12º CONGRESSO BRASILEIRO DE PESQUISA E DESENVOLVIMENTO EM PETRÓLEO E GÁS

TITTLE:

NUMERICAL SIMULATION FOR TUNED WATER INJECTION SCREENING IN ENHANCED OIL RECOVERY (TWIN): EVALUATION OF SURFACE REACTION EQUILIBRIUM CONSTANTS ON SURFACE POTENTIAL

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Abstract

This work presents the development of a tool designed to quantitatively estimate changes in the wettability of a reservoir rock. This rock is composed of a mixture of minerals, including calcite, dolomite, kaolinite, and quartz. The tool is designed to assess how variations in brine composition affect the interaction between the rock and oil in the rock/brine/oil system. Furthermore, the validation of the contact angle was carried out by the code implemented in the tool developed in the present work, which undergoes the validation of the zeta potential. It is essential to employ the zeta potential in the validation of the model, as it is the only potential that can be directly measured experimentally. The zeta potential is derived from the surface potential, which is calculated using the geochemical modeling software PHREEQC, developed by the USGS. To ensure the reliability of estimates for situations not yet tested in the laboratory, it is essential to validate the calculations made by the tool's model with experimental data already available in the literature. This helps to ensure the accuracy of predictions for scenarios not previously explored. The study highlights the significant influence of equilibrium constant variations on calcite surface potential, particularly in magnesium-containing brines, while also demonstrating the crucial role of specific ions, such as sulfate, in driving reactions. These findings contribute to a deeper understanding of the complex interactions within calcite systems and validate previous results through comparison with established data

Keywords: Wettability, SCM, BPS, Zeta Potential.

Introduction

Variations in wettability of an oil-reservoir rock are fundamental parameters that determine distributions and mobilities of fluids within the geological formation. Among the various factors that can influence this property, the composition of the brine present in the rock/brine/oil system plays a significant role).

Changes in salinity, ion type, and concentration of brine components can alter the rock surface and fluid interactions, resulting in variations in wettability. The role played by the rock's surface charge, the ionic composition of formation water (FW), and the polar components of crude oil is important for interactions in the rock/brine/oil system (Erzuah; Fjelde; Omekeh, 2019).

The present work introduces the development of a tool aimed at quantitatively estimating changes in the wettability of a reservoir rock composed of a mixture of minerals, including calcite, dolomite, kaolinite, and quartz. It will assess how these variations in brine composition affect the interaction between the rock and oil within this system.

The parameters used as wettability indicators include the BPS (Bound Product Sum) and the contact angle. Both are derived from the principles of SCM (Surface Complexation Modeling), which describe adsorption through the equilibrium of chemical reactions at the surface. These principles are widely employed for this purpose, along with the DLVO theory (Derjaguin-Landau-Verwey-Overbeek), especially in calculating contact angles.

It's worth emphasizing the importance of utilizing the Zeta potential, a critical factor that influences the surface properties of reservoir rocks and, consequently, wettability and oil recovery

efficiency. Understanding and controlling the Zeta potential enables optimization of extraction operations by adjusting interactions between rock, brine, and oil to maximize hydrocarbon recovery.

Methods

The validation of the BPS calculation was performed using experimental data from Erzuah et al. (2019). The contact angle validation process involves validating the Zeta potential, thus serving as a means to validate the surface potential.

$$\cos\theta_e = 1 + \frac{\varepsilon_0\varepsilon_3\psi_1\psi_2\kappa}{\sigma_{ow}}\operatorname{csch}(\kappa h_0) - \frac{\varepsilon_0\varepsilon_3\kappa}{2\sigma_{ow}}(\psi_1^2+\psi_2^2)\coth(\kappa h_0) - \frac{A}{12\pi\sigma_{ow}h_0^2} + A_s h_s \sigma_{ow} e^{-\frac{h_0}{h_s}} \quad (1)$$

Where ψ_1 and ψ_2 represent the surface potencials of oil and rock; ε_0 ε_3 are the eletrical permittivities of vacuum and brine; κ is the reciprocal of the Debye length; θ_e is the equilibrium contact angle; σ_{ow} is the oil-water interfacial tension; A is the Hamaker constant; A_s is the decay coefficient; h_s is the decay length and h_0 is the equilibrium thickness.

The Zeta potential is derived from the surface potential, which is calculated in the geochemical modeling software PHREEQC developed by the USGS. Once the surface potential is calculated, we can estimate the potential at any distance (x) from the surface using the Poisson-Boltzmann solution as expressed in equations (1)-(2). The Zeta potential corresponds to the potential at the slipping plane also known as the shear plane when ($x = d$), as illustrated in Figure 1.

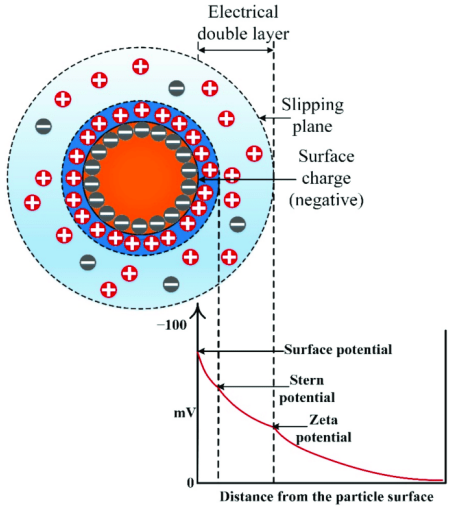


Figure 1 - Representation of charge distribution and potential on the surface and as move away from it until the distance of the slipping plane, where the so-called Zeta potential is located (Sujith; Kim; Lee, 2022).

The solution of the Poisson-Boltzmann equation, applied to the boundary condition of isolated surfaces, provides the potential distribution at any point (x) on the surface, as shown in the following equations:

$$\psi(x) = \frac{4\gamma}{z'}\exp(-\kappa x) \quad (2)$$

$$\gamma = \frac{\exp\left(\frac{z'\psi_0}{2}\right)-1}{\exp\left(\frac{z'\psi_0}{2}\right)+1} \quad (3)$$

Where k_B is the Boltzmann constant $1{,}381 \times 10^{-23}$ J K^{-1}; T is the temperature in Kelvin (K); z' represents the absolute valence or charge number, e is the magnitude of the elementary charge of an electron $1{,}6 \times 10^{-19}$ C; Additionally, γ is an intermediate, dimensionless variable.

The original equilibrium constants were taken as the base values from Table 1. From there, one reaction at a time was varied from -20 to 20 while keeping the others at their original values.

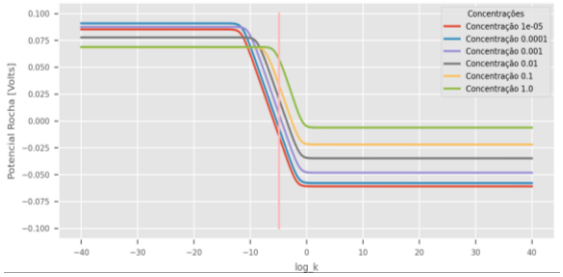
Table 1 – Surface reactions for the mineral Calcite (ERZUAH; FJELDE; OMEKEH, 2019).

Reação	log k inicial
$= CO_3H \Leftrightarrow = CO_3^- + H^+$	-4,9
$= CO_3H + Ca^{2+} \Leftrightarrow = CO_3Ca^+ + H^+$	-2,8
$= CO_3H + Mg^{2+} \Leftrightarrow = CO_3Mg^+ + H^+$	-2,2
$= CaOH + H^+ \Leftrightarrow = CaOH_2^+$	12,2
$= CaOH \Leftrightarrow = CaO^- + H^+$	-17
$= CaOH + 2H^+ + CO_3^{2-} \Leftrightarrow = CaHCO_3 + H_2O$	24,2
$= CaOH + CO_3^{2-} + H^+ \Leftrightarrow = CaCO_3^- + H_2O$	15,5
$= CaOH + SO_4^{2-} + H^+ \Leftrightarrow = CaSO_4^- + H_2O$	13,9

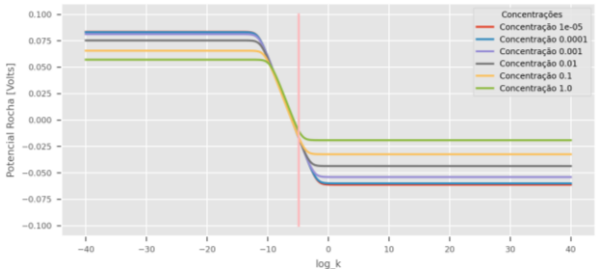
Results and discussions

The experiment investigated the effect of varying the equilibrium constant on the concentrations of two salts, both independently and in combination. It was observed that the surface potential was affected differently at each concentration level. The results, presented in Figures 2 to 5, show specific curves for each concentration.

In Figure 2, the results for the reaction Calcite_coCO3H = Calcite_coCO3- + H+ are presented. In part (a), we have the brine with MgCl2, and in part (b), with NaCl. The original value obtained by Erzuah (2019) is represented by the vertical bar (value of 4.9). It is observed that, in both cases, small variations in the reaction coefficient lead to significant changes in the surface potential. Regardless of the salt present in the brine, the reaction occurs because the reactant side has only one complex on the surface of Calcite.



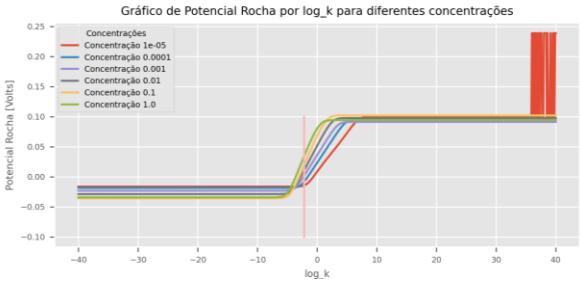
(a) MgCl2



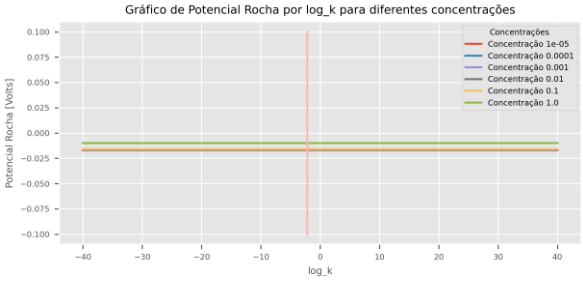
(b) NaCl

Figure 2 – Surface potential versus reaction coefficient for the reaction Calcite_coCO3H = Calcite_coCO3- + H+ (Log k base = 4.9) for the indicated salts and concentrations.

In contrast, in the case of the reaction shown in Figure 3, where magnesium ions are present on the reactant side, only the magnesium-containing brine exhibits surface potential variation when the reaction coefficient is changed. Note that in the case of the NaCl brine, there is no potential variation regardless of the assumed value for the reaction coefficient.



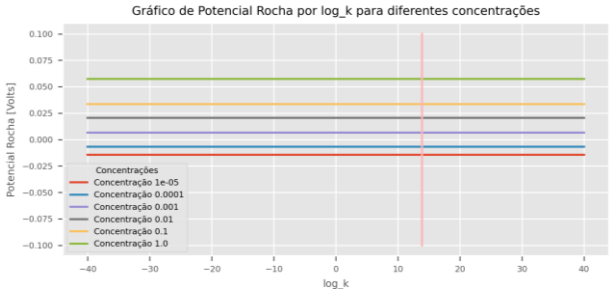
(a) $MgCl_2$



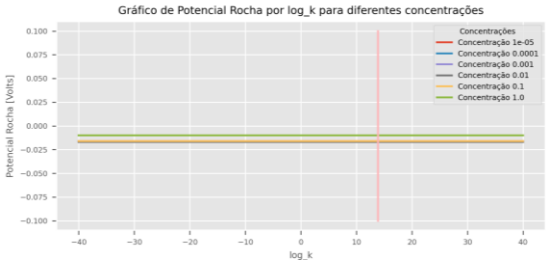
(b) NaCl

Figure 3 – Surface potential versus reaction coefficient for the reaction Calcite_coCO3H + Mg2 = Calcite_coCO3Mg+ + H+ (Log k base = -2.2) for the indicated salts and concentrations.

In Figure 4, the graphs indicate that there is no variation in surface potential with changes in the reaction coefficient for either of the salts. This is because the presence of sulfate ions is necessary for this reaction to occur.



(a) $MgCl_2$

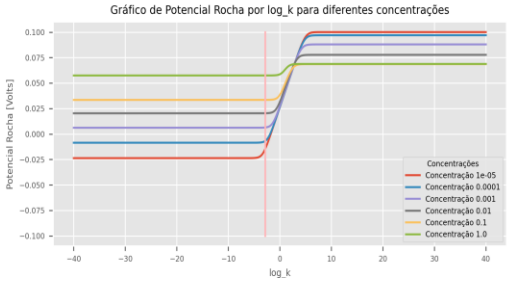


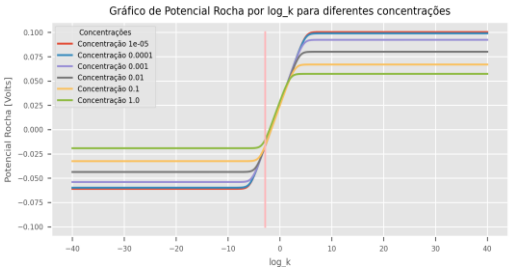
(b) NaCl

Figure 4 – Surface potential versus reaction coefficient for the reaction Calcite_caCaOH + SO_4^{2-} + H^+ = Calcite_caCaSO_4^- + H_2O (Log k base = 13.9) for the indicated salts and concentrations.

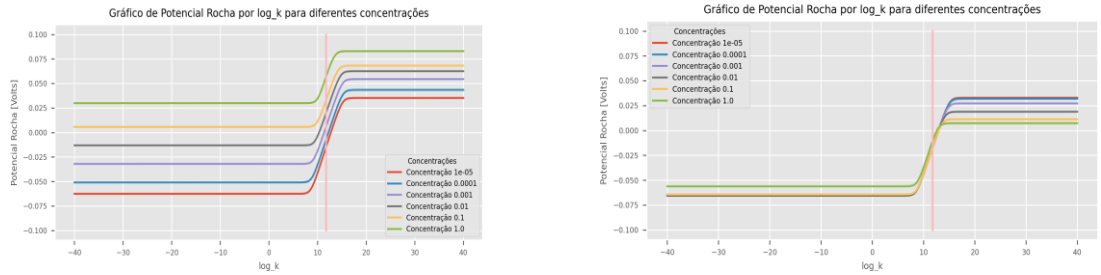
In most of the cases shown in Figures 2 and 5, Erzuah's original value (ERZUAH; FJELDE; OMEKEH, 2019) coincides with the midpoint of the potential change between its two extremes. However, there is an exception in the case of the reaction Calcite_caCaOH = Calcite_caCaO^- + H^+ (log k = -17.0).

Calcite_coCO3H + Ca+2 = Calcite_coCO3Ca+ + H+ (log_k -2.8)

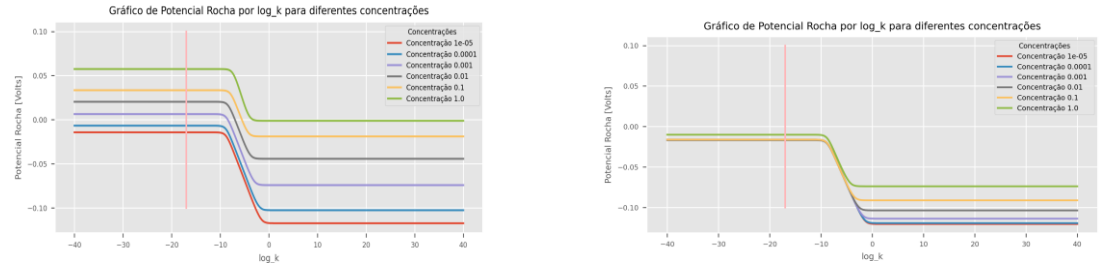




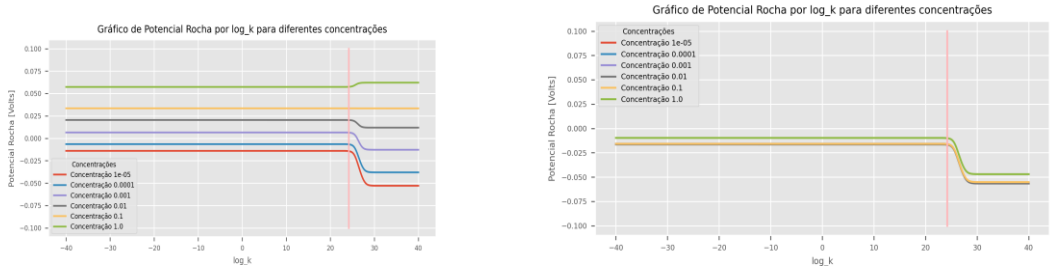
Calcite_caCaOH + H+ = Calcite_caCaOH2+(log_k 11.8)



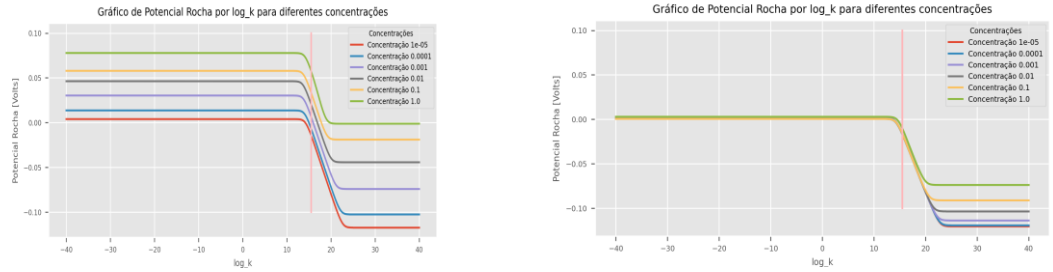
Calcite_caCaOH = Calcite_caCaO- + H+ (log_k -17.0)



Calcite_caCaOH + 2H+ + CO3-2 = Calcite_caCaHCO3 + H2O (log_k 24.2)



Calcite_caCaOH + CO3-2 + H+ = Calcite_caCaCO3- + H2O (log_k 15.5)



(a) $MgCl_2$ (b) NaCl

Figure 5 – Surface potential versus reaction coefficient for the reactions indicated in the corresponding graphs.

Conclusions

The experiment provided valuable insights into the impact of varying equilibrium constants on surface potential in calcite-related reactions. The results demonstrated that changes in the reaction coefficient could significantly affect surface potential, particularly in brines containing MgCl2. In contrast, NaCl brines showed little to no variation in potential for certain reactions, emphasizing the unique behavior of magnesium ions in influencing calcite surface interactions. The findings also highlighted the importance of specific ions, such as sulfate, in driving certain reactions, as shown in Figure 4. The comparison with Erzuah's original data (ERZUAH; FJELDE; OMEKEH, 2019) further validated the results, with most values aligning closely with midpoints between potential extremes. Overall, the study underscores the complexity of surface potential behavior in calcite systems and the critical role of ion composition and equilibrium constants in determining reaction outcomes.

Acknowledgments

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