Multiphase equilibrium flash with salt precipitation in systems with multiple salts

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ABSTRACT

A new methodology for determining simultaneous chemical and phase equilibrium of mixtures of light gases and aqueous electrolyte solutions with the potential for multiple salt deposition is proposed. The novel aspects of this new approach include, but are not limited to (1) a novel tearing algorithm for determining equilibrium ion solubility limits, (2) rigorous proof that the proposed tearing algorithm generates a Cauchy sequence and is therefore guaranteed to converge to the correct equilibrium ion solubility limits (3) and a unique formulation of the combined chemical and multi-phase equilibrium flash problem that accounts for salt deposition but decouples the chemical and phase equilibrium aspects of the flash.

Examples from real EOR and CO_2 sequestration applications are presented. Results clearly show that the proposed numerical approach is reliable, robust, and efficient and can be used to determine salt deposition in multi-phase flash problems. Several geometric illustrations and numerical details are used to elucidate key points of the proposed approach.

1. Introduction: motivation and background

Groundwater aquifers and seawater generally contain a number of ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Cl^-, SO_4^{2-}, CO_3^{2-}, and others. At high enough concentrations, these ions can combine and form salts and precipitate out of solution causing operational difficulties in a wide range of applications. Salt deposited on heat exchange equipment can cause poor heat transfer. A common example of this is scaling on a household water heater from 'hard' water (i.e., water with high levels of calcium, magnesium and carbonate ions). In enhanced oil recovery (EOR) operations, production water containing a wide range of ions is often re-injected into a reservoir in order to avoid the use of municipal water and/or costly water treatment. However, re-use of production water can result in salt deposition, which in turn can plug pores, block injection wells, and/or re-direct or sometimes stop flow through porous media. In CO_2 sequestration, deposition of calcium carbonate can be either a blessing or a curse, depending on where

deposition occurs. Obviously it is desirable if deposition in CO_2 sequestration occurs far from injection well bores. Salt deposition is also important for reservoir modelers to understand, predict, and quantify so that reservoir simulation results correctly reflect physics. In EOR and CO_2 sequestration problems, multiple equilibrium phases often exist within a reservoir due to the presence of light gases and water. Thus the quantification of salt precipitation when multiple salts can form must be considered in conjunction with multi-component, multi-phase equilibrium flash problem, which is a combined chemical and phase equilibrium problem.

1.1. Organization of this article

In this article, a new equation-solving approach to determining simultaneous chemical and phase equilibrium for mixtures of light gases and aqueous electrolyte solutions with the potential for multiple salt deposition is described. Section 2 gives a brief summary of the relevant literature. Basic

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Nomenclature

A	anion
$[A]$	anion concentration
C	cation
$[C]$	cation concentration
$[c_j]$	concentration of the jth ion
$F(z)$	set of nonlinear equations
ΔG_f^0	standard Gibbs free energy of formation
$G(y)$	fixed point map
$G'(y)$	Jacobian matrix of fixed point map
ΔH_f^0	standard enthalpy of formation
K_{sp}	equilibrium solubility product
n_c	number of components
n_A, n_C	number of distinct anions, cations
n_p	number of fluid phases
n_s	number of molecular salt phases
p	pressure
Q_{sp}	ion solubility product
R	gas constant
T, T_0	temperature, reference temperature
v_A, v_C	stoichiometric numbers for anion, cation
x	vector of cation concentrations
y	vector of anion concentrations
z	vector of unknown variables

Greek Symbols

$\phi, \phi\pm$	fugacity coefficient, mean fugacity coefficient
γ	activity coefficient
λ	eigenvalue
μ	chemical potential
ρ	spectral radius

Subscripts

0	initial value
c	component
A	anion
C	cation
f	formation
i	ith component or ith unknown variable

Superscripts

0	standard state
k	iteration counter
*	solution or fixed point

equations and formulations for equilibrium flash, equilibrium ion solubility limits, and the combined chemical and phase equilibrium problem of interest are described in Section 3. Section 4 gives the details of a novel tearing strategy for determining equilibrium ion solubility limits. In particular, cation concentrations are used as unknown variables in an inner loop that enforces mass balances for all species while anion concentrations are used as the outer loop variables to converge chemical equilibrium conditions. Section 5 presents numerical results for two isothermal, isobaric (TP) flash problems with salt deposition. Concluding remarks are given in Section 6.

2. Literature survey

The open literature on multi-phase flash abounds and dates back many years. Thus citation of all papers is not possible. Some of the more notable methodologies and articles for multiphase flash include the inside-out algorithm (Boston and Britt, 1978), tangent plane analysis (Michelsen, 1982a,b), the negative flash (Whitson and Michelsen, 1989), the Mixed Integer Nonlinear Programming (MINLP) approach of McDonald and Floudas, 1995), interval Newton-bisection methods (Stadtherr et al., 1995), homotopy-continuation (Sun and Seider, 1995), and the successive quadratic programming approach (Lucia et al., 2000). Notable methods and articles that address single and homogeneous multi-phase chemical reaction equilibrium include linear programming (White et al., 1958), an equation-tearing approach (Sanderson and Chien, 1973), nonlinear programming (Castillo and Grossmann, 1981), and the work of Smith and Missen (1982).

Elementary information regarding *heterogeneous* chemical equilibrium, equilibrium solubility products, and common ion effects can be found in many standard textbooks on chemical engineering thermodynamics. We refer the reader to the textbooks by Sandler (1999) and Elliott and Lira (2012), which give basic theory for dilute solutions and/or common ion effects involving only a single common ion. In many practical situations, the problem of potential salt deposition can involve a large number of ions.

Although combined chemical and phase equilibrium is well studied in the chemical engineering literature, there is surprisingly little information in the open literature on equilibrium solubility and salt precipitation in the presence of multi-phase behavior and certainly no description of numerical methods for addressing the unique set of computational challenges that characterize these problems. In addition, there is very little experimental solubility data on compounds like calcium and magnesium carbonate because they are considered sparingly soluble, despite the fact that these salts play an important role in carbon mineralization and as a more permanent means of carbon sequestration.

On the other hand, there are empirical correlations for estimating properties of electrolyte solutions (e.g., Lam et al., 2008). There are also more rigorous approaches for determining the solubility of ions in solution and their associated properties such as the use of (1) Debye-Huckel theory, (2) Pitzer expansions, (3) equation of state models (i.e., variants of the electrolyte Predictive Soave–Redlich–Kwong (ePSRK) by Li et al., 2001 and Kiepe et al., 2004), (4) variants of the SAFT equation (Behzadi et al., 2005), and (5) various activity coefficient models as studied by Raatikainen and Laaksonen (2005) and Mohs and Gmehling (2012). Moreover, there is a large body of experimental data for highly soluble chloride, nitrate and some sulfate salts; salts like NaCl, KCl, Na_2SO_4, etc. Unfortunately, all of the computational papers cited deal strictly with the determination of solubility. More importantly, none of the cited papers explicitly address the problem of combined chemical and phase equilibrium where multiple fluid phases and multiple solid salts can co-exist nor do they address the associated numerical issues that can arise.

3. Problem formulations

The problem of interest in this work can be conveniently divided into two parts – equilibrium flash and salt deposition.

3.1. Multi-phase equilibrium flash

The approach to the multi-component, multi-phase isothermal, isobaric equilibrium (TP) flash problem used in this work