Modelling the thermodynamic behaviour of the carbonate system: Application to the prediction of carbonate scaling in oil-field brines

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Carbonate scaling in the wellbore and near-wellbore region of hydrocarbon reservoirs is a major production problem in the North Sea oil fields. Carbonate scale formation mainly results from changes in physical-chemical properties of fluids (i.e. pH, pCO_2, T and P) during production or from chemical incompatility between injected water and formation water. Scale can impair productivity dramatically, thereby increasing hydrocarbon production costs. Prediction remains notoriously difficult, mainly due to difficulties for modelling the thermodynamic behaviour of the carbonate system in high salinity solutions at high temperature and pressure (HS/HT/HP). The Debye-Hückel approach, used for fluids of ionic strength (IS) lower than 0.1 molal, is not applicable to most oil-field brines (typical IS between 0.5 and 5 molal). True activities of dissolved species, accounting for all specific interactions between ions, must be known. The most comprehensive model to calculate activities in brines is the specific ion interaction model of Pitzer. A Pitzer-based computer model, e.g. SCALESIM, is thus being developed as part of an on-going EC-funded project (Qc-Scale; contract JOF3-CT95-0009) for prediction of carbonate scale in oil production operations.

SCALESIM: A Pitzer-based geochemical simulator

The simulator SCALESIM was generated within the ALLAN-NEPTUNIX environment according to the Specific Chemical Simulator approach developed at BRGM (Kervévan and Baranger, 1998, this meeting). SCALESIM calculates aqueous speciation, mineral saturation indices, mineral solubilities and reaction paths, and is specifically designed for HS/HT systems. It integrates the extensive set of Pitzer equations (Greenberg and Moller, 1989) and calculates activity coefficients for the Na-K-Ca-Cl-SO$_4$-OH-H-Ac-CO$_3$-HCO$_3$-CO$_2$-AcH-SiO$_2$-H$_2$O system from 0 to 250°C at Psat. CaSO$_4$(aq) and CaCO$_3$(aq) complexes are explicitly recognized in the system. The Pitzer parameters used in SCALESIM include those validated by Greenberg and Möller (1989) for the Na-K-Ca-Cl-SO$_4$-H$_2$O system between 0 and 250°C, and parameters determined and partially checked in this study for the Na-K-Ca-Cl-SO$_4$-H-OH-HCO$_3$-CO$_3$-CO$_2$-SiO$_2$-H$_2$O system. The dielectric constant of pure H$_2$O, computed after Bradley and Pitzer (1979), was used to calculate the Debye-Hückel parameter A^{ϕ}. The resulting value (0.39147) at 25°C and 1 bar agrees well with the value (0.39145) of Ananthaswamy and Atkinson (1984). This check is a critical step to verify the internal consistency of the model when the chemical system is extended and/or Pitzer parameters added.

The computational soundness of SCALESIM is illustrated in Fig. 1 which compares values of the first (Q1) and second (Q2) ionization quotients of CO$_2$(aq) in 5m NaCl solution determined experimentally by Patterson et al. (1982, 1984) with values calculated with SCALESIM.

Further evidence is provided in Fig. 2. The temperature dependence of calcite solubility computed with SCALESIM agrees well with the experimental data of Ellis (1963).

Application to oil-field brines: preliminary results

SCALESIM was used to calculate the saturation indices of carbonate minerals for typical formation waters from five different oil fields in the North Sea, and compared to values calculated with the B-dot model (using EQ3NR). The investigated brines have TDS values ranging from 68 to 292 g/l, and reservoir
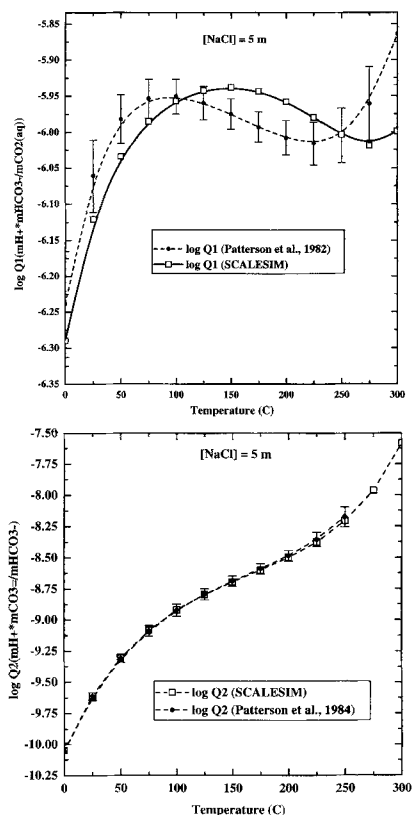
FIG. 2. Solubility of calcite in NaCl solutions at $pCO_2 =$ 12 bar as a function of temperature.

FIG. 1. Computed and measured values of Q1 and Q2 of CO_2(aq) in 5 m NaCl solution as a function of temperature.

temperatures range from 96 to 154°C. Results for calcite are shown in Fig. 3.
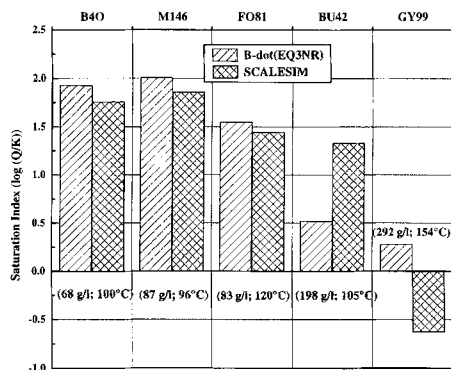
The difference in saturation indices calculated with the two models are small, nearly insignificant, for Na-Cl fluids with low TDS values (<100 g/l) such as B40, M146 and FO81. In contrast, the two models yield significantly different saturation indices for the more complex (Na-Cl-Ca) and saline(TDS > 100 g/l) fluids BU42 and GY99. In the case of GY99, the two models predict opposite saturation states, i.e. under-saturation with SCALESIM versus oversaturation with EQ3NR (Fig. 3). These results illustrate that the use of the Debye-Hückel approximation to describe the thermodynamic behaviour, hence the scaling potential, of complex, high-salinity oil-field brines at elevated temperature may lead to large errors. The Pitzer-based approach, as used in SCALESIM, is considered to yield more accurate predictions.

Similar comparisons, conducted for more concentrated brines (TDS 300 g/l) from the Jurassic carbonate Smackover Formation (Arkansas, USA) lead to similar conclusions.

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FIG. 3. Calcite saturation indices calculated using Scalesim and EQ3NR for typical North Sea brines.