Experience from Chemical Cleaning of a 23 Years Old Intermediate Pressure Superheater in Unit 5 at Asnaes Power Station (ASV5)

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The aim of this paper is to pass on experience gained in connection with the chemical cleaning of a 50 bar intermediate pressure superheater (IP-SH) in unit 5 at Asnæs Power Station (ASV5). The life of the boiler is to be extended to not less than 15 years of additional operation, and this paper primarily concentrates on remaining useful life, oxide deposits and flakes of magnetite in the IP-SH. In particular the hot part of the IP-SH (designated IP Final SH (intermediate pressure final superheater)) had so much oxide deposited that the calculated life was much shorter than 15 years. A choice had to be made between replacing all tubes in the IP Final SH or removing oxide deposits by chemical cleaning. There are 4 different steel materials in the intermediate pressure superheater: 15Mo3 and 13CrMo44 in the intermediate pressure primary superheater (IP Prim SH) and 10CrMo910 (10Cr) and X20CrMoV121 in the IP Final SH. The oxide films in the IP Final SH consisted of chromium oxide, magnetite and (Fe, Cr)$_3$O$_4$ with varying Cr and Fe composition. Oxide films of up to 0.760 mm have been measured in 10CrMo910 in the IP Final SH. A tube sample from the IP Prim SH showed an oxide film of 0.06 mm and no pitting. During the chemical cleaning we were surprised that there were a number of leaks in the IP Prim SH due to severe local pitting. The whole IP Prim SH has been replaced by 13CrMo44 in the summer of 2004.

1. Introduction

Energi E2 owns and operates 7 large power stations/CHP plants and 10 small decentralised CHP plants (Combined Heat and Power plants) in Eastern Denmark. Moreover, E2 owns wind farms in Denmark, Sweden, Greece and Spain and bio fuel plants in Spain, and it is a co-owner of hydropower plants in Norway and Sweden.

Asnæs Power Station is Energi E2's largest power station with 3 active units and a total production capacity of 1,057 MW and 741 MJ/s district heat. Unit 1 at Asnæs Power Station (1959) and unit 3 (1967) were withdrawn from operation in 1998 and 2002, and unit 4 (1968) will probably be withdrawn from operation in 2005. Future operation has been planned for 2 units, ASV2 (1961) and ASV5 (1981). Accordingly, a comprehensive overall plan has been prepared for the power station, which includes an extension of the lives of these 2 units. ASV2 was renovated and rebuilt in 2002.

In the period from 2 April 2004 to 1 October 2004, ASV5 is withdrawn from operation in order to be extensively renovated, rebuilt etc., but some of the preparatory work already started in 2003, among other things the chemical cleaning of the intermediate pressure superheater (IP-SH).

ASV5 is Denmark's largest power station unit, with a nominal capacity of 640 MW electricity, 150 MJ/s district heat and 158 MJ/s process heat for external customers (Statoil and Novo). ASV2 and ASV5 are both capable of using coal and oil as a main fuel. As the first unit in Europe, ASV5 has used Orimulsion from Venezuela as a primary source of energy in the period from 1995 to 2003, at which time supply problems necessitated a reversal to coal firing in the unit.

The life of ASV5 is to be extended by 15 years, corresponding to half the life expectancy of a new unit, but achievable at a price which is approx. 15% of the price of a new unit.

The extension of the life of ASV5 primarily includes:

- Establishment of a deNOx plant
- New automatic control equipment
- Common control room for ASV2 and ASV5
- Boiler: Renovation of superheaters, new injection nozzles, renovation of safety valves etc.

- Renovation of main condenser and main cooling water pumps, turbine examination and renovation etc.

2. Unit 5 at Asnaes Power Station (ASV5)

Figure 1 is a graphical overview of the water-steam circuit of ASV5. The unit consists of 1 high-pressure turbine, 1 intermediate-pressure turbine and 3 low-pressure turbines. At 100% coal firing, the feed pump provides 553.5 kg/s (1,993 t/h) at 238.9 bar. The temperature of the high-pressure steam for the HP turbine is 540 °C at 182 bars. The HP Final SH and steam lines for the high-pressure turbine are made of X20CrMoV121.

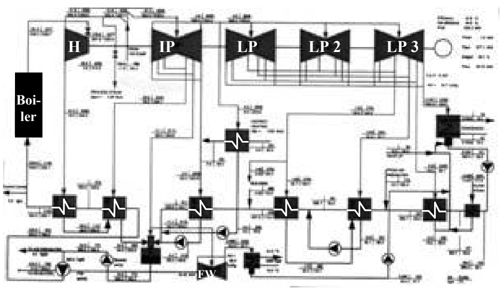


Fig. 1. The water-steam circuit of ASV5.

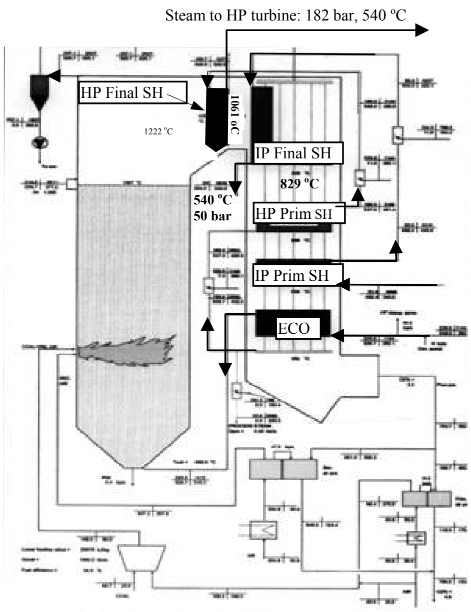


Fig. 2. ASV5. Overview of boiler, first and second pass.

2.1. Description of the IP-SH. From the outlet of the HP turbine to the inlet headers of the IP Prim SH, the steam is carried in 2 steam lines made of 15Mo3 (360 °C at 65 bar) (Fig. 3, Pos. 5). The IP Prim SH "bends" twice inside the boiler at a level of approx. 41-46 m. The IP Prim SH was originally made of 15Mo3, but in 1990/91 and 1998 parts of the IP Prim SH were replaced by 13CrMo44 as a result of corrosive attacks on 15Mo3.

From the outlet headers at level 46 (Pos. 4), the steam is passed on to the top of the boiler (level 68, Pos. 6) and into the IP Final SH. The first two thirds of the IP Final SH are made of 10CrMo910, and at "Pos. 2" (Fig. 3) the material changes over to X20CrMoV121 in the last third, which ends in outlet headers made of 10CrMo910 (Pos. 3). The dimensions are 44.5 x 3.6 mm in the IP Prim SH as well as in the IP Final SH

Steam outlet data: 540 °C at 50 bars. 4 hot reheat piping from headers pass the steam on to the IP turbine.

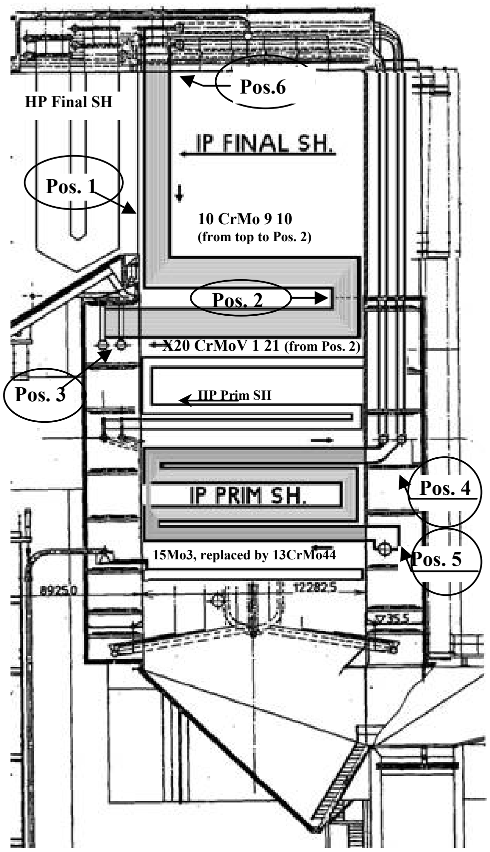


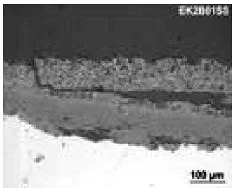
Fig. 3. ASV5. Enlarged sectional view of the second pass.

2.2. Preliminary investigation of the IP-SH tubes In connection with the preliminary investigations regarding the life extension, tube samples have been taken, i.a. from the IP-SH in 1998, 2001 and 2002. In 1998, 3 tube samples were taken from the IP Final SH around the welds between 10CrMo910 and X20CrMoV121 (Fig. 3, Pos. 2). In 10CrMo910, 0.41 mm oxide was found, and in X20CrMoV121 0.16 mm. In 2002, up to 0.450 mm was measured in 10CrMo910 in tube sections with the same position, and 0.143 mm in X20CrMoV121.

In 2001, at 1.5 m above the bottom of horizontal pass (Fig. 3, Pos. 1), oxide films of up to 0.760 mm were measured in 10CrMo910. This position in the boiler is probably the most critical with regard to remaining useful life and flaking (highest temperature flux).

In 2002, a tube sample of 15Mo3 was taken from the IP Prim SH for examination. There was no pitting, and the oxide film measured was 0.066 mm. The results did not give cause for further investigations of the IP Prim SH as the oxide film was not considered critical to life.

The thick oxide films in the IP Final SH cause significant problems, namely 1) flaking where flakes of oxide may damage the IP turbine (→ capacity reduction or erosion/breakdown) or flakes can block up pipes in IPSH → bursting of pipes (due to high metal temperature); and 2) the insulating oxide films result in an increased metal temperature, resulting in a reduced life. In the illustration (Fig. 4), microslip is seen, with clear flaking. Moreover, an investigation of the composition of materials through the oxide films in the 2 steel types in the IP Final SH has been made. In the X20CrMoV121 steel, it is very clear that there is an oxide deposit containing chromium against the steel; the outermost deposit is typically magnetite.



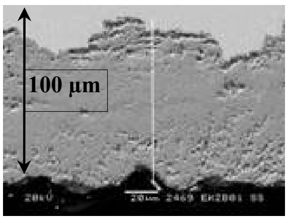


Fig. 4. Fig. 5.

Same tube sample: EK2B01, X20CrMoV121 (in this paper shortened to "X20").

Fig. 4 Flakes of oxide. Fig. 5 shows the section for the elementary analysis in Fig. 6. The samples are numbered from the steel surface (Left at the curves).

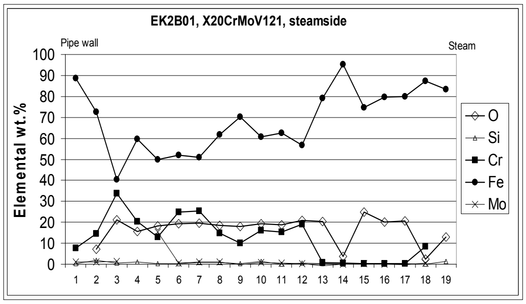


Fig. 6. Elementary analysis of EK2B01, X20.

The corresponding measurements have been made on a tube from the IP Final SH made of 10CrMo910 (in this paper shortened to "10Cr").

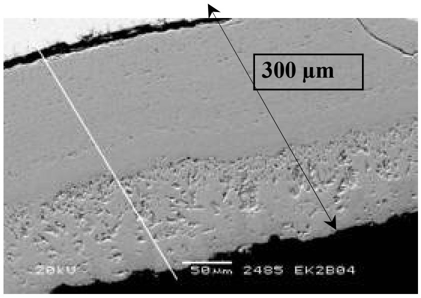


Fig. 7. EK2B04, 10CrMo910 from the IP Final SH. The white line indicates the section for the elementary analysis in Fig. 8.

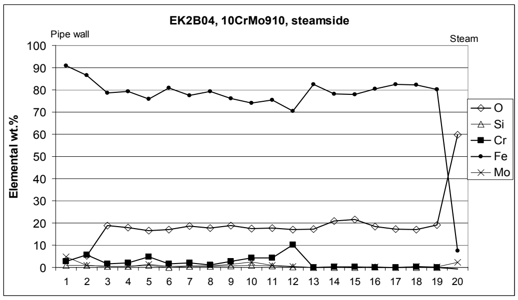


Fig. 8. Elementary analysis of EK2B04, 10Cr.

It can be seen from the elementary analysis that there is also an innermost film containing chromium in 10CrMo910, but this film obviously does not contain that much chromium.

2.3. Calculations of life A number of calculations of life have also been made, which indicate that some of the tubes in the IP Final SH would have used up their lives in a few years. This is due to the thick, insulating oxide deposit, which causes the metal temperature to rise. A rising steel temperature increases the growth rate of the oxide film, whereby consumed life grows exponentially (see Fig. 9). Consequently, the tubes of the IP Final SH had to be replaced or chemically cleaned. According to the calculations, the desired extension of life can be achieved through chemical cleaning, and as chemical cleaning is considerably less expensive than a replacement, chemical cleaning was the chosen solution. Some of the prerequisites for the graph below is an expected performance of the chemical cleaning after 145,000 hours (in the year 2003) and removal of 60% of the oxide film calculated for the tube subjected to the heaviest thermal loaded position: 1.5 m above the bottom of horizontal pass, where the oxide film measured was 0.76 mm.

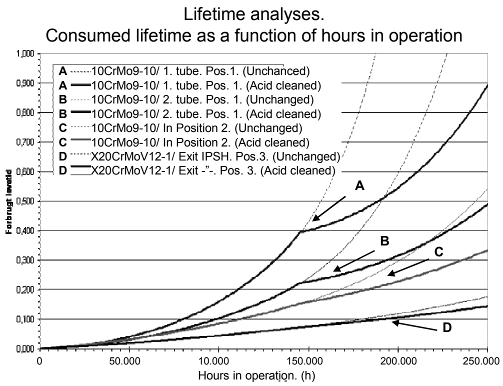


Fig. 9. Calculation scenarios with minimum creep rupture strength data. Positions 1-3 can be found in Fig. 3. For Pos. 1 (curves A and B), this corresponds to 1.5 m above the bottom of horizontal pass, while Pos. 2 is the 10Cr steel just before the transition to X20. Pos. 3 is the IP Final SH (X20) outlet just before the headers.

2.4. Chemical cleaning tests The chemical cleaners made a number of different chemical cleaning tests on tube samples, with different chemical compositions and temperatures. The conclusion was that most of the oxide films could be removed by chemical cleaning, but a porous oxide deposit of 30-50 µm with a high Cr content and limited bonding to the base in X20CrMoV121 would remain. It was expected that this deposit could be removed by subsequent steam blowing. In the samples in question, 0.600 mm had been measured in 10Cr in the tube sample above the bottom of horizontal pass, and 0.500 mm had been measured just before the transition to X20. In X20, 0.120 mm was measured in both samples. After the chemical cleaning, 0.04 mm of oxide was measured in X20, which was not removed by steam blowing at the chemical cleaners. However, we still chose to have the whole system steam-blown, as loose flakes of oxide and any sludge would thus be removed. The tests also showed that when X20 was chemically cleaned at a high cleaning temperature, pitting was observed, possibly because the inhibitor becomes too stressed. Two new tests at lower temperatures showed no pitting problems. The investigations led to the following proposals:

- First treatment: 3 h, 65 °C, 5% HCl, 1% HF and 0.1% Rodine 213.
- Second treatment: Up to 12 h, 60 °C, 5% HCl, 2% HF and 0.1% Rodine 213. If dissolved Fe^{2+} reach 16 g/l, a third cleaning could be relevant.

2.5. Chemical cleaning sequences During pressure testing, 3 leaks were observed in the IP Final SH outlet header made of low alloyed 10CrMo910 (Fig. 3, Pos. 3). This outside corrosion was caused by a too high temperature in the hottest pipes combined with entering sulphur from the flue gas.

The temperature in the IP-SH circuit is raised to 65 °C, and to begin with Rodine 213 is fed for dispersal in the system. 3 h later, hydrochloric acid + inhibitor are first fed and then hydrofluoric acid + inhibitor. HCl and HF are fed over approx. 2 h. The concentration in the IP-SH is now: 5% HCl, 1% HF and 0.15% inhibitor.

After 3½ h of acid treatment, the system is emptied of the acid, which is displaced by nitrogen. Then the IP-SH is flushed with water (deionised water) twice. The first time, the filling and emptying of the whole system is effected in one operation, while the second flushing takes place in 4 stages. At first, the two halves of the IP Prim SH are flushed separately at a flow > 200 kg/s, and then the two halves of the IP Final SH are flushed at a flow > 400 kg/s at the inlet.

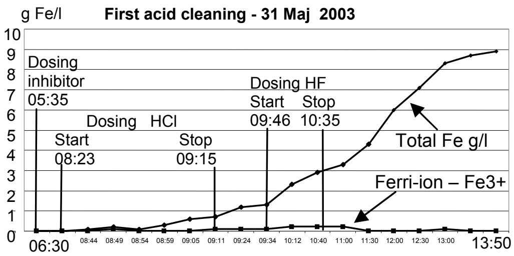


Fig. 10. Sequence and concentration of Fe^{2+} and Fe^{3+} during the first chemical cleaning.

Leaks. Some leaks are discovered in inlet headers as well as in outlet headers of the IP Prim SH. Tube sections are cut out, and leaks are sealed with rubber and clips, or hoses are mounted where tubes have been cut out. Tube samples taken show severe pitting, crack formation and a good deal of sludge at the bottom of the tubes. It was decided to try to patch up all holes and pressure test the IP-SH again. If the attempts at sealing the IP-SH were successful, the cleaning programme would be continued.

After 1½ day of repair work, the IP-SH is filled with water again, and this time the IP Prim SH is flushed at a flow > 400 kg/s in each half.

The second chemical cleaning sequence also starts with heating of water to 65 °C and filling of the IP-SH. Rodine, HCl and HF are fed in the same order as during the first chemical cleaning sequence. This time, the concentration is 5% HCl, 2% HF and 0.15% inhibitor. The acid circulates in the IP-SH circuit for 11 hours before it is drawn off. The acid is displaced by a nitrogen cover in order to reduce corrosive attacks.

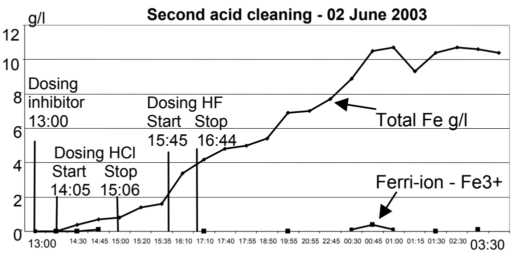


Fig. 11. Sequence and concentration of Fe^{2+} and Fe^{3+} during the second chemical cleaning.

The IP Final SH as well as the IP Prim SH are then flushed in sections (2 sections in each) at a flow > 400 kg/s, resulting in a conductivity of 1 μS/cm at the inlet and < 2 μS/cm at the outlet.

Passivating phase: Preheated 45 °C deionised water with NH_3 is fed to the IP-SH at 170 kg/s. Additional NH_3 is fed, and H_2O_2 is fed over 5 minutes.

When the final flushing has been completed, there is water in the system, the pH is 9.2-9.6, the conductivity is 20–40 μS/cm, and there is no excess hydrogen peroxide. Recirculation is established in the IP-SH via a condensate polishing plant for approx. 19 h whereupon the water in the circuit is so clean that the process is stopped and temporary measures are dismounted.

When the chemical cleaning has been completed, each of the 4 sections is steam-blown in order to detach as much as possible of the loose oxide deposits (which contain Cr) as well as any sludge.

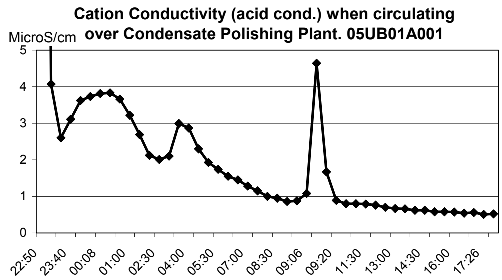


Fig. 12. Acid Conductivity in the IP-SH during recirculation via a condensate polishing plant. The peak at the nine o'clock position is due to shutdown(s) and pressure testing and inspection.

Table 1. Selected chemical cleaning data. The samples have not been analysed for Cr and Ni.

	First acid treatment	Second acid treatment
Temperature	67 °C	62 °C
Duration in system:		
Rodine	7½ h	15 h
HCl	4½ - 5½ h	13 – 14 h
HF	3½ - 4½ h	11½ - 12½ h
Consumption:		
Rodine	250 l	250 l
HCl	30,420 kg	30,420 kg
HF	2,100 l	4,200 l
Dissolved Fe conc.	9.0 g/l	10.6 g/l
Dissolved Fe, total	1,800 kg	2,020 kg
Weight loss on control element placed in circuit:		
10 CrMo 9 10	4.77 g/m^2	2.87 g/m^2
X20 CrMoV 12 1	3.37 g/m^2	3.42 g/m^2

2.6. Investigation of the IP Prim SH The surprising leaks in the IP Prim SH resulted in a major investigation of this section, among other things including an examination of the tubes that were replaced and an endoscopic examination of its condition in November 2003 in order to determine the extent of the pitting etc. in the superheater hoses. The original material in the IP Prim SH is 15Mo3, which does not contain Cr, and which has a thickness of 3.6 mm. In 1990–1991, the centre sections of the 4 lowermost tubes in all of the 208 bulkheads were replaced, and also 86 bends in the 3 lowermost tubes in 1998. The original material has been replaced by 13CrMo 4 4 steel (approx. 1% Cr).

The conclusion from the examination of the condition of the superheater is that there is very widespread pitting in the IP Prim SH. The findings are not systematic and unambiguous, but statistically there is more widespread corrosion in horizontal tubes adjoining an upward tube. In such places, water may also collect if the horizontal tubes have the wrong slope. Tube samples taken have pitting in depths up to 3 mm, which means that only 0.5 mm remains of the thickness. The worst corrosion and the most damage have been detected in the lowermost tubes.

In response to the condition of the tubes in the IP Prim SH, it was decided to replace all of the superheater hoses from inlet header to outlet header, a total of 208 bulkheads of 8 tubes of approx. 57 m each. The new IP Prim SH was made of 13CrMo44 with the dimensions 44 x 3.6 mm. The tubes were chemically cleaned in lengths of 13-14 m by means of inhibited hydrofluoric acid in the workshop. A total of 340 tonnes of tubing for the IP Prim SH has been chemically cleaned and mounted in the boiler during the summer of 2004.

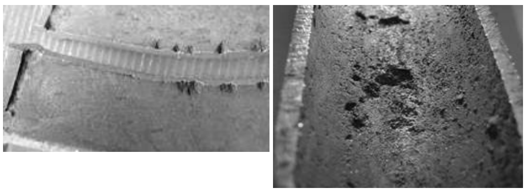


Fig. 13. Pitting in 15Mo3 steel in the IP Prim SH.

3. Conservation

As mentioned in previous chapter, some of the horizontal pipes, especially in IP Prim SH, has the wrong slope, meaning that not all the water can be drained out of the IPSH. (The horizontal parts of the pipes are about 12 m.)

In order to avoid corrosion when tubes with a wrong inclination are idle, and thus the risk of accumulation of water, it is consequently very essential that proper dry conservation measures are taken as regards the IP-SH on shutdown. This will become of even greater importance in the future when the boiler is expected to have another pattern of operation with more start-ups and shutdowns than during the previous 23 years.

As it has turned out to be insufficient to blow dry compressed air through the hot superheater tubes and then mount a Munter's drier, it is necessary to establish new equipment with a sufficient drying capacity. A procedure for correct dehydration of the IP-SH must be prepared where the boiler is purged in the hot state. In immediate continuation of this, while the boiler still has some residual heat, a vacuum must be created for the IP-SH for up to 24 hours. Subsequently, a Munter's drying device must be connected to the IP Prim SH inlet and the IP Final SH outlet, and all vent holes on the IP Final SH inlet must be opened. Moreover, it must be ensured that all shut-off devices against the IP system are tight, including the HP bypass, auxiliary steam bleeder(s) and injection valves.

4. Conclusions

In relation to the extension of life by 15 years of ASV5, the pre-examination of the IP super heater showed, that pipes in IP Final SH, and especially in 10CrMo910, had to be chemically cleaned or replaced because of the heavy oxide layer, while the sampled pipes from the IP Primary SH showed no problems neither with oxide layer or corrosion. The cost for chemical cleaning was about 20 % compared to replacing the whole IP Final SH, and 40 % compared to only replacing the 10CrMo910. The cleaning of the IP Primary SH was an extra benefit.

Tube samples from the IP Final SH taking in summer 2004 are in writing hour going to a thorough examination. But for the time being, there are observed new protective magnetite, and especially in 10CrMo910. Unfortunately there are seen some pitting in IP Final SH, probably some old one, but also some new. A few months after the acid cleaning, and before an adequate magnetite layer was built, a total power breakdown in Eastern Denmark damaged the main transformer for ASV5, an caused a sudden stop followed by a 2 months off-load period, in which the new pitting were formed. The final status of IP Final SH is not finished.

As regarding the IP Prim SH, the investigation focused on calculation of life, and therefore samples were taking in position for the heaviest thermal load. Looking back, we must conclude, that a more thorough general examination of the IP Prim SH could have reduced delays, emergency repairs and extra acid cleaning of the new pipes at workshop (if pipes were replaced before cleaning they could be cleaned in place together with IP Final SH.)

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