Unit 5. Crude Oil Desalting

Assistant teacher
Belinskaya Nataliya Segeevna
Introduction

- When crude oil enters the unit, it carries with it some **brine** in the form of **very fine water droplets emulsified in the crude oil**.

- **Desalting** of crude oil is an essential part of the refinery operation.

- The salt content should be lowered to between 5.7 and 14.3 kg/1000 m³.
Introduction

Poor desalting has the following effects:

- Salts deposit inside the tubes of furnaces and on the tube bundles of heat exchangers creating fouling, thus reducing the heat transfer efficiency.

- Corrosion of equipment.

- Salts carried with the products act as catalyst poisons in catalytic cracking units.
The Presence Salts in Crude Oil

- Salts in crude oil are mostly in the form of dissolved salts in fine water droplets emulsified in the crude oil.

- This is called a water-in-oil emulsion, where the continuous phase is the oil and the dispersed phase is the water.
The Presence Salts in Crude Oil

- The water droplets are so small that they cannot settle by gravity.

- Furthermore, these fine droplets have on their surfaces big asphaltene molecules with the fine solid particles coming from sediments, sands or corrosion products.

- The presence of these molecules on the surface of the droplets acts as a shield that prevents the droplets from uniting with each other in what is called coalescence.
The Presence Salts in Crude Oil

- The salts can also be present in the form of salts crystals suspended in the crude oil.

Salt removal requires that salts be ionized in the water.
Types of Salts in Crude Oil

- magnesium chlorides
- calcium chlorides
- sodium chlorides

- These chlorides, except for NaCl, hydrolyze at high temperatures to hydrogen chloride:
  
  \[ \text{CaCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2\text{HCl} \]
  
  \[ \text{MgCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + 2\text{HCl} \]

- NaCl does not hydrolyze.
Desalting Process

- To remove salts from crude oil, water-in-oil emulsion has to be broken, thus producing a continuous water phase that can be readily separated as a simple decanting process.

The desalting process is accomplished through the following steps:

- Water washing
- Heating
- Coalescence
- Settling
Water washing

- Water is mixed with the incoming crude oil through a mixing valve.

- The water dissolves salt crystals and the mixing distributes the salts into the water, uniformly producing very tiny droplets.

- **Demulsifying agents** are added at this stage to aid in breaking the emulsion by removing the asphaltenes from the surface of the droplets.
Heating

- The crude oil **temperature** should be in the range of **48.9–54.4 °C** since the water–oil separation is affected by the **viscosity** and **density** of the oil.
Coalescence

- The water droplets are so fine in diameter in the range of 1–10 mm that they do not settle by gravity.

- Coalescence produces larger drops that can be settled by gravity.
Coalescence

- **Coalescence** is accomplished through an electrostatic electric field between two electrodes.

- The electric field ionizes the water droplets and orients them so that they are attracted to each other.

- **Agitation** is also produced and aids in coalescence.
Coalescence

- The force of attraction between the water droplets is given by:

\[ F = KE^2d^2 \left( \frac{d}{s} \right)^4 \]

- \( E \) is the electric field
- \( d \) is the drop diameter
- \( s \) is the distance between drops centres
- \( K \) is a constant
According to Stock’s law the settling rate of the water droplets after coalescence is given by

\[
\text{Settling rate} = \frac{k \left( \rho_{H_2O} - \rho_{oil} \right) d^2}{\mu_{oil}}
\]

- \(\rho\) is the density
- \(\mu\) is the viscosity
- \(d\) is the droplet diameter
- \(k\) is a constant
One-Stage Desalter

Figure 1. Simplified flow diagram of an electrostatic desalter

- A typical desalter contains two metal electrodes.
- A high voltage is applied between these two electrodes.
One-Stage Desalter

For effective desalting the electric fields are applied as follows:

- **A high voltage field called the “secondary field”** of about 1000 V/cm between the two electrodes is applied.

  The ionization of the water droplets and coalescence take place here.

- **A primary field** of about 600 V/cm between the water–crude interface and the lower electrode is applied.

  This field helps the water droplets settle faster.

The one-stage desalter achieves **90% salt removal**.
Two-stage desalting

99% salt removal is possible with two-stage desalters.

Figure 2. Two-stage desalting
Two-stage desalting

- A second stage is also essential since desalter maintenance requires a lengthy amount of time to remove the dirt and sediment which settle at the bottom.

- Therefore, the crude unit can be operated with a one stage desalter while the other is cleaned.
Desalter Operating Variables

For an **efficient desalter operation**, the following **variables** are controlled:

- Desalting temperature
- Washing water ratio
- Water level
- Washing water injection point
- Demulsifier injection rate
- Type of washing water
- Pressure drop in the mixing valve
- Desalter pressure
Desalting temperature

- The **settling rate** depends on the **density** and **viscosity** of the crude.

- Since increasing the temperature lowers the density and viscosity, the settling rate is increased with temperature based on the crude gravity.

- Typical desalting temperature can vary between **50 and 150 °C**.
Washing water ratio

- Adding water to the crude oil helps in salt removal.
- Hence, increasing the wash water rate increases the coalescence rate.
- Depending on the desalting temperature, a minimum value should be used.

For example, crude oil having 31.2 API gravity requires 7–8 vol % water addition relative to the crude rate.
Water level

- Raising the water level reduces the settling time for the water droplets in the crude oil, thus improving the desalting efficiency.

- However, if the water level gets too high and reaches the lower electrode, it shorts out the desalter.

- Since the primary electric field depends on the distance between the lower electrode and the water–crude interface, it is always better to keep the level constant for stable operation.
Washing water injection point

- Usually the washing water is injected at the mixing valve.

- However, if it is feared that salt deposition may occur in the preheat exchangers, part or all of the washing water is injected right after the crude feed pump.
Demulsifier injection rate

- **Demulsifiers** are basic copolymers with one end being **hydrophilic** (loves water and attaches to the surface of the water droplet), and the other end being **hydrophobic** (loves the oil and is directed to the oil side).

- When these compounds are adsorbed on the droplet surface, they stabilize the droplet.

- The demulsifier is added to the crude after the feed pump or before the mixing valve at levels between **3 and 10 ppm** of the crude.
Type of washing water

- **Process water** in addition to **fresh water** is used for desalting.
- The water should be relatively soft in order to prevent scaling.
- The water should be slightly acidic with a pH in the range of 6.
- It should be free from hydrogen sulphide and ammonia so as to not create more corrosion problems.
- Therefore, distillation overhead condensates and process water from other units can be used after stripping.
Pressure drop in the mixing valve

- Mixing the washing water with crude oil is necessary in order to distribute the water and dissolve any suspended salts crystals.

- The pressure drop across the mixing valve determines the mixing efficiency.

- On the other hand, the mixing process produces finer (smaller diameter) droplets which tend to stabilize the emulsion and make water separation more difficult.
Pressure drop in the mixing valve

- Therefore, there is a compromise in selection of the appropriate pressure drop across the mixing valve.

- A pressure drop between 0.5 and 1.5 bar (7.4 and 22 psi) is used.
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Desalter pressure

- The operation of the desalter requires that the crude be in the liquid phase during desalting.

- A typical pressure of 12 bar (176 psia) is necessary to achieve this purpose.
Conclusion

- When the process control variables are properly adjusted, a 90% salt rejection can be achieved.
- With a two stage operation the salt rejection can reach 99%.
- Any remaining salts are neutralized by the injection of sodium hydroxide which reacts with the calcium and magnesium chloride to produce sodium chloride.

\[
\text{CaCl}_2 + 2\text{NaOH} \rightarrow \text{Ca(OH)}_2 + 2\text{NaCl}
\]

NaCl does not hydrolyze to the corrosive hydrogen chloride.