Multiscale modelling of supercritical outsalting

TATYANA KUZNETSOVA[2], MARTIN HOVLAND[1], HÅKON RUESLÅTTEN[3], BJØRN KVAMME[2], HANS KONRAD JOHNSEN[4], GUNNAR FLADMARK[5]
[1]Statoil,
N-4035, Stavanger,
NORWAY
[2]Department of Physics,
University of Bergen
Allėgt. 55, 5007 Bergen,
NORWAY
[3]NumericalRocks,
N-7000, Trondheim,
NORWAY
[4]Statoil, R&D Department,
Rotvoll, N-7000 Trondheim,
NORWAY
[5]Department of Mathematics,
University of Bergen,
N-5000 Bergen,
NORWAY
http: http://web.ift.uib.no/php/php/bkvamme.html

Abstract: - Supercritical water has extremely low solubility for normal sea salts. This fact opens up the possibility for the precipitation of salt from seawater that circulates in faults and fractures close to a heat source in tectonically active basins (typically extensional pre-rifts and rift settings). Salts may also precipitate by the boiling of seawater in sub-surface or submarine settings. The theoretical basis for salt precipitation out of seawater attaining certain supercritical regions and its geological ramifications have been examined by molecular modeling and reservoir-scale simulations.

Key-Words: - supercritical brine; water; reservoir modeling; outsalting

1 Introduction

Although the solar evaporation of seawater has long been established as the main origin of terrestrial salt deposits, salt formation by hydrothermal processes is also known to contribute volumes of salts as geological deposits [1, 2]. There exist, however, two basic thermal processes, which have not been seriously addressed, salt precipitation by seawater reaching a certain supercritical region, and salt formation by submerged boiling of seawater. The currently widely accepted conventional evaporite theory states that large and thick salt deposits were formed by solar-induced evaporation of seawater. Despite there being numerous paradoxes and unsolved problems with this model, as admitted and discussed by Warren [2], modern geological literature often treats it as entirely unproblematic. Recent discussions, however, clearly illustrates the severe lack of fundamental data, especially from the deepest portions of salt basins, which prevents us from a full understanding of these economically important deposits and their development through time. Salts readily precipitate from seawater when heated under pressure to beyond the critical point; the large-scale effects of this outsalting in a model lithology were investigated by us in ATHENA reservoir simulator [3]. This 'new' type of hydrothermally produced salts may be more common, abundant, and complex than hitherto realized

2 Salt crossover behavior and brine properties: molecular simulations

We studied the regions of salt precipitation using Molecular Dynamics simulations. SPC/E model [4] was chosen for the description of water-water interactions. The Na^+ and Cl^- ions were modeled using the model by Smith and Dang [4]. Cross interactions were calculated from the standard Lorenz-Berthelot mixing rules [6]. Our model brine system comprised 512 water molecules and 6 molecules of sodium chloride, corresponding to approximately 3.7 wt% salt content. Simulations were performed in a closed system at constant pressure and temperature. The thermostat parameter in the Nose-

Hoover formulation [7, 8], were fixed to 100 fs. The pressure control parameter was set to 8000 fs. Rotational degrees of freedom were handled using an implicit quaternion scheme [9]. Long-range forces were handled using the Ewald summation approach [6]. The simulated structures were in excellent agreement with previous simulations of similar model systems [10, 11, 12].

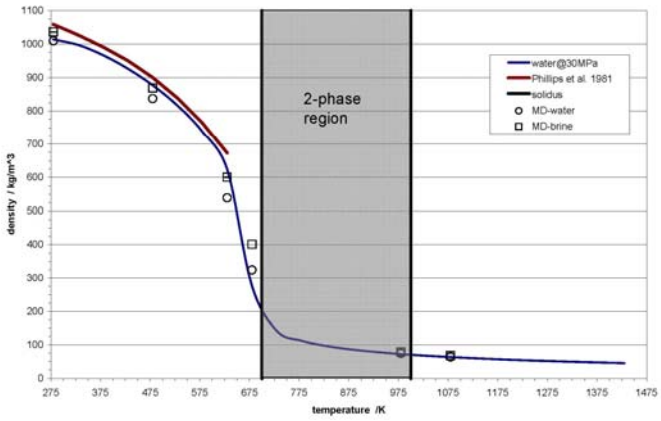

Figure 1: Density of water and 5 % wt. brine as functions of temperature along the 300 bar isobar. Red line is EoS from Phillips et al. [13]; blue line is IAPWS-95 [15]; circles are MD results for pure water; square, MD results for brine.

Figure 1 shows the density of brine as a function of temperature at 300 bar as simulated from Molecular Dynamics simulations together with data from Phillips et al. [13] and the two phase limits of Hodes et al. [14] at 300 bar. When salts dissolve into water, one can distinguish between two different types of configurations: the solvent separated ion pair (SSIP) and the contact ion pair (CIP) configurations. In case of the former, each ion is fully solvated, and the ions are thus screened from each other by their hydration shells (SSIP). CIP, on he other hand, involves an ion pair within the same hydration shell. When in the CIP configuration, the ions behaves almost like dipoles. Figure 3 makes use of the Na^+-Cl^- pair-correlation functions to describe the drastic differences in the strength of solvation at several temperatures below and above the two solidus lines. Note the dramatic changes in the first (CIP) and second (SSIP) peaks of the Na+-Cl- correlation function. A complementary evidence for the different solvation structure was supplied by average coordination numbers for Na+ and Cl- ions. As the temperature increased, the hydrogen-bonded structure of water underwent dramatic changes with two trends emerging. First, the height of the oxygen-oxygen peak (reflecting the strength of the hydrogen-bond structure) decreases with increasing temperature. The lack of any long-range structure at high temperatures was also quite pronounced; water started to behave as a non-polar fluid unable to dissociate dissolved salts. On the other hand, in the same fashion as the effect of the water's dipole moment nearly vanishes at high temperatures, so does the interaction effects of the ion charges albeit at a slower rate. Thus at sufficiently high temperatures, the neutral pairs of ions will dissolve into the supercritical water as non-dissociated salt.

3 Geological Effects of Outsalting: Athena Reservoir Simulator

In order to numerically simulate the spontaneous and rapid precipitation of salt ('outsalting') from seawater as it passes into the SC region, we used the ATHENA reservoir simulator [3] to simulate a representative example of hydrothermal seawater flow. Our numerical model aimed to reproduce a basaltic intrusion occurring at a depth of about 3,000 m. The ATHENA simulator takes temperature, water pressure, and molar masses for each fluid component as its primary variables. A control volume finite-difference box-centred space discretization technique was employed together with a backward Euler scheme for time discrimination of the water pressure and temperature equations and an explicit solver for the mass balance.

The geological domain under study involved a region 3000 m beneath the water surface with dimensions 5 m x 20 m x 220 m. There were three different layers in the *z* direction: sandstone, shale, and sandstone. The sandstone was assigned the porosity, , of 0.35 and permeability, *K*, of 230 mD, shale had = 0.1025 and *K* = 2.9 mD. The boundary conditions included constant pressure of 32 MPa at the sill intrusion points, and 30 MPa at the sea floor. The simulator program added or removed brine from the top or the bottom of reservoir to keep the pressure constant. This yielded an upward water flow. Temperatures were kept fixed at roughly 1400 K and 280 K, for the sill-intrusion and seafloor levels, respectively. The whole domain was subdivided into cells of 5 m height.

Pure water properties were used in the first simulator run. These properties are obtained from the IAPWS-95 formulation of Wagner & Pruss [15], tabulated with the step of 50 K. The actual brine simulations employed temperature spacing of 100 K, with brine enthalpy and density data obtained from molecular modeling described above. Pure water viscosity was used for both water and brine. Instead of modeling a complicated two-phase-system, a quasi-one-phase system was simulated.

The following scenario was proposed to justify this approach: outsalting may occur only at temperatures corresponding to the upper solidus line for pressures equal to 30-32 MPa (980-1020 K [16], see Fig. 1). Thereafter, the brine will be salt-free (pure water) until the upward flow crosses the lower solidus line of Figure

1. Here the salt content of brine is restored due to mixing with the existing brine. The precipitation of salt at the upper solidus line will block the pores and result in decreased porosity and permeability of the given cell. To incorporate this effect of outsalting, we scaled cell porosity by a constant factor, and then applied a simple porosity-permeability correlation to describe the resulting change in permeability. Allowing the porosity to vary during the simulation required slightly longer iteration time to reach steady state.

We have tried several different combinations of porosity and permeability of the sandstone and shale layers. None of this affected the temperature profile; it remained essentially linear and identical to that of pure water. No drift of the outsalting front has been observed either, validating our scenario. On the other hand, the reservoir simulation results displayed in Figures 2 and 3 show that, unlike temperature, pressure and flow velocity have proved to be very sensitive to the variations of porosity and permeability. Figure 2 especially illustrates the effects of the outsalting: the blocking of pores caused by salt deposition leads to an establishment of a stable low-permeability layer. This layer will give rise to a substantial pressure drop over a relatively small region (20 m) and its existence may have drastic practical consequences including unexpected pressure buildup during exploratory boring. The flow velocity profile of Fig. 2 is also quite instructive; though the outsalting will clearly have an impact on the velocity gradient, the effect will manifest itself quite further downstream from the outsalting front.

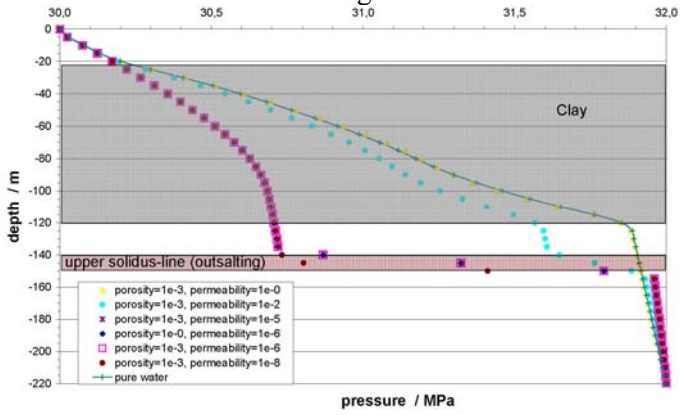

Figure 2: Simulated injection of supercritical brine into a three-layer reservoir: pressure profiles corresponding to different combinations of porosities and permeabilities.

Acknowledgements

We would like to thank Drs. Peter Dietrich, Detlev Leythaeuser, Marian Holness, Klaus Wallmann, and Cristian Hensen for valuable discussions and constructive advice. Special thanks to René Jonsson and Nick Johnston onboard 'Normand Tonjer' for fruitful discussions. We will also thank all of those in Statoil who have contributed with challenging discussions, especially the Nordkapp Basin Group in Statoil-Harstad, Dr. Per Arne Bjørkum; and finally our seniors in Statoil who have provided the opportunity to develop this model and who have given the permission to publish the results.

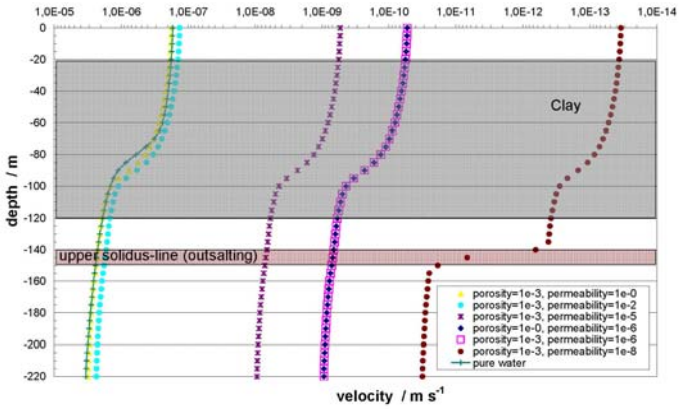

Figure 3: Simulated injection of supercritical brine into a three-layer reservoir: velocity profiles corresponding to different combinations of porosities and permeabilities.

References:

[1] Lowell, R.P.& Germanovich, L.N., 1997. Evolution of a brine-saturated layer at the base of a ridge-crest hydrothermal system. Journal Geophys. Res. 102 (B5), 10, 245-10, 255.

[2] Warren, J.K., 1999. Evaporites: Their evolution and economics. Blackwell Science, Oxford, pp. 438.

[3] SMITH, D.E. & DANG, L.X. (1994) Computer simulations of NaCl association in polarizable water, *J. Chem. Phys.*, 100, 3757.

[4] Berendsen, H.J.C., Grigera, J.R., and Straatsma, T.P. The Missing Term in Effective Pair Potentials. *J. Phys. Chem.* 1987, **91,** 6269-6271.

[5] Garrido, I., Fladmark, G.E., Espedal, M. (2004) An improved numerical simulator for multiphase flow in porous media. *Int. J. Num. Meth. Fluids*, **44**, 447-461.

[6] Allen, M. P., Tildesley D. J., 1987. Computer Simulation of Liquids. Clarendon, Oxford.

[7] Hoover, W.G., 1989. Generalization of Noses isothermal molecular-dynamics – non-hamiltonian dynamics for the canonical ensemble. *Physical Review A* 40, 2814-2815.

[8] Nose, S., 1984. A molecular-dynamics method for simulations in the canonical ensemble. *Molecular Physics* 52, 255-268.

[9] Fincham, D., 1992. "Leapfrog rotational algorithms". Molecular Simulation, 8, p. 165-178.

[10] Lyubartsev, A.P., Laaksonen, A. M.DynaMix - a scalable portable parallel MD simulation package for arbitrary molecular mixtures. *Computer Physics Communications* 2000, **128**, 565-589.

[11] Driesner, T., Seward, T.M., Tironi, I.G., 1998. Molecular dynamics simulation study of ionic hydration and ion association in dilute and 1 molal aqueous sodium chloride solutions from ambient to supercritical conditions. Geochimica et Cosmochimica Acta 62(18), p. 3095-3107.
[12] Chialvo, A.A., Simonson, J.M., 2003. Aqueous Na+Cl- pair association from liquid like to steam like densities along near critical isotherms. J. Chem. Phys., 118(17), p. 7921-7929.
[13] Phillips, S.L., Igbene, A., Fair, J.A. Ozbek, H., Tavana, M., 1981. A Technical Databook for Geothermal Energy Utilization". Lawrence Berkley Laboratory Report, 12810.
[14] Hodes, M., Griffiths, P., Smith, K.A., Hurst, W.S., Bowers, W.J., Sako, K., 2004. Salt solubility and deposition in high temperature and pressure aqueous solutions. AIChE Journal, 50 (9), 2038-2049.
[15] WAGNER, W., PRUß, A., 2002. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Phys. Chem. Ref. Data*, **31**, 387 - 535.
[16] Palliser, C., McKibbin, R., 1997. A model for deep geothermal brines, I: T-p-X state-space description. Transport in porous media, 33, 65-80.