



SPE 82199

## Downhole Measurement of pH in Oil & Gas Applications by Use of a Wireline Tool

Raymond Børeng SPE, Terje Schmidt SPE, Olav Vikane SPE, Liv A. Tau SPE, STATOIL ASA and Bjørn Dybdahl SPE, Tor I. Dale, Oddfinn Thowsen, Petrotech ASA.

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This paper was prepared for presentation at the SPE European Formation Damage Conference to be held in The Hague, The Netherlands 13-14 May 2003.

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### Abstract

The giant Statoil-operated North Sea oil field Statfjord is currently far down its production decline curve. During 23 years of production 60% of the STOOIP has been recovered, and the remaining reserves are characterized by complex distributions of oil, water and gas.

In order to obtain a cost-effective production of the remaining oil, an aggressive drilling and intervention programme is necessary. Future developments might also include a pressure blow down phase of the reservoir. Then large volumes of water will be produced to surface. So far the Statfjord Field has exhibited a fairly mild scale potential. Sulphate scale has been detected in several wells down hole, whereas carbonate scale when found is mainly above the down hole safety valve. Carbonate scale precipitation will be more severe in any future blow down phase with a lowering of the reservoir pressure. To improve carbonate scale prediction a "correct" down hole pH value is necessary. The prediction program will then be capable of performing a better tuning sequence and give more accurate predictions, refer references.

Petrotech has developed a pH sensor system for downhole use. In 2002 Statfjord performed a field test of this system by running it in a well with a "single phase" fluid sampling chamber. The water sample captured down hole was used to get a lab measurement of the pH in the formation water at reservoir temperature and pressure. This sample was then flashed to standard conditions and a full water and gas analysis was performed. The results were used in the MultiScale software program to calculate a pH value. The results indicated good correspondence between the pH values obtained from the down hole sensor, the water sample and the pH value calculated with the scale prediction program.

### Introduction

The Statfjord Field was discovered in 1973, declared commercial in August 1974, and started production in 1979. The field is over 25 km long and averages 4 km in width, and is the largest producing oil field in Europe. Statfjord is located in the Tampen Spur area, in the northern portion of the Viking Graben and straddles the border between the Norwegian and UK sectors. The field is developed by three fully integrated Condeep concrete platforms. All three platforms have tie-ins, as shown in Figure 1. Production is from the Brent, Dunlin and Statfjord reservoirs, with the main reserves in the Brent and Statfjord reservoirs. As of May 2002 the cumulative oil production is 612 million Sm<sup>3</sup>, giving a current recovery of 60% of the STOOIP. The expected recovery factor at abandonment is 65%. 23 years of oil production and injection of water and gas has resulted in a field with complex distributions of all three phases and several fluid contacts. The remaining bypassed reserves are scattered over a wide area and in several reservoirs. Consequently each new well target is gradually decreasing in size and the associated risk of drilling a dry well is increasing. Carbonate scale precipitation will be more severe in a future blow down phase with a reduction of the reservoir pressure. To improve carbonate scale prediction a "correct" down hole pH value is necessary. Statfjord decided to run a pH sensor system for down hole use in a field test together with a "single phase" fluid sampling chamber to gain better pH data.

### Scale predictions

Calcium carbonate scale tendencies are dependent on changes in physical conditions like pressure and temperature as well as the concentration of dissolved salts, gases and pH. Calcium carbonate precipitates due to pressure decrease and release of CO<sub>2</sub> gas. This may occur across the choke or down hole if the draw down is significant. The scaling tendency is reduced as temperature and pH decrease.

Scale predictions for possible blow down phase conditions have been performed using MultiScale. Input data includes the composition of produced water, hydrocarbon data from Statfjord and Brent formations and pressure and temperature data from reservoir conditions to wellhead conditions at water cuts from 70 – 90 %.

Typical diagram for showing iso-saturation lines for 90% water cut is shown in Figure 5.

## Well operation objectives

The objectives for the operation were to run on wire line:

1. A caliper log.
2. A RST-D log.
3. pH-meter sensor system.
4. To perforate one interval in the Ness formation.

The caliper log was run to detect scale build up inside the well bore or any ID restrictions.

RST-D log was run to measure oil and water saturations.

The pH sensor system and sampling chamber were run to measure down hole pH across the Etive perforation interval, refer figure 2 and to take a down hole water sample at perforation depth.

The Ness formation was perforated to increase oil production from the well.

Data gained by the two logs will be used to evaluate the remaining oil potential in the Ness formation and the possibility to plug off existing and new perforation intervals in future operations.

## The well

The well was completed in November 1985. It was initially completed with a 9 5/8" casing and 7" tubing. A work over in 1991 isolated old perforations and a 7" straddle assembly was placed inside the 9 5/8" casing. New tubing was run and the Rannoch formation was perforated. In October 1993 the straddle was perforated and the Etive formation was re opened for production, refer completion drawing in figure 2. At the time of this operation the well produced with a water rate of 2700 m<sup>3</sup>/d (water cut of 95 %). It had a shut in bottom hole pressure of 318 bar and a reservoir temperature of 93° C at top perforation.

## The operational results

The 60-arm caliper log was run successfully. Only traces of scale were measured in the wellbore. Sulphate scale in Statfjord is usually of LRA (Low Radioactive Activity) type. The gamma ray detector run with the RST-D tool had zero readings of unnatural radioactivity. This indicates no scale build up as well. The bottom hole assemblies (BHA) with the pH tool and Bottom hole Sampler were run in hole to top of perforation interval in Etive at 2983,0 m MDRKB. A stable water sample was collected in the sampling chamber and pH measured with the pH-sensor. Then the bottom hole assemblies were pulled out of hole and rigged down. The equipment was brought onshore for further analysis in the laboratory. Following this the Ness formation was perforated in a separate run and the well was back flowed to the test separator.

The wire line run with the pH Tool and Bottom hole Sampler required a total of 7 hours operation. No fault or accidents occurred during the operation. Had the sole purpose of the intervention been for pH determination, the total time would have been 18 hrs, i.e. including time for spotting of equipment, rig up and rig down.

## Sampling chamber

A non-corrosive single-phase down hole sampler was used together with the pH-tool to get a representative sample of the fluid in the well. Sampler volume is about 540 cc. The sampler was triggered by use of a mechanical clock set to trigger when the tools were expected to be at depth, i.e. top of Etive perforation interval.

The single-phase action of the sampler ensured that the gas that was assumed to be present in the water was kept in the solution all the way to surface. At surface, the sample was transferred to a single-phase transport cylinder and shipped to the onshore lab. This sample was later used for a full compositional analysis of both the fluids and gas including pH-measurements at reservoir conditions.

## The downhole pH-probe

The downhole pH-probe system used in this project was developed through a 3-year R&D programme sponsored by Statoil, Saga Petroleum, Exxon Mobil, BP UK and the Norwegian Research Council.

A pre-study was done prior to this project to identify the technology best suited for downhole pH-measurements. In addition to commercially available sensor systems, conceptual technologies were investigated.

Several pH-sensor types and pH-measurement principles were evaluated with respect to suitability for downhole use before ending up with one candidate.

The pH-sensor that was developed demonstrated good temperature stability and showed good performance in oil contaminated water applications and it had a very rigid design. Also, long-term stability was an important parameter when developing the sensor system. This sensor system does not need any pressure correction meaning that changes seen in the sensor signal when pressure increases are related to changes in pH and not a result of changes in the sensor characteristics.

An extensive test programme for the probe was made together with two different research institutions in Norway. Main topics in the test programme were: measurement in NaCl and KCl solutions, measurements in pH-buffers (several buffers with known sodium content were used), measurements in water containing NaHCO<sub>3</sub> saturated with CO<sub>2</sub>, long term stability at elevated temperatures and accuracy tests in oil and water mixtures.

The pH-probe was installed into a HPHT piston cell that was mounted inside a heating cabinet. In and out ports at top and bottom were made to be able to circulate gas through the cell. Temperature was controlled by use of a computer controlled heating cabinet and pressure by use of a pneumatic pump. Cell pressure, pH-sensor signal and temperature were logged on a computer data acquisition system.

In the NaHCO<sub>3</sub> tests mentioned above, a mixture of 97% N<sub>2</sub> and 3% CO<sub>2</sub> was injected by use of a gas booster pump at pressures up to 600 barg. The gas was injected into the lower part of the autoclave and bled off at the top through a needle valve.

The tests demonstrated that the probe was suitable for high pressure and temperature applications had good repeatability

and stability and it behaved as expected with respect to changing temperature and pressure.

Probe specifications:

Max pressure: 1000 barg  
 Max temperature: 175 C  
 pH range: 3-11 (Usable range: 1-12)  
 Accuracy: +/- 0,1 pH \*  
 Resolution: 0,01 pH  
 Max sampling rate: 2 sec

\* This accuracy is based on repeated lab measurements.

The measurement principle of the sensor is based on using two ion-sensitive elements arranged into a differential measurement system. One element is the measurement element and the other the reference element. The reference used in this system is a sodium (Na<sup>+</sup>) sensitive sensor that gives a reference for the other element, which is the pH (H<sup>+</sup>) sensitive element. No electrolyte is used within the sensor to provide a fixed reference for the pH-measurement contrary to more commonly used sensor systems. This means that this is not an absolute pH-measurement since it is measured relative to sodium, but a relative pH-measurement system. Since the pH-measurement depends on the actual sodium content present in the fluid to be measured, the sodium content must be known or at least estimated.

A temperature element is incorporated into the pH-sensor to provide an accurate measurement of the fluid temperature. The fluid temperature is used both in the pH-sensor temperature correction functions and in the pH-calculations itself.

The raw signal used in the pH calculations is the difference between the pH-sensor voltage (in mV) and the reference sensor (in mV).

The pH-measurements system was connected to a downhole datalogger while running the tools into the well at Statfjord.

After the tools were brought to surface, the data were downloaded onto a computer and sent onshore for further processing.

The raw sensor data representing pH (mV) and temperature that was obtained when running the pH-tool and sampled on Statfjord was loaded into a spreadsheet to calculate pH. Since the pH sensor uses a sodium (Na<sup>+</sup>) reference electrode, the sodium content must be known or at least estimated. A value of 10.360 mg/l was first used in the calculation sheet. This value was based on earlier measurements of sodium in fluids from this well. After the laboratory measurement of the captured downhole sample was done, this was later corrected to 11.162 mg/l. The corresponding change in calculated pH is about 0.03 pH units due to this difference. 11.162 mg/l is used in the pH chart (figure 3).

The measured pH was then found to be:

$$\text{pH measured} = 5.8 @ 90\text{C}, 317 \text{ barg}$$

### Laboratory results

The following analyses were performed onshore on the pressurized water sample:

GWR

Ion composition

Organic acids

pH at standard conditions

Total Alkalinity

pH at reservoir conditions

GC analysis to C10+ of flashed gas

Conductivity

Density at standard conditions

The water analysis results are presented in table 1, gas analysis in figure 4 and table 2.

### Laboratory pH at reservoir conditions

The water sample was transferred to a glycol filled piston displacement cell, which was modified to allow for the pH sensor to be fixed into the center of the chamber. This was a different sensor to the one used in the well, but had the same measuring principle. The sample was kept pressurized above reservoir pressure to ensure single phase during transfer. Once the sample was transferred into the pH sample chamber, it was allowed to stand at a pressure of 317 bara and heated to 92 °C and allowed to stabilize.

The laboratory pH was 5.9 at 317 barg and 92°C.

### Simulations

The simulation program MultiScale was used to calculate the pH based on the analysis of the water and gas from the down hole sampler.

### MultiScale model

MultiScale is a computer program design to calculate thermodynamic equilibrium in systems containing water, gas, oil and solids. MultiScale calculates the phases present, and the equilibrium composition of each phase. The following possible precipitations are included:

-NaCl  
 -BaSO<sub>4</sub>, SrSO<sub>4</sub>, CaSO<sub>4</sub>(Both gypsum and anhydride)  
 -FeS  
 -CaCO<sub>3</sub>, FeCO<sub>3</sub>

### Water analysis

The water input contains two parts, the conservative properties and the non-conservative properties. The conservative properties do not change with pressure and temperature if there is no precipitation or water evaporation. These are:

- Ion concentrations: Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Fe<sup>2+</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>
- Concentration of organic acids, entered as acetic acid
- Total alkalinity

The non-conservative data are needed to get the mass balance for CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>S. It is necessary to know the composition and amount of gas dissolved in the water, given as Gas-Water-Ratio, GWR, and the temperature and pressure at the flash conditions.

## Oil and gas analysis

The user can enter both oil and gas analyses.

The oil/gas analysis is similar to most common PVT-programs. The mole% of each component to C9 must be entered together with the moleweight and the density for the heaviest components. The rest is entered as a C10+ fraction. The user can choose to treat the C10+ fraction as C10, or perform a characterization where the C10+ fraction is split up to 9 different pseudo components.

## Mass balances from oil and gas input

To calculate the amount of each compound from the oil analysis, a flash calculation is performed at the pressure and temperature the user has defined.

## Calculation procedure

The calculation procedure is shown schematically in fig. 6.

## Calculation types

In MultiScale there are several calculation options:

- 1) Single point
- 2) Profile calculations, the user can vary pressure or temperature or both
- 3) Multiprofile
- 4) Mixing
- 5) P-T CaCO<sub>3</sub> saturation profile

Calculation type 2 and 3 is simply automatic generation of several single point calculations where the pressure, the temperature or both are varied automatically from some start point to some endpoint. The pressure and temperature is varied linearly from the start point to the endpoint. In Multiprofile, the user can make 4 profiles in one calculation.

Calculation type 4 mixes one water with one or several waters. The user selects which waters that should be mixed and the mixing is from vol%=0 to vol%=100 of the selected waters.

Calculation type 5 is a pressure profile, but the temperature is calculated so that SR (CaCO<sub>3</sub>) equals a selected value. The user must enter a temperature, but this is just to give MultiScale a starting estimate for the temperature.

The above calculation types can be applied to both single streams and multiple streams. However, the mixing profile gives a mixing of streams instead of waters.

There is also an option for automatic tuning of alkalinity and water mass balances.

## Calculation models

There are 2 different ways to perform the calculation:

- 1) Fixed gas composition
- 2) Variable gas composition

In the fixed model, the composition of the hydrocarbon phase (gas and/or oil) is kept constant. That is, the total composition

is not changed even if CO<sub>2</sub>, H<sub>2</sub>S and CH<sub>4</sub> dissolve in the water. When the fixed gas composition model is used, the relative amount of water and oil/gas is not important. The only necessary input is the composition of the gas/oil and the conservative properties of the water (ion concentrations, organic acid and alkalinity). The model is used to:

- Calculate pH and scaling tendency in the water phase for a system where the gas composition is known. For example on a separator.
- Calculate pH and CO<sub>2</sub> concentration in flashed water. (This is done for water when the water analysis and the composition of the flashed gas are given). It is also practical to use this option to check the quality of the water analysis if both the composition of the gas phase and the pH is measured.
- Calculate pH and scaling tendency in pure seawater having air as the gas phase.
- Calculate the effect of gas composition or CO<sub>2</sub> pressure on pH, scaling tendency or bicarbonate concentration.

The "variable gas composition" model is the model that most correctly simulates what happens when oil and water is produced. The composition of all stable phases is calculated by solving the mass balances. The variable gas composition model is designed for cases like:

- The mass balances in a system are known at some conditions, and you want to calculate the amounts and composition of each phase at any given condition.
- If you have a bottom hole oil and water analysis, you know the compositions of the phases at reservoir conditions. The variable model can be used to calculate the amounts and composition of each phase at any given condition in your production system. You may also calculate at what pressure you will reach the bubble point pressure.
- If formation waters from several wells are to be mixed and re-injected into a reservoir, the variable model should be used to calculate the scaling tendency of the water to be injected.

## Simulation results

The options "single point" and "variable gas compositions" were used. The input parameters for simulation are given in Table 1 and 2 in Appendix.

Calculated pH was 5.6 @ 92°C and 317 bar

## Discussion

The following pH results were obtained:

Logging tool: 5.8

Lab pH tool: 5.9

Simulations: 5.6

Two different probes were used in the logging tool and in the lab pH tool. Both are based on the same principle. The difference seen between simulation and actual measurement of +/- 0.3 pH units is acceptable.

The pH tool can be used to monitor pH during stimulation treatments with acid or scale solvers. Precipitation of Calcium carbonate and Napthenates are pH sensitive and can be monitored with the pH electrode. In addition corrosion potential down hole and topside can also be monitored. Oil and gas separation and emulsion formation is sometimes also sensitive to pH were this new pH sensor can give valuable information.

### **Conclusion**

The pH tool has been tested under actual field condition as a logging tool and found to give reliable pH measurement downhole.

### **Acknowledgements**

The authors wish to thank the Staffjord Unit licence owners; BP, Chevron Texaco, Norske Conoco AS, Conoco (UK) Ltd., Enterprise Oil Norwegian AS, ExxonMobil, AS Norske Shell Exploration and Production, and Statoil ASA, for permission to publish this paper.

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1. Kaasa, Baard, Multiscale manual, 2003.
2. B.Kaasa; "Prediction of pH, mineral precipitation and multiphase equilibria during oil recovery", PHD-Thesis NTNU December 1998.

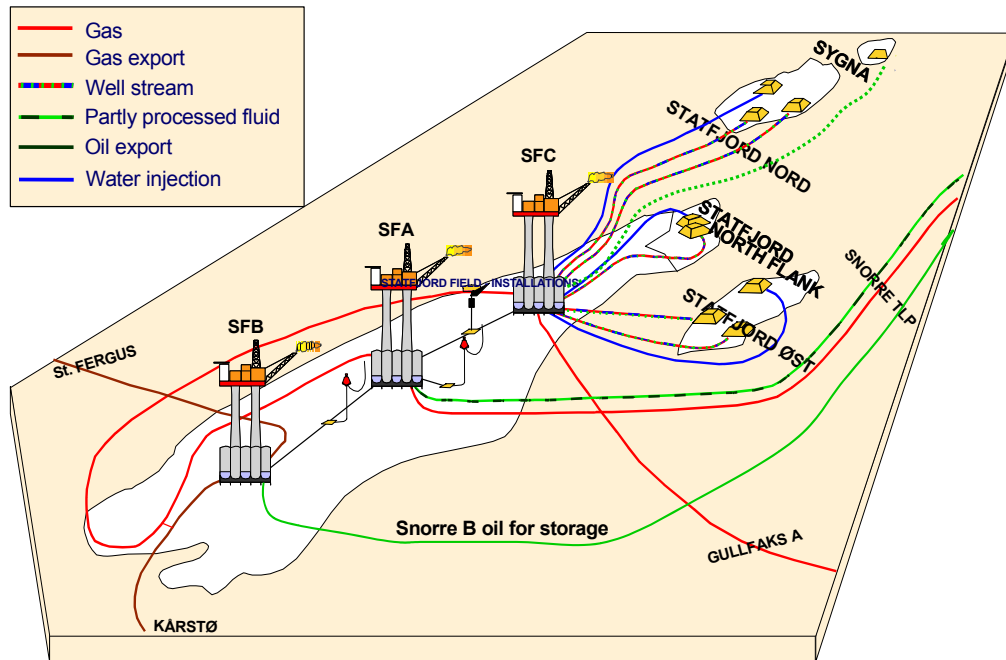


Fig. 1 – The Staffjord Field installations and tie-ins

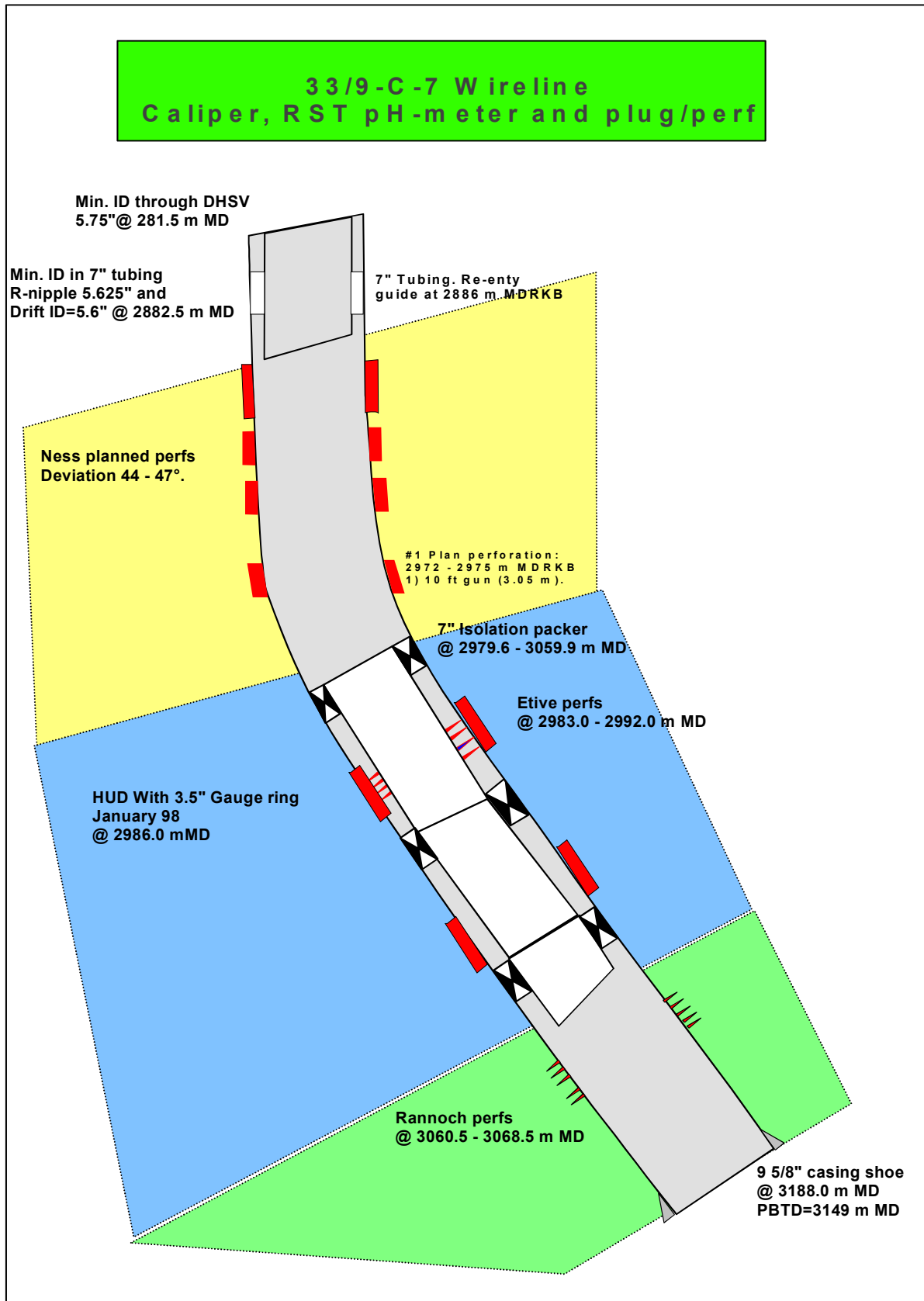


Fig.2 Well completion

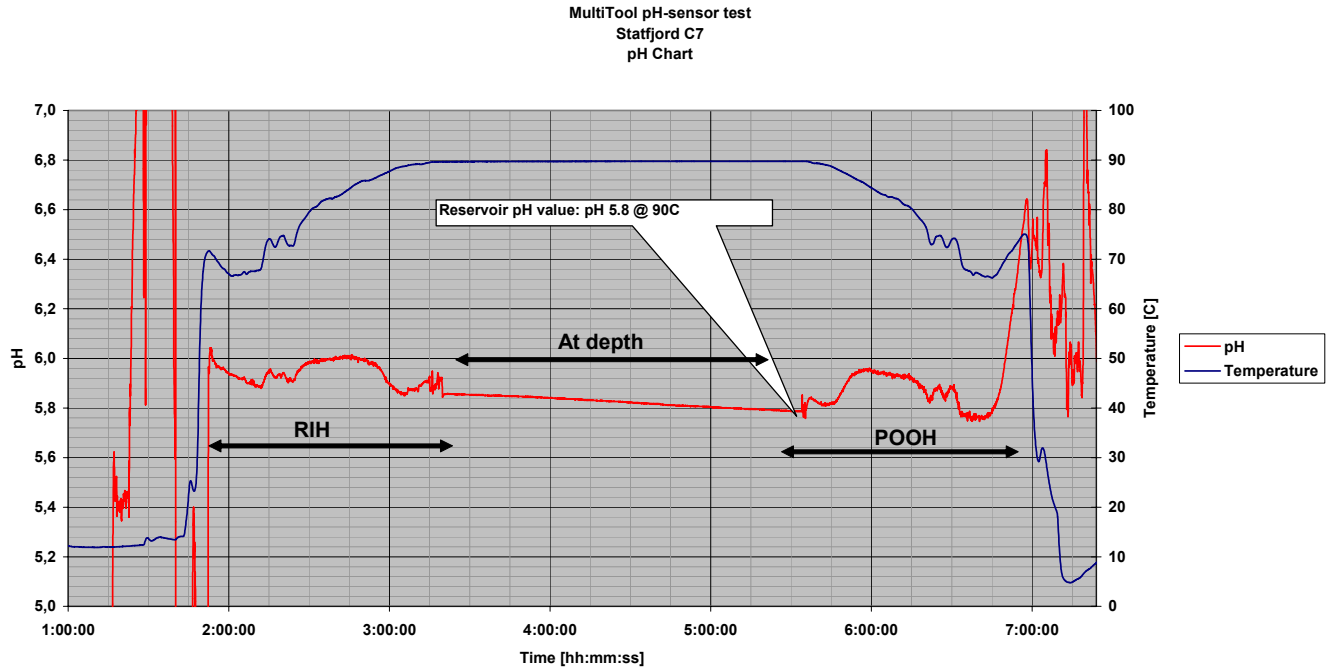


Fig.3 Plot showing the calculated pH and temperature data.



CATIONS	mg/l	meq/l
Lithium	4	1
Sodium	11161	485
Potassium	338	9
Magnesium	1163	96
Calcium	574	29
Strontium	17	0
Barium	0	0
Iron (Dissolved)	0	0
<b>SUM CATIONS</b>	<b>13257</b>	<b>619</b>

ANIONS	mg/l	meq/l
Acetate	49	1
Formate	2	0
Chloride	19519	550
Sulfate	2596	54
Bromide	36	0
Carbonate	0	0
Bicarbonate*	344	6
<b>SUM ANIONS</b>	<b>22546</b>	<b>611</b>

GWR (Sm <sup>3</sup> /Sm <sup>3</sup> )	4.5	
pH	6.74	@32.6 deg.C
Conductivity (mS/cm)	53.0	@25 deg.C
Density (g/ml)	1.026	@15 deg.C
Pressure (bar)	317	
Temperature (°C)	92	
Water cut (%)	100	

**Table 1: Input simulation data**

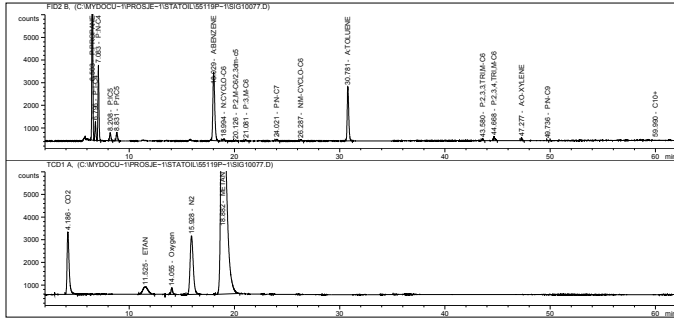


Fig. 4 – Gas chromatogram plot

Component	Weight%	Mol%	MW g/mol
N2	10.211	6.859	
CO2	12.860	5.498	
H2S	0.000	0.000	
C1	72.948	85.564	
C2	2.623	1.641	
C3	0.562	0.240	
iC4	0.044	0.014	
nC4	0.174	0.056	
iC5	0.023	0.006	
nC5	0.025	0.007	
C6	0.008	0.002	86.2
P	0.008	0.002	
N	0.000	0.000	
C7	0.291	0.069	79.1
P	0.013	0.002	
N	0.014	0.003	
A	0.264	0.064	
C8	0.172	0.035	92.3
P	0.000	0.000	
N	0.005	0.001	
A	0.167	0.034	
C9	0.024	0.004	106.8
P	0.001	0.000	
N	0.000	0.000	
A	0.023	0.004	
C10+	0.035	0.004	156.0
<b>Total</b>	<b>100.000</b>	<b>100.000</b>	<b>18.8</b>

Specific gas gravity		<b>0.650</b>	-
Gas density		<b>0.797</b>	<b>kg/m3</b>
Air in sample		<b>2.525</b>	<b>mol%</b>

Table 2: Gas analysis results

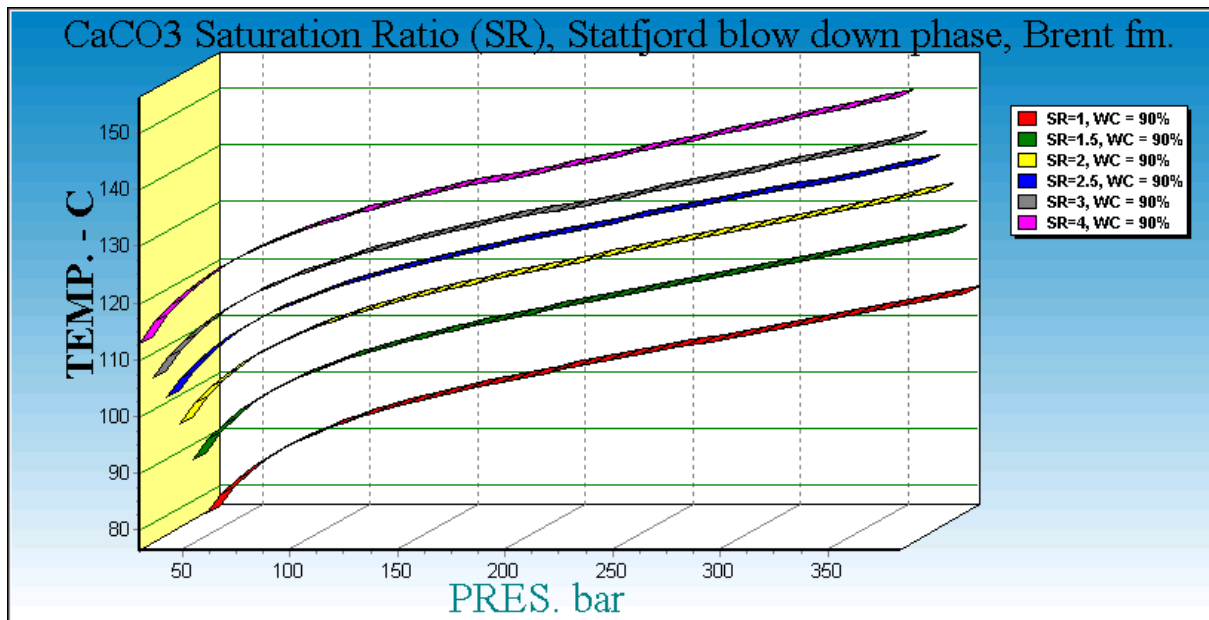
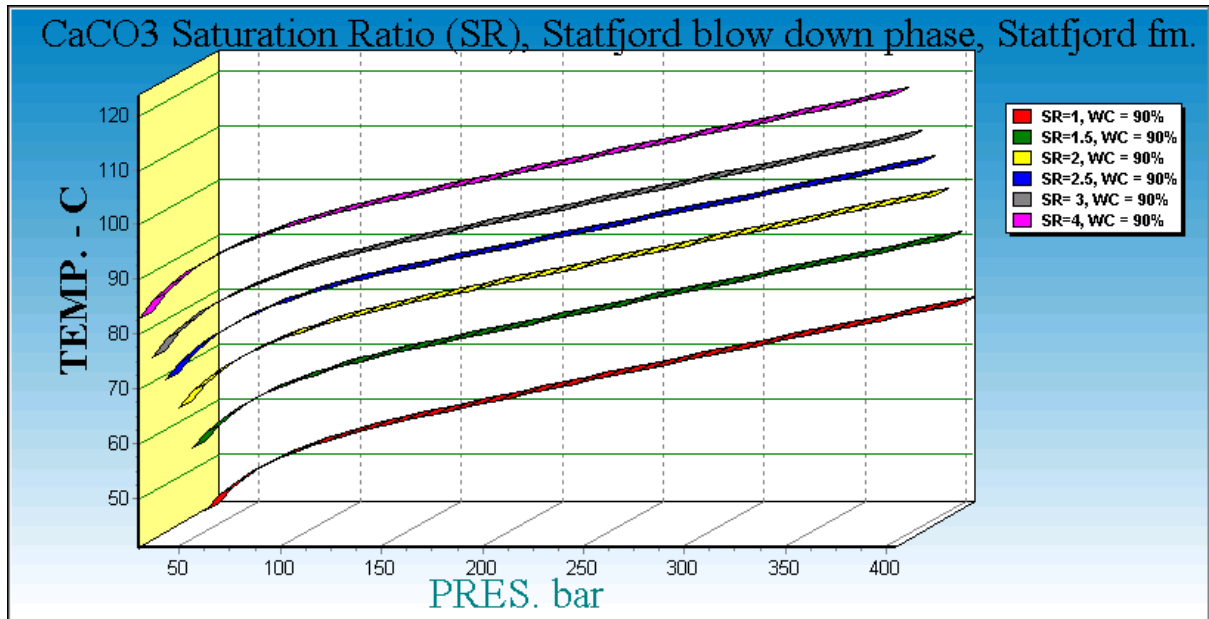
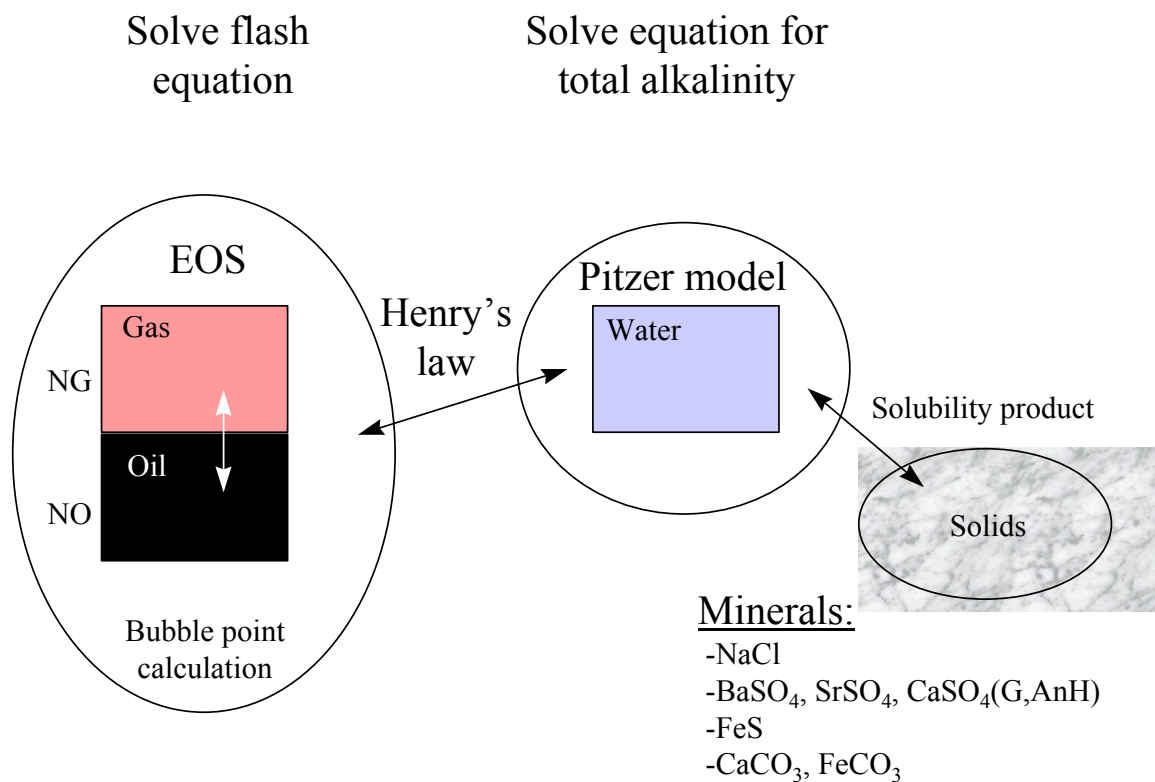


Fig. 5 – CaCO<sub>3</sub>, Iso-saturation lines from MultiScale simulations



**Fig. 6 - Schematic presentation of the MultiScale calculation procedure**