Oil Sludge Deposition in Storage Tanks: A Case Study for Russian Crude Oil in Mo-he Station

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Abstract: The oil tank can form a considerable amount of sludge deposition after continuous accumulation, which causes a seriously negative impact on both the storage capacity and the safe operation of the oil tank. Therefore, it is important to anticipate the rate of sludge deposition in advance so that proper measures can be planned to remove this heavy layer on the bottom. This paper proposes a method using a relatively simple formula for predicting the sludge deposits. The sedimentation mechanism of wax and asphaltene is introduced and summarized from both the micro and macro aspects, the factors causing the interaction between particles and the influence on coalescence were analyzed. We applied our prediction methods to calculate the sludge deposition of four oil tanks in Mo-he Station and compared our results with the data measured by experiments. The results show that our method had a good general accuracy to experimental data and can be used directly for on-site engineers to anticipate real sludge height before measuring the oil level inside the tank.

Keywords: wax; asphaltene; oil sludge; deposition; oil tank

1. Introduction

Particle sedimentation is the movement process of solid in liquid due to various forces. Different solids and liquids have different physical properties and thus the sedimentation processes are different. Crude oil is a complex mixture that contains asphaltene, resin, wax, mechanical impurities, and water. Under certain thermodynamic conditions, asphaltene and wax can coalesce and separate. When they aggregate to a certain particle size and density, they settle under the action of gravity, which is more obvious under weak convection and shear force. The oil tank just meets these conditions. Due to the existence of sedimentation balance, the number of particles that can settle in each batch of oil is limited, and the settlement of wax and asphaltene in the oil tank did not attract much attention from researchers as they do for the case of pipeline wax/asphaltene deposition. However, after a long period of time and continuous accumulation, a considerable amount of sediment can be formed at the bottom of the tank. This effect seriously affects the storage capacity of the oil tanks, and the economic benefits, weakens the buffer capacity of the oil tank and brings challenges to the operation and maintenance. Therefore, if sludge deposition can be anticipated in advance, it can help the oil company to better determine the cleaning period of the sludge and to ensure the safety of the whole oil transportation system, so that maximum benefit can be possibly obtained.

There are a few studies focusing on the mechanism of crude oil deposition. Kynch [547], who was pioneering in the study of the particle sedimentation mechanism, proposed the use of continuity equation to describe the vertical sedimentation process of particles. It is pointed out that after the particles settle for a period, the concentration gradient will be formed below the initial concentration surface in the solution, and the sinking speed of the particles will gradually decrease due to the existence of this gradient. Yan and Fei [7]
studied the viscous sediment suspension system, from the overall consideration of the formation of particles after flocculation, according to the experimental observation. They found that if the volume concentration reaches a certain value, the floc size tends to be consistent because the streamline interferes with each other in the sedimentation process. The muddy water interface will appear, that is, the muddy liquid surface. On this basis, they put forward a formula for calculating the settling velocity of muddy liquid surface. In 1999, Karl et al. used the relationship between effective stress, permeability and porosity to describe the physical properties of slurry, and established a numerical model for slurry settlement. The settlement of kaolin soil suspension in distilled water was used as verification, and the correlation of model prediction was satisfactory. He also pointed out that the model is sensitive to the properties of the slurry. In 2000, Bürger et al. established a numerical model of particle settlement consolidation using Kynch’s solid flux density function and effective stress of solid. This model also requires that the solid concentration, permeability, and effective stress obtained from experiments be known a priori. From the perspective of oil sludge composition analysis, Vazquez et al. carried out a detailed analysis of crude oil sediment components, including suspended matter particles, molecular weight and four components content (saturated hydrocarbon, aromatic hydrocarbon, resin and asphaltene), which laid a foundation for the study of sedimentation mechanism and theoretical prediction. The formation of oil sludge is closely related to its asphaltene and wax components, especially microcrystalline wax, not only because the specific gravity of wax in the oil sludge be much larger than that in the crude oil, but also related to the characteristics of wax crystals, which are easy to form composite structures.

The theoretical basis for idealized particle deposition is the Stokes formula, which relates the settling velocity of particles and liquid density, liquid viscosity and particle diameter under the action of gravity. However, in the actual oil tank, the assumptions for the Stokes law are usually not valid, for instance the no-interaction between the settling particles assumptions or the spherical particles assumption.

When the temperature in the tank reaches the wax precipitation point, wax crystals precipitate and its settlement in the tank is different from that in the pipe flow. In the pipeline, the fluid is moving forward at a fast speed, the shear dispersion and molecular diffusion play dominant roles. In that case the wax forms a uniform ring on the pipe wall. However, for the settlement in the tank, the fluid in the tank is basically static under the storage conditions. Emmanuelle et al. proposed that the wax crystal settlement is mainly caused by Brownian motion and gravity. The wax crystals collide with each other, gather and adhere to the fast settled particles, forming large particles and settling under the action of gravity. Gradually, the concentration of wax or particles in the upper layer is lower than that in the lower layer, resulting in a possible back flux of the small particles. Therefore, after a certain degree of sedimentation, the settlement reaches an equilibrium state, and the sedimentary layer is no longer further thickened, which is called the settlement equilibrium state (see Figure 1).

Figure 1. Schematic diagram of particle settlement.

He also pointed out that the Peclet number (Pe) could be used as a characteristic number to describe the gravity sedimentation and Brownian motion intensity in the simulation. The precipitation process of wax crystal was monitored by a self-made laser turbidimeter.
and analyzed by Pe. Their results show that the gravity and diffusion force almost cancel each other in the absence of wax crystal aggregation. Therefore, Emmanuelle et al. believes that the aggregation of particles is the start of the sedimentation process.

The deposition process of asphaltene is mainly described by two thermodynamic models, the solution model, or the colloidal model. The solution model mainly considers that crude oil and asphaltene are a kind of homogeneous binary mixture, in which asphaltene is a solid solute and crude oil is a solvent. In this model, the amount of asphaltene dissolved in crude oil is determined by the solubility of asphaltene in crude oil, and whether asphaltene precipitates in crude oil is determined by whether the content of asphaltene dissolved in crude oil reaches the saturation state. In the 1980s, Yen. T. F. and Peramanu proposed a colloidal model. The model considers that asphaltene in crude oil is the core part, and the colloid adsorbed on asphaltene constitutes the dispersed phase, while other components constitute the continuous phase. In this model, it is a dynamically stable colloidal system under normal conditions. At this time, the colloid is non-polar, but the dynamic equilibrium of the colloidal system may be broken due to the factors such as temperature, pressure, crude oil composition, precipitant, etc., and the colloidal molecules outside the asphaltene are destroyed, which makes the colloidal particles with polarity. These particles attract each other and collide with each other, and then they settle under the action of gravity.

For the interaction between the two kinds of particles, there is no unified conclusion. Chang and other coupled Langevin type equations were used to determine the collision trajectories of particles. Considering the net gravity, van der Waals force, electric repulsion force and Brownian diffusion force between two particles, the effects of particle size and reduced density ratio on particles were studied, and the adsorption efficiency formula between particles was proposed. For the interaction between wax and asphaltene, Kriz believed that when the asphalt concentration was 0.01%, it would flocculate on the wax crystal structure, while when the asphalt concentration was greater than or equal to 0.05%, it would form a flocculent, which provided conditions for wax crystallization. Leontaritis et al. suggested that asphaltene would lead to the precipitation of amorphous spherical wax particles. Some scholars believe that the interaction between wax and asphaltene is relatively small, but asphaltene may be surrounded by wax crystals. Leontaritis also suggests that asphaltene is the main reason for the formation of the sedimentary layer, because when the density is lower than the crude oil, the wax will precipitate to the bottom since the resin and asphaltene settle together with the wax crystal. He divided the deposition into asphaltene deposition (ADE) and wax deposition (WDE), based on which he determined the deposition mechanism and estimated the deposition amount. After analyzing the composition of five crude oil deposits, Yang et al. suggest that asphaltene and wax would not interact in the precipitation process, but simply adsorb and settle each other. In addition, similar to Leontaritis, they classified the deposits. For the wax dominated sediments, the results showed that the paraffin content and average carbon content in the sediments were higher than those in the crude oil products, because the sediments contained oil residue, asphaltene and a small amount of inorganic salt particles. For the deposits dominated by asphaltenes, the solubility of asphaltenes in sediments was lower than that in crude oil, because they contained some aromatic hydrocarbons and polar substances. This also shows that wax and asphaltene settle together. However, how the two interact and what forces are produced between them need to be further studied at the molecular level. Sun et al. described the self-combination and mutual combination of wax and asphaltene through DLA theory (diffusion limited aggregation), and replaced the consideration of particle interaction with adhesion coefficient by assuming that the adhesion coefficient between asphaltenes was 0.8, the adhesion coefficient between wax and asphaltene was 0.4, and the adhesion coefficient between waxes was 1.0. The change curve of the fractal dimension lays a foundation for exploring the coprecipitation of wax and asphaltene from the molecular level.
Many scholars analyze the settlement process from the experimental point of view. Xu et al. \cite{Xu} used the repeated depth pipette method to trace the viscosity, density, and solid content of four sampling points with three different sources of crude oil as the oil source. They finally obtained four stages of sedimentation: chaotic period, temporary stability period, accumulation, and sedimentation period. Jia \cite{Jia} studied stratification and deposition during crude oil storage through field tests and simulation experiments. In order to obtain the area fraction of the wax crystal, Yang \cite{Yang} used polarized light microscopy (PLM) to observe the wax crystal distribution in crude oil. The results show that with the increase of storage time, the wax crystal concentration in the oil phase decreases gradually, and finally tends to be stable. Ba \cite{Ba} et al. injected the oil into the sedimentation tank for standing sedimentation, and obtained the curve of the deposition rate versus deposition time and sampling port height. The results show that the deposition rate increases with the storage time, and the increasing rate changes from fast to slow; the higher the height from the bottom of the tank, the smaller the deposition rate.

The most closely related problem to production practice is how to predict sludge deposition. Due to the different settling mechanisms of various substances in crude oil, the interaction between them and the influence on sedimentation are not clear. Therefore, it is difficult to predict the amount of sludge deposition according to the type of components. At present, there are three popular methods to predict oil sludge deposition: the thermodynamic model method, colloidal model method and mathematically model method, all of the three are mathematically complicated.

The current popular method is to use the solubility model to predict the deposition of wax and asphaltene. This model considers that wax or asphaltene are dissolved or partially dissolved in oil. They interact with other components in crude oil, and their settlement can be predicted by gas–liquid or solid–liquid equilibrium. The modeling of wax deposition in crude oil is based on the thermodynamic description of solid wax and oil–liquid equilibrium. Firstly, the heavy components in crude oil are characterized, the fugacity of solid and liquid phase is calculated by the equation of state, and activity is calculated by the canonical solution model and canonical solution model and universal quasi–chemical model (UNIQUAC) to describe the thermodynamic equilibrium of the system. Tabatabaiei \cite{Tabatabaiei} established a three-phase thermodynamic model considering gas, crude oil, wax crystal and solid and compared the accuracy of predicting wax appearance temperature (WAT) and wax deposition by adjusting several parameters in the solid model. He found that the fusion temperature was the most appropriate parameter to adjust. Ju \cite{Ju} used the same method to propose a thermodynamic model considering four phases in crude oil to calculate wax and asphaltene deposition. In this model, simplified perturbed chain statistical associating fluid theory (sPC-SAFT) was used to calculate fugacity of the gas phase and liquid phase, UNIQUAC theory was used to calculate activity coefficient, and binary interaction parameter (BIP) prediction was modified to meet the best results.

As for the thermodynamic model of asphaltene deposition, the solubility models are also widely used. Daryasafar \cite{Daryasafar} et al. summarized different thermodynamic models for predicting asphaltene precipitation. According to Flory Huggins model, asphaltene is a macromolecular polymer, which can be represented by virtual components. The liquid properties are obtained by vapor–liquid equilibrium, the oil-rich phase is regarded as a solvent, and asphaltene is regarded as a polymer solute to describe liquid–liquid equilibrium. Modified Flory Huggins (MFH) model divides oil and precipitation into asphaltene and non-asphaltene, the core of the methods is to calculate solubility parameters and molar volume of asphaltene. Panuganti \cite{Panuganti} et al. put forward a more detailed method for prediction by using the perturbed-chain statistical associating fluid theory (PC-SAFT). The model was established according to the definition of Helmholtz free energy reduction. The model accuracy is higher than the traditional cubic-plus-association (CPA) EOS model, however, the crude oil data used is more extensive. CPA EOS model is composed of a cubic equation of the state and SAFT model, which takes into account the attraction and repulsion force between non associated molecules, and also considers the influence of
associating parts, such as the hydrogen bond [1]. Arya et al. [2] used the CPA EOS model to determine the starting point of asphaltene deposition in various oil products. They used a simple crude oil component characterization method, which divided oil into asphaltene and heavy components. They considered association between asphaltene molecules and the association between heavy components and asphaltenes. The solid model combines the monodisperse asphaltene model with the Soave-Redlich-Kwong (SRK) EOS for fugacity calculation. Daryasafar compared the prediction results using the above models based on the experimental data of 12 kinds of asphaltene crude oil. It was found that the PC-SAFT EOS model and CPA EOS model have shown better results.

Another description of asphaltene deposition is the colloidal model. Nellensteyn [3] was the first to study the colloidal structure of asphaltene. Based on the colloidal theory, Victorov [4] et al. analyzed the causes of asphaltene sedimentation in crude oil. Leontaritis [5] analyzed the settlement mechanism of asphaltene under different conditions. He proposed a mathematical method to determine the particle size of deposited particles in the colloidal system. According to the sedimentation equilibrium theory, only the diffusion effect caused by gravity and the concentration gradient of particles was considered, and the calculation of the molecular weight of critical particles was deduced from the equilibrium condition that the sinking amount must be equal to the upward diffusion amount. The formula for calculating the gamma distribution of particles and the packing factor was also proposed. Jia [6] et al. used this method to predict the deposition of different types of crude oil.

As mentioned above, because there are many substances in crude oil, their sedimentation mechanisms are different, and the interaction between them is not clear, the use of the thermodynamic models or mathematical models are an effective method, but the physical property data of crude oil and settling particles are also complex and sometimes difficult to obtain. Therefore, in this article, we propose a method using a relatively simple formula for predicting the sludge deposits. Our formula is easy to be applied to engineering practice with relatively high accuracy and minimum data requirement.

2. Methods

The main equation for sludge prediction is listed as follows [7]:

\[ M_s = M \cdot c \cdot k_a / k_w \]  (1)

where \( M_s \) is predicted sludge mass, kg; \( M \) is the mass of crude oil stored, kg; \( c \) is the wax precipitation amount at storage temperature, %; \( k_a \) is the sedimentation ratio, % and \( k_w \) is the proportion of wax component in sediment, %.

Next, we are going to determine each item in this formula. A simple method was used to estimate the mass of crude oil that produced deposition. The amount of wax precipitation in crude oil at a certain temperature can be measured by experiment. From that, the mass of wax crystals in crude oil were obtained. If we link the calculation process with the actual settlement process, up to now, the initial state of sedimentation has been formed. As a matter of fact, not all of the wax crystals can be settled to the bottom of the tank, some of them continuously moved under the action of molecular gravity, electric repulsion and other forces to collide with other wax crystals or flocs. They continuously gathered into larger particles to settle down. The other parts of the wax crystals that failed to gather successfully or cannot meet the settlement conditions. They continued to suspend in the crude oil. Finally, the settlement balance was achieved in the tank. The aggregate sedimentation ratio of wax crystal is defined as the mass ratio of the two parts as mentioned above. With this important parameter, the mass of wax crystals in sludge is obtained. Through the components’ analysis experiment, the proportion of wax crystals in sludge was determined. Therefore, the important work of deposition prediction is to determine the wax sedimentation ratio at the storage temperature. First, a few assumptions are needed to make before going into details.
2.1. Assumptions

This study is based on the oil storage tank of Mo-he initial station in the second phase project of the China–Russia east oil pipeline. Mo-he station has six 50,000 m$^3$ crude oil tanks, four of them are running continuously. In the tank field, the sludge deposition happens continuously. In fact, for the storage tank on the trunk line, the storage is dynamic. When new crude oil is added or the old left, everything changed. Therefore, the deposition is a dynamic, long-term and constantly changing process. This is a very complex and comprehensive problem to be simplified.

First, for the wax deposition, one of the most important parameters is the temperature. The wax crystallization mainly depends on the changes of temperature. If the temperature is higher than the wax precipitation point, the wax will not precipitate, and there will be no wax deposition. When the temperature drops below the wax precipitation point, the wax begins to separate out. Under a certain temperature, the wax precipitation amount of crude oil is a constant value. The initial distribution of crystal in crude oil was determined. The temperature of the oil in the tank depends on the temperature of the gas above, the tank wall, and the radiation heat brought by the sun. The environmental temperature plays a leading role in the oil temperature. Since the environment temperature changes from morning to night, we assumed that the tank was at the average environment temperature. The temperature of Mo-he station can reach $-30$–$-50$ $^\circ$C in winter, the average temperature in summer is about 10 $^\circ$C, the annual average temperature is $-5.5$ $^\circ$C. Considering the effect of solar radiation heat, the average ambient temperature was considered of 0 $^\circ$C. In addition, Xu et al. proposed the deposition of oil can be basically finished in 48–136 h, due to the long storage time of oil in the tank, the influence of receiving and sending oil can be ignored. The properties of the oil entering the tank remain unchanged for enough time to complete the sedimentation basically.

2.2. Total Mass of Crude Oil Entering Storage Tank

It has been 9 years since the first 6 tanks of Mo-he station were put into use in 2011. To get the sludge deposition all these years, the mass of oil products passed through the oil tanks should be known. The annual turnover of tanks can be obtained from the following formula:

$$V_s = \frac{G K \rho \eta}{K \rho \eta}$$

The $V_s$ is the design capacity, m$^3$; $G$ is the annual transportation mass of the oil, kg; $\rho$ is the density of the oil, kg/m$^3$ and $K$ is the turnover coefficient of the oil. For the primary oil depot, $K$ is taken as 1–3 and $\eta$ is the utilization coefficient of the oil tank. The design capacity of the tank in Mo-he station is 50,000 m$^3$; the density of Russian oil entering the tank is 864.01 kg/m$^3$ at 0 $^\circ$C. The 50,000 m$^3$ oil depot belongs to the first-class oil depot, so $K$ is taken as 3, and $\eta$ is taken as 0.95. Through the above formula, the mass flowing through the tank in one year was 123,121,425 kg, and the mass in nine years was 1,108,092,825 kg.

2.3. Sedimentation Ratio ($k_a$)

As mentioned above, the core of the whole prediction method is the determination of the wax sedimentation ratio. The process of solving the ratio includes the interpretation of the interaction between particles. For the formation mechanism of flocs between wax molecules in the oil storage tank, we generally believe that the combined action of Brownian motion and gravity makes wax molecules collide under the influence of random motion and velocity difference. The collision wax molecules have a certain probability of adsorbing each other to form larger flocs to accelerate the sedimentation. The following describes two methods for calculating the sedimentation ratio.

2.3.1. Polarizing Microscope Observation

One of the methods of observing wax crystal is polarized light microscopy (PLM). It takes advantage of the crystal characteristics. The wax crystal has the anisotropic prop-
property, which can deflect the polarized light, thus it shows the different phenomenon from the surrounding medium in optics. The purpose of using this method is to obtain the particle size distribution and quantity of wax crystals. Then the method proposed by Leontaritis [7] can be used. Based on Kynch’s [7] settlement equilibrium theory, Leontaritis gives an equation for calculating the molecular weight of critical particles according to the equal sedimentation and upward diffusion. Considering the influence of liquid hydrocarbon in the formation of flocs, a formula for calculating the packing factor is proposed. Jia [7] et al. used PLM to observe the distribution of wax crystal, and used software to process the pictures in order to obtain the particle size and volume of wax crystal. She drew the distribution curves of wax molecule size and volume, verified that the particle distribution of wax crystal conforms to gamma distribution. By calculating the critical particle size, the total number of settled and unsettled wax particles can be determined. The sedimentation ratio was obtained. She predicted the indoor simulated deposition of several crude oil and the field deposition of Tarim crude oil. We used the PLM to obtain the area fraction and average particle size of wax at the sedimentation temperature.

As previously assumed, the average environment temperature is 0°C, the wax precipitation point of Russian oil is about 12°C and the condensation point is about −23°C. It is better to eliminate the thermal history of wax crystals before experiment. However, because of the large content of light components in Russian oil, it is easy to volatilize. So, we did not heat the oil and the experiment is carried out at room temperature 18°C, higher than wax precipitation point.

(1) Experimental process:

Slides were cleaned, and proper amount of oil samples were taken using a pipette. Then, oil drops were gently placed in the middle of the slide. To avoid the existence of bubbles, the oil drops should be covered gently by cover glass at one end. The slide was put on the plate, where the temperature can be adjusted. Then, the temperature of plate was reduced 3°C at a time. During the process, the objective lens was adjusted to find the wax crystal and the field of vision was continuously observed on the computer. We found that when the temperature was reduced to 9°C, the wax crystals were observed. With the decrease of temperature, more and more wax crystals were separated out. When the temperature is reduced to the 0°C, the wax crystals were observed for a period of time to let the wax precipitate completely. A suitable view was chosen to take the pictures, and the area contains impurities was avoided.

(2) Pictures processing:

Image-J software was used to analyze the micrographs of the wax crystals. It is a simple and convenient software widely used in medicine and biology. It is mainly used for statistical screening of cells and bacteria. The wax crystals are also small particles in crude oil, so Image-J is well used too. It was applied to binary and boundary segmentation of the wax crystals micrographs. The function particle analysis can output the parameters such as the size, quantity and area of the wax crystal in the image by Excel, which is convenient for subsequent statistics. We obtained the particles area fraction was 0.0102% and the average wax grain size was 1.82 µm.

2.3.2. Two-Dimensional Particle Deposition Simulation Program

Some scholars have done some research in this direction, such as Yang et al. [7] and Jiang et al. [7] have carried out three-dimensional simulation of the accumulation and deposition of sediment particles. Yang et al. [7] have carried out the simulation of wax crystal deposition of oil products in static storage by compiling the MATLAB program, they predicted and analyzed five kinds of crude oil by using the obtained sedimentation ratio combined with experimental data. The calculation of the initial distance.

$$D = \sqrt{\frac{\pi}{r}} \cdot \frac{d_0}{2}$$  (3)
Among them, D is wax crystal grain spacing during program initialization, m; \( \alpha \) is the increase of wax crystal area fraction under the condition of program simulation storage temperature, \% and \( d_0 \) is the initial particle diameter.

Stokes formula was used to describe the settling velocity of the particles. Under the set time step, the particles travel downward for a certain distance. The flocs that reach a certain diameter and density will continue to settle under the action of gravity until the settlement exceeds a certain boundary, which can be considered as part of the sludge eventually.

\[
v_e = \frac{1}{18\eta}(\rho - \rho_1)gd^2
\]

\( v_e \) is the equilibrium sedimentation speed of particles, m/s; \( \rho \) is the density of the dispersed phase, kg/m\(^3\); \( \rho_1 \) is the density of the dispersion medium, kg/m\(^3\); \( \eta \) is the dynamic viscosity of the dispersion medium, Pa s; \( d \) is particle diameter, m, and \( g \) is the acceleration of gravity, taken as 9.81 m/s\(^2\).

For the description of Brownian motion, Einstein’s Brownian motion equation is used to calculate the particle displacement under the influence of Brownian force:

\[
\bar{x} = \left( \frac{RT}{N_A \cdot 1.5\pi\eta d} \right)^{\frac{1}{2}}
\]

where \( \bar{x} \) is the average displacement of the particle along a certain direction in \( t \) time, m; \( N_A \) is Avogadro constant; \( \eta \) is the dynamic viscosity of liquid phase, Pa s; \( T \) is the absolute temperature of liquid phase, K; \( R \) is the molar gas constant and \( t \) is the corresponding displacement time, uniformly take \( t = 1 \) s.

Since the direction of Brownian force is random, the direction of motion is generated by a computer. The random displacement of particles will lead to collision between particles. The result of this collision is either to fuse wax crystals into a new floc or to spring apart. We used a widely used method to describe this interaction, that is, to define an adhesion coefficient to express whether they fuse or not, where the adhesion coefficient is 0.5 under the action of Brownian motion, wax crystals begin to collide and merge, and the diameter and density of the new floccules formed can be expressed by the following formula:

\[
d = N_f D_F \cdot d_0
\]

\[
\rho = (\rho_p - \rho_1) \left( \frac{d}{d_0} \right)^{D_p - 3} + \rho_1
\]

where \( D_F \) is fractal dimension and \( N_f \) is the number of monomer particles in the particle cluster.

After the two particles aggregated, the center coordinates of the particles must be recalculated. This procedure assumes that after the fusion of particles, the center is still on the line of the original center, and its coordinate change value is directly proportional to the diameter of the two particles. Therefore, after the fusion of two particles with different sizes, the new motion center is closer to the larger particles:

\[
\begin{align*}
x &= x_1 \cdot \frac{d_i}{d_i + d_j} + x_j \cdot \frac{d_j}{d_i + d_j} \\
y &= y_1 \cdot \frac{d_i}{d_i + d_j} + y_j \cdot \frac{d_j}{d_i + d_j}
\end{align*}
\]

where \( x, y \) are the horizontal and vertical coordinates of particles; \( i, j \) are the particle numbers and \( d \) is the particle size.

These particles in the program area continued to repeat the above process until they moved out of the simulation area. When the particles accumulated for a long enough time, the program stopped. At this time, the number of particles remaining in the simulation area was obtained, the sedimentation ratio was calculated. Before the calculation, the basic
crude oil physical properties data were needed and the parameters related to the simulation, which will be discussed in the following two parts.

2.4. Acquisition of Crude Oil Parameters

The physical properties of crude oil, including crude oil density, liquid viscosity, wax crystal area fraction, initial wax crystal diameter and fractal dimension, need to be determined by basic physical properties test and wax crystal microscopic test. The area fraction of wax crystals and the initial particle size have been obtained by the previous method, and the selection of fractal dimension is referred to reference [??]. The basic physical properties of this paper are determined by the oil samples taken from Mo-he station. The density and viscosity of the sample at different temperatures are shown in the table below. (Table ??).

**Table 1. Basic physical properties of crude oil.**

| T (°C) | Din (kg/m$^3$) | Vin (mPa s) |
|--------|----------------|-------------|
| 50     | 828.78         | 6.44        |
| 30     | 842.67         | 7.45        |
| 25     | 846.15         | 11.06       |
| 20     | 849.62         | 14.06       |
| 15     | 853.09         | 16.13       |
| 10     | 856.57         | 18.13       |
| 8      | 857.98         |             |
| 6.8    | 858.84         |             |
| 5      | 860.2          | 22.19       |
| 0      | 864.01         | 39.73       |

Where $D_{in}$ is the density of crude oil entering Mo-he station and $V_{in}$ is the viscosity of crude oil entering Mo-he station.

2.5. Selection of Simulation Space–Time Parameters

Selection of the Simulation Area

The selection of simulation parameters is related to whether the computer can truly reflect the actual settlement process. It includes the simulation area size, adhesion coefficient, time step length, time step number, etc. For the bond coefficient and time step, 0.5 and 1s were taken [??]. Since the size of the storage tank is very large, the computer cannot carry out the simulation calculation of this scale. The method of similarity theorem was used to select the simulation size. However, the selection of parameters such as simulation area and simulation temperature are not involved in the existing literature. In this study, the similarity principle is adopted and the similarity characteristic number is used to determine these parameters. The characteristic parameter is the Pe number, which represents the ratio of convection term and thermal diffusion term caused by gravity, which is in line with the hypothesis that wax crystal is affected by gravity and Brownian force.

$$Pe = \frac{4\pi r^3 \Delta \rho g H}{3kT}$$  \hspace{1cm} (9)

where $r$ is the particle radius, m; $\Delta \rho$ is the density difference between the dispersed phase and continuous phase, kg/m$^3$; $h$ is the height of the testing instrument, m, and $k$ is the Boltzmann constant, $k = 1.38 \times 10^{-23}$ J/K. This paper studied the tank of Mo-he station. The size of the tank was $5 \times 10^4$ m$^3$. The diameter of the tank was about 60 m and the height was about 20 m. The results show that the particle diameter was 1.82 µm, the crystal density of crude oil and wax were 864.01 kg/m$^3$ and 900 kg/m$^3$ respectively at 0 °C. K is the Boltzmann constant, equal to $k = 1.38 \times 10^{-23}$ J/K, and G was 9.8 m/s$^2$. The calculated Pe number was 8,202,351. The simulation calculation only needs to ensure that it is equal to the actual calculation. The adjustable parameters were $h$, $R$ and $t$. In this paper, the simulated size was 1000 µm in height and 3000 µm in diameter. The calculated temperature was
0.0137, which was not of practical significance, but was obtained theoretically in order to keep the same Pe number.

2.6. Measurements of the Sludge Deposition Height in Oil Tanks

The measurement process of the oil sludge thickness in Mo-he station is listed as follows: First, the oil surface level \( H_0 \) was measured with a radar level gauge, the data was obtained from the station control. Then a dipstick was used to measure the thickness of the oil layer with the sludge layer excluded: the dipstick was lowered from the top of the tank and stopped when the heavy hammer touches the sludge. At this time, the length of the scale on the dipstick that contacts the oil was recorded as \( H_1 \), and the sludge thickness was calculated from the subtraction of \( H_1 \) from the radar measured level \( H_0 \).

3. Results and Discussion

3.1. Results of the Simulated Sedimentation Ratio

Using MATLAB to run the program, a total of 11,844 particles were generated at the beginning of the settlement. The simulation time was 12 h. Finally, there were 3008 wax crystals settled to the bottom of the tank. It meant the wax sedimentation ratio was 25.40%, so far, the \( M, c, k_a \) and \( k_w \) were already obtained. According to the calculation, the premeasurement of oil sludge deposition at Mo-he station was 3,777,927.215 kg. Here are some important parameters. (Table ??).

| \( X/\mu m \) | \( Y/\mu m \) | \( a_r/\% \) | \( d_p/\mu m \) | Tem | \( k_a \) |
|-----|-----|-----|-----|-----|-----|
| 3000 | 1000 | 0.0102 | 1.82 | 0.0137 | 25.40% |

The \( X \) and \( Y \) are the area of the simulation, \( a_r \) is the area fraction of wax crystal at 0 \( ^\circ \)C, \( d_p \) is the initial average particle size of wax crystal at 0 \( ^\circ \)C and Tem is the simulated temperature.

3.2. Actual Sludge Quality

After getting the key parameter, we could predict the amount of sludge deposition. The actual sludge quality was obtained from the measured sludge volume data provided by Mo-he station. Since the sludge is porous, there must be liquid hydrocarbon filling the gap. In order to obtain the solid sludge deposition, we need to introduce the filling factor, which shows how much space is occupied [? ]:

\[
PF = 1 - \varepsilon
\]  

(10)

The \( \varepsilon \) is the porosity. For the sludge of wax, the \( PF \) is generally taken as 0.5.

The average density of oil sludge is calculated by component analysis of the tank bottom sample. The composition of the tank bottom sample was measured experimentally, details of the experimental methods can be found in reference [? ?]. The results are shown in the table below (Table ??).

| Asphaltene | Resin | Wax | MI | Water |
|-----|-----|-----|-----|-----|
| 0.76 | 6.27 | 7.93 | 1.58 | 0.09 |

A weighted average method is adopted to calculate the content percentage of different components in the oil sludge, and then multiply them by the respective pure compo-
ponent density respectively to obtain the weighted average density of the sludge mixture. The calculation formula is as follows:

\[ \rho_m = \sum_{i=0}^{n} \rho_i x_i \]  \hspace{1cm} (11)

where \( \rho_i \) is the density of each component, kg/m\(^3\), and \( x_i \) is the content of each component in the oil sludge, %. After calculation, the density of the crude oil was 1061 kg/m\(^3\).

The formula for calculating the actual sludge mass:

\[ M_a = V_a \cdot PF \cdot \rho_m \]  \hspace{1cm} (12)

where \( V_a \) is the actual volume of sludge, m\(^3\); it was obtained by a field measurement (Table ??).

Table 4. Actual sludge volume in Mo-he station, m\(^3\).

| Tank Number | 1#   | 2#   | 4#   | 6#   |
|-------------|------|------|------|------|
| Actual sludge volume/m\(^3\) | 7809.616 | 6249.576 | 8308.49 | 9005.059 |

Using the formula above, we calculated the actual sludge quality of four tanks (Table ??).

Table 5. Actual sludge quality in Mo-he station, kg.

| Tank Number | 1#   | 2#   | 4#   | 6#   |
|-------------|------|------|------|------|
| Actual sludge quality/kg | 4,308,721 | 3,448,016 | 4,583,960 | 4,968,271 |

3.3. Actual Calculation and Error Analysis

So far, our prediction method was improved. The prediction error is expressed by the relative error formula:

\[ \delta = \frac{M_p - M_a}{M_a} \times 100\% \]  \hspace{1cm} (13)

\( M_a \) is the actual sludge mass, kg, and \( M_p \) is the predicted sludge mass, kg. When the oil storage temperature was 0 °C, the sludge deposition of four tanks in Mo-he station was predicted. The predicted values and error estimates were as follows:

It can be seen from the Figure ?? that although many assumptions were made in this paper and only a simple method was adopted to estimate the sludge deposition, it was generally in line with the objective facts. The maximum prediction error of sludge deposition was 24%, which was satisfactory in terms of practical use.

Figure 2. Histogram of sludge prediction comparison.
4. Conclusions and Prospect

This paper summarized the previous research on the deposition of oil sludge in storage tanks from different angles. For the settlement mechanism, from the early classical settlement mathematical model, to the combination of the empirical model and mathematical model considering sedimentation thickening consolidation and then to the calculation formula of floc settlement proposed in cohesive sediment, including the theoretical formula derived from the Stokes formula and summarized experience. The research in this field is developing in the direction of considering the molecular level mechanism. It is generally believed that the wax crystal in the tank is affected by Brownian motion and gravity settlement, which can be expressed by Pe number. The settlement of asphaltene is mainly described by the thermodynamic model. The main two models are the solution model and colloidal model. As for the interaction between the two, so far there is no unified conclusion, generally staying in the phenomenon of the interaction between the two and sediment experimental analysis.

In the future, it is necessary to combine the fractal dimension and the force between particles to study the molecular level. Many scholars have analyzed the macro phenomenon of the crude oil deposition process through experiments, and found that the density and viscosity of crude oil in the deposition process exist from top to bottom concentration gradient, and analyzed the change of crude oil deposition with time, and divided the different stages of crude oil sedimentation. In the aspect of oil sludge prediction, thermodynamic model, colloidal model, mathematical model and artificial intelligence or their combination are generally used for prediction. However, the prediction methods are more complex and need various data, which is difficult to be applied to engineering practice.

In this paper, a new method of sediment prediction is proposed. Combined with the method of experiment and computer programming, a relatively simple prediction formula is adopted. The solution of each item only needs the basic crude oil parameters, which can get the prediction results more conveniently and quickly. According to the prediction results, although this method takes some assumptions, the prediction results for the oil sludge in Mo-he station are better, basically in line with the actual situation onsite.

For the future research, in terms of the deposition mechanism, it is necessary to further study the interaction and sedimentation mechanism between wax, asphaltene and other sediments from a microscopic perspective; in the prediction of sludge deposition, considering the influence of various factors such as temperature change and oil receiving and sending, the composition and properties of oil sludge should be analyzed in details in order to obtain better prediction results.

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