

Early Condensate in a Fossil Power Plant using organic treatment.

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An Early Condensate Sampler supplied by Alstom Power Switzerland was used to investigate the early condensate. The tests were done on a drum boiler treated with a mixture of filming and neutralizing amines. Using the Alstom Sampler, we sampled condensate at different moisture contents. Samples were taken in various conditions. Acetate concentrations ranging from 1000 to 6000 $\mu\text{g.kg}^{-1}$ were measured.

1. Introduction

Corrosion in the Low Pressure Turbine is often in the proximity of first condensation. Some [1] state that disc cracking occurred at or downstream of the Wilson line (steam moisture is 3 – 4%) in the turbine. Other studies [2] suggest that the zone of first condensation (1% or less of steam moisture) is already very important.

Nowadays there is a trend to increase the interval between two boiler or turbine inspections. A period of 10 years or more, between turbine inspections, is no longer impossible. The results of our investigations must aware the maintenance managers not to prolong the interval between the turbine inspections. Indeed the alternative treatment is now being used for 4 years and only the boiler has been inspected. Furthermore, it must indicate the need for a very thorough inspection of the LP part of the turbine. A rupture of a LP turbine blade results in an unexpected stop of the power plant.

Turbine blade corrosion in the Low Pressure turbine is often caused by upsets in the water steam cycle chemistry. The pollution of the steam is strengthened in the early condensate. Previous tests have shown that anionic contaminants tend to concentrate in the Early Condensate (EC). This concentration effect is not seen with ammonia.

The Alstom Power Early Condensate Sampler (ECS) has been used in a number of studies in recent years. Tests have been done in units with low ionic contaminants [3] and in units where small amounts of various contaminants were introduced in the cycle[4]. One publication [5] reports on the test done with the ECS in a unit with organic treatment of the water – steam cycle. In this once through unit a mixture containing film forming and

neutralizing amines is used. The drum boiler selected for our test is also treated with a mixture containing film forming and neutralizing amines. There is no condensate polisher in this unit.

The precise organic species used in this commercial mixture are unknown to us but analysis of the superheated steam showed the presence of low molecular mass organics, mainly acetate, and of ammonia as decomposition products. The ionic decomposition products will only be removed during a blowdown of the drum. The conductivity after a cation exchanger (acid conductivity) can climb easily to 1.4 $\mu\text{S.cm}^{-1}$ in the feedwater and in the steam.

The main objective of the test was to quantify the amount of acetates (other organic acids were only present in minor concentrations) in the early condensate. The presence of organic acids, such as acetic acid, which may be formed in the EC if the acetate ions are not balanced by cations, would significantly reduce the pH of the EC.

2. Test Characteristics

2.1. Plant characteristics The tests were performed on a drum boiler unit with a closed circuit and no condensate polisher. The fuel or gas fired unit has at full load a steam flow of 780 t/h @ 12.8 MPa and 540 °C. It is a shifting unit with sliding pressure from 6 MPa to 12.8 MPa. Low loads are often accompanied with high oxygen levels in the pre-deaerator part. 2-to 3-load swings a day are not uncommon.

The water-steam cycle treatment changed from ammonia to a mixture of filming and neutralizing amines in 2000. As the dosing agent is a proprietary product, its exact composition is not known. The

tests, which started in early December 2003, had to be done in a race against time because a change in conditioning agent (for a period of 6 months) was foreseen for early January 2004. Table 1. gives an overview of the most important parameters of the cycle during the test period.

Table 1. Analytical data measured on-line during the test.

	Boiler Water	Steam
pH@25°C	8.8 – 9.1	9.1 – 9.3
Conductivity (μS/cm)	2.3 – 3.3	3.5 – 4.1
Acid Conductivity (μS/cm)		0.8 – 1.2

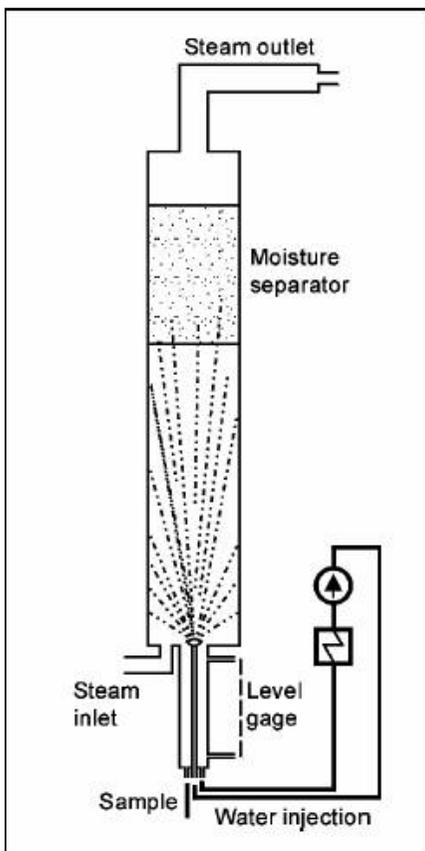


Fig. 1 A schematic diagram of the ECS.

2.2. Apparatus The Early Condensate Sampler (ECS) from Alstom Power Switzerland was used for collecting the samples. Fig. 1 is a schematic diagram of the ECS. A detailed description is given in a number of publications (e.g. in [4][6]) The condensation on pre-formed moisture droplets may differ from the nucleation of moisture in a steam turbine. This is a known disadvantage of the system.

Adjusting the temperature of the injected condensate can set the moisture content of the steam. The early condensate collected during the trials corresponded to moisture contents of 15% to 1%. The time to achieve the required equilibrium, before a sample could be taken, was estimated to be one to six hours in an inverse proportion to moisture content. A major change in the load during a trial has an important influence on the steam pressure at the inlet of the ECS. That is why only 3 representative test runs with at least 3 moisture contents were done (Dec. 9., Dec. 17 and Jan 9) Two other test runs had to be stopped after two samples. Nevertheless their results are comparable with the other.

Samples were taken in glass bottles (Duran ®). The anions were measured using a Dionex DX-120 Ion Chromatograph. As the composition of the dosing product is unknown and we used the Nessler method for the determination of ammonia we are aware of the influence of some amines on this method. Nevertheless we write down the result as being ammonia.

The steam at the inlet of the ECS was taken from the last extraction line from the Mid-Pressure turbine. We tried to keep the pressure at the inlet of the ECS (1.3 bar) as stable as possible (which was not always easy). The temperature at the inlet of the ECS was between 140 – 160 °C.

3. Results

3.1. Water – steam cycle measurements. Prior to the tests we determined the ammonia concentration using the “Nessler” method (ASTM D 1426 - 93). This concentration was used to calculate the pH and to compare it with the measured pH. The results are given in Table 2. This was done for 3 different pH levels with the according acetate concentration found.

The comparable pH's values could be an indication that the "Nessler" analyzing method was valid or that the amount of amines in the cycle was small leaving only ammonia as neutralizing agent.

3.2. Early Condensate Sampler. During the three representative test runs, samples were taken at different levels of moisture (water droplets). The EC samples taken correspond to steam moisture contents of 15% to 1%. The results for acetate are given in Fig. 2. The enrichment (concentration of a species in the EC over the concentration of the same species in the main steam sample) of acetate in the EC is increasing with decreasing moisture contents; from a ratio ± 10 for 8% to 15% moisture content to ± 20 for 4% moisture content. Fig. 3 is an overview.

Table 2. Comparison between measured and calculated pH of the main condensate

Ammonia (ppm)	Acetate (ppm)	Calculated pH@25°C	Measured pH@25°C
0.37	0.2	9.01	9.05
0.87	0.25	9.29	9.30
1.03	0.35	9.33	9.33

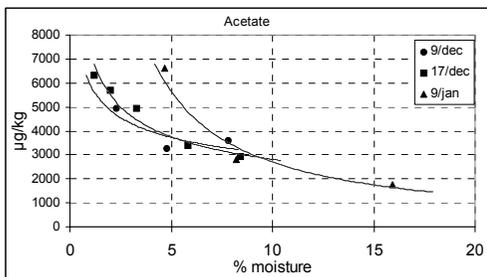


Fig. 2: Acetate in the Early Condensate.

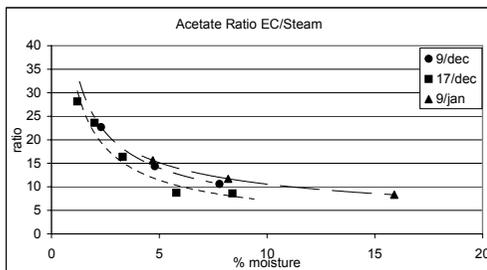


Fig. 3 Acetate ratio EC/Steam.

Chlorides were not always measured in the main steam but the $3 \mu\text{g.kg}^{-1}$ limit is seldom exceeded. The concentration in the EC is not very stable. A clear enrichment could not be detected.

The ammonia concentrations in the EC, measured using the "Nessler" method gave values between $200 \mu\text{g.kg}^{-1}$ and $300 \mu\text{g.kg}^{-1}$. These values were measured while having $\pm 500 \mu\text{g.kg}^{-1}$ of ammonia in the steam. The ratio of ± 0.5 is higher than the ratio found in [4].

Cyclohexylamine determination with GC/MS was below the detection limit of 0.6 mg.kg^{-1} .

As the sodium was not determined (the steam line to the sampler was new, contamination was feared), it is assumed for the calculation of the pH, that the concentration in the EC was $10 \mu\text{g.kg}^{-1}$. This corresponds with values found in earlier investigations, knowing that the level in the main steam is below $2 \mu\text{g.kg}^{-1}$.

Because of the small sample flow ($\pm 3.5 \text{ ml/min}$), pH was not directly measured. The MULTEQ computer code was used to calculate the pH. The calculated pH values are in the range of 4.7 to 5.1 @25°C (see table 3). This low pH is due to the increasing concentration of anions and a fairly stable ammonia concentration in the EC. Assuming the additional presence of 1 mg.kg^{-1} cyclohexylamine raised the pH only 0.1 to 0.3 units.

Table 3 calculated pH (units $\mu\text{g.kg}^{-1}$).

Acetate	NH ₃	
	Na = 0	Na = 10
2500	5.04	5.04
3200	4.9	4.9
5000	4.7	4.69

As mentioned earlier, the treatment product is a proprietary product, which exact composition is not known. The supplier provided the Power Plant with an analyzing method (colorimetric) in order to verify the dosing. The color reaction is developed using an unknown reagent. The result is expressed as mg.kg^{-1} commercial product. A range of 0.7 mg.kg^{-1} to 1.2 mg.kg^{-1} commercial product is an acceptable concentration according to the supplier. This concentration should develop and maintain a reliable film on the surface and a sufficient alkalizing property to the water and steam [7].

The correlation between the analyzing result and the actual concentration of a specific specie is not known. The accuracy of the method could therefore not be examined. The acceptable range is found not only in the boiler water but also in the steam. The same analysis was done on some EC samples. During the December 17th test run the pH in the water – steam cycle was higher than the pH during the other runs; ± 9.3 in the feedwater and steam, ± 9.1 in the boiler water. It was in the EC samples of this test run that the lab measured 0.7 – 1 mg.kg^{-1} commercial product.

5. Conclusions.

The Alstom Power Early Condensate Sampler was used to collect samples of Early Condensate, which were in equilibrium with supersaturated steam containing between 15% and 1% moisture.

As seen in earlier tests, anions concentrate in the early condensate in inverse proportion to the steam moisture content and the ammonia does not concentrate. A deficit of cations makes the EC less alkaline than the bulk condensate.

The mixture of filming and neutralizing amines decomposes in the water - steam cycle. The main organic acid found in the EC was acetic. The concentrations went up to 6 mg.kg^{-1} for 2% to 1% moisture. This resulting in pH as low as 4.7 in the EC.

A high dosing of the treatment product gives higher acetate concentrations in the main steam and thus also in the EC. The non-quantitative analyzing method, provided by the supplier, indicates, in these circumstances, however the presence of active agents in the EC.

The maintenance managers will be given the advice not to prolong the interval between the last and upcoming turbine inspection. A priority one attention must be given to the inspection and analyses of the low – pressure part of the turbine.

Not only is it important to look for possible corrosion but also to verify if there is a presence of a protective organic layer on the turbine internal material. If the film forming properties of the dosing agent are still active, can they protect the turbine material against the presence of fairly high organic acids?

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References and Notes

- [1] Lyle, F., Meminn, A., Leverant, G.R., Low Pressure Steam Turbine Disc Cracking – an update, **1985**. Proc Instn Mech Engrs, Vol. 199, n° A1.
- [2] Dooley, B., Fossil Plant Cycle Chemistry and Steam, **1999**, PowerPlant Chemistry GmbH, Neulussheim, Germany.
- [3] Stodola, J., Svoboda, R., Chemistry of Early Condensate, **1999**, International VGB-EPRI Conference on Steam Chemistry, Freiburg Germany.
- [4] Svododa, R., Phlug, H-D., Warnecke, T., Investigation into the Composition of the Early Condensate in Steam Turbines, **2003**. PowerPlant Chemistry GmbH, Neulussheim,
- [5] Bursik, L., Once-through Boiler as an autoclave for testing an Organic Cycle Treatment Chemical, 2002, PowerPlant Chemistry GmbH, Neulussheim, Germany
- [6] Svoboda, R., Sandmann, H., Romanelli, S., Bodmer, M., Interaction of Iron-Based Materials with Water and Steam (Ed.: Dooley, B. and Bursik, A.), 1993. Electric Power Research Institute, Palo Alto, CA. EPRI TR-102101, 32-1 – 32-16.
- [7] Verheyden, K., Ertryckx, R., De Wispelaere, M., Poelemans, N., Belgian experiences with film forming amines, 2003, 7th International Conference on Cycle Chemistry in Fossil Plants, Houston USA.