EOR Brine Optimization Using Pore-Lining vs Bulk Mineralogy: Integrating Automated Mineralogy and Wettability Alteration Modeling

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Abstract. This study presents an optimization strategy for low salinity and engineered brine injection by integrating automated mineralogy with wettability alteration modeling. Pore-lining mineral phases exert primary control on wettability; however, most existing approaches rely on bulk mineralogical data and do not capture the spatial distribution of pore-lining minerals that control wettability. High-resolution automated mineralogy was used to quantify pore-lining minerals controlling oil adhesion. These data were incorporated into a surface complexation modeling framework to predict the impact of brine composition on wettability and oil recovery. Results demonstrate that incorporating pore-lining mineral characterization significantly improves wettability prediction and enables more reliable brine design. The workflow establishes an optimized brine injection strategies by defining a direct link between pore-scale mineralogy and wettability alteration mechanism.

1 Introduction

Low salinity and engineered waterflooding have become key enhanced oil recovery (EOR) strategies in the oil and gas industry, driven by mechanisms such as wettability reversal toward more water-wet conditions [1–4]. Despite widespread application, the design of optimal injection brine compositions remains a significant operational challenge. This is largely due to uncertainties in predicting wettability response under field conditions, where mineralogical heterogeneity, surface chemistry, crude oil composition, and brine–rock interactions are strongly coupled and difficult to quantify [5,6]. As a result, many waterflood designs continue to rely on empirical approaches, which can lead to inconsistent performance and suboptimal recovery.

A key source of this uncertainty lies in how mineralogical inputs are represented in wettability prediction workflows. Traditionally, weight percent bulk mineralogy (e.g. XRD) has been used as input to these models [7]; however, it often does not adequately represent the reactive surface mineralogy that controls fluid–rock interactions [8]. There has been considerable investigation into the role of thin-films of fluids at the rock-fluid interface [9], but in the overwhelming majority of those publications, the composition of the bulk rock was considered a suitable proxy for the composition of the surface-ling phases. Bulk measurements reflect overall aggregate composition (lab techniques usually homogenize samples to powder, wireline log techniques interpret an interval of volume) rather than the mineral phases exposed at pore surfaces, where oil–brine–rock interactions occur. In contrast, pore-lining mineralogy provides a more representative description of the reactive surfaces, leading to more reliable predictions of wettability response and improved brine design [10].

Automated mineralogy analyses enable rapid, high-resolution mapping of mineral phases through SEM-EDS analyses performed in a pre-defined raster pattern across a flat polished rock surface. This methodology allows quantification of minerals and their spatial distribution within the rock [11], including pore-lining phases that directly control surface chemistry and oil-brine-rock interactions. From an operational standpoint, incorporating pore-scale mineralogical information is the key input for wettability prediction and brine design, reducing uncertainty in waterflood optimization [12].

In this study, high-resolution automated mineralogy is used to identify and quantify pore-lining mineral phases. This information is used to build a surface complexation wettability modeling framework [13] that calculates in situ wettability and its response to waterflood chemistry. The model simulates adsorption and complexation reactions between mineral surfaces, brine ions, and polar oil components, enabling prediction of wettability alteration as a function of brine chemistry and pore-scale mineralogy.

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The objective of this work is to provide a more reliable and predictive approach for brine optimization by directly linking pore-scale mineralogical controls to wettability behavior and, ultimately, oil recovery performance. By incorporating physically observable and pore-accessible mineralogical inputs, this methodology aims to reduce uncertainty, improve decision-making, and enhance the effectiveness of waterflood design. However, field-scale low-salinity and EOR response is influenced by multiple coupled factors, including mineralogical heterogeneity, wettability alteration kinetics, spontaneous imbibition time scales, fracture-matrix interactions, and transport effects. Therefore, the present work is intended to improve one component of the wettability prediction workflow rather than provide a complete mechanistic description of low-salinity recovery processes.

2 Methodologies

2.1 Automated Mineralogy and Pore-Lining Mineral Phase Identification

Automated Mineralogy analysis by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS) was employed to characterize the mineralogical composition and spatial distribution of elements at the pore scale. This analysis enabled identification of pore-lining mineral phases critical for wettability assessment.

Rock samples were cut into small chips representative of the bulk material and dried under controlled conditions to remove residual fluids. The samples were cast in resin and polished to mirror finish to reveal grain centers. To minimize charging effects during imaging, the samples were coated with a thin conductive layer of carbon using a sputter coater.

Automated Mineralogy analysis was conducted under high vacuum conditions; all data were collected using a QEMSCAN® WellSite instrument (Aspex Extreme Scanning Electron Microscope with 5030 Bruker EDS detectors) using the FieldScan mode at 15 kV beam energy and 1 or 4 micron stepping interval. The mineral data were processed in FEI's iDiscover software package using an in-house mineral library developed by Rocktype Ltd and Stratum Reservoir. Although the stepping interval used for analysis was 1 or 4 micron, it should be noted that the volume of investigation at each analysis point is in the size order of 100s of nanometers. Clays with mixed phases or intergrowths are recognized and classified as the dominant phase in the volume of investigation.

The resulting raster mineralogical data were used as inputs for subsequent wettability modeling and brine optimization analyses. Unlike bulk XRD analysis, this approach provides detailed insight into the spatial distribution of mineral phases and their exposure at pore surfaces. Specifically, it enables the quantification of pore-lining versus bulk mineral fractions, by identifying all mineral pixels neighboring pores. This provides a more representative characterization of the mineral surfaces controlling fluid–rock interactions. In contrast, XRD analysis is a semi-quantitative technique in which the angles and intensities of diffracted X-ray beams, generated by scattering from crystal lattice planes, are measured from powdered bulk samples. Bulk mineralogy is then interpreted from the resulting diffractograms through mineral phase identification and semi-quantitative peak analysis [14].

2.2 Wettability Modeling Framework

The surface complexation wettability modeling framework [13,15] was employed to predict the impact of brine composition on oil–rock adhesion and wettability alteration using the pore-lining mineral phases identified through automated mineralogy. The Bond Product Sum (BPS) wettability calculation [16,17] calculates adsorption and competitive exchange reactions among charged mineral surface sites, aqueous ions, and polar oil functional groups, enabling quantification of electrostatic oil–mineral bridging under varying brine chemistries. Representative reactions include competitive sorption of protonated oil base groups and divalent-cation-bridged carboxylates onto negatively charged mineral sites, such as:

$$> Na + -NH^+ \rightleftharpoons > -NH + Na^+ \quad (1)$$

$$> Na + -COOCa^+ \rightleftharpoons > -COOCa + Na^+ \quad (2)$$

Where, for example, -NH^+ is a polar N group exposed at an oil surface and >-NH^+ is the same group, and the oil, attached to a mineral surface. The reactions describe competition from aqueous ions such as Ca^{2+} and Na^+ for surface exchange sites. These reactions are governed by geochemical equilibria that control surface charge development, ion adsorption, and speciation as a function of brine composition, pH, and temperature. Within this framework, the BPS is calculated as the sum of products of surface site densities of oppositely charged species on the mineral surface and polar oil components. This metric serves as a proxy for the strength of electrostatic adhesion between oil and rock surfaces. Higher BPS values indicate stronger oil–mineral interactions and more oil-wet conditions, while lower values correspond to reduced adhesion and more water-wet behavior. The calculated density of electrostatic bridging interactions therefore enables quantitative ranking and optimization of candidate brine formulations.

To specifically examine the effect of fluid chemistry (NaCl salinity) on wettability, all BPS calculations assumed the same representative reservoir porosities of 0.17, TAN/TBN = 1/3; temperature = 90°C, and $P_{CO_2} = 0.032$ atm. TAN is the Total Acid Number of the oil; TBN is the Total Base Number. Note that fluid chemistry (in this case, salinity) is one of the few reservoir parameters that reservoir engineers can readily modify to influence wettability and potentially improve oil recovery.

In general, the calculated BPS values are relatively insensitive to temperature because the underlying surface complexation and aqueous equilibrium constants are only

weakly temperature dependent. Similarly, changing the porosity used in the calculations would not significantly alter the predicted salinity trends. In contrast, variations in P_{CO_2} or TAN/TBN ratios can substantially affect the calculated BPS values, depending on the reservoir mineralogy, particularly the presence of carbonate minerals and the availability of divalent cations such as calcium [12,13,16,17].

3. Results and Discussion

This section presents the results of the experimental and modeling work, followed by a detailed discussion of their implications for wettability alteration and brine optimization. The analysis focuses on linking pore-scale mineralogical characteristics to oil-brine-rock interactions and overall recovery behavior.

3.1 Impact of surface reactive chemistry

Automated mineralogy analysis revealed significant differences between bulk mineral composition and the mineral phases exposed at pore surfaces for Rock A, illustrated in **Fig. 1.** Bulk mineralogical characterization indicated that the sample A was dominated by quartz, with compositions on the order of 70–80%. However, pore-scale analysis demonstrated that quartz exposure at the pore surfaces was substantially lower than suggested by bulk measurements. Instead, pore-lining phases were found to be dominated by clay minerals, particularly illite, which are preferentially located along pore walls and grain boundaries. Note that the crystal size of the pore-lining mineral phases is substantially lower than the grain size of the quartz matrix. The smaller crystal size corresponds to a higher specific surface area (surface area per unit mass), which must be accounted for in wettability calculations. The automated mineralogy map shown in **Fig. 1** was used to scale assumed mineral surface areas (m^2/g), quartz (0.1 m^2/g), calcite (0.1 m^2/g), kaolinite (10 m^2/g), and illite (50 m^2/g) to pore exposure. The relatively low surface areas assigned to quartz and calcite reflect their larger grain and crystal sizes observed in the sample, relative to illite and kaolinite and is consistent with the literature [18]. The relatively higher surface areas associated with clay minerals indicate that they dominate the wettability response to changes in waterflood chemistry. This result highlights the importance of incorporating pore-scale mineral characterization into wettability evaluation and brine optimization workflows.

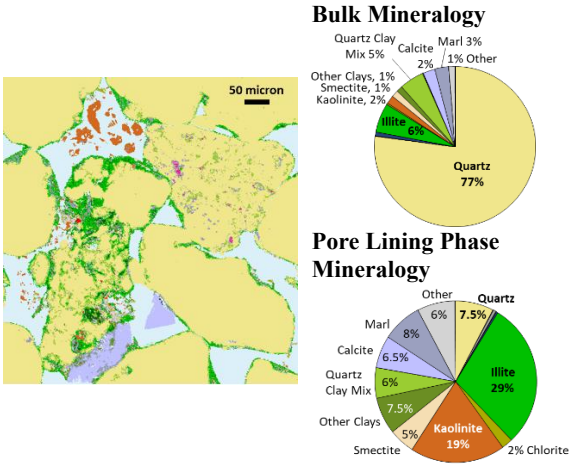


Fig 1. Automated mineralogy map and corresponding bulk and pore-lining mineral composition for Rock A.

Fig 2 presents the calculated wettability for both bulk and pore-scale cases for Rock A, a clay-bearing sandstone with minor calcite. In the bulk case, all mineral surface areas were set identical at 1 m^2/g, whereas the pore-scale case incorporates mineralogy and grain size derived from automated mineralogy. The bulk wettability calculation predicts a strongly water-wet system with only minor sensitivity to salinity. In contrast, the pore-scale calculation indicates substantially more oil-wetting due to the presence of illite within the pore space. This behavior is illustrated schematically in **Fig. 3**. Because the pore-scale model is grounded in the observed pore mineralogy and grain size (**Fig. 1**), it provides a more realistic and informative representation of wettability sensitivity to waterflood chemistry. For example, higher salinity reduces oil adhesion in the illite-rich pores through increased competition of Na^+ ions for illite surface sites that would otherwise be occupied by protonated oil nitrogen bases (see Equation 1).

Salinity was varied in the wettability calculations, as it is a common target in waterflood optimization. The same approach can also be applied by varying other parameters, such as Ca/Na ratio, pH, and sulfate concentration of the injected brine. This enables rapid screening of potential waterflood modifications to maximize oil recovery. The methodology has also been successfully applied to carbonates [12] and kaolinite-rich sandstones [17].

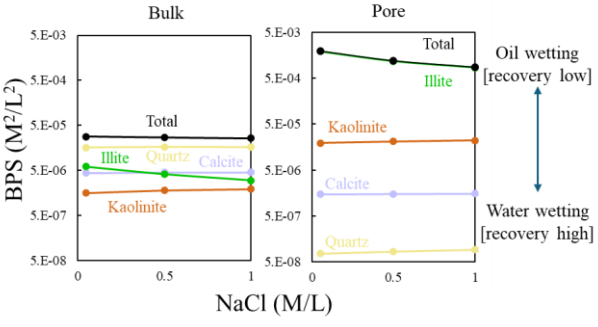


Fig 2. Predicted impact of salinity on oil binding to Rock A in the presence and absence of pore-lining mineral phases. The vertical axis is the calculated BPS of the rock. Color coding:

black-total, green-illite, yellow-quartz, purple-calcite, and brown-kaolinite. Assumptions: OtherClays (Fig. 1) was approximated as illite, the dominant clay in the core. The QuartzClayMix (Fig. 1) was assumed to consist of equal fractions of quartz and illite, while marl (Fig. 1) was represented as an equal mixture of calcite and illite. Muscovite, chlorite, and smectite were also assigned surface chemical properties equivalent to illite, reflecting their comparable basal plane surface charge behavior. Mineral surfaces were numerically pre-equilibrated with the highest salinity brine (1.0 M NaCl), representing connate conditions.

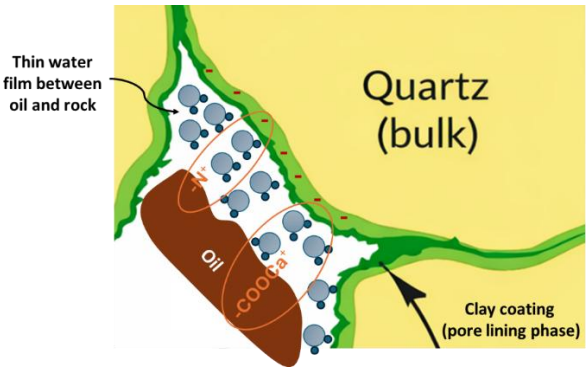


Fig 3. Schematic illustration of clay minerals coating pore walls and interacting with polar oil components.

3.2. Impact of surface roughness

The automated mineralogy-BPS method for wettability prediction was also applied to a rock characterized by pore-lining mineral phases dominated by a mixture of microcrystalline quartz and clay, while the bulk mineralogy is primarily composed of quartz (**Fig. 4**). Automated mineralogy analysis indicates that approximately 55% of the pore lining mineral phase consists of a microcrystalline quartz, with additional contributions from smectite, kaolinite, and other clay minerals. At the pore scale, microcrystalline quartz domains are characterized by dense clusters of fine, needle-like crystals lining the grain surfaces. These features create a heterogeneous and rough surface morphology, significantly increasing the effective surface reactivity compared to clean quartz.

The SEM images shown in **Fig. 5**, present two distinct quartz populations that are critical for understanding rock–fluid interactions. The circled area in **Fig. 5a** shows the surface of a host detrital quartz grain, characterized by flat, euhedral faces indicative of overgrowth cement. These overgrowths partially enclose earlier-developed pore-lining microcrystalline quartz. In contrast, **Fig. 5b** displays clusters of microcrystalline (authigenic) quartz, appearing as fine, needle-like to euhedral overgrowths that precipitated in situ within the pore space.

This distinction is important because these two quartz types exhibit different surface properties and reactive behaviors. Euhedral quartz typically has lower specific surface area and fewer active sites, leading to weaker interactions for instance with polar components in crude oil. Conversely, microcrystalline quartz, with its high surface area, fresh reactive surfaces, and potential association with clays or impurities, can significantly enhance surface charge development and adsorption capacity.

From a wettability standpoint, the presence of microcrystalline quartz or other high-surface area pore-lining phases (such as chlorite or fibrous illite/smectite) can promote stronger rock–fluid interactions, due to increased affinity for aqueous films and ion exchange processes. Therefore, accurately identifying and quantifying these pore-lining phase types is essential for reliable wettability prediction, especially in studies involving low-salinity waterflooding or surfactant EOR, where surface reactivity and mineral heterogeneity directly influence recovery mechanisms.

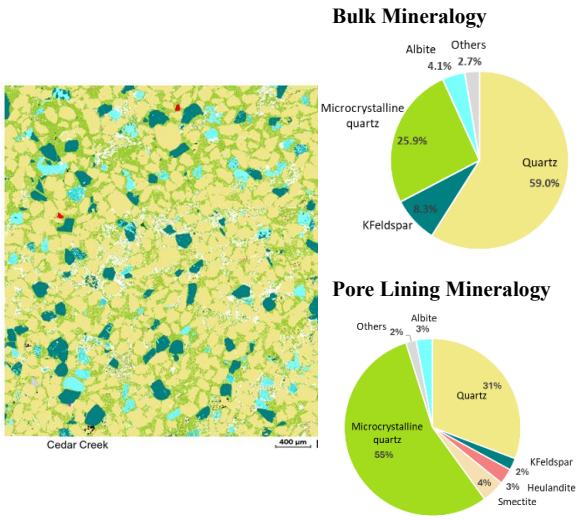
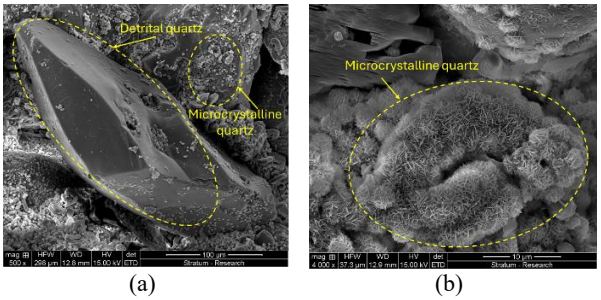


Fig. 4. Automated mineralogy map and corresponding bulk and pore-lining mineral composition for Rock B.



(a) (b)

Fig. 5. SEM images illustrating quartz textures in Sample B: (a) a detrital quartz grain accompanied by localized microcrystalline quartz deposits, and (b) detailed view of pore-lining microcrystalline (authigenic) quartz.

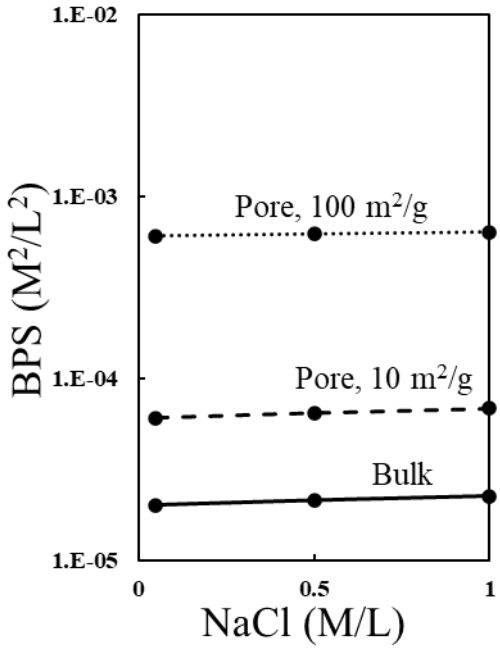


Fig 6. Predicted impact of salinity on oil binding to Rock B in the presence and absence of pore-lining mineral phases as a function of the microcrystalline quartz surface area. Total BPS is shown.

Fig. 6 presents the calculated wettability as a function of salinity for the bulk case, and for three different microcrystalline quartz surface areas (1, 10, and 100 m^2/g). The results show that the automated mineralogy-based inputs consistently predict a significantly higher degree of oil-wetting compared to the bulk-based model. This behavior is primarily attributed to the substantially greater specific surface area associated with microcrystalline quartz, which increases the density of reactive surface sites available for adsorption and ion exchange. Within the surface complexation framework, this leads to enhanced electrostatic bridging between polar oil components and mineral surfaces, particularly through divalent cation-mediated interactions. As a result, the magnitude of oil–mineral adhesion (BPS) increases with increasing microcrystalline quartz surface area. In contrast, the bulk quartz assumption, which underrepresents surface area and reactive site density, yields lower BPS values and therefore predicts more water-wet conditions. These findings highlight the critical role of pore-scale mineral heterogeneity and surface area in wettability prediction, demonstrating that neglecting pore-lining microcrystalline phases can lead to a systematic underestimation of oil-wetness and an overly optimistic assessment of wettability alteration potential under varying brine compositions.

Overall, this example demonstrates that not only the type of minerals present, but also their textural relationships and associations at the pore scale may play a role in controlling wettability. Achieving realistic predictions of oil–brine-rock interactions and for designing more effective brine optimization strategies may be essential to incorporate these effects into modeling workflows in some cases. Future work will focus on integrating dedicated core flow experiments and compatibility testing into the workflow to further validate and quantify the effects predicted by the automated mineralogy and wettability modeling framework. While consistent trends are expected, targeted experimental studies are required to optimize measurement of these differences. Future studies will also incorporate surface roughness characterization and evaluate relationships between automated mineralogy-derived pore surface attributes and experimentally measured surface area metrics such as BET surface area.

Automated mineralogy analysis of pore-lining versus bulk mineralogy may also provide valuable insights for the interpretation of reservoir cation exchange capacity (CEC) behavior and NMR-based pore typing workflows [19,20]. In particular, the distinction between pore-accessible reactive mineral phases and bulk mineralogy may improve understanding of electrochemical behavior, surface relaxivity effects, and fluid-mineral interactions relevant to petrophysical interpretation and recovery processes.

In addition, the potential for scale formation, smectite swelling, and/or migration of kaolinite fines was not discussed above, but their analysis will be a part of the final workflow.

4. Conclusions

This study indicates that wettability behavior is influenced by pore-scale mineralogy, rather than being fully represented by bulk composition. Automated mineralogical analysis in the studied samples showed that pore-lining phases were dominated by clays with high reactive surface areas, which are expected to control oil–brine–rock interactions and lead to more oil-wet behavior than predicted from bulk data. Consequently, wettability models based on bulk mineralogy may underestimate both oil adhesion and sensitivity to brine chemistry, with economic implications when deployed at field scale.

Coupling pore-scale mineral characterization with surface complexation modeling provided a more realistic framework for predicting wettability alteration and optimizing injection water composition. The results also highlighted, for the cases examined here, the importance of surface roughness and mixed-phase mineral structures, such as microcrystalline quartz associations, which enhanced surface reactivity and are not captured by conventional XRD analysis. Overall, incorporating pore-scale mineral exposure and texture into modeling workflows is important for improving wettability prediction and brine design.

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6. Appendix : The BPS Method

The BPS method, described in Section 2.2, assumes that wettability is governed by the electrostatic interactions associated with oil-rock adhesion across an intervening aqueous film, and that oil is exposed to mineral surfaces in the proportions measured by automated mineralogy. The current workflow focuses on the oil-accessible pore system most relevant to hydrocarbon recovery. Water-filled pores or isolated pore corners that are not exposed to oil are therefore not the focus of this study, and their impact on the comparative wettability calculations is expected to be limited.

Surface complexation models are used to calculate the number of oppositely charged chemical species present at the oil-water and mineral-water interfaces, and the BPS is calculated as the product of these interacting surface species. For multi-mineral systems, the overall BPS is calculated as the surface-area-weighted sum of the individual mineral contributions.

Surface equilibrium constants for both minerals and oil functional groups are obtained from the literature and/or estimated using established chemical correlations [12,13,16,17]. The surface complexation calculations require inputs including mineral and oil surface areas, oil TAN and TBN values, and the composition of the aqueous phase. Because the BPS framework enables rapid evaluation of the potential impact of waterflood or frac water chemistry on wettability and oil recovery behavior, it represents a potentially valuable tool for reservoir characterization and reservoir management applications.

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