

## APPLICATION OF THE PITZER'S APPROACH FOR AN ACCURATE DENSITY CALCULATION OF THE NATURAL AND INDUSTRIAL BRINES; A POSSIBLE IMPROVEMENT FOR GROUNDWATER FLOW MODELS

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### ABSTRACT.

Aqueous saline solutions are ubiquitous in both geological systems and engineering practices. With technological and industrial development, salts and saline fluids are more and more exploited for their physical chemistry properties and economical interests. Presently, one is able to apply some specific thermodynamic models (Pitzer, 1991) with more success to industrial and natural brines having a salinity as high as 10-fold that of sea water. A non-exhaustive list of highly saline waters can be drawn as following: high salinity irrigation waters, hydrometallurgy (e.g., Bayer process), ore deposits genesis systems (e.g., MVT-mineralizing brines), oil-brines production (i.e., Smackover Formation, North Sea field, Williston basin, Alberta basin), geothermal brines with well bore scaling (i.e., HDR exchanger in Alsace), and saline Lakes. The complexity of the chemical composition of these brines can induce important uncertainties on the quantification of the brine density, a crucial parameter for many quantification, if the classical simplistic relation density vs salinity is used. Hence, the specificity of dominant salts as their mixtures must be taken into account in calculations of the brine densities for groundwater modelind. A thermodynamic database of the parameters of Pitzer from the literature data (Monnin, 1999; Krumgalz et al., 2000;) valid for temperatures ranging from 0 to 100°C and of salinities up to saturation with various salts (i.e., Dead Sea) was compiled. A numerical module (DensPitz) using Pitzer equations was developed from the initial work of Monnin (1994).

0 25 50 75 100125150175200225250275300325350375400425

0.975

1.000

1.025

1.050

1.075

1.100

1.125

1.150

1.175

1.200

1.225

1.250

1.275

1.300

Hypersaline basins and lakes

Ore deposit systems

Geothermal systems

Density (g/cm<sup>3</sup>)

Salinity (g/kg H<sub>2</sub>O)

NaCl

CaCl<sub>2</sub>

MgCl<sub>2</sub>

KCl

NaBr

KBr

Na-Ca-Mg-Cl

BaCl<sub>2</sub>

Fig. 1 – Evolution of density (g/cm<sup>3</sup>) for specific salts (lines) and for some natural brines (symbols) at 25°C and 1 bar.

Figure 1 shows results of the computed density evolution for simple systems (NaCl, KCl; CaCl<sub>2</sub>, MgCl<sub>2</sub>, BaCl<sub>2</sub>, NaBr, KBr), complex system (Na/Ca/Mg/Cl with ratio 1:1:1:5) and some natural brines. The increasing salinities amplify the discrepancy between the computation results with

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Pitzer approach and simplistic approximation based on total salinity (equivalent NaCl). Figure 1 shows also the repartitions domains of natural brines. The need of using the Pitzer's approach is anticipated for the majority of the industrial, geothermal, oil and metalliferous brines. The mixtures between seawater and basinal brines of the oilfields (i.e., Sorbie and Mackay, 1999; and references therein) can induce significant variations; where only the calculation of the density with the Pitzer's approach is accurate. More detailed results of applications to geological and industrial systems will be presented.

**References:**

- Krumgalz B.S. et al. (2000) J. Phys. Chem. Ref. Data, vol. 29, pp. 1123-1140.  
Monnin C. (1994) Comp. Geosci., vol. 20, pp. 1435-1445.  
Monnin C. (1999) Chem. Geol., vol. 153, pp. 187-209.  
Pitzer K. S. (1991) Activity coefficients in electrolyte solutions, 2<sup>nd</sup> edn, CRC press, 542 p.  
Sorbie K.S. and Mackay E.J. (2000) J. Petrol. Sci. Eng., vol. 27, pp. 85-106.

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