



# Chemical modeling for precipitation from hypersaline hydrofracturing brines



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## ABSTRACT

Hypersaline hydrofracturing brines host very high salt concentrations, as high as 120,000–330,000 mg/L total dissolved solids (TDS), corresponding to ionic strengths of 2.1–5.7 mol/kg. This is 4–10 times higher than for ocean water. At such high ionic strengths, the conventional equations for computing activity coefficients no longer apply; and the complex ion-interactive Pitzer model must be invoked. The authors herein have used the Pitzer-based PHREEQC computer program to compute the appropriate activity coefficients when forming such precipitates as BaSO<sub>4</sub>, CaSO<sub>4</sub>, MgSO<sub>4</sub>, SrSO<sub>4</sub>, CaCO<sub>3</sub>, SrCO<sub>3</sub>, and BaCO<sub>3</sub> in hydrofracturing waters. The divalent cation activity coefficients ( $\gamma_M$ ) were computed in the 0.1 to 0.2 range at 2.1 mol/kg ionic strength, then by 5.7 mol/kg ionic strength, they rose to 0.2 for Ba<sup>2+</sup>, 0.6 for Sr<sup>2+</sup>, 0.8 for Ca<sup>2+</sup>, and 2.1 for Mg<sup>2+</sup>. Concurrently, the  $\gamma_{\text{SO}_4^{2-}}$  was 0.02–0.03; and  $\gamma_{\text{CO}_3^{2-}}$  was 0.01–0.02. While employing these Pitzer-derived activity coefficients, the authors then used the PHREEQC model to characterize precipitation of several of these sulfates and carbonates from actual hydrofracturing waters. Modeled precipitation matched quite well with actual laboratory experiments and full-scale operations. Also, the authors found that SrSO<sub>4</sub> effectively co-precipitated radium from hydrofracturing brines, as discerned when monitoring <sup>228</sup>Ra and other beta-emitting species via liquid scintillation; and also when monitoring gamma emissions from <sup>226</sup>Ra.

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## 1. Introduction

Hydrofracturing technology has greatly enhanced America's ability to extract natural gas from vast geological formation such as the Marcellus and Utica formations in Pennsylvania, Ohio, West Virginia, and nearby states; and from the Barnett and Woodford, Exello/Mulkey, Green River, etc. formations in Texas and other Great Plains states. Using natural gas as fuel inherently releases less CO<sub>2</sub> per amount of energy generated than does coal or gasoline, because eight electrons are transferred per carbon atom when CH<sub>4</sub> + O<sub>2</sub> burns to form CO<sub>2</sub>. In contrast, only four to five electrons are transferred per carbon atom when burning coal or gasoline. In

order to develop this more sustainable natural gas as a fuel, however, considerable water must be employed—both first to develop the well, as propant-laden water is forced at very high pressure into the geologic strata that yield natural gas; and then also to convey the natural gas out of these mile-deep wells. This aqueous fluid is injected and extracted from these wells through repeated cycles. Since these geologic formations often host trapped salts, along with the organic detritus of these former oceans, each water circulation cycle causes more salts to accumulate into these hypersaline hydrofracturing brines—until near-saturation conditions may be reached. Salt levels often reach 120,000–250,000 in northeastern US regions, and up to 250,000–350,000 in dry Great Plains states regions. These levels are 4–10 times higher than in ocean water. These hypersaline brines potentially pose significant environmental challenges, since the brines cannot be released into fresh water sources without profoundly deteriorating that water quality. Moreover, these hydrofracturing brines can include species such as natural occurring radionuclides, trihalomethanes, arsenic and

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Nomenclature		$z_i$	ion charge of $i$ specie
A, B, b	Debye–Hückel parameters	<i>Greek symbols</i>	
$A^\phi$	Debye-Huckel slope factor (0.392 at 25 °C)	$\alpha_1, \alpha_2$	electrolyte type coefficient
$B_{MX}, B'_{MX}, C_{MX}$	ion interaction parameter for ions of opposite signs (Pitzer)	$\beta^{(0)}_{MX}, \beta^{(1)}_{MX}, \beta^{(2)}_{MX}$	$C^\phi_{MX}$ experimental coefficients for Pitzer interaction parameter of single cations with single anions.
COD	chemical oxygen demand	$\gamma_i$	single ion activity coefficient of aqueous species $i$ , kg H <sub>2</sub> O/mol
CPM	counts per minute	$\epsilon(i, k)$	interaction coefficient between the aqueous species $i$ and $k$ (SIT model)
DPM	Decays per minute	$\theta_{ij}$	experimental coefficients for Pitzer second virial interaction parameter for cation or anion pairs.
HSF	hydraulic stimulation fluid	$E\theta'_{ij}(I)$	unsymmetrical electrostatic mixing effects function (Pitzer)
I	ionic strength	$E\theta''_{ij}(I)$	high order ionic interaction term (Pitzer)
IAP	ion activity product	$\Phi_{ij}, \Phi'_{ij}$	experimental coefficient for Pitzer's third virial coefficient mixing parameter, were $c$ and $c'$ are different cations and $X$ is an anion
ICP-AES	inductively coupled plasma atomic emission spectroscopy	$\Psi_{cc'X}$	experimental coefficient for Pitzer's third virial coefficient mixing parameter, were $a$ and $a'$ are different anions and $M$ is a cation
$J_k, J'_k, \chi_k$	functions of the second virial interaction term (Pitzer)	$\Psi_{aa'M}$	
Kd	distribution coefficient for co-precipitation		
$K_{sp}$	solubility product constant		
M or c	cation		
$m_i$	molality of $i$ specie (mol/Kg)		
SIT	Specific Ion Interaction Theory		
TDS	total dissolved solids		
TOC	total organic carbon		
X or a	anion		

selenium, that could pose adverse environmental consequences if they are not properly managed (Vengosh et al., 2014). Yet further, the considerable flow rates of these hydrofracturing waters pose water allocation issues in water scarce areas (Hutchings et al., 2010; Kerr, 2010; Dominc et al., 2011; Fakhru'l-Razi et al., 2009). Herein we use the term hydrofracturing brines to include the hydrofracturing well-development fluids and flow-back fluids—which can be blended and treated together, and then returned as hydraulic stimulation fluid to the hydrofracturess.

In developing technologies for processing these hypersaline hydrofracturing brines, managers may seek to discern the suitability of unit operations that rely on such mechanisms as precipitating anions with cations. Although the conventional thermodynamics of such precipitation reactions are well-characterized by fundamental equations when salt concentrations are low, the relationships are far more complex when 12–30% of everything present in the brine is inorganic ions. Conditions with such high salt contents have rarely occurred in nature (Mantyla, 1987), although highly salty waters appear in the Dead Sea and other saline lakes, and in reverse osmosis brines (Siobhan et al., 1999; Bea et al., 2010; Felmy and Weare, 1986; Hajbi et al., 2011; Krumgalz, 2001; Lerman, 1967; Marcus, 1981). For example, Hajbi et al. (2011) experimentally monitored ions that remained dissolved in reverse osmosis brines as the brines were evaporated up to very high ionic strengths, as presented in Table 1 (see calibration of activity coefficient models to this data set below). This brine originated from the RO retentate of ocean water. The Hajbi data shows that the molality of these species in the supernatant increases with greater evaporation and higher ionic strength, until a threshold is reached where a given species precipitates. For example, Na<sup>+</sup> molality increased up to 4.1 mol/kg at  $I = 7.18$  mol/kg (410,000 mg/L TDS) while Cl<sup>−</sup> increased to 6.3 mol/kg. Then above that threshold, the Na<sup>+</sup> and Cl<sup>−</sup> molalities declined as NaCl precipitated. Intriguingly, at very high ionic strength, Mg<sup>2+</sup> became the predominant cation.

When salt levels are low, and thus the ionic strength ( $I$ ) is low, several equations can be employed to compute activity coefficients

(Bretti et al., 2006; Simon and Whitfield, 1991). The fundamental of all models relies in the Debye-Huckel theory, which accounts for electrostatic and long range interactions between ions in solution, and is valid for  $I < 0.005$  mol/kg. At higher concentrations, some additional terms must be added to the Debye-Huckel equation, obtaining the extended Debye-Huckel equation (for  $I < 0.8$  mol/kg), and the empirical Davies equation (for  $I < 0.5$  mol/kg). In more concentrated solutions, the short range and non-electrostatic interactions becomes significant, thus, requiring models with a more elaborated correction. The simpler approach is the Specific Ion Interaction Theory (SIT), which adds a linear term to the Debye-Huckel equation so as to account for specific short range interactions between aqueous species, while neglecting the interaction between same charge and uncharged species. In its original version, the SIT model has been reputed to accurately estimate activity coefficient values in the range of 0.5–3 mol/kg. However, some authors have identified specific electrolytes that they

**Table 1**

Ionic strength and molality (mol/kg) of reverse osmosis ocean brine that was evaporated to increasingly higher ionic strength (from Hajbi et al., 2011).

$I$ (mol/kg)	$m_{Na}^+$	$m_{Ca}^{2+}$	$m_{Mg}^{2+}$	$m_{K}^+$	$m_{Cl}^-$	$m_{SO_4}^{2-}$
1.050	0.651	0.017	0.090	0.017	0.816	0.047
1.212	0.660	0.020	0.099	0.018	1.052	0.050
1.419	0.745	0.022	0.115	0.025	1.268	0.056
1.579	0.830	0.025	0.133	0.027	1.397	0.061
2.092	1.255	0.034	0.156	0.033	1.824	0.069
2.675	1.450	0.035	0.225	0.041	2.328	0.112
3.248	1.843	0.030	0.277	0.054	2.766	0.131
3.988	2.194	0.021	0.390	0.062	3.459	0.140
5.730	3.090	0.011	0.523	0.090	5.340	0.184
7.179	4.083	0.006	0.711	0.102	6.307	0.243
7.300	3.750	0.003	0.872	0.171	6.053	0.282
7.893	3.430	0.003	1.131	0.188	6.164	0.367
8.755	2.731	0.000	1.607	0.346	5.941	0.515
10.291	2.203	0.000	2.290	0.430	5.785	0.758
12.635	0.686	0.000	3.680	0.544	5.904	0.855
13.924	0.398	0.000	4.677	0.545	5.212	0.746

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