

# Effect of pH and Total Hardness on Stability of Crude Oil Water in Oil Emulsions

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**Abstract-** In this paper, laboratory experiments have described to investigate the effect of pH and total hardness of water on the stability of emulsions. Samples from Mukhaizna field were collected from different three wells AR 2102-PCP, AP 0701 and AR 1612 in respect to prepare standard oil sample for this experiment and shaking by hand. This is because it contains a lot of interfacial active fraction and one of the most stable emulsions in Oman. The wells were selected to have 33% water cut. In the set of experiments, the effect of increasing pH until 10 by added NaOH and decreasing pH until 5 by added HCl to EMO590 Nalco and C117SOS Champion was investigated. Were HCl and NaOH added with 40 ppm of Nalco EMO590 and C117 SOS Champion demulsifiers at 60°C. Knowing that pH of experience sample equals to 8.1. The effect of decrease total hardness by added distillate Water until it equals 500 mg/L and increase total hardness by added NaCl until it equals 5000 mg/L to EMO590 Nalco and C117SOS Champion was investigated. Were distillate Water and NaCl added with 40 ppm of Nalco EMO590 and C117 SOS Champion demulsifiers at 60°C. Knowing that total hardness of experience sample equals to 2500 mg/L. The water's pH influences on emulsions stability. It was found that at pH=10 there is unstable emulsion formed and stable emulsion formed at pH=5. The results show that the stability of emulsions decreases with increases the total hardness.

**Keyword-** Emulsions stability, Emulsions, Total hardness, water pH, Nalco EMO590, C117 SOS Champion.

## 1. Introduction

Emulsion is a heterogeneous system, containing at least immiscible liquid intimately dispersed in another in the form of droplets with a diameter, in general, ranging between (0.1-20) microns, and it is stabilized by an emulsifying agent, asphaltene, resins and finely divided solids. The dispersed phase is known as the internal phase. The liquid surrounding the dispersed droplets is the external or continuous phase. The emulsifying agent separates the dispersed droplets from the continuous phase (Kenneth, 1988). Water-in-oil (W/O) emulsion is formed during the production of oil, which is often accompanied with water. The stability of the emulsion is ranging from a few minutes to years depending on the nature of the crude oil (Bhardwaj and Hartland, 1998). Crude oils consist of a series of hydrocarbons such as alkenes, naphthenes, and aromatic compounds as well as phenols, carboxylic acids and metals. A major fraction of sulfur and nitrogen compounds may be present as well. The carbon numbers of all these

components range from one methane through 50 or more asphaltene. Some of these components asphaltene, resins, wax, and naphthenic acids can form films at oil surfaces. So the tendency to form stable or unstable emulsions of different kinds varies greatly among different oils (Schramm, 1992). The natural petroleum emulsion resulting from the secondary production consists of crude oil as dispersion medium and brine as dispersed phase, normally stabilized by natural chemicals such as asphaltene, resins, and solids such as clays and waxes (Bhardwaj and Hartland 1998). Emulsion stability is the ability of the dispersed phase of the emulsion to resist coalescence or sticking together of droplets. Emulsions are stabilized by the presence of a film between dispersed phase and the continuous phase. Emulsions are undesirable because the volume of dispersed water occupies space in the processing equipment and pipelines, increased operating and capital costs. Moreover, the characteristics and physical properties of oil change significantly upon emulsification. The density of emulsion can increase from (800) kg/m<sup>3</sup> for the original oil to (1030) kg/m<sup>3</sup> for the emulsion. The most significant change is observed in viscosity, which typically increases from a few mPa·sec or less to about 1000 mPa·sec (Fingas, et al., 2003). Emulsion resolution is therefore an important element in handling the petroleum, from the time it is produced until it enters the refining process. In order to minimize the production problems related with crude oil emulsions and environmental concerns, petroleum operators need to prevent emulsion formation or to break it (Gafonova, 2000). The treatment of water-in-crude oil emulsions involves the application of mechanical, thermal, electrical, and chemical processes (Grace, 1992). The main objective of this current research is to investigate the influence of pH and total hardness of water on stability of emulsions.

## 2. Materials and Methods

- ✓ To accomplish the objective of this study, the crude oil samples were obtained from Mukhaizna crude oil field (Specific Gravity 0.8849).
- ✓ Nalco EMO590 and C117 SOS Champion demulsifiers.

### 2.1 Measurement of stability of emulsions

The W/O emulsion was formed by manual shaking the mixture of oil phase and aqueous phase (The wells were selected to have 33% water cut.) in glass bottle of 5L size for 200 times, and the stability of emulsion was determined visually by measuring the oil separated from the emulsion as a function of time (ASTM).

### 3. Results and Discussion

#### 3.1 Effect of pH on Water Separation Efficiency

The pH of the sample water was adjusted by addition of small amounts of HCl and NaOH. A pH meter type (90 Metrohm AG CH -9100 Herisau) with accuracy ( $\pm 0.01$ ) was used to measure pH.

The (W/O) emulsions are stabilized by absorbed film of organic acids and bases in different amounts. The films are very strongly influenced by adding the acids and bases. Consequently, the physical properties of the interfacial film were also affected (Strassner, 1968 Einar, 1989). Tambe and Sharman (1993) studied that oil-in-water emulsions are preferential at low pH value ranging between 4 to 6, while water-in-oil emulsions are favored at high pH values that are between pH 8 to 10. Based on their experiments, the stability of oil-in-water emulsion formed increased as pH was increased from 4 to 6, but further increasing in pH, from 6 to 8 and finally 10 resulted in formation of relatively less stable oil-in-water emulsions and more stable water-in-oil emulsions. (Johansen et al., 1989) concluded that at very high and low pH values, the emulsions seem to be stable, while intermediate pH seems to cause instability. The optimum pH values in treating crude oil emulsions are between 5 to 12. Furthermore, the demulsifiers that are used in treating the emulsion problem are depending on the pH value.

Figures 1 and 2 shows the effect of pH change on water separation efficiency. It can be observed that water separation efficiency increases with increasing of pH, where maximum water separation is 77 % at pH = 8 for pure EMO590 Nalco at 40ppm concentrations and temperature 60 °C. Water separation efficiency increases about 10.7 % when added basic (NaOH) to increasing pH = 10 and the same result founded for C117 SOS champion it increase about 9% from its pure at the same conditions .

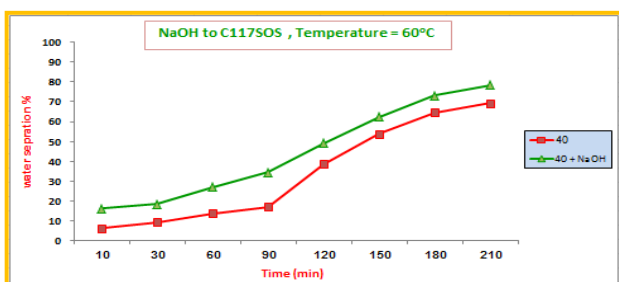


Fig1: Effect of EMO590 + NaOH at Temperature =60°C (pH =10)

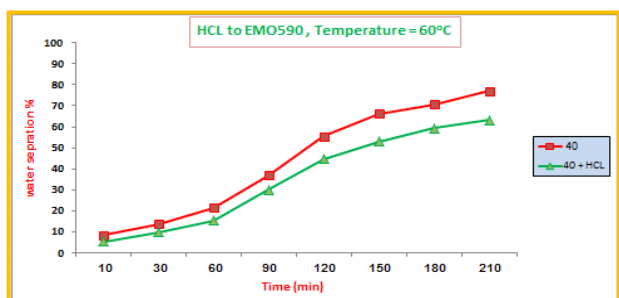


Fig 2: Effect of C117SOS + NaOH at Temperature =60°C (pH =10)

Figures 3 and 4 shows the effect of pH change on water separation efficiency. It was observed that water separation efficiency decreases with decreasing of pH, where maximum water separation is 77 % at pH 8 for pure EMO590 Nalco at 40 ppm concentrations and temperature 60°C. Water separation efficiency decreases about 13.9 % when added Acid (HCl) to dropping the pH 5 and the same result founded for C117 SOS champion it decreases about 14.6 % when it pure at the same conditions .

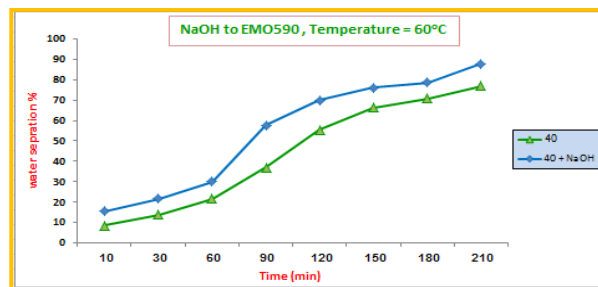


Fig 3: Effect of EMO590 + HCl, Temperature = 60°C (pH = 5)

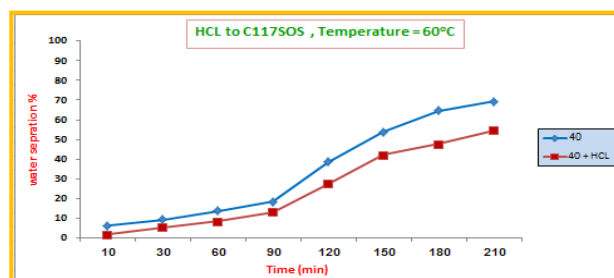


Fig 4: Effect of C117SOS + HCl , Temperature = 60°C (pH = 5)

From the figures 3 and 4 the increasing of water separation causes an increase in pH of the water phase. This is due to that the removal of water increased the amount of salt removed. Hence, the quality of oil will be improved. As depicted in previous, water pH affects emulsion stability decidedly. An emulsion prepared with water at pH 10 was relatively unstable. The polar functional groups contained in the asphaltenic and resinous material originally present in the interfacial film would most likely be ionized at this extreme pH value. The ionization of these polar groups would be capable of creating high surface charge densities that would drastically change the film properties by introducing an internal repulsion in the film, thereby destroying the mechanical properties that give rise to protection against coalescence. The restored or enhanced stability observed at low pH reveals the potential absence of strongly basic polar groups in these particular crude oils.

#### 3.2 Effect of adding Salt on Water Separation (T.H)

The effect of salt concentration in sample by increasing Total Hardness from 2500 to 5000 g/L in water. Figure 5 shows the effect of adding NaCl to EMO590 Nalco on the separation of water from Mukhaizna crude oil emulsion at temperature 60°C and concentration of 20 ppm.

It was observed that the emulsion stability decrease with increase the salt concentration. High salinity increases the ionic force and reduces the thickness of the double layer, favor the agglomeration of drops (F. N. B. Nahui1, M. R. Nascimento, E. B. Cavalcanti and E. O. Vilar. (2008), Anne Finborud, Mator AS, Mark Faucher, SPE, and Erik Sellman, SPE, Alfa Laval Oilfield(1999), Aboutther Thalib Halboose (2010). When the agglomeration of oil drops take place, it is lead to increase the separation of oil because of the increase of oil drop volume causes increase the settling velocity according to Stock's law. In the figure 6 shows the result where obtained when adding NaCl to C117SOS Champion at same conditions .

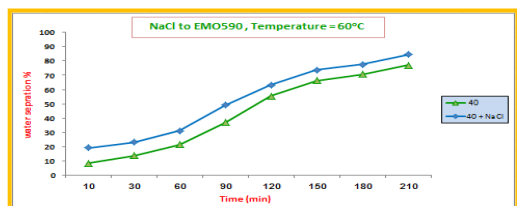


Fig.5: Effect of adding NaCl to EMO590 Nalco on the separation of water from Mukhaizna crude oil emulsion. EMO590 + NaCl Temperature = 60°C, Total Hardness increase from 2500 to 5000 g/L

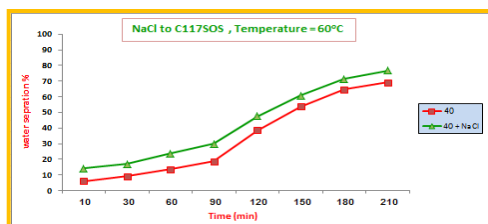


Fig.6: Effect of adding NaCl to C117SOS Champion on the separation of water from Mukhaizna crude oil emulsion. C117SOS+ NaCl Temperature =60°C, Total Hardness increase from 2500 to 5000 g/L

### 3.3 Effect of adding Distil Water on Water Separation

Figure 7 shows the effect of adding distil water to EMO590 Nalco on the separation of water from Mukhaizna crude oil emulsion at temperature 60°C and concentration of 40 ppm. It was observed that the emulsion stability increase with decrease the salt concentration. Low salinity decreases the ionic force and rise the thickness of the double layer, break the agglomeration of drops. When the agglomeration of oil drops reduce , it is lead to decrease the separation of oil because of the decrease of oil drop volume causes decrease the settling velocity .

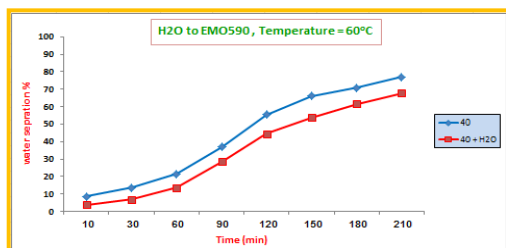


Fig.7: Effect of adding distil water to EMO590 Nalco on the separation of water from Mukhaizna crude oil emulsion. Temperature 60°C, Total Hardness decreases from 2500 to 5000 g/L

In the figure 8 shows the result for adding distil water to C117SOS Champion at same conditions.

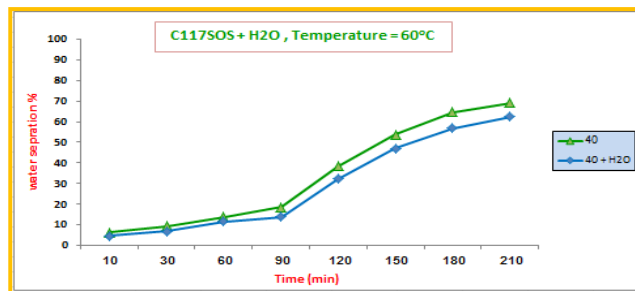


Fig 8: Effect of adding distil water to C117SOS on the separation of water from Mukhaizna crude oil emulsion. Temperature =60°C, Total Hardness decreases from 2500 to 5000 g/L.

## 4. Conclusion

The following conclusions can be drawn from the variables considered in this investigation:

- ✓ The stability of emulsion decreases with increase the salt concentration.
- ✓ It was observed that at pH 10 there is unstable emulsion formed and stable emulsion formed at pH=5.
- ✓ Adding inorganic salts (NaCl) cause the depletion force is reduced at low salt concentrations.
- ✓ At high concentration, rapid aggregation occurs as a consequence of Van der Waals attractive force.
- ✓ The emulsion stability decreases with increase the salt concentration.

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