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PRELIMINARY INVESTIGATIONS OF SCALING AND CORROSION CHARACTERISTICS OF HIGH ENTHALPY GEOTHERMAL WELLS IN HUNGARY

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SUMMARY – A solubility equilibrium program GEOPROF developed earlier was applied for the determination of the bubble point depth, pressure and temperature, plus 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. In addition, the program also determined pH, alkalinity, total carbonate, equilibrium solubilities 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. The concentrations of Ca^{2+}, Ba^{2+}, Sr^{2+}, H^+, OH-, HCO_3^-, CO_3^{2-}, and $H_2CO_3^*$ were computed at the actual temperature and CO_2 pressure, using the Davies and the Pitzer activity calculation methods. The calculated amounts of $CaCO_3$ scaling along the wells and at the surface were used to estimate and suggest a service life of the system. The results from well FAB-4 have high uncertainties because of the estimated gas separation analysis data.

1. INTRODUCTION

Natural geothermal waters are often saturated with silica and fiequently also close to saturation with calcite, calcium sulphate and calcium fluoride. Some acid hot waters 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 scaling 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 distance. Upward, it tapers of to become minor or zero.

The prediction of scaling and their location and shape during production is an important process. Marshall and Reed (1989) calculated saturation index for calcite from the reconstructed reservoir water composition and used a thermodynamic calculation to describe calcium carbonate scaling at Dixie Valley geothermal field. Benoit (1989) and Mercado (1989) investigated the carbonate scaling characteristics and scale incidence on production pipes during some field experiments

It is well known that Hungary has one of the largest low enthalpy thermal water resources in the world. Several higher enthalpy wells also exist in the country, including two wells in South-Hungary Nagyszénás-3 (NSZ-3) and Fabiasnsebestyen-4 (FAB-4). This type of energy resources should be used in the near future. Therefore, it is important that a preliminary investigations of the possible scaling problem during their production be conducted via modelling and measuring processes.

A map of Hungary showing the location of FAB-4 geothermal well is presented in Fig. 1. Two small-medium size geothermal projects are planned in this field. Earlier chemical analysis of scales from FAB-4 and NSZ-3 show that they are mainly calcite precipitates. A suitable description and modelling of these scaling processes along the wells and at the surface during future production is of economic importance.

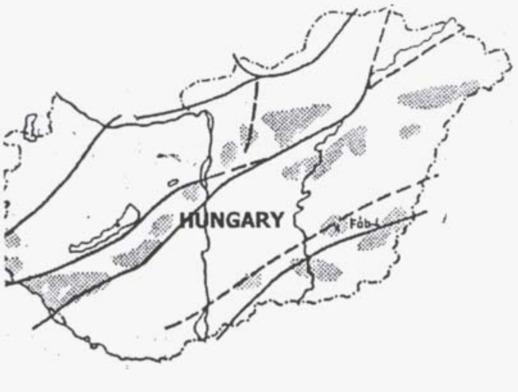

Fig.1 Location map of FB-4

Computer-assisted calculations are commonly used in the prediction of scaling and corrosions (Haarberg, 1989; Plummer and Busenberg, 1982; Harvie et al., 1984; Shiraki and Brantley, 1995; Arakaki and Mucci, 1995). A great advantage of such calculations is their ability to simulate the effects of changes in brine variables, such as temperature, pH and composition, and the probable result on scaling and corrosions. In our earlier research (Pátzay et al; 1997) we developed the computer program GEOPROF to describe these processes, which include the equilibrium solubility and the scaling of calcite and other important scaling components, and the determination of the bubble point and partial pressures of gases.

2. THE MODEL

We have developed a 15-component equilibrium modelling algorithm and program by simplification and modification of the Haarberg model (Haarberg; 1989) 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 each 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 of solving the given equilibrium problem developed by Haarberg (1989). 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. 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, N2, 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 C02 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 is possible inside the geothermal well above the bubble point depth and within the production casing. 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 they are 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 (Kocsis, 1976) 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) and 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 bubbles of dissolved gases starting to collapse, the volume of the gas phase increases until the well head pressure is reached.

3. MODELLING RESULTS FOR WELLS NSz-3 AND FAR4

3.1 Well NSz-3

The average water and gas analysis input data from this well are given in Table 1.

The water contained high TDS with high chloride content including sodium-chloride, and small amount of calcium- and sodium-bicarbonate, sodium-sulphate, but 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 ^{0}C, 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.

The computed bubble point pressure was 230.278 bar, the depth 1079.3 m and the temperature 175.129 ^{0}C. At the bubble point the fluid has a pH 5.762 and the partial pressures of the gas components are: 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 lcm 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 also estimated the 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 2.

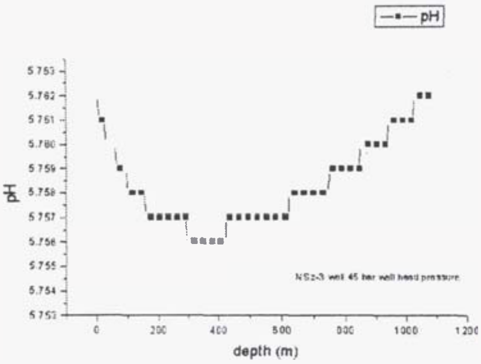

Fig.2 The pH-depth curve in well NSz-3

3.2. Well FAB-4

The average water and gas analysis input data from this well are given in Table 2.

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. The planned well head pressure was 40 bar, the temperature 171 ^{0}C, 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 was 179.5 ^{0}C. At the bubble point the fluid has a pH 4.619 and the partial pressures of the gas components are: p_{CO2}=87.61 bar, p_{CH4}=84.36 bar, p_{N2}=35.18 bar, p_{H2O}=9.776 **bar.** The fluid was 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 lcm 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 parameter.

We estimated also the 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.

The computed equilibrium pH values along the well are shown in Figure 3,

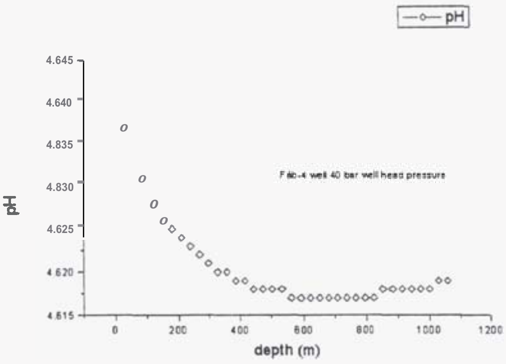

Fig. **3.** The pH-depth curve in well,FAB-4

4. CONCLUSION

A solubility equilibrium program GEOPROF, developed earlier was applied for the determination of the bubble point parameters and the multi-component equilibrium characteristics of two Hungarian high-enthalpy geothermal wells. Scaling characteristics along the well and at the surface were determined and it was concluded that the scaling intensity in well NSz-3 is lower than that in well FAB-4. Because of scaling intensity at surface conditions, it is recommended to keep well head pressure greater than 40 bar during production (especially for well FAB-4), and to reinject the exhausted geothermal water back into the reservoir.

5. REFERENCES

Arakaki, T., Mucci, A. (1995). **A** Continuous Mechanistic Representation of Calcite Reaction-Controlled Kinetics in Dilute Solutions at 25 ^{0}C and 1 Atm Total Pressure, ***Aquatic Geochemistry,*** Vol.1, 105-130.

Benoit, W. R. (1989). Carbonate Scaling Characteristics in Dixie Valley, Nevada Geothermal Wellbores, ***Geothermics,*** Vol. 18(1/2), 41-48.

Haarberg, T.(1989). ***Mineral Deposition During Oil Recovery. An Equilibrium Model,*** PhD Thesis. University of Trondheim, Norway.

Harvie, E. C., Moeller, N. et al. (1984). Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O System to High Ionic Strengths at 25 °C, ***Geochimica and CosmochimicaActa,*** Vol. 86, 723-751.

Kocsis, **J.,** (1976). ***Buborékpont meghatározás termálvizekben,*** Dissertation, Technical University, Budapest, Hungary.

Marshall, J. R., (1989). Thermodynamic Calculation of CalciumCarbonate Scaling inGeothermal Wells, Dixie Valley Geothermal Field, U,S:A., *Geothermics,* Vol. 18(1/2), 269-277.

Mercado, S., Bermejo, F. Et al.(1989). Scale Incidence on Production of Cerro Prieto Geothermal Wells, *Geothermics,* Vol. 18(1/2), 225-232.

Pátzay, G., Stáhl, G. et al. (1998). Modeling of Scale Formation and Corrosion from Geothermal Water, *Electrochimica Acta,* Vol. 43(1-2), 137-147.

Plummer, L.N., Busenberg, E.(1982). The Solubilities of Calcite and Vaterite in H_2O-CO_2 Solutions Between 0 and 90 °C and an Evaluation ofthe Aqueous Model for the System $CaCO_3$-H_2O-CO_2, *Geochimica and Cosmochimica Acta,* Vol. 46, 1011-1040.

Shiraki, R., Brantley, S. (1995). Kinetics of Near-equilibrium Calcite Precipitation at 100 ^{0}C, *Geochimica and Cosmochimica Acta* Vol. 59(8), 1457-1471.

Table 1

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BUBBLE POINT CALCULATION BY KOCSIS METHOD
            C PATZAY GYORGY (1995)

WELLLABEL:  nsz-3
WELL DEPTH (M):  3165.000
WATER FLOW RATE (LITER/MIN):  1313.40
WATER TEMPERATURE (CELSIUS):  171.000
WATER TDS (MG/LITER):  24855.000
WELL GAS FLOW RATE (LITER/MIN):  6986.100
GAS TEMPERATURE (CELSIUS):  171.000
WELL HEAD PRESSURE (BAR):  45.000
WELL  TEMPERATURE  GRADIENT  (CELSIUSM):
.00382568
WELL PRESSUREGRADIENT (BAR/M):   -171656686
WELL SEPARATED GAS-WATER RATIO (NLITER/M3):
1700.000
WELL DISSOLVED GAS-WATER RATIO (NLITER/M3):
3400.000
SEPARATEDGAS COMPOSITION (V%):

 C02   GAS CONCENTRATION(V%):  16.270
 CH4   GAS CONCENTRATION(V%):  79.440
 N2   GAS CONCENTRATION(V%):  4.290

 DISSOLVED GAS COMPOSITION (V%):

 C02   GAS CONCENTRATION(V%):  35.250
 CH4   GAS CONCENTRATION(V%):  61.910
 N2   GAS CONCENTRATION(V%):  2.840

 MOLALITY FOR THE Ca(2+)   ION?
  .1335E-02
 MOLALITY FOR THE Ba(2+)   ION?
  .0000E+00
 MOLALITY FOR THE Sr(2+)   ION?
  .0000E+00
 MOLALITY FOR THE Mg(2+)   ION?
  .3350E-03
 MOLALITY FOR THE Na(+)    ION?
  .3453E+00
 MOLALITY FOR THE K(+)     ION?
  .0000E+00
 MOLALITY FOR THE SO4(2-)  ION?
  .2380E-02
 MOLALITY FOR THE Cl(-)    ION?
  .3179E+00
 MOLALITY FOR THE Br(-)    ION?
  .0000E+00
 MOLALITYFOR THE ATOT      ION?
  .2600E-01
 READ IN THE GAS VOLUME IN M3=
  .0000E+00
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Table 2

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BUBBLE POINT CALCULATION BY KOCSIS METHOD
            C PATZAY GYORGY (1995)

WELLLABEL    fab-4
WELL DEPTH (M):  4239.000
WATER FLOW RATE (LITER/MIN):  3750.70
WATER TEMPERATURE(CELSIUS):  180.000
WATER TDS (MG/LITER):  27200.000
WELL GAS FLOW RATE (LITER/MIN):  46500.00
GAS TEMPERATURE (CELSIUS):  180.000
WELL HEAD PRESSURE (BAR):  40.000
WELL  TEMPERATURE  GRADIENT  (CELSIUSM):
.005800
WELL PRESSURE GRADIENT(BAR/M):  .1920
WELL SEPARATED GAS-WATER RATIO (NLITER/M3):
4400.000
WELL DISSOLVED GAS-WATER RATIO (NLITER/M3):
8000.000
SEPARATED GAS COMPOSITION (V%):

 C02   GAS CONCENTRATION (V%):  76.715
 CH4   GAS CONCENTRATION (V%):  20.899
 N2   GAS CONCENTRATION (V%):  2.5660

 DISSOLVED GAS COMPOSITION (V%):

 C02   GAS CONCENTRATION (V%):  89.30
 CH4   GAS CONCENTRATION (V%):  7.824
 N2   GAS CONCENTRATION (V%):  3.876

 MOLALITY FOR THE Ca(2+)   ION?
  .3081E-02
 MOLALITYFOR THE Ba(2+)    ION?
  .0000E+00
 MOLALITY FOR THE Sr(2+)   ION?
  .0000E+00
 MOLALITY FOR THE Mg(2+)   ION?
  .4540E-03
 MOLALITY FOR THE Na(+)    ION?
  .4284E+00
 MOLALITY FOR THE K(+)     ION?
  .0000E+00
 MOLALITY FOR THE SO4(2-)  ION?
  .2380E-03
 MOLALITY FOR THE Cl(-)    ION?
  .4684E+00
 MOLALITY FOR THE Br(-)    ION?
  .0000E+00
 MOLALITYFOR THE ATOT      ION?
  .1009-01
 READ IN THE GAS VOLUME IN M3=
  .0000E+00
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