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Preservation of boilers and turbines with the surface active substance octadecylamine (ODA)

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1. Basic requirements

Based on the feed-in priority of electricity from renewable energy sources, conventional fossil fuel power plants are faced with new challenges. In times of sinking electricity prices on the one hand and rising fuel costs on the other, the economic running of highly efficient gas and steam turbine power plants is becoming increasingly more difficult. The results are frequent and often lengthy shutdowns. Coal-fired power plants must cope with flexible load requirements and longer run-times in low and part load operation. In contrast, higher reserve capacities, which are often needed quickly, must be made available.

For these reasons, preservation procedures play an increasingly important role. Because of different methods, the operator must decide to what extent and with which technology the system should be protected during downtime. Not only does the cost of the preservation play a role, the method should also provide good protection with simple handling and a flexible management system.

It must also be taken into account that beside the boiler, the steam and water-driven components, including the turbines, are subject to corrosion during shutdowns as well. Thus, these systems of the plant remain unprotected when the preservation method used entails keeping the boiler water warm with nitrogen flushing.

Apart from the classical preservation procedures, preservation with film-forming amines presents an interesting alternative. The preservation procedure using the active substance octadecylamine (ODA) is presented on the following pages. Although a wet-chemical method, the preservation effect remains intact and stable, even after draining or partial draining. This technology of preservation is explained using a practical example.

2. Preservation with octadecylamine

2.1. Development

The use of ODA for the preservation of power plant systems has a long tradition. As early as the 1970s, several publications and patents described the effect and method of preservation with ODA. [1], [2], [3] At that time, the active substance was used in its pure form. As ODA is a water-insoluble solid, the use of the pure substance makes high technical demands on the dosing stations. The active substance has to be melted on site at the facilities and kept in the liquid state for dosing. This poses serious problems. Only by using the stable and water-soluble emulsion developed by REICON, could these problems be overcome. Due to the unavailability of a permanently stable ODA emulsion in Russia, preservation with pure ODA is still carried out at nuclear facilities (e.g. Kola) and conventional power plants to this day. [4, 5]

2.2. Properties of the active substance octadecylamine

ODA is a long-chain, aliphatic amine with the chemical formula $C_{18}H_{37}NH_2$. Due to its volatility and a distribution coefficient similar to that of ammonia, a good distribution in the water and steam cycle is ensured. The active substance has the following characteristics:

Primary amine	> 99 %
Secondary amine	< 1 %
watercontent	0,1 %
Chain length > C15	98,5 %
molar weight	261 g/mol
Water solubility at 20°C	1,1 mg/l

Table 1: Composition of octadecylamine

Apart from the active substance, the emulsion developed by REICON (trade name ODACON®) contains no further additives such as emulsifiers or short-chain amines or polyamines. It is a pure and stable aqueous emulsion. ODACON® is non-hazardous in any normally available concentration. Due to its good biodegradability, the emulsion is classified in water hazard class 1.
Furthermore, it is guaranteed that the ingredients are within prescribed limits:

Chloride	< 2 mg/kg
Sulphate	< 2 mg/kg
Silicate	< 0,5 mg/kg
Acetate	< 1 mg/kg
Sodium	< 1 mg/kg

Table 2: Chemical purity of the emulsion

The methods and results described in the following refer to the use of the ODA emulsion ODACON®.

2.3. The effects of octadecylamine during preservation

Oxygen corrosion

To ensure safe protection during shutdown, it is crucial that direct contact of the material surface with humidity, oxygen or corrosive substances be prevented. To this effect, the formation of a diffusion-resistant, closed protective layer on all system parts is required. The protective layer formed during normal operation is not sufficient and is usually damaged during the starting and shutdown process. ODA, on the other hand, forms a stable, adhesive, non-wettable protective layer on a molecular level on all metallic and oxidic surfaces.

Depending on the temperature and concentration, an adsorption-desorption equilibrium forms in the water-steam cycle and the amino group chemically bonds to the metal (chemisorption) at a temperature over 100°C. At lower temperature, physisorption takes place through van der Waal forces. [6]

At sufficiently high concentration and sinking temperature (e.g. in the shutdown process), the adsorption density increases at the metal surface. The molecules align themselves with their non-polar group perpendicular to the surface. A closed, hydrophobic surface forms on components exposed to both water, as well as steam. Thus, any hazardous substances dissolved in water such as oxygen, carbon dioxide, etc., are unable to reach the component surface to initiate corrosion.

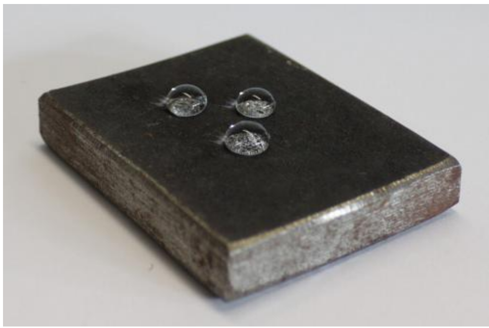

Figure 1: Hydrophobic surfaces after preservation

Local corrosion

It has been shown that, when an ODA molecule adsorbs onto the surface, deposited anions such as chlorides and sulphates are displaced and dissolved. Thus, these can no longer cause corrosion, neither during operation, nor during shutdown. This applies also to construction-based structural cracks and microcracks where the anion concentration is substantially higher. Tests have shown that preservation at a temperature of 150°C for 24h removes more than 60% of chlorides. In practice it means that there is significantly less danger of local cell formation and chloride-induced stress corrosion cracking.

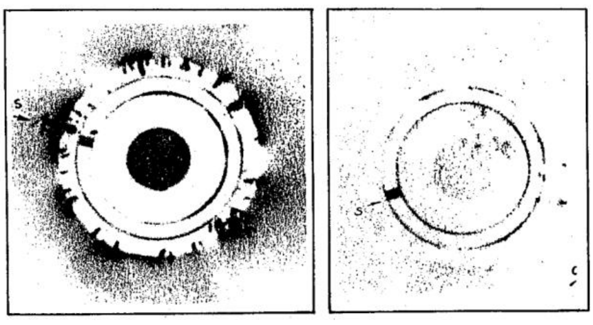

Figure 2: Autoradiography of a strained, austenitic ring-shaped sample: without ODA (left), with ODA (right) (degree of blackening = measure of the chloride accumulation on the surface)

Steam generator fouling

The formation of solid deposits in the steam generator is facilitated by the introduction of impurities, mainly iron particles, from the water-steam cycle. These originate from erosive corrosion and corrosion in the cycle. These processes are promoted by frequent starting and shutdown, as well as occasional short operating cycles during which time stable water chemical parameters are difficult to achieve.

Due to its distribution coefficient, ODA enfolds its protective effect throughout the water-steam cycle. This process is supported by the surface-activity of the substance. This leads to an even coverage of all surfaces and the alkalisation of water droplets. An alkaline boundary layer flow forms on the surface, which improves the formation of protective layers throughout the cycle.

In addition, the diameter of the vapour bubbles and droplets is much decreased due to the reduction of the surface tension of the water. The reduced droplets atomise more quickly upon impact, thus reducing the attack on the surface and material abrasion. This, and the near-surface alkalisation, reduce the erosive abrasion leading to a substantial decrease in the iron content throughout the cycle. Practical experience has shown a tenfold reduction of the iron content after preservation with ODA and re-starting the plant.

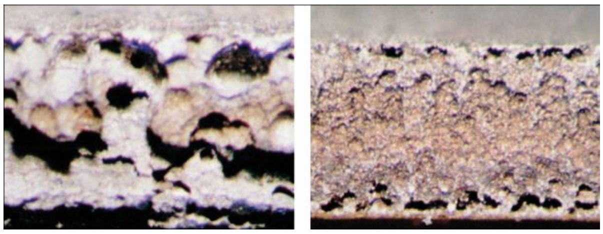

Figure 3: Stereomicroscopic view (magnification 1 : 12) of the leading edge of samples of ST 38, having been exposed to the water regimen with ODA (right) and without ODA (left).

The transition from a filmwise to a dropwise condensation is achieved in the turbine by the reduced water droplets. This reduces the thermodynamic losses as well as drag and braking losses. Depending on the ODA concentration, the efficiency can be increased by up to 2%.

3. Preservation method with octadecylamine

Several methods of preservation with ODA present themselves, depending on the facility characteristic and operating method. No further measures are required, irrespective of the chosen method. The systems can be kept filled or be drained and can be re-started at any time, even with the remaining preservation solution.

3.1. Preservation during downtime

This type of preservation is suited especially for systems which have already been shut down, or those with several boilers delivering steam to a main steam manifold.

The drained systems are filled with feed water at a temperature of ca. 100°C. During filling, the emulsion is dosed to the intake line of the feed water pump. If the boiler is completely full and the ODA concentration of the boiler water sufficient, the boiler water can be circulated externally or simply be left standing without agitation. When the system is cooling down, the adsorption processes described above come into play and the ODA protective layer is formed. Once the temperature reaches

40°C, the boiler can be emptied if required. The boiler water requires no special treatment.
This preservation type only protects those components that come into contact with water while the turbines and condensate system remain untreated.

3.2. Water-steam cycle preservation

If the boiler facilities are started or shut down frequently and out of schedule, or if the systems operate only for a short time, separate preservation can be realised only with difficulty. In this case, a small amount of ODA can be added continuously, while the facility is in operation. The active substance has no negative impact on the normal water chemical operation method. On the contrary, due to the reduced surface tension, the droplet spectrum formed in the saturated vapour is reduced, while the droplet surface is alkalised at the same time. This results in drastically reduced erosive corrosion. [7]
Due to the continuous presence of free ODA molecules in the water-steam cycle, an adsorption-desorption equilibrium is reached. The facility is thus immediately protected from corrosion when shut down. Furthermore, the facility can be re-started at any time without additional measures. In this method, dosing of ODA is best done through the feed water on the intake side of the feed water pump.

3.3. Preservation in the shutdown process

Preservation in the shutdown process presents the best method for preserving a complete power plant unit. The emulsion is added continuously, while the plant is still running. This is done ca. 3 – 10 days before the planned shutdown. The time period depends on the size of the facility, as well as the steam generating capacity and the dosing quantity. Initially, the dosing quantity is kept small and then the ODA concentration required for preservation is slowly increased. This ensures that any mobilisation effects of oxide deposits, as well as those of oils and fats, are controlled. Due to its volatility, the active substance is distributed throughout the water-steam cycle. This not only protects the boiler, but also the steam pipes, the turbine and the condensate system. Once the desired concentration necessary for preservation is reached, dosing is discontinued and the facility can be shut down.

4. Preservation of a 350 MW power plant unit

In the past, preservation with ODA was carried out on numerous nuclear and conventional power plants. In the following, the preservation process of a 350 MW coal-fired power plant unit is described.

4.1. Facility description

The preserved power plant unit is a facility of Huaneng Power Supply in Shangan (China). The main parameters are summarised in the table below:

electric power	350 MW
steam capacity	1060 t/h
operation pressure	170 bar
superheater temperature	540°C

Table 3: Facility parameters of Shangan power station

Under load, the system is conditioned with trisodium phosphate, ammonia and hydrazine.
The chemical parameters are given below:

pH value in feed water	9 – 9,5
conductivity in feed water	< 0,3 µS/cm
oxygen in feed water	< 7 µg/l
oxygen in condensate	< 30 µg/l

Table 4: Chemical parameters

4.2. Preservation method

Preservation work was done in the shutdown process. The relatively short duration of preservation of only 48h, including the shutdown procedure, posed a particular challenge. This required very high ODA concentrations of up to 10 mg/l in the feed water. ODA dosing was started during normal operation ca. 24 h before the actual shutdown process. Thus, dosing of hydrazine was discontinued and ODA was added from the dosing line. In order to minimise ODA-losses in the cycle, the condensate treatment system was shut down. ODA was dosed through the intake side of the water feed pump. Dosing was continued during shutdown and while the system was cooling down. The boiler main stop valve was closed after ca. 35 h, once the temperature reached 285°C. After further cooling, the boiler was drained once the temperature reached 90°C.

4.3. Results of the preservation

ODA concentration

The change observed in ODA concentration is typical for a preservation process. The increase in concentration in the feed water, up to when dosing is discontinued after ca. 35h, can be seen clearly. Due to the very short dwell time, no equilibrium between the concentration of ODA in the feed water and that in steam was reached. The higher concentration of ODA in steam compared to that in the boiler water is indicative of the characteristic distribution coefficient of ODA.

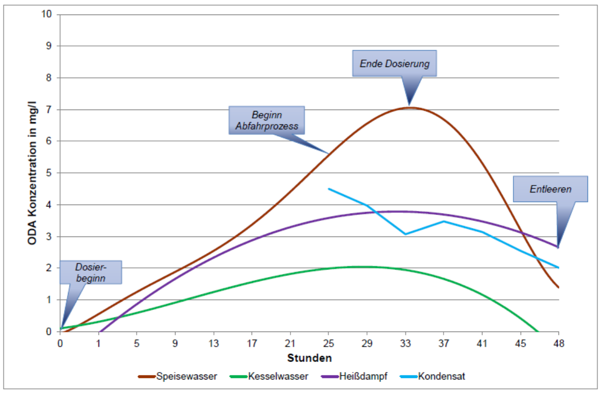

Figure 4: ODA concentration during preservation

Despite a dwell time of only 48h, the ODA concentration was sufficient to form a closed protective layer throughout the facility areas.

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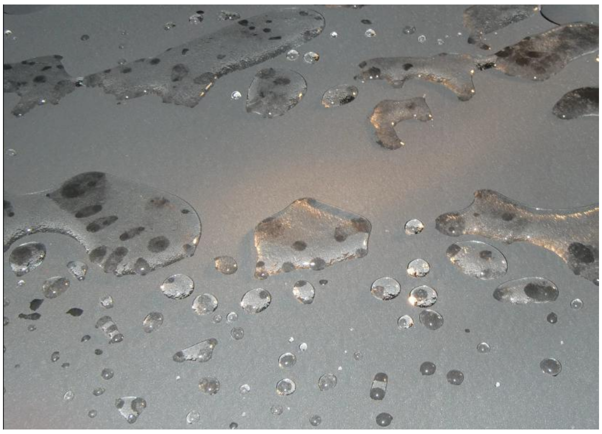

Figure 5: Hydrophobic surface in the condenser

pH Value and Conductivity

The pH was maintained between 9 – 10 during preservation. It was adjusted with trisodium phosphate in the boiler water and with ammonia in the feed water and steam.

The conductivity after cation exchange increased with increasing ODA concentration as expected. Due to the very short dwell time which required a higher ODA concentration, the cation exchanger became saturated quickly, as seen upon sampling. ODA slip induced by the cation exchanger was promoted because of this, resulting in an increase in conductivity.

Iron and silicate values

The iron values in the boiler water were observed to increase markedly from the time of dosing up to when the maximum ODA concentration was reached. The same was observed for the silicate values, but to a lesser degree. The same applies to the superheated steam and the condensate.

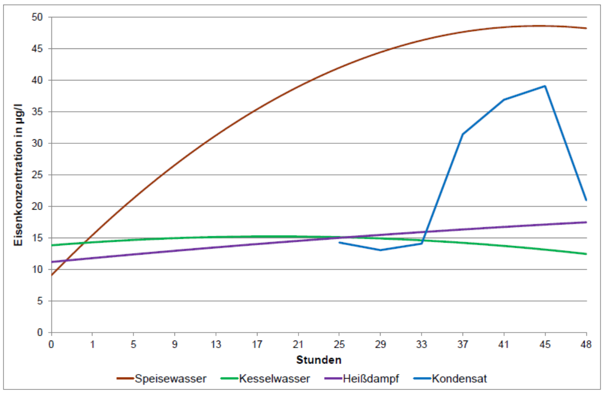

Figure 6: Development of the iron values in relation to preservation dwell time

The increase in the iron as well as the silicate values is proof of the expected mobilisation effect through the use of ODA. The mobilised substances are suspended by ODA and can be eliminated through the steam generator blowdown. Thus, in addition to preservation, a cleaning effect is also achieved.

5. Summary

In line with providing reserve capacity to stabilise the energy grid, it will become necessary to keep power plant facilities in a state of preservation over long periods of time. Preservation with ODA offers the facility operator an interesting alternative to classical preservation methods.

Due to the flexibility of the method, as well as the excellent corrosion protection during downtimes, preservation applications extend from short downtimes right up to long shutdowns. Using one example of many, after 8 years of downtime, a plant was brought back into operation within the shortest period of time. Not only can the systems be drained or left full after preservation, they can also be re-started quickly. Even maintenance or alterations can be carried out on them if required.

This method has broad applications which can be tailor-made to suite the respective situation.

6. References

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