

Test of different measures for the prevention of scaling in the cooling system of Grohnde Nuclear Power Station

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Summary

In the cooling system of Grohnde Nuclear Power Station, heavy carbonate precipitations have occurred for several years in the turbine condenser and in the cooling tower, especially during very limited periods in springtime. Those precipitations cause performance losses and high cleaning costs. Reasons for the intensified precipitation are apparently the biologically upgraded water quality of the river Weser, as well as specific operational conditions of the cooling system (partial recirculation of cooling water).

Well-aimed analyses of measured data of both the plant treatment programme and the river Weser, together with analyses of the deposits, are meant to clarify the releasing factors of the carbonate precipitation.

In a test apparatus built for this special case, the cooling water-side conditions in the turbine condenser are exactly simulated. Scale formation can be observed in 6 heated test tubes, and various countermeasures performed in parallel.

Objective is the clarification of the precipitation processes and the development of countermeasures that are ecologically and economically optimized. For the identification of the conditions for scaling and the well-aimed application of countermeasures, the supervision of the water chemistry is of particular importance.

1 The cooling system of Grohnde Nuclear Power Station

Grohnde Nuclear Power Station is a joint facility of E.ON Kernkraft GmbH and Gemeinschaftskraftwerk Weser GmbH. It is equipped with a pressurized water reactor and has an actual electrical output of 1430 MW. Since its start-up in 1984 Grohnde NPS has reached an average time availability of 92.5% thus taking the lead in the international comparison of all pressurized water reactors.

The turbine condenser has 6 separate cooling water lines. It is equipped with a total number of 72,500 titanium tubes, outside diameter 23 mm, wall thickness 0.7 mm, length 13.8 m. Each of the 6 lines has its own cooling water pump. The cooling water velocity in the tubes is 1.8 m/s, the temperature rise at full load is 12 K.

The required cooling water is extracted from the river Weser and not chemically treated. It can be guided via 2 natural draught wet-type cooling towers. Depending on how the water is guided, and on the temperature of the river Weser, three different cooling methods are possible:

Fresh water cooling (open cycle cooling) is used in the case of sufficient water flow and low temperatures. The cooling water is guided directly back to the river Weser by-passing the cooling towers. Its temperature rise is limited to 3 K.

Discharge cooling becomes necessary at higher temperatures, with the draining cooling water being guided via the cooling towers.

Mixed cooling is applied at low water flow, with part of the draining cooling water from the cooling towers being re-fed to the cooling water intake, thus being operated in a circuit.

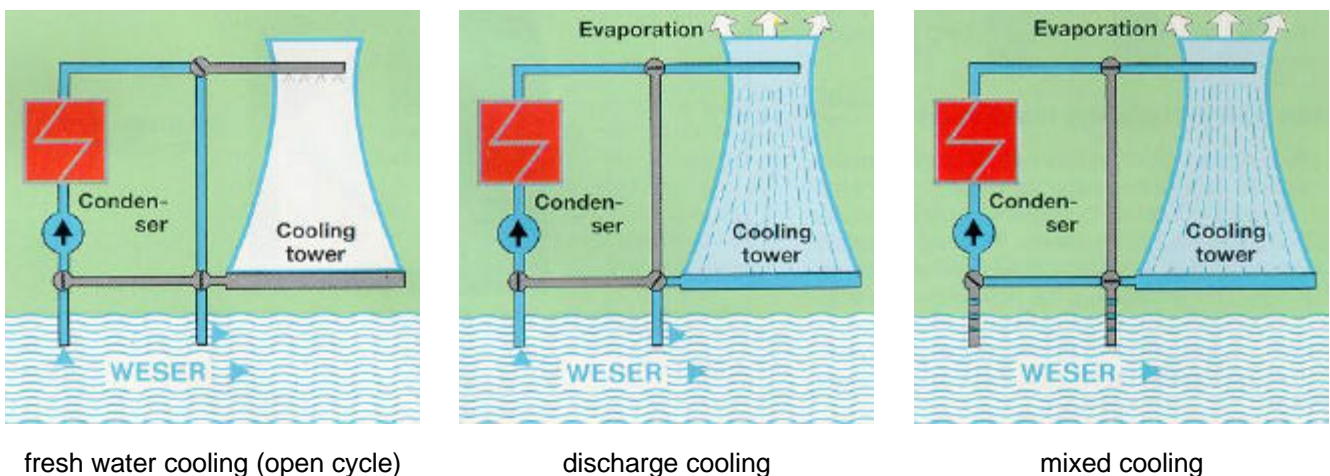


Fig. 1: The three cooling processes of Grohnde NPS

The cooling water requirement for the turbine condenser and the auxiliary cooling systems is 50 m³/s. Due to the fees of 0.02 DM/m³ that are currently levied ("Water-Pfennig") the annual costs amount to approx. 16 million DM. To reduce the extraction of water from the river Weser, more mixed cooling operation is aimed at for the future.

2 Occurrence of scaling

Until around the year 1990 the river Weser was heavily affected by the high salt load of the river Werra coming from the potassium mines in its catchment area. Through shutdowns and environmental protection measures this load could be considerably reduced which resulted in a clear upgrading of the water quality in terms of ecology.

Analysis	1989	2000
conductivity [$\mu\text{S}/\text{cm}$]	6500 (1000-15000)	1900 (600-3300)
pH-value	7.9 (7.3-8.9)	8.1 (7.6-9.1)
m-value [mval/l]	2.1-3.3	2.5-3.3
chloride [ppm]	1500-2500	300-500
calcium [ppm]	70-120	70-100

Table 1: Typical data of analyses from the river Weser 1989 and 2000

As a result of the reduced saline content and an increased pH-value the cooling water has developed a tendency of calcium carbonate precipitation at higher temperatures that had not been existed previously. During the inspection outage in 1994 calcium carbonate scaling was for the first time discovered in the tubes of the turbine condenser and also in the cooling tower. The scaling in the condenser tubes could be removed during the outage by means of jet cleaning, yet not successfully in all cases. By the application of abrasive cleaning balls with corundum coating in the TAPROGGE System the scales could not be removed entirely as they turned out to be extremely hard and adhesive.

In 1995 a TAPROGGE CMS (Condenser Monitoring System) was installed at the turbine condenser. In addition to the exact monitoring of the circulation and the wear of the cleaning balls, the CMS also serves for the measurement of the heat transfer at individual condenser tubes. Once scaling develops in those tubes there is a change of the wear behaviour of the cleaning balls, and the heat transfer coefficient (k-value) drops. In May 1998 the CMS recorded a sudden increase of the ball wear and a decrease of the k-value. At an inspection of a waterbox the examination by endoscope revealed beginning calcium carbonate scaling in tubes that had been clean before. Despite the immediate application of abrasive corundum balls the formation of compact, extremely hard calcium carbonate scales took place in many tubes.

After well-aimed jet cleaning during the inspection outage in April 1999 which focussed on remaining scaling that had been localized by endoscope, all tubes were free from scaling again.

In May 1999 and May 2000, the new development of scaling could be observed particularly well by means of the heat transfer measurement at the monitored tubes. Remarkable is that the scaling in the condenser tubes apparently developed only in strictly limited periods in May. Corresponding performance losses in those periods also point to this fact.

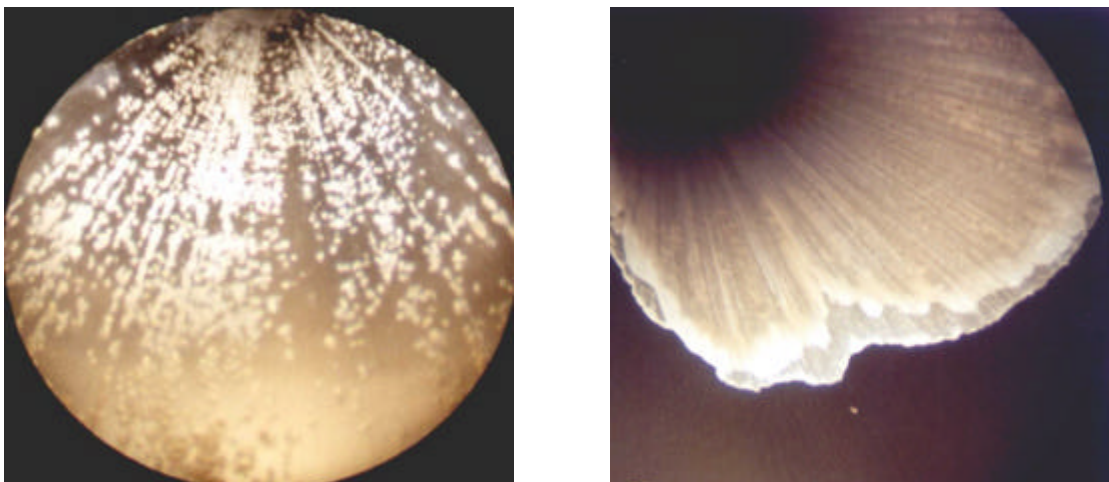
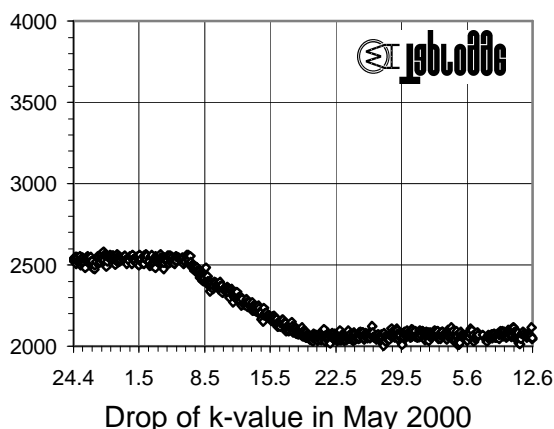
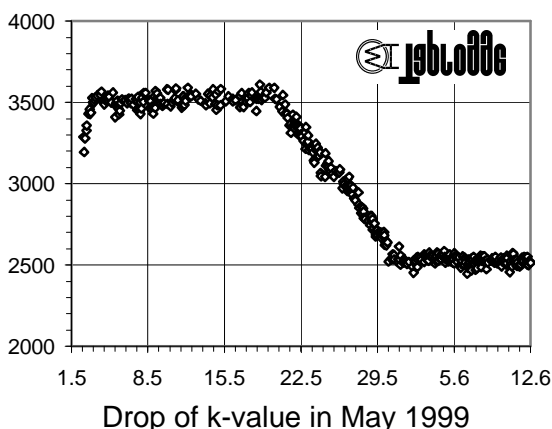


Fig. 2: Scaling in the condenser tubes. Left: initial stage in May 1998 in a tube that had been clean before, 60 cm from the outlet side. Point formation of nuclei is visible. Right: remaining scaling during the inspection outage in April 2000. Traces of abrasion of the injected corundum balls are visible which, however, could not remove the extremely hard, firmly adhesive scaling. The compact, mainly single-layer crystalline structure from the build-up of the scaling in May 1999 is visible at the fracture edge.



Period	k-value in W/m²K	Remark
Re-start after inspection outage 1999 18th – 31st May 1999	3510 drop to 2520	tube without scaling thickness of scaling up to 0.5 mm
Re-start after inspection outage 2000 6th – 18th May 2000	2520 drop to 2050	no cleaning of this tube thickness of scaling up to 0.7 mm

Table 2:

Measured data of the TAPROGGE CMS Condenser Monitoring System. Visible is the strictly time-limited drop of the k-value due to the development of calcium carbonate scaling in the years 1999 and 2000.

In the operation period 1999/2000 the carbonate scaling caused performance losses of up to 15 MW. Additional costs were incurred for the manual cleaning of the turbine condenser and the cooling towers. To avoid such losses the reasons for the scaling in the condenser tubes must be examined, and appropriate countermeasures developed.

3 Releasing factors for the scaling

Generally, cooling water parameters such as, pH-value, temperature and salinity, are responsible for the tendency of calcium carbonate precipitations. Well-known methods for the assessment of the tendency of hardness scales are the calculations according to the Ryznar or Langelier index, or the determination of the differential pH-value as per the German standard method C 10. The latter method is regularly applied at Grohnde NPS within the scope of supervision of the plant chemistry.

According to the differential pH-values that were determined in this way, the cooling water had a tendency of calcium carbonate precipitation throughout the whole summer of 1999 and 2000. However, the scaling in the condenser tubes actually developed only in May. This method alone thus does not provide a reliable forecast of the growth of calcium carbonate scales in the tubes. There must be other factors for the formation of scaling. On the other hand, it can be postulated that despite critical cooling water conditions during other periods the further development of the scaling was avoided by the continuous TAPROGGE cleaning, even if the scaling that had developed in May could not be eliminated by means of abrasive cleaning balls due to its extreme hardness and adhesion.

The analysis of further measured data of operation reveals that during the periods of calcium carbonate precipitation in the condenser tubes the following conditions coincide:

- high pH-value
- average cooling water temperature
- maximum annual values of oxygen content
- first feedback of cooling water (mixed cooling) after the inspection outage

In both years the calcium carbonate scaling coincided with the first mixed cooling operation after the inspection outage. The calcium carbonate build-up ended in both cases at the same time when there was a drop of the pH-value and the oxygen content. As to pH-value and temperature, in July and August of both years conditions occurred that seemed even more critical (higher temperature, pH-value and mixed content), yet they did no longer coincide with extremely high oxygen contents.

These conditions suggest that there is a correlation with the algal flowering time in the river Weser that occurs in the month of May at sufficient solar radiation and results in a particularly high oxygen content. The first cooling water feedback seems to trigger the formation of nuclei on the tube surfaces. Subsequently the calcium carbonate scaling develops very quickly until the pH-value drops again.

The assumption that biological processes have an influence on the formation of nuclei is supported by various other observations. For some years more and more slimy layers have been noticed on the walls, as well as the growth of lichens and snails in the cooling system. During the first commissioning of the tester described below that took place in May 2000, strong growth of slimy biofouling occurring in the test circuit areas with low flow pattern coincided with the build-up of the calcium carbonate scaling in the condenser. However, this phenomenon did not repeat itself during the summer.

The following diagrams give a survey of the development of the different cooling water parameters and the correlation with the scaling in the condenser tubes in the year 2000.

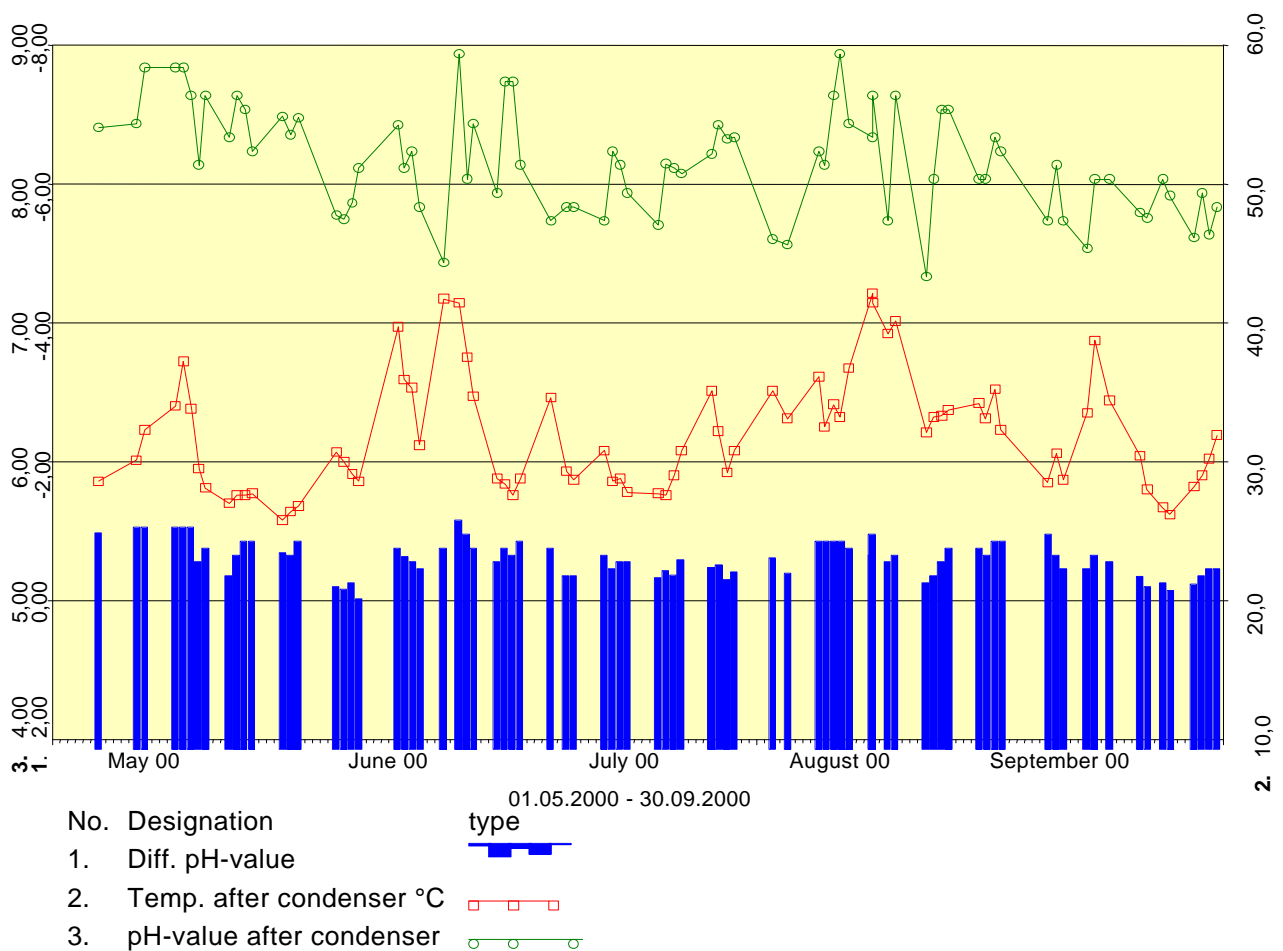


Fig. 3 Cooling water data from downstream of the condenser from the period May to September 2000. Calcium carbonate precipitation in the condenser tubes occurred only from May 6th to 18th, although in June and August higher temperatures and pH-values were reached, and also the differential pH-value was below -1 .

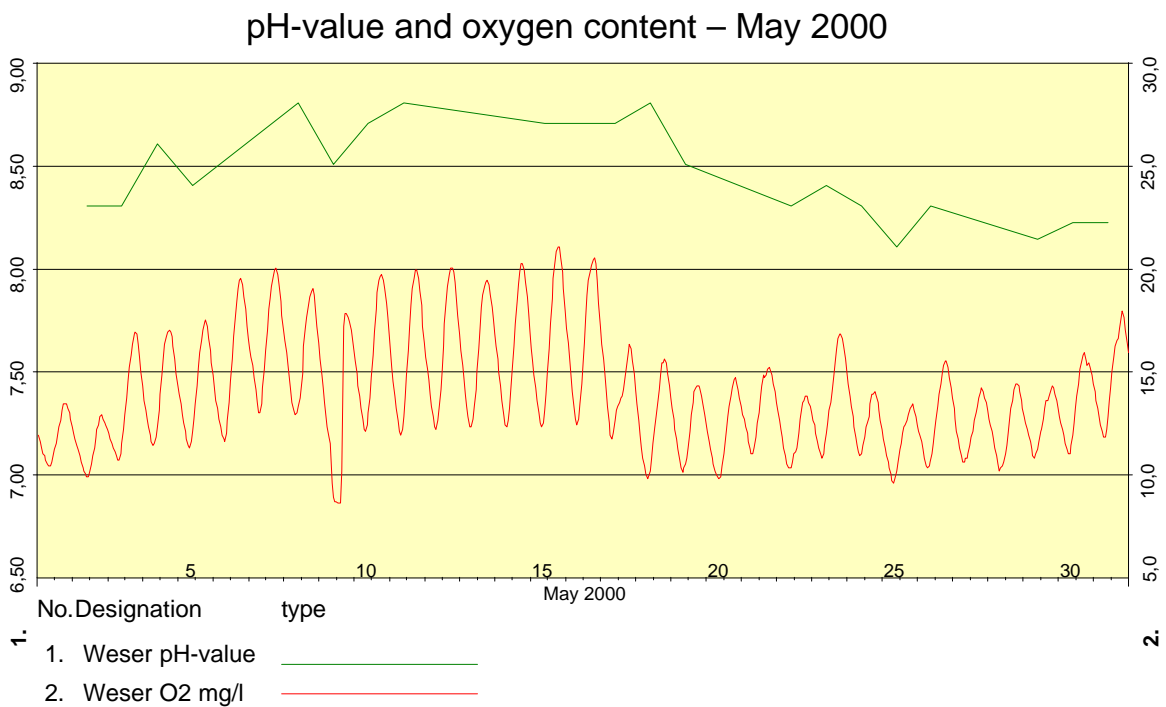
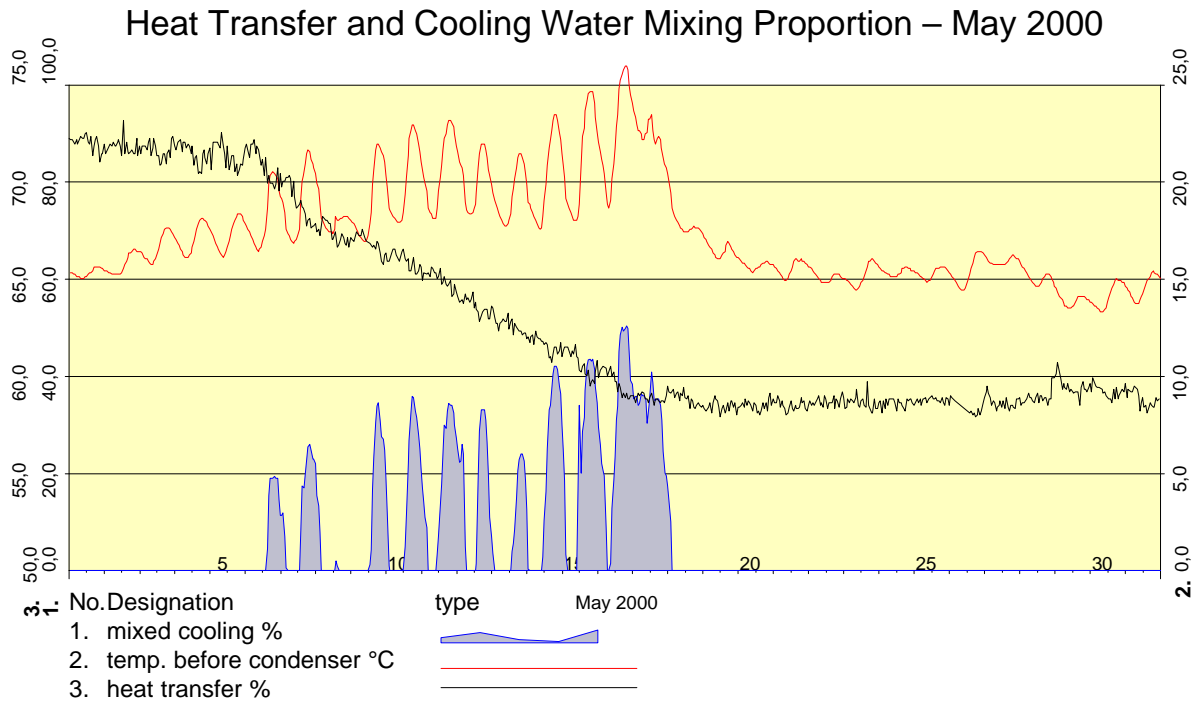


Fig. 4 Measured operational data from May 2000. The growth of the scaling occurred in the period from May 6th to 18th (drop of the measured heat transfer coefficient as Curve 3 in the upper diagram). It coincides with the start of the mixed cooling (Curve 1) and the maximum values of the oxygen content (Curve 2 in the lower diagram).

4 Test of countermeasures

To observe the development of the scaling in the tubes more exactly and to test countermeasures, TAPROGGE installed a tester unit at the turbine condenser of Grohnde NPS. By means of the tester the cooling water-side conditions in the condenser tubes (temperature, flow, TAPROGGE cleaning) can be simulated in 6 heated test tubes of 2 m length each.

The cooling water for this tester unit is extracted directly downstream of the condenser, so that the temperature is already increased and thus the conditions for the carbonate precipitation are even aggravated in the test.



Fig. 5 Tester module with 2 heated test tubes. The temperature and flow conditions prevailing in the condenser, and the automatic TAPROGGE cleaning, can be exactly simulated in the test tubes. In a mixing line the cooling water can be conditioned differently for each test tube. The test tubes can be inspected by endoscope and easily exchanged for laboratory examinations. For the tests in Grohnde NPS three of such modules are being used.

To date the following measures have been tested at the 6 test tubes:

test tube	water treatment	TAPROGGE Cleaning
1	physical treatment of the cooling water by capacitive and inductive coils	yes
2	dosing of a hardness stabilizer as per producer's instructions	yes
3	dosing of CO ₂ (4-8 ppm)	yes
4	dosing of sulfuric acid (5-10 ppm)	yes
5	none	yes
6	none	no

Table 3: tested countermeasures

The test started on June 15th, 2000. As in the condenser, no calcium carbonate precipitation occurred, despite critical cooling water conditions (cooling water temperature 47°C at pH 8.8). The TAPROGGE cleaning was performed with relatively small, non-abrasive cleaning balls and was meant to avoid the deposition of suspended matter in the test tubes only, without influencing the formation of scaling. In tube no. 6 (without cleaning) soft, slimy layers developed especially until mid-July which were repeatedly removed by manual cleaning. To artificially provoke the formation of scaling the pH-value of the cooling water was increased to 9.1 by dosing caustic lye of soda in the intake to the tester starting from July 18th, and additionally, from July 25th the cooling water throughflow was reduced and thus the wall temperature in the test tube increased. Only under such aggravated conditions did calcium carbonate precipitation occur in the test tubes.

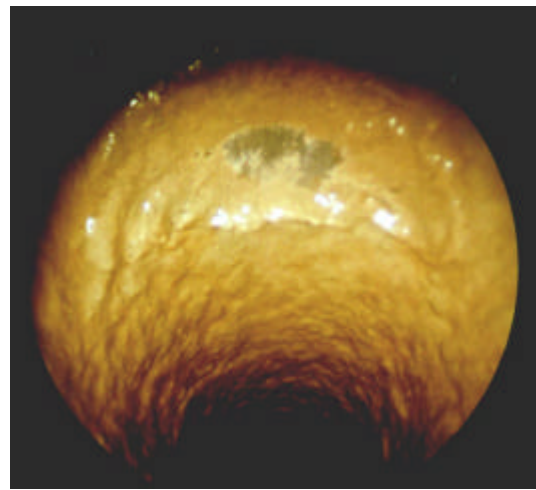
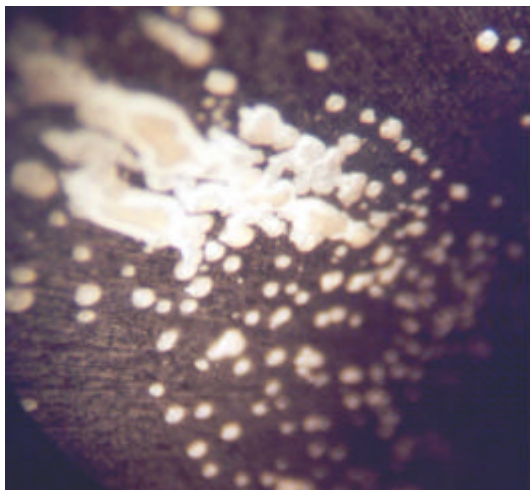


Fig. 6 Left: Calcium carbonate precipitation in an initial stage on August 1st, 2000 (after increase of the pH-value to 9.1 and throughflow reduction). The visual appearance corresponds to that of the turbine condenser.

Right: Condition of tube no. 6 on July 5th, 2000 after 20 days of operation without cleaning. Slimy deposits of approx. 1 mm thickness have developed. They apparently consist of biomass and deposited suspended matter and can be removed by wiping. Those deposits were repeatedly removed to be able to observe the precipitation of calcium carbonate on the tube surface.

The success of the countermeasures was assessed by endoscopic controls during the test and subsequently by laboratory examinations of tube samples at the Allianz Zentrum für Technik. Upon termination of this test phase different layers have developed in the individual test tubes:

Test tube	Treatment	Thickness [mm]	Layer Quantity [g/m ²]	Characteristics
1	physical	1.4	2663	crystalline, hard
2	hardness stabilizing	0.55	959	inhomogeneous crystalline structure, thereby less hard
3	CO ₂ dosing	0.58-0.75	1242	crystalline, hard
4	sulfuric acid	0.23	520	crystalline, less hard
5	ball cleaning only	1.07-1.2	2216	crystalline, hard
6	without cleaning ¹	1.28-1.6	2011	inhomogeneous crystalline structure perturbed by inclusions

1) Soft, slimy layers were manually removed several times during this test

Table 4: Layers in the test tubes

The elemental and X-ray structural analyses revealed that the scaling nearly exclusively consists of calcium carbonate in the form of calcite. A sample of the scaling from the condenser of the inspection outage 2000 showed the same composition.

Remarkable for tube no. 2 (with hardness stabilizer) are an increased silicon content (1.2 % as SiO₂) and traces of CaCO₃ as aragonite in the irregular crystalline structure.

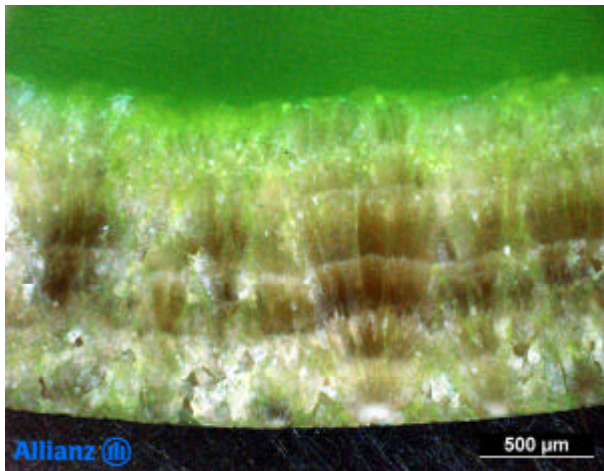
Aragonite is also to be found in traces in tube no. 3 (with CO₂ dosing).

In tube no. 6 the silicon content is also increased (0.9 % as SiO₂), apparently due to the inclusion of suspended matter as a result of missing tube cleaning.

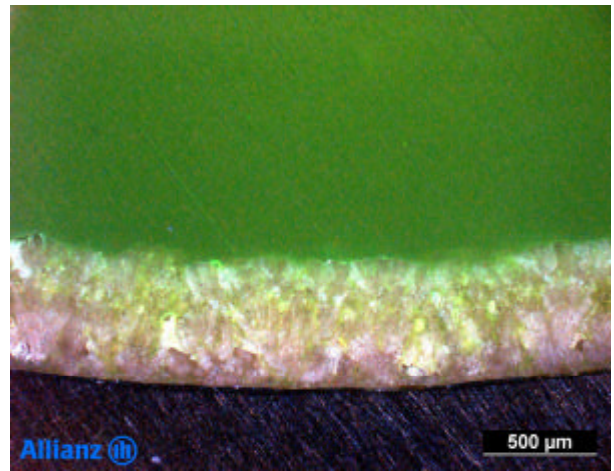
Striking in all samples is a relatively high zinc content of 0.4-0.5 % as SnO₂.

The results show that the formation of scaling can best be countered by hardness stabilizers and the dosing of sulfuric acid for the pH-value reduction in combination with the TAPROGGE cleaning. It is true that *hardness stabilizers* cause scaling which, however, gets an amorphous structure through the inhibition of the crystalline growth. They are thus not very hard and can be removed by abrasive cleaning balls. The drop of the pH-value by 0.3 through *sulfuric acid* has clearly reduced the quantity of scaling. Just a thin film developed that can be reduced by abrasive cleaning balls.

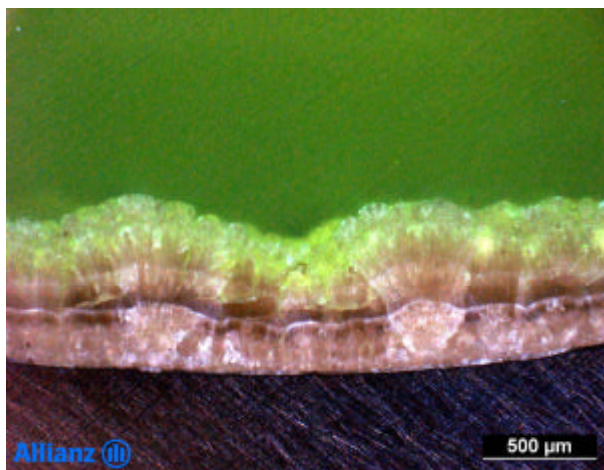
Physical water treatment did not show any effect in this test.



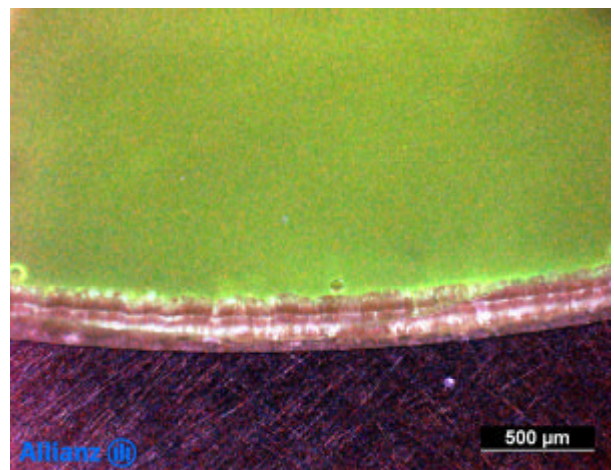
Test tube 1: physical water treatment
very hard, crystalline structure, 1.4 mm



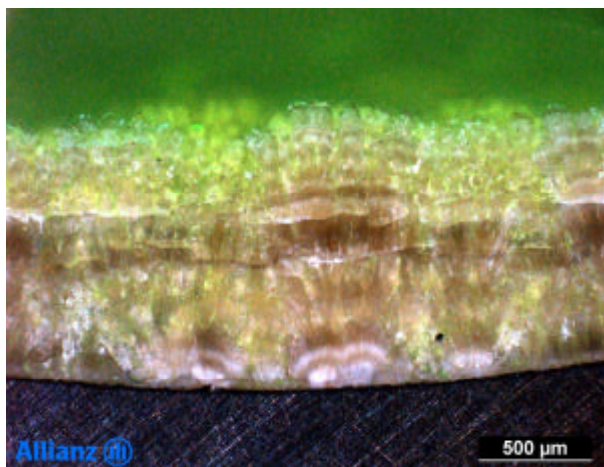
Test tube 2: hardness stabilizing
less hard, inhomogeneous crystalline structure,
0.55 mm



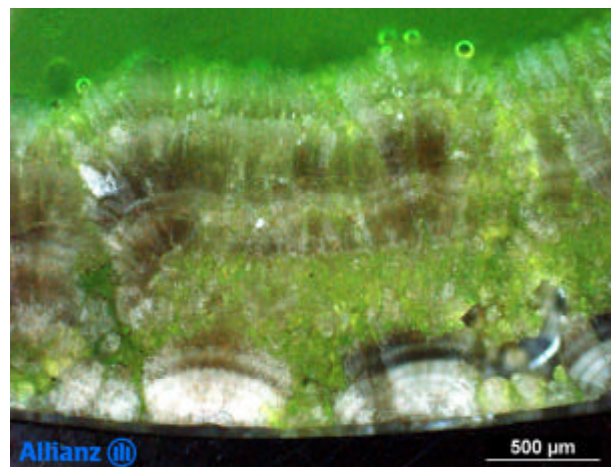
Test tube 3: CO₂ dosing
very hard, crystalline structure, 0.58-0.75 mm



Test tube 4: sulfuric acid dosing
less hard, crystalline structure, 0.23 mm



Test tube 5: cleaning only
very hard, crystalline structure, 1.07-1.2 mm



Test tube 6: without cleaning
disintegrated, inhomogeneous structure,
1.28-1.6 mm

Fig. 7 Micrographs of the scaling in the test tubes

In this test, the dosing of *carbon dioxide* CO₂ was less effective than the dosing of sulfuric acid. However, it is possible that an incomplete solution of the added carbon dioxide may have slightly falsified the result.

Without TAPROGGE cleaning soft, slimy layers develop in the tubes within a few days in the periods of high biological activity of the water. Under conditions of carbonate precipitation, inhomogeneous calcium carbonate scaling develops in the tubes with a crystalline structure that is dramatically perturbed by inclusions of suspended matter. Such layers are not as compact as in the other tubes with TAPROGGE cleaning, thereby causing considerable heat transfer losses. They have a disintegrated structure and a lower hardness

5 Consequences

The results of the examinations performed to date point at promising starting points for the avoidance of calcium carbonate scaling in condenser tubes.

The evaluation of the measured operational data and of the TAPROGGE Condenser Monitoring System revealed that the development of scaling in the condenser tubes took place in limited, short periods only, and that biological activities were a releasing factor for this phenomenon. According to today's knowledge the dosing of sulfuric acid for a reduction of the pH-value, or of a hardness stabilizer to inhibit crystalline formation, can be considered promising countermeasures along with sponge ball cleaning. Such procedures remain to be examined as to their large-technical applicability, economy and probable approval for Grohnde Nuclear Power Station.

These additional countermeasures need to be applied only during the short periods of unfavourable operational conditions with extreme formation of scaling in the condenser tubes, as in the other periods the condenser tubes can be kept clean by cleaning balls alone. By monitoring the wear behaviour of the cleaning balls and the heat transfer at individual tubes the occurrence of calcium carbonate scaling can be detected in a very early stage.

The task of operation monitoring is to clearly forecast such unfavourable operational conditions, so that countermeasures can be applied in an ecologically and economically optimized way.

It is advisable to continue the tests with the testing device during periods that are critical for the cooling water conditions in terms of season, weather, and cooling water system configuration. In such a way releasing factors can be clarified even better, enabling a forecast of the critical conditions. In this regard the cooling water conditioning and the operation of the TAPROGGE tube cleaning can be optimized.