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Desalting of crude oil and some products at Kurdistan region – Iraq

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ABSTRACT

The removal of salt from crude oil for oil-field processing has been and still is a mandatory requirement. Salt in crude oil is, in most cases, found dissolved in the remnant brine within the oil. The chemical composition of these salts varies, but the major portion is nearly always sodium chloride. This remnant water exists in the crude oil as a dispersion of very fine droplets highly emulsified in the bulk of oil. To accomplish desalting, the crude is first heated to (80-110) ºC in order to reach the required viscosity level. About 2-10% wash water added as an extraction agent in addition to 30% emulsifying agents to help dissolve salts and sediments, mixing time was 20 minutes.In this work, we attempt to formulate a method with easier conditions for desalting of Shiwashouk and Kahwergousik fields of operation crude oils (from different wells). The results show a significant decrease in chloride contents.

Keywords: Desalting, crude oil, Kurdistan region.

INTRODUCTION

Crude oils are complex mixtures obtained from many parts of the world and all crudes contain varying degrees of impurities. These impurities consist of naturally occurring water, salts, solids and metals as well as added contamination from well stimulants, gathering methods, storage and transportation. Adverse effects of these impurities are excessive corrosion, fouling and unit upsets. These effects can result in shortened unit run lengths and reduced equipment reliability. To minimize these effects, the refiner often washes the crude oil with water, and uses a desalting vessel to remove the added water and most of the inorganic contaminants from the crude prior to distillation in the crude unit [1].

Production of wet crude because of a rise in the oil/water contact in many oil fields has been a growing field problem, and it has affected the quality of crudes. In almost all cases, salt is dissolved in the water that is dispersed in the crude oil and its separation is not simple because desalting is a critical operation because of the importance of meeting the specifications of acceptable quantities of salt and water in the treated oil [2]. For these reasons, measurements of salt and water content in crude oils are very important in all oil-industry operations, including crude-oil production, processing and transportation and refining [3]. Salt content and acid number are important indices for refining operations. High values of any of these parameters indicate high corrosion tendency of crude oil. The values of these parameters obtained for crude oil blends in the area show that these blends possess very low corrosion potentials [4].

Formerly the desalting of crude oil was conducted only as a measure to decrease corrosion and stabilize operation. In recent years, desalting technology has played an important part in protecting catalysts in the latter refining operations, because after distillation, the majority of salts are left in residual and heavy stocks which lead to the poisoning and deactivation of catalysts in the heavy oil catalytic cracking, hydrocracking, and hydrorefining [5].Another noticeable problem is that a series of enhanced recovery technologies have been widely applied in oil fields, for example, using surfactant, polymer, and alkali flooding to drive heaver oil. At the same time, they can enter into the oil layer and make the emulsion more stable [6].

During the past decades, nonionic surfactants have been widely used as deemulsifiers. Nowadays, alkoxylated polyhydric alcohol, alkoxylated alkyl phenol formaldehyde resin, alkoxylated polyethylene amine, and their derivatives are main de-emulsifiers for the desalting and dewatering of crude oil [5,7]. As the properties of crude oils from different oil fields are different, a deemulsifier fitted to one type of crude oil is usually not as effective with other types. Attempts have been made to correlate the efficiency of deemulsifiers with their surface, interfacial, and chemical properties [8]. Runnac and Tabakovic [9], reported a correlation between deemulsification and the size of the hydrophilic group for block copolymers. Aveyard et al. [10] and Zaki et al. [11] described the correlations between deemulsification efficiency and HLB of deemulsifier. Goldszal et al. [12] investigated whether a relationship exists between deemulsification performance and the properties of the deemulsifier, including relative solubility number (RSN) value and molecular weight. However, there are many works researching the relation between the property of crude oil and the molecular structure of deemulsifiers.

The aim of this method: 1-This method is used to determine the approximate chloride content of crude oils, knowledge of which is important in deciding whether or not the crude oil needs desalting. The efficiency of the process desalter can also be evaluated.2 - Excessive chloride left in the crude oil frequently results in higher corrosion rates in refining units and also has detrimental effects on catalysts used in these units.

MATERIALS AND METHODS

The studies were conducted at the laboratories of oil technology department – Koya technical institute – Koya – Erbil – Kurdistan region – Iraq, by using Salt in crude analyzer (Electrometric method) – model NSB 210 – from Normalab company- France.

The reagents prepared are - Mixed Alcohol Solvent- 63 volumes of 1-butanol and 37 volumes of absolute methyl alcohol (anhydrous). To each liter of this mixture, add 3 ml of water, Calcium Chloride Solution, Magnesium Chloride Solution, Sodium Chloride Solution, Xylene (reagent grade).
Crude oil samples were collected from Shiwashouk and Kourmalah fields and some products from Kawergousick refinery station.

Desalting process: 100 gm crude oil of each sample, 2-10% deionized water and 30% deemulsifier were delivered into a conical flask and stored in a constant-temperature at (90-110) $^{\circ}$C for 20 min. Mixtures shaken for 20 minutes, each time, this ensured uniform distribution of the deemulsifier in the emulsion. First, freshwater was added, followed by the deemulsifier. The mixture was then heated in a water bath. The heated mixture was then mixed and poured into a 100ml centrifuge tube and rotated at 1000 rpm. The final step in completing one cycle was to suck out the top crude volume in the centrifuge tube.
The efficiency of desalting in each experiment is determined by measuring the salt content using standard test method for salts in crude oil (Electrometric method, ASTM D – 3230 -2005a) [13].

Procedure: To a dry, 100 ml graduated, glass-stoppered cylinder, add 15 ml of xylene and pipette (total delivery) in 10 ml of the crude oil sample. Rinse the pipette with xylene until free of oil. Make up to 50 ml with xylene. Stopper and shake the cylinder vigorously for approximately 60 s. Dilute to 100 ml with mixed alcohol solvent, and again shake vigorously for approximately 30 s. After allowing the solution to stand for approximately 5 min, pour it into the dry test beaker [14].

RESULTS AND DISCUSSION

Generally, a small proportion of washing water is mixed with crude oil so that the salts and impurities in oil can be dissolved, the washing water should be dispersed in crude oil to form emulsion, which extracts the salts from oil. However, these brine droplets are prevented from coalescing due to the elastic film on the interface between water and oil. Normally, this film is stabilized by natural emulsifiers in crude oil, such as wax, resin, asphaltene, naphthenic acid, and so forth. The deemulsifier usually has a higher surface activity than these natural emulsifiers, so it can displace them and weaken the film, thereby promoting the droplets of brine to coalesce when they contact each other[13].

Desalting can be performed in a single stage or in two stages, depending on the requirements of the refinery. Dehydration efficiency of a desalter is usually 95% in a single stage and up to 99% in two stages [14].

If mixing is good, dehydration efficiency can be compared with desalting efficiency as most of the salt passed from the organic phase into the water phase. In actual operation, water and oil are preheated and mixed in a good ratio. It has been observed that good mixing allows for appropriate salt removal from oil. During mixing, salt content in oil is washed with the water and emulsion is formed.

Settling rate depends highly on temperature. Liquid density and viscosity usually decrease with temperature. The effect is even greater regarding viscosity as the dependence is exponential. This means that increasing operation temperature will raise settling rate and therefore, improve separation. In a given desalter, separation improvement means that a larger quantity of oil can be desalted in the same time [15]. This would suggest that a higher temperature is more convenient. However, crude oil conductivity increases with temperature and so does the power requirement of the process.

During desalting, water is mixed with oil so that salts can be diluted in water and washed from the organic phase. Some of the mixed water then forms an emulsion that must be demulsified to separate water from oil [16].

The deemulsifier acts to neutralize the effect of the emulsifying agents, freeing more water drops from the surrounding interfacial film. The excessive use of this deemulsifier can decrease the surface tension of water droplets and actually create a more stable emulsion, which is difficult to treat [1].

In the case of crude oil, emulsifiers are present in the form of clay, metallic salts and, most important, asphaltenes. In general, the heavier the crude oil, the greater content of emulsifiers [17].

It has been observed that the suspended water droplets posses an electric charge. For this reason, desalting methods aim at destabilizing the electric array in the droplets. The main element in these methods is the arrangement of two electrodes that generate an electric field among the emulsion. The effect is that droplets vibrate, migrate and, ultimately collide with each other and coalesce. Then the larger drops settle under the effect of gravity. It is worth mentioning that the force that makes coalescence possible is voltage. The amount of electric current is not relevant for droplet coalescence [18].

Typically the relative concentrations of chloride salts in crude oil mimic that of sea water, 70% of the chlorides are in the form of NaCl, 20% $MgCl_2$ and 10% $CaCl_2$. $MgCl_2$ is the primary contributor to overhead corrosion because it almost all hydrolyzes to form HCl [13]. $CaCl_2$ hydrolyzes but to a much lesser extent than Mg. NaCl does not hydrolyze to any appreciable extent. At typical crude unit conditions that about 20% of the salts in the desalted crude could be expected to hydrolyze in the absence of caustic. Besides temperature, acid can increase the % hydrolysis [19].Tables (1) and (2) show the results of crude oil and products desalting. Also, figure (1) shows the Calibration curve of a mixed salt content standard solutions.

Calculations: From the calibration graph, the indicated salt concentration corresponding to the net current (mA) reading of the sample was calculated. The concentration in mg kg^{-1} by using the appropriate equation given below:

$$\text{Salt, mg/kg} = \frac{1000X}{d}$$

Where: X = measured salt concentration in g m^{-3}, d = specimen density at 15º C in kg m^{-3}

Table 1: Salt content of crude oils from Shiwashouk field at Taq area before and after desalting treatment

Sample	Salt content (ppm)	
	Before treatment	After treatment
TT - 02	22899.4	8269.2
TT – 04	46549.6	29269.7
TT – 05	36282.5	21043.8
TT – 07	43539.04	26123.4
TT – 08	39792.4	27779.6
TT - 14	113201.5	84089.7
TT - 15	119732.3	85626.7

Table 2: Salt content of crude oil from Kourmalah and some products from Kawergousick refinery station before and after desalting treatment:

Sample	Salt content (ppm)	
	Before treatment	After treatment
Crude oil (Kourmalah)	232608.1	156738.7
Diesel	5947.5	3545.6
Kerosene	7168.6	5018.02
Gasoline	6093.5	3808.4
Naphtha	12338.03	1542.2

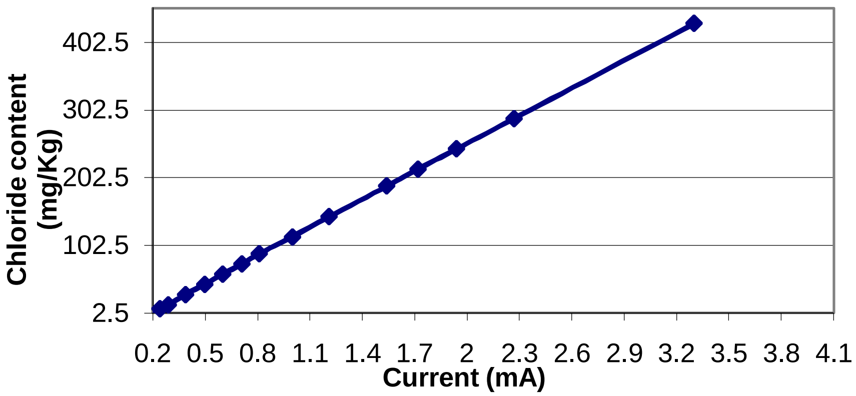
APPLICATION

This method provides a rapid and convenient means of determining the approximate content of chlorides in crude oil and is useful to crude oil processors.

CONCLUSIONS

The desalting of some crude oils with different properties have been studied. Under this study, five parameters will be altered to reach the goal of the study, an optimum combination of parameters. These are: crude temperature, mixing time, settling time, deemulsifier dosage, and the amount of freshwater added in ratio to that of the wet crude's quantity.

Figure 1 : Calibration curve of a mixed salt content standard solutions



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