



Numerical simulation of engineered water injection: Effect of Oil Composition and Rock Charge Distribution

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Abstract. Oil production demands Enhanced Oil Recovery (EOR) techniques. Numerical simulation can simulate recovery techniques such as injecting low salinity water into offshore carbonate reservoirs. However, numerical modeling of LSWI has not been done mechanistically and needs solid scientific foundations. A numerical model based on these foundations was created, using the PHREEQC program and the Python programming language as a tool, to understand the effect of the presence of acidic and basic groups in the oil, positive and negative sites of calcite (typical carbonate rock in Brazilian pre salt reservoirs), in the change of wettability, due to changes in the composition of the injection water. For the development of the algorithm, the Complexation Surface Model (SCM) and the Bond Product Sum (BPS) concepts were applied, aiming to predict the efficiency of the brine injection, to increase the EOR. For oil, the acidic and basic numbers, when increasing, raise the BPS, when decaying, decrease the BPS. But the acid influence is greater. For calcite, the influence of positive and negative sites have the same proportion on BPS, following the same behavior of oil numbers. Because of that, wettability is changed, the higher the BPS, the lower the EOR.

Keywords: Advanced oil recovery, Water injection, Bond product sum, Surface complexation modelling and wettability.

1 Introduction

During the productive life of a reservoir, it is usually interesting to apply Enhanced Oil Recovery (EOR) techniques, because oil exploration needs additional energy, as producing only with natural energy, achieves a yield considered low [1]. Yield that can change with changes in permeability, rock porosity and fluid viscosity.

About 80% to 90% of the world's carbonate reservoirs are preferably oil-wettable, have a greater affinity with oil than with water, and therefore have a low oil recovery factor [2][3]. Wettability can be defined as the preferential tendency of a fluid to adhere or spread to the rock surface, in the presence of other immiscible fluids [2]. In order to mobilize the adsorbed oil to flow, it is necessary to overcome these adhesion forces between rock and oil [4].

Water injection is an advanced oil recovery method that has been widely used, in which a solution, usually seawater, is injected into the reservoir. In offshore carbonate reservoirs, the injection of water with low salinity is an emerging technique, whose objective is to change the wettability of the rock, to make the reservoir surface as less oil-wettable as possible [5]. The technique consists of making compositional modifications to the injection brine so that the salinity of the water is lower than the water present in the formation [6]. Since water is a relatively cheap resource, with easy accessibility and availability, this method becomes advantageous [7].

To predict the effects of wettability, a numerical model can be used to optimize the analyses, as the laboratory test is time-consuming and expensive, making EOR methods more practical and cheaper. Aiming at this, in this article the numerical model was developed with the PHREEQC program and the Python programming language. To carry out studies on the effects of injection water on hydrocarbons interactions with the rock wall, in this case calcite rock.

The concepts of complexation surface and Bond Product Sum (BPS) were applied. As well as the total acid number and total basic number of the oil, applied to determine the effect of the pH of these compounds from the theory of the surface of complexation, on the interaction of calcite and oil ions, influencing oil wettability and consequently changing the recovery factor.

Given this context, the objective of this work is to understand the effect of the presence of acid (carboxylic) and basic (nitrogen) groups in oil, interacting with the positive and negatives sites on the calcite formation, in the change in wettability, due to changes in the composition of the injection water.

2 Theoretical framework

2.1 Surface Complexation Model (SCM)

The complexation surface model is a physicochemical model used to model surface adsorption [8]. It is a technique that characterizes wettability, makes it possible to find the possible pairs of electrostatic bonds on the surface of the formation of carbonate rocks [9].

In this study, the electric model of the double layer, rock surface and fluid (oil) were used. Electrostatic interactions occur between the ions dissolved in the brine layer with these two surfaces, the greater the amount of oppositely charged ions, the greater the bond between them, changing the wettability [9][10]. This case can be exemplified, considering a rock layer interacting with an oil layer, if there is a great electrostatic interaction between them, the oil wettability will be high, hindering an effective oil recovery.

With the SCM it is possible to predict the efficiency of the injection of brine into the reservoir to increase the EOR, through an algorithm. It forms a chemical model, which will be the basis for the numerical model developed in this study, together with the concept product summary described below.

2.2 Bond Product Sum (BPS)

The Bond Product Sum is the sum of all ionic bonds in the dissolved compounds in the layers cited in the surface complexation theory. This concept is fundamental for the study of wettability change, because if the sum of the connections between oil and calcite surface species is very high, the more wettable is the oil surface [11] [5]. One way to exemplify this concept is to consider that if the oil and calcite surface only have species with positive charges, there are no groups of opposite charges, therefore they are not attracted, the BPS would be equal to zero and the reservoir rock would be preferentially wettable to water. On the other hand, if they have species with positive and negative charges, the BPS would be high and consequently the adhesion to the oil would be high [11]. This is the reason for the injection of water, which seeks to reduce the BPS between the rock and the oil, decreasing the bond between the ions in these layers.

The b represent the number of bonds. A equation was developed to exemplify the BPS concept: Eq. 1 below represents it.

$$BPS = \sum_{i=1}^{n=b} [(+bonds\ of\ oil)(-bonds\ of\ calcite) + (-bonds\ of\ oil)(+bonds\ of\ calcite)] \quad (1)$$

To understand the behavior, a computational tool was developed using the methodology discussed in the next section.

3 Methodology

An algorithm was created applying the calculations of the PHREEQC program and the Python programming language. The flowchart in Fig. 1 shows the developed algorithm. Functions are defined from the PHREEQC formula library, which are defined first in Python. With these functions defined, it is possible to apply inputs, base values for calculating BPS, such as TAN, TBN.

The function definition is the part of the algorithm that defines the functions to be applied from the PHREEQC library. The properties of calcite and oil are defined in this section.

The input data is the section of the algorithm that receives the properties and performs previous calculations so that it is possible to complete the subsequent calculations performed in PHREEQC. The Tab. 1 below represents the parameters of reaction and surface reactions.

Table 1. SCM input parameters (oil/calcite).

Reactions	log k at 25°C	Enthalpy (kJ/mol)
Oil Surface		
$= NH^+ \leftrightarrow = N + H^+$	-6.0	34.0
$= COOH \leftrightarrow = COO^- + H^+$	-5.0	0.0
$= COOH + Ca^{2+} \leftrightarrow = COOCa^+ + H^+$	-3.8	1.2
$= COOH + Mg^{2+} \leftrightarrow = COOMg^+ + H^+$	-4.0	1.2
Calcite Surface		
$= CO_3H \leftrightarrow = CO_3^- + H^+$	-4.9	-5
$= CO_3H + Ca^{2+} \leftrightarrow = CO_3Ca^+ + H^+$	-2.8	25.7
$= CO_3H + Mg^{2+} \leftrightarrow = CO_3Mg^+ + H^+$	-2.2	4.5
$= CaOH + H^+ \leftrightarrow = CaOH^{2+}$	12.2	-77.5
$= CaOH \leftrightarrow = CaO^- + H^+$	-17.0	116.4
$= CaOH + 2H^+ + CO_3^{2-} \leftrightarrow = CaHCO_3 + H_2O$	24.2	-90.7
$= CaOH + CO_3^{2-} + H^+ \leftrightarrow = CaCO_3^- + H_2O$	15.5	-61.6
$= CaOH + SO_4^{2-} + H^+ \leftrightarrow = CaSO_4^- + H_2O$	13.9	-72.0

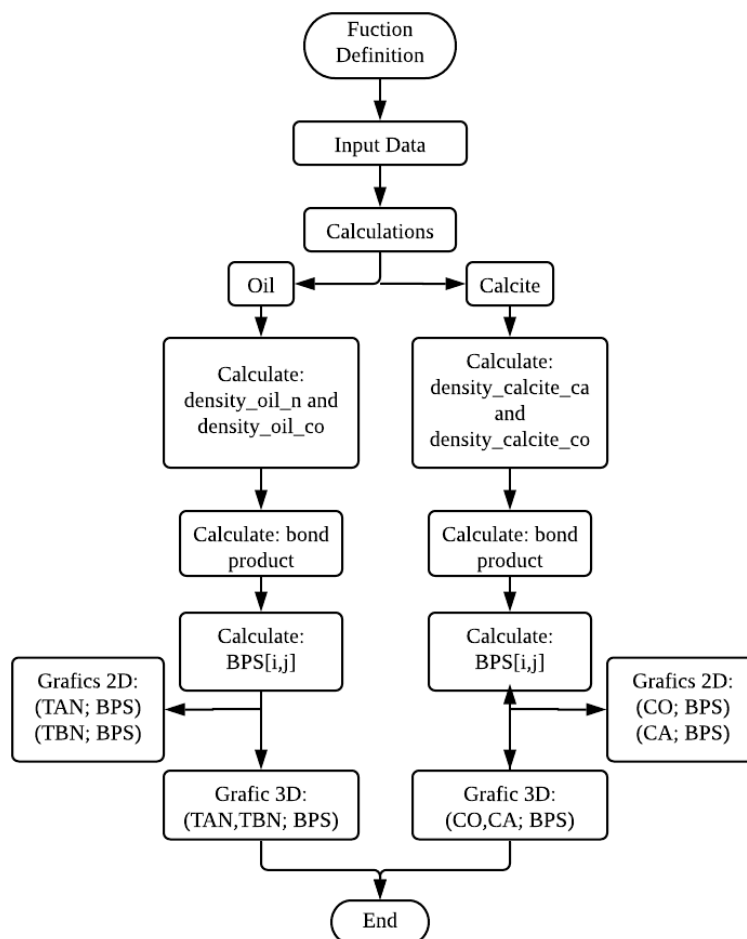


Figure 1. Algorithm for calculating the values of BPS, TAN and TBN.

The terms $density_oil_n$ and $density_oil_co$ are referring to the concentration of presence of acid carboxylic (CO) and basic groups based on nitrogen (N) in oil. The $density_calcite_co$ and $density_calcite_ca$ refer to the positive and negatives sites on the calcite formation, CO is the negative site and CA is the positive.

The main calculation is the oil-site density, it is the concentration of active charged sites in the layer of oil (SCM model of double-layers), based on the TAN and TBN values, the total number of active acid and basic sites respectively, with Equation (2) [9].

$$oil - site\ density\ (\frac{site}{nm^2}) = \frac{TAN\ or\ TBN\ (mg\ KOH/g\ oil)}{MwKOH(\frac{g}{mol})} \frac{N_A}{sur\ face\ area(\frac{m^2}{g})} \quad (2)$$

Oil-site density (sites/nm²) number of active sites per square nanometers, are on the contact surface defined by the SCM. Microgram of potassium hydroxide per gram of oil (mgKOH/goil). The Avogrado's number (N_A) is $6.0221409e + 23$. Molar mass of potassium hydroxide is 56.1 (g/mol).

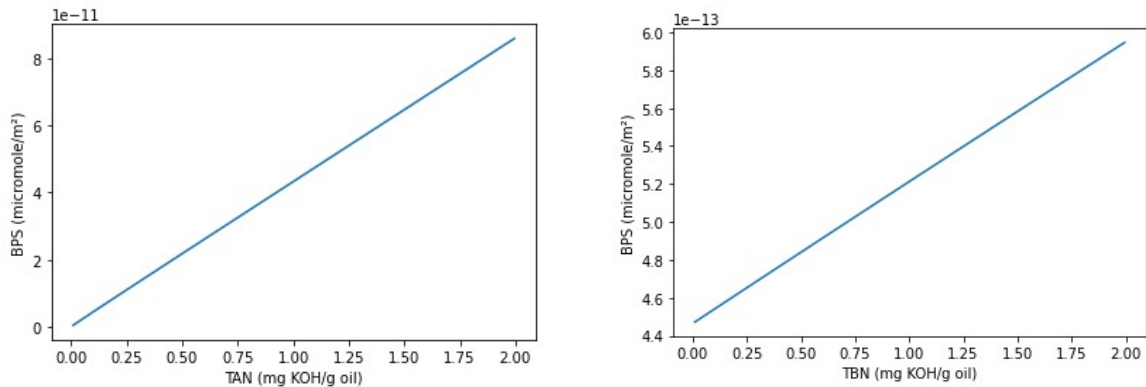
The calculations section performs the particular calculations for oil and calcite, BPS is calculated for each case. These data make it possible to assemble the graphs in the Graphics section, which will be presented in the discussions and results of the article.

4 Results and discussions

The results were divided in two parts, oil and calcite (reservoir). Which one of them was analysed in an individual way.

4.1 Oil data

The relationship between the total acid number of the oil and the sum of the electrostatic bonds in the rock's interaction layer with the oil is represented in Fig. 2.(a). The linear relationship between the variables can be seen in the image. The range of values adopted for TAN is 10^{-12} to $10^{0.3}$ (mgKOH/goil). The calculated BPS is on the order of magnitude 10^{-11} ($\mu\text{mol}/\text{m}^2$). Fixed values of TBN (10^{-2} (mgKOH/goil)) and calcite-site density in 4.9 (sites/nm²) were adopted. It is noteworthy that all figures representing the graphics presented in this article are in the logarithmic scale.



(a) BPS versus TAN, with TBN = 10^{-2} (mgKOH/goil) (b) BPS versus TBN, with TAN = 10^{-2} (mgKOH/goil)

Figure 2. BPS versus TAN on the left and BPS versus TBN on the right, there is a linear relationship both in BPS and in TAN and TBN. A much greater influence of TAN than TBN on BPS is noticeable.

The relationship of the total basic number of oil with the BPS of the rock (calcite) between oil is represented in Fig. 2.(b), the linear relationship between the variables is evident in the image as well. The range of values adopted for TBN is 10^{-12} to $10^{0.3}$ (mgKOH/goil). The calculated BPS is on the order of magnitude 10^{-13} ($\mu\text{mol}/\text{m}^2$).

The difference between the effects of TAN and TBN is in the range of BPS values, which for TBN is on the order of 100 times smaller, when compared to TAN, showing the greater relevance of the acid number of the oil in

the amount of electrostatic interactions between the oil and reservoir rock (calcite). Fixed values of TAN on 10^{-2} (mgKOH/goil) and calcite-site density in 4.9 (sites/nm²) were adopted to build the graphic.

The range of BPS values are different for the same range of TAN and TBN in Fig. 3, which has already been demonstrated in the analysis of Fig. 2.(a) and 2.(b), which states that the acid number of the oil has greater relevance on the amount of electrostatic bonds, most affecting the oil wettability of the reservoir [11] [5].

The ranges of 10^{-2} to $10^{0.3}$ (mgKOH/goil) for TAN and TBN were applied. The values of calcite-site density were set at 4.9 (sites/nm²).

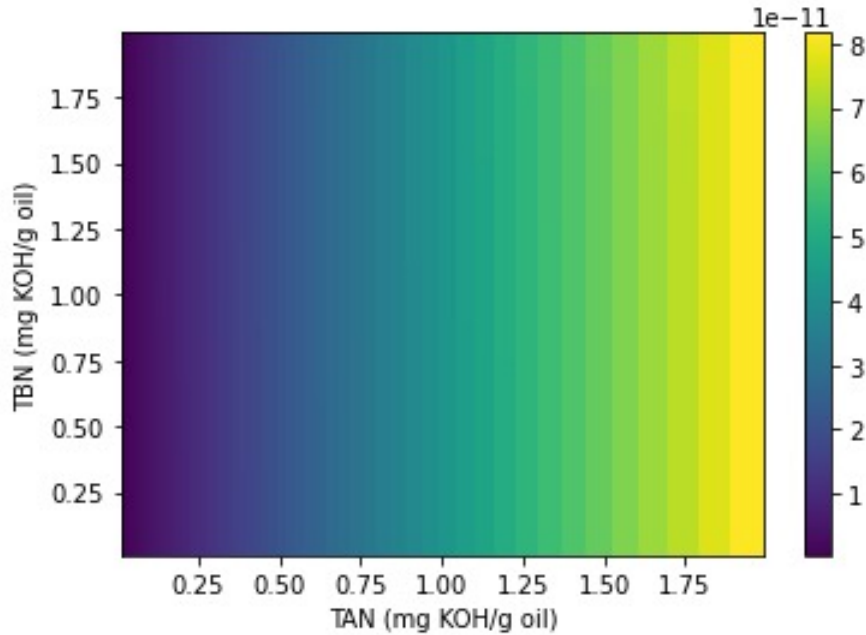


Figure 3. BPS values for varying TAN and TBN.

4.2 Calcite data

The relationship of calcium cation density (Ca^{2+}) released by calcite, represented by positive calcite-site density, with the sum of electrostatic bonds in the rock interaction layer (calcite) with oil is represented by Fig. 4.(a).

The linear relationship between the variables is noticeable in Fig. 4.(a). The values of positive calcite-site density adopted vary from 10^{-12} to $10^{0.3}$ (sites/nm²). The BPS is on the value of 10^{-12} to 10^{-14} ($\mu\text{mol}/\text{m}^2$).

Fig. 4.(b) shows the relationship of density ratio of carbonate ions (CO_3^{2-}), represented by negative calcite-site density, released by calcite, with the sum of electrostatic bonds in the rock-oil interaction layer.

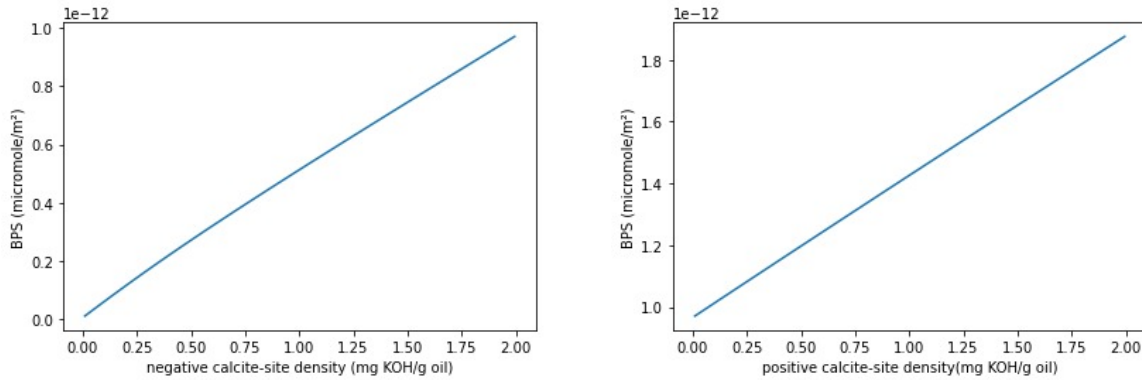
In Fig. 4.(b), the negative calcite-site density value is fixed in 10^{-2} (sites/nm²), TAN and TBN of the oil are static in the value of 0.1 (mgKOH/goil).

The values in Fig. 4.(b), of negative calcite-site density adopted vary from 10^{-2} to $10^{0.3}$ (sites/nm²). The BPS is on the order of magnitude 10^{-12} ($\mu\text{mol}/\text{m}^2$).

The positive calcite-site density value is fixed in 10^{-2} (sites/nm²), TAN and TBN of oil are static in 0.1 (mgKOH/goil).

The range of BPS values are the same for both basic calcite-site density and acid calcite-site density ranges, represented in Fig. 5, showing the fact that both ionic densities share the same relevance on the amount of electrostatic bonds. Because they vary in the same range of BPS, equally affecting the oil wettability of the reservoir [11][5].

The adopted values of calcite-site density range from 10^{-2} to $10^{0.3}$ (sites/nm²). TAN and TBN of oil are fixed at 0.1 (mgKOH/goil).



(a) BPS versus positive calcite-site density, with negative calcite-site density = 10^{-2} (sites/nm²). (b) BPS versus negative calcite-site density, with positive calcite-site density = 10^{-2} (sites/nm²).

Figure 4. BPS versus positive calcite-site density on the left and BPS versus negative calcite-site density on the right. It is observed that the active sites of positive and negative charge have the same influence in relation to BPS.

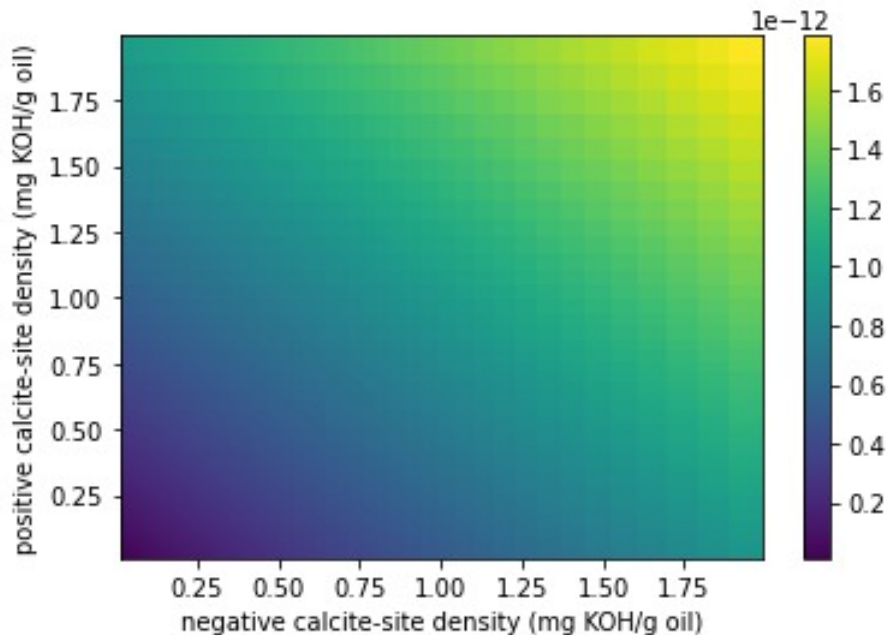


Figure 5. BPS values for varying positive and negative calcite-site density.

5 Conclusions

From the analysis of the oil graphs, it was evident that TAN has a greater influence than TBN in relation to the behavior of BPS, which alters the wettability and affects the recovery factor. For calcite graphs, this difference is not observed for the positive and negatively charged active sites, showing that they have similar influence in relation to BPS.

It is concluded that for a very acidic oil, oil wettability is predominant in the reservoir, generating a low recovery factor. The base number also generates a low recovery factor, however with a smaller influence.

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