Simulation of mineral precipitation in geothermal installations

The Soultz-sous-Forêts case

E. Stamatakis[a,b], C. Chatzichristos[b],
J. Muller[b] , A. Stubos[a] and T. Bjørnstad[b]

[a]National Centre for Scientific Research Demokritos (NCSRD), Athens, Greece
[b]Institute for Energy Technology (IFE), Kjeller, Norway

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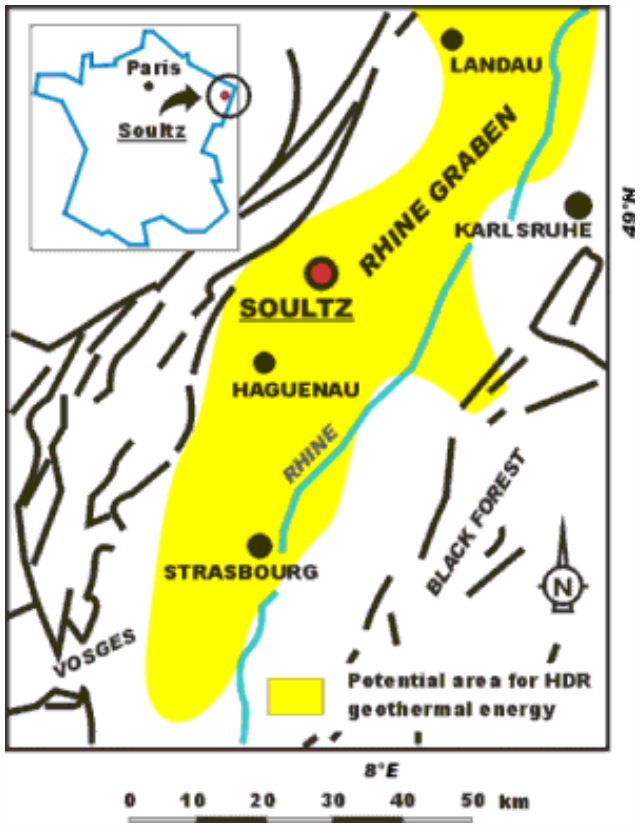
- Parameter estimation
- Optimal design and operation of the plant

The Soultz-sous-Forêts case



The European HDR-project is situated in Soultz-sous-Forêts, France, at the western border of the Rhine Graben

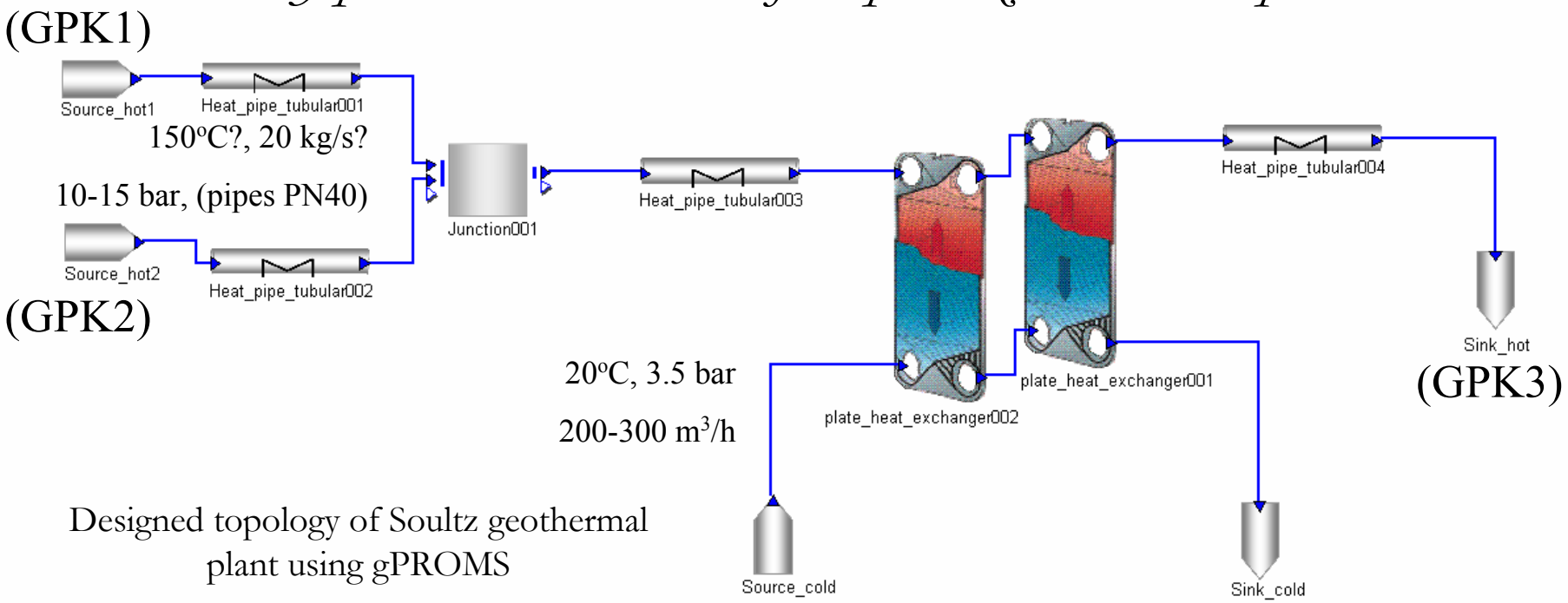
The geothermal field is a HDR reservoir in northeast France. Its fracture network has been explored down to 5000 m depth. The predicted temperature of 200° C was measured at a depth of 4950 m. The final planned Scientific Pilot Plant module is a 3-well system consisting of one injector and two producers.

The geochemical results obtained during a hydraulic stimulation have been provided to our research group in order to study calcite scaling tendency.

Simulations of $CaCO_3$ scale formation

The overall objective is the scaling management optimization (optimize the surface processes in order to minimize the impact of calcite scaling).

The only parameter available for optimization is the pressure.



Designed topology of Soultz geothermal plant using gPROMS

The chemical system

- The main complication is the occurrence of CO2(g) in reaction [1]. The molar volume of CO2(g) varies greatly with both temperature and pressure.

$$CaCO_3(s) + CO_2(g) + H_2O\ Ca^{2+}(aq) + 2HCO^{3-}(aq) \quad [1]$$

$$CaCO_3(s) + CO_2(aq) + H_2O\ Ca^{2+}(aq) + 2HCO^{3-}(aq) \quad [2]$$

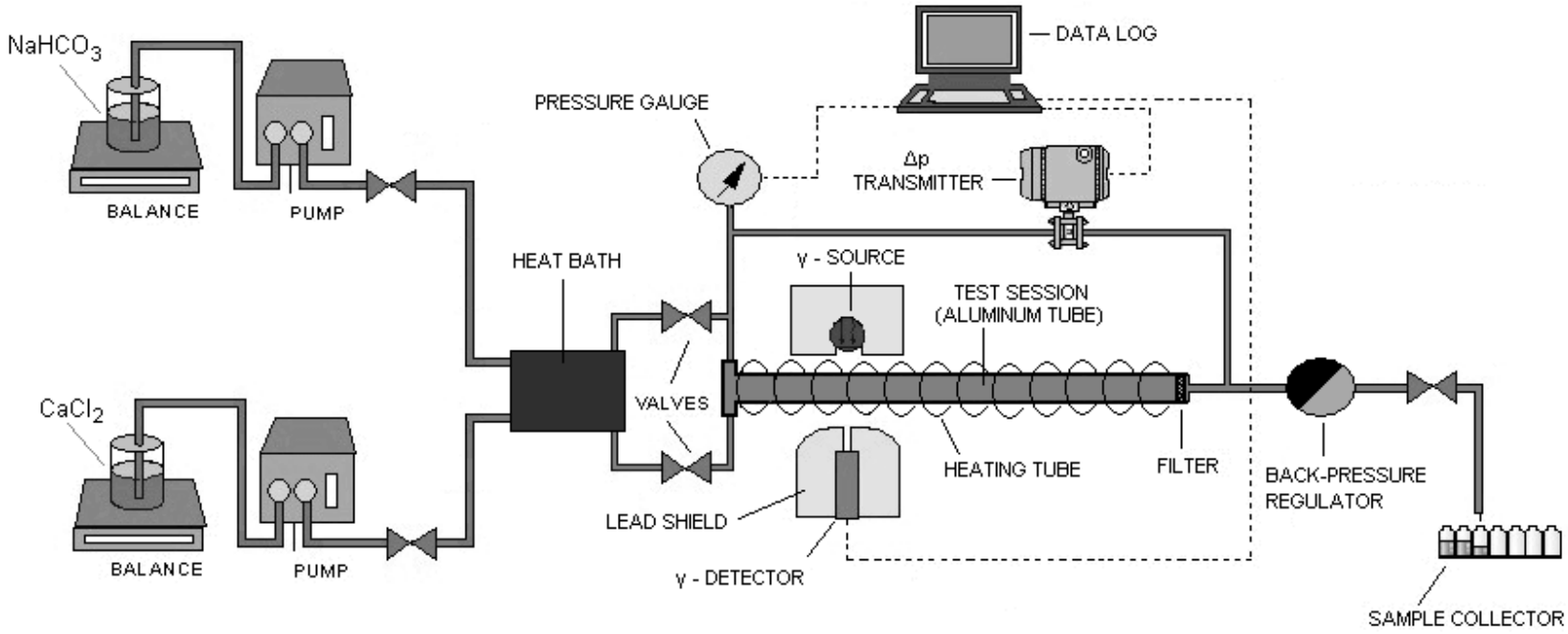
The temperature and pressure dependence of these equilibria is given from the work of Atkinson & Mecik (1994*, 1997**).

*Atkinson G., Mecik M., "$CaCO_3$ scale formation: How do we deal with the effects of pressure?", *Conf. Corrosion 94.*, **Paper 610**, 12pp. (1994).

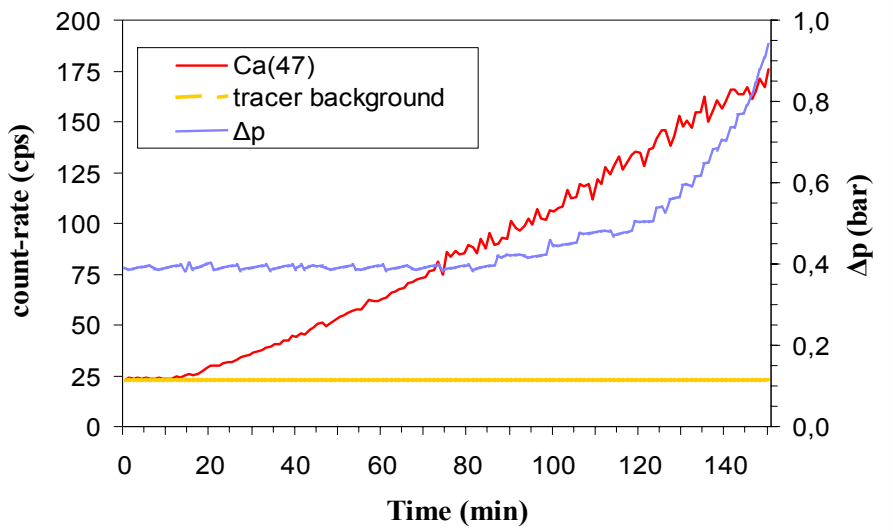
Atkinson G., Mecik M., "The chemistry of scale prediction", *J. Petrol. Sci. Eng.*, **17, 113-121 (1997).

The experimental system

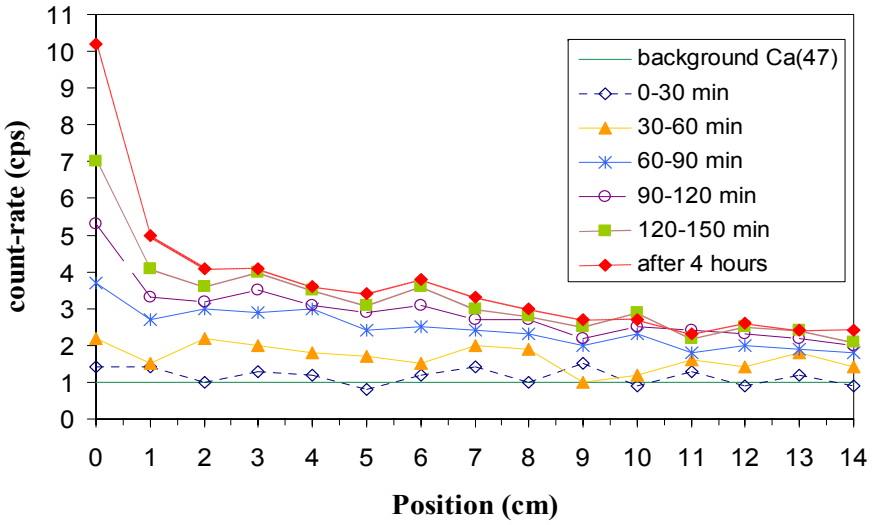
1. Gamma emission based on radioactive tracers added to the flowing and reacting system
2. Gamma transmission based on use of external gamma sources



Typical gamma-emission results

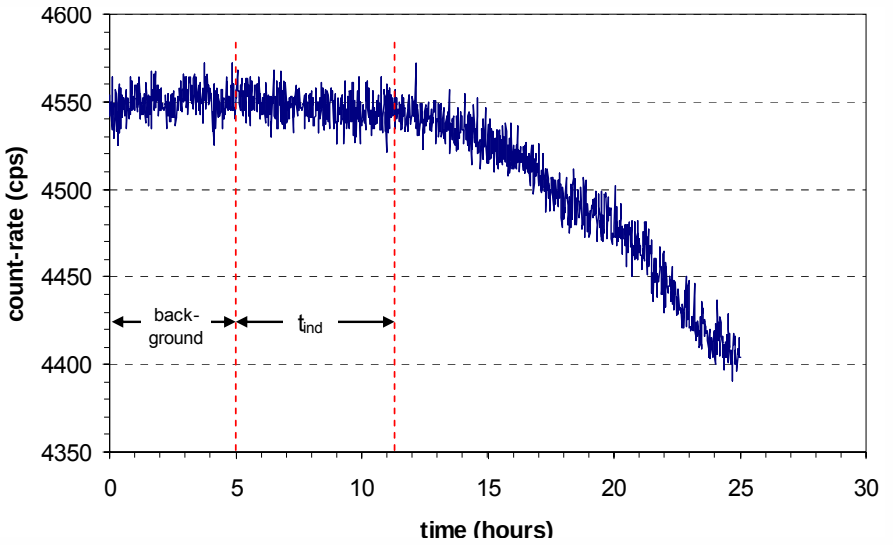


^{47}Ca deposit growth at the inlet and Δp buildup along the tube vs. time

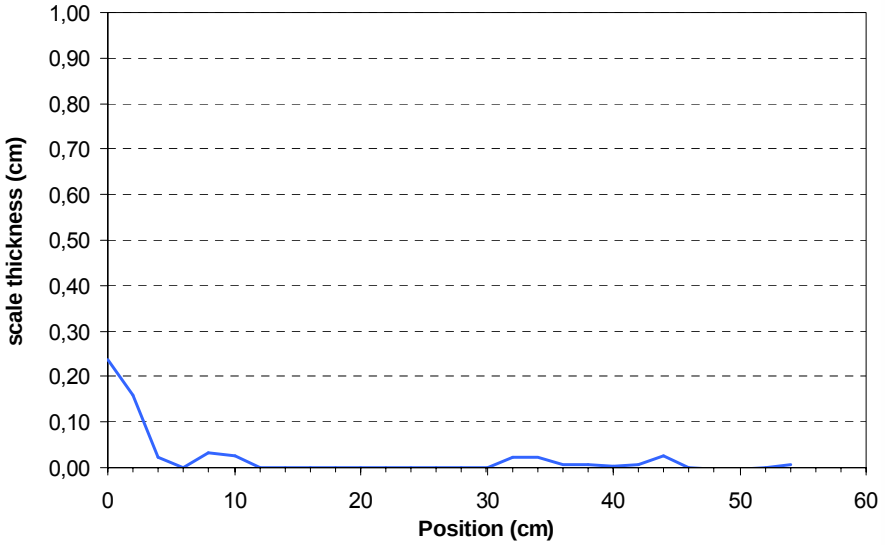


^{47}Ca deposit distribution across the tube at different time-steps

Typical gamma-transmission results



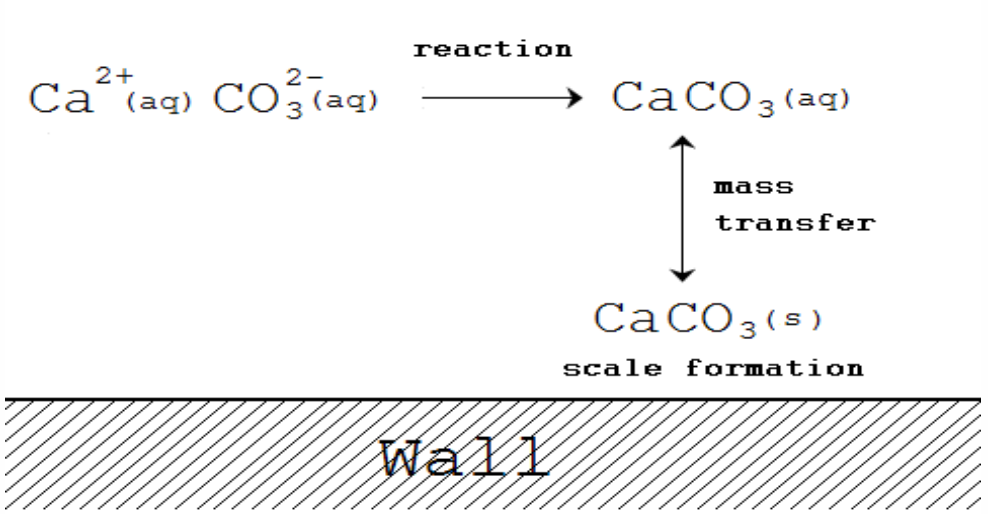
Gamma attenuation measurements for calcite precipitation at the inlet of the tube at 160°C, 15 bars and SR=1.5 (run 2)



Scale thickness distribution across the tube at the end of run 3

Mathematical modeling

- The key step in studying fouling is to capture the interrelationship between the chemical reactions, which give rise to deposition and the fluid mechanisms encountered along the flow path.
- Here, the necessary heat and mass transfer equations are coupled with the equations which describe the formation of calcite deposits in the transfer pipelines and heat exchanger.
- The overall model involves a coupled set of partial and ordinary differential and algebraic equations which can be described in gPROMS using its distributed process modelling capabilities.



The reaction/mass transfer scheme

Mathematical modeling (2)

Simple models are used to account for the hydro and thermo-dynamic characteristics of the fluid with two common assumptions:

- The fluid temperature in the bulk and thermal layer are radially uniform, i.e. the temperature in the bulk and thermal boundary layer are equal and do not change with the tube radius.
- The fluid flows in plug flow at uniform velocity. The velocity in the thermal boundary layer is assumed negligible in comparison.

Mathematical modeling (3)

The simplified one-phase flow case in a circular tube

- The material balance for e.g. $CaCO_3$ in the control volume is given from:

$$\frac{\partial C_{CaCO_3}}{\partial t} + u_z \frac{\partial C_{CaCO_3}}{\partial z} = \underbrace{-K_p C_{Ca}}_{\text{Reaction rate term}} \underbrace{- \left[k_{mCaCO_3} \left(C_{CaCO_{3(s)}} - C_{CaCO_{3(aq)}} \right) + k_w C_{CaCO_{3(s)}} \right]}_{\text{Mass transfer}} + \underbrace{\frac{\partial}{\partial z} \left(D_{CaCO_3} \frac{\partial C_{CaCO_{3(s)}}}{\partial z} \right)}_{\text{diffusion at the axial distance}}$$

- The energy balance (for the heat exchanger) has the form:

$$\frac{\partial T_s}{\partial t} + u_z \frac{\partial T_s}{\partial z} = -\frac{1}{\rho C_{pw}} U a_s \left(T_s - T_{cold} \right)$$

Quantifying fouling

The rate of deposition is related to the concentration of $CaCO_3$(s) by the mass transfer coefficient k_w. The Biot number is used to express the change of heat transfer due to fouling and it is related to the rate of deposition according to:

$$\frac{\partial Bi}{\partial t} = \beta k_w C_{CaCO_3}, \qquad \beta \text{ is a constant}$$

- Deposit thickness and mass at each position z along the heat exchanger:

$$x_d(z) = \frac{\lambda_d Bi(z)}{U_o},$$

$$mass(z) = \frac{\lambda_d Bi(z)}{U_o} \rho_d$$

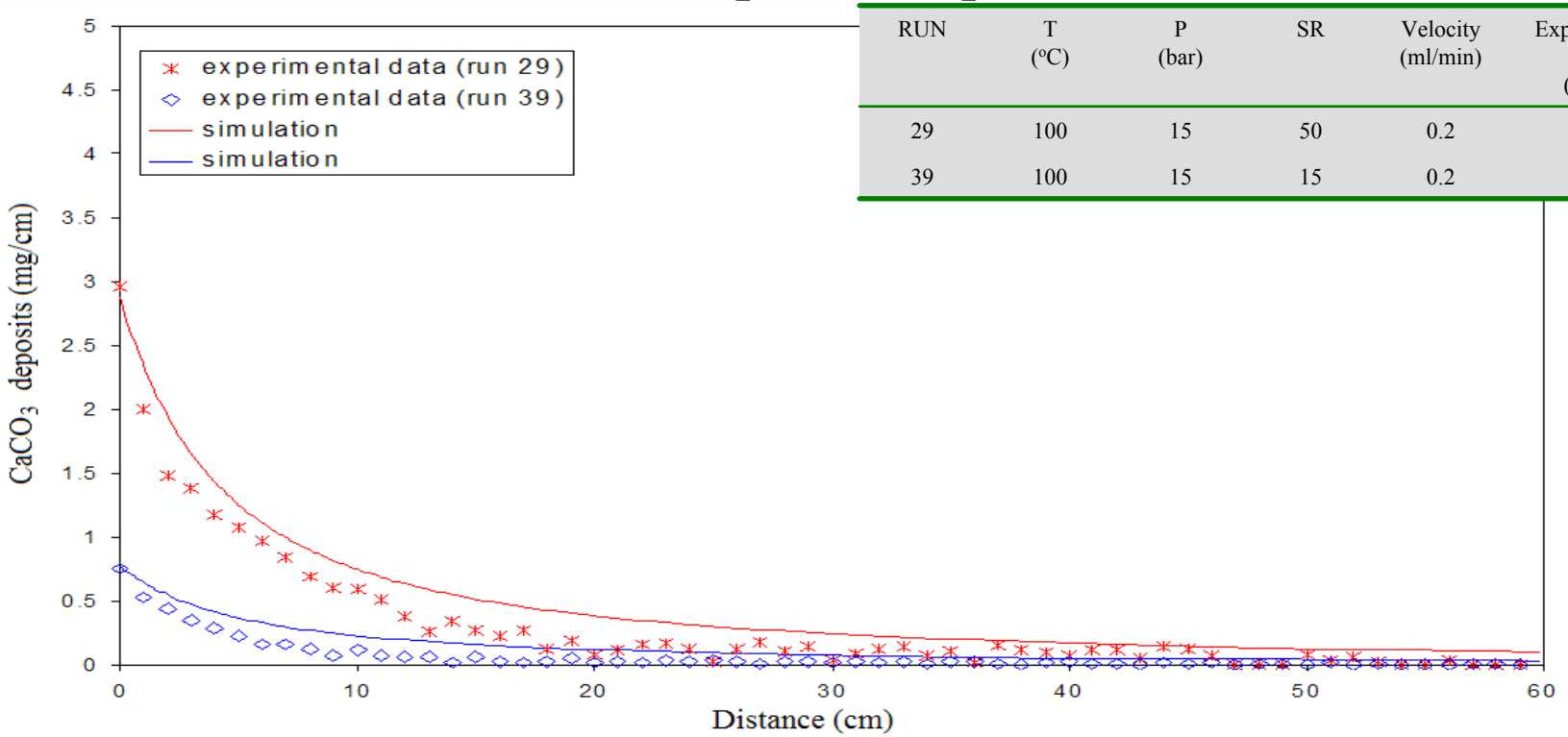
Parameter estimation

- Before using the model to predict the dynamic behaviour of the process, we need to validate it and estimate the values of several unknown model parameters based on the data gathered from our experimentations.
- This type of analysis can be easily performed using the built-in parameter estimation capabilities of gPROMS.
- Thus, the mathematical model is used to estimate the values of the unknown parameters, such as heat transfer coefficients, that best match the experimental data over time.

Preliminary simulation results

- Here, for the purpose of parameters estimation and verification we tried to simulate two specific experimentations.

RUN	T (°C)	P (bar)	SR	Velocity (ml/min)	Experimental Time (hours)
29	100	15	50	0.2	12
39	100	15	15	0.2	12



Optimal design and operation of the plant

- Fouling in geothermal installations is a major problem and, virtually, represents additional costs to the industrial sector such as:
  - capital cost due to cleaning equipment and services
  - lost of production
  - waste of energy and heat
- A detailed economic objective function is going to be used to account for all the important factors related with calcite precipitation and a number of operating constraints will be imposed.

Optimal design and operation of the plant (2)

- There are two main issues which must be taken into consideration when establishing optimal control strategies for this problem. The first issue is to ensure that no precipitation occurs and the system operates above its bubble point at all times. The second issue is to seek for the best economic performance.
  - The complexity of the dynamic optimization problem arises primarily from the distributed and highly nonlinear nature of the system model
  - Because of the complexity of the underlying physical process, it is often difficult to define simple strategies in order to address all important issues and take at the same time into account all operating constraints

Thank you!

Temperature-dependent constants for lnk

$$\ln k = \frac{\Delta A \ln T}{R} + \frac{\Delta B T}{2R} + \frac{\Delta C}{2RT^2} - \frac{\Delta I_h}{RT} - \frac{\Delta I_g}{R}, \text{ (T in K)}$$

Solid	ΔA	ΔB	$\Delta C\ (\times 10^{-6})$	ΔI_h	ΔI_g
Calcite	-239.623	0.18866	9.0767	83810.8	-1540.62
$CaCO_{3(s)} + CO_{2(g)} + H_2O \leftrightarrow Ca^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)}$, K_1					
Range: 0 - 300°C					
Calcite	282.476	-0.7958	-14.5318	-102360	1772.44
$CaCO_{3(s)} + CO_{2(aq)} + H_2O \leftrightarrow Ca^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)}$, K_1					
Range: 0 - 200°C					
	-80.384	0.18166	6.1255	31661.2	-495.94
$CO_{2(g)} \leftrightarrow CO_{2(aq)}$, K_H					
Range: 0 - 250°C					

Effect of pressure on $CaCO_3$ dissolution

$CaCO_{3(s)} + CO_{2(g)} + H_2O \leftrightarrow Ca^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)}$, K_1

$$\ln\left[\frac{K_P}{K_1}\right] = \frac{-\left[\Delta\overline{V}^0_{s,1} - \Delta\overline{V}^0_{CO_{2(g)}}\right]}{RT}(P-1) + \frac{\Delta\overline{K}^0_{s,1}}{2RT}(P^2-1)$$

$$\Delta\overline{V}^0_{s,1} = -26.69 + 0.146365t - 15.7085\times10^{-4}t^2 - 1.0566\times10^{-6}t^3$$

$$\Delta\overline{K}^0_{s,1}\times10^{-3} = 11.8837 + 2.853\times10^{-2}t - 8.5531\times10^{-4}t^2 + 5.3145\times10^{-6}t^3$$

$\Delta\overline{V}^0_{CO_{2(g)}}$ from interpolation of the CO2 molar volumes reported by Angus et al. (1976)

$\Delta\overline{V}^0_{s,1}$ in cm^3mol^{-1}, $\Delta\overline{K}^0_{s,1}$ in $cm^3bar^{-1}mol^{-2}$, t in °C

Range: 0 - 150°C, 1 - 200bar

$CaCO_{3(s)} + CO_{2(aq)} + H_2O \leftrightarrow Ca^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)}$, K_1

$$\ln\left[\frac{K_P}{K_1}\right] = \frac{-\Delta\overline{V}^0}{RT}(P-1) + \frac{\Delta\overline{K}^0}{2RT}(P^2-1)$$

$$\Delta\overline{V}^0 = -61.9 + 20.231\times10^{-2}t - 24.45\times10^{-4}t^2 - 0.603\times10^{-6}t^3$$

$$\Delta\overline{K}^0\times10^{-3} = 13.517 + 3.222\times10^{-2}t - 15.1385\times10^{-4}t^2 + 12.919\times10^{-6}t^3$$

$\Delta\overline{V}^0$ in cm^3mol^{-1}, $\Delta\overline{K}^0$ in $cm^3bar^{-1}mol^{-1}$, t in °C

Range: 0 - 225°C, 1 - 2000bar