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Scaling prediction based on thermodynamic equilibrium calculation — scopes and limitations

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Abstract

A comprising thermodynamic approach is presented to investigate the behavior of saline solutions with respect to $CaCO_3$, $CaSO_4$ and SiO_2 scaling in water treatment processes. The Pitzer activity coefficient model is used to describe the aqueous species activities and the corresponding equilibrium reactions are solved to determine the saline solution composition. A well evaluated parameter set for the system H-Na-Ca-Mg-OH-Cl-CO_3-HCO_3-CO_2-SO_4-HSO_4-SiO_2 at 25°C is compiled and applied for calculation of the pure scale solubilities as well as mixture effects such as $CaCO_3$/$CaSO_4$ coprecipitation and silica adsorption. New data on silica removal dependant on the saline solution composition are used to estimate the ratio of silicate formation and silica adsorption onto other precipitating salts. Whereas the saturation states for pure scales are found to be well predictable at varying conditions, only qualtitative estimations for mixed scale formation can be achieved. Here, the predictability by thermodynamic equilibrium calculation is shown to meet its present boundary and its valuable service for understanding the mechanisms of scaling and the species involved is highlighted.

Keywords: Scaling; $CaCO_3$; $CaSO_4$; SiO_2; Thermodynamic equilibrium; Pitzer model; Softening; Silica removal

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1. Introduction

The scaling phenomenon, the precipitation and deposition of sparingly soluble salts in process equipment remains to be a decisive factor in water treatment systems. Scale formation affects heat and mass transfer within the process equipment and causes increased operating costs due to scale inhibition measures, chemical cleaning and damaged equipment replacement. Moreover, the application of antiscalants restricts operational parameters (e.g. the top brine temperature at multi-stage-flash desalination process) and thus further decreases the process efficiency. The

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answer to this problem is a sound prediction of scaling propensities for optimum design of pretreatment steps and operating conditions.

The most commonly identified inorganic scalants in thermal and membrane desalination processes are calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$) and silica (SiO_2). The basic condition for scales to form is excess of the solubility limit, i.e. the solubility product at thermodynamic equilibrium. A broad range of short-cut scaling potential indices (SPI) is available to predict these limits for the single salts (several short-cut SPIs for calcium carbonate have been compiled (e.g. [1]); similar procedures for calcium sulfate have been offered (e.g. [2,3]). These formulas are designed for easy application and therefore take only few system parameters into account (e.g. pH, alkalinity, ionic strength, etc.). Effects of varying composition as well as coupled equilibria cannot be taken into account. A more profound but also more costly approach is to calculate scaling limits from the Gibbs Free Energy.

Thermodynamic equilibrium is characterized by a minimum value of the system Gibbs Free Energy, which can be calculated by a set of linear independent mechanism equations containing all the contributing species and reactions. The general form of these equations, the laws of mass action, read:

$$K = \exp\left(-\frac{\sum_i \nu_i \cdot \mu_i^{\mathrm{ref}}}{RT} \right) = \prod_i \left(a_i \right)^{\nu_i}$$

$$\sum_i \nu_i \cdot \mu_i^{\mathrm{ref}} = \sum_i \nu_i \cdot \Delta_f G = \Delta_f G$$

For a solution/precipitation reaction $S_{(s)} \leftrightarrow S_{(aq)}$ or $S_{(s)} \leftrightarrow A^+ + B^-$, the equilibrium constant is the thermodynamic solubility product. The ratio of the ionic activity product (IAP) and the solubility product (K_{sp}) is known as the saturation index (Ω) and can be used as a measure for scaling potential:

$$\Omega = \frac{IAP}{K_{sp}} \begin{cases} \leq 1: \text{no scaling potential} \\ > 1: \text{ scaling potential} \end{cases}$$

This approach has been used widely to investigate natural waters from the point of geochemistry (e.g. [4]). Here, the Pitzer model is widely accepted for calculation of the aqueous species activity (e.g. [5]). Only recently the application of this method to industrial scaling problems was introduced. Hamrouni and Dhabi [6] presented a microcomputer program incorporating the Gibbs Free Energy approach for scaling prediction in desalination processes. Huff [7] applied the geochemical modeling code PHREEQC to assess the potential for scale formation during reverse osmosis desalination. Sheikholeslami [1] proposed a Scaling Potential Index (SPI) for $CaCO_3$ based on Gibbs Free Energies.

In this study, the practicability of scaling prediction by thermodynamic equilibrium calculation is investigated. The scaling limits for calcium carbonate ($CaCO_3$), calcium sulphate ($CaSO_4$) and silica (SiO_2) in mixed electrolyte systems are computed by the equilibrium network method (see below) and compared to empirical data. These predictions can serve for determining the scaling propensity of raw waters as well as estimating the efficiency of pretreatment steps, e.g. softening measures. Whereas the pure mineral solubilities are shown to be well predictable for different scenarios, the phenomena of co-precipitation and mixed scales are not reproducible by an equilibrium approach. However, the results presented serve for defining scaling thresholds, for ruling out certain presumptions and for pointing out the next steps in research.

The equilibrium network method applied consists of graphical representation of the reactions