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Experimental Study of Dehydration Effect of Crude Oil in Multi-Purpose Station

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Abstract
Crude oil dehydration process in multi-purpose station is of great importance, in which there are a lot of confounding factors and parameters. In order to solve the dewatering difficulty in multi-purpose station of Liaohe Oilfield during operation, we designed a laboratory experiment of thermo-chemical setting dehydration, and analyze these factors impacting the liquid mixture separation of oil and water from the districts, including to liquid water content, dehydration temperature, PH value of crude oil solution, demulsifier dosing concentration, produced fluid composition. This research shows that: adjusting the technological parameters in a reasonable range, is both beneficial to dewatering and improving heavy oil dehydration effect, and of great significance of improving the downstream production standard.

Key words: Heavy oil; Multi-purpose station; Crude oil emulsion; Demulsification

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INTRODUCTION

In Jinzhou oil production plant of Liaohe oilfield, the water cut crude oil comes from three blocks, including district two, four and five , whose daily processing fluid volume is 14,000 m^3, and the water content of crude oil is in the range of 85% - 95%, and the purification of the crude oil requires that the water content is less than 1%. Their main functions are: crude oil heating, tank settling dehydration, measuring output, and so forth. During 2009 to 2012, the multi-purpose station performs worse effect on dehydration when enters in winter (October to February), mainly for that, the water content of external transport purifying raw oil exceeds the standard (the water content of crude oil outside the station regularly exceeds the standard), and the oil content in water which is dehydrated from settling tank increases. In order to make sure that the water content of external transport oil is below 1%, and reaches the required handover standard, we carry out the indoor experimental study of heavy oil thermal chemical dehydration, so as to make clear the relationship between the demulsifier dosage, dehydration temperature, water content, pH value and heavy oil separation of oil and water in multi-purpose station, and by adjusting each parameter, we solve the problem of disorder of the water content of the crude oil to improve the dewatering efficiency of heavy oil.

1. THE SECTION OF EXPERIMENTS

1.1 The Experimental Device and Reagents

The digital viscoscope of BROOKFIELD DV-II + Pro; the ZJ- II thermotank, whose accuracy of temperature controlling is 0.1℃; HH-4 digital thermostatic water bath; the high shearing and dispersing type mulser; HA-805 intelligent and infrared high efficient dehydration apparatus; hydro tester; PH meter; 250 beakers, 250 ml dosimeters, rubber plugs and so on.

The samples of heavy oil, demulsifier, sodium hydroxide (analytical) and concentrated hydrochloric acid, which were provided by Liaohe oilfield, the PH value of the water sample which uses in indoor simulation experiment is 7.86, performing weakly alkaline, which can be regulated by hydrochloric acid and sodium hydroxide solution; using sodium chloride, potassium chloride, calcium chloride, magnesium chloride adjusting water mineralization degree, and the degree of mineralization is as Table 1.

Table1
The Indoor Experimental Water Mineralization Degree (mg/L)

$Na^{+}+K^{+}$	Mg^{2+}	Ca^{2+}	CL^{-}	SO_4^{2-}	HCO_3^{-}	The mineralization degree in total
466.9	9.7	24.1	266	38.4	854.3	1,659.3

1.2 Experimental Methods

In this experiment, we referred to the SY/T 5281-2000 standard of petroleum and natural gas industry, the methods of using and properties testing of crude oil demulsifier (bottle test), according to the national standard GB/T 8929-2006, crude oil water content testing (distillation), we measure the water ratio in upper oil after dehydration. The specific operation as follows:

(a) The preparation of a different pH values of water samples, whose range is 4, 5….10, 11;

(b) The preparation of the crude oil emulsion of[1-2] different moisture content; The moisture content range is 30%, 36%, 40%;

By many times of field sampling, we found that, water cut oil samples was about 28% - 43%, which is large range; At the same time, as the storage time is different, the moisture content will change. In order to make uniform conditions, we first use efficient dehydration instrument to dehydrate the viscous oil samples in Jin's exploitation, keeping that the water content is less than 1%. When preparing the crude oil emulsion, we should unity emulsifying machine speed and emulsifying time[3]. Each group of experimental oil samples should be completed in one time, to ensure that the crude oil emulsion properties are uniform. Using the prepared emulsion as soon as possible, the storage time should not exceed three days, in order to reduce the aging emulsion influence of indoor experimental accuracy.

The preparation steps of crude oil emulsions including: a) Before mixing the two-phase oil-water mixtures, we process fully preheated; b) After sufficient preheating, we adjust mixing time, control mixing speed, and emulsify oil-water mixture proportion appropriately; c) Then proper amount of demulsifier was added to low speed stirring.

(3) The crude emulsion will be moved to the plugged cylinder, ensuring good sealing , then we place it into the constant temperature box in advance preheat fully in 24 hours;

(4) According to experimental program, we process crude oil dewatering, in first 2 hours, we observe phenomena each 15 minutes; after 20 hours, we change the time interval to 1 hour and observe phenomena. We should record precipitation water, oil-water interface layer state, and the turbidity degree of separated water turbidity degree. And calculate the moisture content.

2. THE EXPERIMENTAL RESULTS AND DISCUSSIONS

2.1 The Temperature Impact on the Settling Dehydration

Under the condition of constant PH value of crude oil emulsion, liquid water content, demulsifier concentration, constant temperature box will be set respectively for 80℃, 85℃, 90℃, 95℃ and record the seperated water content, oil-water interface layer, and separated water turbidity degree.

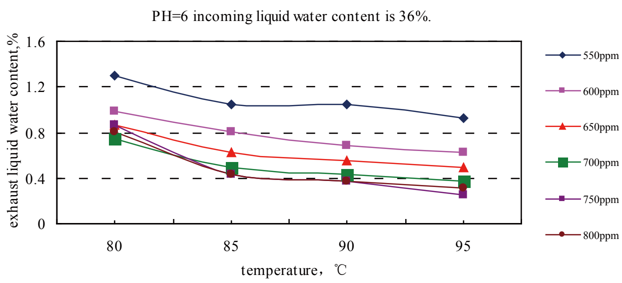

Figure 1
Different Demulsifier Concentration, PH = 6, the Liquid Water Content is 36%, the Curve of Crude Oil Changes With Different Temperature

As shown in Figure 1, when liquid moisture content, pH value and adding demulsifier are at the same concentration, the water ratio of crude oil processed decreases with the increase of dehydration temperature, and the oil-water emulsions' separation which effected by temperature directly responses at curve steepness of temperature, that is, the curve is more steeper, and the temperature effects more intensely. This role in the temperature is most significant between 80℃ and 90℃, and its value is about 0.72% - 1.5%. Despite the significant effect of temperature, but at high temperature, which is 90℃ - 95℃, at this time the water content of crude oil has been very low, and continued heating effecting on the oil-water separation is restricted.

In the experiment, with the increase of temperature, moisture content remained basically decrease trend. Its mechanism is as follows:

The law Stokes：

$$V_d = \frac{d_d^2 g(\rho_w - \rho_o)}{18\mu}$$

In the formula:
V - The settling velocity of water droplet, m/s;
d_d - The diameter of water droplet, m;
ρ_1 - The e water density, Kg/m;
ρ_2 - The e oil density, Kg/m;
g - The gravity acceleration, 9.8 m/s^2;
μ - The viscosity of crude oil, p·s.

As the law Stokes[4] shows, the degree of difficulty of oil-water separation mainly depends on the density difference phase and oil viscosity. Therefore, to accelerate the dehydration, it should be done of increasing the density difference between oil and water and reduce the viscosity of the oil phase. With the increase of temperature, the interfacial shear viscosity of heavy oil emulsion is gradually reduced, and thermal motion of droplet dispersed is strengthened, reducing the viscosity of the oil phase, increasing the oil-water density difference, which favor the droplet coalescence and aggregation, and reduce the stability of the emulsion; at the same time, it also has the thermal diffusion in favor of demulsifier molecule. In addition, with the increasing of the demulsifier, the moisture content is not always reduced, which requires the indoor experiment on demulsifier.

2.2 The PH Value Impact on the Settling Dehydration of Second Stage

Under the same conditions of dehydration temperature, liquid water content, and demulsifier concentration, the crude oil emulsion were prepared for pH value of 4, 5...11, recording the separation of content, studying the effect of oil-water separation, first determining that either the acidic or alkaline is beneficial to the dehydration of crude oil, and then on this basis, in the narrow pH range experiment, investigating the oil-water interface layer and separated water turbidity degree.

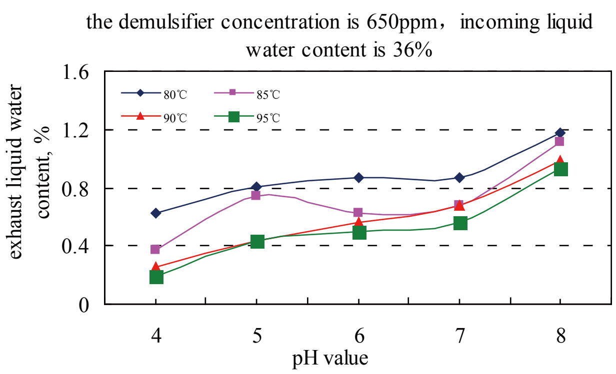

Figure 2
Demulsifier concentration is 650 ppm, and Liquid Moisture Content is 36%, the PH Value Curve of Crude Oil Changes With Different Temperature

As shown in Figure 2, unchanged in other cases, since the pH = 4 is increased to pH = 5, the change of this section of water rate is about 0.2% - 0.5%, a turning point in the first; then, moisture content remained basically unchanged; when pH value is larger than 5, the water content increased faster, and the increasing trend is maintained to pH = 6, but the pH value is below 7.5 the, the rate of water cut crude oil processed keeps at a low level; as the pH value is greater than 7.5, the water cut of crude oil increased faster.

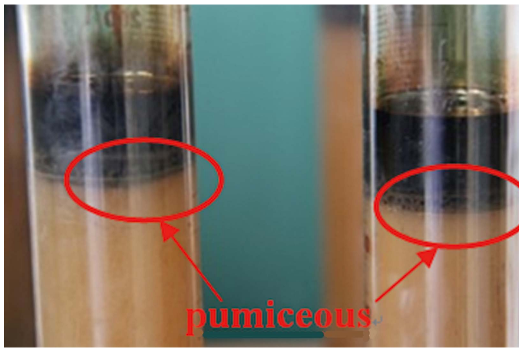

Figure 3
The Picture of Emulsion Dehydrated of Temperature is 85 ℃, Liquid Water Content is 85%, PH = 10

Besides, we also find that: when pH = 4 - 7.5, the color of emulsions of dehydrated water is clear, the oil-water interface is distinctly, the middle layer is thin, and the oil droplets to the wall of the container are less and also smaller particle size; when pH > 7.5, the color of emulsions of dehydrated water is turbidity, oil-water interface is not neat, the middle layer is thin, the oil drops and flocs adhered to the wall of the container are more, and even performs the emergence of foam (Figure 4), and dehydrated water is also reduced. The color of water pulling out becomes clear with the fall of pH, which explains the decrease of pH value can not only improve the water dehydrated, but also can decrease the oil content in the sewage, and improve the effect of oil-water separation.

Through the indoor experiment to the effect of pH on the stability of crude oil emulsions, we found that the addition of alkali enhanced the stability of the emulsions[5-6], with the enhancement of contact time of prolonged stability of alkali and oil , one of the reasons is the reaction between alkali and acidic substances in oil generation and then generate into oil soluble surface acting agent. This surface active agent can react with hydrophilic radical of the original surface active agent, and can enhance the space resistance and repulsion force of interfacial film to make the film more powerful, moreover, the polymer can strengthen the viscosity of the liquid, and has a great influence on the drops of poly. Alkali can make the type and structure of emulsion more complex.

At the same time, the conclusions can be obtained: changing the pH value of dehydrated water, majorly adjusting the dehydrated water quality, such as whether the oil-water interface is equal, and the oil content in the water dehydrated. If the water in crude oil performs alkaline, it will be easily turbid, and when adding acidic substances to dehydrated water, the pH value becomes smaller, so the water is easy to clean. While the dehydrated sewage of old multi-purpose stations' pH = 7.86, weakly alkaline, it is according with the indoor experiment conclusions, we should add an acidic substances to regulate.

2.3 Demulsifier Concentration Impacting on the Settling Dehydration of Second Stage

Under the same conditions of the pH value of crude oil emulsions, temperature, water content, we change the demulsifier concentration into 550 ppm, 600 ppm, 650 ppm, 700 ppm, 750 ppm, 800 ppm, and record the separation of content, study the oil-water interface layer, and separated water turbidity degree.

When demulsifier impacts on the oil-water separation, the effect is not always improved with the increase of drug concentration. As shown in Figure 4, for example, when pH = 5, the dehydration temperature is 85℃, and the demulsifier concentration is between 550 ppm to 580 ppm, the water content after treatment will increase with the decreasing of demulsifier concentration; When the demulsifier concentration is between 580 ppm and 750 ppm, the liquid water content is no longer reduced; but when the demulsifier concentration is over 750 ppm later, a liquid water content increases, showing the trend that it is not conducive to the separation of oil and water.

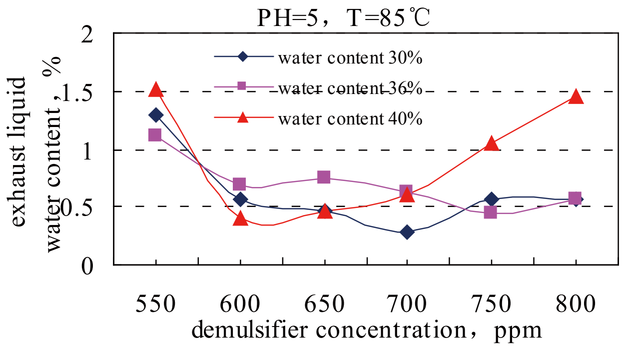

Figure 4
pH = 5, T = 85℃, the Curve of Different Water Content Changes With Temperature

Because of the joint demulsifier, the demulsifier breaks up to the oil-water interface, and adsorbs to the interface, and part displaces the natural emulsifier molecule which adsorbs on the interface, making the interface film's viscoelasticity reduce, which connects with the formed film and develop into the mixed film whose intensity is lower, so the resistance between two water droplets' collision and coalescence becomes smaller, and coalescence probability is more larger, eventually leading to dehydration[7]. In the experimental concentration range, more larger is the demulsifier concentration, smaller is the water in the oil rate. This is because with the increasing demulsifier concentration, the demulsifier molecule constantly replaces active substances on the oil-water interface, the interface transverse force among the adsorbed molecules decreases, oil film strength becomes smaller, so that the film life is shorter, and interfacial film is thickness, when the film thickness is thinner than a limit value, the membrane will rupture, eventually led to the demulsification and dehydration.

Demulsifier is surface active agent in the end, overusing will appear the phenomenon of two times emulsification, demulsification rate decreased in the opposite. The average amount of satisfactory effect is in 650 ppm - 750 ppm. Because of the increase of demulsifier dosage, the interaction of emulsifier molecules and emulsion reaches equilibrium at the interface, interfacial film strength becomes lower, and the water droplets are most easily coalescent, but excessive addition of demulsifier can make the demulsifier molecule form a new interfacial film, it can't help droplets coalescence, but will hinder.

2.4 Water Content Impacting on the Settling Dehydration of Second Stage

Under the same conditions of pH of crude oil emulsions, temperature, dehydration demulsifier concentration, we setup the crude oil emulsions rate into 30%, 35%, 40%, and record the separate water case, and investigate the oil-water interface layer, and separated water turbidity degree.

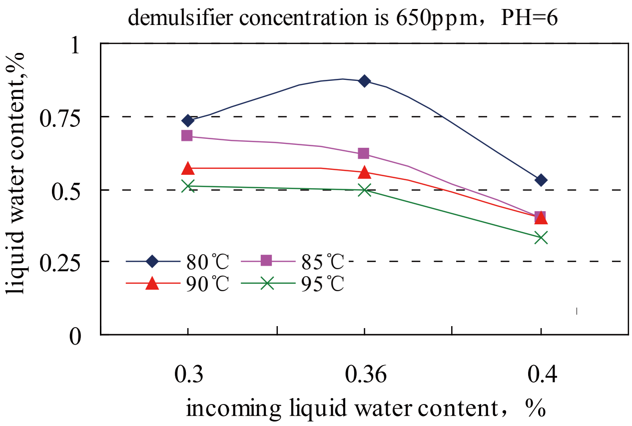

Figure 5
PH = 6, Demulsifier Concentration is 650 ppm, the Curve of Crude Oil Changes With Different Temperature

When the liquid water content is 36%, the difference corresponding to each temperature point of liquid water content is maximum. As shown in Figure 5, for example, when the demulsifier concentration is 650 ppm, pH = 6, the dehydration temperature grows slowly, and the growth trend is not significant, but when the liquid water content is in 36% to 40%,the liquid water content drops sharply.

Through the indoor experimental study and analysis of experimental results, we found that: the moisture content is higher, and the required demulsifier concentration is lower. When the other factors are constant, and liquid water content is 30%, the demulsifier optimal concentration is 700 ppm - 750 ppm; when the liquid water content is 36%, the demulsifier optimal concentration is 650 ppm - 750 ppm; when liquid water content is 40%, the demulsifier optimal concentration is 600 ppm - 650 ppm.

3. THE APPLICATION PROCESS OF DEHYDRATION IN MULTI-PURPOSE STATION

We synthesize the dehydration parameters (dehydration temperature, pH value, liquid water content, adding demulsifier concentration) from indoor experimental and the obtained data of water content .According to the experimental data, we use the 1stOpt to fit out 15 empirical formulas and verify whether the formula is correct. Verification methods are as follows: We take interval 30 groups of data in the range of the formula, and calculate out of liquid water cut by the formula, then input them in Excel; at the same time, the experimental results of the corresponding condition data will be input in Excel, comparing the difference. After determining the reliability of the empirical formula, we can take advantage of C# language to compiler, and it is convenient for operation personnel to select the parameters for reference.

CONCLUSION

(a) Through the indoor experiment study, we found that, for the crude-oil-saline water system from joint station, the lower pH value (That is acidic) is in favor of oil-water separation, and there are the most suitable pH interval is from 6 to 7.5, the stability of the emulsion is the worst in this range.

(b) When the dehydration temperature is higher, the oil-water separation effect is better. Dehydration temperature reasonable range is from 80℃ to 90℃ in the second dehydration stage.

(c) When the dehydration temperature and pH value are in the optimum range, liquid moisture content is 34% - 37%, the optimum range of demulsifier concentration is 600 ppm - 750 ppm.

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