is defined as

$$K_{SP}(\text{MX}) = \frac{K^0{}_{SP}}{\gamma_{M^+} + \gamma_{X^-}} \tag{3-9}$$

where a and γ are the activity and activity coefficient, and m is the molality of the ion.

According to the definition of SR, there are three possible scenarios.

SR < 1: solution is undersaturated. No precipitation will take place. If there are any solids, they will be dissolved.

SR > 1: solution is supersaturated, high possibility of precipitation. There may be precipitates, but this will depend on the kinetics of the precipitation reaction. Some salts need a trigger to start precipitation even if they are many hundred times super-saturated.

SR = 1: solution is at equilibrium with the precipitating phase, i.e. the solution is saturated. Neither precipitation nor dissolution will occur.

3.4.3.1 Influence of Temperature

Any changes in temperature will result in a change of chemical equilibrium of the reservoir brine. However, any change of the condition results in a change of chemical equilibrium.

Influences of temperature and pressure are closely connected. During production of the well, the brine is moved to a lower temperature and pressure.

$CaCO_3$ shows a contrary behaviour compared to most other scales. With increasing temperature it becomes less soluble, i.e. the hotter the water the more likely the $CaCO_3$ precipitation.

This implies that a temperature drop will increase the solubility of $CaCO_3$ and thus decreases the SR for $CaCO_3$. This is true for $CaCO_3$, $FeCO_3$, $CaSO_4$ and $SrSO_4$. Most other salts have an increasing SR with increasing temperature.

3.4.3.2 Influence of Pressure

For $CaCO_3$ the influence of pressure is the opposite of the influence of the temperature. As pressure increases, the solubility of $CaCO_3$ will also increase and thus decreases its SR. Figure 12 shows the behaviour of $BaSO_4$ at different pressures. It is clearly to see that the solubility of $BaSO_4$ decreases with decreasing pressure.

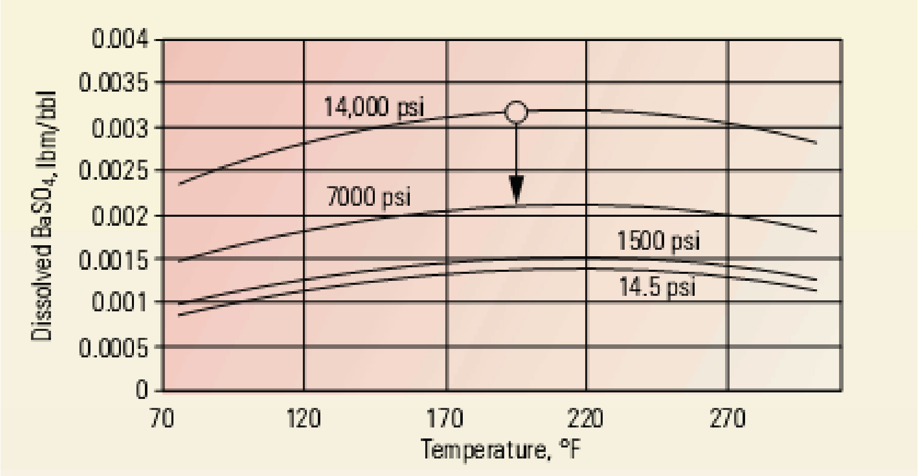

Figure 12: Mineral solubilities vs. Pressure

3.4.3.3 Influence of CO_2 Partial Pressure [17]

For prediction of carbonate scales, it is also important to know the chemical reactions within the brine and CO_2 in the gas phase. Many oilfield reservoirs contain carbonate mineral cements and CO_2, thus the formation water is saturated with $CaCO_3$ under reservoir conditions where the temperature can be up to 200°C and the pressure up to 30 MPa.

When this CO_2 gets in contact with water, it will dissolve and form carbonic acid according to Eq.(3-10). The carbonic acid itself ionises to form hydrogen ion and bicarbonate ion.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \tag{3-10}$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \tag{3-11}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{3-12}$$

$CaCO_3$ does not exist in solution as calcium ions and carbonate ions, but as calcium ions and bicarbonate ions. Therefore, the precipitation of $CaCO_3$ can be expressed as:

$$Ca^{2+} + 2HCO_3^- \leftrightarrow Ca(HCO_3)_2 \leftrightarrow H_2O + CO_2 + CaCO_3 \downarrow \tag{3-13}$$

According to the principle of LeChatelier, an increase of the CO_2 concentration results in formation of more calcium bicarbonate. A decrease in CO_2 content, however, leads to formation of calcium carbonate. This shows that the solubility of $CaCO_3$ is very influenced by the CO_2 content of the water. The conclusion is that the amount of CO_2 that will dissolve in water is proportional to the partial pressure of CO_2 in the gas over the water, which is the product of mole fraction of CO_2 in gas phase and the total pressure of the system. According to this, an increase in system pressure or percentage of CO_2 in the gas will lead to an increase of dissolved CO_2 in the water and the pH of the water therefore decreases.

However, this effect becomes less effective as the temperature increases. Then the reverse will take place.

3.4.3.4 Influence of pH

Not every scale has a dependency on pH. Sulphates are more or less independent of pH, whereas the solubility of carbonate and sulphide scales shows a strong dependency of pH. This complicates the prediction of carbonate and sulphide scales because it is necessary to calculate both pH and the concentrations of all carbonate and sulphide species.

When looking on Eq.(3-14), it can be seen that a decrease in pH takes place when precipitation occurs.

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3(s) + H^+ \tag{3-14}$$

During $CaCO_3$ precipitation, the pH increases due to loss of CO_2 from the aqueous phase to the oil and gas phase as the pressure drops. The lower the pH, the less likely $CaCO_3$ precipitation will occur.

3.4.3.5 Mixing of Incompatible Fluids

Incompatible fluids are fluids, which precipitate minerals when mixed together. In oilfield industries, it is common that seawater is mixed with formation water by injecting seawater into the reservoir to maintain the reservoir pressure and thus to increase the oil recovery. This is inasmuch problematic that seawater contains high concentrations of SO_4^{2-} and low concentrations of Ba^{2+} and Sr^{2+}. In addition, formation water often has the opposite composition. The logical consequence would be precipitation of $CaSO_4$, $BaSO_4$ and $SrSO_4$.

3.4.3.6 Influence of Materials/Surfaces [1]

The first metal-petroleum fluid contact happens on well tubing and thus this equipment is more exposed to changes of pressure, temperature, pH and fluid velocity. Furthermore, the co-produced water contains high concentrations of ionic materials dissolved from the overburden rock and afterwards deposited in the reservoir minerals. As the well provides a point of exit, a pressure drop is the result and this causes a disturbance to the conditions of equilibrium. In addition, the temperature drops and as a result, salts may deposit as scale, depending on how massive the change is. The presence of the metallic tubing also induces a change of pH. As production proceeds the metal/fluid interface is continuously replaced by fresh fluid and thus changing the fluid composition on this interface.

Well tubing is usually fabricated by extrusion or welded seam method; each has advantages and disadvantages for the petroleum industry. [1]

The more expensive extruded tubing is also more resistant to corrosion and thus in an indirect way to scale depositions. These depositions depend on the physical makeup of the tubing and the prevailing conditions of the well. Welded seam tubing, for example, has a metal-metal boundary that may consist of variable crystal coordination states or grain boundaries. These are the locations where the attack of metal is most probable because of interstitial spaces thus providing a site for the formation of scale.

3.5 Common Scale Scenarios

There are four typical situations during hydrocarbon production, which are responsible for scale formation.

3.5.1 Mixing of Incompatible Fluids

Mixing of fluids is done by injecting seawater into the reservoir during secondary and enhanced-recovery waterflooding operations. The purpose of this is to enhance the recovery and to maintain the depleting reservoir pressure.

Table 3 shows a comparison of compositions between formation water and seawater. As it can be seen in this case the seawater contains a lot more SO_4^{2-} anions than the formation water. A combination with formation water that is rich in divalent cations like Ba^{2+} and Sr^{2+} gives the perfect base for scale. This mixing produces new fluids containing the combined ion concentrations that exceed the solubility limits for sulphate minerals.

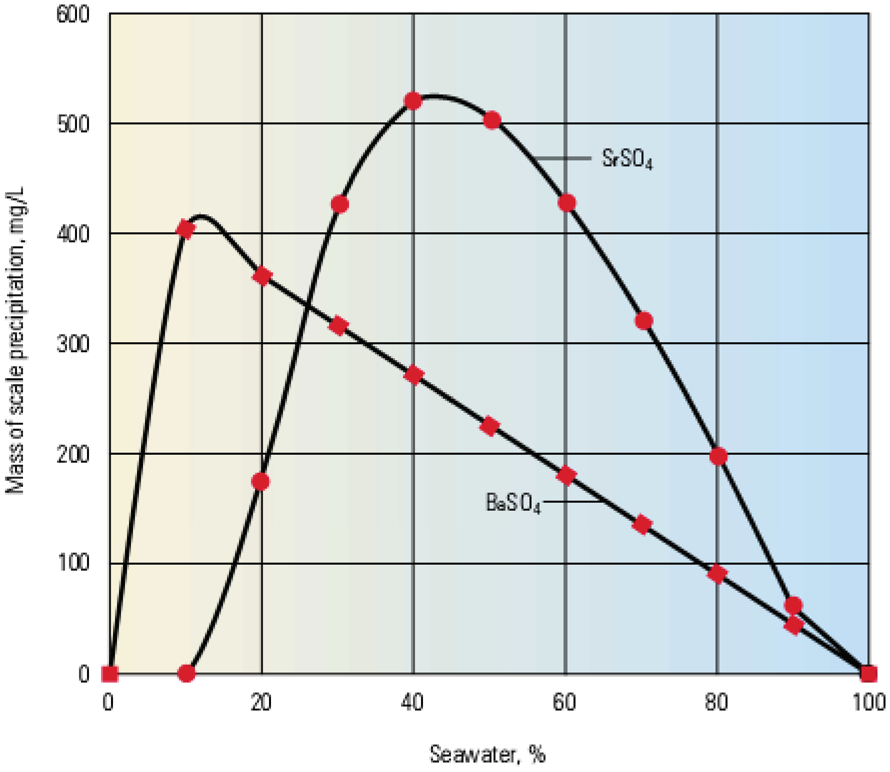

Figure 13: Amount of scale precipitations at different mixtures of seawater and formation water

Generally, one can say that there is a distribution of what scale type will form in what formation. $CaSO_4$, for example, will mainly form in limestone formations, whereas $BaSO_4$ and $SrSO_4$ will form in sandstone formations. Scale occurring in the formations is very difficult to remove, mechanically as well as chemically. However, incompatible water mixing not only occurs in formation but also in tubing where it is possible to remove the precipitated scale chemically and mechanically.

3.5.2 Autoscaling

Autoscaling or self-scaling happens when changes in temperature and pressure cause the exceeding of the solubility limit of a mineral. These changes are accompaniments of production of reservoir fluids.

Pressure changes can be within the wellbore but also at any restriction downhole and can lead to precipitation of sulphate and carbonate scales. Large temperature drops, for example, can cause sodium chloride scale – halite – to form.

This autoscaling problem is aggravated when acid gases are present. Pressure drops during production causes the fluid containing the gases to outgas, thus raising pH and leading to scale deposition. This scale deposition can start in the near-wellbore matrix, goes up the tubing and ends in the surface equipment because on the way to surface the produced water experiences a series of temperature and pressure changes.

Another important observation is that for carbonate scales, temperature effects often work against pressure effects. As the fluid travels up the tubing to surface temperature and wellhead pressure, the resulting temperature drop may override the pressure effect, thus reducing scale formation in the tubing. On the other hand, subsequent release of pressure from the wellhead to surface can lead to massive deposits of scale in surface equipment and tubing. [8]

3.5.3 Evaporation Induced Scale

As it is known, fluids containing gas can also lead to scale formation it is easy to draw the conclusion that simultaneous production of hydrocarbon gas and formation brine is a potential trigger for scale formation. The process would be the following: the hydrostatic pressure will decrease in production tubulars and lead to an expansion of the hydrocarbon gas. Simultaneously the still hot brine phase will evaporate. The results are dissolved ions and thus a salt concentration exceeding the solubility limit leading to salt precipitation. Although other scales may form, this cause is quite common for halite scaling in high pressure – high temperature (HPHT) wells.

3.5.4 Gas Flood

In secondary recovery operations, the formation is flooded with CO_2 gas to enhance recovery and this used CO_2 can lead to scale depositions. The reason for that is when water contains CO_2 it becomes acidic and will dissolve calcite in the formation. However, subsequent pressure drops in the formation surrounding a producing well can cause the CO_2 to come out of solution and induce carbonate scale precipitations. These depositions can occur in the perforations and in the formation pores near the wellbore. As the scale production in the near wellbore region goes on, the pressure is reduced further and thus causing even more precipitation. On this way, the perforations can get completely sealed or an impermeable wall between the borehole and reservoir can be created within a few days. The consequence would be a complete shutting down of the production.

3.6 Occurrence of Scale

Damages in surface and subsurface oil and gas production equipment due to scale formation have been long known. Furthermore, scale formation has been also recognised as a major cause of formation damage in injection as well as producing wells. Precipitation of salts leads to permeability decline. Additionally, scale causes equipment wear and corrosion and flow restriction. All these problems will lead to a decrease in oil and gas production.

Scale precipitation in the formation can limit or even block oil and gas production by plugging the oil-producing formation matrix or fractures and perforated intervals. Thus reducing the initial permeability to 30% or up to more than 90%, depending on the solution composition, temperature, flow rate and solution injection period in case of injection wells.[14] Furthermore, the porous media in the formation can get impermeable to any fluids. Scale in the near wellbore region has a finer particle size than tubing scale, thus it can block gravel packs and screens, but also matrix pores.

Besides, scale also precipitates in downhole pumps, tubing, casing flowlines, heater treaters, tanks and other production equipment and facilities. This implies that scale can occur at any point in the production system, at which supersaturation is generated, both downstream and upstream. This is because supersaturation is generated by changing the pressure and temperature conditions or by mixing two incompatible fluids.

Additionally, $CaCO_3$ is formed, when there is a sharp pressure reduction, such as given between the formation and the well bore and across any constriction in the production tubing, e.g. check and safety valves. This reduction in pressure causes the CO_2 to break out of the solution and go into the gas phase.

In production tubing scale occurs inside of the tubing, where it forms layers, which can be several centimetres thick. Scale deposits in tubing cause an increase of pipe surface roughness and reduction of the flowing area, thus lowering the production rate.

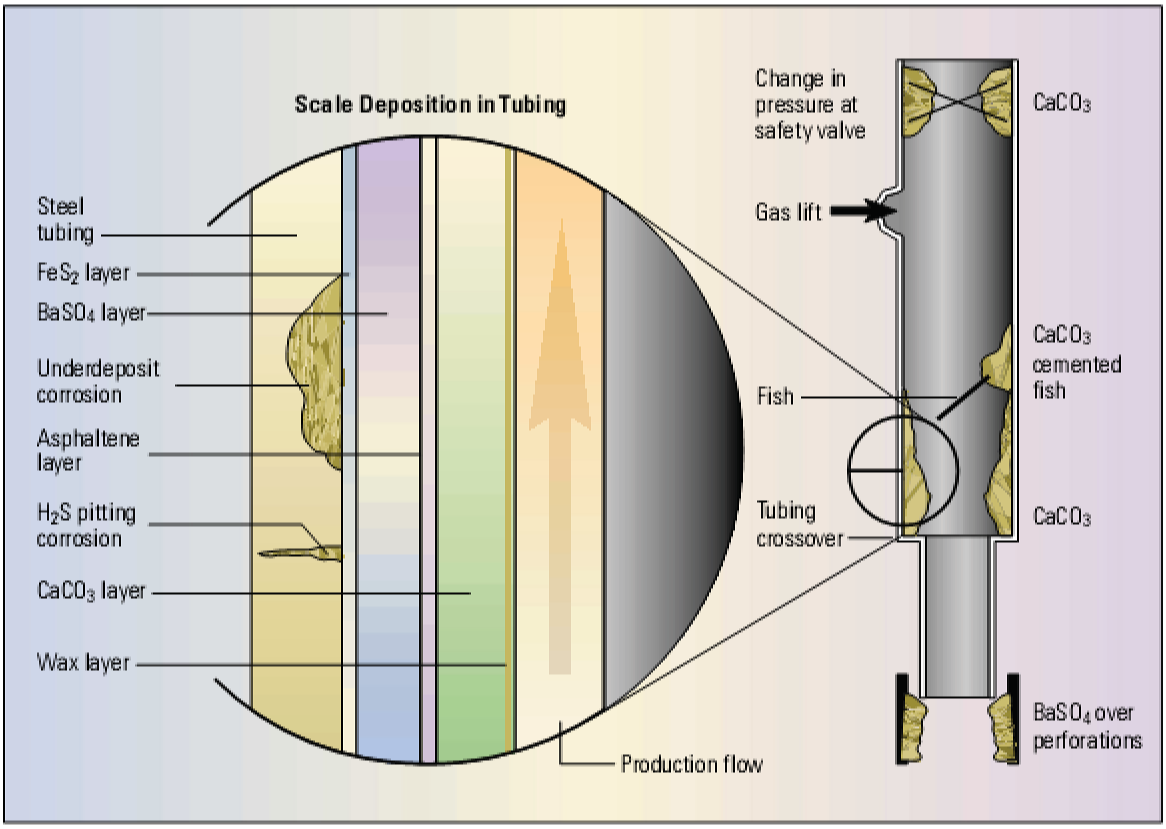

Figure 14: Scale in tubing. It is common that scale is covered with a waxy or asphaltene coating. [11]

Figure 14 shows a common scenario of scale deposits inside tubing. Scale deposits can often contain layers of wax or asphaltenes and the layers closest to the tubing may additionally contain iron sulfides, carbonates or corrosion products. Therefore, not only scale problems occur but also corrosion.

In surface production equipment, scale can cause clogging of valves, flowlines, etc. This can be quite dangerous, especially in case of blocked safety valves. Therefore, it is very important to detect scale deposits as quick as possible. This can be done with NODAL analysis, which can indicate scale deposits in tubing if a well suddenly show restrictions that were not present earlier. Another indication of scale formation in case of water injection is the increased water cut and thus decreased oil production. This is a sign that injection water has broken through and scale is beginning to form.

3.7 Prevention

The saying “prevention is better than cure” is also true for oilfield practice. Keeping producing wells healthy is ultimately the most efficient way to produce hydrocarbons.

Scale prevention and removal is based on prediction of scaling formation damage provided by mathematical modelling. Nevertheless, to ensure the best results of an inhibitor it is unavoidable to test the inhibitors in the laboratory and later on in the field.

Scale can be best prevented by using chemical methods. Mechanical methods are not that useful because scale is very hard and this will lead to a very fast wear of the equipment. The most common prevention method is chemical inhibition, which can range from the basic dilution methods, to the most advanced and cost-effective methods of threshold scale inhibitors.

Dilution is commonly applied to control halite precipitation in high salinity wells. In this process, the saturation in the wellbore is reduced by continuously delivered fresh water to the sandface. It is the simplest method to prevent scale formation and requires only a macaroni string through the production tubing.

3.7.1 Chemical Inhibition

The function of a scale inhibitor is to prevent or delay crystal growth at threshold concentrations. Inhibitor efficiency is usually described by three main mechanisms: nucleation inhibition, crystal growth retardation and chelating.

Nucleation inhibition means that scale crystals form but are then disrupted or re-dissolved by the action of the inhibitor molecules. In case of crystal growth inhibition the inhibitor adsorbs on or interacts with the active crystal growth sites, i.e. growing edges or spirals, to retard or stop the crystal growth process. Other inhibitors act as chelating agents, i.e. they break up the scale by isolating and locking up the scale metallic ions within their closed ring-like structure, thus breaking the re-precipitation cycle. One of the best-known chelating agents is EDTA, which is still used today. Since chelating agents consume scale ions in stoichiometric ratios, the efficiency and cost-effectiveness of them as scale inhibitors are poor. [11]

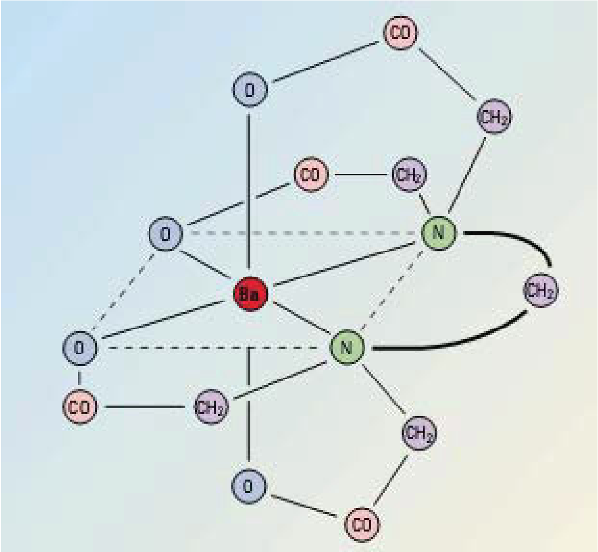

Figure 15: An EDTA molecule shares electrons from oxygen and nitrogen atoms with barium ions, thus forming a barium-EDTA chelate compound [11]

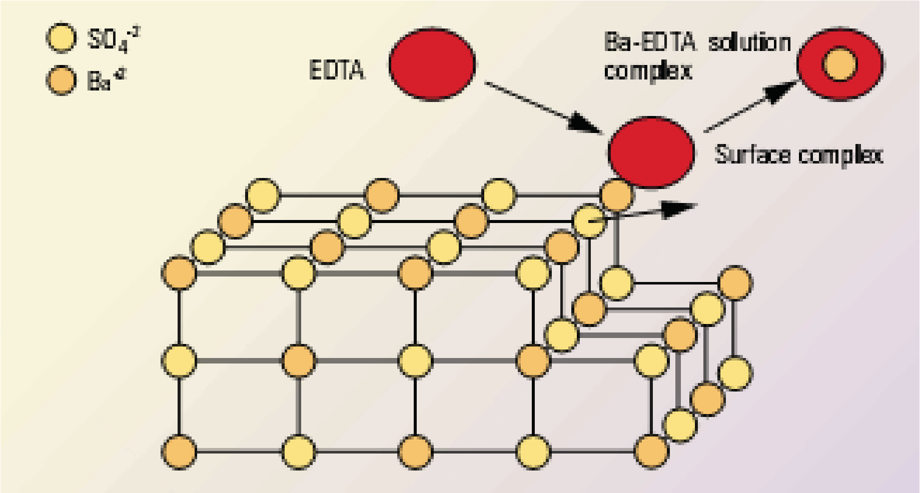

Figure 16: Dissolving $BaSO_4$ scale

The effectiveness of the processes depends on the inhibitor concentration. There exists a certain MIC, i.e. minimum inhibitor concentration, where the mineral scales are inhibited at threshold levels.

It is not compelling that an inhibitor operates only through one of the above explained mechanisms. Phosphonates and polymeric species are inhibitors that operate through both of the mechanisms. Therefore, it is very important to choose the right scale inhibitor and its concentration, and this can be done by several laboratory tests.

3.7.1.1 Inhibitor Types

There are many inhibitor types available, depending on their functionality. However, all commercial scale inhibitors belong to one of the following chemical families: [16]

- Polymers,
- Esters of phosphoric acid,
- Phosphonates

Polymers

Polymers act as nucleation inhibitors. Their activities also include crystal modification, flocculation and dispersion. The polymer docks on a growth site, thereby blocking it and causes the scale microcrystal to grow unnaturally. The crystals may reach certain sizes and shapes and cannot continue growing.

Polymers acting as scale inhibitors are mainly of the polyacrylamide or polyacrylate type. They have good temperature stability and might be used in HT conditions (up to 200°C) to control $CaCO_3$, $CaSO_4$, $BaSO_4$ and $SrSO_4$ scale. Because of their temperature stability and their good adsorption behavior, they are ideal candidates for squeeze treatments. Unfortunately, they are quite difficult to be traced in low concentrations. Nevertheless, they are very effective in scale control in production systems and oily water clean up units when added at the wellhead manifold.

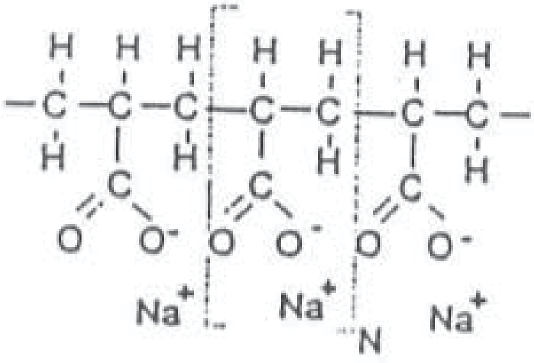

Figure 17: Example for a polymer – Polyacryl [14]

The newer generation of this group of scale inhibitors are phosphino-substituted polycarboxylic acid inhibitors, where the active ingredient is a phosphorus containing polycarboxylic acid. This phosphorus ensures that the product can be monitored even at low concentrations, which is quite important for squeeze treatments. As with all polymers, polycarboxylate also show high temperature stability. They are primarily designed to inhibit $BaSO_4$ and $SrSO_4$ scale but also display some effect against $CaCO_3$.

Esters of phosphoric acid (phosphate esters)

In contrast to polymers, phosphate esters have a lower thermal stability (<121°C) and are therefore commonly used in low temperature conditions, e.g. surface equipment. Phosphate esters belong to the so-called threshold nucleation inhibitors, i.e. they form sparingly soluble salts with one of the mineral lattice ions of the growing scale microcrystal. On this way, further crystal growth will be inhibited.

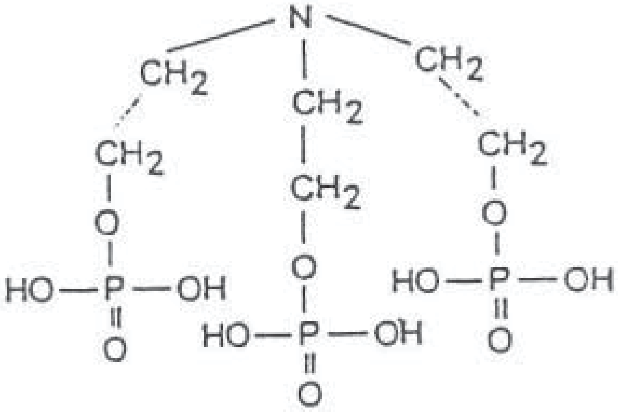

Figure 18: Phosphate ester [14]

They show good to excellent inhibition efficiency against sulphate scales. Inhibition of $CaCO_3$ however, is sometimes totally insufficient.

A drawback of using phosphate esters as scale inhibitors is the possible formation of emulsions, which is caused by some phosphate esters. Emulsification can happen during and after the application and are hard to analyze. Sometimes emulsifications are indicated by decreased productivity, and in other cases, the effective heater treatment of the oil becomes impossible.

Phosphonates

Phosphonates are effective threshold inhibitors for low solubility sulphate and carbonate salts over a broad supersaturation range, especially against $CaSO_4$. These scales can be completely inhibited or markedly reduced. Diphosphonates are likewise useful inhibitors over wide concentrations of supersaturation except in the case of $CaSO_4$ stabilization. The effective concentrations cover a range, which varies with temperature, pressure, degree of supersaturation, type of scale forming deposit, etc.

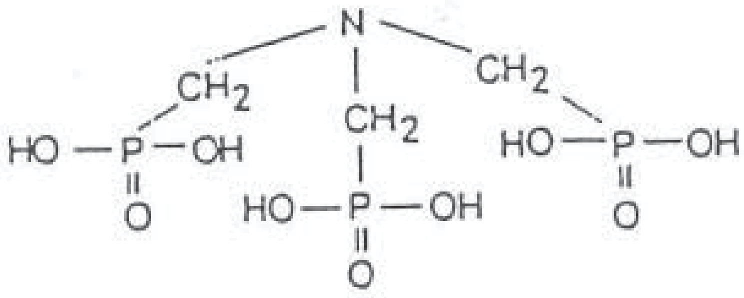

Figure 19: Phosphonate [14]

Furthermore, phosphonates and diphosphonates are recognized as good inhibitors against water-formed scales, which deposit in oilfield formations and on equipment in contact with unstable or supersaturated waters.

Additionally, this group has a good temperature stability, which reduces the risk of precipitation of byproducts.

Since OMV has the philosophy not to use scale inhibitors containing phosphonates in Austria, this group is of no interest for this thesis. When using phosphonates the biological processing step in the waterflood plants will be disturbed.

These chemical compounds minimize scale deposition through a combination of crystal dispersion and scale stabilization.

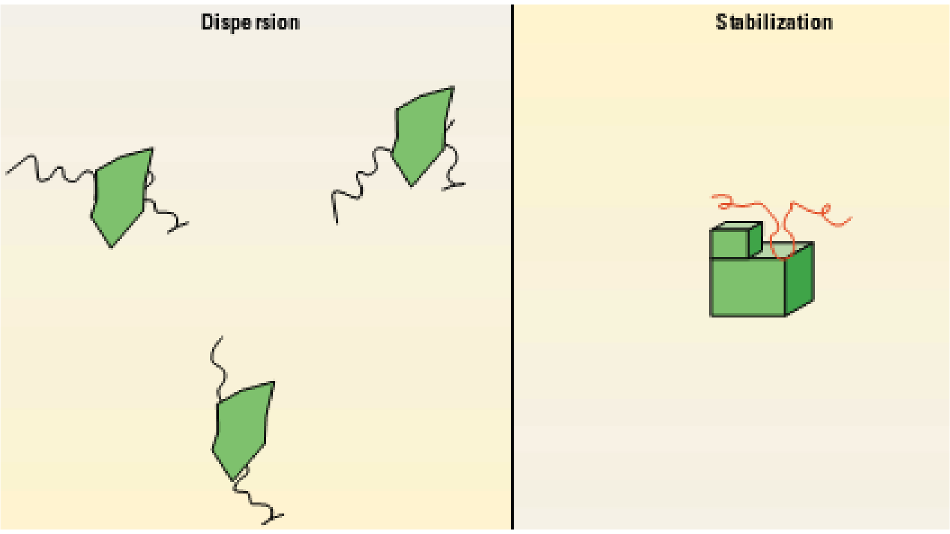

Figure 20: Dispersion and stabilization

Dispersion prevents seed crystals of scale from adhering to tubing walls and other crystal particles. During stabilization, the deposited scale structure is modified by the phosphonates in such a way that further crystal attachment is prevented.

When using the chemical method, there are two possibilities to apply the inhibitor, namely squeeze treatment and continuous treatment.

3.7.1.2 Inhibitor Squeeze Treatment

In this process, the inhibitor is pumped directly into the formation, where it adsorbs on the rock surface or precipitates in the pore space, whereby the pump pressure is below the frac pressure to ensure the uniform distribution of the inhibitor in the pores. With the help of water or another fluid, the inhibitor is further squeezed into the formation, where it adsorbs to the pores of the formation. Although scale formation should be prevented the squeezed inhibitor can lead to a so called *Pseudoscale* with the same consequences of normal scales. This is the case when the solubility limit is exceeded and thus leading to crystallization of the inhibitor.

With time, the inhibitor is released to prevent the deposition of scales. This treatment ensures a longer inhibitor life, thus reducing the frequency of descaling.

Carbonate formations are good candidates for squeeze treatments since the inhibitor is strongly adsorbed by Ca^{2+} and Mg^{2+} ions. Therefore, it is common to repeat the treatment after a few years, usually after three years, whereas in sandstone formations it is possible that the inhibitor can lose its efficiency after a few months. This effective time is quite short because the adsorption capacity of sandstone rocks under reservoir conditions is limited.

This method helps to avoid scale depositions in the formation as well as reduction of the permeability. If the inhibitor concentration drops below a certain value then the process has to be repeated. Treatment lifetimes for this method depend on the surface chemistry, the temperature, and the pH of the liquid contacting the formation. Core tests showed that the lifetime of the inhibitor after the repetition are shorter than after the first treatment but the volume is less. The disadvantage of this method is the consumption of large volumes of chemicals, the need of coiled tubing for placement, and large amounts of vessel resources to complete. Furthermore, the concentration of the inhibitor has always to be controlled during production to know the time of a new treatment. However, the key factor in performance of an inhibitor treatment is the proper inhibitor placement.

Below the advantages and disadvantages of a squeeze treatment is listed. [14]

Advantages of the squeeze treatment:

- There is no skin in the formation
- There are no deposits on completion equipment
- The tubing has not to be pulled out
- In general an easy job for service companies
- Only periodic controlling is necessary

Disadvantages of squeeze treatment:

- Treatment has to be repeated regularly
- Predictions about the efficiency are very difficult, sometimes impossible, especially with new wells
- Composition of inhibitor can not be changed afterwards
- Risk of formation damage
- Corrosion prevention and control is more difficult
- Need of coiled tubing

3.7.1.3 Continuous Inhibitor Treatment

Continuous treatment is suited for every kind of inhibitor. The inhibitor is brought down the wellbore through gas lift valves, an own tubing or directly through the annulus. For the inhibitor to be efficient it must be present in the aqueous phase in sufficient concentration, which will be determined by the bulk concentration, by the rate of transport to the surface and by the rate of consumption of the inhibitor.

When transporting the inhibitor through gas lift valves, the inhibitor prevents the plugging and blocking of the valves and the standpipes. On the other hand, the inhibitor itself can lead to blocking by evaporation or coagulation. However, this can be avoided by choosing the proper composition of the inhibitor or by diluting the inhibitor solution.

The way through the annulus is the simplest way to transport the inhibitor. Of course, this can only be done when there is no packer inside the well. Care should be taken when choosing the inhibitor concerning the dispersion in the production stream and influence on other kinds of inhibitors. The inhibitor should be uniformly dispersed within the produced fluids to ensure the full efficiency.

Another possibility to apply continuous inhibition is to install an additional string in the wellbore. This string can also be used for other inhibitors, such as corrosion inhibitors and the concentration can be changed every time if necessary. On the other hand, an additional string means additional expenses and energy. Furthermore, the installation of such a macaroni string is often not possible with horizontal or strong deviated wells.

In OMV, the few concerned wells and lines are treated by the continuous method.

3.7.2 Magnetic Fields

The working principle of magnets in oilfield wells is the following: when a fluid goes through a strong magnetic field, the charged particles are influenced, thus influencing crystal growth, morphology, solubility and deposition rate. The influence on crystal growth is such that crystals are getting larger and therefore, attachment to other crystals is not that easy as before.

The advantage of this technology is that with installation of a permanent magnet no maintenance and additional installation are required. According to the companies every 500 metres depth one magnet is needed for a proper prevention.

Since there is no maintenance of the installation necessary no additional personnel is needed either and thus reducing costs and time. On the other hand, a wrong installation of the permanent magnets can impede the efficiency.

3.7.3 Changing the Production Parameters

Production parameters can be changed in order to inhibit and prevent scale formation. Above all, reducing the number of gas lift installations would minimise scale depositions in many standpipes. Furthermore, an increase in pressure would prevent or at least delay the formation of $CaCO_3$, because less CO_2 can break out of formation brine.

3.8 Scale Removal

When scale is already formed, scale removal methods must be quick, non-damaging to the wellbore, tubing or formation environment, and effective at preventing precipitation. Knowing the type and quantity of scale and its composition or texture, are the most important prerequisites to perform the best removal technique. Strengths and textures of scales vary from delicate, brittle whiskers or crystals with high microscopy, to rock-like, low permeability layers. Furthermore, impurities in scale deposits can affect the resistance to removal methods. Pure $BaSO_4$, for example, is extremely resistant to chemical removal, and can be very slowly removed by mechanical techniques. Mixed scales with $BaSO_4$, however, can be removed by both methods, chemical as well as mechanical.

3.8.1 Mechanical Methods

Mechanical methods provide a wide range of tools and techniques that are appropriate for wellbore tubulars and the sandface. The choice of the correct method depends of course on the scale deposit and the well.

In earlier days, explosives were used to rattle pipe and break off brittle scale. They were effective in removing scale but also effective in damaging tubulars and cement, since the explosives provided high-energy impact loads. This principle was improved further and further. Today, the method of string shots is still used. For that a few strands of cord are detonated by an electric cap. With this method, scale blockages in perforations and thin scale films inside tubulars are successfully removed.

Very hard scale deposits, where the porosity is too little for a chemical treatment, can be removed by impact bits and milling technology. These bits are run on coiled tubing inside the tubulars and function like drill bits. Impact bits are reciprocating tools that work much like a jackhammer with a rotating bit and work best on brittle scale deposits. As with mills, they need a fullbore access to be effective and they seldom clean scale completely from the steel walls.

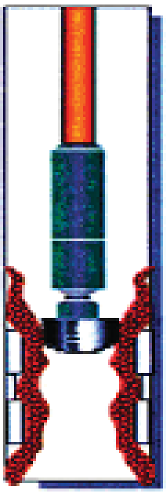

Figure 21: Milling action of a mill

Another possibility would be fluid jetting methods, where tools with multiple jet orifices achieve full wellbore coverage. Usually water is used as jetting fluid, although chemicals can be added. Not only chemicals can be added to the stream but also solids to make the jetting fluid even more effective. These solids are abrasive and improve the ability of the water jet to cut through scale drastically. Sand as additive is widely used. However, not only scale is cut through but also the tubing. Therefore, it is necessary for the jet to exploit the difference in hardness between wellbore scale and the underlying steel. With time, the sand particles will erode the surface of the ductile material by a cutting and plowing action, thus may leading to potential corrosion problems.

Figure 22: Different nozzle configuration for jetting tools

3.8.2 Chemical Methods

Chemical methods are sometimes the only way to get access to scale deposits. Besides, they are the first and lowest cost approach and the remaining possibility if mechanical methods are ineffective or too expensive to be carried out.

Like mechanical methods the selection of the appropriate chemicals depends on the scale type. Sulphate scale, for example, can be best treated by strong chelating agents. $CaCO_3$ scale, however, has a higher acid solubility than sulphate scales and can be therefore easily removed by HCl acid, yet taking care of precipitation of by-products through spent acid solutions.

For most chemical treatments, the surface-area-to-volume ratio or equivalently the surface-area-to-mass ratio is an important parameter. This parameter controls the speed and thus, the efficiency of the removal process. This means, that porous materials, e.g.: clay-like particles and hair-like projections react quickly, since they have large reaction surface areas. Scale deposits in tubings have a small surface area for a large total deposited mass; therefore, the reactivity of chemicals is slow to be effective.

The different methods and chemicals are previously described in more detail.

4 Laboratory Experiments

Scale inhibitors can be tested in the laboratory with static tests or dynamic tests. The following part contains a detailed description of these tests and the results of the tests done for this thesis.

4.1 Static Tests

Static tests are used to determine the most effective inhibitor and its best application level, i.e. concentration. For that, the water sample is mixed with the scale inhibitor in various concentrations. The beakers containing the mixtures are then kept at a certain temperature for a fixed period of time. Usually the mixtures are held at 70°C for 16 hours. After that the mixtures are filtered and the concentrations of calcium, barium, and strontium remaining in the solution are then determined. When plotting the results a ranking of the tested inhibitors can be made. [19]

Basically, this method measures the precipitation of scale forming solids, e.g. calcium carbonate, calcium sulphate, barium sulphate or strontium sulphate in the presence of an inhibitor with varying concentrations. The results of the different inhibitors are compared with each other. The more solids that could be kept in solution by a given amount of inhibitor, or the less inhibitor is needed to keep a given amount of solids in solution, the more effective the inhibitor is.

- In static tests, the inhibitor is added to unstable water or a mixture of incompatible ions.
- For evaluation monitoring over time has to be performed:

  Measurement of the ionic concentration change or
  Measurement of the onset of turbidity or
  Quantification of the precipitation (floating and adhesive).
- These tests normally are performed at field application temperature.
- Scale inhibitor is added in various concentrations.
- The inhibitor providing best protection at lowest dosage is the most efficient product.

4.1.1 Experimental Setup and Methodology

When doing static tests one has to ensure that the flasks are clean and free of any impurities. Therefore, the very first step in doing static tests was to clean the Erlenmayer flasks with HCl acid and to rinse out the flasks with bidistilled water to remove all the acid. The acid should not be too weak otherwise the flasks would not be clean enough. In this case, a 16% HCl acid was used. After cleaning, the flasks were dried in a drying cabinet to remove water left from the cleaning. Each dry flask was filled with 100 ml of the water samples and the inhibitor, whereas four flasks were blank, i.e. there was no inhibitor. When finishing the preparation of the flasks, they were put into the drying cabinet again at the desired temperature for one week.

The tests were done with water samples from the Romanian well 16 Sampetru German. This well was chosen randomly. It did not matter which well should be tested, the main thing was that a well was tested to compare the results.

EM [ml]	50
Total hardness [°dH]	34.22
Ca [mg/l]	178

Table 4: Analysis of the water sample for the static test

For this test, four scale inhibitors out of the initial 23 inhibitors, including scale inhibitor A, were tested concerning their efficiency. The dosage of the inhibitor was increased in 2 ppm steps, starting with a concentration of 4 ppm and for each concentration step there were two flasks available, containing the water sample. Altogether, there were two flasks with a concentration of 4 ppm, two flasks with 6 ppm, etc. until 10 ppm, and four flasks containing only the water samples. This means that there were in overall 36 filled flasks, which were dried in the drying cabinet at a temperature of 40°C for one week. This temperature was taken because it was the wellhead temperature, where big problems due to scale deposits occur.

When analyzing the samples after a week, it was recognised that the thermometer of the drying cabinet was not that precise, i.e. the temperature in the drying cabinet was in reality only 33.4°C although the cabinet was set to 40°C. Nevertheless, this was only an experiment to confirm the results of the dynamic tests.

However, a first optical analysis was done. On the first sight, it can be seen that the precipitations did not occur uniformly, i.e. there were precipitations in one flask and in the other flask with the same concentration there were none of them. Moreover, in some flasks containing the inhibitor there were more precipitations than in the flasks without inhibitor. The reasons for these results could be the instability of the water samples or the flasks were not closed and cleaned properly.

Optical analysis									
Concentration	0	4_1	4_2	6_1	6_2	8_1	8_2	10_1	10_2
Blank 1	++								
Blank 2	+								
Blank 3	+								
Blank 4	/								
A		-	-	+	-	-	-	+	-
B1		+	+	-	-	/	+	-	/
M3		-	+	-	-	+	-	/	-
M5		-	+	-	+	-	+	-	-

Table 5: Results of optical analysis

Due to the irregular results from the optical analysis the measurement of the calcium concentration in the filtrate were not done further.

4.2 Dynamic Tests

Dynamic tests are carried out in order to evaluate the efficiency of different chemical inhibitors to prevent the formation and deposition of mineral scales and to investigate the effect of increasing temperature and pressure on scale formation.

For this thesis, the Dynamic Tube Blocking Test (TBT) method was used. With this method, the MIC required to prevent scale formation can be determined and the testing of different scale inhibitors at the same conditions can be accomplished.

The basic principle of a dynamic test is always the same. The method is based on the rate at which the pressure drop increases through a capillary tubing. This pressure increase indicates that something in the capillary is precipitated and hinders the flow through it.

There exist many variations of the testing unit, but generally, the testing unit consists of several pumps, a water bath, a mixing chamber and a pressure recorder.

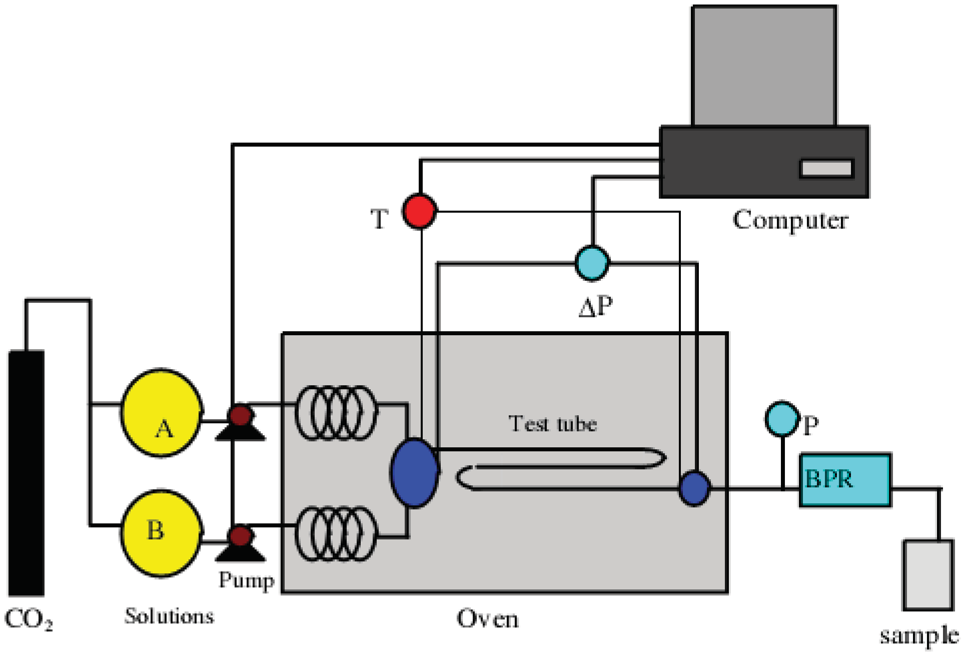

Figure 23: General setup of a TBT apparatus [20]

In this configuration, two pumps are driving two solutions, containing scale forming cations and anions respectively. The solutions go through pre-heating coils that bring the solution to the desired test temperature and are then combined to a solution with a positive SI. The new solution passes through the test tube, where scale crystals nucleate and grow on the circumference of the tubing. By measuring the scale forming ion concentrations at the outlet sampling point and the pressure drop across the tube, the process of scale formation can be monitored. A BPR is used to maintain the pressure. The pressure drop across the test section is measured either, to monitor tube blockage, i.e. ΔP increases. In overall, solution temperature and ΔP are logged by the computer to visualize the process of scale formation in the test tube.

4.2.1 Experimental Setup and Methodology

Although there exist variously modified testing units, the basic principle is always the same. The method depends on the rate at which the pressure drop increases through a standard length of capillary tubing. For this work, however, the apparatus was modified a little bit.

The tubing bore diameter in this case was 0.5 mm and the length 1 m. Generally, stainless steel tubing wound into a coil is used. The flow rate was set at 5 ml/min and kept constant.

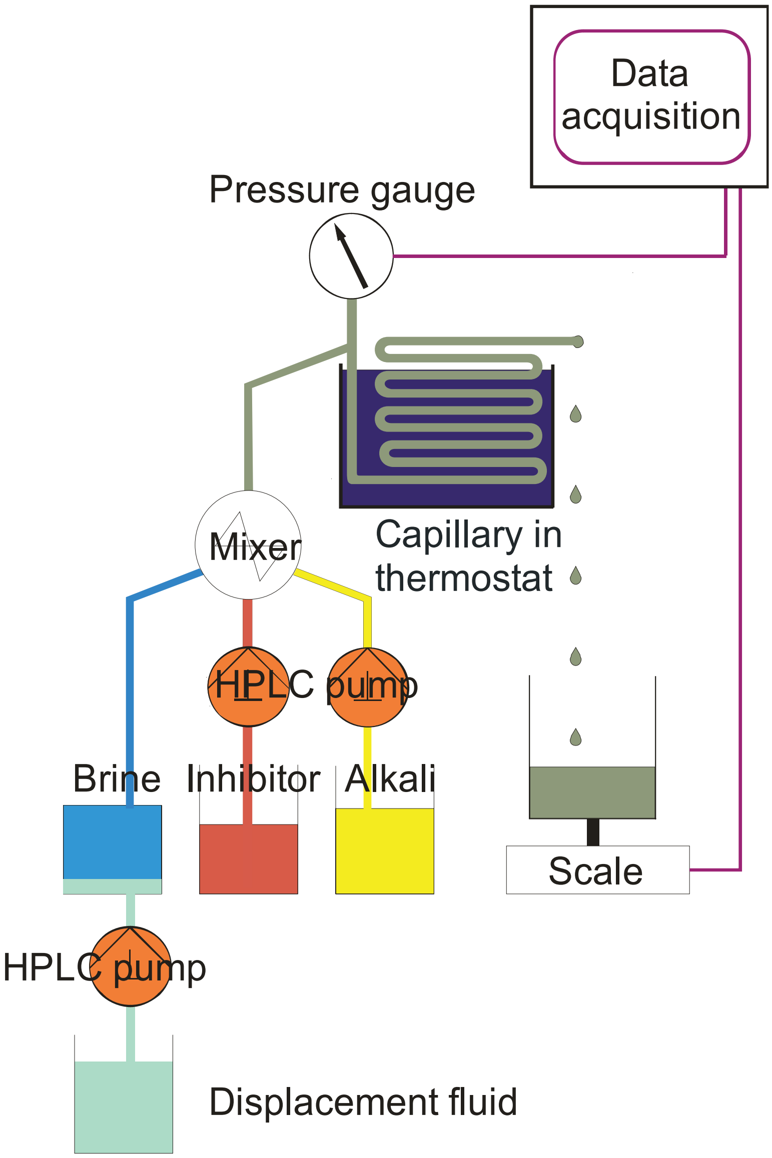

Figure 24: Scale apparatus from OMV

The apparatus consisted of a water bath with a capillary tubing inside. The water was heated up to the desired temperature and kept at this temperature.

HPLC pumps, one for each fluid, were used to pump the fluid through. These pumps are very sensitive to solids and precipitations, and therefore, the fluid containing the carbonate ion for potential scaling was pumped indirectly by displacement into the mixing cell. Inside the mixing chamber, a magnetic stirrer mixed the incoming fluids - water sample, NaOH base to destabilize the water sample and the inhibitor – before entering the steel tubing. A base was needed to raise the pH to 8.5 because very little precipitation took place by itself and therefore, the process would take too long. Although, this was a change of the real conditions it was still possible to demonstrate the performance of the tested inhibitors.

Since the pumps were designed as constant flow units, a decrease in bore diameter due to scale deposition inside the test coil would result in an increase of fluid velocity and hence pressure drop across the coil. The tubings from the pumps were connected to the injection needles on the top of the mixing cell. The outlet of the cell itself was connected via silicone tubing to the inlet on the rear of the pressure transducer. In addition, the outlet of the pressure transducer was linked to the inlet of the coil.

A digital balance measured the weight of the droplets coming out of the capillary and thus checking for flow irregularities. The pressure and the weight were monitored and plotted in a diagram in real time by a software called VEE Agilent Pro, which is a visual programming and dataflow programming language.

Figure 25: Apparatus setup

The water samples were analysed prior to the experiments. Total hardness, Ca content, Mg content, pH and base consumption to pH = 8.5 were measured. This pH value was taken empirically and because it was a good average value, where scale precipitation occurs.

For measuring the total hardness, a certain amount of the water sample was mixed with a Ca-Mg-buffer solution and an indicator buffer pill. When the pill was completely dissolved, the mixture was titrated with an m/20 Komplexon until the previous red colour of the mixture changed into green. The value was then taken for calculating the total hardness with the following formula:

$$°dH = V_{\sum} * m * F * 5.608 * \frac{1000}{EM} \quad (4\text{-}1)$$

The same procedure was used for measuring the amount of calcium in the water sample. For measuring this amount, a Ca-buffer solution and calconcarboxylic acid were mixed with the water sample. The initial pink colour should change into blue. The amount was then calculated with the following formula:

$$mg / lCa = V_{Ca} * m * F * 40.08 * \frac{1000}{EM} \quad (4\text{-}2)$$

The Mg amount is calculated from the difference between those two volumes. When having this, the amount in mg/l could be calculated as following:

$$mg / lMg = (V_{\sum} - V_{Ca}) * m * F * 24.305 * \frac{1000}{EM} \quad (4\text{-}3)$$

The base consumption was also done by titration with a 0.1N NaOH base solution. This value was needed to adjust the pump for the test.

The inhibitors were diluted with distilled water, depending on the needed concentration and injected into the mixing cell.

After each test run, a 5% citric acid solution was used to remove the remaining deposits in the tubing. Distilled water was then used to flush out the left acid, which otherwise would retard the initiation of any precipitation.

4.2.2 Tests with Synthetic Water Samples

For understanding and getting familiar with the apparatus the handbook of the scale apparatus suggests working with synthetic fluid samples. The fluid samples were mixed according to the handbook with one solution containing the precipitation inducing $NaHCO_3$ and the other containing a mixture of various kinds of chlorides. When mixing them up in the mixing cell, precipitation in the coil will occur after a certain time.

For the test runs with synthetic fluid samples, three inhibitors were tested at a temperature of 70°C. When adding the inhibitor, the amount of the fluid sample was reduced to keep the flow rate of 5 ml/min constant. After each run, the capillary was cleaned up with a solution of 5% citric acid and distilled water to make sure that the test coil was clean for the next run.

Three scale inhibitors were tested concerning their performance against carbonate scale formation for a Libyan oilfield of OMV, where carbonate scale occurs in masses and leads to production problems.

Temperature	70°C
Solution 1	NaCl, KCl, $CaCl*2H_2O$, $MgCl_2*6H_2O$ pH = 6.18
Solution 2	NaCl, $NaHCO_3$ pH = 7.96
Scale inhibitor A	Polycarboxylic acid – based inhibitor
Scale inhibitor S1	Carboxylate type inhibitor
Scale inhibitor B	Blend of organic phosphates and polymers
Initial inhibitor concentration	6 ppm
Flow rate	5ml/min
Inhibition pressure	0.35 bar

Table 6: Test conditions with synthethic brine

The first test was done without any addition of inhibitor, i.e. a blank line was run to get a reference curve. In the following tests the inhibitors were added at a predetermined pressure, in this case p = 0.35 bar. This value was chosen arbitrarily; nevertheless, one has to be aware that there should have been enough time for a proper pressure build up. Furthermore since the pressure transducer has a limit of only one bar the pressure for adding the inhibitor has to be chosen carefully. Hence the risk of blocking the test coil is greater, the higher the prescale pressure. The concentration of the inhibitors was set to 6 ppm and should be increased in 2 ppm steps after every 30 minutes if the inhibitor was not effective.

4.2.2.1 Results

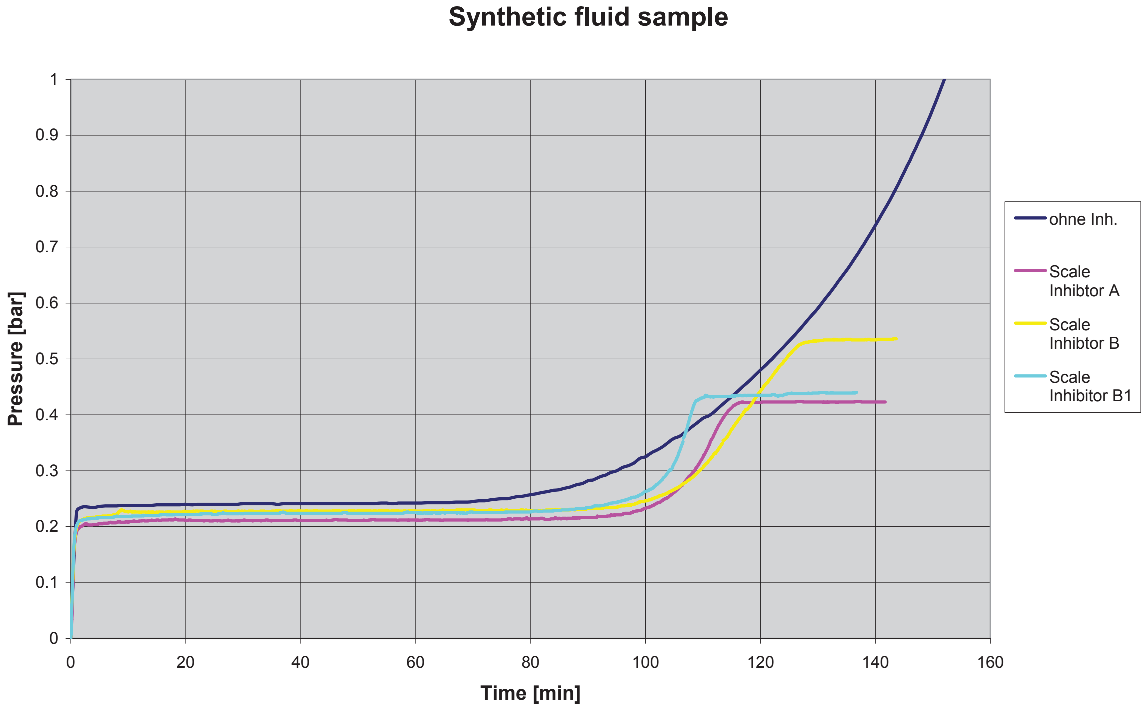

Figure 26: Pressure profiles of the tested scale inhibitors with synthetic water samples

This diagram shows the results of the tests with the inhibitors and the blank line in one diagram. As it can be seen, all three inhibitors were successful in inhibiting further scale formation. The curves differ from each other because the time of nucleation of the scale crystals is varying and the water quality changes over time. Besides, it is not possible to get the test coil into the same condition as before again although the testing conditions are kept as constant as possible. For a better interpretation, the curves can be adjusted.

As scale started to build up in the test coil, the monitor showed a gradual rise in pressure. Reactions do not occur instantaneously. A time delay occurs once all of the reactants have been added together. They must come together in the reaction media to allow the reaction to happen. The time required before a reaction begins is termed the induction time.[19] When the pressure reached 0.35 bar the inhibitor was injected via the second pump. In the case that the inhibitor was efficient, the pressure would flatten out. Otherwise, the pressure would increase again and the dosage has to be increased further. In this test run, all three inhibitors showed good inhibition efficiency because the pressure stayed constant after adding the inhibitor.

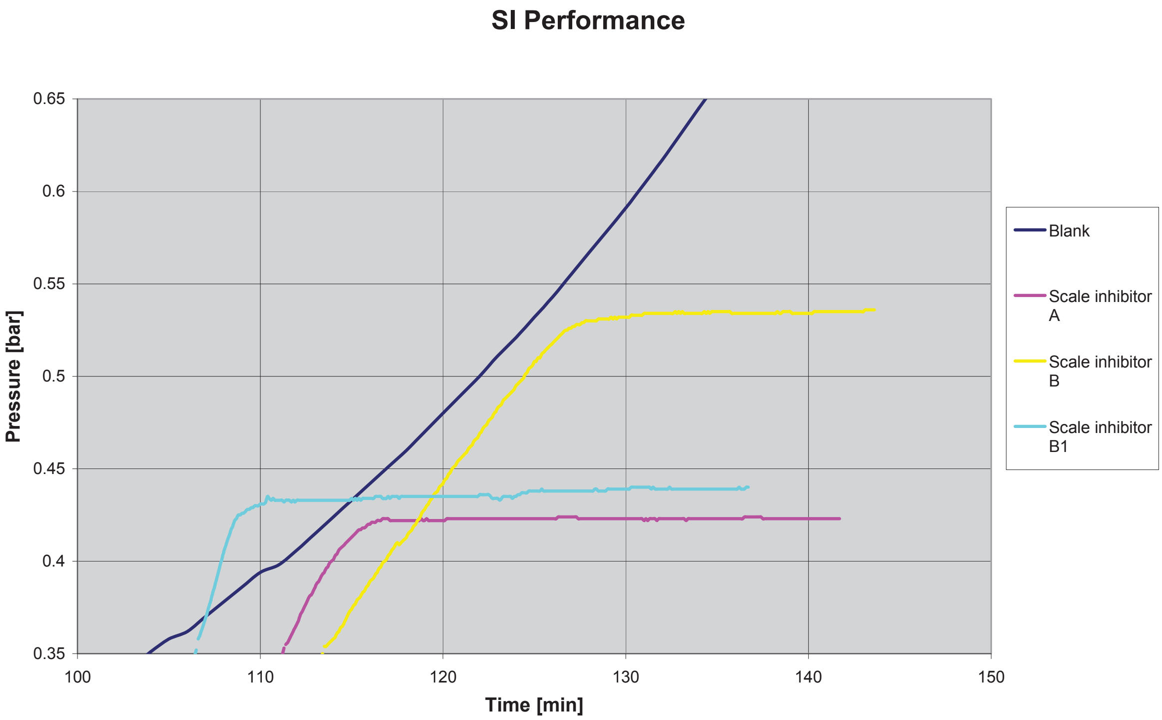

Figure 27: Enlargement of the relevant part of the previous diagram

This diagram is just an enlargement of the previous diagram. A curve adjustment, e.g. an overlapping of the curves, is not necessary in this case because the results are quite clear. All three inhibitors are effective at a concentration of 6 ppm. Since scale inhibitor A showed the earliest pressure plateau, it was recognised as the inhibitor with the best inhibition performance. Nevertheless, the other two scale inhibitors made a good job too, thus the decision what inhibitor to take, would depend on price and availability.

4.2.3 Tests with Water Sample from Matzen

Matzen 172 is a well in Austria, which is still producing but with a high percentage of water. Problems with carbonate scales in the Matzen field occur in gas lift wells, heat exchangers at gathering stations and subsequent flowlines.

A few years ago, 12 phosphate-free scale inhibitors were tested with brine samples from this well in order to find an alternative product to the still used scale inhibitor A. The inhibitors were tested and screened through a TBT and afterwards through static tests. Inhibitor A, which was already in use for about 15 years, was run as a benchmark in those tests. Field tests were carried out either to prove the performance of the tested inhibitors. Finally, inhibitor A was again the best and cheapest one among those tested inhibitors. This scale inhibitor is still used today. Part of this work was to check, whether this inhibitor is still effective or not and to use it again as a benchmark for the new scale inhibitors to be tested.

After testing the apparatus and practising with the synthetic fluid samples tests were run with fluid samples from the well Matzen 172 and the same three scale inhibitors as before. Since this water is not susceptible to extreme scaling the dosage of inhibitor added was very limited.

Before doing the tests the water sample was filtered and analysed concerning the total hardness, Ca amount, Mg amount, pH and base consumption to pH = 8.5.

Again, when adding the inhibitor the amount of the water sample was reduced with respect to the amount of the added inhibitor to keep the flow rate constant at 5 ml/min. Furthermore, reducing the amount of the base would be meaningless since there was only a small amount of base added. However, the initial concentration of the inhibitors was reduced to 2 ppm and increased in 2 ppm steps every 30 minutes if the inhibitor did not show any inhibiting behaviour.

Temperature	70°C
Total hardness	42.64°dH
Ca amount	189 mg/l
Initial pH	7.94
NaOH consumption	0.1 ml/5ml
Flow rate	5 ml/min
Inhibition pressure	0.35 bar
Initial inhibitor concentration	2 ppm

Table 7: Test conditions for Matzen 172

4.2.3.1 Results

The performance of the three tested inhibitors is shown in the diagram below. The time of increasing the inhibitor concentration is marked by small breaks in the curves.

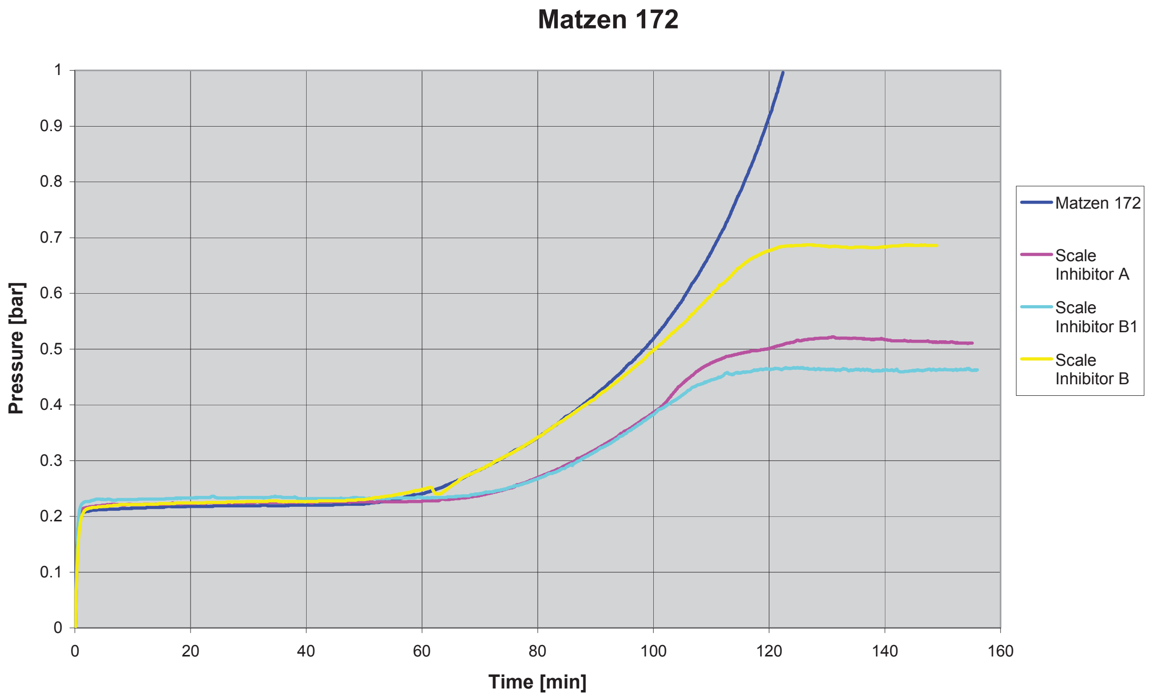

Figure 28: Pressure profiles of the tested scale inhibitors with water samples from Matzen 172

For analysing this diagram, it is not necessary to adjust the curve since it is very easy to see what inhibitor acts at best.

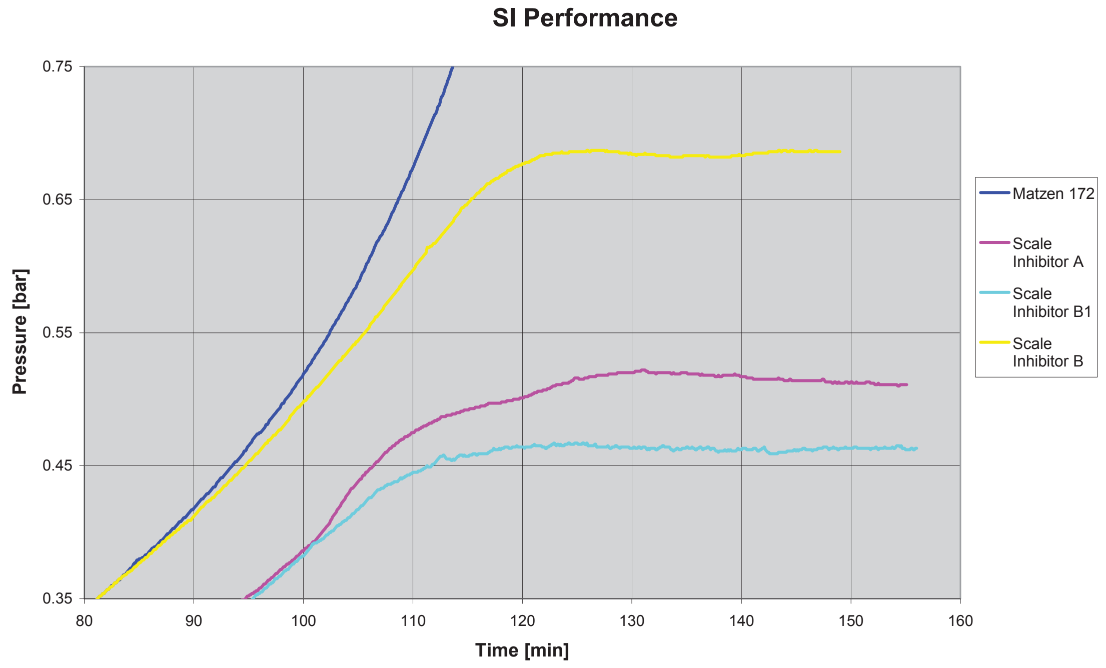

Figure 29: Enlargement of the relevant part

The small spikes only show the presence of small or often tiny gas bubbles, which indicate dissolution of some deposits in the tube.

The results show that in case of water samples from Matzen 172 inhibitor A, which is used as benchmark, takes the second place, right behind the new scale inhibitor S1. Scale inhibitor B, which is used in Libya, brings up the rear.

4.2.4 Tests with Water Sample from Libya

When analysing the Libyan water sample and comparing the results with those from Matzen 172, one can see that the Libyan water sample contains far more Ca^{2+} ions than the Austrian water sample.

Temperature	70°C
Total hardness	771°dH
Ca amount	4,278 mg/l
Initial pH	7.44
NaOH consumption	0.25 ml/5ml
Flow rate	5 ml/min
Inhibition pressure	0.35 bar
Initial inhibitor concentration	20 ppm and 10 ppm

Table 8: Test conditions for Libya

The sample was taken from the wellhead of a production well since scale depositions occur in the flowline between manifold and separator, where a pressure drop favourites depositions.

The conditions of the water have changed within four years. One of the major reasons is that the watercut from this field increased from 50% to 80%. In order to keep the oil production rate constant the gross production rate was then increased. As a result, the temperature increases, which together with the higher water rate enhance scale precipitation. Before enhancing the production rate, the inhibitor was injected after the manifold just before the produced fluids enter the separator. Now, after realising that the depositions occur earlier, the injection point of the inhibitor is about 50 metres away from the separator, i.e. before the produced fluids go through the manifold. Another fact why scale precipitation is favoured in this section is that the diameter of the flowline upstream the manifold is different to that after the manifold. The flowline is getting smaller downstream the manifold. Therefore, it will come to a pressure change, which will enhance the scale precipitation.

Due to the results from the sample analysis, the amount of the base is increased to get the pH value of 8.5. Nevertheless, the first blank line was run without any addition of the base; just to see whether precipitation occurs in the pre-set time or not.

Scale inhibitor A was tested only once at the beginning with the Libyan water sample, after that not any more. This is because this inhibitor is not available in Libya. Therefore, only two scale inhibitors were left.

4.2.4.1 Results

Since two cans of water samples were tested, the results from tests with water from the cans may differ from each other.

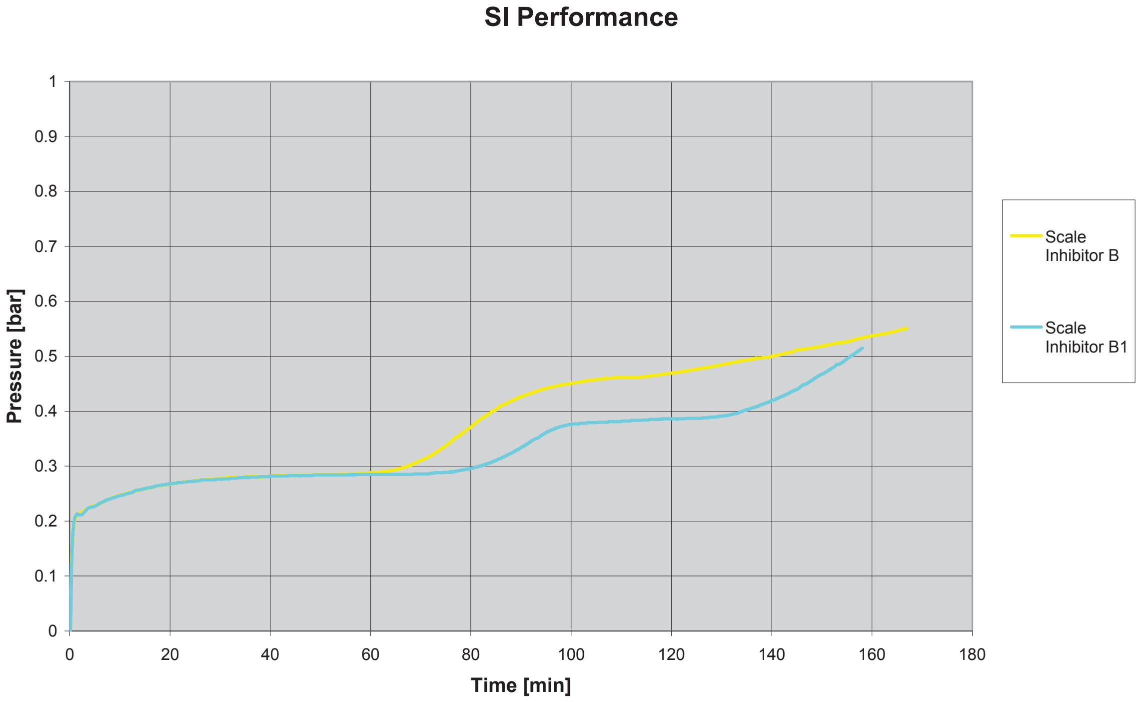

Figure 30: Pressure profiles of tested scale inhibitors with Libyan water sample

The initial inhibitor concentration was 20 ppm and was increased every 30 minutes by 10 ppm, i.e. at the end the concentration was 40 ppm. The amount of the brine was reduced by the amount of the added inhibitor to keep a constant rate of 5 ml/min. According to the diagram, none of the scale inhibitors was efficient in inhibiting scale precipitation because the pressure still increased although the concentration was very high.

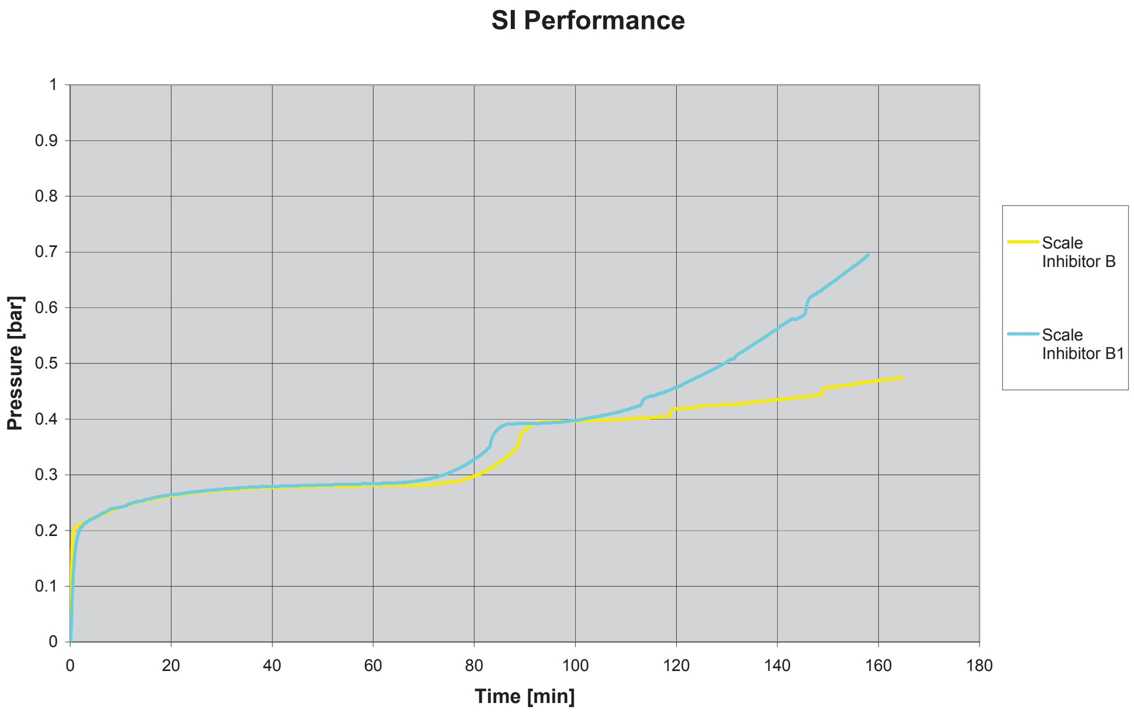

Figure 31: Pressure profiles with Libyan water samples at increasing flow rate

During these runs, the amount of brine was not reduced by the amount of added inhibitor. Therefore, there are pressure jumps shortly after adding the inhibitor. In the previous test runs the brine amount was reduced when the inhibitor was added. In doing so, the pH increased because the solution got more alkali and thus leading to even more precipitations. The initial concentration was still 20 ppm and ended up with 40 ppm.

Although the initial concentrations were quite high and the concentrations were further increased, the pressure still increased and showed no flattening. The explanation for this behaviour could be overdosing of the inhibitors. In case of an inhibitor overdose, precipitation of additional products can occur and the inhibitor causes more precipitation than as otherwise.

For this, the next tests were done with a lower initial inhibitor concentration.

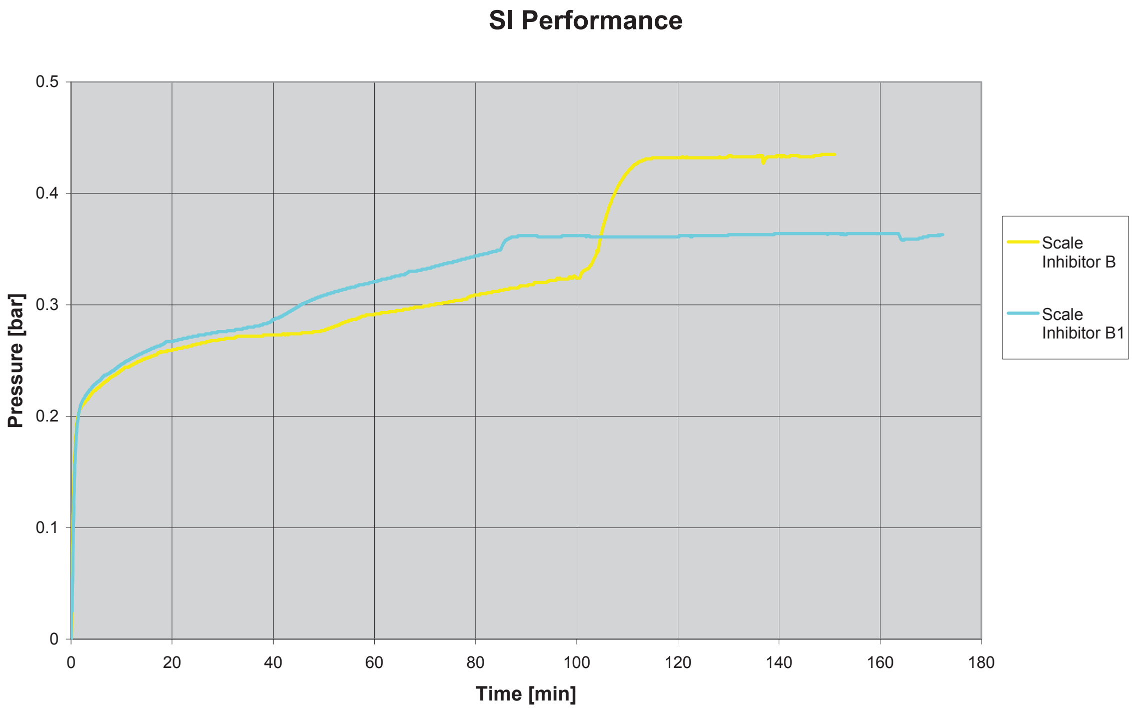

Figure 32: Pressure profiles with Libyan water samples with reduced initial inhibitor concentration

The initial concentrations for these tests were set at 10 ppm. Reducing the concentrations was a good idea because now the inhibitor showed a much better performance than before. Both of them are effective at a concentration of 10 ppm, whereas scale inhibitor S1 performed better than scale inhibitor B, because the pressure flattened out in more than half of the time of B.

4.3 Observations and Conclusions

When going through the results of these tests, it can be said that scale inhibitor A, which was tested a few years ago and is still used today, is still doing a good job, although this inhibitor belongs to an older generation of scale inhibitors. However, the selection of the scale inhibitors was quite good since all of them did a good job.

A very important point is the dosage of the inhibitor. As stated before, an overdose can lead to even more precipitation and thus causing more damage.

The pressure increase at the beginning of the tests showed some differences. While the pressure plateaus of the tests with water samples from Matzen 172 and synthetic brine were pretty flat during the induction time, the pressure plateau of the tests with Libyan water samples were more round. The reason may be that the composition of the Libyan water contained far more Ca^{2+} ions and therefore the pressure is constantly increasing due to a constant precipitation. Another reason may be the high viscosity of the brine, thus leading to a more viscous solution in the mixing chamber.

In overall, all three chosen scale inhibitors showed good inhibition efficiency, even at a low inhibitor dosage.

4.4 Screening of Scale Inhibitors from the Global Tendering

An important part of this thesis was to make a screening of scale inhibitors from the Global Tendering of OMV. Rising costs and the opportunity to use a competitive product made the Global Tendering necessary.

Companies, which want to take part of this competition, had to be aware of the following criteria:

- There should be no phosphate or phosphate-generating compounds for Austria
- There should be good inhibitive properties at competitive cost
- Flow should be possible even at low temperatures

If possible, green inhibitors will be preferred because of their environmental effect.

According to these criteria, scale inhibitors of three companies were selected and should be tested in the laboratory by screening tests. With these tests, the performance of the inhibitors should be evaluated and the best one should then be tested in the field.

Another reason for this inhibitor screening was the scale problem situation in Romania, where scale deposits can completely plug tubing within a short time. However, the wells there were not treated with scale inhibitors but with HCl acid, although the problems were not eliminated but further aggravated.

Therefore, the tests were done with brine samples from Romanian wells either to ensure that the testing conditions are as real as possible.

As mentioned before, scale inhibitors from three well-known companies were tested concerning their performance with brine samples from OMV wells. At the beginning, there were in overall 23 scale inhibitors, whereas only continuous scale inhibitors were taken for the tests.

The first screening was done with brine samples from well Matzen 172, simply because at that time there was no brine from Romania available. The tests were carried out like the previous one, i.e. analyzing of the brine sample, blank line, etc.

4.4.1 Screening with Water Sample from Matzen 172

Primarily, screening with brine samples from Matzen 172 should be done at various temperature conditions to evaluate the temperature dependency of the water sample. Three different temperatures were tested and are shown in Figure 33. At the end, the temperature was set to 50°C, since the pressure build up at 70°C was too fast and at 30°C too slow.

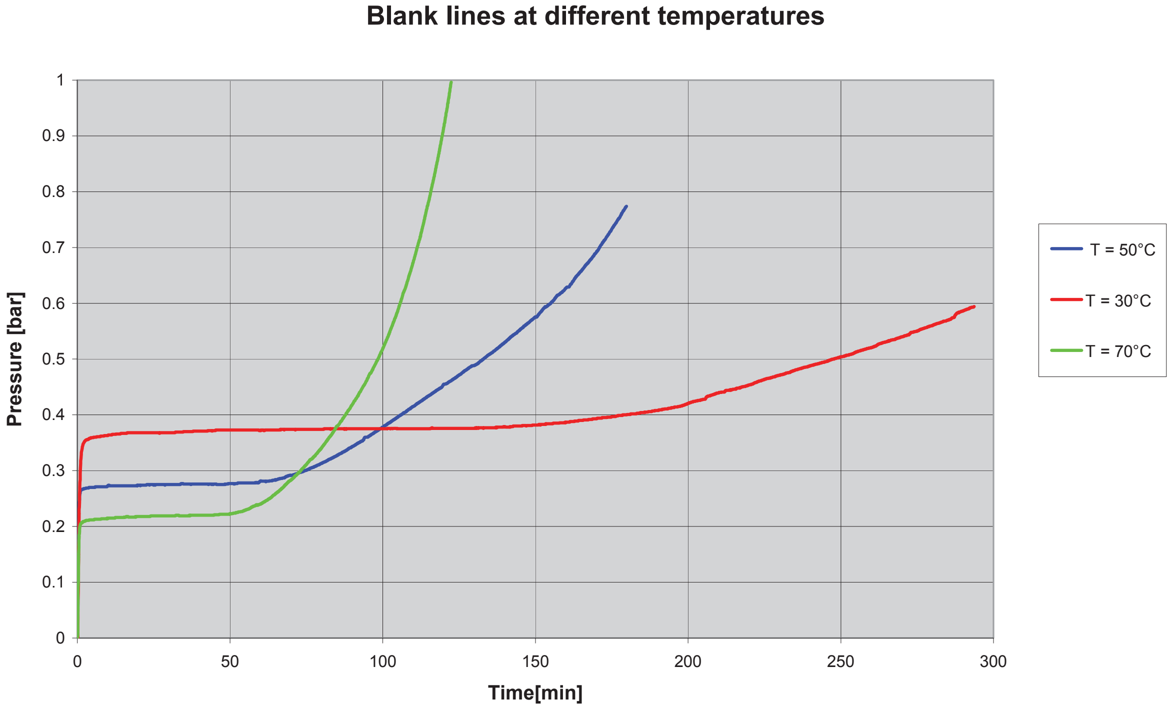

Figure 33: Blank runs with Matzen 172 at different temperatures for inhibitor screening

Temperature	50°C
Total hardness	44.04°dH
Ca amount	186 mg/l
Initial pH	7.58
NaOH consumption	0.1 ml/5ml
Flow rate	5 ml/min
Inhibition pressure	0.4 bar
Initial inhibitor concentration	2 ppm

Table 9: Test conditions for screening with Matzen 172

The inhibition pressure was changed to have more clearance for a proper pressure and scale build up.

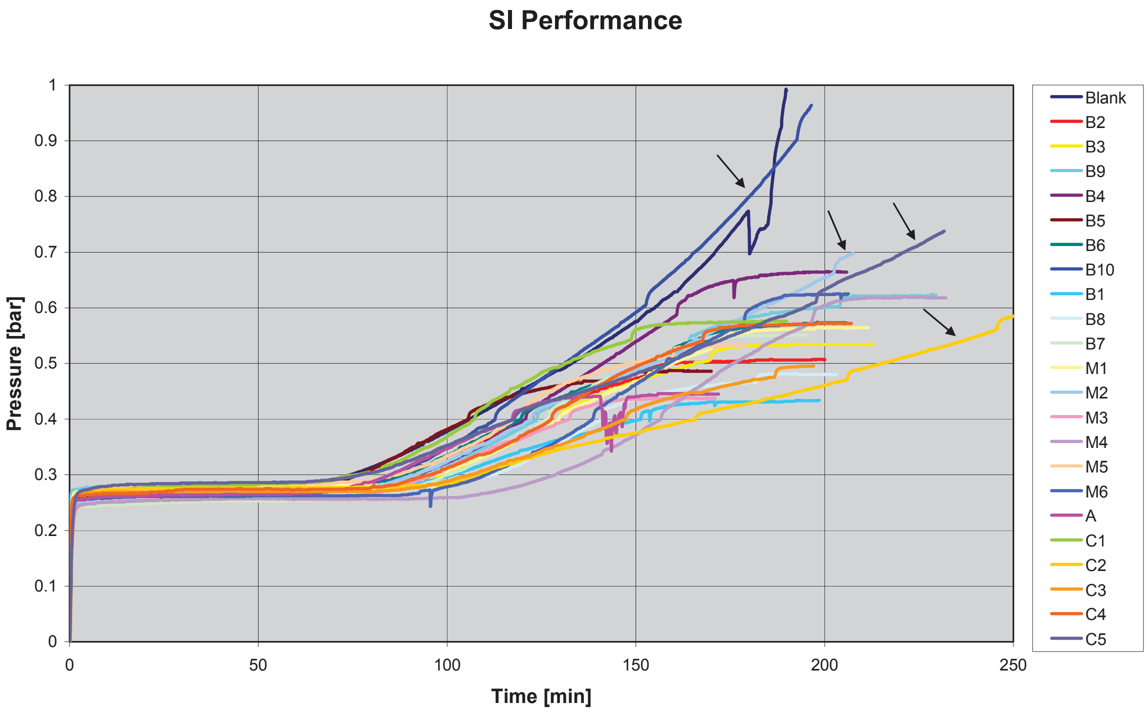

Figure 34: Pressure profiles from screening with Matzen 172

This diagram looks a little bit chaotic; however, it shows the performance of all tested scale inhibitors. It is possible to eliminate those inhibitors, where the pressure profiles do not correspond to the pre-determined requirements, i.e. the pressure still increases. The corresponding curves are marked with arrows in the diagram.

For a better analysing, the curves are adjusted and shifted.

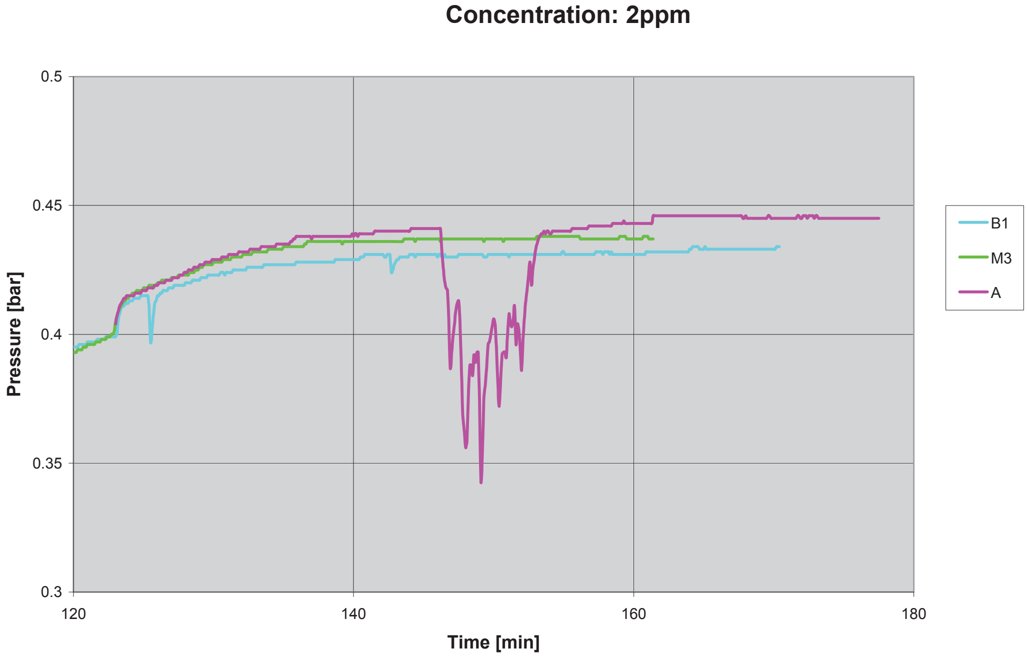

Figure 35: SI performance with water samples from Matzen 172 at 2 ppm

Only three scale inhibitors were efficient at a concentration of 2 ppm. Again, scale inhibitor A was one of them.

The bulk of the tested inhibitors were efficient at a concentration of 4 ppm. Their pressure profiles are shown in Figure 36. The curves are already adjusted for a better analysing.

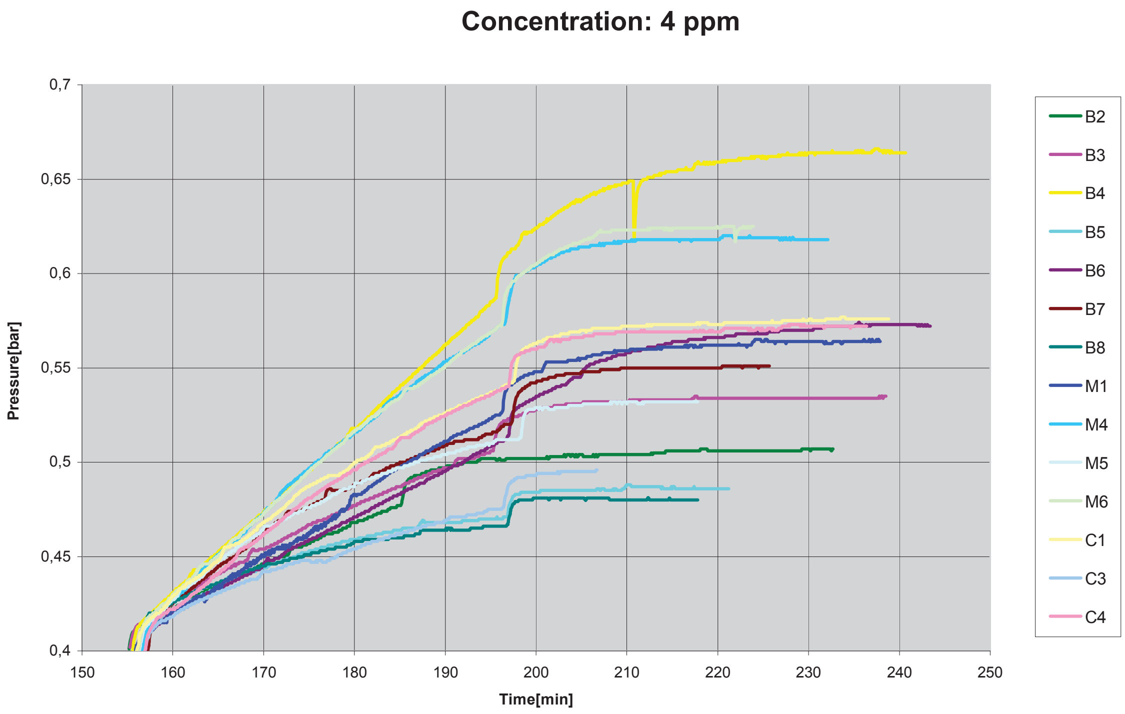

Figure 36: SI performance with water samples from Matzen 172 at 4 ppm

According to the results from the diagrams, the following ranking could be done:

B1 > M3 > A

B8 > B5 > C3 > B2 > M5 > B3 > B7 > M1 > B6 > C4 > C1 > M4 > M6 > B4

For ranking the scale inhibitors, the time when the curve starts to flatten out is the important aspect to be considered. Thus, the earlier the curve flattens out, the better the performance of the scale inhibitor, because this is a sign that the inhibitor starts to be effective.

4.4.2 Screening with Water Sample from Turnu Est – Romania

The same procedure as before was applied to brine samples from the Romanian well Turnu Est, Sonda 402. However, this time only 17 scale inhibitors were tested. Those 17 scale inhibitors were left from the screening with brine from Matzen 172, i.e. those were the best out of initial 23 scale inhibitors.

Temperature	55°C
Total hardness	54.43°dH
Ca amount	226 mg/l
Initial pH	7.46
NaOH consumption	none
Flow rate	5 ml/min
Inhibition pressure	0.35 bar

Table 10: Test conditions for screening with Turnu Est

As always, the first test was a blank run to see, how the brine sample acts. This time three blank runs were done, to see what NaOH dosage should be added to the brine. Concerning the titration, 0.45 ml NaOH should be added to the brine to get a pH of 8.5. This is shown by the blue curve. Another test was done with a reduced base dosage, but the pressure increase was still too fast. Therefore, a test without any base addition was done and the result was finally all right.

The small bumps at the beginning of the tests only show that the tube still contained HCl acid and some deposits. When starting the tests with the brine, the remaining acid in the tube dissolved the remaining deposits and thus leading to a pressure increase at the beginning and a constant pressure profile afterwards when there were no deposits anymore. According to the amount of left deposits in the tube, the pressure increase was different.

After analysing the pressure profiles, it was decided to run the subsequent tests without any addition of NaOH and to flush the coil again with distilled water.

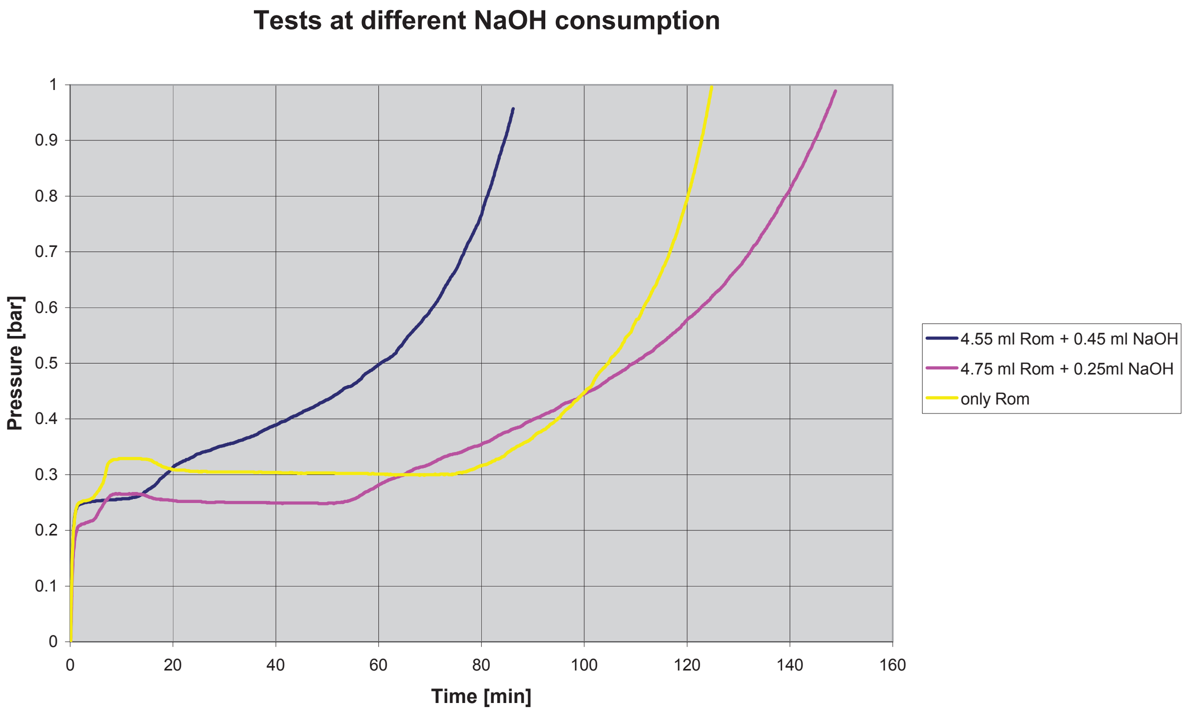

Figure 37: Blank runs with water samples from Turnu Est with different NaOH consumption

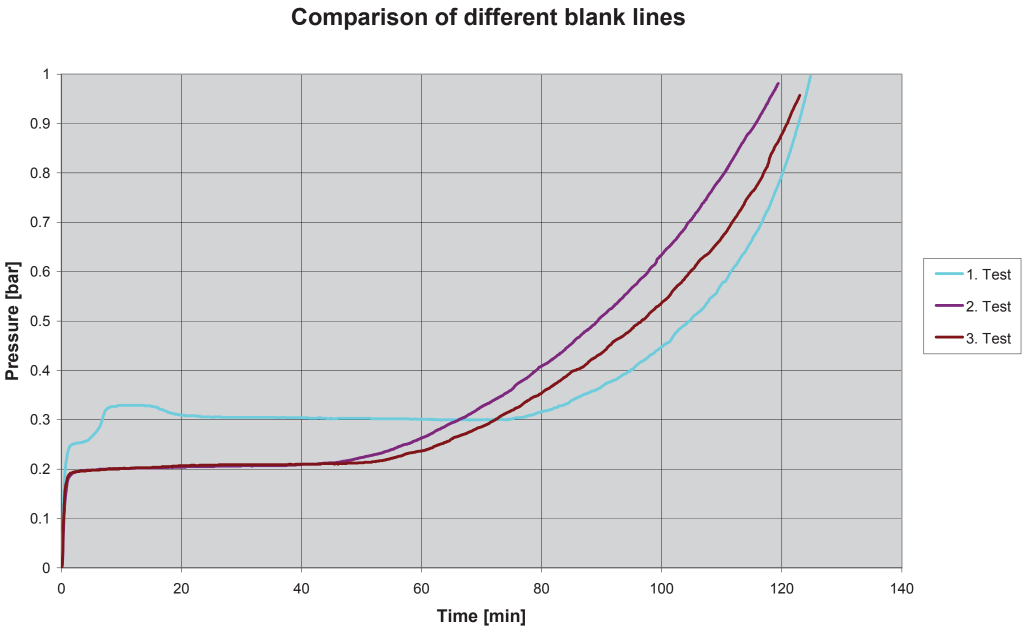

Figure 38: Blank runs without NaOH addition to verify the reproducibility

The purpose behind these tests was first, to ensure the repeatability of the tests and second, to do the same tests as before but with a cleaner tube. As it can be seen, the pressure profile of a cleaner tube looks quite different from the one of a tube still containing deposits. Since the pressure was very low at the beginning, the scale inhibitor would be added at a pressure of 0.35 bar again.

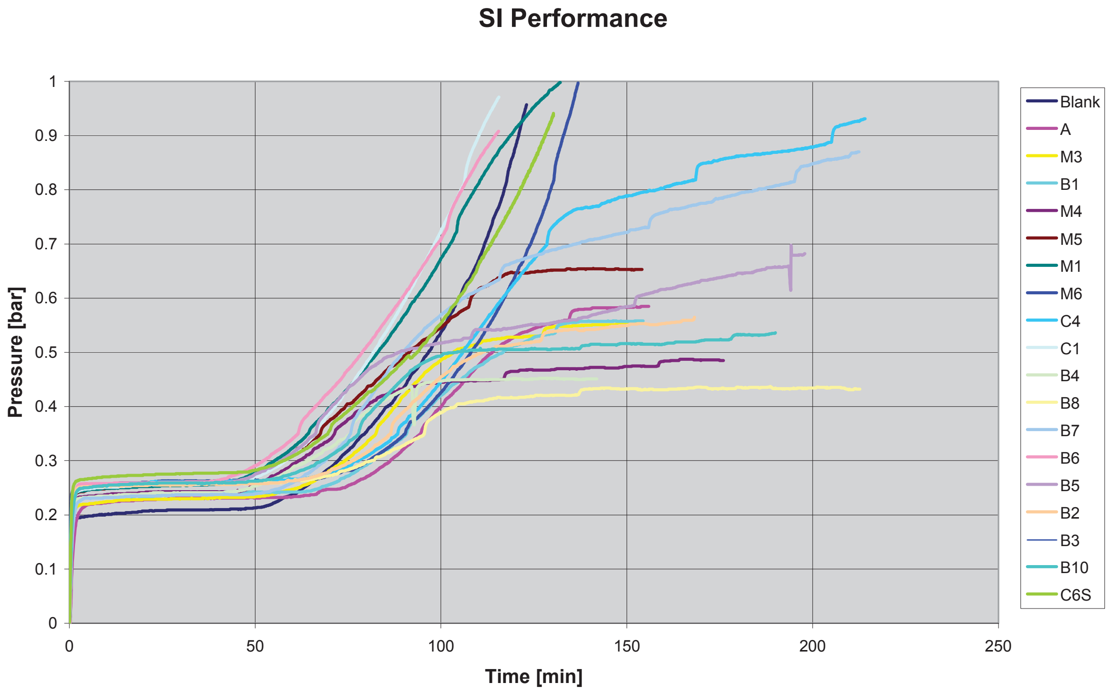

Figure 39: SI performance with water samples from Turnu Est

Originally, only 17 scale inhibitors should be tested with the brine sample from Romania, but since the people there started to test scale inhibitors on their own, their tested scale inhibitors should also be regarded as well in these tests. Therefore, the 18th scale inhibitor in this test was the added one, which was tested in Romania. This scale inhibitor was not in the assortment for this thesis, because it was a scale inhibitor for squeeze treatments.

From this diagram, those inhibitors can be dropped out, which showed no scale inhibition, i.e. where the pressure still increased.

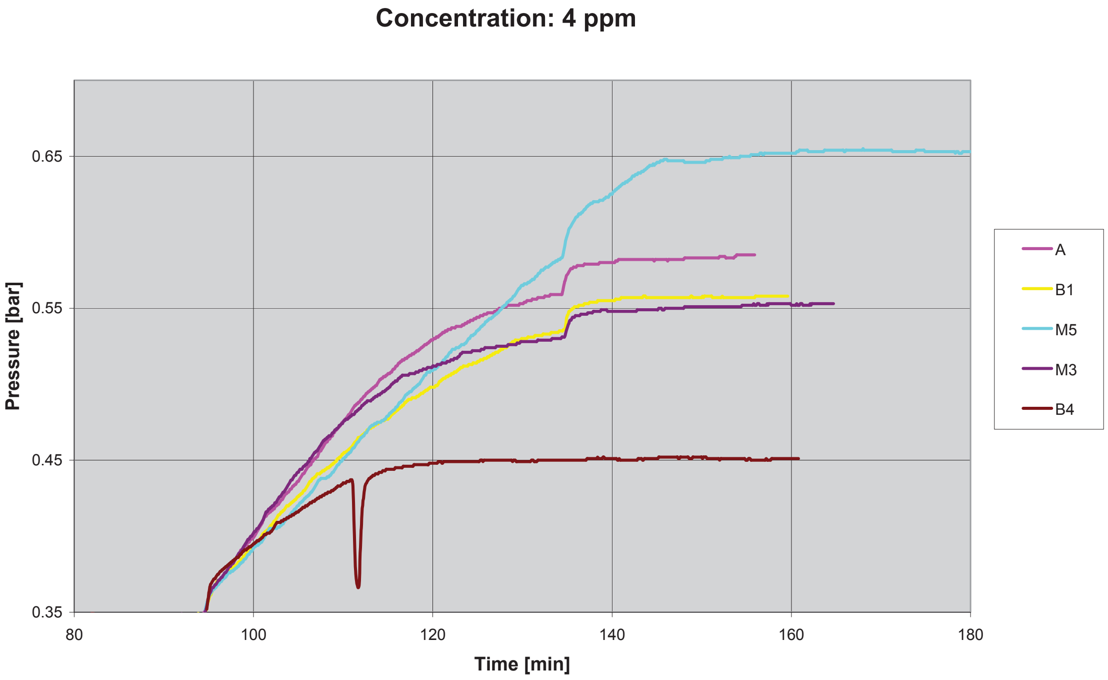

Figure 40: SI performance with water samples from Turnu Est at 4 ppm

For the diagram in Figure 40, those inhibitors were selected, which were efficient at a concentration of 4 ppm. The sharp pressure decline in curve B4 maybe showed a release of a solid in the tube.

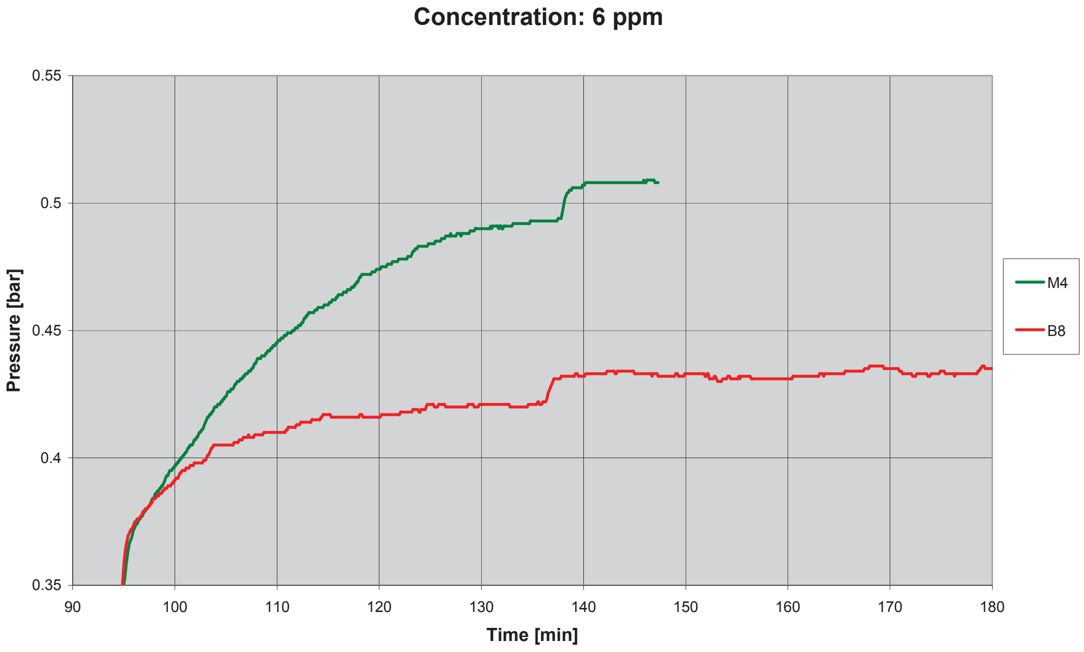

Figure 41: SI performance with water samples from Turnu Est at 6 ppm

In overall, seven scale inhibitors out of initial 17 were left after the screening. According to the results, a ranking of the best scale inhibitors can be made for the well Turnu Est.

B4 > M3 > B1 > A > M5 > B8 > M4

Whereas, the last two scale inhibitors of this ranking needed a concentration of 6 ppm to be efficient.

4.4.3 Screening with Water Sample from 16 Sampetru German – Romania

For the following two Romanian wells only those scale inhibitors were tested, which remained from screening with brine from Turnu Est. Therefore, only seven scale inhibitors were tested concerning their inhibition efficiency.

In well 16 Sampetru German scale depositions have plugged the standing valve and causes problems in surface equipment by clogging and plugging the flowlines.

Temperature	40°C
Total hardness	48.7°dH
Ca amount	206 mg/l
Initial pH	7.33
NaOH consumption	0.35 ml/5ml
Flow rate	5 ml/min
Inhibition pressure	0.4 bar
Initial inhibitor concentration	2 ppm

Table 11: Test conditions for screening with 16 Sampetru German

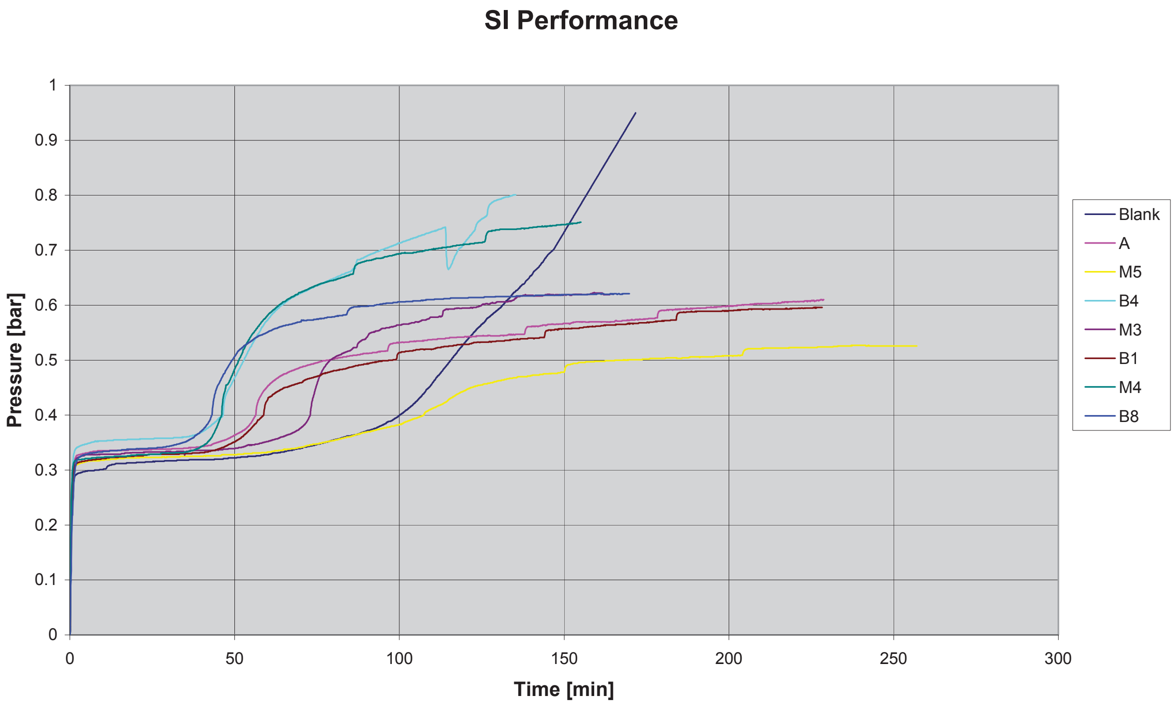

Figure 42: SI performance with water samples from 16 Sampetru German

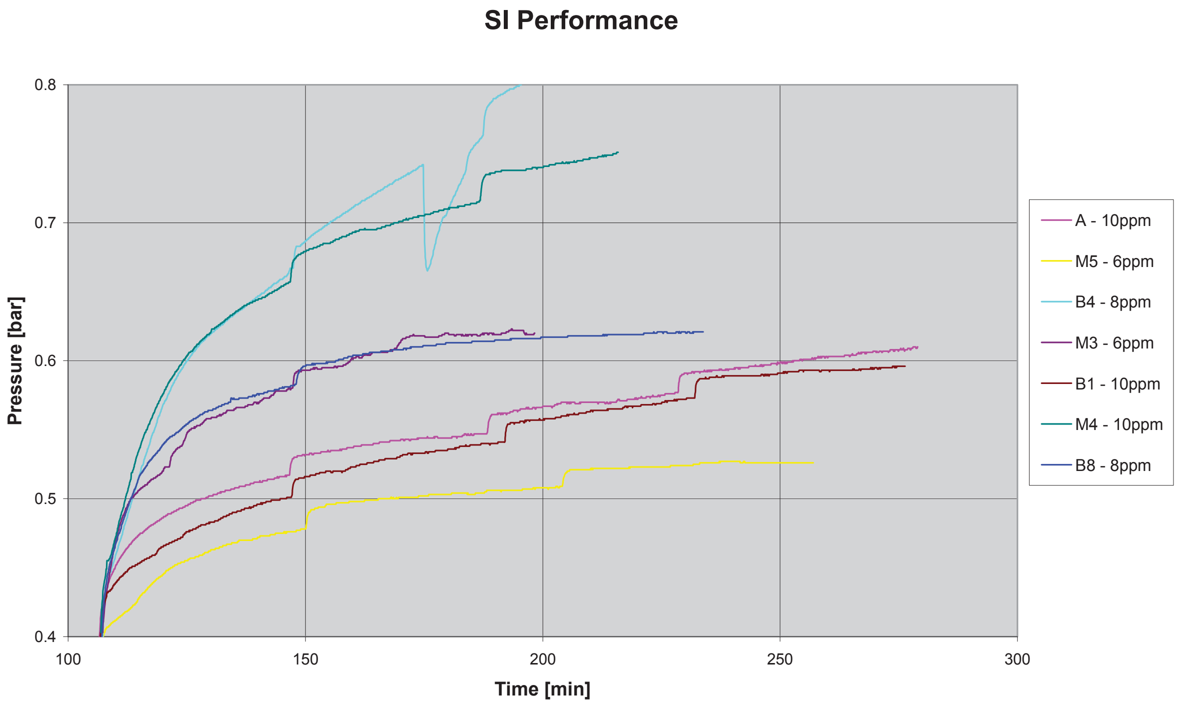

Figure 43: SI performance with water samples from 16 Sampetru German after curve adjusting

Now it will be easier to analyze the performance of the tested scale inhibitors. Some of the inhibitors were tested several times due to failures of the pumps, not proper cleaned test tube or not correct selected initial inhibitor concentration. Therefore, some of them had different initial inhibitor concentration, which had to be considered when ranking the products.

The only inhibitor, which started with 2 ppm was scale inhibitor M5.

Products, whose initial inhibitor concentration was 4 ppm are ranked below:

M3 > B1, A

M3 is preferred because the pressure stayed constant when the inhibitor was increased to 6 ppm. The pressure profiles of the other two inhibitors showed no sign of a constant pressure, although the concentration was increased up to 10 ppm.

The remaining scale inhibitors were added at a concentration of 6 ppm and are ranked as following:

B8 > M4, B4

When summing up those inhibitors, which were really effective in inhibiting scale formation, then the final ranking would be:

M5 > B8 > M3

4.4.4 Screening with Water Sample from 8 Sampetru German – Romania

The same seven scale inhibitors were tested with brine samples from the well 8 Sampetru German. The scale problems for this well occur downhole in the wellbore, therefore the temperature is set to bottomhole temperature.

Temperature	66°C
Total hardness	29.9°dH
Ca amount	104 mg/l
Initial pH	7.14
NaOH consumption	0.25 ml/5ml
Flow rate	5 ml/min
Inhibition pressure	0.35 bar

Table 12: Test conditions for screening with 8 Sampetru German

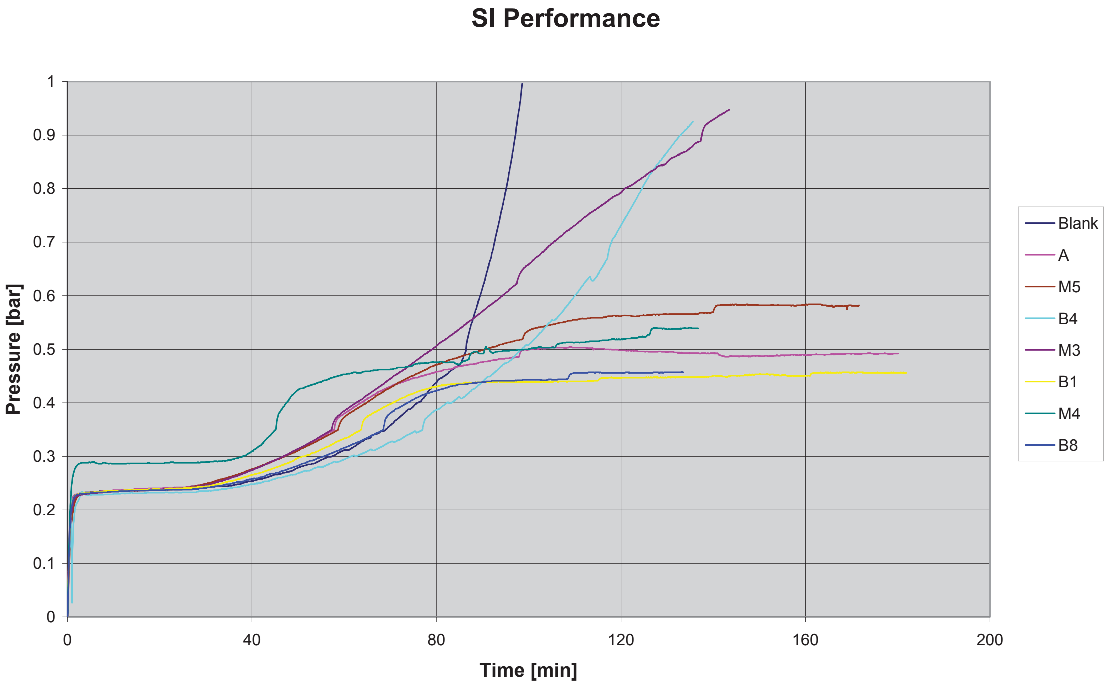

Figure 44: SI performance with water samples from 8 Sampetru German

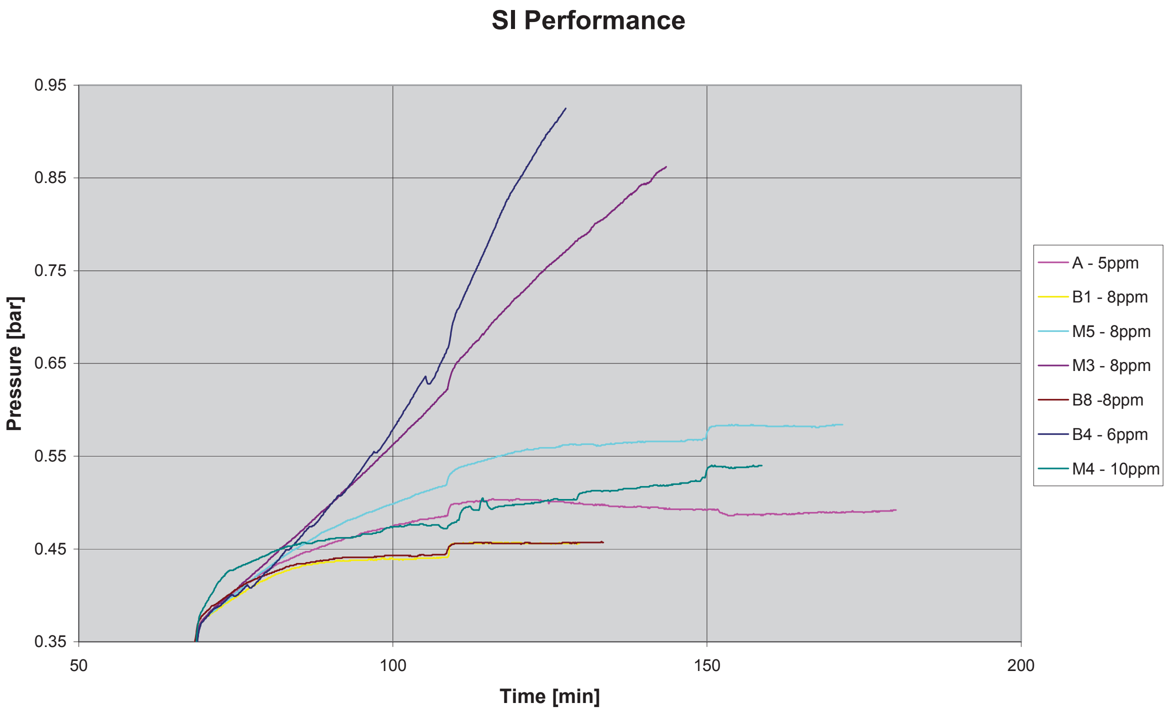

Figure 45: SI performance with water samples from 8 Sampetru German after curve adjusting

For this screening five scale inhibitors were added with an initial concentration of 4 ppm and the other two with an initial concentration of 6 ppm. Thus, the following ranking could be made:

A > B1, B8 > M5 > M4 > B4, M3

4.5 Conclusion

The dynamic tests gave a good overview about the performance of the tested scale inhibitors. When performing the tests, care should be taken concerning the cleanliness of the test tube. As it can be seen, a tube containing acid left from the cleaning process, can lead to a different pressure profile.

It was not possible to run the tests always at the same conditions, since the water quality and temperature varied with varying wells. Besides, the water quality changed over time, i.e. the hardness, pH, etc. changed with time thus the curves differ from each other, especially the pressure increase at the beginning of each test. Nevertheless, the optimum testing conditions had to be found. In some cases, it was unavoidable to do the same test several times at different conditions to find out the best test conditions.

However, dynamic tests are very good in screening inhibitors, since they do not take so much time as static tests, although static tests are good to confirm the dynamic test results.

Nevertheless, these tests often give different selection and ranking of scale inhibitors, as it was the case here. This is due to several factors: [22]

- Short residence time – TBT generally has a residence time less than 10 seconds, whereas static tests have a residence time of several hours or even days.
- Dispersant/ anti-agglomerant properties of certain inhibitor species
- Differences between nucleation and crystal growth inhibition effects
- Impact of scale adhesion on the walls of the micro-bore tubing

The scale inhibitors were tested concerning their ability to inhibit or even stop further scale formation. It would be interesting, to test the scale inhibitors without prescaling, i.e. adding the inhibitor right from the start to the brine. Do the inhibitors show the same performance, or does their performance differ? Although, this kind of testing was done with two inhibitors and the results coincided with the ones with a prescaled tube, it would be wrong to generalize. Furthermore, it is not easy to put the effective scale inhibitors into one chemical group. This means, that those scale inhibitors, which are left, belongs to the polymeric, phosphonate, carboxylate and polyaspartate group. After those long lasting tests, it can be said, that the efficiency of the scale inhibitors strongly depends on the water composition. Nevertheless, two scale inhibitors showed a good performance with all four water samples and those scale inhibitors belong to the phosphonate and the polymeric group.

Scale Inhibitor	Matzen 172	Turnu Est	16 Sampetru	8 Sampetru
A	✓	✓		✓
B1	✓	✓		✓
B2	✓			
B3	✓			
B4	✓	✓		
B5	✓			
B6	✓			
B7	✓			
B8	✓	✓	✓	✓
B9				
B10	✓			
M1	✓			
M2				
M3	✓	✓	✓	
M4	✓	✓		✓
M5	✓	✓	✓	✓
M6	✓			
C1	✓			
C2				
C3				
C4	✓			
C5				
C6S	✓			

Table 13: Screening results

Table 13 shows the results of the screenings with various brine samples. All of the initial 23 scale inhibitors were tested with brine samples from the well Matzen 172. Those, which performed best were tested with brine samples from the Romanian well Turnu Est. Seven scale inhibitors out of 17 were then tested with brine samples from the wells 16 Sampetru German and 8 Sampetru German. Finally, it is shown that five scale inhibitors are applicable to the well 8 Sampetru German and only three from seven were successful in inhibiting scale for well 16 Sampetru German.

Below there are two diagrams showing the maximum pressure and price/kg of the tested inhibitors. Those curves are taken from the screening with brine samples from Matzen 172. The first diagram contains the results of those inhibitors which were effective at a concentration of 2 ppm.

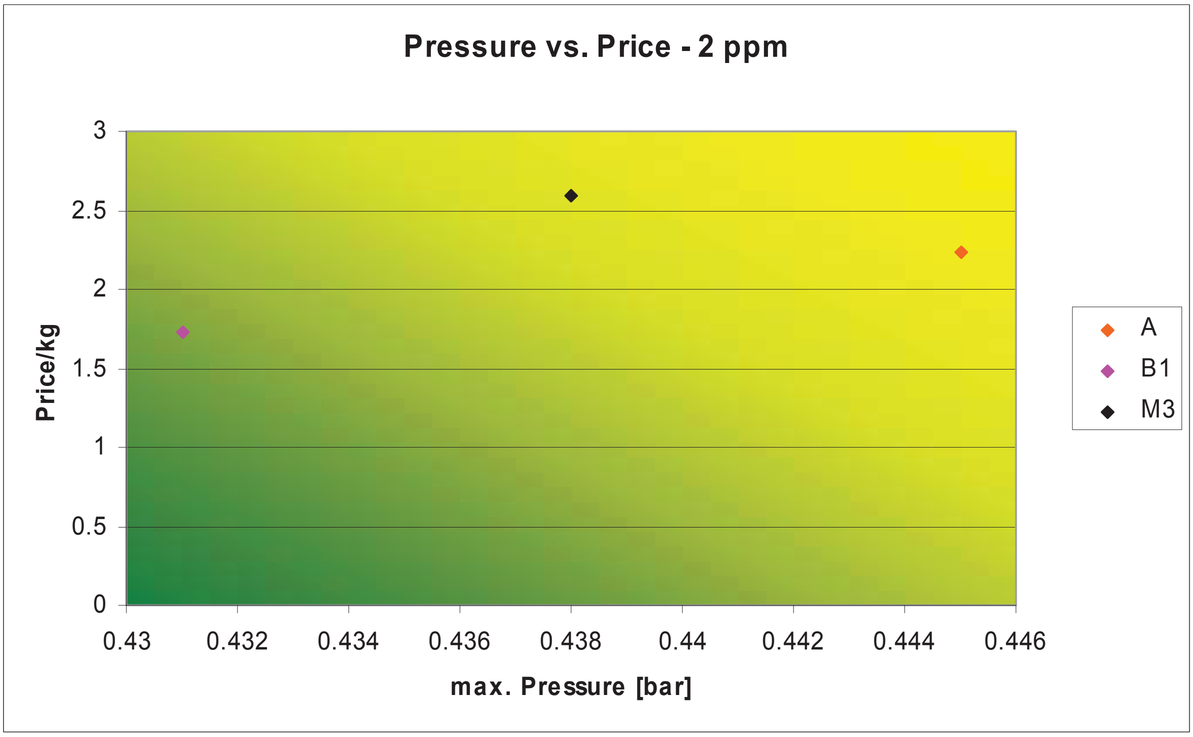

Figure 46: Diagram Pressure vs. Price for screening with Matzen 172 at 2 ppm

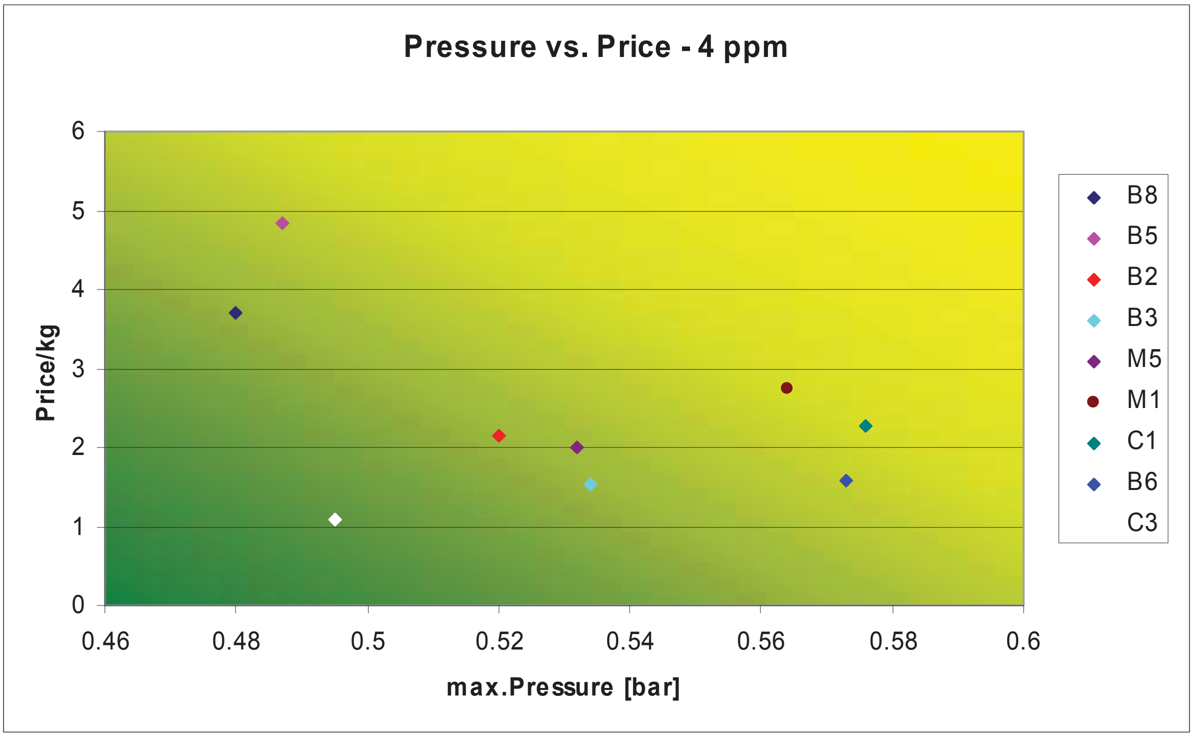

Figure 47: Diagram Pressure vs. Price for screening with Matzen 172 at 4 ppm

However, the last decision what scale inhibitor to take depends on the results of the field tests and on the price and its availability.

5 Computer aided Scale Prediction

5.1 MultiScale®

MultiScale® is a computer program designed to calculate equilibriums in systems containing water, gas, oil and solids and to predict scale formation. Through the input, the user defines temperature, pressure and the concentration of each compound. MultiScale® then calculates the phases which are present and the equilibrium composition of each phase. [23]

Many prediction models available are good in predicting sulphate scaling but fail when predicting carbonate scale because for predicting carbonate scale it is necessary to calculate the pH and the phase distribution of acidic gases in the water sample. Nevertheless, all models use thermodynamic principles and geochemical databases and all of them rely on basic input data such as concentration analysis, temperature, pressure and gas-phases compositions. With the help of models, one can predict the effect of incompatible mixing or changes in temperature and pressure.

MultiScale® includes a PVT-model, which uses an equation of state to describe and calculate the volumetric behaviour of the gas and the phase equilibriums between gas and oil. Besides, the software contains an aqueous chemical equilibrium model, which uses the Pitzer ion interaction model to calculate the activity coefficients.

MultiScale® considers pressure and temperature changes, which lead to precipitations, pH and the amount and phase distribution of acidic gases. Furthermore, it is possible to make predictions about FeS and NaCl and the kinetics of water evaporation, which is controlling NaCl precipitation but also sulphates and carbonates, is included.

All in all, MultiScale® is a useful tool to predict sulphate scale and does not fail in predicting carbonate scale, including all necessary calculation steps.

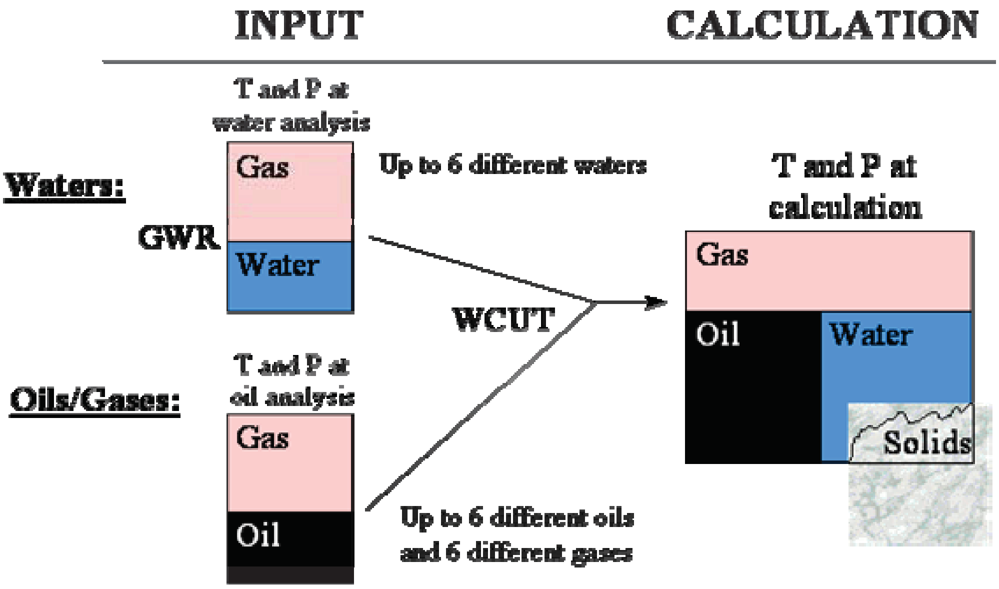

Figure 48: Schematic figure of the MultiScale® model [23]

According to the model shown in Figure 48, the user can mix a number of different components and phases into one calculation point.

The user has to put in the water composition, i.e. the water-soluble ions such as Na^+, Cl^-, Ba^{2+} and organic acid and GWR. In case, the water contains water-soluble hydrocarbons, amounts of CO_2, H_2S and CH_4 are also necessary as input. The hydrocarbon phases can be oils or gases and the rate in m^3/d and the corresponding pressure and temperature have to be entered. For oils and gases, it is necessary to enter the mole% of each component up to C9 together with the mole weight and the density for the heaviest components. The rest is entered as C10+ fraction or can be splitted up to nine different pseudo-components.

After entering the necessary data, the software performs a flash calculation at the given pressure and temperature to calculate the amount of each component from the entered volume rate.

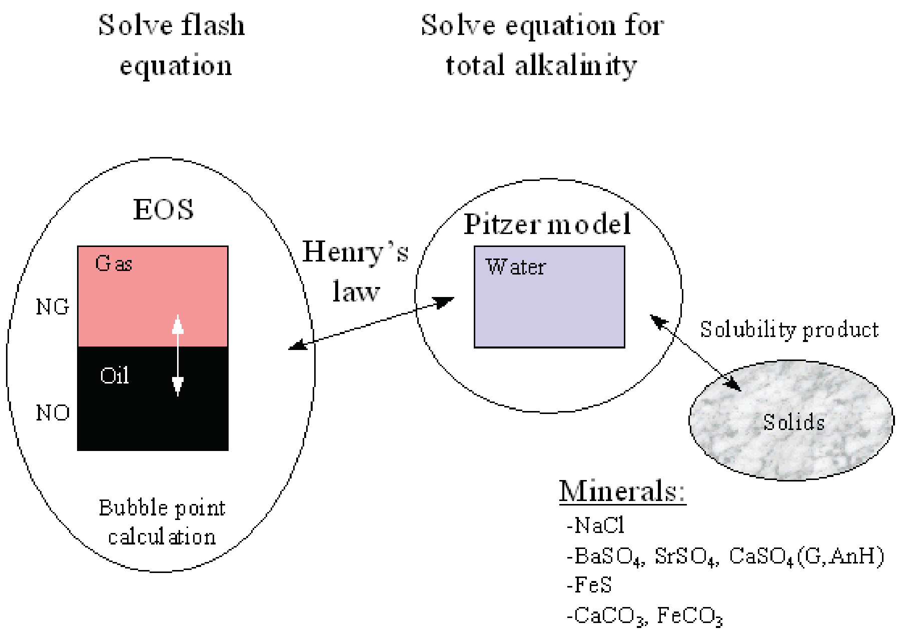

Figure 49: Schematic presentation of the calculation procedure [22]

The calculation steps of the software are listed below:

- Calculation of mass balances out of input data
- Calculation of thermodynamic equilibrium constants at calculation pressure and temperature
- Calculation of stoichiometric equilibrium constants based on an initial guess of water composition
- Solving of flash equation with all hydrocarbons, i.e. inclusive CO_2 and H_2S, from the hydrocarbon phase
- Assuming that the amounts and properties of the gas and oil are constant, the amounts of CO_2, H_2S and CH_4 dissolved in the water phase are calculated. The amount of water, which will evaporate is calculated either.
- Since CO_2, H_2S and CH_4 switched from the hydrocarbon phase to the water phase and evaporated water from the water phase to the hydrocarbon phase, a recalculation of the concentrations in the water phase will be necessary. The Pitzer model is used to calculate the activity coefficients.
- Repeating of the flash calculation with a different composition of the phases
- Adjusting of the concentrations of CO_2, H_2S and CH_4 in the water phase and the amount of water in the hydrocarbon phase.
- Repeating the procedure from step 7 until there is a convergence

- Calculation of saturation ratios. Supersaturated salts will precipitate and salts, which are undersaturated and solid, will dissolve.
- Output data are written

The results of the calculations are the total amount and the total mass rate of all compounds for all oils, gases and waters. Furthermore, the distribution of the compounds in the hydrocarbon phase, the water phase and precipitated phases are listed.

With MultiScale® it is possible to calculate a single point calculation, a profile calculation with varying pressure or temperature or both, a multiprofile, a mixing profile or a P-T $CaCO_3$ saturation profile.

However, this tool helps in calculating and predicting scale if the inputs are correct.

5.2 Comparison: Calculations – Laboratory Tests

Part of this thesis was to use this program to predict scale precipitation potential from water samples from the Libyan well, wherewith scale inhibitors were tested.

However, the results from the program are only guidelines, to see whether scale will precipitate or not, especially if two waters should be mixed. This means, that the compatibility of those two waters can be easily checked with this tool. In this case, the program was helpful in predicting scale precipitation and confirming the results from the dynamic tests.

5.2.1 Calculation with Libyan Water

First, the ionic composition of the water sample was entered into MultiScale® for a “single point calculation”.

pH	7.02
Cl^-	103,204 mg/l
Br^-	391 mg/l
SO_4^{2-}	367 mg/l
Total alkalinity	6.46 mmol/l
Alkalinity	5.68 mmol/l
Organic acids (acetate)	90.5 mg/l
Na^+	58,115 mg/l
K^+	775 mg/l
Mg^{2+}	777 mg/l
Ca^{2+}	4,185 mg/l
Sr^{2+}	416 mg/l
P	320 psi – 22.06 bar
T	84°C
WC	80%
Rate	2,000 bbl/d – 327.318 m^3/d
Gas	19,003 m^3/d
GLR	157.9
Analysis p	1 bar
Analysis T	20°C
CO_2	2.77 mol%

Table 14: Input data for MultiScale® calculation

After saving and verifying the water a “single point calculation” could be performed. The results are shown below.

```
       Property              Initial        Equilibrium
---------------------------------------------------------------
         pH            :          7.0200         5.8631
         Water activity:          0.8891         0.8891
  Total CO2(aq) :          5.2159         3.3110  mmole/kgH2O
  Total H2S(aq) :          0.0000         0.0000  mmole/kgH2O
  Total CH4(aq) :          8.8259         8.7750  mmole/kgH2O
  Alkalinity    :          6.8693         3.0603  mmole/kgH2O
   Ionic strength:          3.2692         3.2630  mole/kgH2O
  Charge balance:          0.0000         0.0000  mmole/kgH2O
   Diss salts    :    181328.5913    181203.4719  mg/kg H2O
   Diss gases    :       156.8387       217.3610  mg/kg H2O
   Other species :       405.6743       192.5082  mg/kg H2O
   Tot diss spec :    181891.1042    181613.3412  mg/kg H2O
      Density       :          1.1113         1.1110  kg/l
---------------------------------------------------------------

          SATURATION RATIOS AND PRECIPITATED AMOUNTS
---------------------------------------------------------------
  Salt      Initial     Precipitate   Equilibrium   Solubility
         SR          g/M3          SR          product
---------------------------------------------------------------
FeS            0.000          0.0        0.000         4.6258E-03
FeCO3          0.000          0.0        0.000         3.4947E-09
CaCO3(C)      41.393        190.6        1.000         2.2708E-07
CaSO4(A)       0.380          0.0        0.346         1.1765E-03
CaSO4(H)       0.372          0.0        0.338         1.2028E-03
CaSO4(G)       0.139          0.0        0.126         3.2242E-03
BaSO4          0.000          0.0        0.000         9.6617E-08
SrSO4          1.163         61.1        1.000         1.7589E-05
NaCl           0.110          0.0        0.110         7.8539E+01
```

Figure 50: Result file from MultiScale

This is one part of a typical output sheet of the program. In this case, only the saturation ratios are shown to see what salt will precipitate and what not. On the first sight, the high saturation ratio of $CaCO_3$ jumps right into the eyes. Therefore, it is of no surprise that 190.6 g $CaCO_3/m^3$ water will precipitate at these conditions. $SrSO_4$ will also precipitate in large amounts and maybe there would be $BaSO_4$ too, but there were no input data available.

The results of the prediction model coincide with those of the dynamic tests. It is now proven, that there are a lot of $CaCO_3$ precipitations and there are scale inhibitors available, which are effective against those scale deposits.

5.2.2 Calculation with Romanian Water

The same procedure was applied to the Romanian water samples. The results are shown below.

```
                 SATURATION RATIOS AND PRECIPITATED AMOUNTS
 ----------------------------------------------------------------
   Salt       Initial     Precipitate   Equilibrium   Solubility
          SR           g/M3           SR           product
 ----------------------------------------------------------------
 FeS            0.000           0.0         0.000       5.1815E-04
 FeCO3         11.500           1.3         1.000       1.9402E-10
 CaCO3(C)      15.590         481.1         1.000       4.9034E-08
 CaSO4(A)       0.000           0.0         0.000       5.1546E-04
 CaSO4(H)       0.000           0.0         0.000       5.0977E-04
 CaSO4(G)       0.000           0.0         0.000       6.8920E-04
 BaSO4          0.000           0.0         0.000       7.6633E-09
 SrSO4          0.000           0.0         0.000       5.5816E-06
 NaCl           0.001           0.0         0.001       8.7135E+01
```

Figure 51: Result file for Turnu Est

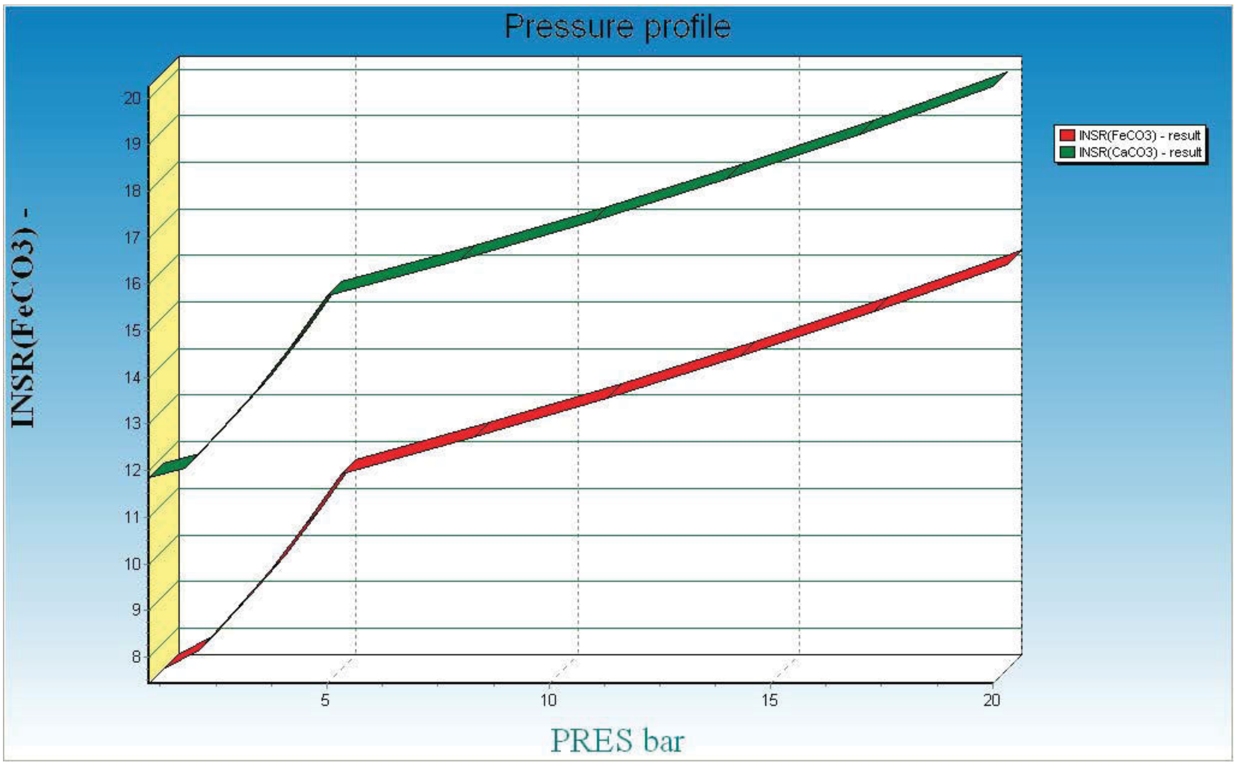

Figure 52: INSR vs. Pressure for Turnu Est

As the results show, there can be some $FeCO_3$ precipitations, which is quite rare for OMV wells. There could be some iron impurities in the water because of tubing, etc. when sampling the water or the formation water may contain dissolved iron. However, this has no effect on the results since the precipitates only contain a minor amount of iron. Well 16 Sampetru German and well 8 Sampetru German show the same profile when calculating the possible precipitations.

```
              SATURATION RATIOS AND PRECIPITATED AMOUNTS
----------------------------------------------------------------
  Salt      Initial    Precipitate   Equilibrium   Solubility
           SR          g/M3          SR          product
----------------------------------------------------------------
FeS            0.000          0.0        0.000        4.4530E-04
FeCO3         19.447          1.6        1.000        2.4465E-10
CaCO3(C)      23.977        474.2        1.000        5.7984E-08
CaSO4(A)       0.000          0.0        0.000        6.8802E-04
CaSO4(H)       0.000          0.0        0.000        6.8891E-04
CaSO4(G)       0.000          0.0        0.000        6.9508E-04
BaSO4          0.000          0.0        0.000        5.2791E-09
SrSO4          0.000          0.0        0.000        6.1966E-06
NaCl           0.001          0.0        0.001        8.4131E+01
```

Figure 53: Result file for 16 Sampetru German

```
              SATURATION RATIOS AND PRECIPITATED AMOUNTS
----------------------------------------------------------------
  Salt      Initial    Precipitate   Equilibrium   Solubility
           SR          g/M3          SR          product
----------------------------------------------------------------
FeS            0.000          0.0        0.000        5.2317E-04
FeCO3         76.179          5.9        1.000        1.5234E-10
CaCO3(C)      13.011        233.7        1.000        4.0557E-08
CaSO4(A)       0.000          0.0        0.000        4.0142E-04
CaSO4(H)       0.000          0.0        0.000        3.9707E-04
CaSO4(G)       0.000          0.0        0.000        6.5161E-04
BaSO4          0.000          0.0        0.000        9.2372E-09
SrSO4          0.000          0.0        0.000        4.9384E-06
NaCl           0.001          0.0        0.001        8.7769E+01
```

Figure 54: Result file for 8 Sampetru German

6 Conclusion and Outlook

Scale is a formation of hard minerals, which precipitates on surfaces and then accumulates there. In oilfields, in case scale occurs in the tubing, this will reduce the effective tubing diameter, and thus hindering hydrocarbons and cash respectively to flow.

The present situation in OMV concerning scale deposits are not that dramatic, except in Romania, where scale deposits can rapidly form in the tubings. Since these scale deposits are mainly $CaCO_3$ scale, it is easy to prevent them by use of appropriate chemicals, i.e. scale inhibitors.

Therefore, OMV did a global tendering for oilfield chemicals, e.g. scale inhibitors with the purpose to purchase inhibitors from selected companies, thus ensuring constant product quality, better delivery times and better prices. Although this was successful with tubing, it is much harder to get all needed chemicals of only one company, because it is quite rare that one company offers the whole product range needed. Hence, this thesis was done to select a small number of scale inhibitors for all affected wells.

The present thesis shows a dynamic screening of a newer generation of scale inhibitors, to select the best one for field tests and future application. The screening was done with a scale apparatus, assembled by the LEP staff. Although the apparatus was not state of the art, it did a good job. Besides, a new scale apparatus should have been ordered to compare the results from each apparatus, but the delivery of the new apparatus was delayed, so that the tests could not be carried out anymore.

Also part of the work was to test inhibitor A, which was used for 15 years and is still used today, in order to evaluate its efficiency and to use it as a benchmark.

The tests were done with different brine samples, i.e. brines from a Libyan well, three Romanian wells and one Austrian well. It was quite important to do the tests under as real as possible conditions to be able to draw authentic conclusions.

Most of the tested scale inhibitors were efficient at even very low concentration, thus making the scale treatments quite cheap. Nevertheless, the inhibitors should be tested in the fields to see whether they really work or not.

Another part was to do scale predictions with a scale prediction software, in order to compare the results with those from the dynamic tests. This was done with MultiScale® for the Libyan brine sample. The software is a useful tool in predicting scale precipitation and checking the compatibility of different waters to avoid sulphate scaling.

However, in times of intelligent wells it will be a good option to install intelligent completions with permanent monitoring systems in order to detect changes in water chemistry. These downhole scale sensors are still in research and development but nevertheless, there are integrated scale management systems installed, which use downhole electrochemical sensor sensitive to pH and ion concentrations along with temperature and pressure. It is also possible to install multiphase flow measurement advises in order to detect potential carbonate buildup and to help regulating chemical dosages for scale control.

Nevertheless, the best way to test and rank scale inhibitors is to do both tests, dynamic and static test, and to compare the results. The scale inhibitors should then be tested in the field under real conditions.

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7.2 Abbrevations

e.g	Exempli gratia – for example
i.e.	id est – that is
OPEC	Organization of the Petroleum Exporting Countries
IGU	International Geographical Union
EOS	Equation of state
ppm	Parts per million
API	American Petroleum Institute
Pas	Pascal second
°C	Celsius degree
ID	Inner diameter
PI	Productivity Index
EDTA	Ethylenediamenetetraacetic acid
CAPEX	Capital Expenditure
MPa	Mega Pascal
HPHT	High Pressure High Temperature
EM	Einmaß - Input
F	Factor of the Titriplex III solution
m	Concentration of Titriplex III solution in mol/l
mg	milligram
ICP OES	Inductively coupled plasma – optical emission spectroscopy
SI	Saturation Index
etc.	et cetera
PBR	Back Pressure Regulator
ΔP	Pressure differential
mm	millimetres
ml/min	Millilitre per minute
HPLC	High Performance Liquid Chromatography
pH	Potential of hydrogen
GWR	Gas-Water-Ratio

8 Appendix

8.1 Definitions

Proven reserves

Proven reserves are reserves that can be produced using the current technology at current prices, with current commercial terms and government consent.

Solubility product

The K_{sp} expression for a salt is the product of the concentrations of the ions, with each concentration raised to a power equal to the coefficient of that ion in the balanced equation for the solubility equilibrium.

LeChatelier Prinicple

This principle can be used to predict the effects of a change in conditions on a chemical equilibrium. According to the principle, the equilibrium will shift in order to counter-act the imposed change.

Threshold effect

Threshold effect is the large effect of comparatively small concentrations of inhibitors on scale formation. The right inhibitor concentration in a well depends on its scaling conditions.

Flocculants

Flocculants are additives that cause crystals to form loose agglomerations rather than hard deposits, i.e. crystals stay in liquid phase.

Dispersants

Dispersants prevent agglomeration of scale crystals too, they keep them suspended in the flowing phase.

Pseudoscale

Pseudoscale is often caused by interactions between Mg^{2+}, Ca^{2+} and Ba^{2+} ions in the brine and the applied inhibitor. The precipitations act like real scale. Therefore, the applied chemical not only fails in preventing scale formation but also causes additional problems by deposition of pseudoscales.

EDTA

Ethyleneediamenetretraacetic acid is a chemical that dissolve and chelate $CaCO_3$ and can break the reprecipitation cycle. [8]

ICP OES

Inductively Coupled Plasma Optical Emission Spectroscopy is a type of emission spectroscopy and uses a plasma to produce excited atoms that emit electromagnetic radiation at a wavelength characteristic of a particular element. The concentration of the element within in the sample can be evaluated through the intensity of the emission. [23]

HPLC pumps

High Performance (Pressure) Liquid Chromatography is a form of column chromatography used in analytical chemistry.

Green Inhibitor

A green inhibitor is an inhibitor that is less toxic, not environmentally persistent, not bioaccumulative, biodegradable to non-toxic byproducts and efficient in their manufacturing process. [24]

Henry's law

William Henry stated that at a constant temperature, the amount of a given gas dissolved in a given type and volume of liquid is directyl proportional to the partial pressure of that gas in equilibrium with that liquid.

8.2 Water Analysis

Libyan water sample

Water sample from 29.11.2006	
Total hardness [°dH]	772
Ca amount [mg/l]	4,278
pH	7.44
NaOH cons. [ml]	0.25
T [°C]	70
p [bar]	0.35
Water sample from 3.1.2007	
Total hardness [°dH]	749
Ca amount [mg/l]	4,115
pH	7.78
NaOH cons.	0.1
T [°C]	70
p [bar]	0.35
pH	7.2
NaOH cons. [ml]	0.38
Water sample from 9.1.2007	
Total hardness [°dH]	751
Ca amount [mg/l]	4,100
pH	7.29
NaOH cons.	0.23
T [°C]	70
p [bar]	0.35

Water sample: Turnu Est

Water sample from 14.2.2007	
Total hardness [°dH]	54.43
Ca amount [mg/l]	226
pH	7.46
NaOH cons. [ml]	0.45
T [°C]	55
p [bar]	0.35

Water sample from 21.2.2007		
	Total hardness [°dH]	51.09
	Ca amount [mg/l]	244
	pH	7.43
	NaOH cons.	-
	T [°C]	55
	p [bar]	0.35
	Water sample from 28.2.2007	
	Total hardness [°dH]	44.95
	Ca amount [mg/l]	258
	pH	7.26
	NaOH cons.	-
	T [°C]	55
	p [bar]	0.35

Water sample: 16 Sampetru German

Water sample from 8.3.2007		
	Total hardness [°dH]	29.95
	Ca amount [mg/l]	115
	pH	7.45
	NaOH cons. [ml]	0.4
	T [°C]	40
	p [bar]	0.4
Water sample from 14.3.2007		
	Total hardness [°dH]	44.97
	Ca amount [mg/l]	245
	pH	7.37
	NaOH cons.	0.35
	T [°C]	40
	p [bar]	0.4

Water sample: 8 Sampetru German

Water sample from 20.3.2007		
	Total hardness [°dH]	30.3

		3
	Ca amount [mg/l]	112
	pH	7.45
	NaOH cons. [ml]	0.35
	T [°C]	66
	p [bar]	0.35