DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 2003/14

Prediction of scaling problems likely to occur during geothermal heat production using the FFC-01 well

Estimation of saturation indices for saline formation waters

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MINISTRY OF THE ENVIRONMENT

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G E U S

Abstract

Formation waters obtained from Zone A (1610 m) and B (1840 m) of the FFC-01 well in Malmö are very saline having TDS = 170,000 and 190,000 mg/l respectively. The main solutes are sodium, calcium and magnesium chloride.

The results of the chemical analyses were used to calculate the saturation indices of various salts at different temperatures in order to predict if scaling problems were likely to occur during geothermal heat production. Two different computer programs MULTISCALE and SHEMAT were used to calculate the saturation index $\log(AP/K_T)$, the ratio between the activity product of ions in solution and the solubility product for a number of salts. Differences between the results obtained using two programs were insignificant. Barium sulphate is the only salt for which super saturation will occur when the temperature of the formation water is lowered. No precipitation of barium sulphate is however, expected to occur as the rate of precipitation of this salt is slow.

The concentration of suspended solids in the formation water determined by filtration during a production test of Zone A is very low, only 0.3 mg per litre.

Contents

Introduction

Sydkraft Värme Syd AB have asked The Geological Survey of Denmark and Greenland (GEUS) to assess the risk of scaling (precipitation of salts) during geothermal heat production from a geothermal well in the city of Malmö. Two potential reservoirs of the Malmö area were tested by air-lift testing during September-October 2002 in the newly drilled FFC-01 well. Furthermore, pressurised formation water samples were obtained using a bottom hole sampler shortly after the tests. Analysis of these samples show that the formation water of the two geological formations, the Anager Grönsand/Höganäs formation (Zone A, 1610 m) and the Kågeröd formation (Zone B, 1860 m) is very saline, Table 1.

Table 1. Chemical composition of formation water samples from Malmö geothermal well FFC-01

Sample ID	Formation	Depth M	pH	HCO3	Cl	SO4	Br	Na	Ca	Mg	K	Sr	Fe	NH4	Ba	Zn	SiO2	I	Density g/cm3 20 °C
				g/l										mg/l					
815183	Arnager/	1610	6.3	0.056	105	0.045	0.63	42.2	21.8	1.10	1.25	1.01	0.069	40	17	<0.5	5.4	7.6	1.116
815182	/Höganäs	1610	6.3	0.069	103	0.041	0.55	42.7	20.1	1.00	1.19	1.01	0.065	40	16	1.2	5.4	7.2	1.116
813561	Kågeröd	1840	6.1	0.069	119	0.027	0.54	45.0	22.5	1.60	0.36	0.96	0.007	40	27	1.2	7.1	8.9	1.129
815183	Kågeröd	1860	6.1	0.069	103	0.048	0.68	38.6	19.2	1.31	0.46	0.81	0.008	40	23	1.7	5.9	8.0	1.129

Due to the high salinity of the water (5 times that of sea water) precipitation of salts may occur due to cooling, which could lead to clogging of the re-injection well or the geothermal plant itself. Since geothermal production requires large volumes of water, usually over 100 cubic metres per hour, precipitation of just 1 mg of salt per litre of fluid may cause large problems if the precipitate form in critical parts of the plant. Therefore, it should be examined if the formation water will become supersaturated with respect to certain salts i.e. the solubility of various salts in the fluid should be known for different temperatures.

The solubility of most salts in pure water are known from laboratory measurements at room temperature and atmospheric pressure. However, the solubility of a given salt varies with both temperature and the salinity of the water and unfortunately, solubility data for different salinities and temperatures are limited. Therefore, often one has to interpolate/extrapolate using relatively few data points to determine the solubility at the salinity and temperature needed.

Computer software has been developed to calculate the solubility of various salts for different salinities at different temperatures. However, one should not expect to obtain identical results using different software because different models and different databases are being used. This is due to the fact that most computer programs have been developed for various specific purposes, therefore, one should select among those most suited for saline formation waters in sedimentary basins. No commercial computer program has yet been developed that specifically solve problems with saline geothermal fluids, however, programs used by the oil industry to tackle scaling problems can be used for geothermal plants as well since similar types of waters are operated with.

In this report a short description is given of the salts that may precipitate during geothermal heat production using saline formation waters. Furthermore, saturation indices of various salts at different temperatures for the two formation waters of the Malmö FFC-01 well (Table 1) have been calculated using two different computer programs. The scientific basis of the model used in the programs is explained shortly, and the results obtained using the two programs have been compared in order to get an impression of the accuracy of the calculations.

Even if super saturation predicted by the computer calculations should occur, this does not imply that precipitation will take place in the geothermal plant nor in the injection well. The rate of precipitation may be so slow due to kinetics, that precipitation is prevented in critical parts of a geothermal doublet. Laboratory experiments on barium sulphate briefly mentioned in this report may serve as an example of such phenomena.

Experience in geothermal production with formation waters from the sedimentary basin extending into Southernmost Sweden, have been obtained in the Danish area. In order to take advantage the Danish experience in exploration and exploitation of geothermal energy a brief introduction to the types of formations waters encountered in the Danish Sub basin is given.

During the production test of zone A (1610 m) in December 2002, the amount of suspended particles in the water was determined by filter paper tests on two occasions. The results of the tests are described in this report and a number of photos have been included for documentation.

Finally conclusions are drawn with respect to the potential risk of clogging of a geothermal plant in Malmö using the formation waters of the Arnager Grönsand/Höganäs and the Kågeröd formations.

Saline formation waters in the Danish Sub basin

Most information on deep formation waters in the Danish Sub basin has been obtained from geothermal exploration wells. However, production tests that provide the most reliable results were only performed in four wells. Therefore, also formation water from air-lift tests and water obtained from centrifuge extraction of core samples have been analysed to extend the data base on formation water chemistry. The results of the latter samples do not provide information on volatiles (gases) of the formation fluid and concentrations of minor constituents cannot be considered reliable. However, data on major ions is considered to be representative for the formation waters and have been included in the plots of formation water chemistry versus depth, Fig. 1. The well locations relevant for the formation water plots are shown in Fig. 2.

The salinity of formation waters almost increases linearly with depth approaching saturation with respect to halite (sodium chloride) at 3000 m (Fig. 1A). Close to salt diapirs salinity increases more rapidly with depth as is seen for the Erslev and Tønder wells (Fig. 1A and Fig. 2). The smooth increase in formation water salinity with depth is probably due to diffusion of salt from the large Zechstein salt deposits present in the large parts of the basin (Fig. 2). The relatively high bromide to chloride ratios of most formation waters does not indicate dissolution of salt as being the primary source, since halite has a lower bromide to chloride ratio compared to sea water (Fig. 1B). The source is more likely the residual brines left after the precipitation of the Zechstein salts.

The calcium concentration increases more rapidly than salinity with depth (Fig. 1C). This is probably due the diagenesis of plagioclas, whereby anorthite is transformed into albite (eq. 1).

$$CaAl_2Si_2O_8 + 2Na^+ + 4SiO_2 \rightarrow 2NaAlSi_3O_8 + Ca^{++} \qquad (1)$$

The degree of diagenesis depends on both temperature and time, and this could explain why calcium concentration increases relative to salinity with depth since both temperature and age of the formation increases with depth.

The calcium to magnesium ratio increases generally with depth, primarily because of the diagenetic reaction mentioned, but also because of dolomitisation of calcite which decreases the magnesium concentration relative to salinity (Fig. 1D).

Sulphate, one of the major ions of seawater (2800 mg/l), is often quite low in formation waters due to the microbial process of sulphate reduction. Sulphate concentration is often below 50 mg/l in waters of geological formations containing organic matter. In organic lean formations like chalk and the reddish brown terrigeneous Triassic deposits sulphate concentration may be higher.

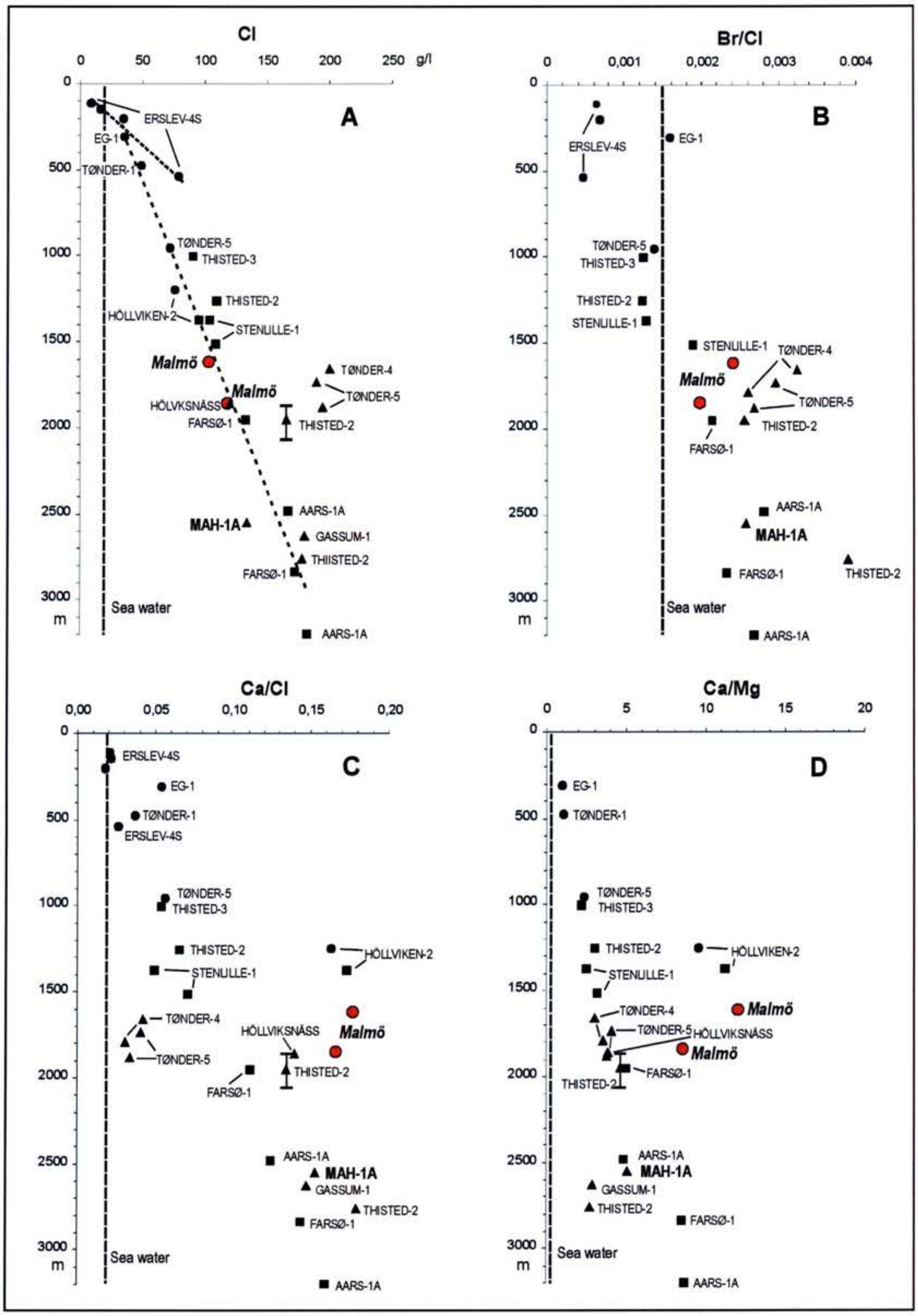


Fig. 1. Chemistry of formation waters in the Danish sub basin. Triangles = Triassic, squares = Jurassic and circles = Cretaceous-Tertiary. Ion-ratios are in mole units. Malmö FFC-01 geothermal well data are indicated by red circles.

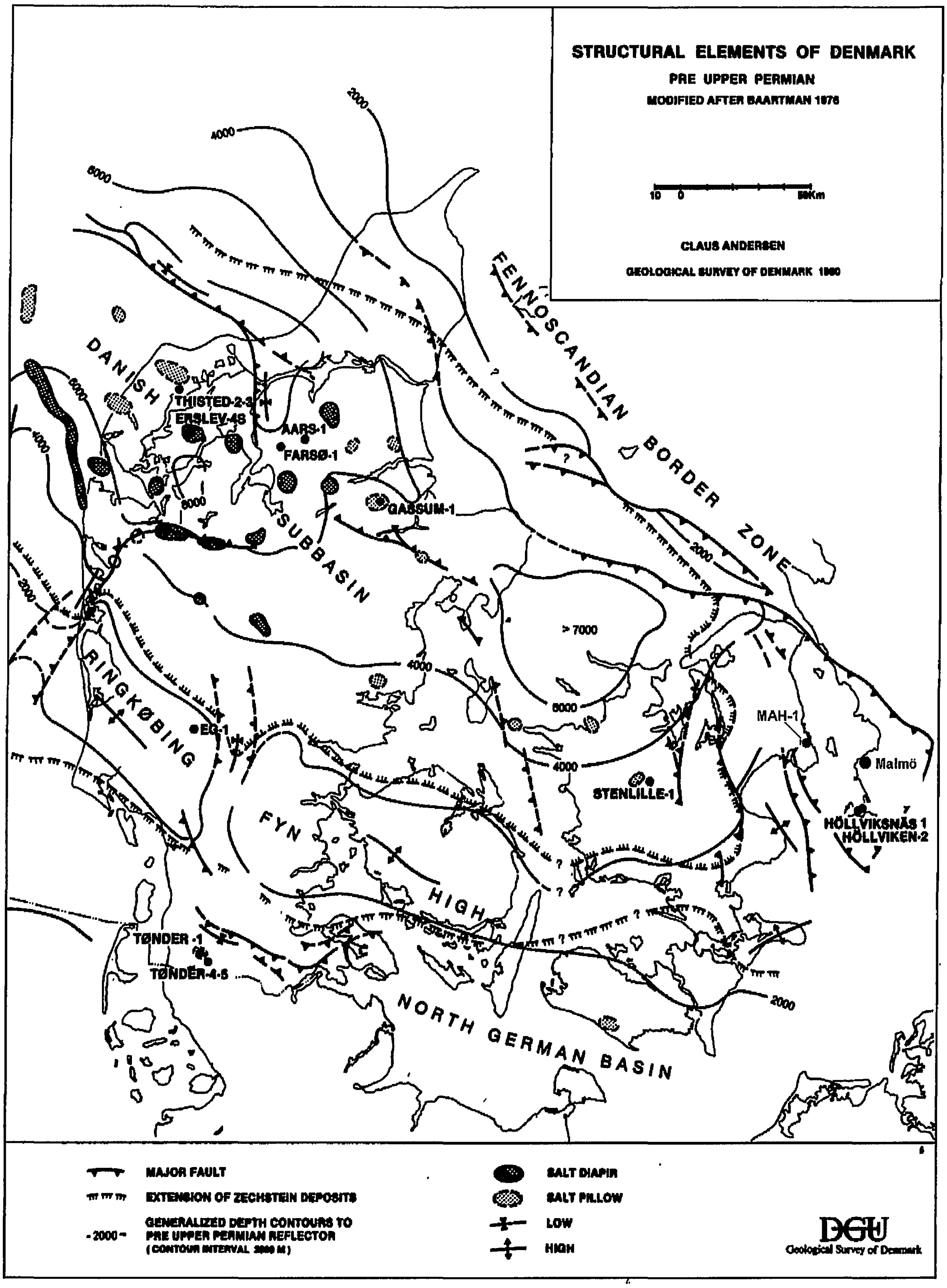


Fig. 2. Location map indicating the position of wells from which data on formation water chemistry have been obtained.

Formation waters in the area outside the massive Zechstein deposits indicated on figure 2 do not differ significantly from waters within the area with respect to chemical composition, as is seen for data obtained from wells in southernmost Sweden (Fig. 1). The high salinity of the formation waters outside the Zechstein area is most likely also due to the salt deposits, although it is not possible to decide by which mechanism salts were transferred from the Zechstein area.

Precipitation of salt from saline waters - general considerations

Most high-enthalpy geothermal plants have scaling problems with silica SiO_2 due to a major drop in temperature of the formation fluid during heat production. In low enthalpy geothermal plants (<100 °C) silica precipitates do not form because the formation waters remain under saturated with respect to silica at all times. In geological formations the SiO_2 concentration of the formation water is controlled by equilibrium with quartz, which is much less soluble than silica. However, precipitation of quartz is so slow that quartz never forms in low enthalpy geothermal plants. Amorphous silica precipitates of much faster than quartz, and will start to form when the fluid becomes supersaturated with respect to this mineral. Thus, precipitation of silica will only occur when exploiting formation waters with initial temperatures well above 100 °C.

In low enthalpy geothermal plants scaling problems will most likely be due to precipitation of sulphates or carbonates. As mentioned in the previous chapter calcium concentration increases with depth, thus formation waters may become saturated with respect to anhydrite ($CaSO_4$). This is more likely to happen for the organic lean deposits e.g. the terrigenous Triassic deposits, where sulphate concentration may be higher due to absence of sulphate reduction. Whether or not the formation water is saturated with respect to anhydrite may be examined in two ways. 1) By studies of the mineralogy of the formation to see if anhydrite is present or 2) by comparing the ion product of calcium and sulphate of the formation water with the solubility product for anhydrite. The latter approach, require the use of computer programs in order to calculate the solubility product of anhydrite in the specific formation water. This is then related to the ion product of calcium and sulphate by calculation of an anhydrite saturation index for the formation water in question. Comparison of calculated solubility products with experimental solubility data are seldom published. However, Kaasa (1998) did compare calculations by MULTISCALE with experimental data for anhydrite, Fig. 3.

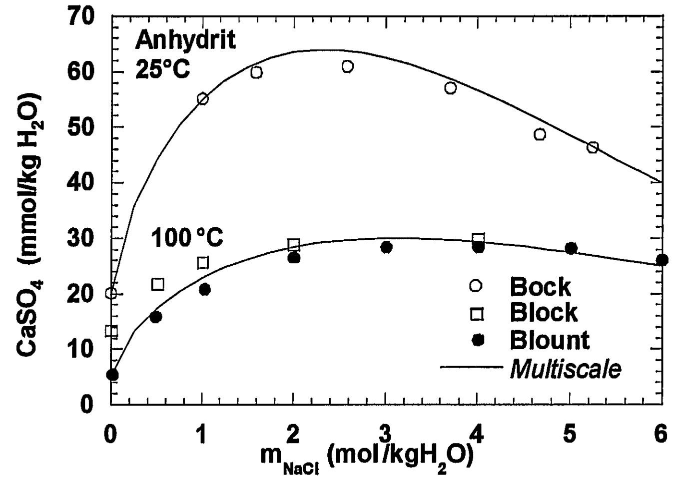


Fig. 3. Solubility of anhydrite as a function of salinity, at 25 °C and 100 °C. Curves represent values calculated by MULTISCALE *(Kaasa, 1998). 1 m_{NaCl} ~ 50 000 mg/l TDS.*

The solubility increases markedly with increasing salinity of the solution from 0 – 3 molal (ca. 150 mg/l). At still higher salinity, the solubility of anhydrite decreases due to the ”salting out” effect. The increase in solubility with increasing salinity is generally observed for all salts, and can be explained by a decrease in the activity of the calcium and sulphate ions, i.e. a decrease in the “effective” concentrations of the two ions. This decrease is due to the “shielding” of the calcium and sulphate by other ions in solution.

Strontium sulphate is less soluble than anhydrite, but its solubility varies similarly with temperature and salinity. Though its temperature dependence is less significant compared to that of anhydrite, Fig. 4.

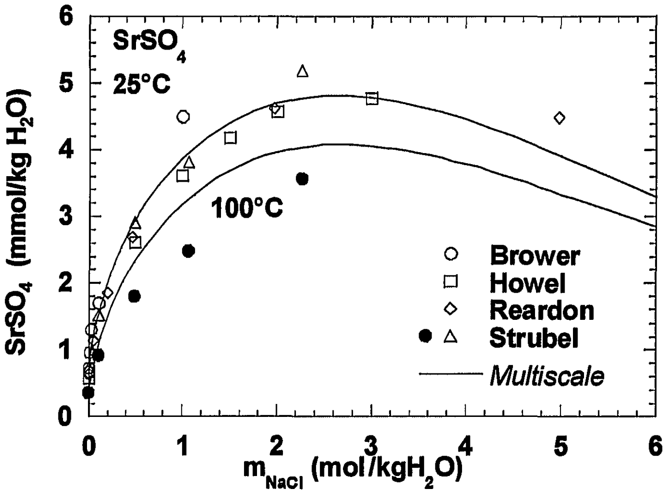


Fig. 4. Solubility of strontium sulphate as a function of salinity at 25 °C and 100 °C. Curves represent values calculated by MULTISCALE (Kaasa, 1998).

The solubility of barium sulphate decreases with decreasing temperature, therefore the formation water will become supersaturated with respect to this salt, if initially saturated with respect barite in the geological formation (Fig. 5)

The amount of barium sulphate that could precipitate upon cooling of the formation water will be modest anyhow, because of the low concentrations of both barium and sulphate (Table 1).

The vast literature on barium sulphate scaling is mainly related to problems encountered by the oil industry during enhanced oil recovery operations. Mixing of injected seawater having a high sulphate concentration (2800 mg/l) with formation water high in barium (up to 300 mg/l) may lead to precipitation of significant amounts of barium sulphate.

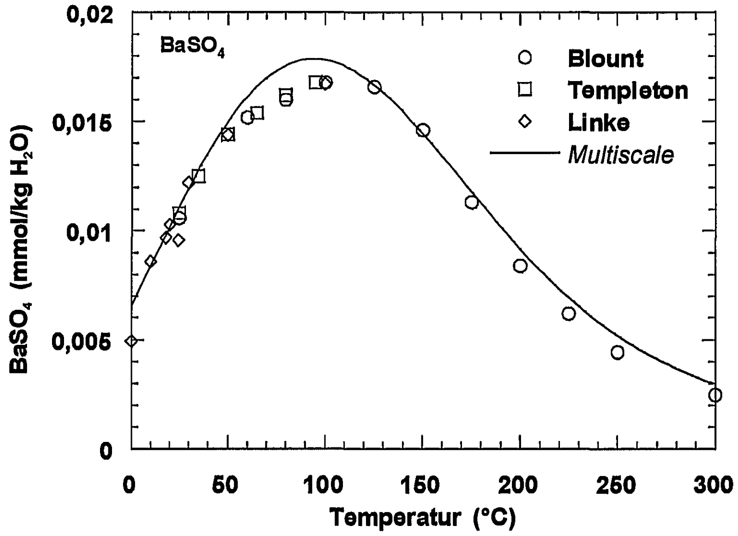


Fig. 5. Solubility of barium sulphate in pure water measured and calculated as a function of temperature. Curve represent values calculated by *MULTISCALE (Kaasa, 1998).*

The solubility of calcite increases with decreasing temperature, Fig. 6. Therefore, precipitation of calcite should not occur upon cooling of the formation water during heat production.

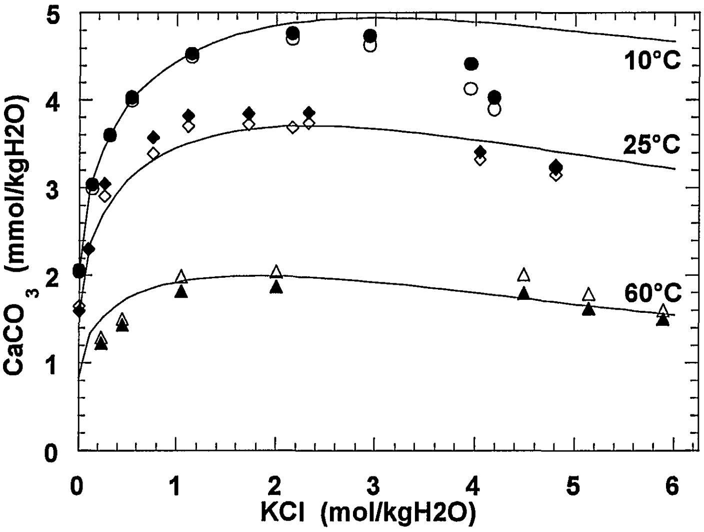


Fig.6. Solubility of calcite as a function of salinity measured and calculated at three different temperatures. Experimental data based on calcium analyses are shown as solid symbols. Data based on carbonate analyses are shown as open symbols. Curves represent values calculated by *MULTISCALE (Kaasa, 1998).*

Precipitation of calcite may, however occur if CO_2 is lost from solution as a result of pressure reduction. Loss of carbon dioxide will increase pH and shift equation 2 to the right.

$$Ca^{2+} + 2HCO_3^- \rightarrow Ca^{2+} + CO_3^{2-} + \uparrow CO_2 + H_2O \rightarrow CaCO_3 \downarrow + H_2O \qquad (2)$$

pH measurements as well as bicarbonate analyses on formation waters are usually performed after loss of CO_2. Therefore, it is difficult to make realistic calculations of the saturation index for calcite and dolomite. Super saturation with respect to carbonate minerals is often indicated by computer calculations because too high pH values have been entered.

Computer software for predicting scaling problems

No commercial computer software has yet been developed specifically to predict scaling problems that may occur during geothermal heat production using low-enthalpy saline waters. However, software like SOLMINEQ88 (Kharaka *et al.*, 1988) and MULTISCALE (Kaasa, 1998), developed for the oil industry to calculate the saturation index for various salts at different temperatures and pressures are adequate for geothermal production as well. Oil field waters like geothermal waters are very saline and have similar chemical composition, except for the much larger gas content in the former. The high gas content makes prediction of scaling problems in oil production wells more difficult than in geothermal wells. In oil and gas production, however, it is not so important what happens when the water reach the surface and cools down, since water is quickly separated from the oil. Also the volumes of water produced in oil production is usually minor compared to those produced during geothermal production. Given the large volumes of water involved and the fact that it has to be re-injected after cooling very precise calculations of saturation indices are needed for waters used for geothermal heat production. SOLMINEQ88 was primarily developed to calculate saturation indices for mixtures of different waters that may result from enhanced oil recovery. This could help the oil industry to decide what type of water should be chosen for injection in order to avoid problems with scaling. MULTISCALE will serve this purpose even better and in addition this software may be used to predict scaling problems in primary production as it capable to do calculations for a three phase system: water-gas-oil.

Besides the two computer-programs mentioned a fairly large number of programs have been developed to simulate geochemical processes in groundwater as wells as in surface waters, However, these programs are not suitable for calculations on very saline waters as they use a different approach for calculating saturation indices. The computer code for one program (PHREEQ) was modified to calculate saturation indices using the Pitzer equations, which are the most suitable for saline waters. This program, PHRQPITZ (Plummer *et al.,* 1988), may be downloaded from the homepage of the U.S. Geological Survey. PHRQPITZ uses the same approach as MULTISCALE except that it does not offer the possibility to calculate the effect of pressure on solubility of various salts. However, the effect of pressure on solubility is minor compared to that of temperature. Furthermore, little experimental data are available that allow check of pressure effects on solubility (Kühn *et al.,* 2002). The databases, which are used by PHRQPITZ for calculation of saturation indices are separated from the computer code itself. Thus the user may up-date the databases when more data and better data become available. As pointed out by Plummer *et al.* (1988) one has to be very careful in selecting data for up-dating their database, as the data for the various Pitzer parameters must be consistent. One example presented by the authors show fairly large discrepancies in the calculated solubility of a particular salt by arbitrarily picking Pitzer data published by different authors. Recently Kühn *et al.*(2002) published an extended database for the PHRQPITZ code, which is used in their computer program SHEMAT.

Ion-pair models for low to moderate salinity waters, Debye-Hückel equation

The first computer programs were based the ion-pair model, and this model is still being used as the databases with this model allow calculations with respect to a large number minerals relevant for environmental studies. The "Pitzer model" extends the Debye-Hückel equation by specific ion-interaction terms that allow more accurate calculations to be made for saline waters. However, ion-interaction terms (Pitzer parameters) have so far only be determined for a limited number of ions, mostly the major ions of seawater.

As shown in figure 3 the solubility of anhydrite increases with the salinity of the solution. This is due to "shielding" of calcium and sulphate by the other ions in solution. The degree of "shielding", expressed by the activity coefficient (γ_i) depends on the ion strength of the solution and may be calculated using the Debye-Hückel equation (eq. 3).

$$\log\gamma_i = \frac{\div A_\gamma z_i^2\sqrt{I}}{1+a_i^\circ B_\gamma\sqrt{I}} \qquad (3)$$

I is the ion strength that may be calculated from the total concentration of ions in solution taking into account the charge of the ions. A_γ and B_γ are Debye-Hückel constants. a_i^o is ion radius for the ion in question and z_i its charge. Activity coefficients for different ions as a function of salinity ($I = m_{NaCl}$) are shown in figure 7.

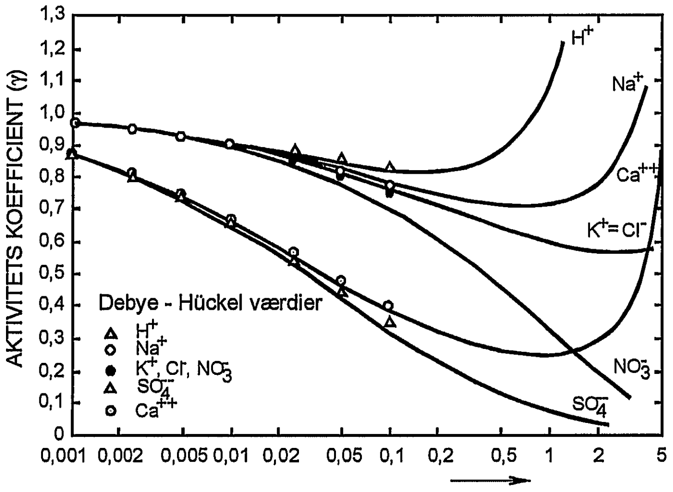
The Debye-Hückel equation should only be applied for dilute solutions. For less dilute solutions ion pairing has to be taken into account. Ion pairs may be neutral like $CaSO_4$ or have a positive or negative charge like $CaHCO_3^+$. Equation 4 expresses the formation of the calcium sulphate ion pair where K_{eq} denote the equilibrium constant for the reaction.

$$Ca^{2+}+SO_4^{2-}=CaSO^\circ_{4(aq)}\ ; \qquad K_{eq}=\frac{a_{CaSO_4}}{a_{Ca^{2+}}\cdot a_{SO_4^{2-}}} \qquad (4)$$

Equilibrium constants for several ion pairs are included in the databases used by the different computer programs. Executing the program equations for all ion pairs are being solved simultaneously by the computer, using an iteration procedure. In this way the activities of all ions i.e. the "effective" concentrations are being determined. The activity product of various ions (AP) are then related to the solubility products of different salts (K_{sp}) for example calcium sulphate (eq. 5) to give the saturation index $\log(AP/K_{sp})$. This may be negative indicating that the solution is not saturated or positive if the solution is supersaturated with respect to that particular salt.

$$CaSO_{4(s)}=Ca^{2+}+SO_4^{2-}\ ; \qquad K_{sp}=\frac{a_{Ca^{2+}}\cdot a_{SO_4^{2-}}}{a_{CaSO_4}}=a_{Ca^{2+}}\cdot a_{SO^{2-}_4} \qquad (5)$$

The Activity of solid salt equals 1 by definition.



Figur 7. Activity coefficients for different ions as a function of ion strength I, in a NaCl solution, after Garrels & Christ (1965). I =1 ~ TDS = 50 000 mg/l

Ion-interaction model for saline waters, Pitzer equations.

The ion interaction model proposed by Pitzer (1973; 1975) extend the Debye-Hückel model by taken into account the specific interactions of all ions in solution. Of course it is not possible to determine all specific interactions between ions experimentally. However, by thorough theoretical work Pitzer and others succeeded in reducing significantly the number of parameters needed to be determined experimentally. The model was tested successfully by predicting the right succession of precipitates forming upon seawater evaporation at 25 °C (Harvie and Weare, 1980; Harvie *et al.* 1984).

When the computer code for PHRQPITZ was published in 1988 Pitzer parameters were only available for few ions in a fairly narrow temperature interval around 25 °C. Since then, the number of ions have increased and the temperature interval extended up to 150 °C (Moller, 1988; Greenberg and Moller, 1989; Kaasa, 1998; Kühn *et al.*, 2002). However, use of the model is still limited to calculations of saturation indices for simple salts, not the more complex silicate minerals.

Accuracy of calculated saturation indices

It is obvious that the accuracy of the calculated saturation indices very much depends on the accuracy of the formation water analyses. Generally analysis of minor ions e.g. barium and sulphate are less accurate than that of major ions. Even if accurate analytical data were available for the formation fluid the calculated saturation indices would still not be 100 per cent accurate due to the uncertainties in the experimental solubility data used for calculation of the solubility products of various salts. The parameters of the Pitzer variables are also due to uncertainties depending on the experimental set-up and accuracy of the analytical instruments used for determination of the specific parameters.

Calculations of saturation indices for Malmö FFC-01 formation waters

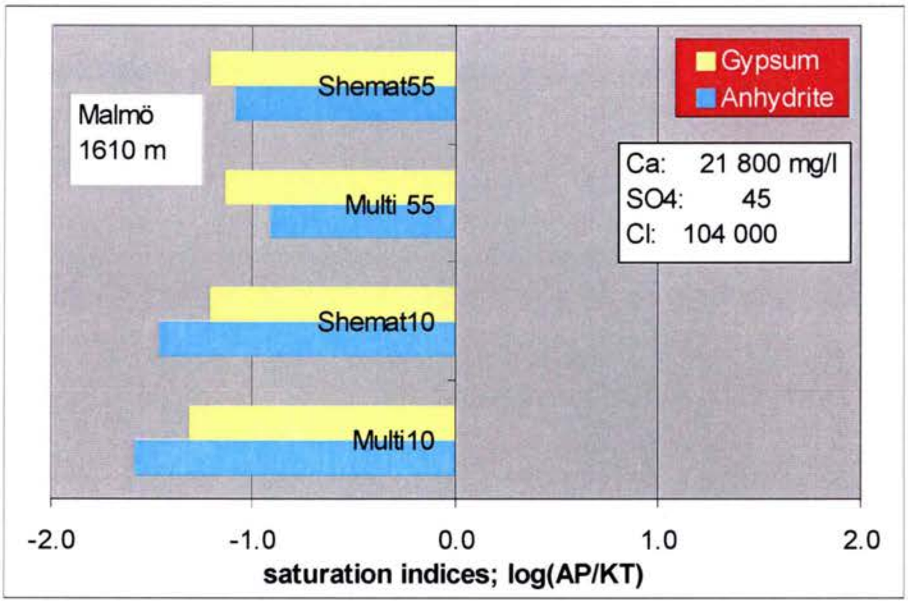
In order to get an impression of the uncertainties of the computer calculations saturation indices have been calculated using two different programs: MULTISCALE and PHRQPITZ. The database for the latter was obtained from Kühn *et al:* (2002) which they use in their SHEMAT program. The experimental data for both solubility and Pitzer parameters used in both programs were obtained from the same published literature. Even so, the saturation indices calculated by the two programs differ although not much as can be seen in the tables and figures below. At higher temperatures (>50 °C) the saturation indices calculated using the SHEMATE database are lower than those calculated by MULTISCALE. The opposite is the case at low temperature (10 °C). Calculations by SHEMAT include formation of a $CaSO_4^{\circ}$ ion pair as is also used by Greenbeerg and Moller (1989). Formation of this ion pair will lower the concentration of "free" sulphate and thus lower the activity product (AP) of calcium sulphate. However, MULTISCALE calculation does include this specific ion pair. Kaasa (1998) concluded that MULTISCALE calculations made a better fit to published solubility data than did the method of Greenbeerg and Moller (1989). However, the data are too limited to decide which of two sets of saturation indices is the most accurate one. In view of the uncertainties with respect to formation water analyses as well as solubility products and Pitzer parameters the difference in calculated saturation indices is considered to be insignificant. The pressure condition used in all calculation was equal to 1 bar, since PHRQPITZ does not include an option for calculations including higher pressures. Also, the effect of pressure on solubility is much less important than that of temperature.

Only the results for the sulphates have been shown in the figures and tables below, as the calculations showed that the formation waters of the FFC-01 well was under saturated with respect to other types of salts. Calculations by both computer programs show that the formation water will become supersaturated with respect to barite as the water temperature is lowered to 10 °C. Details of MULTISCALE calculations on barium sulphate including the amount that may precipitate due to super saturation at different temperatures is shown in table 2.

Table 2. MULTISCALE results on barium sulphate.

Temperature °C	Zone A Sample 815183		Zone B Sample 813561		Zone B Sample 815183	
	log(AP)/Ksp	mg/l	log(AP)/Ksp	mg/l	log(AP)/Ksp	mg/l
63			-0.083	0	0.098	6.3
55	0.024	1.3				
15	0.459	18.2	0.418	21.6	0.609	27.2
10	0.527	19.9	0.485	24.2	0.679	28.9
5	0.599	21.4	0.555	26.6	0.753	30.5

Malmö FFC-01 Zone A, 1610 m, sample 81583



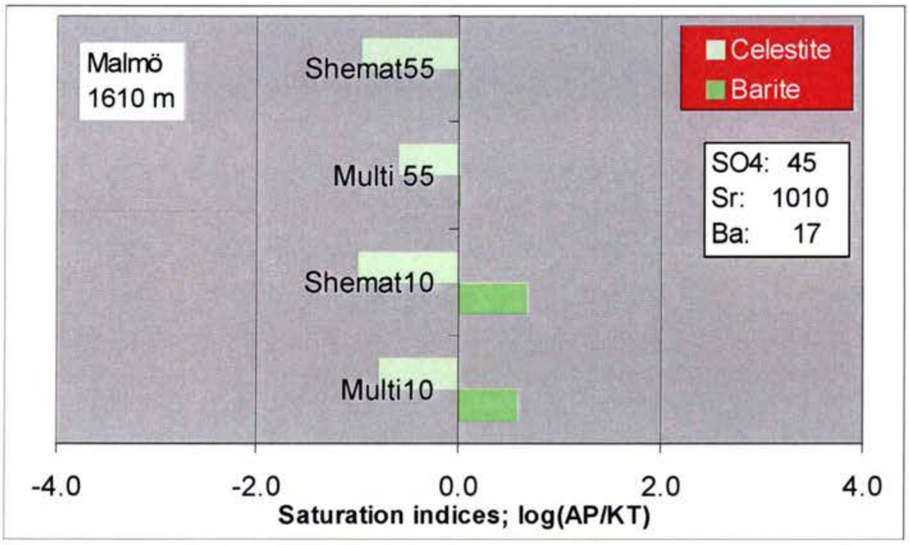
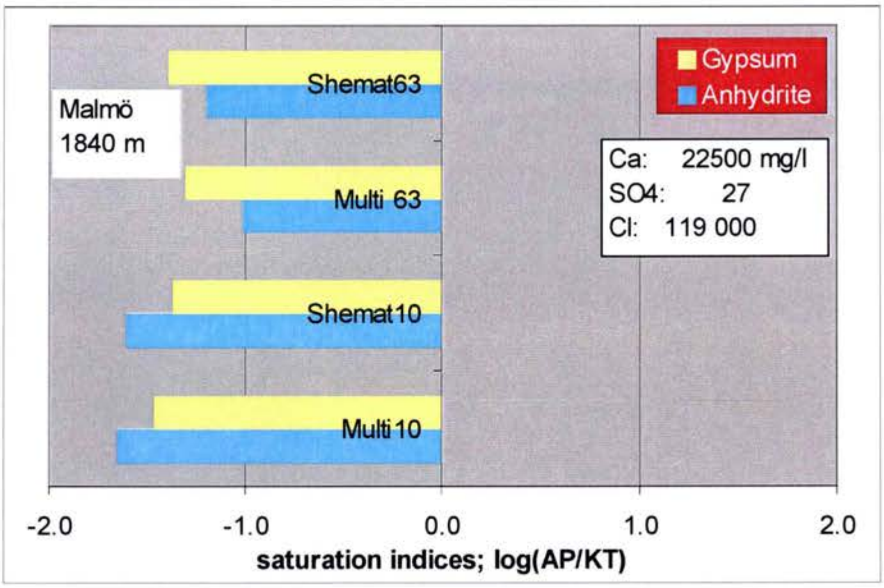


Fig. 8. Saturation indices calculated for four salts of sulphate. Bottom Hole Sample 815183.

Table 3. Saturation indices of Zone A, 1610 m formation water. Bottom Hole Sample 815183

ID	Anhydrite	Gypsum	Barite	Celestite	Temp.	Model type
Multi10	-1.585	-1.319	0.527	-0.788	10	Multiscale
Shemat10	-1.466	-1.211	0.667	-0.989		Shemat
Multi 55	-0.907	-1.131	0.013	-0.595	55	Multiscale
Shemat55	-1.087	-1.214	0.009	-0.953		Shemat

Malmö FFC-01 Zone B, 1840 m, sample 813561



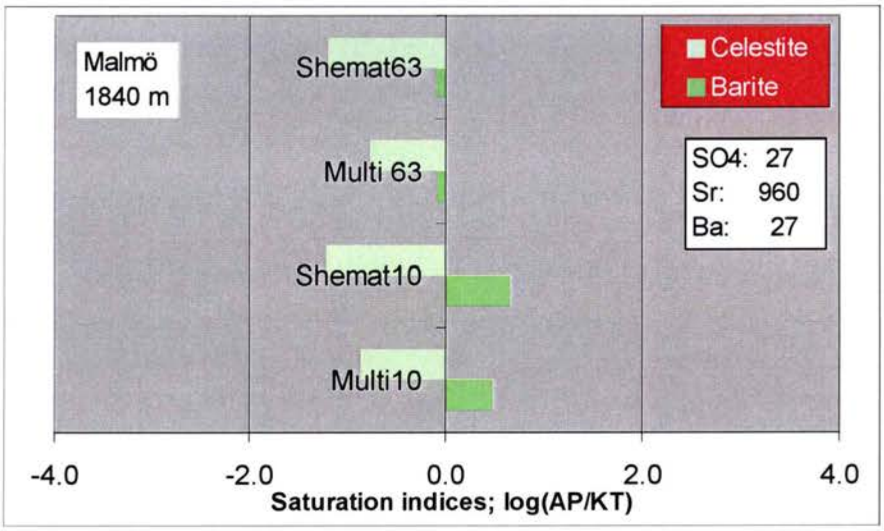
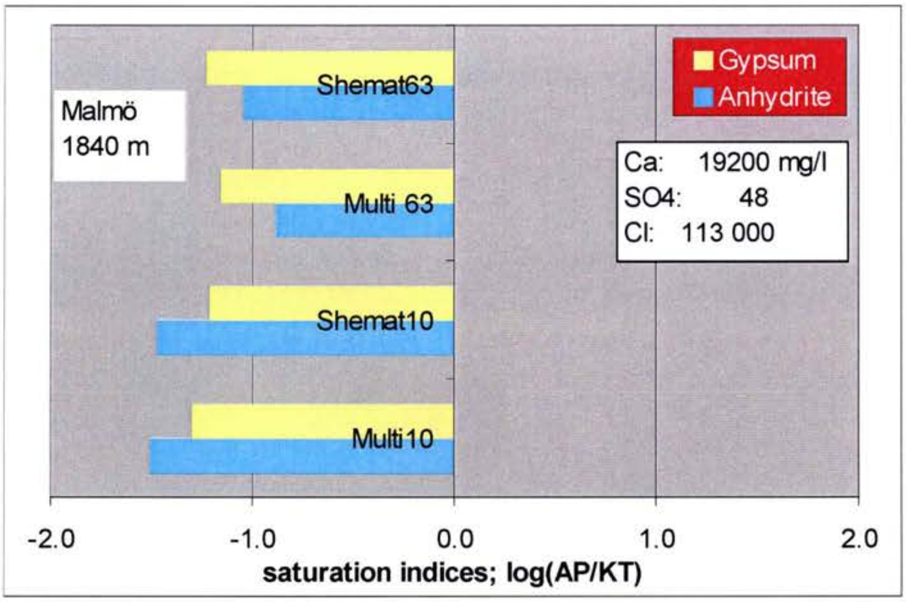


Fig. 9. Saturation indices calculated for four salts of sulphate. Bottom Hole Sample 813561

Table 4. Saturation indices of Zone B, 1840 m, formation water. Bottom Hole Sample 813561

ID	Anhydrite	Gypsum	Barite	Celestite	temp	Model type
Multi10	-1.658	-1.469	0.485	-0.860	10	Multiscale
Shemat10	-1.608	-1.368	0.664	-1.213		Shemat
Multi 63	-1.009	-1.310	-0.083	-0.770	63	Multiscale
Shemat63	-1.196	-1.396	-0.102	-1.193		Shemat

Malmö FFC-01 Zone B, 1860 m, sample 815183.



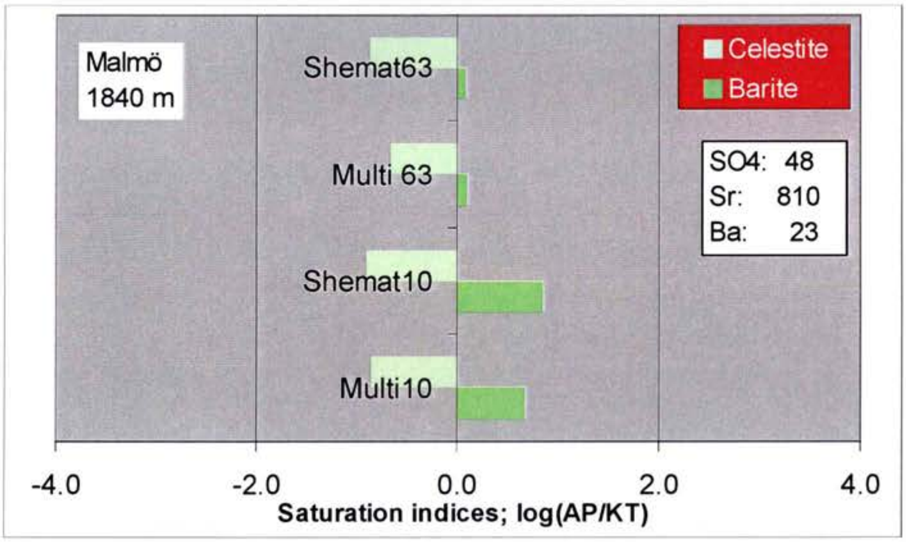
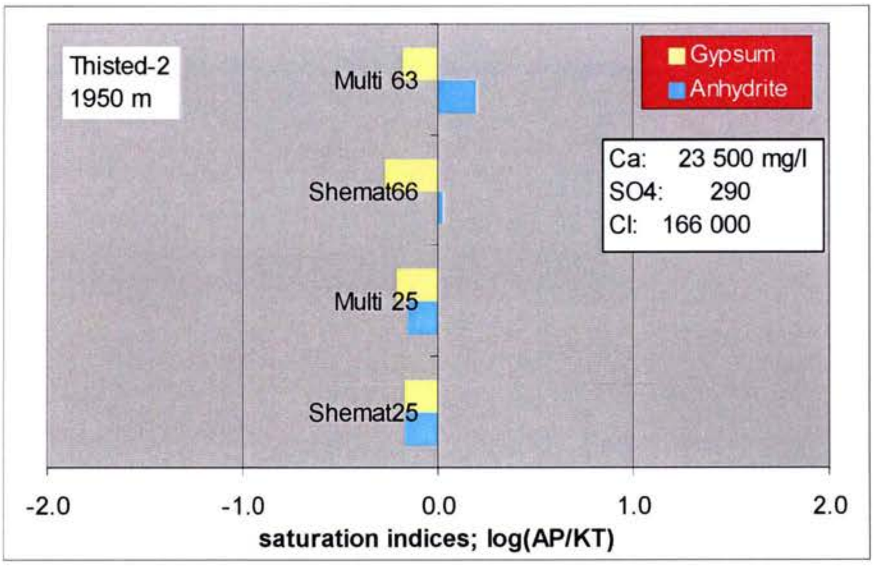


Fig. 10. Saturation indices calculated for four salts of sulphate. Bottom Hole Sample 815183.

Table 5. Saturation indices of Zone B, 1860 m, formation water. Bottom Hole Sample 815183

ID	Anhydrite	Gypsum	Barite	Celestite	temp	Model type
Multi10	-1.509	-1.301	0.679	-0.851	10	Multiscale
Shemat10	-1.479	-1.216	0.840	-0.900		Shemat
Multi 63	-0.879	-1.155	0.098	-0.654	63	Multiscale
Shemat63	-1.049	-1.225	0.086	-0.868		Shemat

Danish well Thisted-2 – another example of barite super saturation



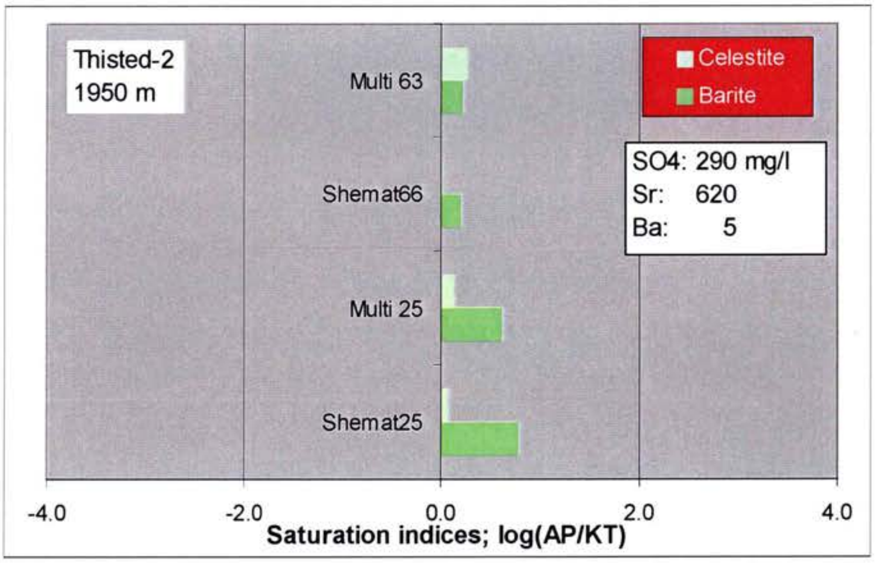


Fig. 11. Saturation indices calculated for four salts of sulphate. Thisted-2 formation water sampled during production testing (10 m^3/h) of the Skagerrak Fm. (1950 m) May-June 1982.

Table 6. Saturation indices of Thisted-2, Skagerrak Formation water 1950 m.

ID	Anhydrite	Gypsum	Barite	Celestite	Temp.	Model type
Shemat25	-0.168	-0.166	0.786	0.066	25	Shemat
Multi 25	-0.148	-0.204	0.605	0.120	25	MultiScale
Shemat66	0.024	-0.269	0.198	0.022	66	Shemat
Multi 63	0.198	-0.177	0.213	0.261	63	MultiScale

From the calculations presented in the figures and tables in this chapter precipitation of barite appear to be the most serious problem with respect to scaling. As the amount of barium and sulphate in the formation water is low large amount of barite is however, not expected to precipitate, Table 2. The calculation of saturation indices for the formation water obtained from a Danish geothermal well near the city of Thisted (Fig. 2) also indicate super saturation with respect to barite (Fig. 11; Table 6). However, no sign of barite deposits were observed in the small geothermal pilot plant that had been sat up to study problems of scaling during long term testing of the Triassic sandstone of the Skagerrak Formation in this well (Laier, 1982a). Thus, indication of super saturation with respect to barite, does not imply that barite will actually start to precipitate in the geothermal plant of Malmö. Slow rate of precipitation may prevent barite from precipitation at all in the geothermal plant, as will be explained in the next chapter.

Slow precipitation kinetics minimise the risk of scaling in case of supersaturation

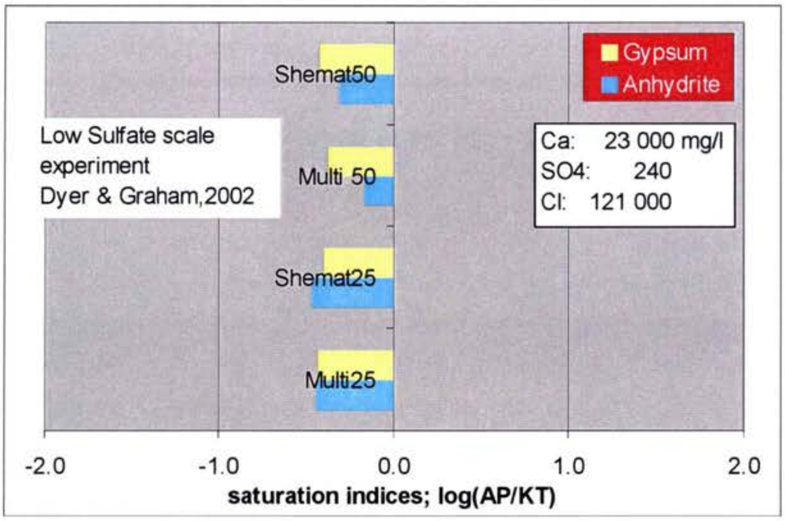
Problems with scaling are often encountered by the oil industry during enhanced oil recovery. Injecting fluid into an oil reservoir in order to improve recovery causes mixing of fluids that may be incompatible i.e. precipitation of various minerals may occur. If sea water is injected, which is often the case, precipitation of sulphate minerals are likely to occur, because sulphate concentration in sea water is high (ca. 2800 mg/l) compared to most oil field waters (< 5 mg/l). Formation water on the other hand is normally highly enriched in calcium, strontium and barium relative to sea water. In order to minimise problems with scaling several laboratory experiments have been carried out mixing sea water with various types of formation waters.

Dyer and Graham (2002) carried out several experiments in order to determine which commercial scale-inhibitors were the most suitable in preventing scaling caused by barite. They also determined how much of a particular inhibitor should be added in order to avoid scaling. The two researchers observed that barite first started to precipitate when the mixed waters became very supersaturated with respect to barite. Furthermore, the rate of precipitation of barite from highly supersaturated (100x) solutions was so slow that the mixed solutions remained supersaturated (70x) even after 22 hours. Experiments on temperature dependence of the precipitation rate of barite indicated a clear decrease in rate with decreasing temperature.

Comparing saturation indices for the ”least supersaturated ” mixed solutions studied by Dyer and Graham (2002) (Table 7; Fig. 12) with those for the Malmö geothermal water Figs. 8 – 10, it is obvious that super saturation due to cooling of the geothermal water is far less than for the mixed laboratory fluids. Thus, due to the slow kinetics of barium sulphate precipitation, no scaling due to barite formation is expected to occur, even if the geothermal water should become a little supersaturated due to cooling.

Table 7. Saturation indices for sulphate minerals. Low sulphate scaling test (Dyer and Graham, 2002).

ID	Anhydrite	Gypsum	Barite	Celestite	temp	Model type
Multi25	-0.445	-0.426	2.263	-0.194	25	Multiscale
Shemat25	-0.465	-0.391	2.389	-0.189		Shemat
Multi50	-0.165	-0.368	1.997	-0.092	50	Multiscale
Shemat50	-0.306	-0.416	2.033	-0.184		Shemat



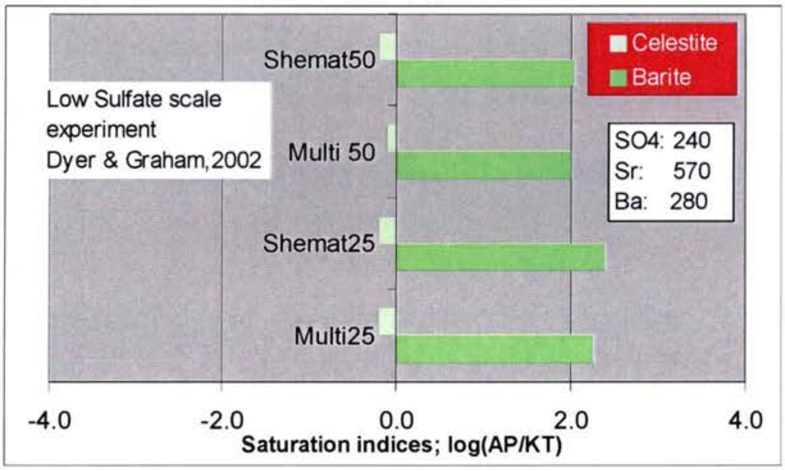


Fig. 12. Saturation indices for four sulphate-minerals. Low sulphate scaling test of Dyer and Graham (2002)

Suspended particles in formation water

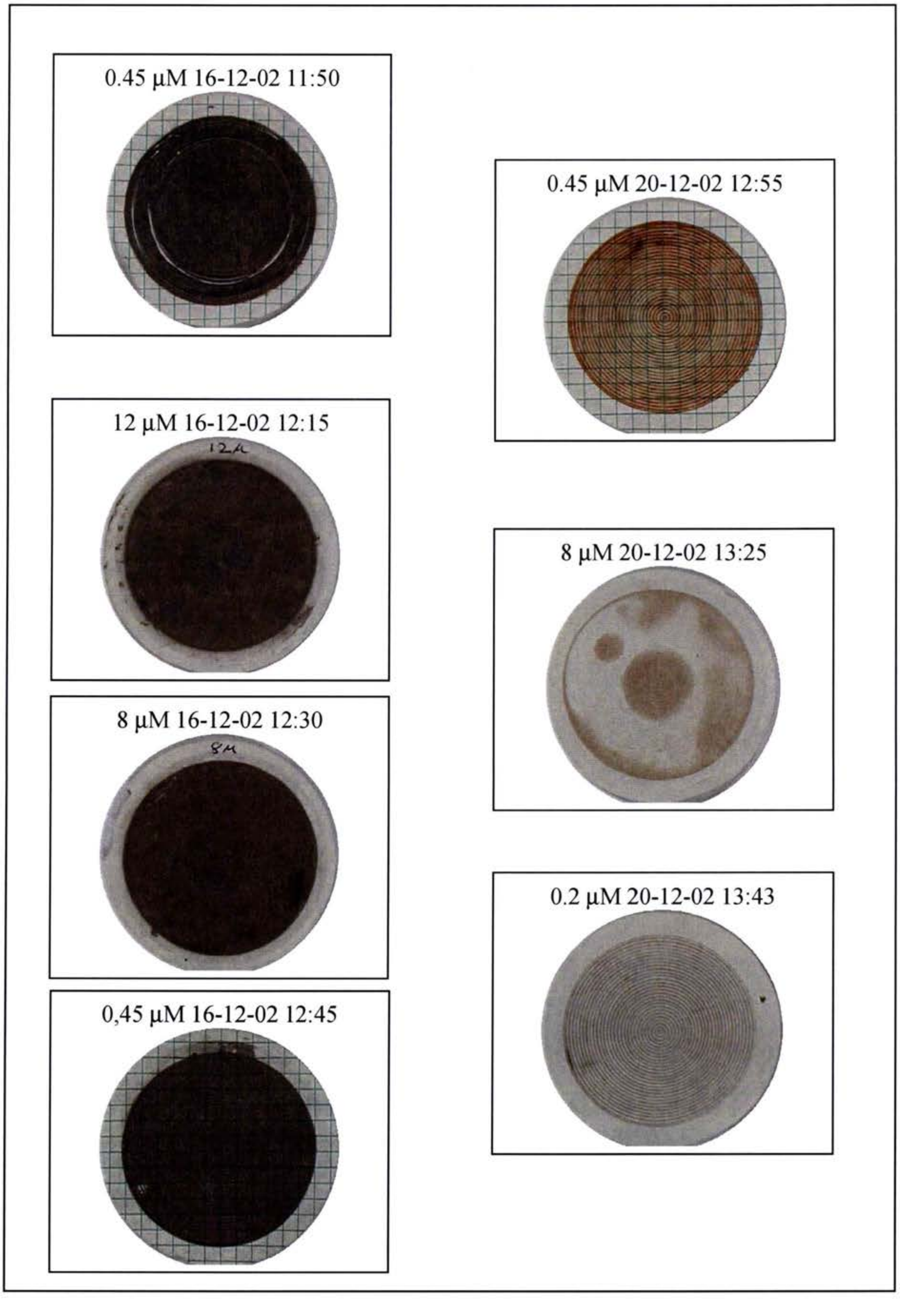
The amount of suspended matter in the formation water was determined by filtration on two occasions. During the production test of zone A, 1610 m, part of the water was conducted through 50 mm diameter filters with different pore sizes 0.2 to 12 µm. The volume of water filtered varied from 6 to 20 litres depending on the amount of suspended particles in the water. After filtration the filters were gently flushed with pure water in order to remove formation water, to avoid precipitation of salts. Subsequently, the filters were dried at 60 °C for 5 hours, and finally weighed. Subtracting the weight of the filter itself the amount of solids on the filter was determined, and thus the concentration of particles in the formation water (Table 8).

Table 8. Concentration of particles in formation water determined by filtration.

date	time	**filter size µm**	filter paper weight; mg	plus particles; mg	particles; mg	volume water; L	**mg/l**
16-12-02	11.15	*start of pump, pumping rate = 130m^3/h*					
	11.50-12.10	**0.45**	79.1	99.5	20.4	8	**2.6**
	12.15-12.25	**12**	77.2	114.5	37.3	12	**3.1**
	12.30-12.40	**8**	71.1	92	20.9	10	**2.1**
	12.45-13.05	**0.45**	78.6	92.5	13.9	6	**2.3**
19-12-02	13.00	*start of pump, pumping rate = 130m^3/h*					
20-12-02	12.55-13.20	**0.45**	78.1	84.9	6.8	20	**0.3**
	13.25-13.39	**8**	70.6	77.7	7.1	20	**0.4**
	13.43-14.05	**0.2**	98.3	106.2	7.9	20	**0.4**

The concentration of suspended particles was ten times higher during the first time filtration was performed compared to the second time. This is most likely due to the fact that first filtration was performed only one hour after the production test had started (Table 8). The second time filtration was done, the pump had been working continuously for more than 24 hours. Previous experience with this type of measurements showed repeatedly fairly high concentration of suspended particles shortly after the pump had been switched on (Laier, 1982b)

The amounts of reddish brown solids (most likely iron oxide due to corrison) appear to be higher on the first filter compared to the two latter ones of the second set of filters (Figs. 13 and 14). This may be due to the fact the valve to which the filtration unit was attached had not been thoroughly flushed before the first filtration was performed. Thus, any material that may have collected around the valve connection to the tubing (during the production test) was mobilised at the start of filtration and transferred to first filter.



0.45 µM 16-12-02 11:50

12 µM 16-12-02 12:15

8 µM 16-12-02 12:30

0,45 µM 16-12-02 12:45

0.45 µM 20-12-02 12:55

8 µM 20-12-02 13:25

0.2 µM 20-12-02 13:43

Fig. 13 Filters, 50 mm diameter, used to determine the concentration of suspended particles.

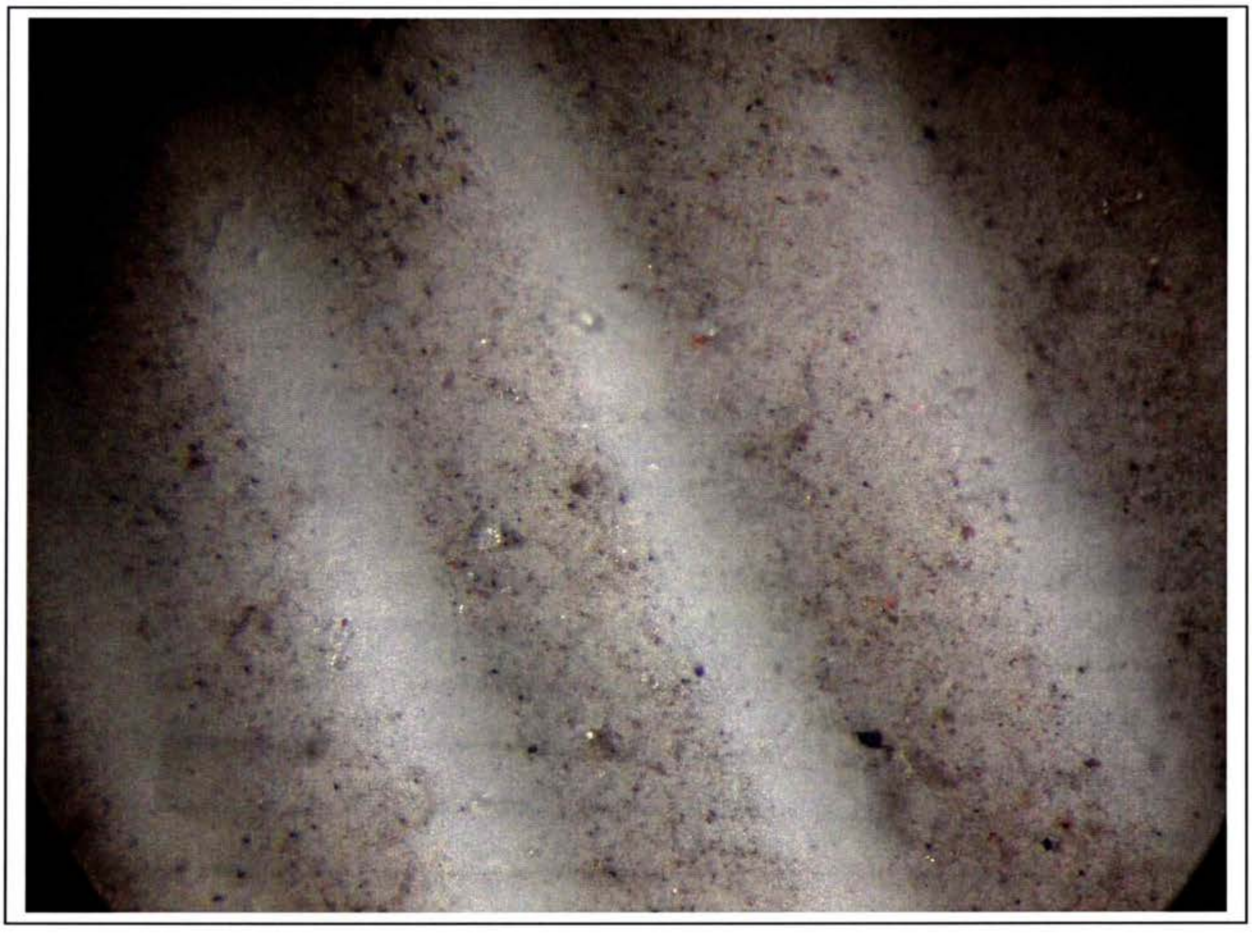


Fig. 14. Suspended particles collected on filter papers, Upper = 0.45 µm filter of 20-12-02, lower = 0.2 µm filter of 20-12-02. Area covered by photo equals 3x2 mm^2

The amount of suspended particles in the formation water of Zone A of the Malmö FFC-01 well is of the same order of magnitude as observed for Danish formation waters (Laier, 1982b), including the one exploited in the Thisted plant, which has been in operation for approximately ten years. Thus, no special treatment of the FFC-01 formation water appear to be needed, other than the general precautions taken for re-injection as observed by similar geothermal plants e.g. Thisted.

The suspended matter examined by filtration is limited to that fraction of solids that are brought to surface (well head) during the production test. Larger particles produced from the formation during the production test, may however collect on the bottom of the well and therefore not be detected by filtration. After the test, well logging did not indicate a reduction of well depth, Appendix 1. Therefore it can be assumed that the amount of solids produced from the formation is insignificant.

Solids in a Bailer sample collected after the production test consisted of corrosion products (80%) and formation material (20%) mostly quartz (Appendix 1).

Conclusions

Results of calculation of saturation indices for various salts indicate that super saturation will only occur with respect barite when the temperature of the formation water decreases. The super saturation is, however, minor compared to that of laboratory mixtures from which barite hardly precipitated even after 22 hours. Thus, it is concluded that no precipitate will form during geothermal heat production exploiting the formation waters of the Malmö FFC-01 well.

The concentration of suspended particles measured in the formation water during a production test of Zone A is low, in the order of 0.3 mg/l. Therefore no special treatment of the fluid should be necessary, other than the normal precaution taken for re-injection of a geothermal fluid.

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