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ENHANCED OIL RECOVERY THROUGH WETTABILITY ALTERATION USING NANOTECHNOLOGY TECHNIQUE FOR ABU ROACH C AND D MEMBERS INBADR AL-DIN 15 FIELD AT NORTH WESTERN DESERT, EGYPT

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ENHANCED OIL RECOVERY THROUGH WETTABILITY ALTERATION USING NANOTECHNOLOGY TECHNIQUE FOR ABU ROACH C AND D MEMBERS INBADR AL-DIN 15 FIELD AT NORTH WESTERN DESERT, EGYPT

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ABSTRACT

The majority of enhanced oil recovery mechanisms purposefully alter the wettability of the reservoir rock from oil-wet to water-wet; to increase the amount of oil recovered from it. Wettability is the ability of a fluid to stick to a solid surface in the presence of other immiscible fluids. Wettability alteration is crucial as it affects the amount of oil recovered from a given reservoir. It was concluded that the Nano silicate and aluminum were the best Nano concentration from ***1.0 to 4.0 g/L*** *and Nano scale* ***28-32 nm*** *to change the rock wettability form oil wet to water wet .By doing so these will be reflect on the amount of producing oil. So it can be increased oil productivity by wettability change from oil wet to water wet which was the target of our research.*

Keywords: *Wettability Alteration, Nano materials, Enhance oil Recovery*

1. INTRODUCTION

The contact angle is defined as the edge of a droplet of fluid placed on a flat surface. The edge of the droplet when in contact with a surface is divided into three different regions, which are a free surface, a planar interface and a transition region. The planar interface is the region where the droplet adheres to the solid surface and is different from the nature of the liquid. The transition region connects the spherical cap to the droplet planar portion. The radii and the tangent are varying accordingly from zero at the planar interface to pi-theta at the spherical cap. This will change the energy with changes in separation when they get close to each other [1]. This contact angle measurement method involves depositing a water, which is brine in the majority of the cases so as to simulate the reservoir saline condition, drop on the rock surface and adding volume to the drop until the maximum volume allowed is reached without increasing the three-phase line. The advancing angle is the maximum possible angle measured resulting from the volume increase. The increase in volume step is followed by a volume removal one where the maximum volume that can be extracted before disturbing the drop profile’s geometry is removed and the resulting contact angle is measured [2]. This angle is the receding angle which when subtracted from the advancing contact angle yields a value referred to as the contact angle hysteresis The difference between the advancing angle and the receding angle is the hysteresis contact angle $H = \theta_{\mathbf{a}} - \theta_{\mathbf{r}}$ [3]. Wettability of rocks is classified into five categories, which are Water Wettability, oil wettability, neutral or in- terminate wettability, fractional wettability, and finally, mixed wettability. In water-wet reservoirs, the reservoir rock is preferentially wetted with water which occupies the small pores and contacts most of the rock surface forming a thin film of water that coats the formation matrix[4,5]. For effective oil transport and recovery, the water-wet condition is a favorable one [6].

2. Nanomaterials used in Experimentation

2.1 Aluminum [Al]

Aluminum is an effective material in this experiment as it has great potential in adhering or adsorbing on to surfaces which is main focus of the material being used in the enhancement for oil recovery, which, it gives us a new area for developing new material with desired functionality [7].

2.2 Silica [Si]

Silica has been studied extensively in the past years due to their superior physic-chemical properties. These properties are classified as follows: higher thermal and chemical stability, hardy mechanical strength, catalytic activity and strong surface acidity [8].

3. Methodology

The aim of the research is to investigate the effect of various nanomaterials on the wettability of sandstone and limestone reservoirs and particularly the effect of these Nano-materials on the water phase contact angle with the surface of the rocks. Changes in the reservoir rock wettability are more interest in the oil field industry as they reflect on the amount of oil recovered from the reservoir. When the reservoir wettability is altered from water-wet to oil-wet, severe impairment is caused to the productivity, therefore, treatments that lead the reservoir to a more water-wet condition are favorable ones.

The use of the Silica and Aluminum are justified by the fact that none of the previous researchers tested its efficacy in the oil industry in contrast to oxides that have been extensively used in the field for oil recovery. The concentration of the above mentioned nanomaterials was kept constant at **1.0 to 4.0 g/L** in the study making the type of material variable. The study is conducted at ambient conditions except for the saturation of core plugs that was conducted at a pressure of 2000 psi. The different instruments used throughout the study are explained in the experimental section.

The contact angle meter was used for measuring the contact angle that each nano-fluid makes with the rock in an attempt to settle on one with the greatest positive impact on oil productivity.

The following are the wettability categories that surfaces lie in depending upon the range in which their contact angle falls:

$0^\circ \leq \theta < 90^\circ$	**Water-wet**
$\theta = 90^\circ$	**Neutral or Intermediate wet**
$90^\circ < \theta \leq 180^\circ$	**Oil-wet**

The relation between the contact angle and the interfacial energies is governed by Young's equation:

$$\sigma_{os} - \sigma_{ws} = \sigma_{ow} \cos\theta$$

θ	=	Contact angle measured through the water phase at Rock/Oil/Brine interface;
σ_{os}	=	Interfacial energy between Solid and Oil, dyne/cm;
σ_{ws}	=	Interfacial energy between Solid and Water, dyne/cm;
σ_{ow}	=	Interfacial energy or tension between Oil and Water, dyne/cm.

Contact angle measurement. Several contact angle measurement techniques are present such as the tilting plate method, the capillary rise method, and the sessile drop method. The method that is most widely used in the petroleum industry is the sessile drop method [9]. The sessile drop measurement is conducted by placing a drop of water on a mineral surface that is suspended below the oil's surface horizontally [4]. The measurement takes place by taking a photograph of the system where the angle is measured through water, that is, the denser phase [10]. This is the basic principle of the sessile measurement technique. Modifications carrying different natures were introduced to the sessile drop method. This work explains the "Sessile - Add and Remove Volume Method" as it is the method of measurement adopted by the contact angle meter device that is used for measuring contact angles in the experimental section.

Limitations Associated with Contact Angle Measurement. Encountered during contact angle measurements is contact angle hysteresis where a liquid drop can make several stable contact angles with the rock surface. Hysteresis is a result of surface heterogeneity and roughness **[11].** Another cause of hysteresis while measuring contact angles is surface immobility where the surface does not allow the necessary motion for the fluid to reach an equilibrium contact angle value **[10]**. **Figure 1** illustrates that Water advancing and receding contact angles measured by the sessile drop method.

4. EXPERIMENTAL WORK and PROCEDURES

4.1 Materials

The materials used in the experiment were core samples from a sandstone and limestone reservoir obtained from a well producing in the Western Desert – Egypt, distilled Water prepared in the Lab. The density of distilled Water was 1.00 gm/cm^3, oil that has a density of **0.9434 g/ml.** Nanomaterials obtained were Silica and Aluminum. A concentration of different Nano solution of each nanomaterial was prepared by dispersing it in distilled Water using magnetic stirrer.

4.2 Setup and Procedures for Experimental work

Core plugging was done for the sample rock using the plugging machine in AUC Lab. cores sample were cut off from the sample rock where four core plates samples, sandstone has average diameter **38.10 mm**, lengths ranging from **28.30 to 38.12 mm** and limestone has average diameter **35.12 mm,** lengths ranging from **25.18 to 33.14 mm**.

The core samples were trimmed using the Trim Saw and then, there were left into the Dean stark device to be cleaned from any undesirable fluids in the pores. Then, the core samples were put into the oven to be dried and it was heated at 62˚C as above this temperature, the clays in the samples might break down affecting porosity and permeability of the cores.

Routine core analysis was done to get

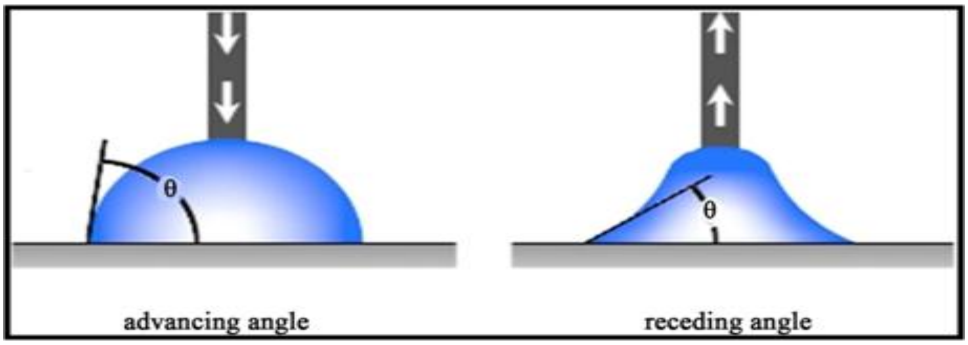

Figure 1: Water advancing and receding contact angles measured by the sessile drop method.

Table 1: Routine core analysis results for core plate samples used in this study.

Sample No.	Weight	Diameter	Length	Bulk volume	Grain Density	Pore Volume	Porosity	Cal. Pore Volume	Absolute Permeability	Oil Saturation	Initial Water Saturation
	gm	mm	mm	cm^3	gm/cm^3	mm	%	cm^3	*md*	%	%
Plate 1	88.19	38.20	34.81	43.69	2.93	1.62	21.45	1.25	2427.15	86.2	13.8
Plate 2	77.88	38.09	33.16	39.67	2.90	1.63	23.58	1.50	2575.60	90.4	9.6
Plate 3	78.38	38.04	32.90	37.69	2.86	2.12	25.12	1.98	2596.12	92.6	7.4
Plate 4	74.12	38.04	30.48	37.39	2.83	1.85	20.45	1.14	2695.36	87.5	12.5
Plate 5	68.02	38.10	28.30	34.75	2.79	2.47	22.61	2.20	2698.24	85.7	14.3
Plate 6	63.43	38.10	34.81	32.26	2.81	2.25	24.87	2.11	2715.53	88.1	11.9
Plate 7	75.19	38.15	31.53	36.14	2.82	3.24	17.52	2.90	2369.47	80.5	19.5
Plate 8	80.12	38.22	29.72	37.26	2.85	3.61	15.45	3.16	2286.18	78.2	21.8

porosity and absolute permeability using Helium Porosimeter and Air Permeameter, then the eight core plugs (Plates) was put inside the manual saturator to be saturated with mineral oil under pressure 2000 psi and ambient temperature for eight or ten hours. Each of the eight core plates were injected with distilled water and different nanomaterial at concentration from **1.0 to 4.0 g/L** and were achieved the measurement of contact angles for their and surface tension measured between air, distilled water and different nanomaterial at ambient conditions (Atmospheric pressure and room temperature) using Optical Tensiometer device into the Egyptian Nanotechnology Central **(Figure 2**) and Force Tensiometer device into the AUC Lab. (**Figure 3).**

Figure 2: Optical Tensiometer

Figure 3: Force Tensiometer

4.3 Measuring contact angle, Surface Tension and Interfacial Tension

The change in surface or interfacial tension between oil, distilled water and several of nano-fluid, and air are the main mechanism when wettability reversal to water-wet condition, reduction of interfacial tension will lead to a reduction of the capillary pressure within the pores. Surface tension is measured in the laboratory by **Force Tensiometer–K100** and **Optical Tensiometer,** which can be used by Du Nouy Ring. The difference between interfacial tension and surface tension is the liquid-liquid interface instead of the liquid-air interface. Interfacial tension can be used to describe immiscibility of these two liquids, which it does consider the interface between the phases. The molecules on the first surface have forces acting upon it from the first liquid and from the surface molecules of the second liquid and vice versa. **Table 2 and 3** are shown as the results of measurement of the surface tension and interfacial Tension by using of AUC Device (by Force Tensiometer–K100) and ENC Device (Optical Tensiometer).

In addition to the **Table 4 and 5** are shown as the results of measurement of the contact angle by using of AUC Device (by Force Tensiometer–K100) and ENC Device (Optical Tensiometer).

By using different types from Nano concentration Silica and Aluminum applied on sand stone and limestone samples To figure out the relation between surface tension and distilled water with different Nano concentration. The surface tension was dropping from **85.35 to 55.09** dyne/cm as shown in **Figure 6**, when using different Nano concentration from 0.25 to 4.0 g/L, while the surface tension was dropping from **71.76 to 69.06** dyne/cm as shown in **Figure 7**, when it using different Nano concentration from **0.25 to 4.0 g/L.**

These mean that the surface tension between fluids drop and the air decreasing by increasing Nano concentration, which it be needed for easy to displace the oil drops.

By using different Nano concentration of silicate and Aluminum applied on sand stone and limestone core samples to figure-out the relation between Interfacial Tension and distilled water with different Nano concentration.

Table 2: Surface tension and interfacial Tension results of measurement by using of AUC Device (by Force Tensiometer–K100).

Core sample ID	Nano ID	Nano Concentration, % by weight	Surface Tension, dyne/cm	Interfacial Tension, dyne/cm
1-A	1-S	0.25	58.99	37.80
2-A	2-S	0.5	65.12	36.41
3-A	3-S	1.0	67.33	37.69
4-A	4-S	2.0	70.96	36.46
5-A	5-S	3.0	70.03	36.88
6-A	6-S	4.0	63.54	37.71
1-B	1-AL	0.25	71.76	36.89
2-B	2-AL	0.5	71.32	37.47
3-B	3-AL	1.0	72.26	38.82
4-B	4-AL	2.0	72.20	39.50
5-B	5-AL	3.0	71.69	38.52
6-B	6- AL	4.0	69.60	38.02
1-D	2-S	0.5	58.99	37.80
11-D	4-S	2.0	65.12	36.41
111-D	6-S	4.0	67.33	37.69
2-D	1-AL	0.25	58.99	37.80
22-D	3-AL	1.0	65.12	36.41
222-D	5-AL	3.0	67.33	37.69

Table 3: Surface tension and interfacial Tension results of measurement by using of ENC Device (Optical Tensiometer).

Core sample ID	Nano ID	Nano Concentration, % by weight	Surface Tension, dyne/cm	Interfacial Tension, dyne/cm
1-A	1-S	0.25	60.57	37.76
2-A	2-S	0.5	65.01	43.39
3-A	3-S	1.0	80.89	38.55
4-A	4-S	2.0	76.17	29.97
5-A	5-S	3.0	80.32	34.89
6-A	6-S	4.0	84.24	45.54
1-B	1-AL	0.25	85.35	41.99
2-B	2-AL	0.5	72.49	16.21
3-B	3-AL	1.0	61.36	29.88
4-B	4-AL	2.0	81.69	13.60
5-B	5-AL	3.0	60.04	37.06
6-B	6- AL	4.0	55.09	13.72
1-D	2-S	0.5	47.66	33.68
11-D	4-S	2.0	46.99	33.61
111-D	6-S	4.0	64.35	19.97
2-D	1-AL	0.25	46.83	39.54
22-D	3-AL	1.0	57.25	42.83
222-D	5-AL	3.0	40.41	17.56

Table 4: Contact Angle results of measurement by using of AUC Device (by Force Tensiometer–K100).

Core sample, ID	Nano ID	Nano Concentration, % by weight	Contact angle, degree	
			Before	After
1-A	1-S	0.25	125.27	83.87
2-A	2-S	0.5	128.32	84.43
3-A	3-S	1.0	130.51	70.02
4-A	4-S	2.0	118.68	67.77
5-A	5-S	3.0	134.58	74.43
6-A	6-S	4.0	135.0	78.36
1-B	1-AL	0.25	115.23	89.17
2-B	2-AL	0.5	132.47	85.32
3-B	3-AL	1.0	126.65	85.18
4-B	4-AL	2.0	129.85	88.87
5-B	5-AL	3.0	133.24	75.66
6-B	6- AL	4.0	128.64	86.25
1-D	2-S	0.5	126.21	89.20
11-D	4-S	2.0	114.58	84.85
111-D	6-S	4.0	121.25	79.55
2-D	1-AL	0.25	125.39	83.87
22-D	3-AL	1.0	127.23	84.43
222-D	5-AL	3.0	125.0	70.02

Table 5: Contact Angle results of measurement by using of ENC Device (Optical Tensiometer).

Core sample, ID	Nano ID	Nano Concentration, % by weight	Contact angle, degree	
			Before	After
1-A	1-S	0.25	125.27	74.72
2-A	2-S	0.5	128.32	78.24
3-A	3-S	1.0	130.51	75.19
4-A	4-S	2.0	118.68	69.68
5-A	5-S	3.0	134.58	72.95
6-A	6-S	4.0	135.0	59.59
1-B	1-AL	0.25	115.23	77.17
2-B	2-AL	0.5	132.47	58.26
3-B	3-AL	1.0	126.65	69.62
4-B	4-AL	2.0	129.85	55.50
5-B	5-AL	3.0	133.24	74.30
6-B	6- AL	4.0	128.64	55.63
1-D	2-S	0.5	126.21	72.65
11-D	4-S	2.0	114.58	72.13
111-D	6-S	4.0	121.25	61.82
2-D	1-AL	0.25	125.39	73.98
22-D	3-AL	1.0	127.23	77.64
222-D	5-AL	3.0	125.0	69.52

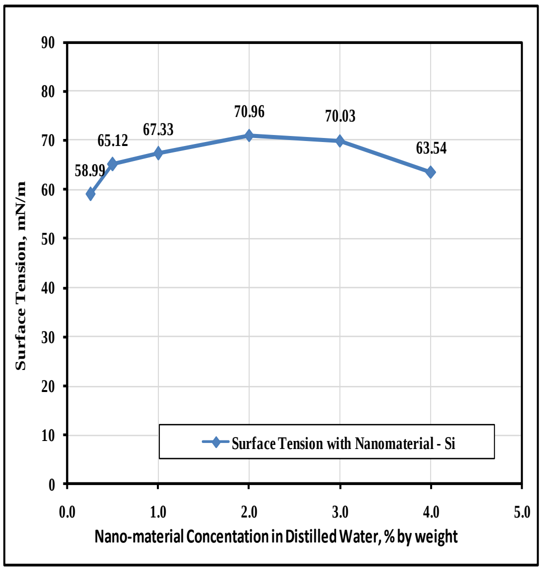

Figure 5: Surface Tension measurement by Force Tensiometer (Si)– AUC Device.

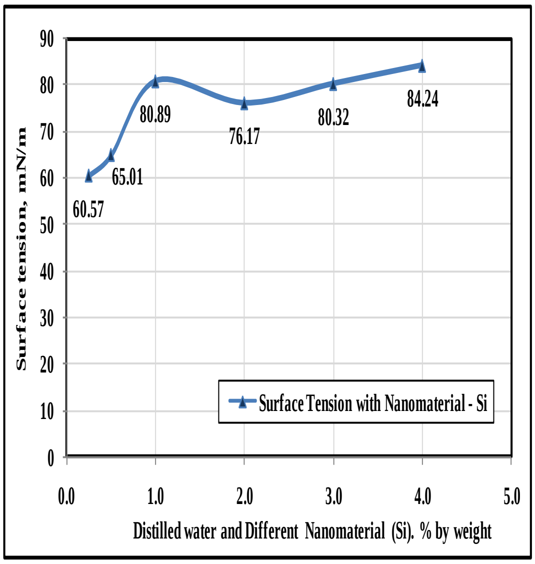

Figure 4: Surface Tension measurement by Optical Tensiometer (Si)–ENC Device.

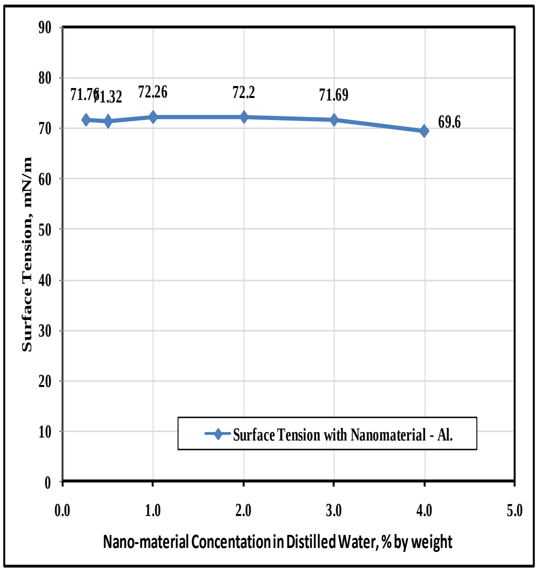

Figure 7: Surface Tension measurement by Force Tensiometer (Al)– AUC Device.

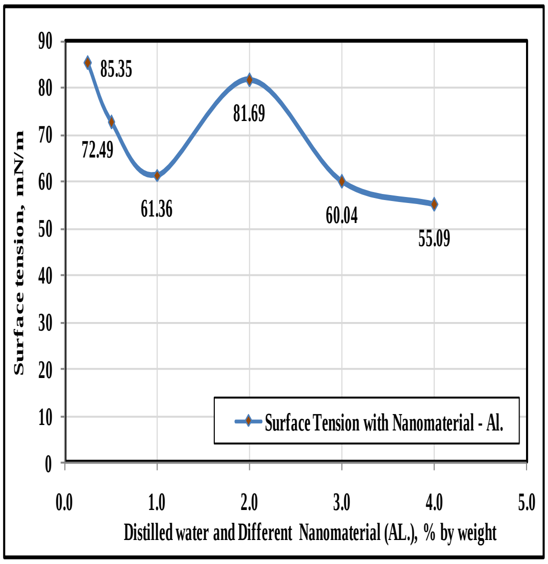

Figure 6: Surface Tension measurement by Optical Tensiometer (Al)–ENC Device.

The Interfacial tension was increasing from **37.76 to 45.54** dyne/cm as shown in **Figure 8** when using different Nano concentration from **0.25 to 4.0g/L,** while, the interfacial tension was increasing from **36.89 to 38.02** dyne/cm as shown in **Figure 11,** when using different Nano concentration from **0.25 to 4.0 g/L.** These mean that the Interfacial tension between oil and water increasing by increasing Nano concentration which it be needed for easy to displace the oil drops.

By using different Nano concentration of silicate and their applied on sandstone and limestone samples for to figure out the relation between contact angle and distilled water with different Nano concentration. The contact angle decreased from **83.87^0 to 78.36^0** in **Figure 12** where using different Nano concentration from **0.5 to 4.0 g/L**, while the Contact angle was decreasing from **89.2^0 to 79.55^0** in **Figure 16**, where using different Nano concentration from **0.25 to 4.0 g/L.**

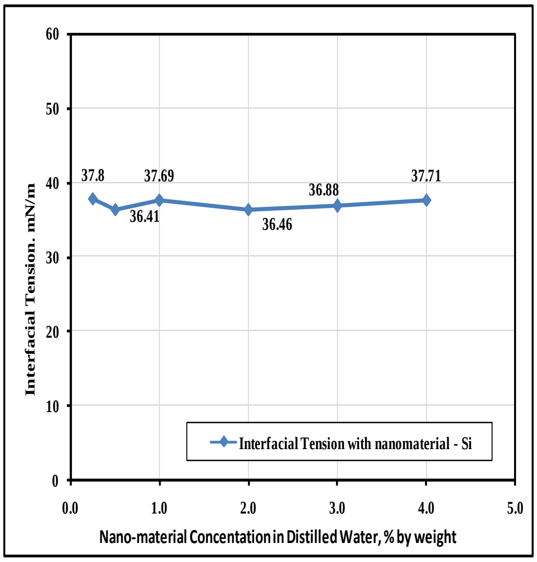

Figure 9: Interfacial Tension Measurement by Force Tensiometer (Si)– AUC Device.

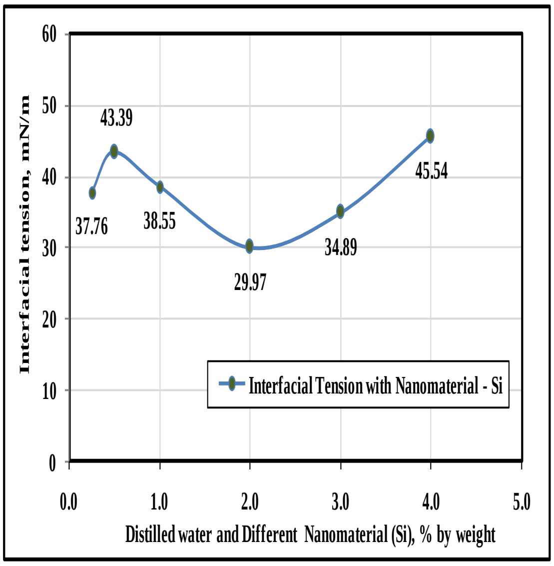

Figure 8: Interfacial Tension Measurement by Optical Tensiometer (Si)–ENC Device.

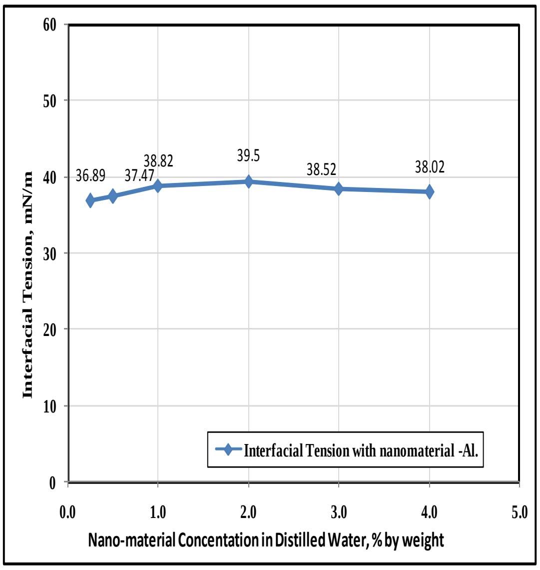

Figure 11: Interfacial Tension Measurement by force Tensiometer (Al)– AUC Device.

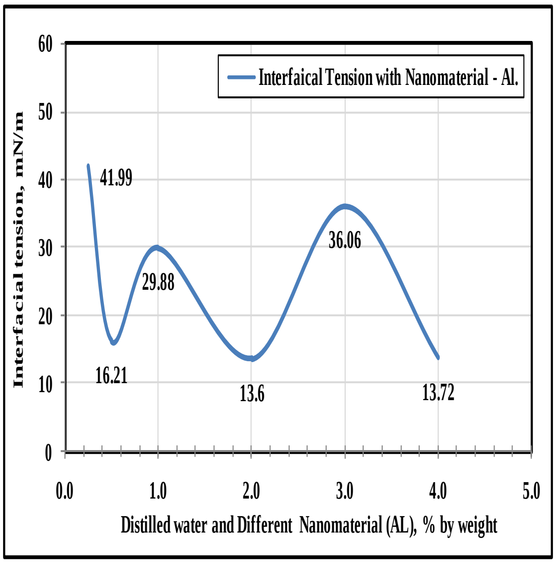

Figure 10: Interfacial Tension Measurement by force Tensiometer (Al)–ENC Device

In the **Figure 17**, it could be show that the contact angle was decreasing from **72.65^0 to 61.82^0** when using different Nano concentration from **0.25 to 4.0 g/L,** while the contact angle was decreasing from **73.98^0** to **59.59^0** in **Figure 19** when using different Nano concentration from **0.25 to 4.0 g/L**. These mean that the contact angle between oil and the water decreasing by increasing Nano concentration and it be needed for easy to displace the oil drops to be more water wet which is our target.

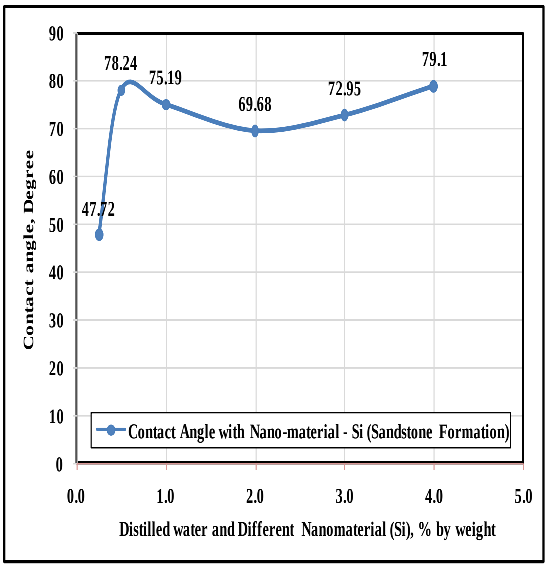

Figure 13: Contact angle Measurement by Optical Tensiometer in Sandstone Formation (Si)–ENC Device

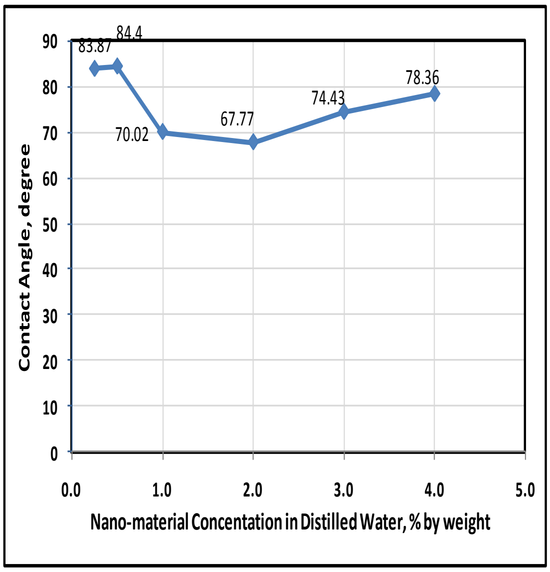

Figure 12: Contact angle Measurement by Force Tensiometerin Sandstone Formation (Si)– AUC Device.

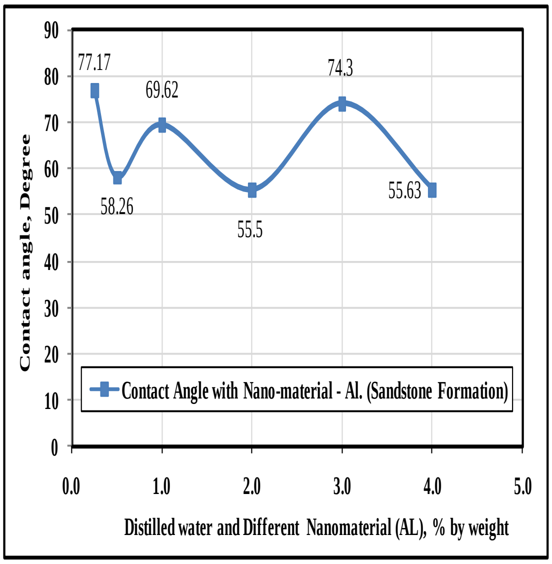

Figure 15: Contact angle Measurement by Optical Tensiometer in Sandstone Formation (AL)–ENC Device

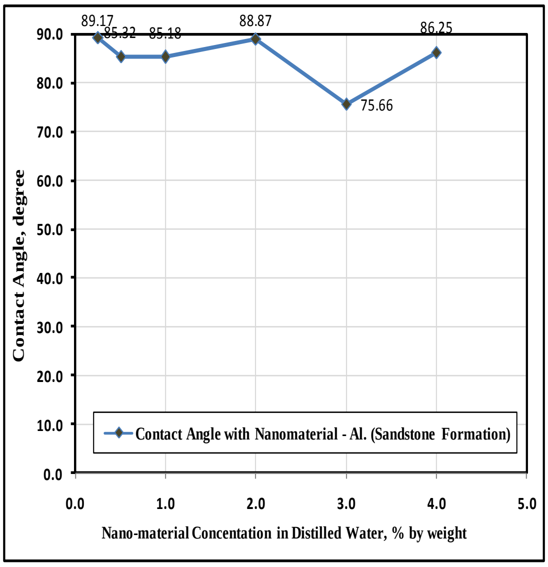

Figure 14: Contact angle Measurement by Force Tensiometer in Sandstone Formation (AL)– AUC Device.

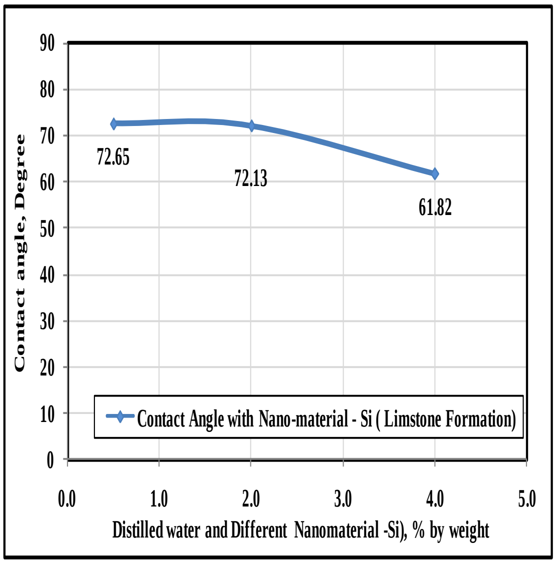

Figure 17: Contact angle Measurement by Optical Tensiometer in Limestone Formation (Si)–ENC Device

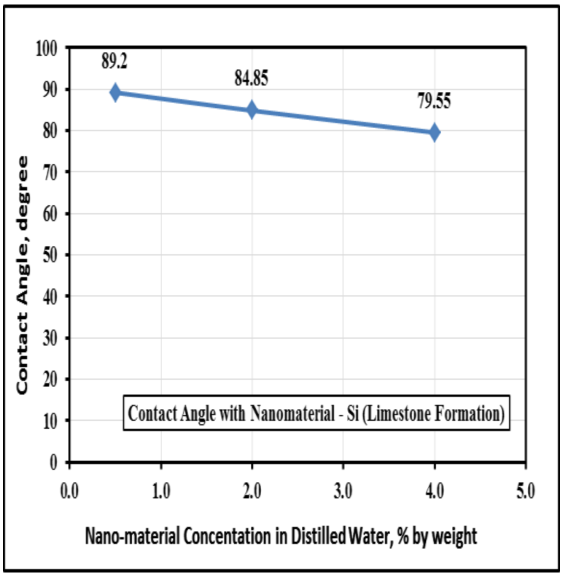

Figure 16: Contact angle Measurement by force Tensiometer in Limestone Formation (Si)– AUC Device.

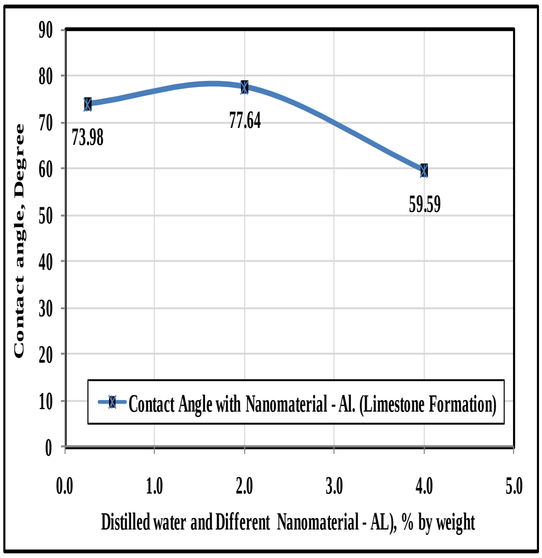

Figure 19: Contact angle Measurement by Optical Tensiometer in Limestone Formation (Al)–ENC Device

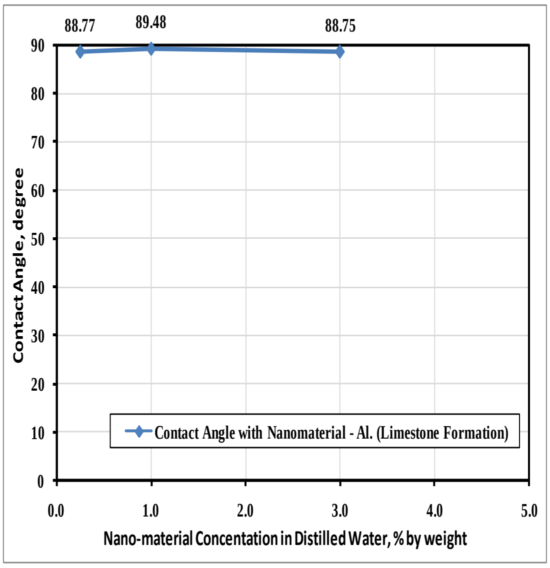

Figure 18: Contact angle Measurement by Force Tensiometer in Limestone Formation (Al)–AUC Device.

5. RESULTS AND DISCUSSION

Nanomaterials are being used in the oil industry in the domain of Enhanced Oil Recovery where there are injected into core samples in the laboratory and the resulting increase in oil recovery is recorded. The oil phase contact angle changed from **129.85 ^{0} to 55.50^0.** Their results prove that significant amounts of oil can be recovered after water is injected into the core plug aged with Si and Al Nano fluids. Moreover, the concentration of the nanoparticles enhances the oil recovery as when it increase the concentration of the nanoparticles in distilled water mix solution nanoparticles Silica & Aluminum, the surface tension and the contact angle decreases. The concentration of Silica and Aluminum nanoparticles could introduce considerable alteration to the rock wettability from oil-wet to water-wet [18]

To settle on the optimum concentration of Silica nanoparticles to be injected into a sandstone core sample, its applied their study on a concentration range of **1.0 - 4.0 g/L.** Six of plug core samples from sandstone formation and two samples from limestone formation were cleaned, polished, trimmed; to minimize contact angle hysteresis, and saturated with mineral oil. Oil droplets were deposited on the sample surfaces and the oil phase contact angle, in the presence of distilled water, was measured. Graph of oil phase contact angle [degrees], in the presence of distilled water, versus several nano-fluid concentrations [g/L] was plotted and so the optimum concentration appeared to be **1.0- 4.0 g/L.** The range between **1.0- 4.0 g/L** concentration changed the oil phase contact angle from **129.85^0 to 55.50^0** indicating a wettability shift from oil-wet to water-wet.

The change in angle was a consequence of the increase in the interfacial tension between oil and water according to Young’s equation. The wettability alteration reflected on oil recovery by an increase to 78.0% in the amount of oil recovered after nano-fluid injection. Eight core plates of a length of approximate 1.0cm each sample and cleaning samples using a trimming machine and polished to achieve a flat and relatively smooth surface which used to measure of contact angle are accuracy values results. These sample plates were saturated with oil at room temperature and a pressure of **2000 psi** under Lab. Conditions. Four different solutions were prepared such that each solution is to be deposited on one of the rock plates using a syringe.

6. CONCLUSION and RECOMMENDATIONS

The authors run experimental work on AUC, EPRI and Egyptian Nano Center – Cairo University. The selected sample Abu Roach 'C' and 'D' members were subjected to complete core analysis and run all experimental tests to measured surface and interfacial tension, and contact angle,. The optimum concentration of Nano silicate was from **1.0 to 4.0 g/L** to decrease surface tension from **75.35 to 63.54** dyne/cm in sandstone formation by using AUC Device (Force Tensiometer), while the optimum concentration of Nano Aluminum was from **1.0 to 4.0 g/L** to decrease surface Tension from **76.35 to 69.6** dyne/cm in limestone formation by using ENC Device (Optical Tensiometer). Tthe optimum concentration of Nano silicate was from **1.0 to 4.0 g/L** to increase interfacial tension from **37.76 to 45.54** dyne/cm in sandstone formation by using ENC Device (Optical Tensiometer). The optimum concentration of Nano silicate was from **1.0 to 4.0 g/L** to decrease interfacial tension from **36.89 to 38.02** dyne/cm in limestone formation by using AUC Device (Force Tensiometer). Using AUC Device (Force Tensiometer), The optimum concentration of Nano silicate was from **1.0 to 4.0 g/L** to decrease contact angle from **118^0 to 67.77^0** in sandstone formation, while optimum concentration of Nano Aluminum was from **1.0 to 4.0 g/L** to decrees contact angle from **133.24 ^{0} to 75.66^0** in sandstone formation, while optimum concentration of Nano silicate was from **1.0 to 4.0 g/L** to decrees contact angle from **121.25^0 to 79.55^0** in limestone formation .The optimum concentration of Nano Aluminum was from **1.0**

to 4.0 g/L to decrease contact angle from **125.0^0 to 70.02^0** in limestone formation, while using ENC Device (Optical Tensiometer). The optimum concentration of Nano silicate was from **1.0 to 4.0 g/L** to decrease contact angle from **135^0 to 59.59^0** in sandstone formation. While optimum concentration of Nano Aluminum was from **1.0 to 4.0 g/L** to decrease contact angle from **129.85 ^{0} to 55.50^0** in sandstone formation. While optimum concentration of Nano silicate was from **1.0 to 4.0 g/L** to decrees contact angle from **121.25^0 to 61.82^0** in limestone formation .The optimum concentration of Nano Aluminum was from **1.0 to 4.0 g/L** to decrease contact angle from **125.0^0 to 69.52^0** in limestone formation. From all the pervious discussion it was concluded that the nano-silicate and aluminum were the best Nano concentration from **1.0 to 4.0 g/L** and Nano scale from **28 to 32 nm** to change the rock wettability form oil wet to water wet .By doing so these will be reflect on the amount of producing oil. So, it can be increased oil productivity by wettability change from oil wet to water wet which was the target of our research.

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