Analysis and Treatment of the Deterioration Products of Fire-Resistant Oil

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Abstract. The 300 MW unit of a power plant is resistant to fuel, and its color is reddish brown. The acid value and resistivity are in line with the standard requirements. However, a large amount of sludge appears in the same grade of oil, causing the filter to be blocked and unable to supply oil. After the oil is filtered by the online oil filtering device, the degraded anti-fuel oil and the new oil are mixed and there is still sludge. In order to solve this problem, the components in the anti-fuel oil were tested and the acid value, moisture, resistivity, particle size and sludge precipitation test were tested. The cause of the sludge in the mixed oil was found and the treatment method was found. The oil samples were adsorbed by diatomaceous earth, activated clay and strong polar silica-alumina, and the parameters were analyzed after treatment. It was found that both activated clay and polar silica-alumina adsorbent have better purification functions, but the polar silica-alumina adsorbent is better and effectively solves the problem of fuel resistance degradation.

1. Introduction
With the continuous development of power industry technology, large-capacity and high-parameter units are put into operation more and more. In order to improve the operation stability of the unit, reduce the risk of fire, and ensure the safe and economic operation of the unit, the turbine control system mostly uses phosphate anti-fuel [1-3] (hereinafter referred to as anti-fuel) as a control solution. Anti-fuel is the abbreviation of synthetic phosphate anti-combustion hydraulic fluid, which has excellent heat-resisting fire resistance and lubricating properties. Anti-fuel as the control system of the speed control system, the lubricating oil of the single-machine capacity million-kilowatt steam turbine, the side-discharge oil and the main pump motor lubricating oil system use anti-fuel as the lubricating medium. However, compared with mineral oil, anti-fuel is expensive, has poor stability, and is more susceptible to deterioration. Resistance to fuel oil can cause its antioxidant properties to decrease, acid value to rise, resistivity to decrease, and sludge to be produced. For the speed control system, the anti-fuel degradation will cause the control system components to corrode and jam, and the flexibility of the sleeve movement is reduced [4-6]; For the lubrication system, the anti-fuel degradation will destroy the lubricating function of the oil, affect the heat exchange of the oil cooler and the cooling of the bearing bush, so that the oil near the bearing bush is in a high temperature overheating state, thereby accelerating the deterioration of the oil [7-9]. At present, there are many kinds of regeneration treatment methods for degraded anti-fuel oil [10-13], some of which can achieve better regeneration effect, but the oil quality after regeneration treatment is unstable, and after a short period of operation, various indicators will deteriorate. Therefore, research on the stability against fuel degradation prevention measures is of great significance for extending its service life.
In this paper, the problem of degradation of phosphate ester anti-fuel in a 300 MW unit of a power plant is found. After the regeneration of the oil filter bypass, the acid value, moisture and electrical resistivity are all in compliance with the standard requirements, and the fuel system is replenished. A large amount of sludge, the filter is not timely and the fuel oil circuit is blocked, causing the turbine to stop. Aiming at the degraded anti-fuel oil, the effects of non-metallic materials, moisture, oil temperature and purification ability of bypass regeneration device on fuel quality in anti-fuel system were analyzed, and different adsorbent adsorption effects were studied through experiments.

2. Test

2.1. Instruments and reagents
Anti-fuel chlorine content analyzer (Shandong Zhonghui Instrument Co., Ltd.), anti-fuel resistivity tester (China Changzhou Detong Power Instrument Co., Ltd.), ZSXPrimusIX science fully automatic sequential scanning X-ray fluorescence spectrometer (Nippon Scientific Co., Ltd.), Constant temperature heating magnetic stirrer, electronic balance (METTLER TOLEDO Instrument Co., Ltd.), Optima 8000 inductively coupled plasma optical emission spectrometer (PE company in the US), absolute ethanol (analytical grade), petroleum ether (analytical grade), D60 (dearomatized solvent), diatomaceous earth, activated clay (industrial), strong polar silica-alumina adsorbent.

2.2. Test sample
Unit 1 of a power plant was put into operation in 2015, the color of the anti-fuel oil turned reddish brown, and the oil sample was taken for testing. The resistivity, acid value and moisture content met the operating oil standard. After filtering oil through the online oil filtering device, the color of the anti-fuel oil did not change significantly. The resistivity was $1.21 \times 10^{10} \ \Omega \cdot \text{cm}$, the acid value was 0.083 mgKOH/g, the moisture content was 389 mg/L, and the test items were all in accordance with DL/T 571-2014. The "Guidelines for Operation and Maintenance of Phosphate Anti-Fuels for Power Plants" standards require anti-fuel quality during operation.

2.3. Test plan and method
The degraded anti-fuel sludge was subjected to component analysis by X-ray fluorescence spectrometer, and its composition was further examined by scanning electron microscopy (X-ray spectroscopy). The resistivity was measured in accordance with the DL/T 421-2009 "Electrical Oil Volume Resistivity Measurement Method" standard. The chlorine content was determined in accordance with DL/T 1206-2013 "Determination of Phosphate Anti-Fuel Chlorine Content by High Temperature Combustion Microcoulometric Method". The acid value is determined in accordance with GB/T 28552-2012 "Transformer oil, turbine oil acid value determination method (BTB method)". The sludge was measured according to the standard of DL/T 429.7-2017 "Measurement method for oil sludge deposition". The content of metal elements in the oil is determined in accordance with GB/T 17476-1998 "Use of additive elements, wear metals and contaminants in used lubricating oils and determination of certain elements in base oils (inductively coupled plasma optical emission spectroscopy)"[14-18].

2.3.1. Comprehensive analysis of samples. The fuel resistance was tested for metal element content, acid value, moisture content, chlorine content and electrical resistivity to investigate whether the fuel resistance was deteriorated due to excessive chlorine content. The resistivity, moisture and acid value of the fuel-resistant sample before and after the regeneration of the filter oil were compared.

2.3.2. Oil mixing test. (1) In order to verify that the running oil itself is free of sludge, this test produces sludge when mixed with new oil in different proportions. Take 100ml of running oil and four beakers respectively, add 10ml, 20ml, 50ml and 100ml new oil, labeled as A, B, C, D four mixed oil samples.
(2) Perform the sludge deposition test on the running oil, take the plug cylinder and weigh 25g of running oil, add petroleum ether to make up to 100ml, and place it in the dark for 24 hours to see if there is sludge.

2.3.3. Anti-fuel treatment. Take 30g of diatomaceous earth, activated clay and strong polar silica-alumina adsorbent, put it into three beakers, add 1000g of anti-fuel oil, and carry out adsorption treatment. The adsorbed anti-fuel was again subjected to component analysis and acid value, moisture, chlorine content and resistivity test.

3. Results and discussion

3.1. Anti-fuel fuel indicators
Analyze whether the dissolvable sludge is caused by the anti-fuel degradation caused by the excessive chlorine content in the anti-fuel. Take No. 1 machine anti-fuel 2g after D60 dilution treatment, oxygen atomization, analysis of metal element content by inductively coupled plasma emission spectrometer and detection of chlorine content in oil by anti-fuel chlorine content analyzer, see data table 1.

| Metal element | Cl | Fe | Ni | Cu | V | Zn | Mn | Cr | Al | Mg | Ca | Na | K | Si |
|---------------|----|----|----|----|---|----|----|----|----|----|----|----|----|----|
| Content μg/g  | 93 | 0.46 | - | 0.23 | - | 7.86 | 0.022 | 6.6 | - | 0.343 | 0.203 | 0.68 | 0.42 | - |

Note: "-" in the table indicates that the element is not detected.

The online oil filtering device can reduce the particle size, moisture and acid value in the fuel resistance and increase the electrical resistivity. The oil sample is used to detect the moisture, acid value and electrical resistivity in the fuel resistance. Through the oil filter device, the acid value, moisture and resistivity index are better than the oil resistance index before and after the filter oil regeneration, see Table 2.

| Name | Before filter oil regeneration | After filter oil regeneration |
|------|-------------------------------|------------------------------|
| Moisture (mg/L) | Acid value (mgKOH/g) | Resistivity (Ω·cm) | Moisture (mg/L) | Acid value (mgKOH/g) | Resistivity (Ω·cm) |
| Content | 989 | 0.133 | 7.1×10^9 | 389 | 0.083 | 1.21×10^10 |

3.2. Analysis of mixed oil test results
After taking 100ml of oil filter, put the anti-fuel in A, B, C, D beakers, add 10ml, 20ml, 50ml and 100ml of the same brand of new oil, stir evenly and then let stand for a period of time and find that the bottom of the beaker has sludge.

After the oil filter was taken for oil sludge precipitation test for 24 hours, it was found that sludge was deposited at the bottom of the plug cylinder. It can be found that after filtering oil through the oil filter, some indicators of anti-fuel oil meet the requirements of DL/T 571-2014 “Guidelines for Operation and Maintenance of Phosphate Anti-Fuel for Power Plants”, but the sludge is not removed by the oil filter. Through the above tests, it was found that these sludges were dissolved in the anti-fuel, and existed in combination with the organic acid in the anti-fuel, which reduced the acid value of the fuel resistance and dissolved enough sludge. When a new oil is added, the dissolution balance is broken, the acid value is not greatly reduced, and the dissolved sludge is precipitated due to insufficient solubility.

Weigh 250g Unit 1 anti-fuel oil in a 1000mL volumetric flask, add petroleum ether and let it stand for 24h. Then, the produced sludge is filtered with a 3 μm filter membrane, and the filter is dried in an
oven at 80°C. The filter was analyzed by EZ scan using a fully automatic sequential scanning X-ray fluorescence spectrometer. The test data (using the normalization method) are shown in Table 3. The dried sludge precipitate on the membrane was scraped off for X-ray energy spectrum analysis, and the test data (using normalization method) are shown in Table 4.

**Table 3. Content of components of sludge precipitates**

| Name        | Content/\% | Name        | Content/\% |
|-------------|------------|-------------|------------|
| Na₂O        | 0.93       | MgO         | 3.04       |
| Mg          | 3.92       | Al₂O₃       | 0.22       |
| Al          | 0.17       | SiO₂        | 3.44       |
| Si          | 1.17       | P₂O₅        | 70.63      |
| P           | 57.9       | SO₃         | 3.92       |
| Si          | 1.17       | Cl          | 0.75       |
| Cl          | 1.67       | K₂O         | 0.25       |
| K           | 0.51       | CaO         | 0.95       |
| Ca          | 1.45       | TiO₂        | 1.05       |
| Ti          | 1.40       | V           | -          |
| V           | 0.07       | Cr₂O₃       | 0.25       |
| Cr          | 0.35       | MnO         | 0.07       |
| Mn          | 0.13       | Fe₂O₃       | 6.98       |
| Fe          | 11.77      | NiO         | 0.02       |
| Ni          | 0.03       | CuO         | 0.08       |
| Cu          | 0.18       | ZnO         | 7.41       |
| Zn          | 15.97      |             |            |

Note: "-" in the table indicates that the element is not detected.

**Table 4. Content of components of sludge precipitates**

| Weight/\% | C   | O   | Mg  | P   | S   | Ca  | Fe  | Zn  |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|
|           | 71.34 | 24.71 | 0.16 | 2.81 | 0.17 | 0.16 | 0.20 | 0.45 |

From Table 2-4, it can be seen that the main component of the sludge precipitate on the filter membrane is carbon oxide, followed by the metal elements zinc, iron, magnesium, and a small amount of chlorine, sulfur, calcium, copper, titanium, and aluminum. According to the composition analysis of the sludge precipitates, it can be roughly inferred that the fuel oil is mainly due to self-aging problems. Some parts of the operation have hot spots, and the moisture in the fuel is high, which accelerates the aging of the fuel.

### 3.3. Regeneration treatment and analysis of diatomite, activated clay and strong polar silica-alumina adsorbent

The unfiltered anti-fuel oil was regenerated with diatomaceous earth, activated clay and strong polar silica-alumina adsorbent, and the treatment effects of the three adsorbents were compared. Weigh 30g diatomaceous earth, activated clay and strong polar silica-alumina adsorbent in a 1500ml beaker, add 1000g of untreated anti-fuel, and put it in a 40 °C constant temperature magnetic stirrer for 3h, let stand precipitation and suction filtration. Observe the color change after processing. It can be found that all three adsorbents can make the reddish brown anti-fuel into the same pale yellow color as the new oil. The regenerated oil sample was taken for resistivity, metal element, chlorine content, acid value, and sludge deposition detection. The specific data are shown in Table 5.
Table 5. Test data of fire-resistant oil after treatment

| Test items                  | Diatomite  | Activated clay | Strong polar silica-alumina adsorbent |
|-----------------------------|------------|----------------|--------------------------------------|
| Exterior                    |            |                |                                      |
| Resistivity (Ω·cm)          |            |                |                                      |
| Acid value / (mgKOH/g)      |            |                |                                      |
| Moisture content (mg/L)     |            |                |                                      |
| Sludge precipitation        | qualified  | qualified      | qualified                            |
| Cl (μg/g)                   | 65         | 68             | 61                                   |
| Fe (μg/g)                   | 0.007      | 0.009          | 0.005                                |
| Ni (μg/g)                   | -          | 0.031          | -                                    |
| Cu (μg/g)                   | 0.008      | 0.006          | 0.004                                |
| V (μg/g)                    | -          | 0.006          | -                                    |
| Zn (μg/g)                   | 0.022      | 0.013          | 0.008                                |
| Mn (μg/g)                   | 0.018      | 0.025          | 0.02                                 |
| Cr (μg/g)                   | 5.19       | 6.03           | 1.08                                 |
| Al (μg/g)                   | 0.010      | -              | 0.009                                |
| Mg (μg/g)                   | 0.32       | 0.29           | 0.021                                |
| Ca (μg/g)                   | 0.21       | 0.46           | 0.032                                |
| Na (μg/g)                   | -          | -              | -                                    |
| K (μg/g)                    | 0.039      | 0.054          | 0.009                                |
| Si (μg/g)                   | 0.42       | 1.78           | 0.23                                 |

Note: "-" in the table indicates that the element is not detected.

It can be seen from Table 5 that the chlorine content in the oil sample degreasing after diatomite, activated clay and strong polar silica-alumina adsorbent is not obvious, the reason is that the oil is mainly composed of organic chlorine, and the other items are all reached. The anti-fuel quality standard in operation, the effect of polar silica-alumina adsorbent is better than that of diatomite and activated clay. After treatment with activated clay, the silicon and calcium ions in the oil increase, and the chromium ion has no obvious change. The metal ions are substantially reduced after treatment with the silica-alumina adsorbent.

4. Conclusions
(1) It is found through research that a large amount of organic acid is produced after the fuel-resistant aging of the No. 1 unit, and the acidic substance can dissolve the sludge generated by the deterioration and form a dissolution balance, so that the ordinary oil filtering device cannot remove the acidic substance and the sludge. When a new oil is mixed, the acid concentration is lowered, thereby destroying the dissolution balance and causing sludge to precipitate.
(2) At the same time, the unit should be put into the anti-fuel online regenerative dehydration device to remove the acidic substances, magazine particles and moisture in the fuel.
(3) It is recommended to use a strong polar silica-alumina adsorbent for the adsorbed substances in the in-line filter and the bypass regeneration device to prevent the introduction of new ions such as Ca and Mg by the adsorbent of the diatomaceous earth to accelerate the deterioration of the fuel resistance.

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