Oxidative Deterioration Effect of Cavitation Heat Generation on Hydraulic Oil

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ABSTRACT The thermal effects of cavitation on hydraulic oil is very important. From a micro perspective, the evolution of bubbles, will release amount of energy, especially its collapse in high-pressure area. The energy is converted into heat, which will be absorbed by hydraulic oil, which is indirectly converted into vibration and noise, and other forms. In order to study the effect of cavitation on hydraulic oil from an energy perspective, we investigated the oxidative deterioration of surrounding hydraulic oil during the compression of cavitation bubbles by using theoretical analysis and experimental comparison methods. Firstly, the cause of cavitation heat generation in hydraulic system was analyzed. Secondly, two kinds of hydraulic oils were tested for corrosion under the environment of cavitation heat generation, and the chemical properties changes of these hydraulic oils in the simulated cavitation heat production environment were analyzed. Finally, the thermogravimetric analysis and comparison of the two kinds of hydraulic oils in a simulated cavitation heat-generating environment were performed, and obtained the reason why hydraulic oil was oxidized to form solid carbon particles. The results showed that cavitation heat generation will cause oxidative deterioration of hydraulic oil, which enhanced the corrosion of hydraulic oil, and subsequently generated solid particles in hydraulic oil. The inner surface of hydraulic components will be scratched when solid carbon particles move with hydraulic oil flow in hydraulic system.

INDEX TERMS Cavitation heat generation, hydraulic oil, oxidative deterioration, corrosion, high temperature carbonization.

I. INTRODUCTION

As an energy transmission medium in hydraulic system, hydraulic oil is not only responsible for energy transmission, but also plays a pivotal role on cleaning, lubricating, heat dissipating, and cooling in hydraulic system. To a large extent, the hydraulic components work normally, and even the reliable and stable operation of the entire hydraulic system depends on the quality of hydraulic oil. According to incomplete statistics, 80% of the hydraulic system failures are caused by hydraulic oil pollution [1], [2]. As early as the mid-1960s, the NFPA (National Fluid Power Association) also concluded that “at least 75% of hydraulic system failures were caused by hydraulic oil pollution” [2], [3].

Therefore, to ensure the hydraulic oil is not deteriorated and not polluted is an important prerequisite for stabling operation of hydraulic system [4]–[7].

In hydraulic system, when hydraulic oil in internal flow field is cavitating, the air dissolved in hydraulic oil will separate out gradually in the low pressure area. Because the flow field pressure is lower than the air separation pressure, and free in form of bubbles in hydraulic oil. Because the flow field pressure is lower than that of saturated vapor pressure, part of hydraulic oil will also be vaporized into hydraulic oil vapor, and exists in the hydraulic oil together with free air in a gas phase state. In the high-pressure area, the separated air bubbles will be compressed and re-dissolved into the hydraulic oil. This
process is often accompanied by the release of a large amount of heat, that is, cavitation heat generation. In the process of cavitation heat generation, hydraulic oil will be affected by local high temperature, and directly contact the oxygen in separated air. Therefore, the chemical properties of hydraulic oil will be changed under the local high temperature and oxygen, which will be studied below.

II. CAVITATION HEAT GENERATION ANALYSIS OF INTERNAL FLOW FIELD IN HYDRAULIC SYSTEM

Some scholars have confirmed that when a single bubble is compressed or even collapsed in a high pressure area, a high pressure and temperature will be generated inside the bubble, in the theoretical and experimental research on the dynamics of single bubbles [12], [13]. The specific analysis on the separation process of bubbles in hydraulic oil and the heat generation process of bubbles under high pressure have been conducted as follows.

A. SEPARATION OF CAVITATION BUBBLES

Generally, the diameter of air dissolved in hydraulic oil is very small (0.05mm-0.5mm). When the bubble is filled with air, the static relationship is [14], [15].

\[(p_s + p_g)\pi R^2 = p \pi R^2 + 2\sigma \pi R^2\]  
(1)

where: \(p_s\) is the air separation pressure; \(p_g\) is the air pressure inside the bubble; \(p\) is the oil pressure outside the bubble; \(R\) is the radius of bubble; \(\sigma\) is the surface tension.

Among them, the pressure could be obtained according to the ideal state equation [16], [19].

\[p_s = \frac{3mkT}{4\pi R^3}\]  
(2)

where: \(m\) is the mass of a single bubble; \(k\) is the gas constant; \(T\) is the absolute temperature.

Putting Equation 2 into Equation 1, we could get the following equation.

\[p - p_s = -\frac{2\sigma}{R} + \frac{3mkT}{4\pi R^3}\]  
(3)

If we took the right part of Equation 3 as a function of \(P(R)\), and when \(T\) and \(k\) were constant, let \(dP/dR = 0\), we could find the minimum of Equation 3.

\[\frac{2\sigma}{R_c^2} = \frac{9mkT}{4\pi R_c^4}\]  
(4)

where: \(R_c\) is the critical radius.

\[R_c = \left(\frac{9mkT}{8\pi \sigma}\right)^{\frac{1}{2}}\]  
(5)

From the above analysis, it could be known that the critical radius of bubble is \(R_c\), which increased with the increase of the mass of a single bubble, which was hardly affected by the volume of the bubble. When \(m\) was constant, the pressure increase would cause the bubble radius to decrease. When the hydraulic oil pressure dropt, the bubble radius would increase until the bubble radius approached the critical radius. When the hydraulic oil pressure was lower than the critical pressure (air separation pressure), that is: \(P < P_c\), bubbles would be separated and cavitation would occur.

B. BUBBLES GENERATE HEAT DUE TO COMPRESSION

Free air bubbles flow with hydraulic oil flow, when it moves to high pressure area in hydraulic system, the volume of air bubbles is compressed until crushed, which making the air bubbles re-dissolved into hydraulic oil. At this time, the volume occupied by the original air bubbles becomes a vacuum, and the surrounding high-pressure oil will quickly fill this vacuum with a very high flow speed. Because this process takes a very short time, a severe physical impact will occur in that area. In this area, the pressure and temperature will rise rapidly [18], [19]. During the process of compressing the bubbles, the density of the bubbles increases as the volume of the bubbles decreases, due to the constant mass of the bubbles. The relationship between bubble density and internal pressure during the adiabatic process is as follows.

\[P_1 = \rho n \left(\frac{R_1}{R_0}\right)^{3n}\]  
(7)

where: \(\rho\) is the bubble density; \(n\) is the bubble radius at any time; \(R_0\) is the original radius of the bubble; \(P_1\) is the bubble pressure at any time; \(P_0\) is the original pressure of the bubble; \(n\) is the adiabatic coefficient.

It takes a very short time for the air bubble to be compressed because of the rapid change of the pressure in hydraulic system. Therefore, the process of air bubble compression can be considered as adiabatic compression process. According to the knowledge of thermodynamics, air features satisfies the following equation in adiabatic compression process [20].

\[\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}\]  
(8)

where: \(P_1\) and \(P_2\) are internal pressures of air bubble at two different times (unit MPa); \(T_1\) and \(T_2\) are internal temperature of air bubble at two different times (units K); \(k\) is adiabatic index of air.

In hydraulic system, assumed the original condition of bubble as \(T_1 = 27^\circ\) (300 K) and \(P_1 = 10\) MPa, when the hydraulic oil containing air bubbles was transported to the high pressure area \(P_2 = 35\) MPa), the temperature inside the air bubble would sharply rise to \(T_2 = 1377^\circ\) (1650 K). The process of temperature change inside air bubble was visually described in Figure 1.

In Figure 1, a→b: an air bubble in hydraulic oil was gradually transported from low pressure area \((P_1)\) to high pressure area \((P_2)\) with the oil flow. In this process, the temperature inside the air bubble sharply increased from \(T_1\) to \(T_2\) due to the compression of the bubble.
b→c: a large amount of heat in the air bubble transferred rapidly to surrounding oil, and finally reached a new thermal equilibrium state. The inside temperature of the air bubble and the temperature of hydraulic oil were gradually equal, and the temperature reached $T_3$.

The above two processes described a process in which air bubbles in hydraulic oil release a large amount of heat to surrounding oil during the compression process, that is cavitation heat production process.

III. EFFECT OF CAVITATION HEAT GENERATION ON CHEMICAL PROPERTIES OF HYDRAULIC OIL

It could be known from the above analysis that when air bubbles appear in the internal flow field of the hydraulic system, the bubbles will be migrated to the high pressure area with hydraulic oil flow. When the air bubble is compressed or even crushed in the high pressure area, a large amount of heat is released instantly. At this time, the hydraulic oil in the area where the bubble is located is affected by the dual effects of high temperature and oxygen contained in the air bubble. In the following, we would analyze the changes in the chemical properties of hydraulic oil during this process.

A. THE DESIGN OF CORROSION TEST

According to the previous studies, the chemical properties of hydraulic oil will change to some extent, mainly affected by acid value, after high temperature oxidation of hydraulic oil. The acidic substances in hydraulic oil mainly comprise of high-molecular organic acids, low-molecular organic acids, polybasic acid salts, ester compounds, phenol compounds, amine salts, metal salts, weakly alkaline salts and so on. Among these acidic substances in hydraulic oil, the organic acid compounds produced from the oxidative deterioration and especially the low-molecular-weight organic acids are highly corrosive to metals and cause great harm to hydraulic systems [21]–[24].

The depravation of hydraulic oil can mainly reflected by the change of its corrosion degree. Therefore, according to the national standard “GB/T5096-8 Petroleum Products Copper Strip Corrosion Test Method”, two types of hydraulic oil were tested for corrosion degree in simulated cavitation heat generation environment, and then analyzed the effect of cavitation heat generation on the chemical properties of hydraulic oil.

B. CORROSION TEST OF HYDRAULIC OIL

1) SELECTION OF TESTED HYDRAULIC OIL

In order to analyze the effect of cavitation heat generation on the chemical properties of hydraulic oil, we selected two types of hydraulic oil used in construction machinery hydraulic system for corrosion test. The two tested hydraulic oils were 46# and 68# anti-wear hydraulic oil.

2) THE PROCESS OF CORROSION TEST

In the first step, the two tested hydraulic oils were filled in the test tube and marked respectively.

In the second step, the standard test copper sheets that have been polished and decontaminated were placed in the test tube respectively, and made them to be immersed in the tested hydraulic oil.

In the third step, the test tubes were simultaneously heated in an oil bath and kept at 100° for 2 hours.

In the fourth step, the test copper sheets in the test tube were taken out with tweezers after 2 hours in the oil bath. They were compared with the corrosion standard color plate to determine the corrosion level after washing.

The tools used in the experiment were shown in Figure 2 - Figure 4.
3) THE RESULTS OF CORROSION TEST

We tested the two types of hydraulic oils in accordance with the above test procedures, and recorded the test results every 2 hours. The test time was 10 hours in total. Five test results were measured for each type of hydraulic oil. And the experimental results were shown in Figure 5 and 6.

FIGURE 5. Corrosion test results of 46 # hydraulic oil.

FIGURE 6. Corrosion test results of 68 # hydraulic oil.

The color of copper sheets changed from light orange to dark orange gradually as the test time increased (Figure 5). The result indicated that 46 # hydraulic oil was oxidized in the environment of high temperature oxygen and produced corrosive substances. With the increase of test time, more and more corrosive substances were generated, and the corrosion of standard copper sheets became more and more serious.

The results of corrosion test on 68 # hydraulic oil were similar with 46 # hydraulic oil. And the corrosion of 68# hydraulic oil was more serious than 46 # hydraulic oil.

In order to show the test results more clearly, the corrosion test results of two kinds of hydraulic oils were obtained, and the respective corrosion levels were shown in Table 1.

| Tested time | 46# hydraulic oil | 68# hydraulic oil |
|-------------|-------------------|-------------------|
| 2h          | 1a                | 1a                |
| 4h          | 1a                | 1a                |
| 6h          | 1a                | 1a                |
| 8h          | 1a                | 1b                |
| 10h         | 1b                | 1b                |

From Table 1, it could be seen that with the corrosion test time increased, the corrosion level of the copper sheets in two kinds of hydraulic oils were getting higher and higher. It indicated that with the increase of contact time between hydraulic oil and oxygen in a high temperature environment, the chemical properties of hydraulic oil gradually changed, more and more corrosive substances were generated. It suggested that hydraulic oil would undergo oxidative deterioration gradually and its corrosion would increase gradually in the process of cavitation heat generation.

C. INFRARED SPECTRUM COMPARATIVE ANALYSIS OF HYDRAULIC OIL BEFORE AND AFTER CORROSION TEST

In order to analyze the chemical properties of hydraulic oil more accurately during cavitation heat generation, infrared spectrum comparative analysis have been conducted on the two kinds of hydraulic oils before and after corrosion test. Through the infrared spectrum comparison analysis, we could know the changes of their main chemical bonds and functional groups, and then their chemical properties.

1) INFRARED SPECTRUM ANALYSIS OF 46 # HYDRAULIC OIL

By simulating the cavitation heat generation environment of the flow field inside hydraulic system, the 46 # hydraulic oil was subjected to a corrosion test. The infrared spectrum analysis was performed before and after corrosion test. The test results were shown in Figure 7 and 8.

FIGURE 7. Infrared spectrum of 46# hydraulic oil before corrosion test.
By comparing Figure 7 and 8, we found that the chemical composition of 46 # hydraulic oil had some changes before and after corrosion test.

The structure of saturated alkane in 46 # hydraulic oil: absorption peaks mainly included carbon-hydrogen stretching vibration and in-plane bending vibration absorption peaks, and strong multiple peaks appeared in the range of 3000 cm\(^{-1}\) to 2845 cm\(^{-1}\). After cavitation, the intensity of the absorption peak at 3000 cm\(^{-1}\) to 2845 cm\(^{-1}\) remained unchanged, which indicated that cavitation had no effect on the structure of saturated alkanes.

The 46 # hydraulic oil contains an aldehyde structure: C-H stretches and vibrates in the aldehyde structure. Two characteristic peaks with approximately equal intensities appeared at the characteristic absorption peaks of 2820 cm\(^{-1}\) to 2700 cm\(^{-1}\). The intensity of these two absorption peaks was significantly weakened after cavitation. The position of the peak was basically unchanged, which indicated that the aldehyde structure activity was reduced and the dipole moment was changed.

The 46 # hydraulic oil contains a benzene ring skeleton structure: two unsubstituted benzene ring skeletons vibrated at 1500 cm\(^{-1}\) and 1600 cm\(^{-1}\). After cavitation, the absorption peak at 1600 cm\(^{-1}\) was obviously weakened, which indicated that its molecular structure became more symmetrical.

The 46 # hydraulic oil contains a phosphate ester structure: a characteristic peak of P = O structure at 1250 cm\(^{-1}\), a characteristic absorption peak of PO\(_4\)^{3-} at 980 cm\(^{-1}\), and a characteristic absorption peak of C = O ester at 1740 cm\(^{-1}\). These peaks were significantly weakened. This showed that cavitation had a greater influence on the phosphate or phosphate structure, and the polarity and symmetry of its functional groups have changed obviously.

2) INFRARED SPECTRUM ANALYSIS OF 68 # HYDRAULIC OIL

The infrared spectrum analysis of 68 # hydraulic oil was performed before and after corrosion test. The test results were shown in Figure 9 and 10.

By comparing Figure 9 and 10, we found that the chemical composition of 46 # hydraulic oil had some changes before and after cavitation.

The saturated alkane structure in 68 # hydraulic oil: absorption peaks mainly included carbon-hydrogen stretching vibration and in-plane bending vibration absorption peaks, and strong multiple peaks appeared in the range of 3000 cm\(^{-1}\) to 2845 cm\(^{-1}\). After cavitation, the absorption peaks of 3000 cm\(^{-1}\) to 2845 cm\(^{-1}\) became broader and the intensity increased, which indicated that the high-temperature oxygen environment affected the symmetry and intermolecular dipole moment of saturated alkanes.

The 68 # hydraulic oil contains an aldehyde structure: C-H stretches and vibrates in the aldehyde structure, and two characteristic peaks with approximately equal intensities appear at 2820 cm\(^{-1}\) to 2700 cm\(^{-1}\), but the intensity of the peak was weak, and it was impossible to analyze whether belongs to other structures. After cavitation, the intensity of the two absorption peaks changed slightly, and the positions of the peaks were basically unchanged, which indicated that the molecular dipole moment of the aldehyde structure changed.
The 68 # hydraulic oil contains a benzene ring skeleton structure: the unsubstituted benzene ring skeleton vibrates at 1500 cm$^{-1}$ and 1600 cm$^{-1}$. After corrosion tests, the absorption peak at 1600 cm$^{-1}$ was significantly enhanced, which indicated that its molecular structure has appeared asymmetrically, the high temperature oxygen environment affected the strength of the hydrogen bonds on the benzene ring, changed its dipole moment, and increased the intensity of absorption peak.

The 68 # hydraulic oil contains a phosphate ester structure: a characteristic peak of $P = O$ structure at 1250 cm$^{-1}$, a characteristic absorption peak of $PO_4^{3−}$ at 980 cm$^{-1}$, a characteristic absorption peak of $C = O$ ester at 1740 cm$^{-1}$. The characteristic peak of $P = O$ structure at 1250 cm$^{-1}$ was obviously enhanced, and the polarity and symmetry of other functional groups did not change much. This showed that the high temperature oxygen environment test had a greater impact on the phosphate or phosphate structure.

3) THE ANALYZE OF INFRARED SPECTRUM FOR HYDRAULIC OILS

By simulating the cavitation heat generation environment of the flow field inside hydraulic system, the two types of hydraulic oil were tested for corrosion, and the infrared spectrum comparison analysis was performed before and after corrosion test. With the increase of time, two types of hydraulic oil corrosion were increasing gradually, which indicated that their chemical properties have changed to some extent. However, since the temperature of cavitation heat generation environment simulated by the corrosion test was relatively low, only 100°C, and the corrosion test time was also short, only 10 hours. Therefore, the corrosion of two hydraulic oils on copper sheet in the standard corrosion test was slight relatively, and the changes in the peak position or characteristic absorption peak of the four infrared spectra were not significant. However, it could be known from the above experiments that cavitation heat generation does affect the chemical properties of hydraulic oil, which would increase the corrosion of hydraulic oil, and further caused chemical corrosion to other components in hydraulic system.

IV. HIGH TEMPERATURE CARBONIZATION EFFECT OF CAVITATION HEAT GENERATION ON HYDRAULIC OIL

According to the II.B of this study, the oil temperature was $T_1 = 40^\circ$ (313 K) and the pressure in low pressure area was $P_1 = 0.1$ MPa during normal operation of hydraulic system. At that time, if hydraulic oil containing air bubbles was transported to the high pressure area $P_2 = 6.2$MPa, the temperature inside the air bubble in the hydraulic oil would rise to $T_2 = 766.29^\circ$ (1039.29 K) sharply. Because the pressure of flow field in hydraulic system changes very quickly(often less than 0.02s), when air bubble collapses, the surrounding hydraulic oil will not only be affected by local high temperature, but also contact the oxygen in air bubbles directly. Therefore, the hydraulic oil would be carbonized at the dual effects of local high temperature and oxygen, which would be studied below.

A. THE DESIGN OF THERMOGRAVIMETRIC TEST

In order to analyze the high temperature carbonization of hydraulic oil generated by cavitation heat generation in internal flow field of hydraulic system, we used thermogravimetric analysis technology to simulate cavitation heat generation environment in 46 # and 68 # anti-wear hydraulic oil. The mass fraction changes of the two hydraulic oils in a high temperature aerobic environment and a high-temperature anaerobic environment were compared and analyzed. In order to minimize the experimental error, ten thermogravimetric tests were performed for each hydraulic oil, and the thermogravimetric analysis data of the two kinds of hydraulic oils were obtained by averaging the ten sets of test data.

B. THE PROCESS OF THERMOGRAVIMETRIC TEST

Thermogravimetric analysis technology can reflect the relationship between the mass and temperature of the tested sample. The instrument can accurately set the speed of temperature rise through the built-in program. It can analyze the thermal stability and composition of the tested sample ingredient [25]–[27].

Thermogravimetric tests were performed on 46# and 68# hydraulic oils in air and nitrogen atmospheres, respectively. The air atmosphere simulated that the hydraulic oil has been in contact with and reacts with oxygen during the continuous temperature rise. During the whole process, air was always blown to the hydraulic oil sample. As the temperature of hydraulic oil increased gradually, some of the hydraulic oil would be oxidized into solids and remain in the crucible. The nitrogen atmosphere simulated that the hydraulic oil has been in an oxygen-free environment during the continuous rise in temperature. During the entire process, nitrogen has been blown to the hydraulic oil sample. As the temperature of hydraulic oil increased gradually, the hydraulic oil would be gradually vaporized and blown away by airflow, and its mass fraction would always decrease.

C. THE ANALYZE OF THERMOGRAVIMETRIC TEST RESULTS

The 46 # and 68 # anti-wear hydraulic oil samples were placed in an air atmosphere (simulated aerobic environment) and a nitrogen atmosphere (simulated anaerobic environment) for thermogravimetric test. The test curves of the two hydraulic oil samples were shown in Figure 11 and 12.

Figure 11 showed that the mass fraction of 46 # anti-wear hydraulic oil was basically maintained at 100 % under 200° in both air and nitrogen atmosphere. In nitrogen and air atmosphere, the mass fraction of 46 # tested oil sharply decreased between 200° and 350°C. In nitrogen atmosphere, when the temperature exceeded 350°, the decline rate of mass fraction of 46 # tested oil slowed down gradually, while the same change trend occurred in air atmosphere, when the temperature exceeds 380°. The mass fraction of 46 #
tested oil changed to zero at 500° in nitrogen atmosphere. That is to say, the oil completely vaporized in the process of rising temperature until the final mass was zero in nitrogen atmosphere. In air atmosphere, the mass fraction of 46 # tested oil gradually became a fixed value (4%) from 475°, and kept constant. This result showed that a part of 46 # tested oil was oxidized and formed solid oxide in the process of rising temperature.

Figure 12 showed that the mass fraction of 68 # anti-wear hydraulic oil was basically maintained at 100% under 200° in both air and nitrogen atmosphere. In nitrogen atmosphere, when the temperature exceeded 350°, the decline rate of mass fraction of 68 # tested oil slowed down gradually, while the same change trend occurred in air atmosphere, when the temperature exceeds 410°. The mass fraction of 68 # tested oil changed to zero at 450° in nitrogen atmosphere. That is to say, the oil completely vaporized in the process of rising temperature until the final mass was zero in nitrogen atmosphere. In air atmosphere, the mass fraction of 68 # tested oil gradually became a fixed value (5%) from 475°, and kept constant. It showed that a part of 68 # tested oil was oxidized and formed solid oxide in the process of rising temperature.

In practical hydraulic system, the effect of cavitation heat production on carbonization of hydraulic oil was confirmed by analyzing the sediment at the bottom of construction machinery oil tank. It was found that there are some solid carbon particles in the sediments at the bottom of oil tank besides iron chips (Figure 13).

Cavitation heat production provided a sufficient heat and oxygen concentration in the process of bubble being crushed. Solid oxide resulted from the high temperature carbonization. One of the important factors of hydraulic oil pollution is solid carbon particles, which formed by the high temperature carbonization of some hydraulic oil during cavitation heat production. When solid carbon particles move with hydraulic oil flow in hydraulic system, the inner surface of hydraulic components would be scratched. This is one of the important reasons why cavitation heat production causes damage to inner surface of hydraulic components.

V. CONCLUSION
(1) 46 # and 68 # hydraulic oil were oxidized in a high temperature oxygen environment, and produced corrosive substances gradually. When prolonged the reaction time, more corrosive substances were generated. These results suggested that the hydraulic oil will undergo oxidative deterioration and its corrosion would increase gradually during the process of cavitation heat generation in hydraulic system internal flow field.
(2) In a nitrogen atmosphere, two kinds of hydraulic oils were vaporized completely when temperature increased. In an air atmosphere, the mass fractions of the two kinds of hydraulic oils became a constant value eventually. This result showed that most of hydraulic oils were vaporized during the process of temperature rising, but a small fraction was oxidized and formed oxides.
(3) In the process of air bubble collapse, the cavitation heat generation provided enough heat and air bubbles provided oxygen, which carbonized a part of hydraulic oil to solid oxides at high temperature.

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