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A New Approach for Determination of Carbonate Rock Electrostatic Double Layer Variation towards Wettability Alteration

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Abstract

Focus on the molecular scale of low salinity brine effects seems to be necessary to clarify the possible mechanisms of carbonate rock wettability alteration. This study aimed at investigating the effects of different operational parameters such as pH, salinity and types of ions on wettability alteration (WA) during low salinity brine injection as a tertiary recovery process. In the present study, using the electrostatic double-layer concept and molecular behavior, along with a good view of the past studies, led to the justification of the obtained results. The studied reservoir is one of the Middle East carbonate reservoirs which is considered for low salinity brine injection plan. Although the concept of ζ potential is ill-defined in electrostatic or/and electrokinetic topics, nonetheless, to the extent possible, has been tried to use this concept to illustrate and justify underlying mechanism during low salinity process beneficially.

Resultant findings have shown that pH value directly affects carbonate rock powder ζ potential and determine the type of surrounding ions that form Stern layer and ion distribution in diffuse layer as well. A close examination at two temperatures of 25 °C and 80 °C, showed that active ions in WA e.g. Ca^{2+} and Mg^{2+} and SO_4^{2-} as an agent facilitator to access active ions to the rock powder surface, have profound impacts on the Stern layer. The obtained optimal ions concentrations, (i.e., 1000 ppm sulfate + 1000 ppm magnesium @ 80 °C) and (500 ppm calcium and 800 ppm sulfate @ 25 °C) have changed the ζ potential of oil wet rock powder in Seawater form -23.6 mV to -6.71 mV and -8.7 mV respectively, using a new designed procedure. In the present study, influence of ion valence on the electrostatic double layer variation of an oil-wet rock powder has been led to directly link this alteration to the wettability state changes. Therefore, this approach could be very helpful to monitor the wettability state of the rock powder in molecular scale.

Keywords: Wettability alteration, Electrostatic double layer, ζ potential alteration index, Ion concentration, Carbonate rock, Low salinity.

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1-Introduction

On average, two-third of initial oil in place of reservoirs remains un-swept after primary and secondary (conventional water injection) oil recovery methods. Other oil recovery methods such as thermal or non-thermal methods could increase the producible in-place oil and consequently expand the reservoir life. Generally, most of enhanced oil recovery (EOR) methods are seeking to improve the reservoir recovery factor by these main aims: a) reduction of interfacial tension between fluid and reservoir rock, b) oil swelling, c) reduction of oil viscosity, d) change of wettability and d) change in phase behavior (PVT)[1–8].

Two decades ago, Yildiz & Morrow[9] continued a research which was started by Jodhunadan & Morrow [10] on the effect of brine salinity and composition on oil recovery efficiency improvement. From that time to now, there are numerous indications from experimental and field studies which showed brine injection with salinity less than 4000 ppm has greater influence on oil recovery[6–8,11–14].

Success of low salinity brine injection is proven as an efficient EOR method but the underlying mechanisms of recovery improvement are still not entirely clear. On the other hand, Lagar et al. [15] reported 14% oil recovery increment by low salinity brine injection and researcher consider understanding the mechanisms of this process could help improving that valuation. One of the proposed mechanisms in literature is electrical double-layer expansion at mineral interface. For visualizing of ionic environment around a charged particle like colloid, double-layer model is being presented. This model tries to explain the repulsive forces in vicinity of a charged particle. It assumes two layers around the charged particle named Stern and diffused Layer and a shear plane which is located in between and Zeta (ζ) potential is attributed to it [16].

Stern layer symbolizes a close layer of charged particle around the surface that is filled by high concentration counter-ions. Moreover, other counter-ions are attracted by charged particle but prevented to get closer by Stern layer ions. This dynamic equilibrium causes diffuse layer which is filled by counter-ions with a density less than the Stern layer. Furthermore, co-ions distribution will gradually increase far from the charged particle surface. Concentration and type of ion in solution affect the double-layer thickness. Accordingly, surface charge and double-layer thickness determine the magnitude of surface potential. The most measurable parameter to evaluate the surface potential of a charged particle in electrostatic and electrokinetic studies is ζ potential. This parameter presents the electrical potential of where Stern and diffused layer meet (shear plane). Figure 1 tries to illustrate the aforementioned concepts[8-9].

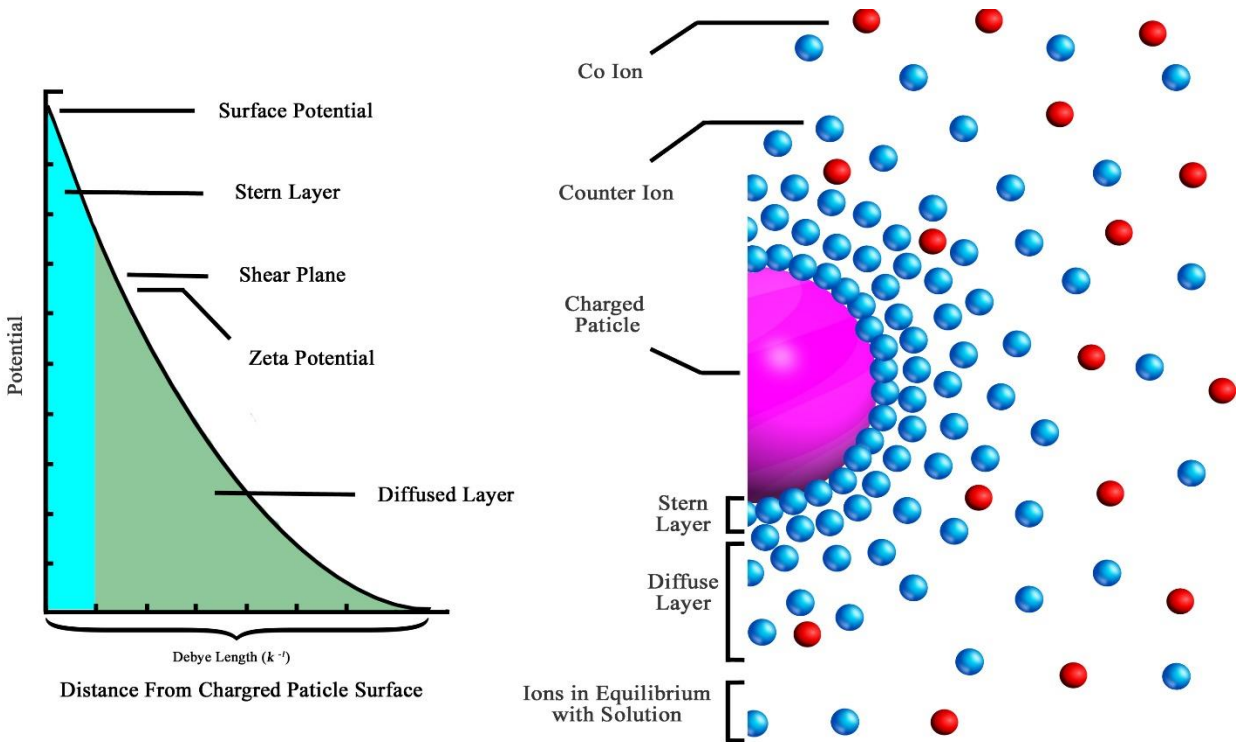


Figure 1: A visual presentation of double-layer model

Sign of ζ potential of the particle dictates direction of the movement toward anode or cathode. Obviously, its magnitude determines speed of particle motion in the electrolyte cell. The dominance state of net charges in diffuse and Stern layer over the intrinsic charge of the particle is controlled by pH, type and concentration of existing ions in solution that specifies speed of suspended particles in solution when an electric field is applied. To express this speed in terms of ζ potential, Smoluchowski [5] introduced the following equation.

$$\zeta = \frac{4\pi\eta}{\varepsilon} \times U \times 300 \times 300 \times 1000 \quad (1)$$

η is solution viscosity, ε is dielectric constant and $U = v/(V/L)$ represents electrophoretic mobility, which symbols of v , V , and L demonstrate speed of particle (cms^{-1}), voltage (volt), and the distance of electrodes (cm), respectively.

Double layer expansion is considered as one of the simplest and efficient way to explain how the wettability state alters during low salinity injection process. Based on this theory, counter-ions in brine film adsorb to brine/oil and brine/rock interfaces which are charged negatively. Therefore, a double layer system is formed at each interface and screens the repulsion between those interfaces. The characteristic length of the screening is named Debye length (k^{-1} , equation 2), given by[17]:

$$k^{-1} = \left(\frac{\epsilon_r \epsilon_0 k_B T}{2 N_A e^2 I} \right)^{1/2} \quad (2)$$

where ϵ_r and ϵ_0 are the relative permittivity of brine (dielectric constant) and free space respectively, T is temperature, k_B is the Boltzmann constant, N_A is Avogadro number, e is an electron charge and I is ionic strength which is given by[17]:

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (3)$$

which depends on molar concentration (c_i) and charge of ionic species i (z_i). Because of the ionic strength decreases during lowering the brine salinity, Debye length increases. Consequently, it expands double layers and makes them more diffuse in addition screening becomes weaker.

To easily imagine the mobility of a charged particle in a solution subjected to an electric field, Figure 2 is designed. Figure 2 shows a comprehensive view of a ζ test and a magnified view very close to the surface of the colloid particle. Some researchers tried to simulate conditions of ζ potential test using Molecular Dynamics (MD). Dimensions of simulation box in MD studies usually are in order of Angstrom (10^{-10} meter) which is 3 to 5 order of magnitude smaller than diameter of a colloid particle. Considering a large simulation box which contains colloid particles and surrounding fluid, makes these simulations computationally expensive. To overcome this difficulty, electroosmotic conditions is applied to MD simulation by researchers. The filling fluid in a ζ cell is stationary with respect to an imaginary system of coordinates located in an arbitrary point like one of the electrodes. However, the colloid particle moves toward the oppositely charged electrode relative to that coordinate system like what is shown in Figure 2-I (Eulerian coordinates). In MD simulation the Lagrangian coordinate is applied by locating the origin of the coordinate system on colloid particle. Therefore, particle surface is fixed in position and the neighboring fluid beyond the slipping plane moves toward the electrode with charge similar to that of the particle (Figure 2-II). Thus, the ζ potential calculated in MD is different in sign and close in magnitude to the experimental results [8,10 ,11, and 12].

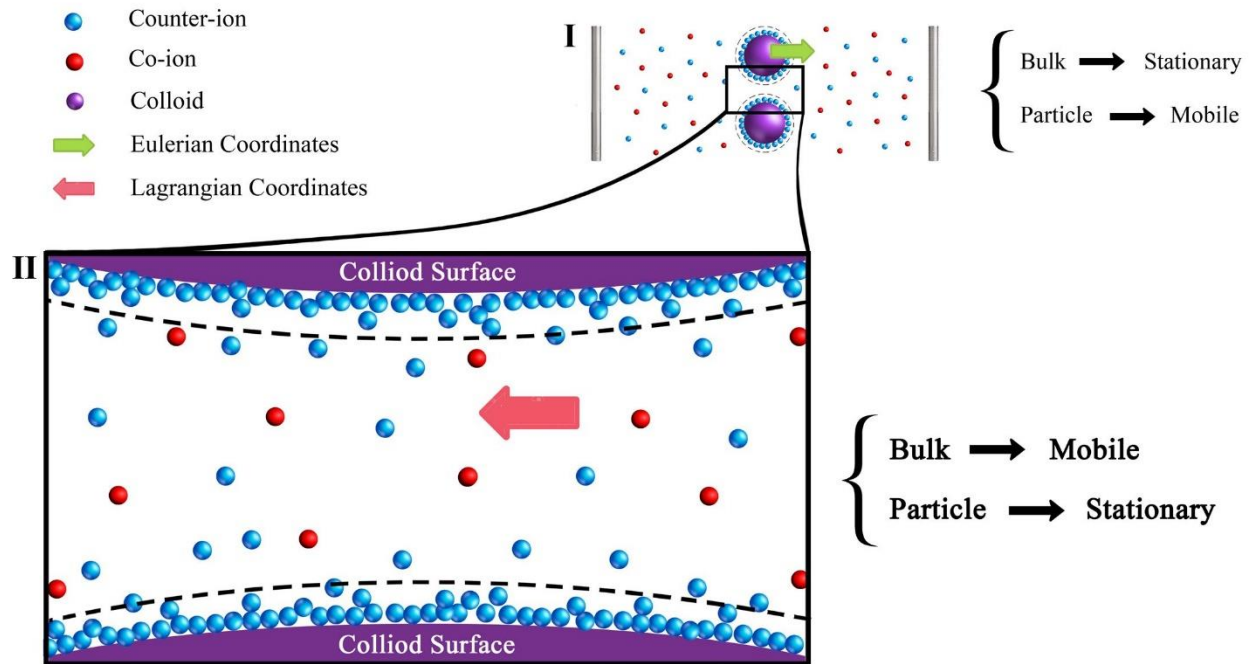


Figure 2: Surrounded colloid by EDL in an electric field I) colloid movement towards electrodes II) bulk movement towards electrodes

Several studies have been performed about water based EOR methods over the last decade to understand the true underlying mechanisms. Agbalaka et al. in 2009 [21] experimentally evaluated the impact of salinity and wettability on efficiency of oil recovery. They examined the potential of low salinity waterflooding as tertiary oil recovery method and compared to the results of low salinity waterflooding potential as secondary oil recovery process. Furthermore, in the same year, RezaeiDoust et al. [22] presented the chemical mechanisms in smart water waterflooding in both carbonate and sandstone reservoirs and tried to demonstrate their differences and similarities. The most bolded point in their work was that they claimed a different chemical mechanism for wettability alteration from evidence of different chemical boundary mechanisms of polar component from crude oil onto the negatively charged quartz/clay and the positively charged carbonate minerals. Moreover, in 2010 Austad et al. [23] suggested a new mechanism for low salinity EOR method based on the effect of pH quantity on acidic adsorption.

In the read more, Berg et al. in 2010 [24] done several experiments and provided straight evidence about advantages and disadvantages of each high salinity and low salinity waterflooding processes. Low salinity waterflooding released more crude oil but caused serious formation damages meanwhile the high salinity process was not as efficient as low salinity in crude oil production but nearly insignificant amount of clay swelling was observed. After that, in 2010 Fathi et al. [25] studied the effect of salinity and smart water composition on oil recovery at different temperatures of 100, 110 and 120 °C at chalk surface and compared with water flooding with Seawater as the base fluid. Also, they confirmed that the concentration of the

active ions such as Ca^{2+} , Mg^{2+} and SO_4^{2-} are not the only important factors for wettability changes but also the amount of non-active ions such as Na^+ and Cl^- can affect the WA process. They proved this statement by discussing over double-layer effect at chalk surface. Then in the same year Veldder et al. [27] reported a successful WA upon to low salinity waterflooding in one of the mixed-to-oil wet sandstone reservoirs in Syria. From their observation, they estimated the wettability changes was nearly to complete and leading an associated incremental 10-15 % stock tank oil initial in place recovery.

In 2011 Alotaibi et al. [28] stated that ionic strength of injection water has the main impact on low salinity waterflooding process in sandstone reservoirs and wettability is the main changeable parameter during this method. They reported that several factors such as salinity, temperature and rock mineralogy have great effect on rock wettability. Moreover, it was reported that the double-layer thickness is expanded by low salinity layer based on ζ potential measurements. This expansion provides a greater chance to change the wettability and efficiency of the process. Next year in 2011 Suijkerbuijk et al. [29] determined the impact of formation water, imbibing water and crude oil composition on WA during low salinity waterflooding operation. They explained and discussed their results within the context of several mechanisms which have been presented in previous studies. In addition, Nasralla et al. in 2013 [30] investigated the idea of ionic strength effect on the electrokinetic charges in sandstone reservoirs again. In their study, low salinity waterflooding showed lower contact angle rather than high salinity for two types of crude oil. Besides, based on their ζ potential results low salinity waterflooding had ability to make surface charge strongly negative at rock/brine and also oil/brine interface. They concluded when any increasing in repulsive forces between rock and oil surface is occurred, the double-layer expands. Consequently, it causes WA and more oil recovery improvement.

Although Nasralla et al. in another work in 2014 [31] introduced sweep efficiency improvement, interfacial-tension reduction and multicomponent ionic exchange as low salinity mechanisms but they believed none of them is the primary mechanism. Thus, they tried to quantify the extent of recovery due to electrical double –layer mechanism. Their study showed that reduction in pH value recovers smaller amount of crude oil. Also, by ζ potential measurement it was concluded that decreasing pH value of low salinity brines makes electrical charge at brine/rock and oil/brine interface slightly negative, decreases the double-layer expansion and consequently rock becomes more oil wet. In 2015 Mahani et al. [32] studied the kinetics of low salinity waterflooding effect in sandstone environment. Their results indicated that kinetics of wettability changes correlate with buoyancy-over force balance. In another work and in the same year Mahani et al. [33] demonstrated the positive results of low salinity flooding application as carbonate reservoir EOR process. Also, they tried to explain the underlying mechanisms specifically in carbonate rocks. Their results implied that oil detachment from dolomite surface needs a larger reduction adhesion forces at the contact line that limestone. They stated that the change in surface charge is the primary mechanism which reveals that there is a positive low salinity effect in carbonate rocks without mineral dissolution.

Myint et al. in 2015 [17] stated that double-layer expansion is closely related to the brine films thickness and stability. They reviewed the last studies about WA mechanisms during low salinity

waterflooding process which affect interaction between brine/rock and brine/oil interface of thin brine film. Then in 2016 Jackson et al. [34] demonstrated efficiency of controlled Salinity Water (CSW) is strongly correlated to ζ potential alteration at both oil/brine and mineral/brine interface. For optimum designing of a (CSW) composition, they stated that the polarity charged of ζ potential must be known for both interfaces. They suggested that the lack of identification about positively charged oil-water interface may be the reason for failures in using conventional approach to CSW. Just after them Mahani et al. [35] presented a comparative study about electrokinetic of different types of carbonate rock. They entered the effect of wide range of salinity, brine composition and pH value into their experimental study. For all cases they found the surface charge was positive in high salinity water. For lower salinity like SW or/and diluted SW the ζ potential decreased toward negative values. Also, they revealed pH value had a great effect on ζ potential. Their results were discussed about surface charge and effect of different salinity on four different carbonate rocks. Finally, in 2017 Song et al. [36] tried to facilitate understanding of the rock role of electrostatic forces in calcite WA by presenting an experimental study and surface complexation modeling (SCM) of synthetic ζ potential in mixed brine (Mg^{2+} , SO_4^{2-} , Ca^{2+} and CO_3^{2-}). Their work and model prediction showed calcite ζ potential is sensitive to CO_2 pressure and calcite surface will be positively charges in all brines in presented CO_2 environment. Table 1 shows the summery of recent studies over low salinity waterflooding.

Table 1: Summery of literature survey

Researcher	Year	Conclusion
Agbalaka et al.	2008	Evaluating the impact on salinity and wettability on efficiency of oil recover
RezaeiDoust et al.	2009	Discussing on similarities and differences in the chemical mechanisms of smart water flooding between carbonate and sandstone reservoirs
Austad et al.	2010	Investigation over chemical mechanism of low salinity flooding in sandstone reservoirs
Berg et al.	2010	Finding evidence of WA by low salinity flooding
Fathi et al.	2010	Study on the effect of salinity and ion composition on wettability modifying
Veldder et al.	2010	A successful low salinity flooding in a filed wide scale and proving of WA
Alotaibi et al.	2011	Investigating the wettability changes using low salinity water in sandstone reservoirs
Suijkevbuijk et al.	2012	Using parameter isolation to investigate the relation between wettability and low salinity flooding
Nasralla et al.	2013	Study on oil recovery improvement and its relation with WA in sandstone low salinity flooding
Nasralla et al.	2014	Introducing Double layer expansion as a primary mechanism in low salinity flooding
Mahani et al.	2015	Investigation of kinetic of low salinity flooding effect
Mahani et al.	2015	Investigation of the low salinity flooding mechanisms in carbonated reservoirs
Myint et al.	2015	Study on pervious clarified mechanisms and its effect on thin liquid films in IOR
Jackson et al.	2016	Explaining the impact of ζ potential during controlled salinity waterflooding
Mahani et al.	2016	Bring the surface complexation model to explain the electrokinetic of carbonate/brine interface in low salinity flooding
Song et al.	2017	Expanding the surface complexation modeling to characterizing carbonate wettability during waterflooding

In all previous studies, the zeta potential and its relation to the wettability state are not reliable. Because zeta potential value strongly depends on ion strength of brine, type of ions, as well as the amount of colloid charge and the ability of ions to gather in stern layer. Disjoining pressure in an oil, water, and rock system only can represent whether rock surface attract the oil or not, and its is not able to discuss about wettability state change of the rock. But in this study, tracking of wettability state change and its effect on zeta potential has been possible.

Although, finding a correct zeta potential range to investigate the variation of electrostatic double layer is a process in which would be obtained by a series of experiments that reveal the behavior of fluid phases and the colloidal particles when are in contact with each other. In other word, a chemical upon to its components behaves differently and has a miscellaneous effect on zeta potential. For instance, asphaltene molecules based on their structure might increase or decrease the value of zeta potential [34,37]. At the same way, minerals of the rock powder and the composition of the selected reference fluid also have a deceive role in the zeta potential measurement. Therefore, to recognize the behaviors of used material it is necessary to implement try and error experiments to find a suitable range for wettability state examination.

Though so far, there are many studies on ζ potential and wettability state, but the approach of ζ potential variation during WA process has not been followed due to the lack of the key idea of this paper to investigate the change of ζ potential in same situation before and after WA. In fact, ion strength as well as fixed concentration of each ion type to have an equal access opportunity to get closer to the rock surface and forming the Stern layer and shear plane is the fundamental idea of this research to design a procedure which results in record of any changes in an oil wet (OW) carbonate rock Stern layer.

In this paper, first, the methodology and procedures are presented. Then, at result and discussion section the results of asphaltene molecules stimulation by various ions, zero potential charge (ZPC) of used rock powders, influences of different ions and ion strength, and ultimately variation of electrostatic double layer have been investigated.

2- Methodology & procedures

This study aimed at investigating different ions influences on modification of a colloidal particle stern layer which has been surrounded by various ions. This study gives a good molecular scale knowledge about zeta potential as well as wettability alteration. The difficulties of this study were the sensitivity of zeta potential results to any possible contaminant in the test tube and also the solubility of the rock powder in brine which should be controlled by setting water pH up before mixing with rock powders. Further more details are discussed in these regards.

2-1- Stepwise road map

Figure 3 indicates the Stepwise road map to investigate the effects of active ions on the wettability alteration during modified ionic liquid flooding.

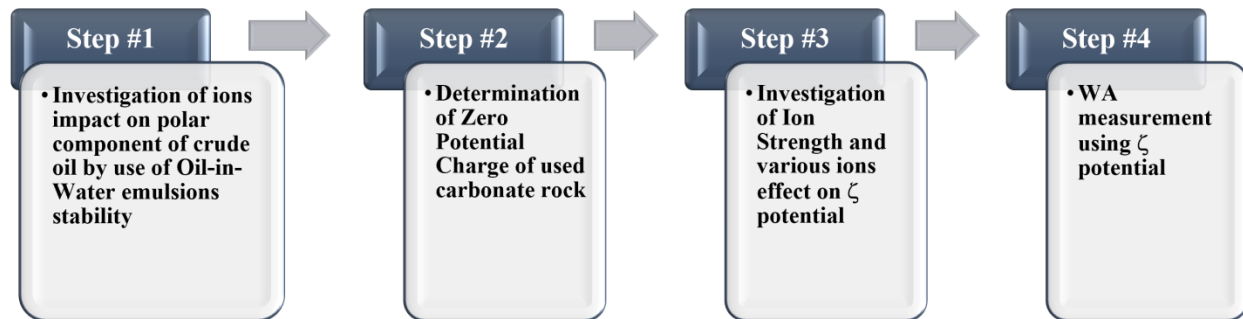


Figure 3: Investigation of the ions effect on the wettability alteration methodology

In section 2-3 the procedures of all steps are represented with specific titles, and at results and discussion section (section 3) the related results are explained with same titles (with heading of 3-X-...).

2-2-Materials

Used oil is obtained from one of Middle East fields which along its low specific gravity has a noticeable asphaltene content. 3.46 wt% and 11.46 wt% and 34 are the values which have been reported for its asphaltene and resin contents, and °API gravity, respectively. The water wet (WW) and OW Rock Powders (RP) contain about 84% calcite and 5% dolomite. All synthetic brines were made using Merck company products but the used Seawater was provided from sea.

2-3-Methods

2-3-1-Aging process

To run ζ potential investigation experiments with OW rock powder and compare the results with WW state, aging process was performed as follow:

I- Clean rock powder (with size of equal or less than 20 micron) and crude oil were mixed using a mechanical stirrer for 24 hrs.

II- The mixture of rock powder and crude oil was poured into a cylinder and its pressure was raised to 2500 psi.

III- High-pressure cylinder was kept in an oven at 80 ° C for 800 hrs.

All these steps are illustrated in Figure 4. After aging process accomplishment, the OW rock powder was washed using decalin to remove the crude oil components that have not chemically bonded to the rock surface.

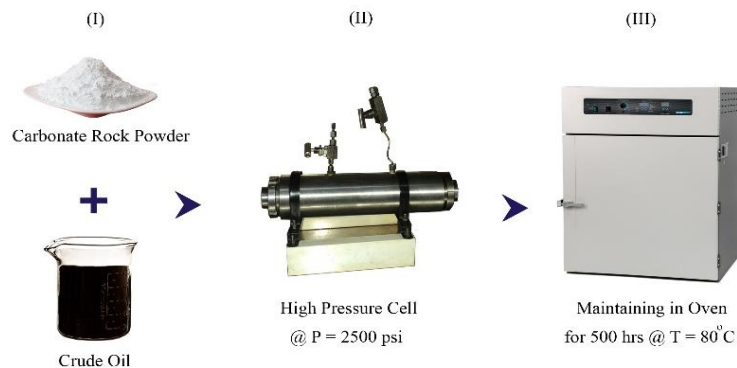


Figure 4: Steps of aging process

2-3-2- Procedures of step#1 → Investigation of the ions impact on polar component of crude oil by use of oil-in-water emulsions stability

2-3-2-1- Investigation of the oil-in-water emulsions ζ potential

To investigate the effects of salinity on the polar molecules of crude oil and its impact on ζ potential of the oil-in-water emulsions, following procedure has been performed which is shown in Figure 5.

I- Proportion 1 to 4 of crude oil was added to aqueous (ultra-pure water, 10 times diluted Seawater, and Seawater (SW)).

II- The crude oil was dispersed in the water base solution using ultrasonic for 10 min. (The oil-in-water emulsions formation was checked by a microscope)

III- The emulsions were allowed to get balance for 48 hrs.

IV- pH was set to value of 7.5 using HCl and NaOH.

V- Baker of Emulsions was placed on a magnetic stirrer to get the balanced pH, and step IV was repeated until fixing pH to 7.5.

VI- Measuring and recording ζ values of samples.

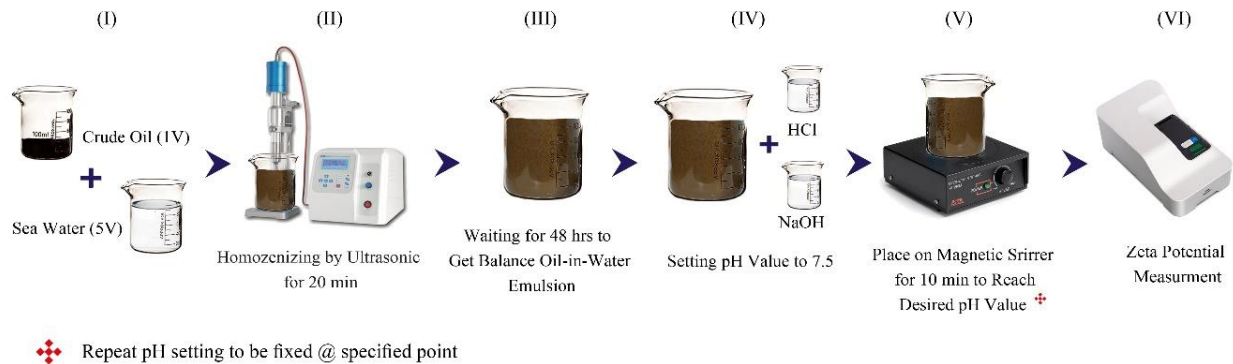


Figure 5: Oil-in-water emulsion preparation procedure

2-3-2-2-Emulsion stability determination

A sample of all prepared emulsions before and after the step III were placed on a glass lamella. Using ImageJ software, the number of O-in-W emulsion ratio with size of less than $1000\mu\text{m}^2$ was calculated

2-3-3- Procedures of step#2 → Potential of Zero Charge Determination (PZC) of the carbonate rock

2-3-3-1- PZC determination

Following is the procedure which is done to determine PZC of used carbonate rock (Figure 6).

- 1- 2.5 gr washed and clean WW rock powder was added in to 250cc SW ($\zeta_{\text{SW}}=-4.23$) (7 samples for performing the experiments in 5,6,7,8,9,10, and 11 were prepared).
- 2- The added WW rock powder was dispersed using Ultrasonic with power of 200W for 5 min.
- 3- pH values of seven prepared samples were set up to 5, 6, 7, 8, 9, 10, and 11 using NaOH and HCl (repeat this step in a multiple time interval until obtaining a fixed pH).
- 4- Measuring and recording ζ values of samples.

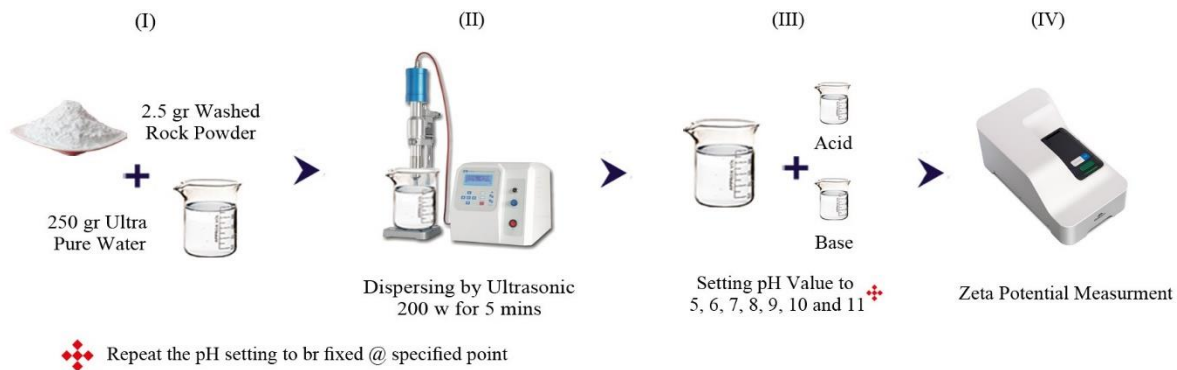


Figure 6: Procedure of Finding PZC

2-3-4- Procedures of step#3 → Investigation of the ion strength and various ions effect on ζ potential

2-3-4-1-Effect of ion strength on ζ potential

Ion strength reduces by dilution of an ionic liquid using ultra-pure water. SW was diluted 5 and 20 times and WW RP were dispersed within them. Their pH was set up to 7.5 using HCl and NaOH. After ensuring that the pH value does not change, ζ potential was measured.

2-3-4-2- Effects of various ions on ζ potential

In this step of the work, the impacts of various ions on ζ potential of WW and OW RP have been examined. In order to check the electric charge of cations and anions, the anions (SO_4^{2-} , PO_4^{3-}), cations (Ca^{2+} , Mg^{2+}) and monovalent (Na^+ , K^+) were selected. In addition of ions type effects, OW and WW rock powder were used to check the effects of wettability states on the ζ potential as well. Figure 7 represents the followed steps for sample preparation to measure ζ potential.

I- Enough amount of RP was added in to distilled water for elimination of any possible contaminate.

II- The washed RP were kept in the oven at 90°C until complete drying.

III- 2.5 gr clean and washed WW RP were added in to 250cc ultra-pure water ($\zeta_{\text{UPW}}=0$)

IV- The added WW RP were dispersed using Ultrasonic with power of 200W for 5 min.

V- 300, 500, 800, and 1000ppm of anionic divalent (SO_4^{2-} , PO_4^{3-}), cationic divalent (Ca^{2+} , Mg^{2+}) and monovalent (Na^+ , K^+) were dissolved in the prepared solutions in step IV, individually. A calculated amount of Na_2SO_4 , Na_3PO_4 , CaCl_2 , MgCl_2 , NaCl , KCl were dissolved so that 300, 500, 800, and 1000ppm of the target anions or cations be present in the solution.

VI- pH values of prepared solutions were set up to 7.5 using NaOH and HCl (this step repeated in a multiple time interval until obtaining a fixed pH).

VII- Measuring and recording ζ values of samples.

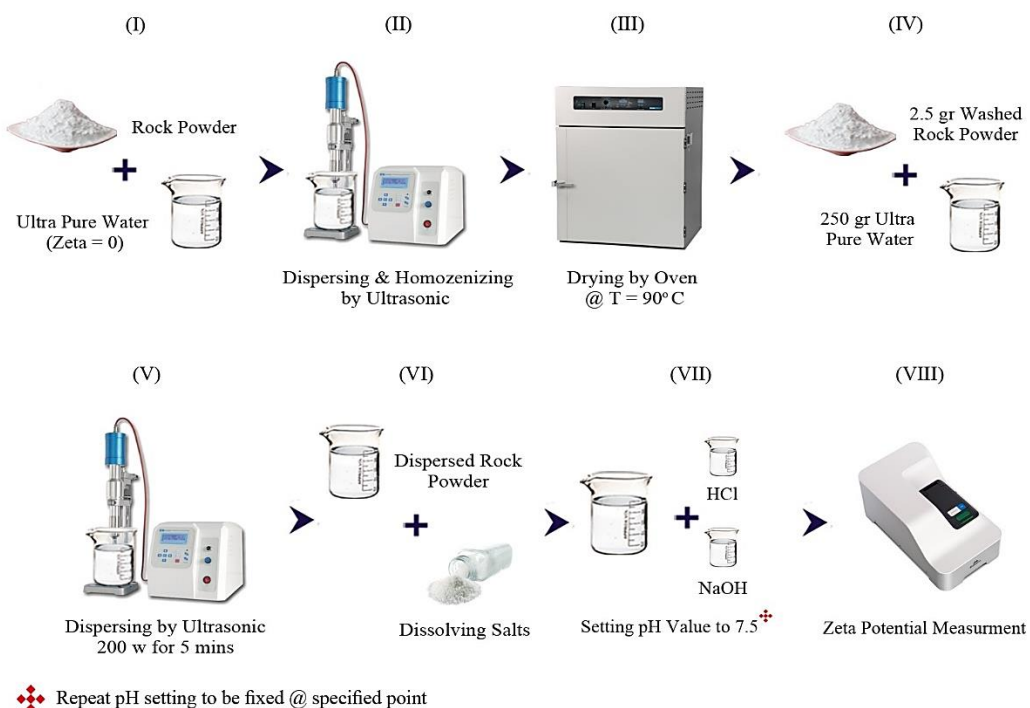


Figure 7 : Procedure of check the various Ions Effect on ζ Potential

2-3-5- Procedures of step#4 → WA measurement using ζ potential

The active ions such as magnesium and calcium have a crucial role in wettability alteration processes [9,10, 18 and 19]. Their tendency to react with carboxylic acid components which have been stuck to the rock surface cause to change the rock wettability state from OW towards water wetness. Forming metal-organic complexes need the active ions to get closer to the rock surface [38], and therefore, the role of sulfate ions seems to be vital for the wettability alteration process to be implement. Based on the negative charge of sulfate anions, they gently reduce the intrinsic positive charge of rock and then reduce the repulsive forces between the cations and rock surface, conclusively increasing the accessibility of the cations to the diffusive layer. In the final step, the impacts of active ions and sulfate have been examined to check ζ potential variation when OW RP are in contact with the solution that involves active ions. The following are the procedure which have been conducted to calculate ζ potential alteration index:

I-2.5 gr OW rock powder was added in to 250cc ultra-pure water ($\zeta_{UPW}=0$).

II- The added WW rock powder was dispersed using Ultrasonic with power of 200W for 5 min.

III- pH values of prepared solutions were set up to 7.5 using NaOH and HCl (this step repeated in a multiple time interval until obtaining a fixed pH= 7.5).

IV- Different concentrations of cationic divalent (Mg^{2+} , Ca^{2+} , and SO_4^{2-}) was dissolved at 25°C and 80°C in the prepared solutions in step III. Figure 8 and Figure 9 Indicate the concentrations of dissolved salts and the methodology that has been followed to determine optimum salinity for WA.

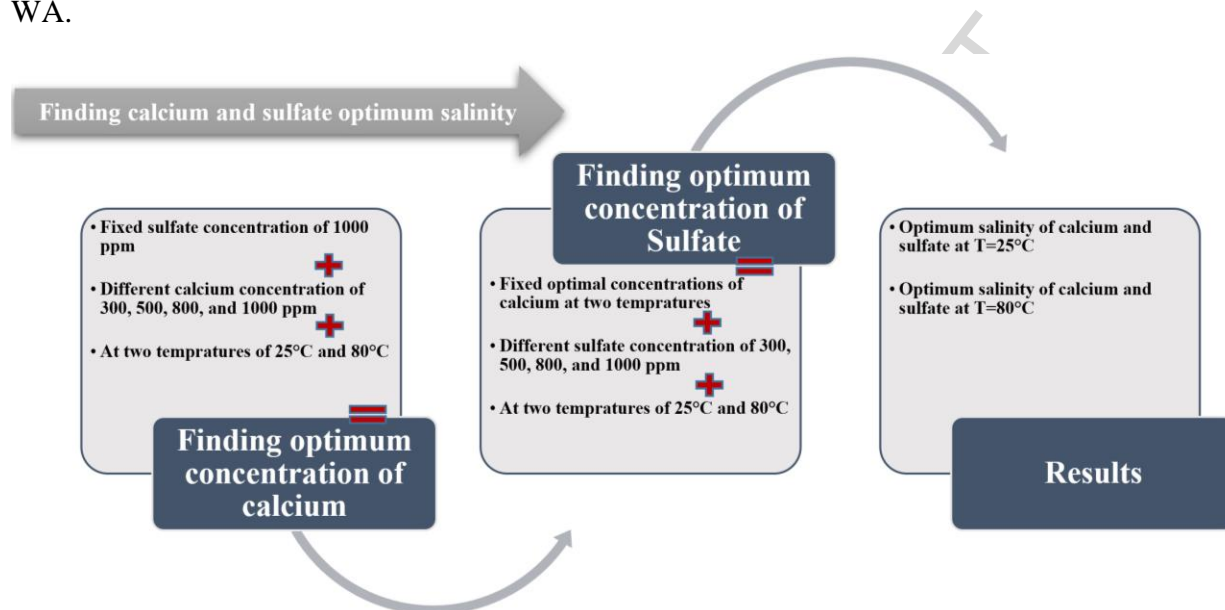


Figure 8: Finding optimum salinity of calcium and sulfate

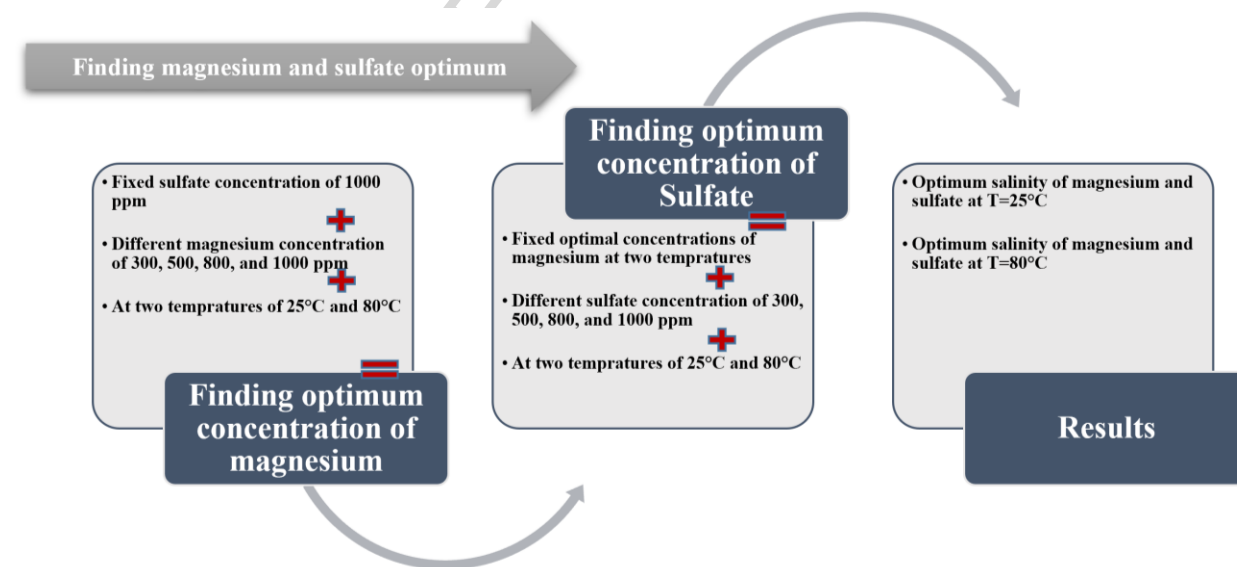


Figure 9: Finding optimum salinity of magnesium and sulfate

V - pH values of prepared solutions were set up to 7.5 using NaOH and HCl (this step was repeated in a multiple time interval until obtaining a fixed pH= 7.5).

VI- After obtaining a fixed pH from the prior step, the solution was allowed to achieve a balance (in order to obtain its balance ions distribution in the Stern layer, shear plane and also diffusion layer).

VII- After removing the number of crude oil components (which was stuck to the Stern layer) upon to reaction with dissolved active ions, the suspended RP (which their Stern layer were chemically modified) were filtered by a 9-micron filter paper using a vacuum pump.

VIII- To obtain reassuring of evacuating any salts from the filtered rock powder, they were washed using ultra-pure water and then were dried in an oven at 60°C.

IX- The dried RP were added to SW and then its dispersion was done by use of ultrasonic apparatus.

X- pH values of prepared solutions were set up to 7.5 using NaOH and HCl (this step was repeated in a multiple time interval until obtaining a fixed pH= 7.5).

XI- ζ potentials of the fixed pH solutions were measured.

XII- Having ζ potential of the OW RP after aging process, and the measures ζ potential of previous step, the ζ potential alteration index (ζ PAI) can be calculated. All these steps are illustrated in Figure 10.

$$\zeta \text{ PAI} = \left[\frac{\zeta_{oil-wet} - \zeta_{Altered wettability}}{\zeta_{oil-wet} - \zeta_{water-wet}} \right] \quad (4)$$

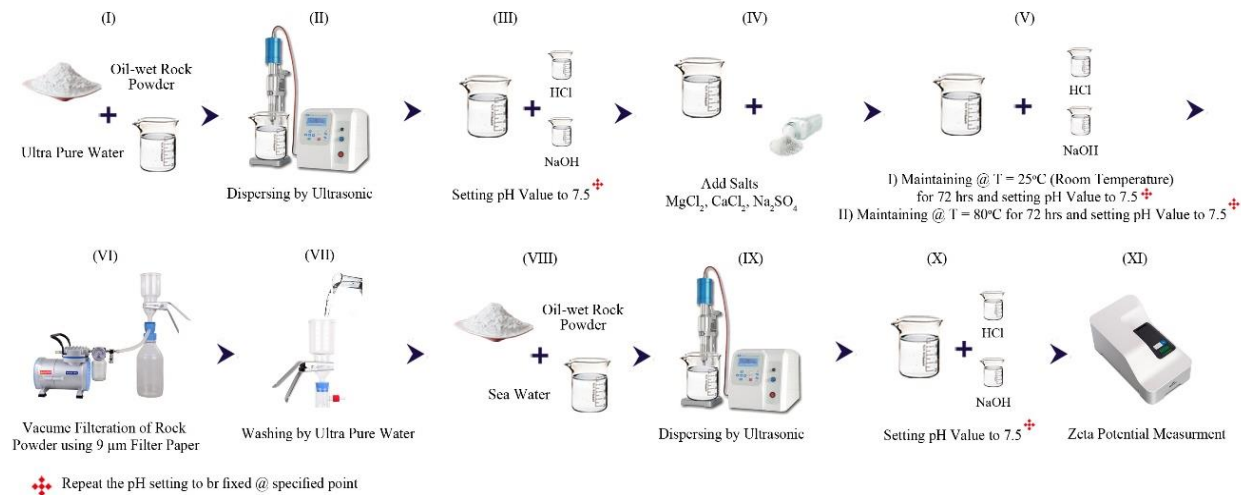


Figure 10: procedure to find ζ potential alteration index

2-3-5-1-Determining the optimum salinity of the calcium and sulfate

Owing to the roles of active ions such as magnesium calcium and complementary role of sulfate in WA, this part of the work has been designed in such a way that at temperature of 25°C and 80°C, the changes on ζ potential in a basis fluid to be record. To clarify the usage reason of this methodology, the ζ potential of aged rock powder (OW RP) was measured in SW. Thereafter, the procedure of Figure 10 was conducted to apply the changes by active ions on the Stern layer and then after filtering, the rock powder with changed Stern layer dispersed in the SW again to measure ζ potential

2-3-5-2-Determining the optimum salinity of the magnesium and sulfate

Same procedures which have been conducted for optimization of calcium and sulfate ions are repeated for magnesium and sulfate optimization.

3-Results and Discussion

3-1- Results of step #1 → Investigation of the ions impact on polar component of crude oil by use of oil-in-water emulsions stability

3-1-1-Investigation of the oil-in-water emulsions ζ potential

The obtained results indicate that ζ potential increases with increasing the salinity so that SW with salinity of 45000 ppm has the minimum ζ potential with value of -31.7 with respect to 10 times diluted SW and ultra-pure water with value of -17.4 and -8.4, respectively. The presence of various ions in the water phase, will stimulate the polar molecules (such as asphaltene and resin) which have a bit water solubility and tends to accumulate on the oil/ water interfaces (Figure 11). Therefore, the measured ζ potential showed a negative value. With decreasing salinity, accumulation of the asphaltene will reduce and the charge of emulsions will increase (less negative respect to SW). Due to the used crude oil, behavior of the polar molecules on ζ potential will vary [34] and the order of change magnitude depends on the molecules structure and effects of some atoms such as nitrogen, oxygen, and sulfur and their reaction tendency with rock [37]. With increasing (more negative) the value of ζ potential, the stability of emulsions due to boosting the repulsion forces will increase[39].

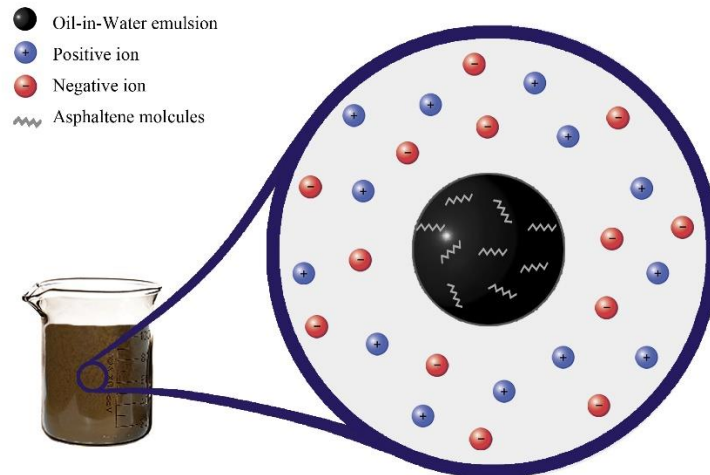


Figure 11: Balanced oil-in-water emulsion

3-1-2- Emulsion stability determination

The ratio of oil-in-water emulsion number to the number of all emulsions were considered as stability indicator (SIn)[40]. The stability indicators demonstrate values of 0.63 and 0.59 for formed emulsion in SW before and after given balance time. Due to crude oil polar component accumulation on the oil/water interfaces, interfacial tension decreases and emulsion can be formed in smaller size with more stability. Therefore, stability of emulsions due to the presence of polar molecules on the interface enhance and they can be able to stay suspended in the continues water phase due to appropriate ζ potential [41]. Table 2 represents the value of emulsion stability of three samples.

Table 2 : ζ potential and stability indicator of ultra-pure water, 5 times diluted SW, and SW

Continues phase	ζ potential	SIn before balance	SIn after balance
UPW	-8.4	0.08	0.06
10 diluted SW	-17.4	0.28	0.15
SW	-31.7	0.63	0.59

3-2- Results of step #2 → PZC of used carbonate rock

3-2-1- PZC determination

PZC of carbonate rock usually is located in the range of [9-11], lower and upper of this point, intrinsic charge of calcite is negative and positive, respectively. In this work, the obtained results of the PZC finding procedure also confirms the reported results in the literature review. As Figure 12 demonstrates, the PZC for the used carbonate rock is placed at pH of 9.14. It represents that, due to positively and negatively charged of used rock powder and used oil, respectively, in the pH of 7.5 (all of the prepared samples were set up to pH=7.5) the attraction forces leading an OW rock powder below PZC.

Depending on the sign of ζ potential around the PZC, the change in the pH of the solution could strengthen or weaken ζ potential. This means that, if ζ potential value of a solution is positive, H^+ increasing in the solution will boost the positive charge in the diffuse layer and increase the ζ potential value. Similarly, if the ζ potential is negative, OH^- increasing will affect the ζ potential and reduce it. On the other hand, concentrations of H^+ and OH^- could be able to affect the polarity and dominant system charge so that in a special concentration (PZC), the colloid charge will probably tend to be neutralized (with crystal structure consideration) due to atomic electronegative change. Less than or more than of PZC, electric cloud arrangement will change in such a way that the surface charge of the colloid (rock powder) be positive or negative. Figure 12 indicates that less than 9.14, Stern layer of carbonate RP is occupied with negatively ion charged, and in case of more than PZC vice versa.

According to the intrinsic charge of the calcite particle at a specific range of pH, Stern layer will host the counter ions [27-28]. Several studies have been done to check the tendency of ions to stick to the colloid on the Stern layer and specify the colloid behavior in an electrical field. The

tendency of colloid to attract the ions and get them together on the Stern layer determine its movement direction in an electrical field, In fact, the impact of electrical field on the ions that are stuck to the particle on Stern layer and those ions which are under the influence of particle charge and accompany it during its movement, represent the particle surface charge in that bulk which has been suspended in it.

The intrinsic charge of calcite RP varies with change of pH [6], [19-21], [23][42]. Concentration of H^+ and OH^- in the solution control and change the colloids polarity and affect the interaction between ions and colloids. Usually the range of [9-11] is reported for PZC of carbonate rock [36]. lower than this range the carbonate surface charge is positive and vice versa. When for setting up the solution pH, sodium hydroxide and chloric acid are used, below the PZC the calcite charge is positive and tends to attract the counter ions (Cl^-) and consequently, the measured ζ potential is negative, and on the contrary, upper then PZC, Na^+ is counter ion and measured ζ potential is positive. Hereafter, in all figures, the markers which are in blue and black indicate WW and OW states of RP, respectively.

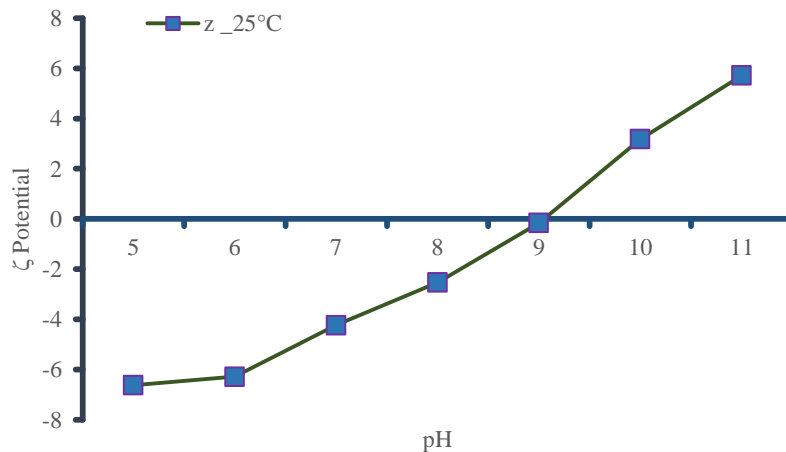


Figure 12: ζ potential changes over different pH value at constant temperature 25° C

3-3- Results of step #3 → Investigation of the ion strength and various ions effect on ζ potential

3-3-1-Effect of the ion strength

Figure 13 depicts the measured ζ potential for suspended WW rock powder into SW, 5, and 20 times distilled SW at 25°C and 80°C. The resultant findings indicate that, distillation of SW decrease the ion strength and consequently the accessibility of active ions (magnesium and calcium) to the rock surface will increase. At high temperature the ions penetration into diffuse layer will increase and intensify the potential difference between diffuse layer and the bulk (Figure 13).

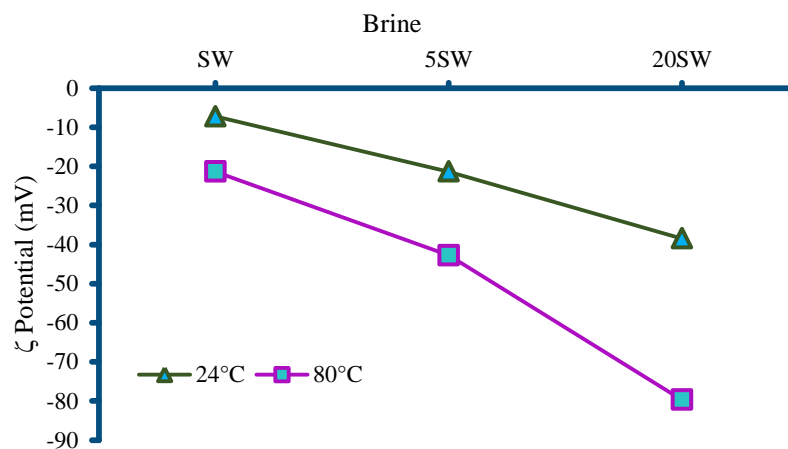


Figure 13: potential for combination of WW rock powder and different brines

3-3-2-Effects of various ions on ζ potential

3-3-2-1-Effects of anions on ζ potential

Generally, the values of measured ζ potential for OW rock are more negative than those of WW Figure 14. Although, depending on type of used crude oil this result may be vary due to the bond atoms to polar molecules such as NSO which can affect the electron cloud arrangement [34,36,43]. Nevertheless, penetration of polar molecules of the used crude oil in the Stern layer and sticking to the rock surface with intrinsic positive charge in pH=7.5, leading a negative ζ potential.

Scrutiny of ζ potentials results of this work and the literature survey reveal that different dissolved salts with different concentration, ion valences, and pH, when calcite rock powder is present as a charged colloid, the ζ potential depends on many parameters which vary from a salt to another. The first parameter which is important to consider for determination of ζ potential is the ratio of the ions valences (Co-Ion^A : Counter-Ion^B , A and B are ions electrical valence, for

instance, $Mg^{2+}:-1Cl$, for $MgCl_2$) which forming a salt as well as its concentration. The general rule for ζ potential which can be observed from the results of the present study and also literature survey outline that in a colloidal system with dissolved salts. In case of having more counter ions charge than co ions (i.e., $B>A$), from the beginning, counter ions decisive the sign of the measured ζ potential. As concentration increases, co-ions will pervade the diffuse layer and alleviate the electric potential of Stern layer and shear plane as well, and consequently salinity increases and double layer electrostatic (EDL) will be compressed. When the counter ions have less charge than co ions (i.e., $B<A$), at very low concentration (about 0.01%wt [37]), counter ions form the Stern layer and shear plane and determine the sign of ζ potential. With increasing the co-ions concentration, their charge weighs the bulk condition and will quickly change the ζ potential sign [16]. In case of electrical charge equivalency (i.e., $B=A$), the counter ions will be attracted by calcite rock powder and form Stern layer and shear plane, and the ζ potential sign will be the same which counter ions are. Generally speaking, by ions concentrations increasing (regardless of ions charge type and valency) the Debye length will decrease and the ζ potential will be weakened.

Ions distribution around the rock powder will be affected by entrance of trivalent or divalent anions into the solutions. As Figure 14 demonstrates, the recorded ζ potential value for sodium phosphate (Sodium+1:3-phosphate) show a more negative ζ than that of sodium sulfate (sodium+1:2-sulfate). Because the sulfate anions have one negative valence more than phosphate, thus will be attracted more by RP and are occupied Stern and shear plane in low concentrations of 300 and 500ppm. With increasing their concentrations, the amount sodium cation will increase and impose the co-ions to diffuse layer and reduce the impact of counter-ions in WW and oil wet (OW) states[37]. Moreover, increasing the salinity will compress the EDL due to reduction of iso-potential surfaces power which is created by RP. Therefore, the electric field which is applying by ζ potential measuring instrument, feels less the created potential by rock powder and consequently, the mobility of RP decreases and ζ potential will reduce as well. Figure 16 illustrates the ions distribution around a calcium RP with WW and OW states.

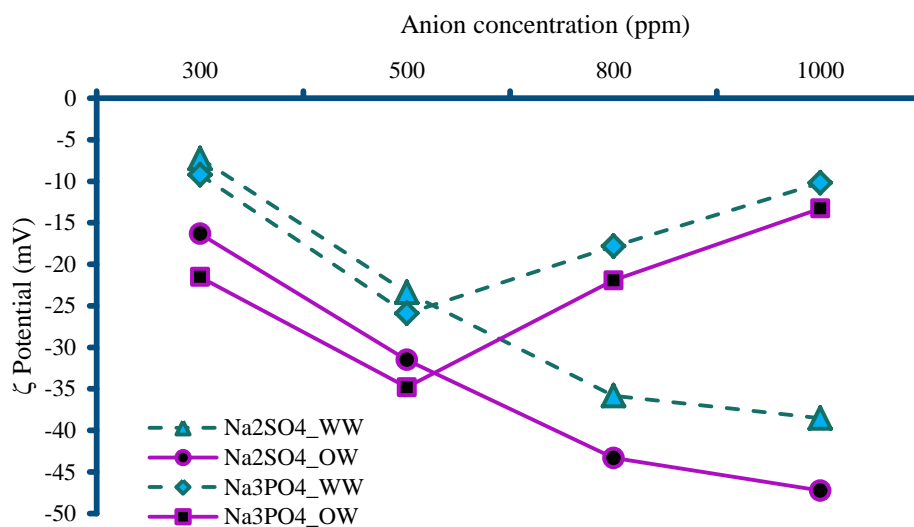


Figure 14: Effect of anion concentration on ζ potential at constant temperature 25°C

Resultant findings at 80 °C outlined that, increasing of temperature will intensify the penetration of ions within the diffuse layer and boost the ions chance to stick to the rock on the Stern layer. Figure 15 indicates that the salt of Na₂SO₄ due to its anion (SO₄²⁻), has less effect than anions of Na₃PO₄ (PO₄³⁻) and its ability is lower than that of phosphate for decreasing ζ potential (i.e., to be more negative). In cases of suspension of OW rock powder at 80°C, the trends which was seen in WW rock powder, have been repeated. But in concentration of more than 800ppm, due to more molarity of Na⁺ in Na₃PO₄ than Na₂SO₄, the amount of sodium will increase and penetrate into diffuse layer and consequently, alleviate the negative charge of rock powder, thus, the measured ζ potential will increase (become less negative).

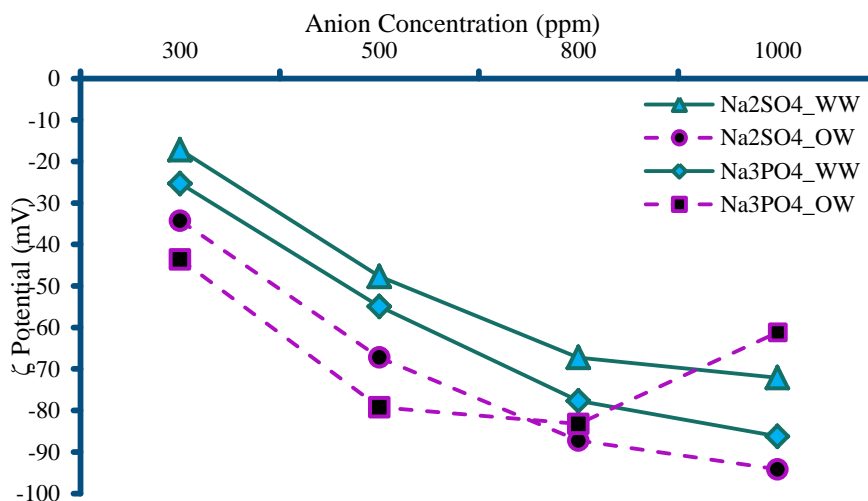


Figure 15: Effect of anion concentration on ζ potential at constant temperature 80 °C

In case of anions penetration into diffuse layer of a positively charged rock powder as counter-ion (Figure 16), they will form the Stern layer and shear plane as well. In low concentration, the ability of the co-ions to enter the diffuse layer and also to get closer to the shear plane and Stern layer (with more intensity) will decrease. When carboxylic molecules are stuck on the Stern layer the penetration ability of co-ions into diffuse layer will increase.

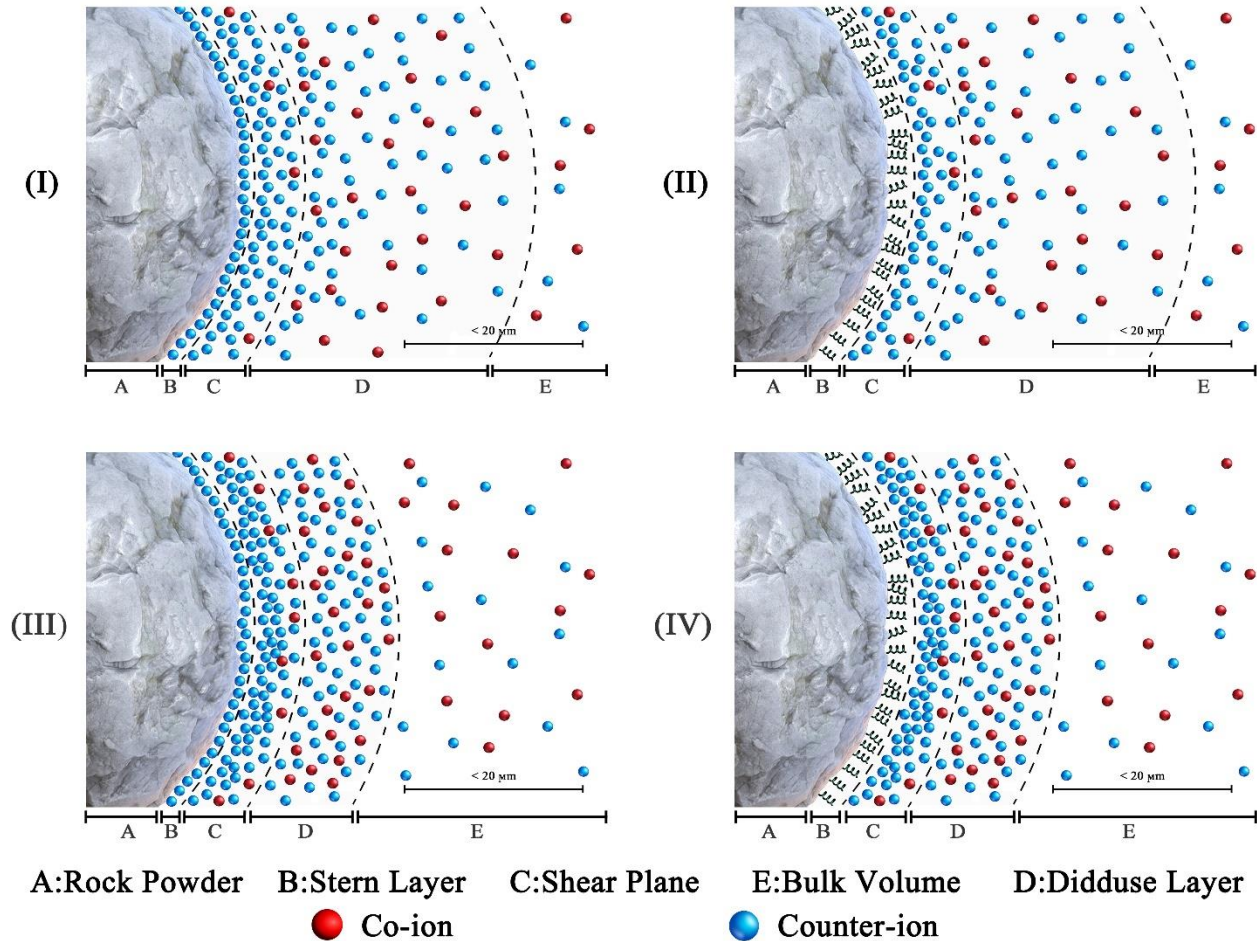


Figure 16: Anion distribution around a carbonate rock powder [I] WW RP, low concentration, expanded EDL, II) OW RP, low concentration, expanded EDL, III) WW RP, high concentration, compressed double layer, VI) OW RP, high concentration, compressed double layer]

3-3-2-2-Effects of cationic divalent on ζ potential

(Magnesium+2:1-Chloride) and (Calcium+2:1-Chloride) are the salts which their cations have more electric valence than their anions. In very low concentrations [34,37], the Stern layer of the rock powder will occupy with chloride (Cl^-) and lead to a negative ζ potential. Affecting of the shear plain and diffuse layer by positive charge of cations cause positive ζ potential. That is why in high concentration, presence of magnesium and calcium cations outweigh the chloride anion and change the ζ potential towards positive values. Salinity increasing causes electrostatic

double layer compression and consequently leading power reduction of the iso-potential surfaces around the rock powder as well as mobility reduction in the electric field. Performing the experiments using OW RP recorded the lowest ζ potential for MgCl_2 due to negatively charged component of crude oil and also less activity of magnesium ion respect calcium at 25°C temperature (Figure 17), whereas calcium ions due to more ability to penetrate within the diffuse layer lead to ζ potential increasing with sharp slope in higher concentrations. Moreover, the negative charge of the carboxylic component on the Stern layer and also the tendency of calcium ion to form metal-organic complexes with carboxylic acid [2], [12], [19], [30-33] are the reasons that calcium ions tend to more invading diffuse layer. Figure 19 indicate the distributions of ions in the Stern and diffuse layer of WW and OW RP.

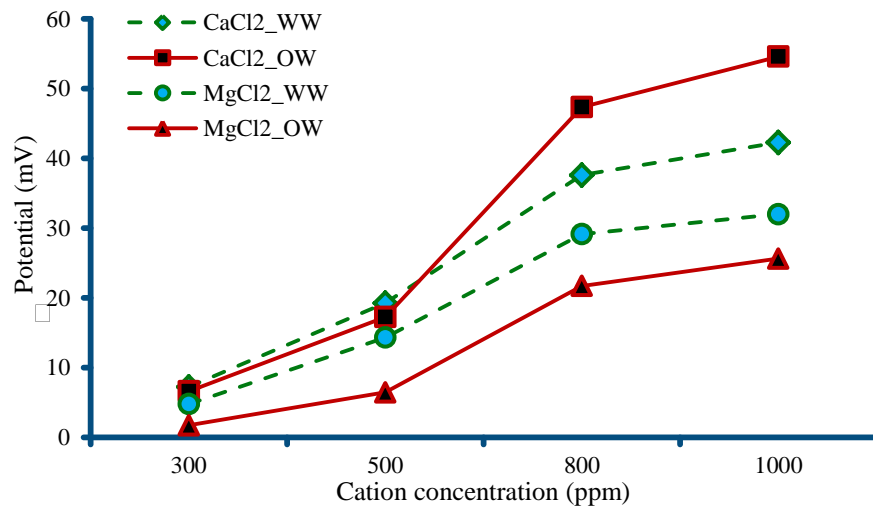


Figure 17: Effect of cation concentration on ζ potential at constant temperature 25°C

Magnesium ions are more active than calcium [9-10], [18-19] in high temperature. As it can be observed from Figure 18, in case of dissolving MgCl_2 at temperature of 80°C , measured ζ potentials are more positive for OW and WW RP. As stated earlier, calcium and magnesium have more tendency to occupy the diffuse layer of OW RP than WW. The recorded ζ potentials of OW RP indicate that, in low concentration, the presence of carboxylic acid in Stern layer leading less increasing (less positive) of measured ζ potential, while with concentration increasing in solution with suspended OW rock powder, EDL compression as well as gathering of cationic ions in the diffuse layer results in more ζ potential recording (Figure 19).

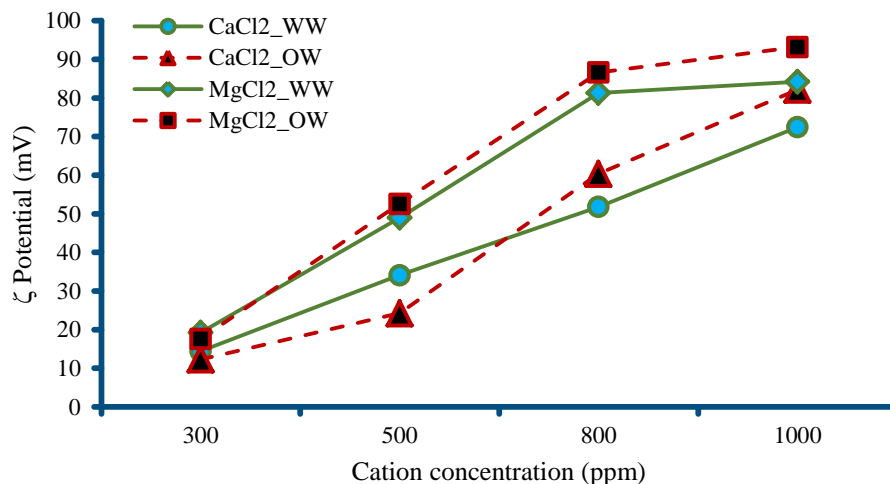


Figure 18: Effect of cation concentration on ζ potential at constant temperature 80 °C

In low concentrations, the counter ions will place in the Stern and diffuse layers and cause a negative measured ζ . As concentration increases, due to more valences of cations such as magnesium (+2) and calcium (+2) than the anion (Chloride (-1)), their charge overcome the charge of Stern layer and the sign of ζ potential will be changed to positive rapidly [37]. In this work the used salts concentration of MgCl₂ and CaCl₂ is high enough to outweigh the primary negative ζ potential in lower salinity than 300 ppm. What is more, in all tests, for having no significant effects on the salinity when acid and base are adding for setting up the pH, very low concentrations (<300 ppm) were not selected.

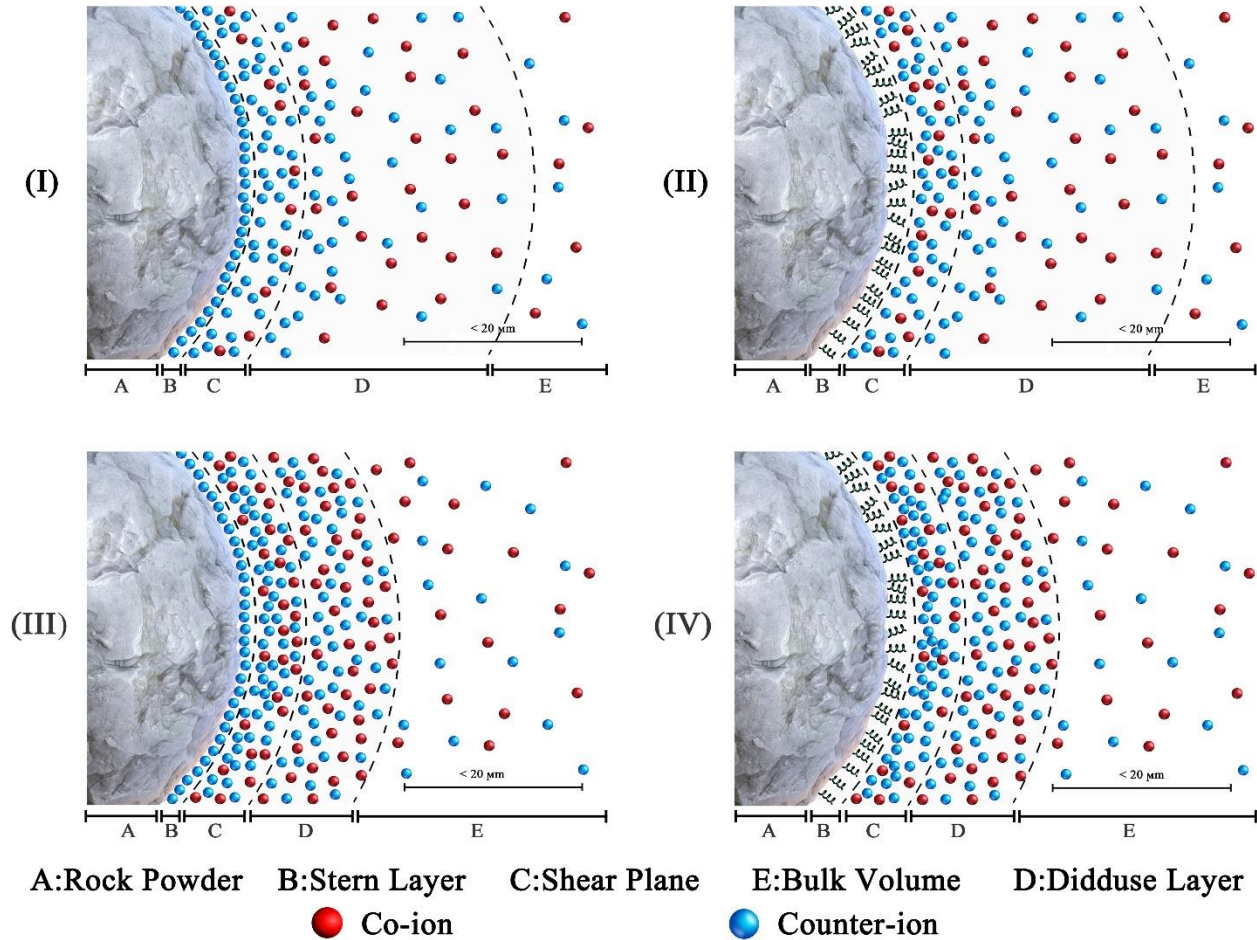


Figure 19: Cation distribution around a carbonate rock powder, I) WW RP, low concentration, expanded double layer, II) OW RP, low concentration, expanded double layer, III) WW RP, high concentration, compressed double layer, VI) OW RP, high concentration, compressed double layer

3-3-2-3-Effects of monovalent on ζ potential

(Na+1:1-Cl) and (K+1:1-Cl) are monovalent salts which their anion and cation have equal valences. At low concentrations, negative measured ζ potential is due to occupying of Stern layer and shear plane by chloride anions. As concentration increases, the number of cations will increase and penetrate the Stern layer and alleviate the negative ζ potential (become less negative). Figure 20 illustrates that the growing trends have occurred at lower concentrations for NaCl than KCl for OW and WW RP. This can be because of the sequences of sodium and potassium location in the periodic table of elements. As the atomic radius of sodium is less than potassium, its charge density is more effective in increasing ζ potential (become less negative). Therefore, potassium concentration should be more to show a ζ potential increasing like what happen for NaCl. Like what happened for previous salts (Figure 14, Figure 15, Figure 17, and

Figure 18) for NaCl and KCl the measured ζ potential of OW is more negative than WW rock powder.

At temperature of 80°C, the ability of Cl^- , Na^+ , and K^+ for penetration into diffuse layer will increase. As it is obvious from Figure 21, all concentrations of NaCl and KCl have a more negative ζ potential value than those which conducted in ambient temperature. Comparison of NaCl propensity at 25°C and 80°C, results in a decreasing of Na^+ performance upon to the attraction between positive charge of rock powder and Cl^- . All the obtained trends in Figure 21 depict that, in 800ppm concentration, the salinity is high enough to highlight the role of cations in increasing ζ potential values. Furthermore, the steeper slope of ζ potential increment (less negative) of dissolving NaCl with a concentration of 1000 ppm in the OW rock powder solution, is another proof of the assert of the superiority of Na^+ than K^+ for negative charge alleviating in the diffuse layer.

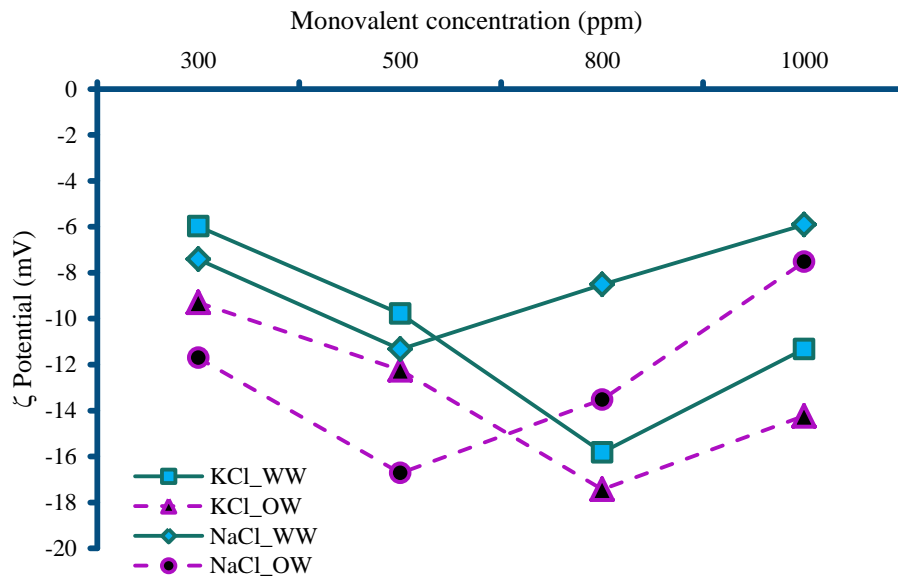


Figure 20: Effect of monovalent concentration on ζ potential at constant temperature 25 ° C

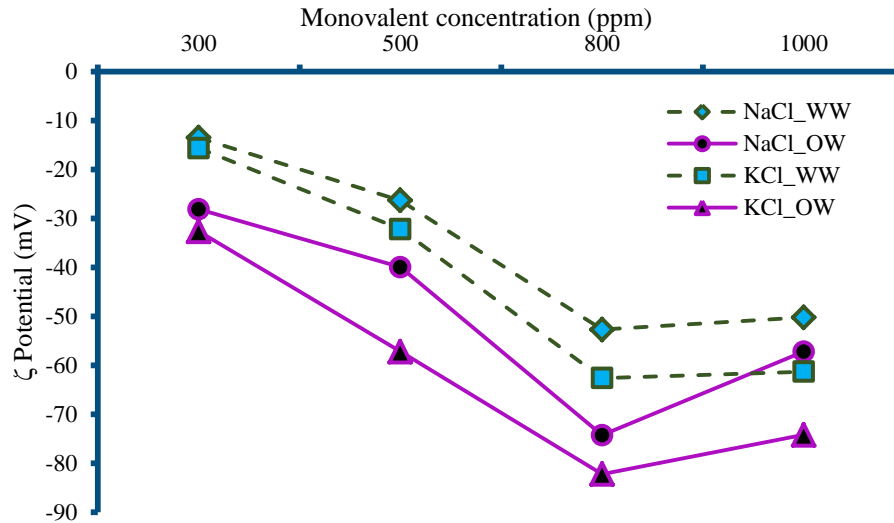


Figure 21: Effect of monovalent concentration on ζ potential at constant temperature 80 °C

3-4- Results of step #4 → WA measurement using ζ potential

3-4-1-Determining the optimum salinity of the calcium and sulfate

The recorded difference between the two value of ζ potential in SW, represent the created WA by added salts. SW was selected as reference solution for ζ measurements. Before and after every change on the RP, ζ potential of same RP was measured in SW again. It is necessary to point out that, for comparison accuracy of ζ changes along a designed experiment, ζ should be measured in one reference fluid with the same ionic strength and proportion of electrolyte concentrations.

SW was selected as basis fluid due to the difference between measured ζ potential of OW and WW states (-23.6 and -4.2, respectively). The difference between these two numbers indicate that, the negative charge of crude oil component causes the ζ potential to be more negative in same SW. An important point which mentioning it seems to be crucial is that, after many try and errors SW was selected as references fluid, and other used fluids showed a shorter range than that of is obtained for SW i.e., [-23.6, -4.2]. Therefore, after ions effects on the stern layer, recording any ζ potential value within this range, is a good indication for WA towards water wetness.

According to Figure 10, to find the optimum salinity of calcium, in constant sulfate concentration of 1000 ppm, the calcium was dissolved at two temperatures of 25°C and 80°C with concentration of 300, 500, 800 and 1000 ppm. The optimum for two temperatures of 25°C and 80°C have happened in brines of 1000 ppm sulfate + 500 ppm calcium, and 1000ppm sulfate + 1000 ppm calcium, which their ζ potential have been recorded by -9.7 and -8.7, respectively (Figure 22). In the continuation of the work, for the obtained optimum concentrations of calcium

(500 ppm and 1000 ppm @ 25°C and 80°C, respectively), the measuring ζ potential was performed to investigate the impact of variation of sulfate concentrations (300, 500, 800 and 1000 ppm) (Figure 23). Resultant findings indicate the optimum salinity for calcium and sulfate with concentrations of 800 ppm sulfate and 500 ppm calcium at 25°C results in ζ potential of -7.5 and for 1000ppm sulfate and 1000ppm calcium at 80°C the ζ potential measured by -8.7.

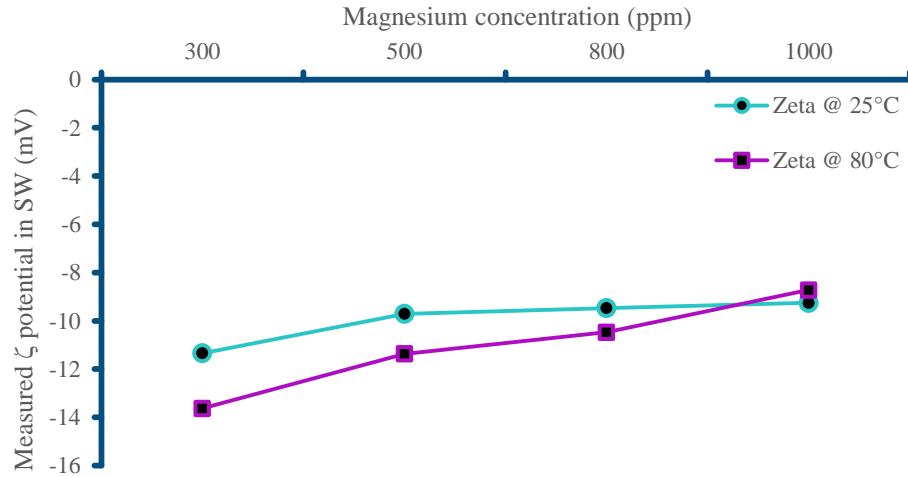


Figure 22: Effect of calcium concentration on ζ potential at two different temperatures of 25 & 80°C and fixed sulfate concentration 1000 ppm.

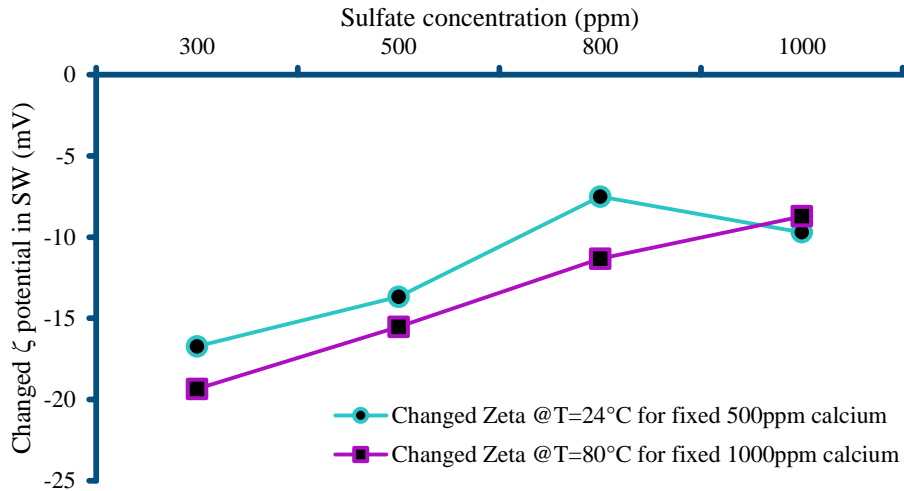


Figure 23: Effect of sulfate concentration on ζ potential at two different temperatures of 25 & 80 °C and fixed calcium concentration 500 & 1000 ppm.

3-4-2-Determining the optimum salinity of the magnesium and sulfate

At fixed concentration of sulfate the values of -13.1 and -6.7 are obtained as maximum (optimum or less negative) ζ potential for magnesium concentration of 800 and 1000ppm,

respectively (Figure 24). Thereafter, the combination of different sulfate concentration with the optimal concentration of magnesium (Figure 25) have shown that optimum sulfate and magnesium concentrations, 800ppm of magnesium + 500 ppm of sulfate, and 1000ppm of magnesium + 1000 ppm of sulfate, at the temperature of 25°C and 80°C with results in ζ potential values of -8.3 and -6.7, respectively.

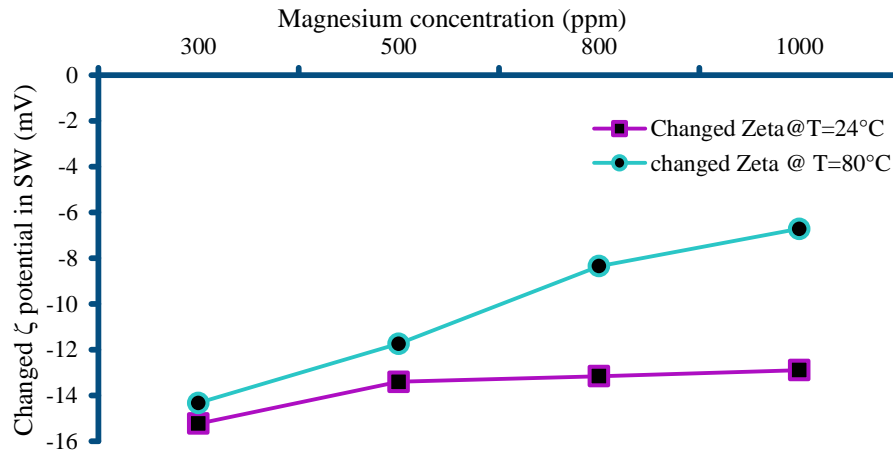


Figure 24 : Effect of magnesium concentration on ζ potential in two different temperatures of 25 & 80 °C and fixed sulfate concentration 1000 ppm.

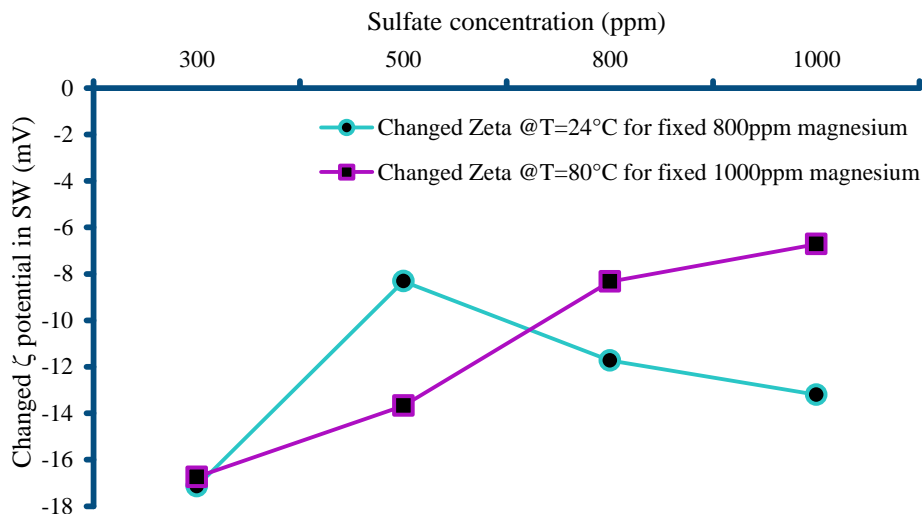


Figure 25: Effect of sulfate concentration on ζ potential in two different temperatures of 25 & 80 °C and fixed magnesium concentration 500 & 1000 ppm.

3-4-3- ζ Potential Alteration Index (ζ PAI)

ζ PAI values have been calculated for all designed brine combination (the brines of Figure 22 to 25) using the defined formula in step XII of procedure #7. According to the results of ζ potential measurements, the closer values to ζ of WW rock in the base solution (in this study Sea Water), has higher value of ζ PAI (Figure 26, Figure 27, and Figure 28). The obtained data which are used to calculate ζ PAI are provided in the Tables 2, 3 and 4 in the Appendix. These results show that, at two temperatures of 25°C and 80°C, the maximum ζ PAIs are obtained for optimum concentrations of (800ppm of calcium and 500 ppm of sulfate) and (1000ppm of magnesium and 1000 ppm of sulfate) are 0.83 and 0.87 (Figure 27 and Figure 28), respectively.

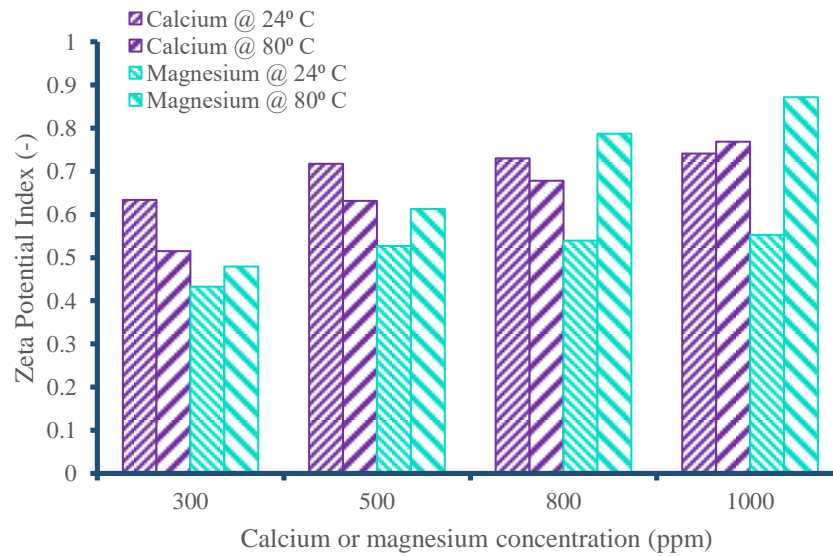


Figure 26: ζ PAI of brines with constant sulfate concentration of 1000 ppm.

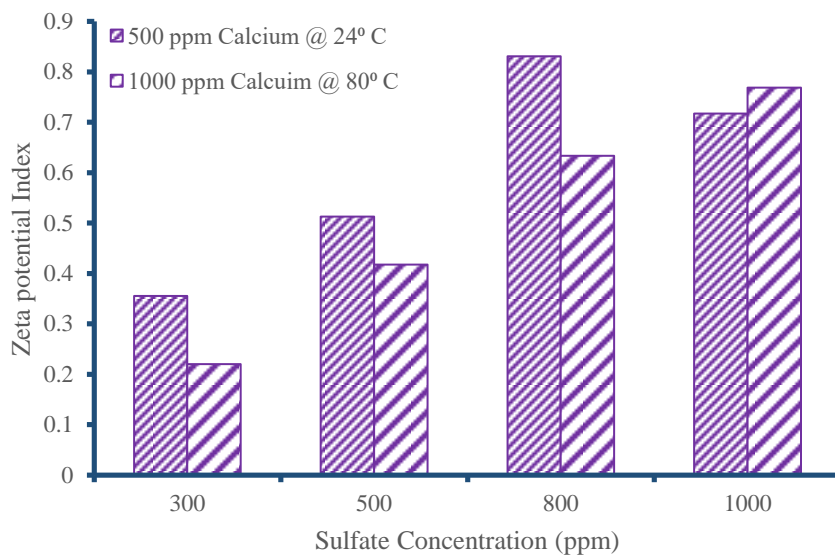


Figure 27: ζ PAI of brines with fixed optimum concentrations of calcium.

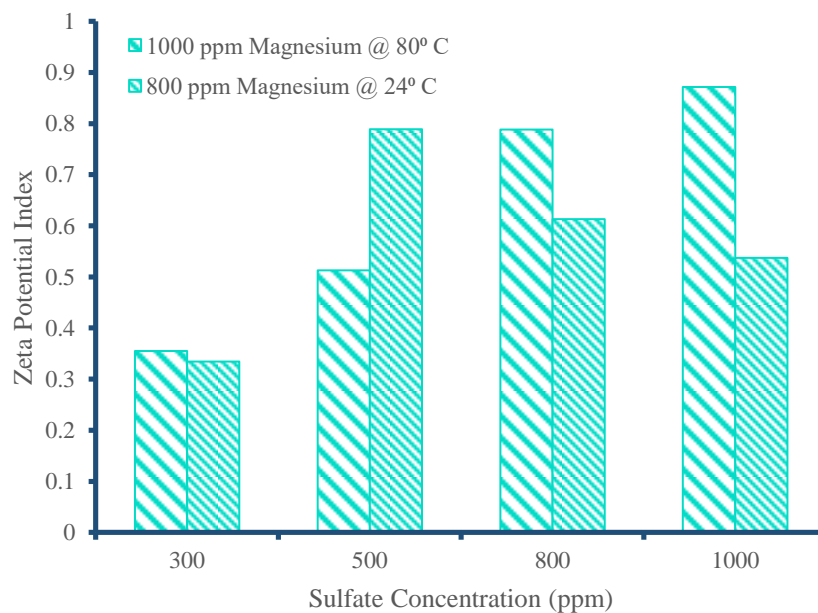


Figure 28: ζ PAI of brines with fixed optimum concentrations of magnesium.

3-Conclusion

As shown in the essay, several parameters affect the layers around carbonate rock powder which are occupied by co and counter ions. Amongst them, the pH of the solution specifies the inherent charge of the rock's surface molecules, and upon its charge, the ions distribution will locate around the rock powder. Furthermore, co and counter ions molarity and concentrations as well as their valences, determine the ζ potential trend and also its changes. Resultant findings have shown that with increasing the co-ions molarity, the ascending (more positive) or descending (more negative) trends will stop or revers until the compression of double layer electro static. The comparison of divalent cations (magnesium and calcium) and monovalent cations (sodium) performances when their concentration increase, will rise the importance of the ion valence role to create sharp change in the measured ζ potentials. In addition, the different valences of phosphate (-3) and sulfate (-2) anions concentrations affect the measured ζ potentials proportional to the amount of their negative charge as well.

At the present study, for the first time, novel experimental procedures have been designed to relate the measured ζ potential values to the wettability alteration. The results of the experiments, is another proof of proposed theories about the effectiveness of calcium and magnesium as active ions and the role of sulfate ions as the accelerator of their performance in wettability alteration process towards water wetness. Moreover, the superiority of calcium at low temperature (25°C) and magnesium at high temperature (80°C) concluded. Considering the determiner impact of rock mineralogy and crude oil composition on the measured ζ potential, the obtained results outlined that the composition of the used oil wet rock powder causes the ζ potentials values of -4.2 and -23.6 for water wet and oil wet rock powder, respectively. The best ζ potential alteration indexes were obtained for combination of calcium (500 ppm) and sulfate (800 ppm) at 25°C and combination of magnesium (1000 ppm) and sulfate (1000 ppm) at 80 °C.

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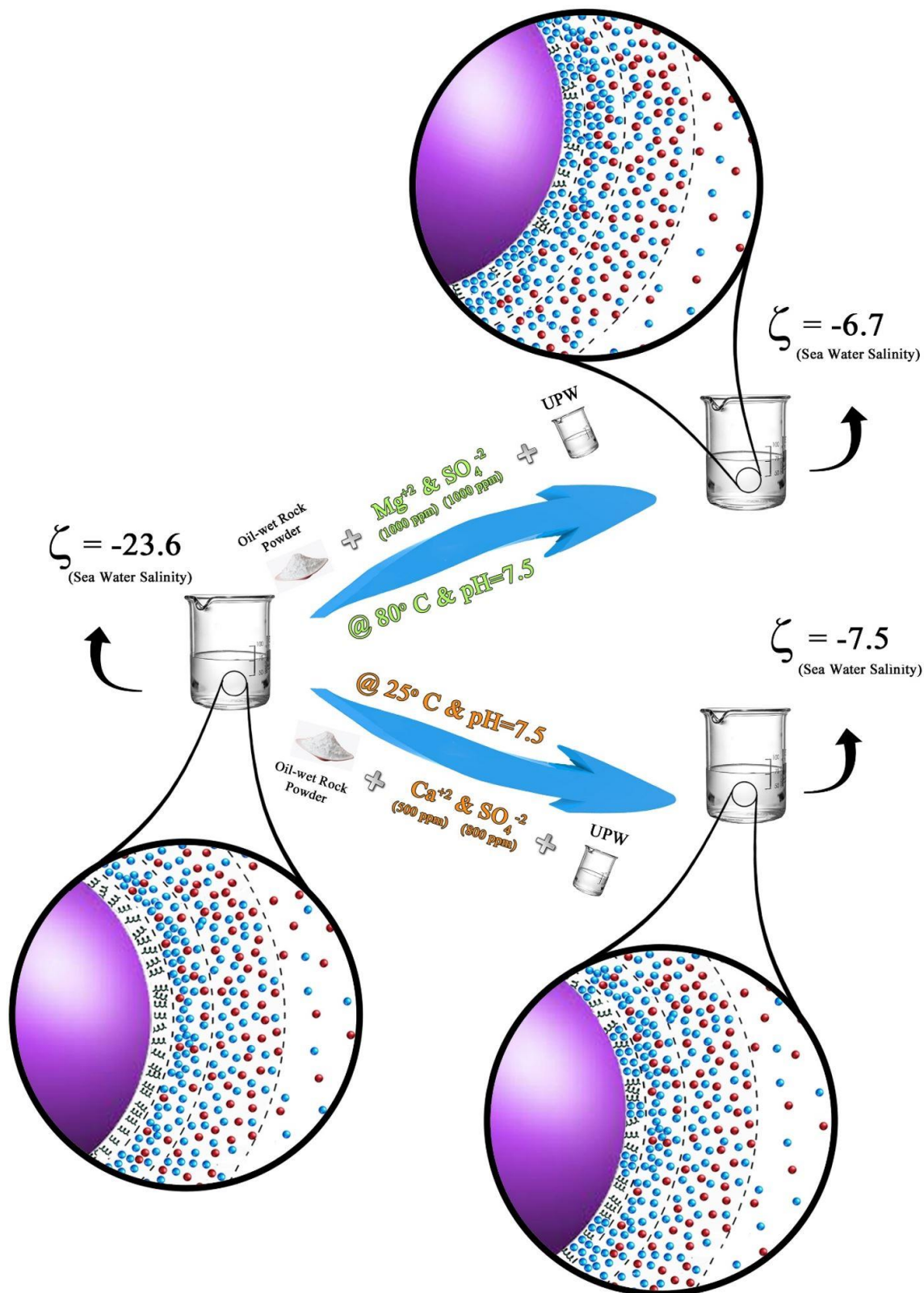
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Graphical abstract

Highlights

- **Ions roles in Wettability Alteration (WA) process is investigated using introduced ζ PAI.**
- **Ions valences and concentrations affect the trend of ζ potential.**
- **Stability of oil-in-water emulsions enhanced by ion strength increment.**
- **EDL around carbonate rock is expanded with decreasing ion strength.**