Modeling the properties of geothermal two-phase multi-component fluids

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Estimating the properties of the multicomponent geothermal fluids are requisite. Imprecise knowledge of geothermal water properties, e.g. isobaric heat capacity, leads to inaccurate knowledge of geothermal water heat content and thus to inaccurate knowledge of heat input to geothermal power plants (Schröder et al., 2015). In early geothermal process simulations the geofluids were idealized as pure water, nonetheless many geothermal reservoirs contain significant amounts of salts and non-condensable gases (NCGs) including H_2S, N_2, NH_3, H_2, CH_4 and CO_2 (Michaelides, 1982), where the mass fractions of gases could be as high as 10 percent (Fatma Bahar Hosgor, 2015).

Presence of salts and/or non-condensable gas can seriously complicate any geothermal fluid simulation. For instance, by diss/exsolution of salts and/or NCG, density of the geofluid can be significantly affected. The density has a strong influence on the calculated volumetric flow-rate of the production pump (Francke and Thorade, 2010). In case of the thermosiphon doublet, density affects the thermosiphon effect, i.e. mass flow-rate of geofluid which is generated by the density difference of the geofluid between injection and production wells (Adams et al., 2014). In other circumstances, NCG breakout (exsolution) plays important role to scaling of some precipitant, i.e. calcite, stibnite, which are associated with CO_2, H_2S concentration ex/dissolved in brine (Baran Kaypakoglu, 2015). (Grimes, 2013) showed that sulfide stress corrosion cracking of low-alloy steels is correlated with the fugacity (or equivalently activity) of H_2S. Salts and NCGs would also obscure accurate pressure-drop computations in geothermal wells (Hasan and Kabir, 2010). Furthermore, the properties of water-salts-NCG is prerequisite for geo-pressurized resources and carbon capture storage hybrid simulation. The potential for compensating the cost of CO2 capture and storage by producing large quantities of valuable methane and geothermal energy is obviously significant (Ganjdanesh et al., 2013).

Consequently, more realistic representations of geothermal fluids must include salts and NCGs. The common independent variables of the properties of the salts/NC-gases are pressure and temperature (p, T), however the thermodynamic state of two-phase fluid have to be defined by specifying any other combination of two independent state properties. In fluid simulation, the known variable are usually pressure and specific enthalpy (p, h). Therefore, the Equation of State (EOS) described in this study will be based on them. It consisted of mainly two models (1) Vapor-

Liquid Equilibrium (VLE) of liquid (aqueous) and gas (non- aqueous) phase, (2) thermophysical properties, i.e. density, isobaric heat capacity/enthalpy, viscosity, and thermal conductivity.

To develop the VLE or gas solubility model, generally two approaches are used, that are fugacity-fugacity $(\phi - \phi)$ and fugacity-activity $(\phi - \gamma)$. The first term $(\phi - \phi)$ uses one EOS to compute fugacity of all phases in equilibrium, and the equations are solved by fugacity equality of different phases. Recent examples are involving work of (Li et al., 2015) on modification of (Ingolf Soreide, 1992) model. It can reproduce single-gas and gas-mixture – brine experimental data with good accuracy. Nevertheless, the effect of other electrolytes (salts) which commonly exists in geothermal system has not been included. Further, (Battistelli and Marcolini, 2009) lately took an important step by presenting the EOS TMGAS coupled into TOUGH2 to model brine and gas mixtures (CO_2, H_2S and hydrocarbons). The TMGAS model can accurately reproduce the gas–brine equilibrium in wide temperature and pressure range. Nevertheless, for salt molality higher than 2 mol/kgw, the accuracy derived from the comparisons with the experimental data declines.

The second term, $(\phi - \gamma)$ predicts the gas solubility by implementing ideal gas, virial, or cubic, e.g. Peng-Robinson (PR), Soave Redlich Kwong (SRK) equation to compute gas (non-aqueous) phase fugacity. While, the activity model is used for coefficient of liquid (aqueous) phase calculation. The equations are solved with chemical potential equality of both phases. Recent work of this approach is presented by (Springer et al., 2015) on extension of speciation based model for mixed-solvent electrolyte systems (Peiming Wang, 2002) to comprise CO_2–H_2S–brine system. Unfortunately, not all details of the EOS seem to have been released in publications, e.g. TMGAS and (Springer et al., 2015), which are proprietary software. Thus, they are not easily available or reproducible for broader academic investigations in geothermal energy. Duan Research Group, gave wide-ranging studies for the single gas component solubility in pure water or brine measurements of CO2, N2, CH4 and H2S (Duan and Mao, 2006; Duan et al., 2006; Mao and Duan, 2006; Mao et al., 2013; Zhenhao Duan, 2003, 2007). But their work does not implicate about gas mixture solubility which is of more practical significance in actual field applications. (Francke et al., 2013) has unified these Duan’s single-gas solubility functions to model CO_2–N_2–CH_4 mixture solubility. However, it still considers the gas phase as an ideal gas (fugacity coefficients equal to unity) which tends to fail at higher pressure and for gas with strong intermolecular forces, i.e. water-vapor. While, to calculate the solubility, fugacity of pure gas system is used with sum of water-vapor and gas partial pressure as input to the auxiliary functions.

The VLE model in our work is also based on fugacity-activity $(\phi - \gamma)$ approach, which is more computational efficient (less iterative) than fugacity-fugacity approach. The model is based on improvements of (Francke et al., 2013) model. It uses Peng-Robinson real-gas equation for fugacity calculation and fusion of Duan Research Group solubility models for each NCG – brine system to address gas-mixture, with total pressure as input to the auxiliary functions since it corresponds to aqueous-phase pressure. This model covers mixture of CO2–N2–CH4–H2S and brine of Na+, K+, Mg2+, Ca2+, Cl- and (HCO3)-.

The thermophysical properties model, i.e. density, isobaric heat capacity/enthalpy, viscosity, and thermal conductivity are already assembled by some workers for single electrolyte (salt) or seawater. But, the accurate models of mixed electrolytes (salts) system is mostly available only for density. (Francke et al., 2013) describes detailed model of geofluid thermophysical properties (not only density) which is limited to NaCl, $CaCl_2$, and KCl. In our paper, parameters of other salts, i.e. $MgCl_2$, $NaHCO_3$, were added. Improvement on explicit model for enthalpy, effect of dissolved gas, and gas (non-aqueous) phase properties were also carried out.

The results is delivered as a pressure-enthalpy (p,h) based EOS for geothermal fluid by fusion of H2O-salts binary and brine-NCG binary systems. It delivers easy-to-reproduce, open-source, and merely extendable or replaceable EOS. The phase partitioning model covers pressure, temperature, and salt molality up to 60 MPa, 227 ºC, 4.5 mol/kgw for the system CO2 – N2 – CH4 – H2S – brine; 100 MPa, 227 ºC, 4.5 mol/kgw for the system CO2 – H2S – brine, as can be seen in Fig. 1; 150 MPa, 300 ºC, 4.5 mol/kgw for the system CO2 – CH4 – brine. These validity ranges is sufficient for mid-enthalpy geothermal reservoir/wellbore simulation. For simplified model of the system CO2 – H2O – NaCl, the model is valid up to 150 MPa, 460 ºC, ∞ mol/kgw (halite) which is suitable for very high-enthalpy application, e.g. supercritical resources. The phase partitioning of this system can be seen in Fig. 2.

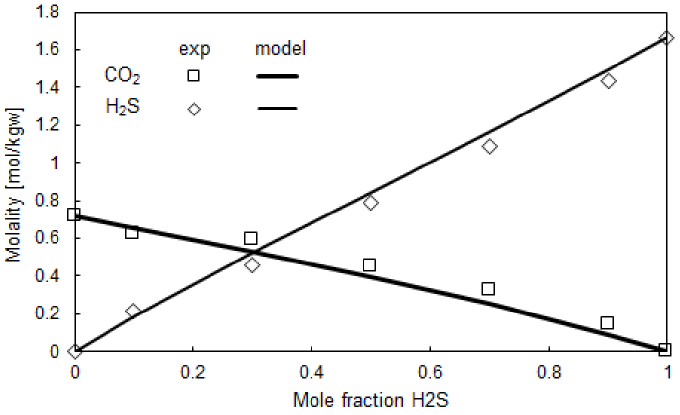

Figure 1 Molality of CO_2 and H_2S varying with H_2S mole fraction in dry gas-phase: Dots are calculated results from (Bachu and Bennion, 2009), and predicted values (solid lines). The experiment was set according to $\mathrm{p} = 13.5\ \mathrm{MPa}$ and $\mathrm{T} = 61°\mathrm{C}$, with NaCl concentration of 11.9% (mass fraction).

The present model has been validated using a complete dataset of the VLE and thermophysical properties of geofluid in the temperature range between 32 and 177 ºC under conditions corresponding to total pressure of 0.5 – 50 MPa, which represents conditions for geothermal applications. The evaluation of properties was based on a comprehensive literature review for the appropriate selection of the most widely acceptable procedures and methods as well as NCGs and water thermophysical properties, which were employed as input parameters for the calculations.

At lower temperature, when the heat has been extracted, salts tend to precipitate. Hence, we would like to accurately predict solubility of salts by implementing additional geochemical speciation solver, such as PHREEQC.

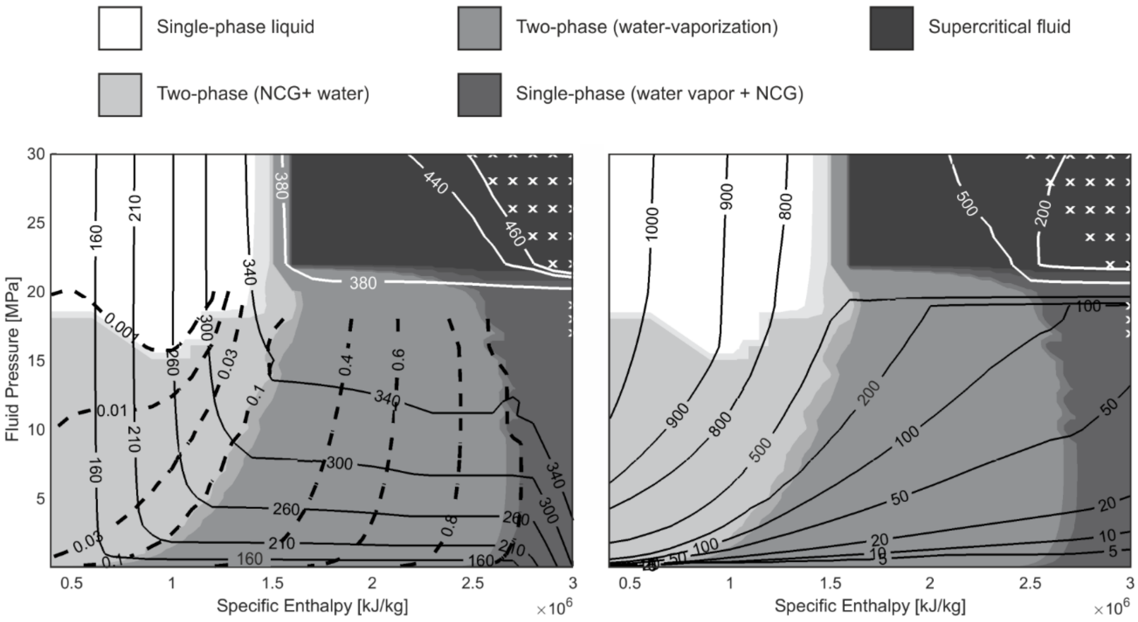

Figure 2 Phase diagram of geofluid with 3 wt% CO2 and 10 wt% NaCl. Solid lines depict the temperature profile. Dashed lines show the gas (non-aqueous) phase quality. x point indicates zone outside the validity range of CO_2 solubility model.

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