Tikrit University

The College of Petroleum Processes Engineering Petroleum Systems Control Engineering Department

Petroleum Refining Processes

Fourth Class

Lecture 4

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Oil Emulsion

- → The fluid produced at the wellhead consists usually of gas, oil, free water, and emulsified water (water—oil emulsion).
- ♣ Before oil treatment begins, we must first remove the gas and free water from the well stream. This is essential in order to reduce the size of the oil—treating equipment.
- ♣ The gas and most of the free water in the well stream are removed using separators.
- ♣ Gas, which leaves the separator, is known as "**primary gas.**" Additional gas will be liberated during the oil treatment processes because of the reduction in pressure and the application of heat. Again, this gas, which is known as "**secondary gas,**" has to be removed.
- The free water removed in separators is limited normally to water droplets of 500 μM and larger. Therefore, the oil stream leaving the separator would normally contain free water droplets that are 500 μM and smaller in addition to water emulsified in the oil.
- ♣ This oil has yet to go through various treatment processes (dehydration, desalting, and stabilization) before it can be sent to refineries or shipping facilities.
- ♣ The objective of dehydration stage treatment is first to remove free water and then break the oil emulsions to reduce the remaining emulsified water in the oil.
- ♣ Depending on the original water content of the oil as well as its salinity and the process of dehydration used, oil-field treatment can produce oil with a remnant water content of between 0.2 and 0.5 or 1%. The remnant water is normally called the basic sediments and water (B.S. &W.). The treatment process and facilities should be carefully selected and designed.

Salt water is thus produced with oil in different forms as illustrated in Figure 1.

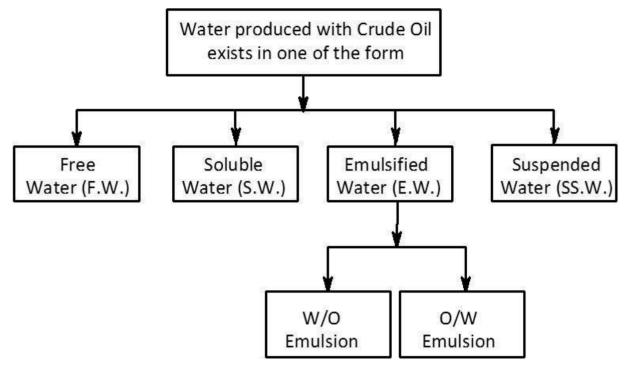


Figure 1: Forms of saline water produced with crude oil.

- ♣ A part f r o m free water, emulsified water (water-in-oil emulsion) is the one form that poses all of the concerns in the dehydration of crude oil.
- → Oil emulsions are mixtures of oil and water. In general, an emulsion can be defined as a mixture of two immiscible liquids, one of which is dispersed as droplets in the other (the continuous phase), and is stabilized by an emulsifying agent. In the oil field, crude oil and water are encountered as the two immiscible phases together. They normally form water-in-oil emulsion (W/O emulsion), in which water is

dispersed as fine droplets in the bulk of oil. This is identified as type C in Figure 6. However, as the water cut increases, the possibility of forming reverse emulsions (oil-in-water, or O/W emulsion) increases. This is type B in Figure 2.

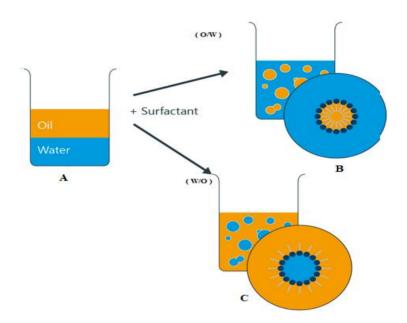


Figure 2: Schematic representation of (A) a non-dispersed system, (B) an O/W emulsion, and (C) a W/O emulsion.

The basic principles for the treating process are as follows:

- 1) Breaking the emulsion, which could be achieved by either any, or a combination of the addition of heat, the addition of chemicals, and the application of electrostatic field.
- 2) Coalescence of smaller water droplets into larger droplets.
- 3) Settling, by gravity, and removal of free water.

For two liquids to form a stable emulsion, three conditions must exist:

- 1) The two liquids must be immiscible.
- 2) Sufficient mixing time for diffusion of the discontinuous phase into the continuous phase.
- 3) There must be the presence of an emulsifying agent.

Emulsifying Agents

Emulsifying agents, which are commonly found in crude oil or water in the natural state or introduced in the system as contaminants during drilling and/or maintenance operations, create this film. Some of the common emulsifiers are as follows:

- 1) Asphaltic materials;
- 2) Resinous substances;
- 3) Oil-soluble organic acids;
- 4) Dispersed solid materials such as sand, carbon, calcium, silica, iron, zinc, aluminum sulfate, iron sulfide, and so on.

These emulsifying agents support the film formation encasing the water droplets, hence the stability of an emulsion.

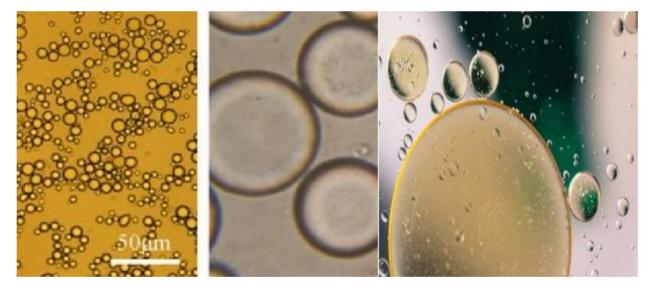


Figure 3: Photomicrograph of loose emulsion containing about 30% emulsified water in the form of droplets ranging in diameter from about 50 μM downward.

A very stable emulsion is known as a "tight" emulsion and its degree of stability is influenced by many factors. Accordingly, we can best understand the resolution problem and, hence, the treatment procedure if we consider the following factors:

- 1. Viscosity of oil
- 2. Density or gravity difference between oil and waterphases
- 3. Interfacial tension between the two phases (which is related to the type of emulsifying agent)
- 4. Size of dispersed water droplets
- 5. Percentage of dispersed water
- 6. Presence of emulsifying agents

The method of treating "wet" crude oil for the separation of water associated with it varies according to the form(s) in which water is found with the crude. Free-water removal comes first in the treating process, followed by the separation of "combined" or emulsified water along with any foreign matter such as sand and other sediments. The basic approaches of handling "wet" crude oils are illustrated in Figure 3.

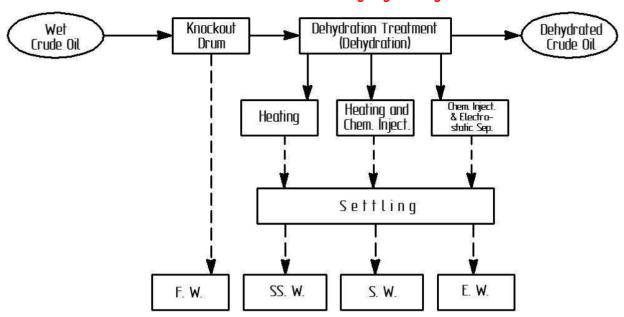


Figure 3: Basic approach of handling wet crude oil (F.W. = free water, SS.W. = suspended water, E.W. = emulsified water).

Dehydration Process:

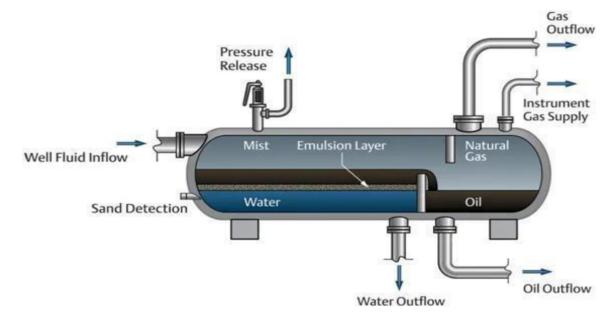
- ➤ Crude oil from separators normally contains up to 2% produced water in addition to water emulsified in the oil.
- ➤ When the product specification calls for a BS&W less than 0.5 %, electrostatic coalescer is commonly used.
- ➤ In dehydration stage by electrostatic coalescer, up to 10% water in inlet oil reduces to less than 0.2% volume water in oil after coalescing.

Successful dehydration of crude oil is carried out in three step:

- > Destabilization of the emulsion
- > Coalescence of small drops into large drops
- > Settling out of large drops and separation of the two phases.

Destabilization of the Emulsion

- ➤ During crude oil production and processing, unfavorable formation called emulsion is formed due to dispersion of a liquid (dispersed phase) in the form of droplets, entirely in another liquid (continuous phase).
- ➤ Emulsion is an unwanted formation that causes serious corrosion in pipelines, processing equipment, and increase in operational and capital cost.



Stable inter-facial films can be broken down by:

- > Chemical demulsifiers
- ➤ Heat treatment
- > PH treatment
- ➤ Increased salinity.

Coalescence of water droplets

This is achieved by introduction of electric field into the oil—water emulsion. When the emulsion passes through the electric field, the water droplets are electrically charged, and then dipole will be created. Dipole attraction between water droplets causes the coalescence of droplets. The attraction between water droplets in an electric field is given by:

$$F = \frac{K_s \varepsilon^2 (d_m)^6}{S^4}$$
 with $S \ge d_m$

F: attractive force between droplets

Ks: constant for system

ε: voltage gradient

dm: diameter of droplets

S: distance between droplets

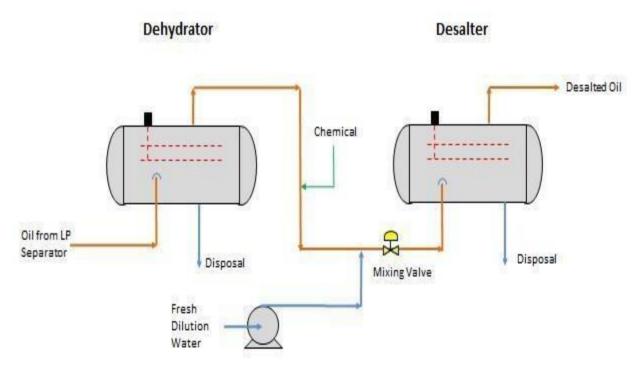


Figure 5: Typical Dehydrator and Desalter Arrangement.

Why crude dehydration?

Crude oil often contains water, inorganic salts, suspended solids, and water-soluble trace metals. As a first step in the refining process, to reduce corrosion, plugging, and fouling of equipment and to prevent poisoning the catalysts in processing units, these contaminants must be removed by dehydration and desalting.

Desalting of crude oil:

- ♣ The removal of salt from crude oil for refinery feed stocks has been and still is a mandatory step. This is particularly true if the salt content exceeds 20 PTB (pounds of salt, expressed as equivalent sodium chloride, per thousand barrels of oil).
- ♣ The most economical place for the desalting process is usually in the refinery. However, when marketing or pipeline requirements are imposed, field plants are needed for processing the salty oil prior to shipping.
- ♣ Salt in crude oil is, in most cases, found dissolved in the remnant brine within the oil. The remnant brine is that part of the salty water that cannot be further reduced by any of the dehydration methods.

Table 1: shows the amount of salts found in oils for various regions in the world

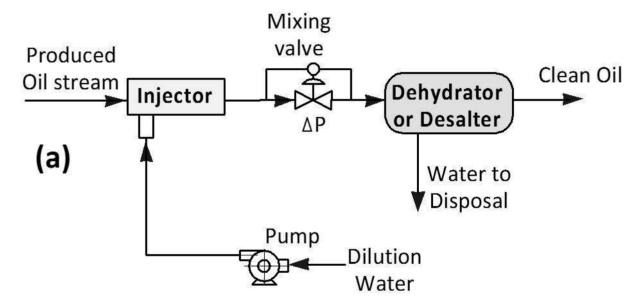
Table 1: Average Values for the PTB for Some Typical Crude Oils.

Source of oil	Avg. salt content (PTB)
Middle East	8
Venezuela	11
United States	
Pennsylvania	1
Wyoming	5
East Texas	28
Gulf Coast	35
Oklahoma and Kansas	78
West Texas	261
Canada	200

- → The method of reducing the PTB by lowering the quantity of remnant water WR is usually referred to as the treating process of oil dehydration.
- → The other alternative of reducing the PTB is to substantially decrease the dissolved salt content of the remnant water (i.e., its concentration, SR). This practice is known as desalting.
- → Desalting of crude oil will eliminate or minimize problems resulting from the presence of mineral salts in crude oil. These salts often deposit chlorides on the heat transfer equipment of the distillation units and cause fouling effects.
- ♣ The removal of these salts is aimed at providing an economical operating cycle in the refining process of crude oil. The reduction of salt content down to 5 PTB is feasible.

Description of the desalting process

♣ We cannot economically achieve a satisfactory salt content in oil by using dehydration only (single stage). This is particularly true if the salinity of the water produced with oil is much greater than 20,000 ppm (formation water has a concentration of 50,000–250,000 mg/L). Accordingly, a two-stage system (a dehydration stage and a desalting stage) is shown in Figure 7. Under certain conditions, however, a three-stage system may be used which consists of a dehydration stage and two consecutive desalting units as shown in Figure 7(b).



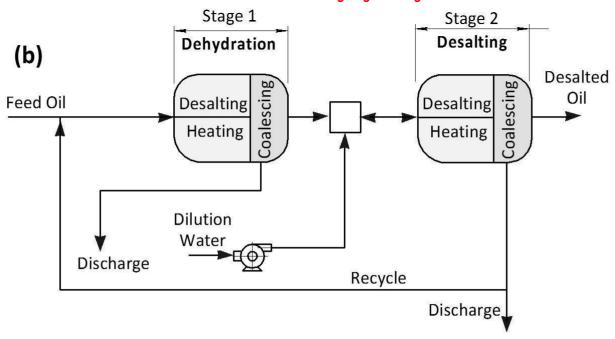


Figure 7: (a) Single-stage desalting system. (b) A two stage desalting system.

- Wash water, also called dilution water, is mixed with the crude oil coming from the dehydration stage. The wash water, which could be either fresh water, or water with lower salinity t h a n the remnant water, mixes with the remnant water, thus diluting its salt concentration. The mixing results in the formation of water—oil emulsion. The oil (and emulsion) is then dehydrated.
- ♣ The separated water is disposed of through the field-produced water treatment and disposal system.
- ♣ In the two stage desalting system, dilution water is added in the second stage and all, or part, of the disposed water in the second stage is recycled and used as the dilution water for the first desalting stage. Two-stage desalting systems are normally used to minimize the wash water requirements.
- The mixing step in the desalting of crude oil is normally accomplished by pumping the crude oil (which is the continuous phase) and wash water (which is the dispersed phase) separately through a mixing device. The usual mixing device is simply a throttling valve. The degree of mixing can be enhanced if the interfacial area generated upon mixing is increased.

The chemical desalting process involves adding chemical agents and wash water to the preheated oil, followed by settling, is shown in Figure 8. The settling time varies from a few minutes to 2 h. Some of the commonly used chemical agents are sulfonates, long-chain alcohols, and fatty acids.

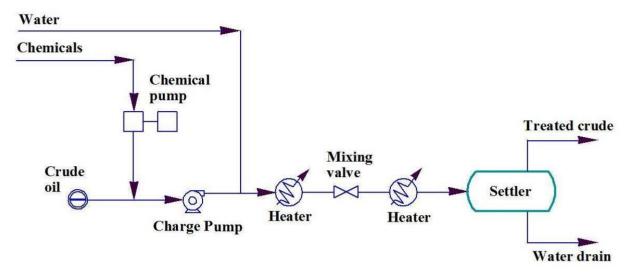


Figure 8: Chemical desalting.

Electrostatic Desalting

In this case, an external electric field is applied to coalesce the small water droplets and thus promote settling of the water droplets out of the oil. The electric field may be applied in any of the following manners:

- 1. ac field devices for water-rich emulsions.
- 2. ac/dc field for maximum dehydration
- 3. Variable gradient field for maximum saltreduction.

In the electrical desalting process, a high potential field (16,500–33,000 V) is applied across the settling vessels to help coalescence, as shown in Figure 9.

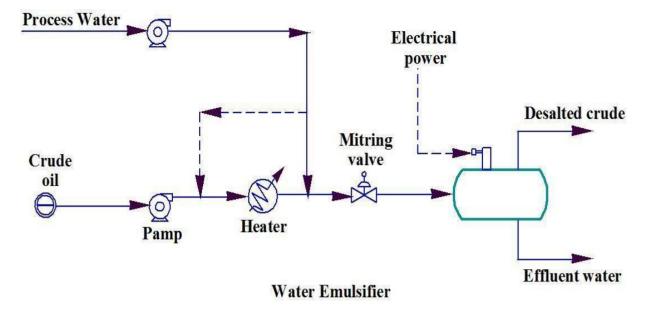


Figure 9: Electrical desalting.

The chemielectric concept utilizing both chemical agents and electrical field is schematically illustrated in Figure 10. In the desalting process, it is a common practice to apply enough pressure to suppress any loss of hydrocarbon due to vaporization of the oil. The pressure normally used in a desalting process is in the range 50–250 psi.

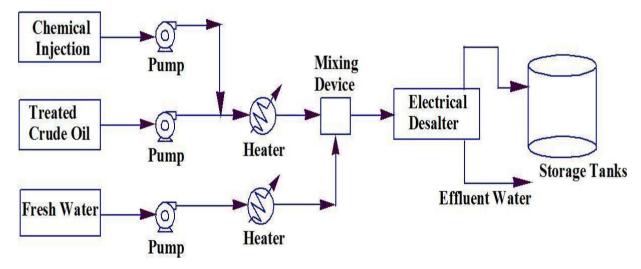


Figure 10: A typical desalting system utilizing chemelectric approach.

The efficiency of desalting is dependent on the following parameters:

- 1. Water-crude interface level.
- 2. Desalting temperature.
- 3. Wash water ratio.
- 4. Pressure drop in the mixing valve.
- 5. Type of demulsifiers.

Table 2: Average Desalting Conditions.

Crude gravity	Desalting temperature	Minimum water
(°API)	(°C)	ratio (vol%)
>40	110	2–4
30–40	110	4–8
	120	4–7
<30	130	8–10
	140	>10