Preliminary Investigations of Scaling and Corrosion Characteristics of High Enthalpy Geothermal Wells in Hungary

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Abstract

A solubility equilibrium program GEOPROF developed earlier was applied for the determination of the bubble point depth, pressure and temperature as well as the partial pressure profiles of the gases CO_2, CH_4 and N_2 between the bubble point depth and the well head in two high enthalpy geothermal wells NSZ-2 and FAB-4. Additionally the pH, the alkalinity the total carbonate, the equilibrium solubility for $CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$ along the well depths in Na-K-Mg-Ca-H-Ba-Sr-Cl-Br-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system were determined and the concentrations of the Ca^{2+}, Ba^{2+},Sr^{2+},H^+, OH^-, HCO_3^-, CO_3^{2-}, and the $H_2CO_3^*$ were computed at the actual temperature, CO_2 pressure using the Davies and the Pitzer activity calculation methods. The calculated amounts of scaling $CaCO_3$ along the wells and at the surface were used in the estimation of the suggested service life. The results for the well FAB-4 have high uncertainties because of the estimated gas separation analysis data.

Keywords

Scaling and corrosion, calcite precipitates; Hungarian high enthalpy geothermal well, modelling, concentration and gas pressure profile along the well

Introduction

Natural hot thermal or geothermal water or steam are saturated with silica and frequently close to saturation with calcite, calcium sulphate and calcium fluoride. Some acid hot water also contain appreciable concentration of heavy metals. Changes in temperature and pressure disturb the equilibria and will generally lead to scale formation. Calcite and silica deposits are the most frequent scale formation materials. The most troublesome calcite deposits usually occur in the well casing at the level of first boiling (the bubble point) with heavy band of calcite being deposited over a short length. Upward it tapers of to become minor or zero.

The prediction of scaling and the description of the location and shape of scale during production is an important process. Marshall and Reed[1] calculated saturation index for calcite from the reconstructed reservoir water composition and used a thermodynamic calculation for the description of calcium carbonate scaling at Dixie Valley geothermal field. Benoit[2] and Mercado[3] investigated the carbonate scaling characteristics and scale incidence on production pipes with field experiments

It is well known that Hungary has one of the biggest resource in the world of low enthalpy hot water, although there are several higher enthalpy wells also in the country, among others the wells in South-Hungary Nagyszénás-3 (NSZ-3) and Fábiásnsebestyén-4 (FAB-4). This type of energy should be used in the near future and the possible scaling during their production should be preliminary estimated via modelling and measuring processes. A map of Hungary with the location of the NSZ-3 and FAB-5 geothermal wells is shown in Fig. 1.

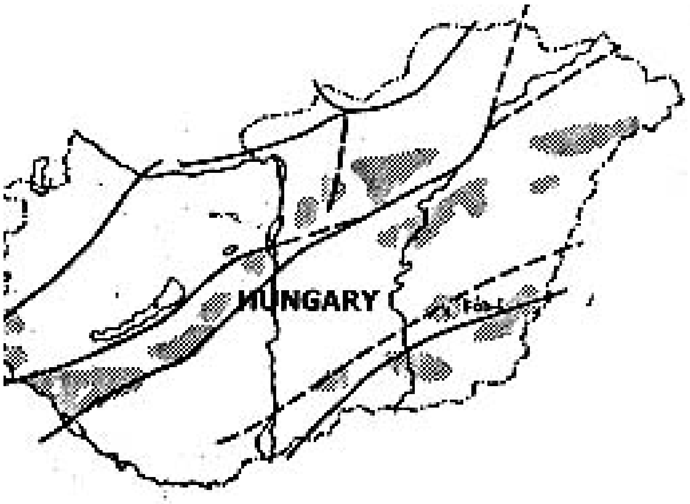

Fig.1 Hungarian high enthalpy wells

Two small-medium size geothermal projects are planned in this field. According to the chemical analysis data of the earlier collected scales, in these wells the scaling are due mainly to calcite precipitation. A suitable description and modelling of these rather complicated scaling processes during the future production along the wells and at the surface is of economic importance.

Scaling and scaling profiles

- **Scales: carbonates (calcite, aragonite, vaterite), silica (amorf or non-amorf silica), sulfate (calcium-sulfate, barite, anhydride), sulfide (Pb, Zn, Fe, Cu)**
- **Scaling processes:**
  -Boiling after the bubble point in the well, separator or two phase fluid flow in the pipes-MOST IMPORTANT!
  -Scaling from the water drops from the steam in the separator, turbine or pipe.
  -Scaling during recharge from the single phase fluid.
- **Scaling after boiling:**
  -Concentration is increasing through the evaporation.
  -By the expansion the temperature will drop and the solubility will decrease.
  -Debubbling of the dissolved gases (CO_2, H_2S) will increase the pH and decrease the solubility.
  -The higher the salt content and the lower the temperature of the fluid, the higher is the supersaturation after the bubble point .
  -At high temperatures the evaporated steam causes the cooling of the fluid, and the solubility will increase, small crystalline particles could dissolve again.

-The calcite scaling kinetics is not well explained, we know that the velocity is higher at higher supersaturation and at the higher temperature

- **$CaCO_3$ scaling:**
  -Above 310 ^{0}C no calcite, above 270 ^{0}C no aragonite scaling, vaterite scaling is very rare.
  -At the bubble point two phases are generated, the steam(vapor) phase contains small amount (~1%) of water, main components are CH_4, CO_2, N_2, H_2S.
  -$CaCO_3$-CO_2-H_2O equilibrium is very important, first the slightly soluble, non condensable gases (CH_4, N_2) segregate more intensively, CO_2 will escape later at smaller pressures.
  -The solubility of the CO_2 at 160-180 ^{0}C is the smallest, boiling in these temperature range causes the highest calcite scaling.
  -The CO_2 escape increases the pH and the amount of the carbonate ions.
- **The starting position of scaling in the well**
  -At adiabatic boiling the scaling usually starts at 20-40 ^{0}C lower then the bubble point temperature
  -The higher the salt content and the lower the temperature of the fluid, the higher is the supersaturation after the bubble point .
  -At high temperatures the evaporated steam causes the cooling of the fluid, and the solubility will increase, small crystalline particles could be dissolved again.
  at the highest supersaturation and at the highest temperature.
- **The length of scale and other characteristics of scaling in practice**
  -Scaling in several US wells [2,3] caused 1,69-2,9 cm thick scale causing 45% cross section reduction without flow problem at the well head.
  -During the well production the bubble point could move down- and upward, the path is very often sevaral 100 m long.
  -Calipering the scales in these wells, scaling were nearly uniform (±3 mm), and followed the roughness of the pipe walls, the yellow-brown scale contained 100% calcite with a density of 2,67 g/cm^3.
  -At 7 investigated wells during well production the boiling (bubble) point moved between 0-300 m, the scaling lenght were between 290-500 m. Because the quick precipitation the scales contained impurities (Mg, Fe, Ti, Ba, Sr)
  -In wells having changing cross sections the scaling started often near the cross section change.
  -There was no direct functional relationship between the volume of the produced water and the mass of the precipitated scale.
  -The amount of scale depended on the pH, bicarbonate, carbonate, calcium ions and on CO_2 content, but the critical parameter was the calcium ion content.
  -Using the measured volume of the scales and using 2,67 g/cm^3 scale density the Ca content of the fluid before scaling were 3,54-12,89 mg/dm^3 and 2,93-11,6 mg/dm^3 calcium precipitated as scale, so 0,6-1,3 mg/dm3 calcium remained in dissolved form.
  -The thickness of the scales depended on the length of the supersaturated region, shorter supersaturated region (no change in the boiling depth) caused thicker and shorter (180-250 m) scale. At changing depth of boiling and at higher velocities the scale was longer and thinner (see Figure 2.[3]).

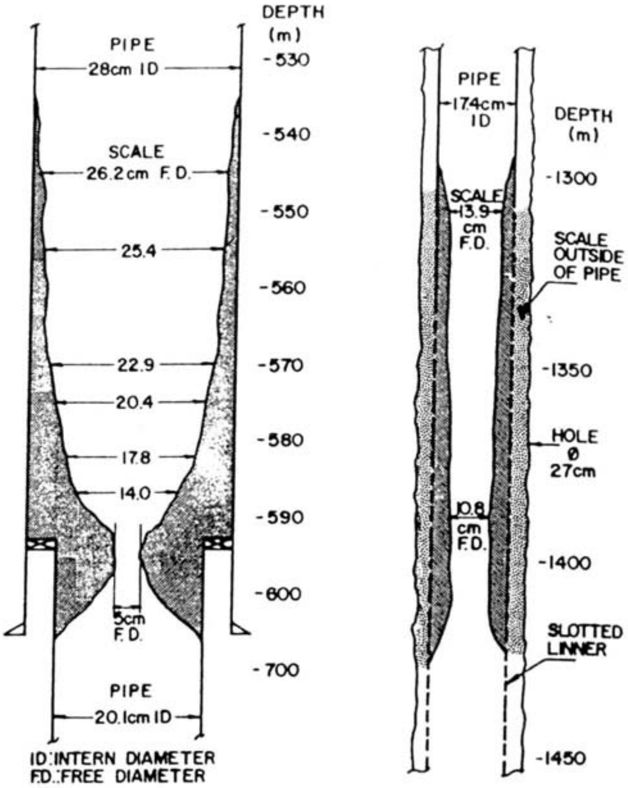

Fig.2 Typical scale profiles

-0,69 bar well head pressure change caused about 60 m change in the boiling depth. the change in the well head pressure caused the change of the depth of the bubble point so the changing well head pressure determines the length of scaling.

-The length of scale shows the length of intensive CO_2 debubbling and the length while precipitation particles reached the wall of the well.

-In wells where the inflow part of the well is covered by scale the regulation by changing well head pressure will not affect the bubble point depth.

-In wells with uniform diameter (22,4 cm) the production was limited by the maximal allowed scale thickness.

-In other wells the 25,5 cm and 31,5 cm diameter pipes narrowed at depth 992-1151 m to 22,4 cm and if the bubble points were shifted into the narrower region quicker scaling occured and more frequent cleaning was needed.

-A functional relationship was found between the deepest final bubble point depth of the smallest well head pressure and the lower end of the scale.

-The following Figure 3.[2] shows the normalized scale profiles of 7 US wells.

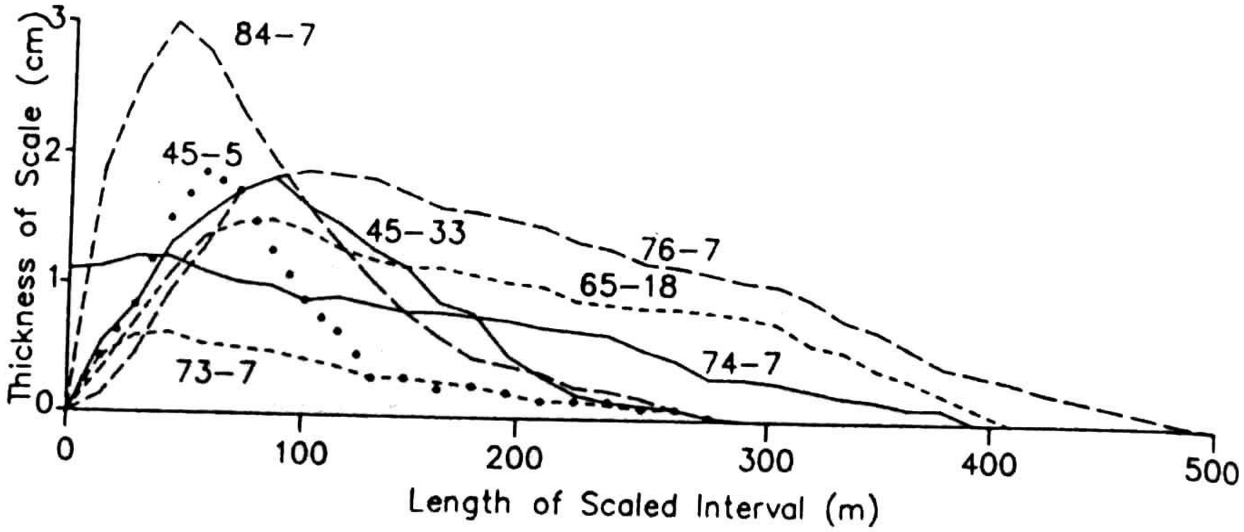

Figure 3. The normalized scale profiles in 7 US wells

-The scale was developed first on a 147-317 m long surface, the 84-7 and 45-5 labeled scaling was detected in wells 45-60 m above the relative constant bubble point depth. Decreasing well head pressure (deeper bubble point depth) caused longer and thinner scale profiles(76-7).

-The cross section of the well is an important parameter, affecting the velocity of scaling. Increasing the diameter the pipe surface area/fluid volume ratio decreases. Cleaning was necessary after 65-70% cross section reduction. The bigger was the cross section of the well, the longer was the service period before cleaning.

- Inhibition or diminishing the scaling and scale removal

  -In low enthalpy wells the scaling could be diminished through limitation of degassing and pH shift

  -In high-enthalpy wells boiling could not be avoided, precipitated scale could be removed from the surfaces by chemical and/or mechanical methods.

  -Using chemical inhibitors scaling will not eliminated only the scaling process will slow down. Inhibitor overdose could cause „pseudo" scale generation, optimal inhibitor concentration is about several hundred ppm (see Figure 4[4].).

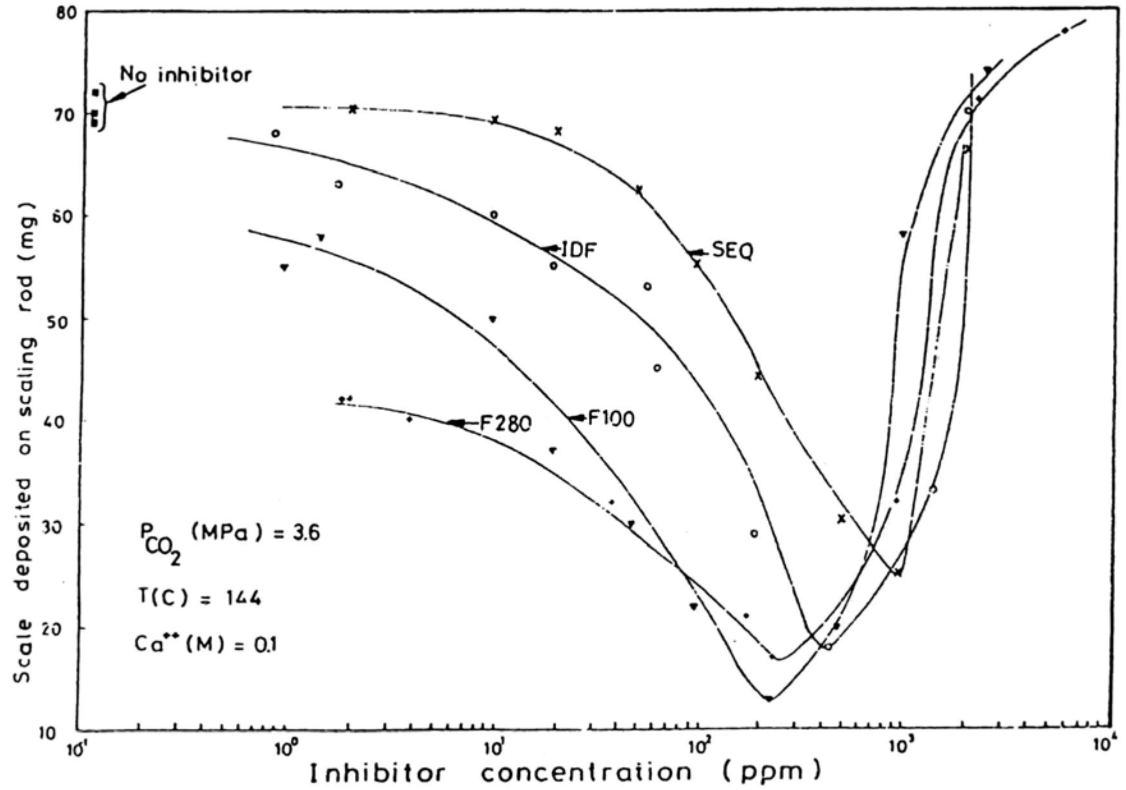

Figure 4. Scaling and inhibitor concentration

-Generally the scaling could be diminished by increasing the well head pressure if the scaling area is shifted into wider cross section. Scales at moderate depth could be removed mechanically and /or chemically.

Modeling of scaling with the GEOPROF code

Computer-assisted calculations are finding increased use in the prediction of scaling and corrosion Haarberg[5], Plummer and Busenberg[6], Harvie et al.[7], Shiraki and Brantley[8], Arakaki and Mucci[9]. A great advantage is the ability to simulate the effects of changes in brine variables, such as temperature, pH and composition, and the probable result on scaling and corrosion. In our earlier research Pátzay et al.[10] we developed a simulating tool, a computer program GEOPROF to describe these processes, the equilibrium solubility and the scaling of calcite and the other important scaling components and the determination of the bubble point and the partial pressures of gases.

We have developed a 15 component equilibrium modelling algorithm and program by simplification and modification of the Haarberg model [10] to describe the equilibrium solubility of calcium carbonate, calcium sulphate, barium sulphate and strontium sulphate in thermal water system under various carbon dioxide pressure, temperature and concentration of the 15 components. For the Na-K-Mg-Ca-H-Ba-Sr-Cl-Br-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system the model is based on the solution of the following set of equations:

- material balances
- elctroneutrality balances

- phase equilibria equations
- reaction equilibria equations

We used the strategy in solving the given equilibrium problem developed by Haarberg[5]. The resulting non-linear equations can then be solved for hydrogen and bicarbonate molality by a regular Newton-Raphson solver in two variables using iteration.

In addition to determination of equilibrium solubilities, we calculated the initial and the equilibrium pH values and determined the Langelier and Ryznar saturation indexes. For industrial water, concentrations of specific species must be kept at a level that is slightly scale-producing. A slightly scale-producing condition results in a thin, self-healing layer of oxidized metal and calcium carbonate that inhibits corrosion. For this condition to be met, the Ryznar index must be kept at 6.5±0.3 and the Langelier indexes must range from 0 to 0.5.

In addition we have developed a model and program to determine the bubble point and the partial pressures of gases between the bubble point depth and the well head in thermal and geothermal well. As hot water rises toward the surface the pressure imposed on it by overlying fluid decreases. Eventually it reaches a level at which a vapour phase separates and migrates to the surface independently - i.e. boiling occurs. This pressure is called the bubble point pressure and the depth where the first boiling occurs the bubble point depth. When steam separates from a liquid during boiling, gases like H_2, N_2, CH_4 move preferentially into the vapour phase. The more soluble gases (CO_2, H_2S, NH_3) are partially retained in the residual liquid. It is possible to calculate gas concentrations in both vapour and liquid phases resulting from such process. From the calcite dissolution equations (for a $CaCO_3$-CO_2-H_2O system) it is quite clear that removal of CO_2 to a steam phase during flashing leads to calcite supersaturation even though the accompanying temperature drop itself leads to calcite saturation increase. Since most reservoir fluids are close to saturation with calcite, carbonate scaling inside the well above the bubble point depth and inside production casing is a possibility for all geothermal wells. The solubility of calcium carbonate minerals in aqueous solution at any particular temperature increases with increasing partial pressure of CO_2. Boiling leads to strong reduction in CO_2 partial pressure due to effective transfer of CO_2 into the steam phase. The presence of other gases in the geothermal fluid, especially if less soluble in water then CO_2 will enhance degassing of the CO_2 during boiling.

In our simulation model we modified the Kocsis method [11] for the determination of the bubble point pressure and depth and developed a computation algorithm for the determination of the H_2, N_2, CH_4 partial pressures between the bubble point depth and the well head . The method is based on the assumption that in the pressure range of the usual bubble point the sum of the chemical activity of the components in the liquid phase equals one.

The computation is started after the input of the gas separation and chemical analysis data with the determination of the bubble point. The concentrations (activities) of the volatile and non-volatile dissolved components could be computed at this depth using the surface analysis data and the steam fraction Decreasing the total pressure by sufficiently small value ($\Delta p<0.1$ bar), using the new total pressure we can determine the new smaller depth closer to the well head.

Using at the new depth the computed partial gas pressures the new equilibrium solubilities could be computed for the dissolved components and possible precipitations and/or dissolutions are determined. At smaller pressures and depths the dissolved gases start to debubble, the volume of the gas phase increases till reaching the well head pressure.

Results

Modelling results for wells NSZ-3 and FAB-4

Well NSz-3

The average water and gas analysis input data are given as follows:

Input parameter	Value	Unit
Well depth	3165.0	m
Water flow rate	1313.4	dm^3/min
Water temperature	171.0	^oC
TDS	24855.0	mg/dm^3
Gas flow rate	6986.1.0	dm^3/min
Gas temperature	171.0	^oC
Wellhead pressure	45.0	Bar
Separated GWR	1700.0 CO_2 16.270 vol%, CH_4 79.440 vol% N_2 4.290 vol%	Ndm^3/m^3
Dissolved GWR	3400.0 CO_2 35.250 vol%, CH_4 61.910 vol% N_2 2.840 vol%	Ndm^3/m^3
Water composition	Ca^{2+} $1.335.10^{-3}$ Mg^{2+} $3.350.10^{-4}$ Na^{2+} $3.453.10^{-1}$ SO_4^{2-} $2.380.10^{-4}$ Cl^- $3.179.10^{-1}$ A_{TOT} $2.600.10^{-2}$	mol/kg mol/kg mol/kg mol/kg mol/kg mol/kg

The water contained high TDS with high chloride content including sodium-chloride, and small amount of calcium- and sodium-bicarbonate, sodium-sulphate, without calcium-sulphate and calcium-chloride. The analysed scale samples basically contained calcium-carbonate with trace impurities. The separated gas phase contained approximately 80% methane, 16% carbon-dioxide and 4% nitrogen, the mean gas-water-ratio was 5.1 Nm^3/m^3. The planned well head pressure was 45 bar, the temperature 171 ^0C, the water flow rate was 1313.4 dm^3/min, the gas flow rate 6896.1 Ndm^3/min. The program used the experimental pressure-depth and temperature-depth profiles instead of the gradients.

The computed bubble point pressure was 230.278 bar, the depth 1079.3 m and the temperature 175.129 ^0C. At the bubble point the fluid has a pH 5.762 and the partial pressures of the gas components: p_{CO2}=12.66 bar, p_{CH4}=191.0 bar, p_{N2}=17.7 bar, p_{H2O}=8.93 bar. The fluid was supersaturated (SR_{CaCO3}=2.341) and a precipitation was expected above the bubble point depth ($6.248.10^{-4}$ g $CaCO_3$/kg fluid). According to our estimation a 1 cm thick (average value) scale on a 100 m pipe length will developed at a 226800 kg/h production during a 390 day service period, which is a good parameter.

We estimated also the expected scaling at the surface at atmospheric pressure. The computed mass of scale at the surface at 226800 kg/h production was 5.216 kg $CaCO_3$/h. The computed equilibrium pH values along the well are shown in Figure 5.

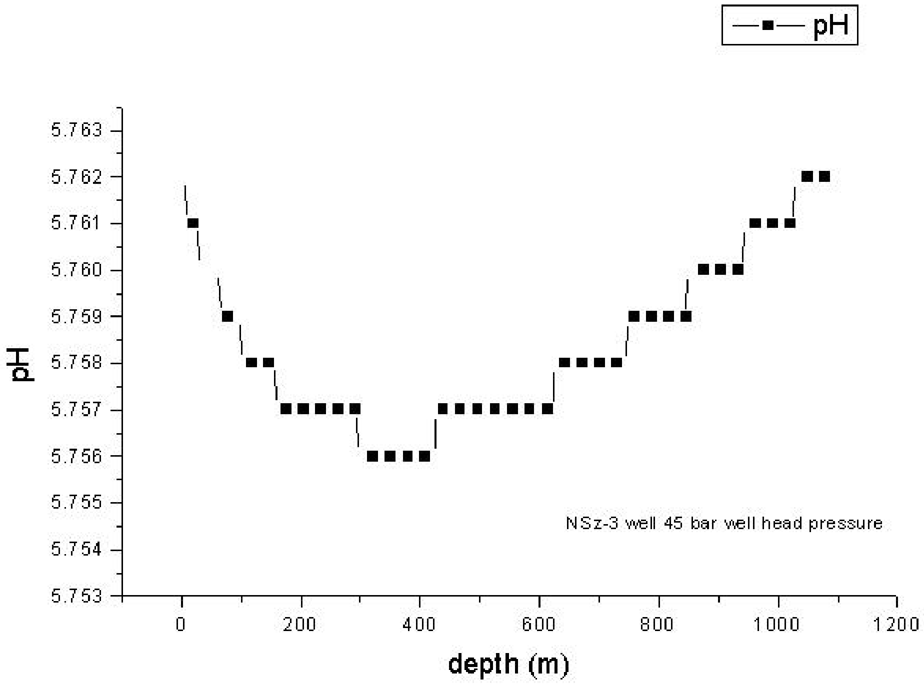

Fig.5 The pH-depth curve in well NSz-3

Well FAB-4

The average water and gas analysis input data are given as follows:

Input parameter	Value	Unit
Well depth	4239.0	m
Water flow rate	3750.7	dm^3/min
Water temperature	180.0	^oC
TDS	27200.0	mg/dm^3
Gas flow rate	46500.0	dm^3/min
Gas temperature	180.0	^oC
Wellhead pressure	40.0	Bar
Separated GWR	4400.0 CO_2 76.714 vol%, CH_4 20.899 vol% N_2 2.566 vol%	Ndm^3/m^3
Dissolved GWR	8000.0 CO_2 89.300 vol%, CH_4 7.824 vol% N_2 3.876 vol%	Ndm^3/m^3
Water composition	Ca^{2+} $3.081.10^{-3}$ Mg^{2+} $4.540.10^{-4}$ Na^{2+} $4.284.10^{-1}$ SO_4^{2-} $2.380.10^{-4}$ Cl^- $4.684.10^{-1}$ A_{TOT} $1.009.10^{-2}$	mol/kg mol/kg mol/kg mol/kg mol/kg mol/kg

The water contained high TDS with high chloride content including sodium-chloride, and small amount of calcium- and sodium-bicarbonate, sodium-sulphate, without calcium-sulphate and calcium-chloride. The analysed scale samples basically contained calcium-carbonate with trace impurities. The separated gas phase contained approximately 2.70% methane, 76.7% carbon-dioxide and 2.7% nitrogen, the mean gas-water-ratio was estimated 12.4 Nm^3/m^3 (no measured value was available). The planned well head pressure was 40 bar, the temperature 171 ^0C, the water flow rate was 1313.4 dm^3/min, the gas flow rate 46500 Ndm^3/min. The program used the experimental pressure-depth and temperature-depth profiles.

The computed bubble point pressure was 220.8 bar, the depth 1067.3 m and the temperature 179.5 ^0C. At the bubble point the fluid has a pH 4.619 and the partial pressures of the gas components: p_{CO2}=87.61 bar, p_{CH4}=84.36 bar, p_{N2}=35.18 bar, p_{H2O}=9.776 bar. The fluid was heavily supersaturated (SR_{CaCO3}=221.3) and a precipitation was expected above the bubble point depth ($4.944.10^{-3}$ g $CaCO_3$/kg fluid). According to our estimation a 1cm thick (average value) scale on a 100 m pipe length will developed at a 225036 kg/h production during a 58 day service period, which is an acceptable, but not very good parameter.

We estimated also the expected scaling at the surface at atmospheric pressure. The computed mass of scale at the surface at 225036 kg/h production was 109.8 kg $CaCO_3$/h, which is a huge amount.

The computed equilibrium pH values along the well are shown in Figure 6,

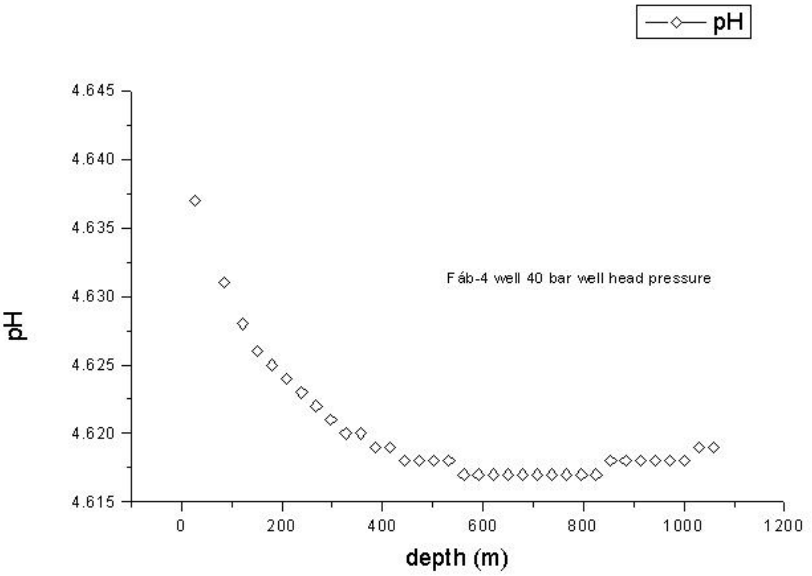

Fig. 6. The pH-depth curve in well FAB-4

Conclusion

A solubility equilibrium program GEOPROF, developed earlier was applied for the determination of the bubble point parameters and the multicomponent equilibrium characteristics of two Hungarian high-enthalpy geothermal wells. Scaling characteristics along the well as well as at the surface was estimated and it was concluded that in the NSz-3 well the scaling intensity is lower then in FAB-4 well. Because the intensity of scaling at surface conditions it is recommended to keep the production at well head pressure not lower then 40 bar, especially in the case of the FAB-4 well, and reinject the exhausted geothermal water back into the reservoir.

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