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Determining The Role of ION Exchange in Permeability Alteration During ASP Injection: A Laboratory-Scale Study Using CMG® Reactive Transport Modeling

Dike F Putra[1,2,3], Mohd Z Jaafar[2], Tengku Amran T. M[3], M. Haidar T. Putra[4], Noviarita[1], Agus Dahlia[2], and Ichsan A Lukman[5].

[1]Petroleum Engineering Department, Faculty of Engineering, Universitas Islam Riau
Kaharuddin Nst Street No.113, Simpang Tiga, Bukit Raya District, Pekanbaru City, Riau 28284, Indonesia.

[2]Petroleum Engineering Department, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia
Iman Street, 81310 Skudai, Johor Darul Ta'zim, Malaysia.

[3]Faculty of Chemical Engineering, Universiti Teknologi Mara, Shah Alam.
Ilmu Street 1/1, 40450 Shah Alam, Selangor, Malaysia.

[4]Earth Science Department, University of Calgary.
Calgary, AB, Canada.

[5]Center of Energy Studies (PSE), Universitas Islam Riau.
Kaharuddin Nst Street No.113, Simpang Tiga, Bukit Raya District, Pekanbaru City, Riau 28284, Indonesia.

Corresponding author: dikefp@eng.uir.ac.id

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ABSTRACT - Electrokinetic-based Enhanced Oil Recovery (EK-EOR) presents a novel method that applies electric fields to mobilize trapped hydrocarbons in formations with low permeability. This work investigates the impact of ion exchange and mineralogical reactions on permeability behavior during Alkali-Surfactant-Polymer (ASP) flooding, integrating laboratory-scale sand-pack experiments with reactive transport simulation in CMG-GEM. During ASP injection, a marked rise in differential pressure indicated abrupt changes in permeability caused by polymer accumulation, mineral dissolution, and early-stage ion exchange. Two numerical scenarios were assessed: one involving only aqueous-phase chemistry, and another incorporating fluid reactions and solid-surface ion exchange. The latter case required minimal calibration to match experimental data, while the former demanded unrealistic permeability upscaling. The results underscore ion exchange as a vital mechanism influencing fluid transport in EK-EOR. Although wettability alteration is often associated with ASP processes, this study suggests that under short exposure periods, changes in permeability dominate recovery performance. The findings improve reservoir modeling by promoting geochemical integration into simulation workflows.

Keywords. Electro-kinetic EOR, ion exchange, permeability evolution, reactive transport simulation, ASP injection.

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INTRODUCTION

Enhanced Oil Recovery (EOR) technologies have significantly improved in recent decades, particularly in managing production from aging reservoirs characterized by challenging geological conditions. Among the various EOR methodologies, Electro-kinetic EOR (EK-EOR) has emerged as a particularly promising technique, especially for mobilizing trapped oil in formations with low permeability or complex heterogeneity. This method involves the application of a low-voltage direct current (DC) electric field across the reservoir, which initiates electrochemical and physicochemical processes including electroosmosis, electromigration, and electrophoresis that collectively modify the transport behavior of fluids and the interfacial characteristics within porous systems (Alshawabkeh 2009; Revil & Mahardika 2013).

Unlike traditional chemical or thermal recovery methods, EK-EOR offers operational advantages regarding environmental sustainability and energy efficiency. It is especially valuable in scenarios where thermal injection leads to energy losses in deep or fractured reservoirs, or where chemical additives risk causing formation damage (Alghamdi et al. 2019; Ikpeka et al. 2022).

One of the pivotal effects of EK-EOR is its ability to influence rock permeability through interactions between electrochemically induced fluid migration and in-situ mineral transformations. These transformations may involve the dissolution or precipitation of minerals, ion exchange at mineral surfaces, and modifying the pore network structure and flow connectivity (Putra et al 2024). Additionally, changes in zeta potential and wettability, induced by the applied electric field, can shift capillary dynamics and enhance oil displacement efficiency (Revil & Pezard 1999; Tang et al. 2023).

Despite its potential, EK-EOR still requires a deeper understanding, particularly regarding the complex interplay between geochemical reactions and fluid flow under electrical stimulation. This study seeks to address that gap by evaluating how ion exchange processes and mineral reactivity influence permeability changes during ASP flooding, combining experimental observations with reactive transport simulation using CMG-GEM (Putra et al. 2025)

Review on previous studies

Electro-kinetic phenomena in porous media

A range of coupled electro-kinetic phenomena is activated when a DC electric field is applied across a fluid-saturated porous medium. Chief among these is electroosmosis the bulk movement of fluid driven by interaction with the electric double layer (EDL) present at mineral-fluid interfaces. In minerals such as quartz and various clays, which generally possess negative surface charges, the EDL facilitates the transport of positively charged ions and water molecules in the direction of the electric field (Nazarova et al. 2018; Xie et al. 2019). Electroosmotic flow becomes particularly effective in low-permeability or fine-grained media where traditional pressure-driven flow is minimal (Lawson Scientific 2010).

Simultaneously, electromigration causes dissolved ions such as Na^+, Ca^{2+}, Cl^-, H^+, and OH^- to move in response to the electric potential gradient. Electrophoresis further drives the movement of suspended colloidal particles or oil droplets. These combined processes are influenced by fluid properties such as ionic strength, pH, temperature, and zeta potential. Compared to conventional flooding, electroosmotic flow tends to be more uniform and directional, which enhances sweep efficiency in layered or anisotropic formations (Alizadeh et al. 2023; Jaafar 2013; Thanh 2018).

Coupled electrochemical reactions and mineral alterations

Applying an electric field alters the chemical environment of the porous matrix. At the anode, oxidation generates protons (H^+), which lower pH and lead to dissolution of susceptible minerals, such as carbonates (e.g., calcite and dolomite):

$$CaCO3 + 2 H+ \rightarrow Ca2+ + CO2 + H2O \quad (1)$$

Conversely, at the cathode, reduction reactions produce hydroxide ions (OH^-), increasing local pH and often leading to the precipitation of compounds like iron hydroxides, silica, or alumina. This spatial pH gradient creates zones of mineral transformation that modify pore structures, potentially enhancing or obstructing permeability depending on mineral composition (Glover 2018; Khaledialidusti et al. 2015; Xie et al. 2019).

Ion exchange is another critical mechanism between pore fluids and mineral surfaces. Exchangeable cations (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}) can be released or captured at mineral interfaces, altering surface charges and affecting electroosmotic mobility. Over time, such interactions can either increase permeability through dissolution and pore widening or decrease it through clogging and mineral deposition (Alshawabkeh 2009; Probstein & Hicks 1993, Saputra et al. 2022).

Effect on permeability and fluid flow

Permeability is a key parameter controlling flow behavior in EK-EOR. Experimental studies have documented cases where permeability improves due to the disintegration of cementing agents or acid-induced swelling of clays. On the other hand, clogging can occur when high pH at the cathode causes precipitation of insoluble materials, narrowing pore throats (Bartels et al. 2002; Kim et al. 2019; Park et al. 2006).

These outcomes are highly dependent on the mineralogy of the formation, the intensity and duration of electric field exposure, and the initial chemical environment of the system. While acidic zones near the anode can enhance permeability by dissolving silicates, the resulting dissolved species may reprecipitate in alkaline zones, potentially offsetting gains in flow capacity. Hence, careful control of these geochemical reactions is essential to optimize permeability evolution (Hosseini et al. 2023).

Moreover, electric field exposure can shift reservoir wettability from oil-wet to water-wet states by modifying surface charge conditions, thereby improving the mobility of trapped oil. These wettability and relative permeability changes can significantly boost recovery in mixed-wet reservoirs (Korrani & Jerauld 2018; Sadeqi-Moqadam et al. 2016).

Laboratory and simulation approaches

Laboratory investigations of EK-EOR often employ core flooding or column-based setups. These experiments involve saturating the core with brine or formation water and monitoring real-time voltage, current, pH, ionic concentrations, and permeability. Such controlled conditions enable tracking of fluid front movement and reaction kinetics (Jaafar et al. 2015; Putra et al. 2024, Tobing & Eni 2014).

Simultaneously, simulation tools like CMG-GEM, TOUGHREACT, PHREEQC, and COMSOL complement laboratory studies. These platforms model electrochemical transport, reactive flow, and mineral alterations at the lab and field scales. By integrating electrical, hydraulic, chemical, and thermal processes, these tools support comprehensive optimization of EK-EOR design parameters and prediction of long-term performance.

METHODOLOGY

Research rationale

Although electro-kinetic principles have been widely applied in environmental engineering, particularly for soil decontamination, their application in petroleum EOR remains relatively underexplored especially in how electric field-induced geochemical processes influence permeability. Most EK-EOR studies have focused on experimental observations without quantitatively bridging those findings to field-scale predictive modeling.

This study addresses that gap by integrating laboratory data and numerical modeling to evaluate the influence of mineral reactions and ion exchange on permeability alteration. It specifically targets the behavior of tight or heterogeneous reservoirs, where conventional injection strategies face mobility and sweep challenges.

Experimental setup

A set of core-flooding experiments was performed using a custom-designed sand pack system. This apparatus consisted of a transparent resin casing, 40 cm in length, filled with a synthetic sandstone analogue and embedded with stainless steel electrodes placed at 10 cm intervals. The system allowed real-time monitoring of electric potential, pressure differential (ΔP), and effluent properties. A DC power source was used to apply electric current throughout the experiment.

Three operational phases were defined:

Phase 1: brine pre-flushing

Synthetic brine was injected into the sand pack to establish baseline saturation and remove mobile oil. Effluent samples were collected to analyze ionic composition and initial electro-kinetic behavior. ΔP and voltage were recorded continuously.

Phase 2: ASP injection

Following brine stabilization, the alkaline-surfactant- polymer (ASP) slug comprising sodium carbonate (alkali), sodium dodecyl sulfate (surfactant), and HPAM (polymer) was introduced at constant flow. Interactions between injected chemicals and mineral surfaces were expected to initiate ion exchange and mineral dissolution or precipitation, altering the flow paths.

Phase 3: post-injection monitoring

After ASP injection, further sampling was carried out to measure concentrations of key ions such as Na^+, Ca^{2+}, Mg^{2+}, and Al^{3+}. Permeability changes were evaluated by comparing ΔP values before and after chemical flooding. Residual oil saturation (Sor) was also determined.

ASP formulation

The chemical flooding formulation was based on widely accepted ASP concentrations for sandstone EOR. Each additive plays a specific role, such as sodium dodecyl sulfate (SDS), which reduces interfacial tension, Na_2CO_3, which facilitates saponification and ion exchange, and HPAM, which enhances sweep efficiency by increasing water viscosity (Nasution & Putra 2022).

Numerical simulation framework

Numerical modeling was conducted using CMG-GEM, incorporating reactive transport features to simulate laboratory conditions in one-dimensional space.

Model initialization:

The digital model geometry replicated the sand pack dimensions. Rock and fluid properties including porosity, permeability, and initial brine composition were calibrated using experimental measurements.

Permeability control:

A user-defined function adjusted permeability based on local ionic concentration (particularly Ca^{2+} and Cl^-) and pH. They helped simulate dynamic permeability alterations caused by ion exchange and mineral reactions.

Reactive transport integration:

GEM's built-in geochemical module was employed to simulate mineral dissolution (e.g., calcite at the anode) and precipitation (e.g., silica and iron hydroxides near the cathode). Reaction rates were governed by Arrhenius-based kinetics with threshold values for ion activity.

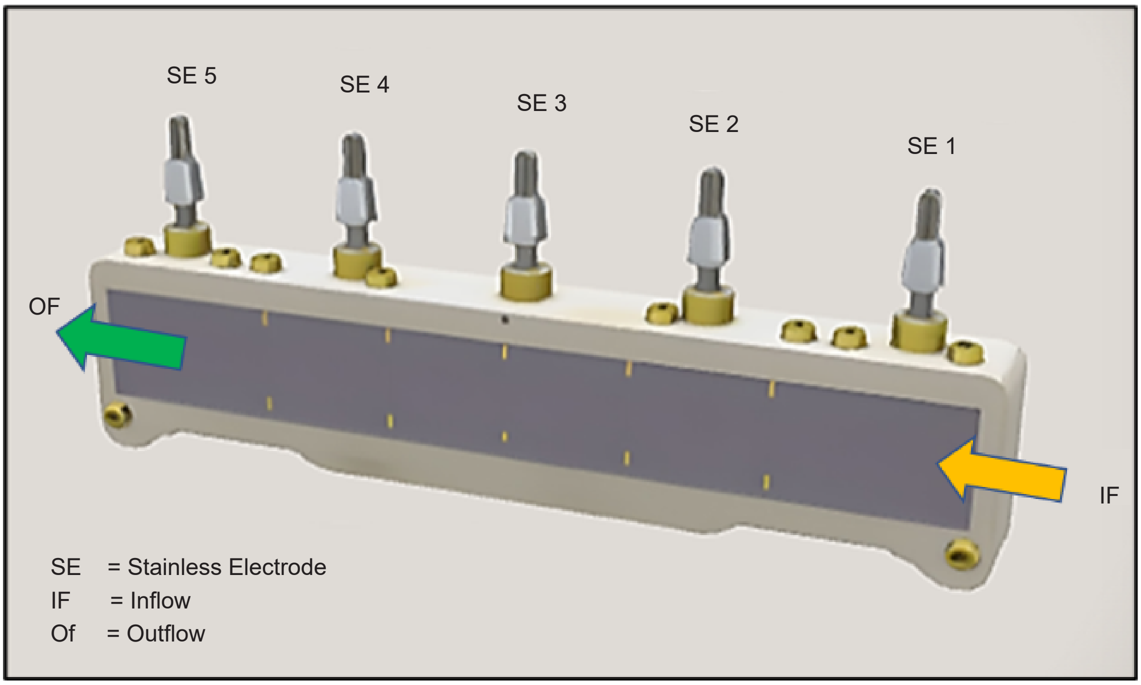


Figure 1. Sand pack cell for laboratory experiments (Putra et al. 2025)

Table 1. Chemical components of fluid injection (Putra et al. 2025)

Component	Primary Function	Concentration
Sodium Dodecyl Sulfate (SDS)	Surfactant	2000 ppm
Sodium Carbonate (Na_2CO_3)	Alkali	5000 ppm
Hydrolyzed Polyacrylamide (HPAM)	Polymer	0.075 wt%

Model validation and sensitivity:

Simulated permeability trends, ion concentration profiles, and oil recovery factors were compared against lab data. Sensitivity analysis was performed on electric field strength, brine salinity, initial mineralogy, and applied pressure gradient.

RESULT AND DISCUSSION

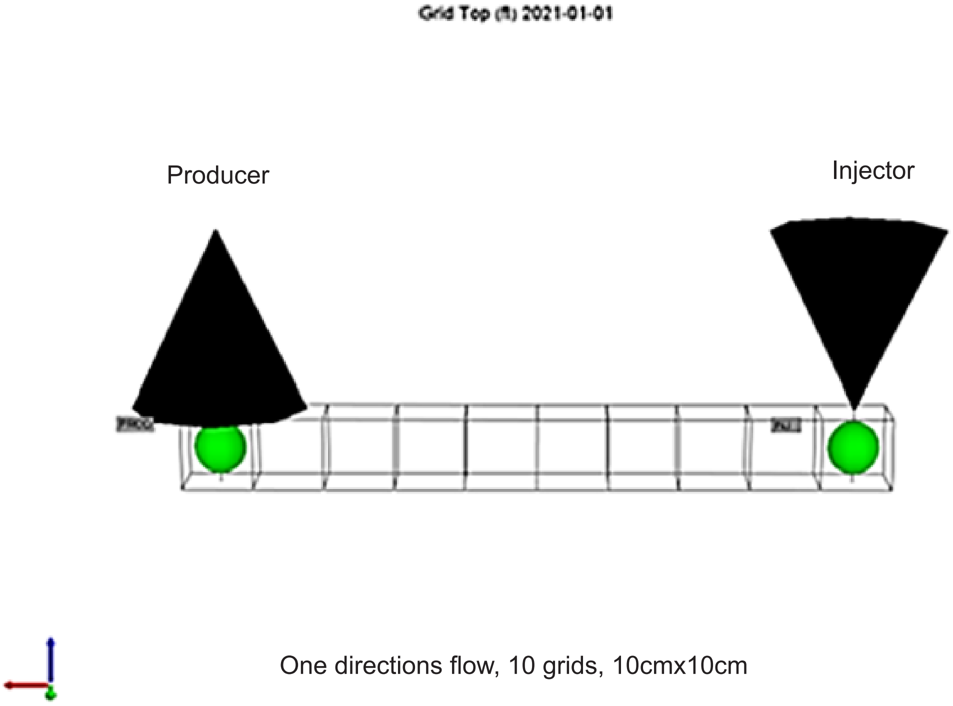
Experimental observations

The laboratory flooding test on a high-porosity synthetic sand pack ($\phi = 0.398$) revealed significant permeability changes following ASP injection. The formation was composed predominantly of quartz, with embedded carbonate and clay minerals including calcite, magnesite, illite, and kaolinite. The injection protocol consisted of a 10-minute brine pre-flush, followed by a 5-minute ASP slug. The ASP formulation included 2000 ppm SDS, 5000 ppm Na_2CO_3, and 0.075 wt% HPAM.

Upon ASP injection, the differential pressure (ΔP) rapidly rose from approximately 2.5 psi to over 17 psi at a fixed injection rate of 1 mL/min. This spike suggests a sudden permeability decline, likely caused by polymer retention, interaction between polymers and clays, and chemically induced pore-scale transformations.

Surface reaction mechanisms

Two reactive transport models were developed to evaluate the contribution of surface interactions. The first model incorporated only homogeneous aqueous reactions, while the second included both aqueous and mineral surface ion exchange reactions. Representative ion exchange reactions included;



One directions flow, 10 grids, 10cmx10cm

Figure 2. Sand-pack model - one direction (Putra et al. 2025)

$$(CaCO_3)+(H^+)\rightarrow(Ca^{++})+(HCO_3^-) \quad (2)$$

$$(MgCO_3)+(H^+)\rightarrow(HCO_3^-)+(Mg^{++}) \quad (3)$$

$$(K.6Mg.25Al_2.3Si_3.5O_{10}(OH)_2)+8(H^+)\rightarrow2.3(Al^{+++}) +5H_2O+0.25(Mg^{++})+3.5SiO_2 \quad (4)$$

$$(Al_2Si_2O_5(OH)_4)+6(H^+)\rightarrow2(Al^{+++})+5H_2O+2SiO_2 \quad (5)$$

These reactions indicate carbonate dissolution and clay destabilization can liberate multivalent cations by initiating exchange with injected Na ions under acidic and alkaline gradients, common during EK-EOR.

Simulation-based permeability evolution

The CMG-GEM simulation provided a compelling contrast between the two models. The ion-exchange-inclusive scenario required only a modest permeability increase from 0.0004 md to 0.0008 md, consistent with observed experimental behavior. This twofold enhancement reflects a realistic effect of surface charge modification and improved flow conductivity due to electrochemical interactions.

In EK-EOR, the permeability alteration plays a vital role in reflecting how subsurface flow properties evolve under electric field stimulation. Examining the permeability adjustments in the simulation models reveals key insights into the mechanisms at play.

Figure 3 shows the matching evidence of both models. A significant difference displays both results, while the curve of ion exchange exhibits a better similarity with the lab result.

In contrast, the model that excluded ion exchange demanded an exaggerated permeability uplift, from 0.0004 md to 0.00945 md, to match oil recovery trends. Such a drastic adjustment is unlikely under practical field conditions and reveals the limitation of omitting mineral surface reactions in EK-EOR simulations. The need for such forced calibration indicates that essential physics, specifically the electro-kinetic coupling between fluid and solid phases, is missing in the no-exchange model.

During the ASP injection phase, the differential pressure (ΔP) sharply increased from ~2.5 to ~17 psi at a constant 1 mL/min injection rate, signalling a rapid permeability reduction (Figure 4). The ASP injection dramatically increased ΔP, consistent with the onset of polymer retention and geochemical alteration. Notably, the simulation model incorporating ion exchange closely mirrored the experimental data, requiring only a twofold increase in permeability. This alignment underscores the importance of electrochemical interactions at the mineral-fluid interface, mainly the exchange of potential determining ions such as Ca^{2+} and Mg^{2+} for Na^+ introduced in the alkali phase.

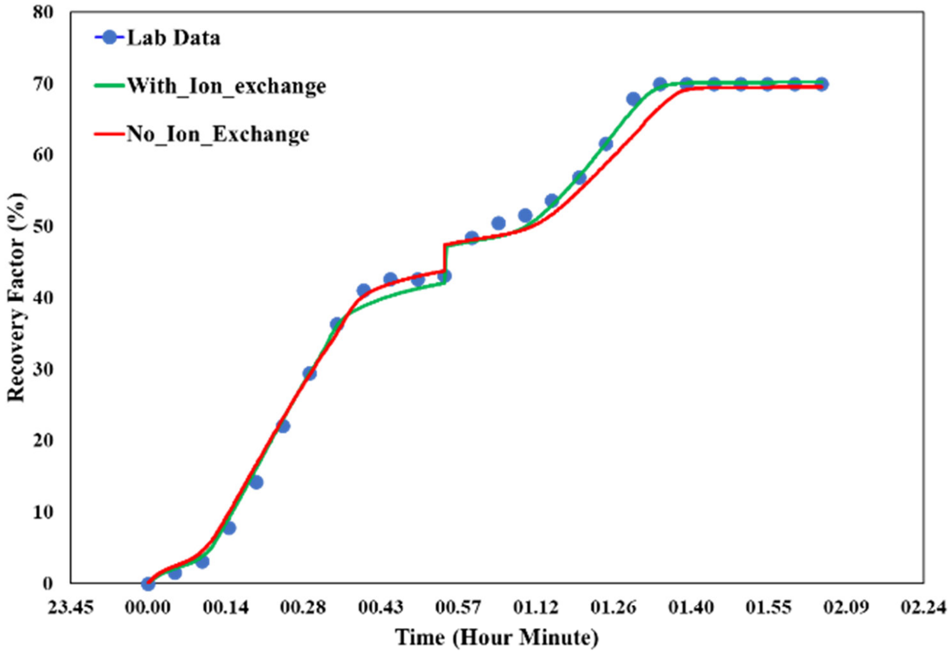


Figure 3. History matching of laboratory data with and without ion exchange

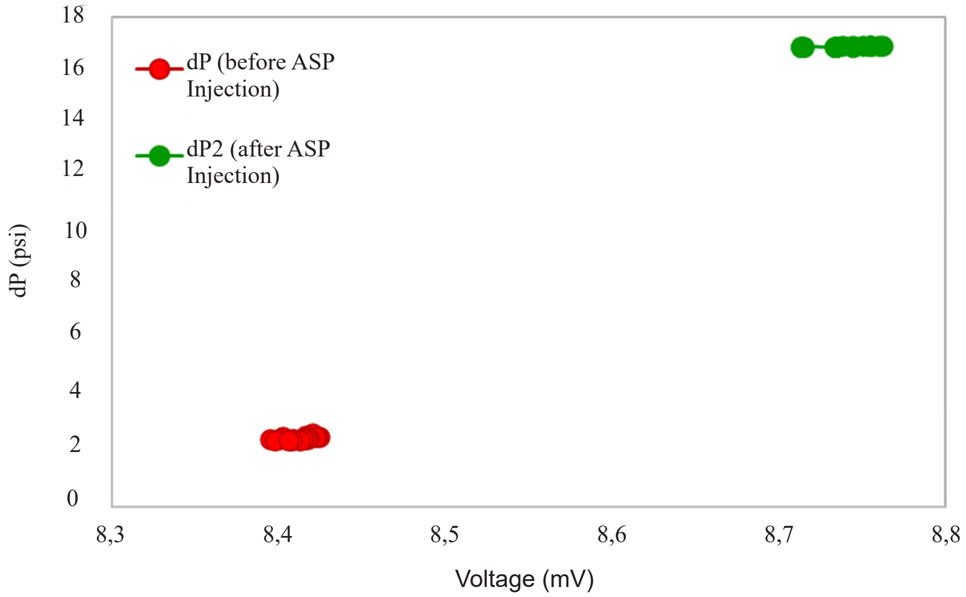


Figure 4. Correlation of pressure gradient and voltage during the 15-minute experiment

This phenomenon is primarily attributed to polymer retention within pore spaces, mineral-clay interaction (especially with kaolinite and illite), and geochemically-induced mineral surface reactions. These changes occur almost immediately and are the dominant mechanism affecting fluid flow during short-duration injection.

Streaming potential and early-time effects

During the ASP injection period, the streaming potential increased slightly from 8.4 mV to approximately 8.75 mV. This small but measurable shift suggests changes in the electric double layer (EDL) properties due to the replacement of divalent ions (Ca^{2+}, Mg^{2+}) by monovalent Na^{+}. These changes reflect early-stage restructuring of the mineral-fluid interface but fall short of triggering large-scale wettability alteration due to the limited exposure time.

The simultaneous rise in ΔP and streaming potential underscores the dominance of permeability control mechanisms over wettability effects during short-duration injection. Polymer-clay interaction, clay swelling, and immediate ion exchange reactions are likely responsible for the altered flow resistance.

Role of potential determining ions (PDIs)

Reactions involving carbonate minerals such as:

$$\begin{aligned} &CaCO_3 + CO_3^{2-} \rightarrow Ca^{2+} + 2CO_3^{2-} \\ &MgCO_3 + CO_3^{2-} \rightarrow Mg^{2+} + 2CO_3^{2-} \end{aligned} \tag{6}$$

Produce divalent cations that act as potential determining ions (PDIs). When these PDIs interact with clays like illite and kaolinite, which have high cation exchange capacities, they significantly affect surface charge and electro-kinetic behavior. Over time, these effects may lead to enhanced water-wetness, but under the 5-minute ASP regime, permeability change, not wettability shift, emerges as the dominant recovery mechanism.

While the surfactant (SDS) in the ASP solution can facilitate wettability alteration by reducing interfacial tension and desorbing organic films, such changes are time-dependent and require prolonged contact to manifest at the mineral-fluid interface. In formations containing illite and kaolinite, wettability alteration is also influenced by the balance of PDIs on the surface and in the solution. Under extended injection periods, ion exchange would continue displacing divalent cations with monovalent ones, pushing the system toward a more water-wet condition through mineral surface recharging. However, in this short-duration experiment, the initiation of such mechanisms is only partially realized.

These early-stage interactions influenced the structure of the electrical double layer (EDL), subtly altering streaming potential and indicating initial wettability transitions. However, the brevity of ASP exposure limited the extent of this transformation, placing permeability modification at the forefront of enhanced recovery in this context.

In summary, the combined evidence of a sharp ΔP increase, minor voltage shift, and the presence of carbonate and phyllosilicate minerals supports the conclusion that permeability alteration driven by polymer-clay interactions and early-stage PDI-controlled surface reactions is the dominant mechanism in this experiment. The mineralogical composition adds complexity to the geochemical interactions, mainly due to the buffering effect of carbonate minerals and the high CEC of illite, which delays but eventually enables wettability transformation via ion exchange. The full manifestation of wettability alteration would require longer exposure time, allowing ion exchange and EDL restructuring to reach equilibrium and contribute more substantially to enhanced oil recovery.

The no-ion-exchange model, by contrast, failed to replicate lab outcomes without invoking unrealistic permeability increases. This result emphasizes the necessity of coupling geochemical mechanisms with flow dynamics in EK-EOR simulation, especially under low-voltage, short-duration applications where traditional wettability models fall short.

Collectively, these findings highlight the interplay of physical, chemical, and electro-kinetic mechanisms in dictating reservoir behavior and reinforce the need for integrative simulation approaches in EK-EOR strategy design.

CONCLUSIONS

This research confirms that during short-duration electro-kinetic ASP flooding, permeability alteration rather than wettability change is the dominant mechanism influencing fluid mobility. Laboratory observations supported by numerical simulations showed a marked increase in differential pressure, which signals a rapid reduction in permeability due to interactions between injected chemicals and formation minerals, especially polymer retention, clay swelling, and geochemical surface reactions.

Minerals such as calcite, magnesite, kaolinite, and illite played active roles in early-stage ion exchange and dissolution, releasing multivalent ions like Ca^{2+} and Mg^{2+}. These ions modified the electric double layer (EDL) and contributed to a minor increase in streaming potential. However, due to the limited contact time (only five minutes of ASP exposure), wettability alteration had little time to evolve fully. Instead, the permeability reduction driven by electrochemical and physicochemical reactions emerged as the primary factor impacting flow resistance.

Importantly, the model incorporating ion exchange accurately reproduces experimental trends with only a modest increase in permeability. In contrast, the model excluding ion exchange required an unrealistic permeability upscaling to match recovery behavior. It reinforces the idea that including mineral surface interactions is essential for physically valid and predictive EK-EOR simulations.

In conclusion, the study offers a practical framework for evaluating permeability evolution under electro-kinetic conditions. It also emphasizes integrating geochemical and electro-kinetic mechanisms into modeling workflows. For future studies, longer injection durations are recommended to explore the transition from permeability-dominated to wettability-driven recovery processes comprehensively.

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GLOSSARY OF TERMS

Symbol	Definition	Unit
ASP	Alkaline-Surfactant-Polymer	
EK-EOR	Electro-Kinetic Enhanced Oil Recovery	
RF	Recovery Factor	%

IFT	Interfacial Tension	dynes/cm
DC	Direct Current	API
CMG	Computer Modeling Group	
SDS	Sodium Dodecyl Sulfate	
HPAM	Hydrolyzed Polyacrylamide	
SP	Streaming Potential	
Sor	Saturation Oil Residual	
EDL	Electric Double Layer	
PDI	Potential-Determined-Ions	
CEC	Cation Exchange Capacity	
ΔP	Differential pressure	

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