A SIMPLIFIED APPROACH TO TRANSLATE CHEMICAL ALTERATION IN CORE EXPERIMENTS TO FIELD CONDITIONS

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ABSTRACT

We present a method for upscaling the chemical alteration observed in chalk core flooding experiments to the field scale. Chemical reaction rate constants are determined from constant temperature core flooding experiments and are used by a flow line model to predict chemical alteration when cold seawater is injected into a 130°C chalk reservoir. Injection rates and conditions are similar to a section of the Ekofisk field. The simulations show that for activation energies of 65kJ/mol significant alteration extends ~400m from the injection well. Approximately 1.5wt% of calcite is dissolved and 1.5wt% of dolomite is precipitated near the injection well, after 40 years of simulated seawater injection. The dissolution and precipitation are almost equal in magnitude, thus the net chalk dissolution predicted is <1wt%. Porosity near the injection well is predicted to increase by 1 to 2%, partly due to the fact that the precipitated mineral, dolomite, is denser than the dissolved mineral, calcite. Anhydrite is predicted to precipitate at high temperatures, but will thereafter redissolve as the reservoir is cooled by the injection water. These chemical alterations may be a contributing mechanism of the compaction of the Ekofisk reservoir observed after the start of the waterflood.

When comparing our chemical predictions with analysis of produced water from the Ekofisk field, similar trends as found from the effluent profiles in the core experiments are observed. Seawater breakthrough is mainly identified by a decline in the chloride and sodium concentrations. The breakthroughs of sulphate and magnesium are delayed relative to the injection water front, whereas a net gain of calcium in the produced water is observed. These field observations are also in accordance with the predicted precipitation of anhydrite and dolomite, and dissolution of calcite.

INTRODUCTION

Core flooding experiments and field tests carried out during the last decade have demonstrated the impact of water chemistry on oil recovery. On the Norwegian Continental Shelf, seawater injection is widely used as secondary oil recovery strategy. Most Norwegian reservoirs are initially at 50-150 °C, but portions of some of these reservoirs have been cooled down to 50°C or less due to water injection. In nature, fluids are in equilibrium with the rock if the temperature is above 70°C, and consequently, even if the pore water was originally sea water (usually it is more saline), the chemistry of the aqueous pore fluid in the reservoir (formation water) now differs from the chemical composition of seawater. When seawater or any brine with a different chemical composition or temperature than the formation water is injected into the reservoir, the reservoir rock will be chemically altered. The alteration will entail physical changes (due to dissolution/ precipitation of minerals) and also change in surface chemistry (surface charge, zeta potential). These changes can affect the amount and rate of water imbibition (and oil expulsion), change the rate of reservoir rock compaction (e.g. Ekofisk and Valhall field), and exacerbate or moderate the scaling potentials in the production wells.

In this paper, we propose to quantify the alteration of injected water chemistry by building a flow line model for the chemical changes that occur as the injected fluid moves from an injection to a production well. The chemical changes have been calculated by assuming that the flow occurs in flow zones (fractures or permeable strata). Similar methods have been developed in earlier work to study precipitation and dissolution in near wellbore reservoir[1, 2], and to simulate the dissolution and deposition of silica during intrusion-driven hydrothermal circulation, the generation and titration of CO_2 during steam injection, and the development of alteration halos around fractures during the formation of porphyry copper ore deposits[3-5].

THE BASIC FLOW LINE MODEL

The thermodynamic model used to calculate the equilibrium concentration of the chemical reactions between a brine and the rock has been described in [6-8]. In the following section we will introduce the advective reactive transport model, and we make the following assumptions:

1. One dimensional flow of an incompressible single aqueous phase
2. No dispersion or diffusion
3. Mineral dissolution and precipitation is described through a linear rate equation
4. No redox reactions take place
5. Porosity changes due to chemical reactions do not affect the residence time of the fluid in each node

In the following we will start by describing the flow line model in a linear case, which will be used to fit the chemical rate constants in the model to the lab data. A sketch of the model setup is shown in Figure 1, for a special case, where the flow line has a constant thickness. If the flow line contracts or diverges, the nodes will not be distributed

evenly. The important constraint is that the fluid moves from one node to the next in time step Δt.
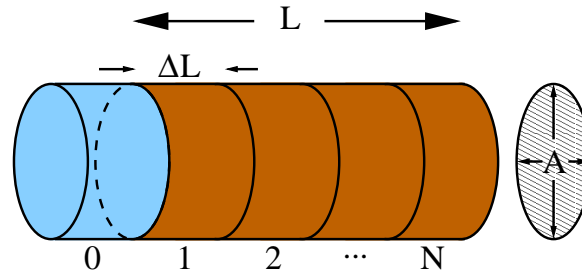

Figure 1: A schematic drawing of the uniform linear flow line model. The flow goes from left to right. L is the length of the system, ΔL is the length of one sub volume and A is the area of the cross section. The 0 sub volume is used to specify the fluid, while sub volumes 1 to N contain the rock fluid system.

We assume that the fluid composition that enters from the left, at node 0, is known. Along the flow line, cross sectional area, temperature, pressure, and mineral composition is known. Thus the fluid advects one node, equilibrates partially with the rock, then moves to the next node, partially equilibrates etc. At some distance from the inlet, the fluid will be in equilibrium with the rock and no more chemical alterations occur. If the fluid injected has a temperature different from the rock, there will be additional alteration induced by the temperature gradients from inlet to outlet, until the fluid is in thermal equilibrium with the rock.

In this work we use a linear rate equation, and the rate at which a chemical species will equilibrate with the rock minerals inside a fluid node is thus:

$$\phi \frac{\partial \Delta c_i}{\partial t} = -k(T)\Delta c_i. \tag{1}$$

ϕ is the porosity of the rock, k(T) is a temperature dependent rate constant. $\Delta c_i = c_i - c_i^{eq}$, is the difference between the total concentration of a chemical species, c_i, and the equilibrium concentration, c_i^{eq}. Equation (1) can be integrated over the time step Δt:

$$\Delta c_i(t + \Delta t) = \Delta c_i(t)\, e^{-\Delta t/\tau}, \text{ where } \tau = \frac{\phi}{k(T)}, \tag{2}$$

where we have assumed that the equilibrium concentration does not change during the time step. The rate constant has a temperature dependence described by the Arrhenius equation, see e.g.[9, 10]:

$$k(T) = k(T_0)\exp\left\{\frac{E_a}{RT}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right\}, \tag{3}$$

E_a is the activation energy, and has a typical value of 20-80 kJ/mol [10] for dissolution/ precipitation reactions.

MINERALOGICAL AND POROSITY CHANGES

The mineralogical compositions along the flow line are given by mass fractions:

$$x_i = \frac{M_i}{M_r},$$ (4)

where M_i is the mass of mineral i and M_r is the total mass of the rock. A change in the fluid composition along the flow line is in this work only related to mineralogical alterations. Thus, the mineralogical alteration is completely determined by the changes in pore water chemistry:

$$\delta x_i = \frac{\phi}{\rho_r (1 - \phi)} M_{w,j} (S_{i,j})^{-1} \Delta c_j,$$ (5)

where ρ_r is the rock density, and S^{-1} is the inverse stoichiometric matrix, which defines the composition of the minerals in terms of basis species, e.g. if only calcite is present a change of one molar in the calcium concentration correspond to a one molar change in calcite. If more than one mineral is present, a system of linear equations needs to be solved. The porosity change along the flow line can be estimated by the following arguments: The change in porosity, $\delta\varphi$, during one time step is given by:

$$\delta\varphi = \frac{V_f + \delta V_f}{V_b + \delta V_f + \delta V_r} - \frac{V_f}{V_b}.$$ (6)

δV_f is the change in fluid volume, and δV_r is the change in rock volume, $V_b = V_f + V_r$ is the bulk volume. Assuming that the change in fluid volume is equal, but of opposite sign as the rock volume, i.e. $\delta V_f \approx -\delta V_r$, we get:

$$\delta\varphi = \frac{\delta V_f}{V_b} = -(1 - \varphi)\rho_r \sum \frac{\delta x_i}{\rho_i},$$ (7)

where ρ_i is the mass density of mineral i, and δx_i is the change in the mass fraction of mineral i during one time interval. The changes in porosity are recorded but are not reintroduced into the calculations. The presented model is, as of yet, a model for transport only. The inclusions of porosity changes would need a model that incorporates the rock mechanics of the reservoir and the alteration in the flow due to these changes. This is outside the scope of this work, but we will acquire knowledge of the position and size of the initial porosity changes.

TEMPERATURE MODEL

The temperature is based on the knowledge of the initial rock temperature, T_r, the temperature of the injected fluid, T_f, together with the specific heat capacities c_r and c_f for the rock and fluid, respectively. The heat transfer, ΔQ, is given as

$$\Delta Q = C \Delta T,$$ (8)

where ΔT is the temperature difference and the C is the heat capacity. Here we have assumed that the heat capacity is close to constant for the considered temperatures. The heat capacities for the rock and fluid are given as:

$$C_r = V_r \rho_r c_r = (1 - \varphi) V \rho_r c_r \text{ and } C_f = V_f \rho_f c_f = \varphi V \rho_f c_f.$$ (9)

From the conservation of energy together with the assumption that the system is closed we obtain that

$$\Delta Q_r + \Delta Q_f = 0.$$ (10)
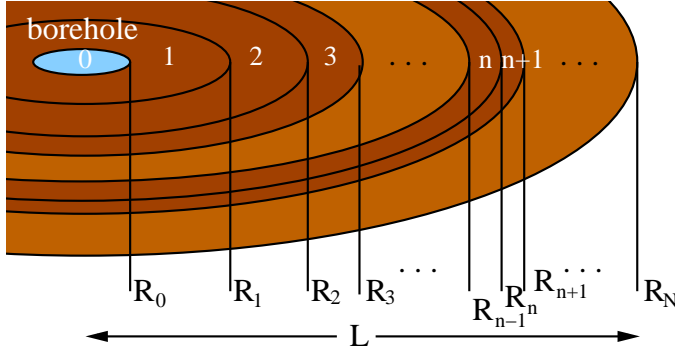
Combining the above relations we get that:

Figure 2: An illustration of the cylindrical setup. R_0 is the radius of the borehole and R_1 to R_N are the radii of the concentric shells.

$$C_r \Delta T_r + C_f \Delta T_f = 0$$
$$(1 - \varphi) V \rho_r c_r \Delta T_r + \varphi V \rho_f c_f \Delta T_f = 0$$ (11)
$$\Delta T_r + a \Delta T_f = 0,$$

where $a = (\varphi \rho_f c_f)/((1-\varphi) \rho_r c_r)$.

The amount of heat transferred is dependent on the systems and rates involved, but, given the above assumption, this is easily coded into the model. In this paper we have chosen the situation that the rock and fluid comes into thermal equilibrium, so that after the heat exchange both the rock and the fluid have the same temperature T_{eq}. This gives the following update rule for the temperature:

$$T_{eq} = \frac{T_r + a T_f}{a+1}.$$ (12)

CYLINDRICAL GEOMETRY

In the above calculations we have assumed that the flow through the system is represented by a closed tube or flow line. By extending the model to a cylindrical geometry, we can make large scale prediction assuming isotropic conditions. In this model we consider the sub volume to consist of cylindrical shells. The radii, R_n, defining the shell structure are given by the constraint that the volume contained in the cylindrical shells should be equal. Assuming that the reservoir has constant thickness, we get that

$$R_{n+1}^2 - R_n^2 = R_n^2 - R_{n-1}^2.$$ (13)

The boundary condition are given such that R_0 is the radius of the borehole and $R_N = L$, the length of the system. N is the number of sub volumes. Solving the above difference equation we get that

$$R_n = \left((L^2 - R_0^2) \frac{n}{N} + R_0^2 \right)^{\frac{1}{2}}. \tag{14}$$
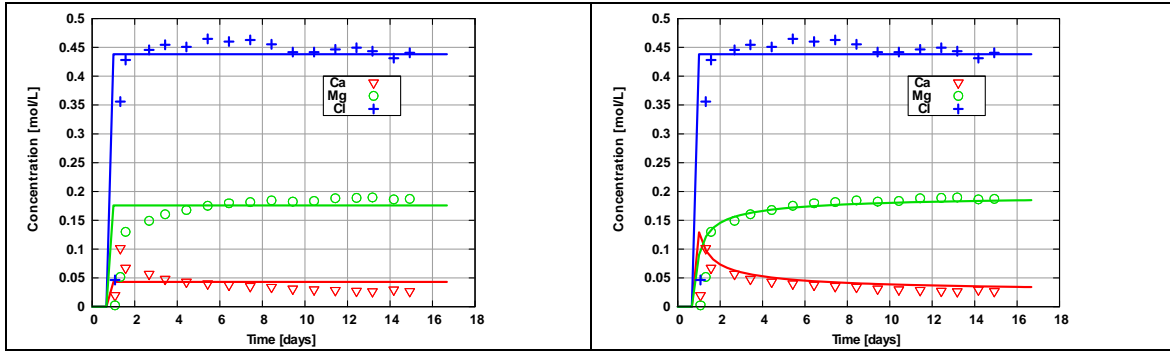

Figure 3: Measured (points) and simulated effluent profile (solid lines), when 0.219M MgCl$_2$ is injected at a constant flooding rate of 1PV/day at 130°C. Loss of magnesium and the gain in calcium are attributed to calcite dissolution and dolomite precipitation in the model. (Left) Kinetic decay time of τ=4.45 days. (Right) Effluent profiles when equation (16) is used.

Given the fluid flux at the borehole walls, q_f, we get the time increment, that is the time it takes to move the fluid through a shell, as:

$$\Delta t = \frac{\phi}{2 q_f} \frac{L^2 - R_0^2}{N R_0}. \tag{15}$$

All the calculations we have discussed for the tube geometry are based solely on variables intrinsic to each sub volume. Hence, the previous presented calculations do not change when applied to the cylindrical geometry. The only change is the positioning of the sub volumes.

COMPARISON WITH LAB EXPERIMENTS

We will compare the flow line approach with the data published in [11]. The experiments were performed at 130°C, and with a constant flooding rate of 1PV/day, the porosity of the core was 50%. We will fit the rate constant in equation (1) when 0.219M MgCl$_2$ is injected. The result is shown to the left in Figure 3, a decay time of τ=4.45 days is used. However as is discussed in [12], there seems to be an initial period of fast dissolution, and then the calcite dissolution rate is gradually lower. It is known that magnesium may inhibit the dissolution rate of calcite [13], thus it was suggested that formation of magnesium bearing minerals inside the core could explain the transient effects observed in the core scale experiment[12]. This effect can be included in the model, by making the following substitution:

$$k \rightarrow k_1 \frac{1 + k_2 c_{dolomite}}{1 + k_3 c_{dolomite}}, \tag{16}$$

where k_1=0.46/days, k_2=5.6·10^{-2}l/mol, k_3=18 l/mol, the concentration of dolomite is given in mol/l pore volume. Using this rate equation, we get the results shown to the right in Figure 3. We will use equation (16), and the same value of the constants in the rest of the paper. We can now use the flow line model to predict effluent profiles in other core flooding experiments. In Figure 4 to the left is the effluent profile shown when seawater with reduced level of NaCl is injected [11]. In addition to the loss in magnesium, there is
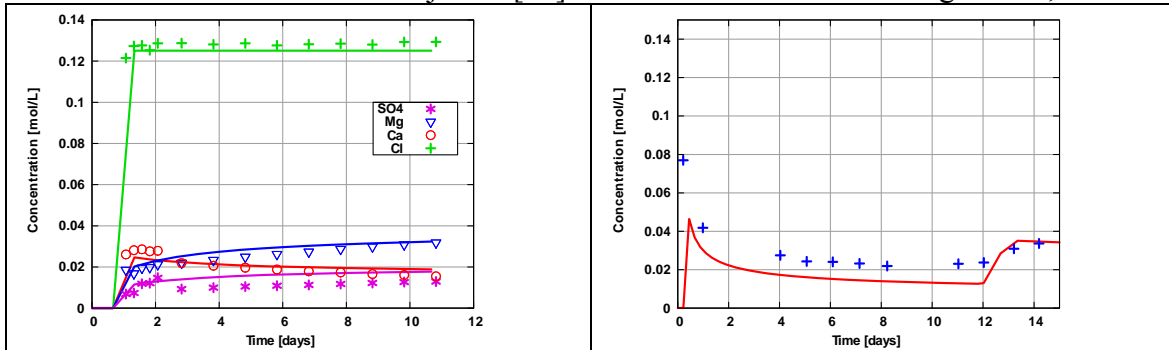

Figure 4: (Left) Measured (points) and simulated effluent profile (solid lines) when seawater with a reduced level of NaCl is injected at a constant flooding rate of 1PV/day at 130°C. (Right) 0.219M MgCl₂ is injected at a constant flooding rate of 3PV/day, after 12 days the flooding rate is lowered to 1PV/day. Only the calcium concentration was measured.

a loss of sulphate, which in the model is attributed to anhydrite precipitation. The match with the experimental data is striking; the model even correctly predicts the intersection of the calcium and magnesium concentration profiles. To the right in Figure 4, the flooding rate was changed from 3PV/day to 1PV/day after 12 days, this experiment was not included in [11]. As the model in this paper is to be used in a cylindrical case it is important to check if the model can reproduce conditions when the flooding rate is changed.

RADIAL GEOMETRY

In this section we will run the flow line model in a radial geometry, with physical parameters relevant for the Ekofisk field. We assume the ratio between the heat capacity for the rock and the brine is $c_r/c_f = 0.2$, an average injection rate of 30.000 bbl/day at a bottom hole temperature of 25°C, and a well radius of 10cm. The water is injected into a 100m interval of chalk with average porosity of 30%. The activation energy is set to 65 kJ/mol. The primary mineral in the field is assumed to be calcite in this example. But adding a percentage of dolomite initially, will not change the results as dolomite starts to form immediately when seawater is injected. The composition of the injection water (seawater), and the formation water are listed in Table 1.

Seven years after injection the concentration profiles from the well, the change in porosity, and the mineralogical alteration is shown in Figure 5 and Figure 6. In the beginning of the injection period, the reservoir is hot and anhydrite is precipitated, later when the reservoir is cooled anhydrite redissolves. During the injection period dolomite forms and calcite dissolves, and because the primary mineral calcite is replaced by the secondary mineral dolomite, the net change in porosity is not that great. As can be seen

from the left figure in Figure 6, the net change in porosity is positive where anhydrite has been dissolved because of the temperature front, and negative in the hot areas where anhydrite is precipitated.
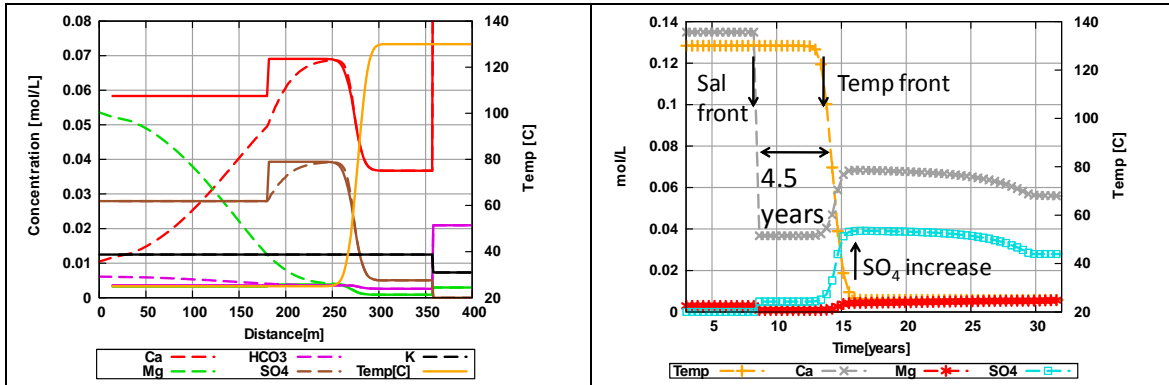

Figure 5: (Left) Concentration profiles from the well seven years after injection, the solid lines are the equilibrium concentrations and the dashed lines are the predicted concentrations. The jump in the equilibrium concentration at 170m is due to the fact that anhydrite that was precipitated when the reservoir was hot has now dissolved. The change in concentration later on is due to the temperature increase. (Right) The effluent profile at 400m from the well, note that the temperature profile is lagging behind the seawater breakthrough.

The effluent curve to the right in Figure 5 clearly demonstrates that there is a stripping of magnesium and sulphate from the injection water and a gain in the calcium concentration. The net gain in calcium concentration is equal to the magnesium loss minus the sulphate loss, on a molar basis. Five years after seawater breakthrough the temperature front arrives, and a sharp increase in calcium and sulphate concentration is observed. Thus sulphate breakthrough in the producer could be an indication of the position of the temperature front.

To summarize:
1. The alteration is greatly affected by the activation energy of the dissolution/precipitation rate constants. Activation energy of 65kJ/mol will induce alterations as far as 400m from the injection well, but only a 1wt% change in calcite concentration close to the well after 40 years of simulated injection. If the activation energy is close to 20kJ/mol, the alteration only extends 100m from the well, but after 40 years of simulated injection close to 35% of calcite is dissolved and replaced by dolomite. (Figures not included in the paper)
2. Chemical alteration is not only driven by advection, but more importantly by temperature gradient induced by the injection water. Anhydrite precipitates when the reservoir is hot, and dissolves when the reservoir cools down.
3. The change in calcium concentration is linked to dolomite precipitation and anhydrite dissolution, and the stoichiometry is such that the change in calcium

concentration is equal to the loss in magnesium minus the loss in sulphate concentration (on a mol/L basis).
4. The arrival of the temperature front is accompanied by an increase in sulphate and calcium concentration.
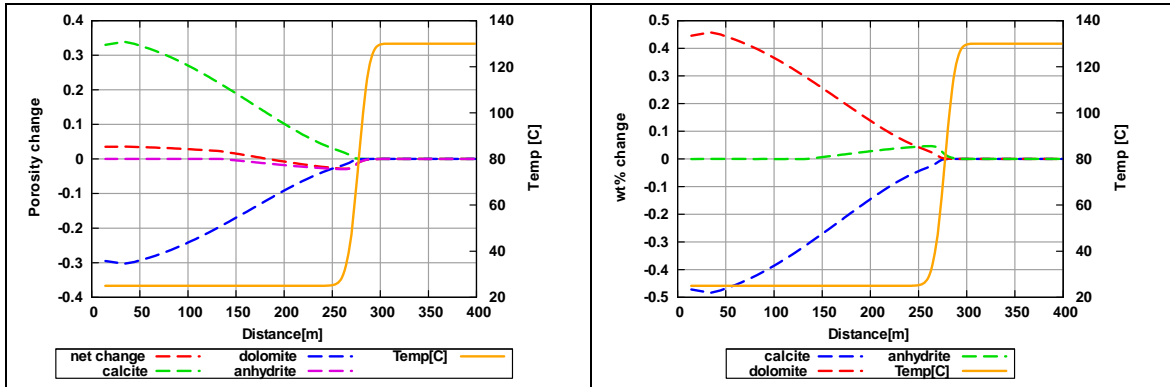

Figure 6: Seven years after injection. (Left) porosity changes, note that the porosity decreases in the area where anhydrite is precipitated (Right) wt% mineralogical alteration, note that the alteration in dolomite precipitation is almost equal but opposite in magnitude as calcite.

COMPARISON WITH ION ANALYSES FROM PRODUCED WATER

We have compared the results obtained in the previous section with produced water analyses from a well at the Ekofisk field. The average injection rate of the nearby injector was 20-30000bbl/day, at a distance of 300-400 m from the producer. The average porosity is 35%. The well experienced seawater breakthrough in 2001. Assuming that chloride acts as an ideal tracer (i.e. does not participate in any chemical reactions), the fraction, f, of injection water in the produced water is given as:

$$f = \frac{c_{Cl}^{PW} - c_{Cl}^{FW}}{c_{Cl}^{IW} - c_{Cl}^{FW}},$$ (17)

where c_{Cl}^{IW} and c_{Cl}^{FW} are the chloride concentration in the injected and formation water respectively, and can be found in Table 1. Based on this we can predict the other ion concentrations in the produced water assuming no chemical reactions in the reservoir:

$$c_i^{PW}(\text{predicted}) = f c_i^{IW} + (1 - f)c_i^{FW}.$$ (18)

The calculated initial ion concentrations (i.e. assuming no chemical reaction, just injection and formation water mixing) of the produced water are shown as solid lines in Figure 7. From the concentration profiles it is evident that chemical reactions are taking place in the reservoir. Magnesium and sulphate are lost and a corresponding gain in calcium is observed. From the discussion in the last section; if the change in ion concentrations observed in the producer is due to formation of new mineral phases one should expect the gain in calcium concentration to be equal to the loss in magnesium minus the loss in sulphate concentration. From Figure 7 it follows that this is indeed the

case i.e. loss of magnesium is ~0.033mol/L, loss of sulphate is ~0.02 mol/L, thus the gain in calcium should be 0.013mol/L in January 2005. Note also that it takes about 3 years before the sulphate concentration increases in Figure 7, which is about the same time as
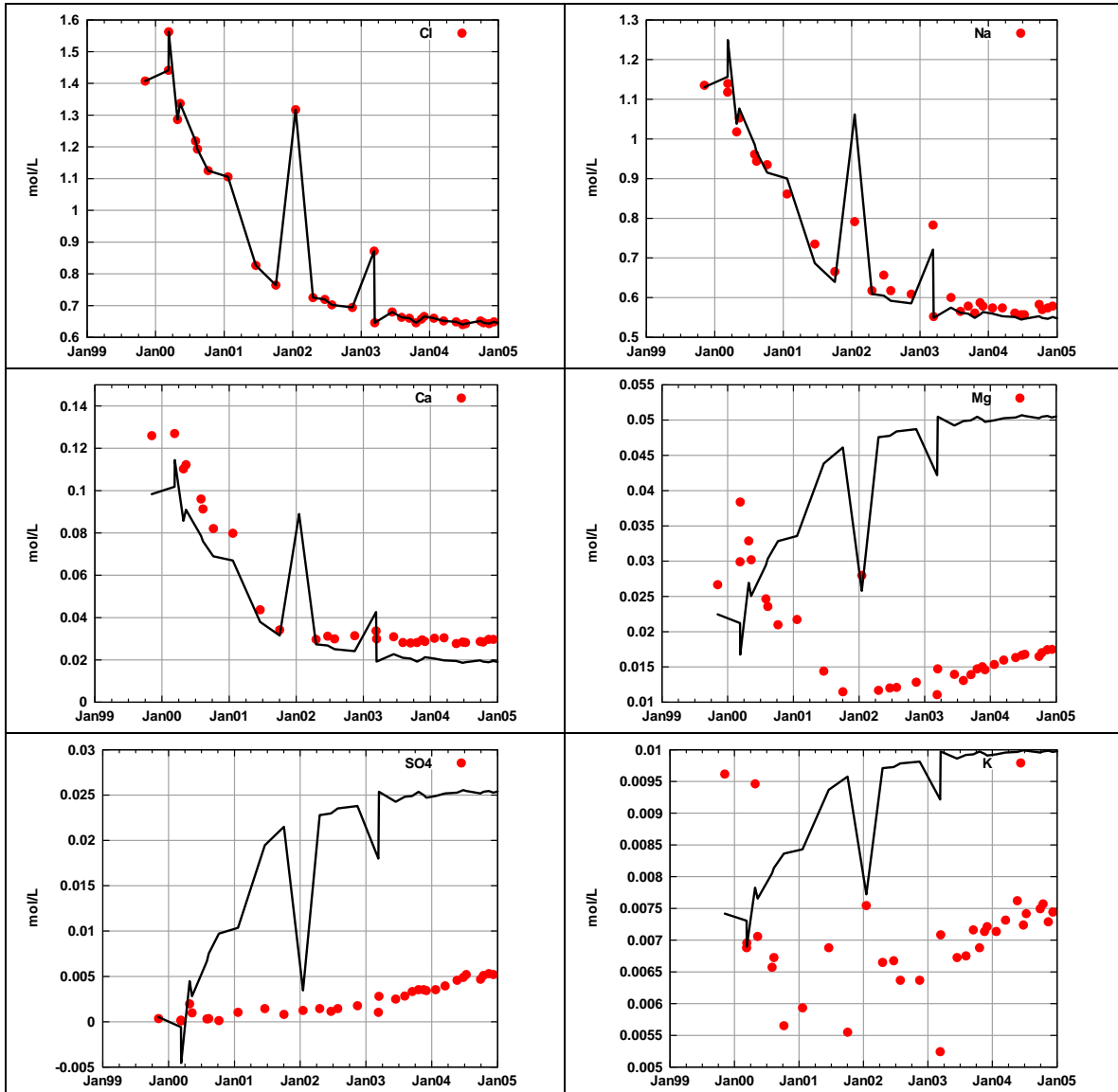

Figure 7: Analyses of produced water (points), the solid lines are the predicted ion concentrations assuming that chlorine is an ideal tracer, and that the drop in chloride concentration is solely due to mixing between Ekofisk formation water and seawater. The gap between the solid lines and points is then attributed to precipitation or dissolution.

predicted to the right in Figure 5. The delay between the salinity and temperature arrival depends on the distance travelled and the sediment porosity. As long as these parameters are estimated reasonably correctly, the delay predicted should be reasonably robust.

SUMMARY AND CONCLUSION

We have proposed a method to translate chemical alterations at the core scale to the field scale. One set of rate constants was found to match effluent profiles from core floods at 130°C where $MgCl_2$ was flooded at 1PV/day in one core and in another case the flooding rate was changed from 3PV/day to 1PV/day. The same set of rate constants was also used to predict effluent profiles when seawater like brine was flooded at 1PV/day at 130°C. These rate constants were then applied to predict chemical alteration when seawater at 25°C is injected into a calcite-rich reservoir formation at 130°C and at typical Ekofisk injection rates. The alteration predicted by the flow line model seems to fit well with the observations from one of the production wells at the Ekofisk field. Sulphate, and magnesium stripping is observed in the produced water which indicates that the injection water induces chemical alterations in the reservoir. The predicted alteration in the model is strongly related to the activation energy, if the activation energy is 65kJ/mol, the alteration extends 400m from the well with a 1wt% change in calcite close to the injection well. If the activation energy is close to 20kJ/mol, the alteration only extends 100m from the well, but the alteration close to the well is 35wt%, where calcite has been converted to dolomite. The chemical alteration is tightly connected to the temperature front, and it could be possible to extract information about the temperature front from produced water ion analyses.

ACKNOWLEDGEMENTS

Table 1: Ekofisk formation and injection water (seawater) compositions used in the predictions and calculation of injection water fraction in the produced water (field data)

Ions	EF Water mmol/L	Seawater mmol/L
Na^+	1142.8	484.6
K^+	7.4	10.3
Mg^{2+}	21.9	53.6
Ca^{2+}	99.9	10.5
Cl^-	1423.2	561.9
SO_4^{2-}	0.0	27.9
HCO_3^-	3.9	2.4

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