# Copper deposits in power pressure equipment – Problems in operation and maintenance

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**Kurzfassung**

### Kupferbeläge in Kraftwerkskomponenten – Ein Betriebs- und Instandsetzungsproblem

*Im Laufe der letzten Jahre konnten in zahlreichen polnischen Kraftwerken und Heizkraftwerken, sowohl in den verhältnismäßig neuen als auch in den lange betriebenen, die sich immer intensiver auswirkenden Probleme im Zusammenhang mit bisher außergewöhnlichen Mengen an Kupfer und seinen Verbindungen in Belägen an den Aussenflächen von Strahlheizrohren und übrigen Komponenten im Wasser-Dampfkreislauf beobachtet werden.*

*Ein solcher Zustand ist aus einer Reihe an Parametern und Faktoren abzuleiten, die im Falle der Nichterkennung bei Untersuchungen oder der Vernachlässigung durch die Betreiber dazu führen, dass Kupfer und seine Verbindungen freigesetzt werden und sich an unterschiedlichen Komponenten absetzen. Dadurch verursachen sie möglicherweise regelmäßige Betriebs- und Instandsetzungsprobleme.*

*Im vorliegenden Beitrag werden die Probleme im Wasser-Dampfkreislauf eines Dampferzeugers mit Wirbelschichtfeuerung dargestellt.*

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## Characteristics of the power unit under examination

The cases described below concern the power unit equipped with a hard coal-fired, fluidised bed boiler with natural circulation. The boiler operates at live/reheat steam pressure of 16.1/3.8 MPa and at 560 °C having a steaming capacity of 425 t/h.

The work performed within the years 2004 to 2009 covered a vast scope of issues connected with both the operation and maintenance of the power unit. The major part of the work concerned the problems of the water-steam cycle being contaminated with copper compounds on both working medium side and equipment side.

Limited possibilities of performing analyses due to an insufficient number of measurement posts presently installed on the power unit equipment made it impossible to precisely determine the areas of occurrence and total amount of copper compounds being transported with working medium through the water-steam cycle under standard operating conditions.

An additional obstacle rendering an accurate identification of the problem difficult resulted from the general tendency to reduce both the scope and number of physical-chemical tests performed during standard operation, accompanied by generally limited scope of diagnostic examination carried out within the period of equipment overhauls. Which is why the current condition of the equipment is poorly identified whereby possible countermeasures taken by the users are often incorrect.

As time went by, the problem of copper compound in the deposits in water-steam cycle became more and more serious causing trouble in the performance of maintenance activities. Most important, however, was the reduction in the target power of the turbine whereby a further correct operation of the power unit was jeopardised.

## Physical-chemical conditions in the water-steam cycle

Since commissioning of the power unit until November 2005, the working medium has been chemically conditioned with trisodium phosphate only, batched into the boiler water. The feedwater was also conditioned with carbohydrazide added on the suction side of the feedwater pumps.

The initial guidelines concerning the quality of the working agent in the water-steam cycle of the unit are presented in Table 1. In the majority of cases the physical-chemical conditions maintained in the water-steam cycle were satisfying the above recommendations. The only significant deviation was found with copper compounds whose contents in condensate and feedwater frequently exceeded the recommended value of 3 µg/dm$^3$, Figure 1.

## History of experience connected with copper occurrence in the deposits

Case 1

In 2004 the deposits caused a total clogging of the tube coil in the cooler of the condensate sample probe. The internal surface of the tube was found to be covered over its whole diameter with loose, reddish-brown deposits up to 2.0 mm in thickness, easily detachable from tube metal. Chemical analysis of the deposits indicated more than 90 % (by weight) of copper with a small admixture of iron compounds (Table 2).

*Table 1. Initial cycle chemistry limits in water steam cycle.*

| Locations | $Cl^-$ ppb | $SiO_2$ ppb | Fe ppb | Cu ppb | $O_2$ ppb | $P_2O_5$ ppm | Cation conductivity µS/cm | pH |
|---|---|---|---|---|---|---|---|---|
| Cold condensate tank | | < 20 | < 20 | < 3 | | | < 0.3 | 6.8 ÷ 7.2 |
| Condensate | | < 20 | < 20 | < 3 | | | < 0.3 | |
| Feedwater | | < 20 | < 20 | < 3 | < 20 | | < 0.3 | |
| Boiler water | < 200 | < 310 | < 70 | < 5 | | 0.5 ÷ 2 | < 30 | 9.1 ÷ 9.6 |
| Saturated steam | | < 20 | < 20 | < 3 | | | < 0.2 | |

*Table 2. Chemical analysis of the deposits from the tube coil in the cooler.*

| Constituent | % (by weight) |
|---|---|
| Fe ($Fe_2O_3$) | 4.00 |
| Cu (CuO) | 95.40 |
| Si ($SiO_2$) | 0.60 |

*Table 3. Elemental analysis of the deposits from the feedwater pump.*

| | Constituent % (by weight) | | | | | |
|---|---|---|---|---|---|---|
| Measurement | Cu | Sn | O | Fe | Si | Zn |
| I | 55.43 | 1.02 | 28.47 | 15.09 | – | – |
| II | 54.84 | 0.88 | 28.78 | 14.60 | 0.23 | 0.67 |

## Case 2

During an overhaul of the main feedwater pump in 2005, a large amount of deposits was found on the surface of the rotor. An elemental analysis of the deposits indicated copper and iron compounds to be the prevailing constituents (Table 3). The deposits were further subjected to X-ray structural analysis which revealed copper oxide (CuO) as a dominant phase with iron compounds (mainly as $Fe_2O_3$) not exceeding 5 %.

Along with the analyses, the condenser tubing from the steam side (Figure 2) and tube bundles of the LP regenerative heaters from the feedwater side (Figure 3) were visually inspected for surface condition and found free from any characteristic corrosion/erosion damage.

## Case 3

During the maintenance work performed on the fluidised bed boiler in 2007, test sections were taken from the water wall tubes situated directly above the fluidised bed and from the boiler roof tubes, to assess the condition of their surfaces.

### *Water wall tubes located directly above the fluidised bed*

The whole internal surfaces were covered with process deposits of a uniform brown coloration, firmly adhering to the metal, but they were free from large deposit clusters and from corrosion pitting.

### *Boiler roof water wall tubes*

The internal surfaces of the tubes from the roof (fireless side) were covered with a thin layer of dust-free, process deposits with the coloration changing from light to dark-brown. The surfaces were found free from corrosion damage.

The internal surfaces of the tubes directed towards the furnace (fire side) were covered with the layer of grey-brown deposits 0.5 to 0.6 mm in thickness which was exfoliating and coming off the metal in the form of flakes (Figure 4). Corrosion pitting was found on the surfaces under the deposits. The pitting was filled with the deposits precipitated during an intense evaporation of water and with corrosion products. The walls of the tubes from the fire side were found considerably thinned showing a minimum of 3.8 mm in comparison with the nominal dimensions (diameter 63.5 x 6.0 mm).

Both the amount and chemical composition of the deposits were examined to indicate that the fraction of copper compounds varied from 29 % (by weight) with the tubes from the fluidised bed area to 64 % (by weight) with the boiler roof tubes, which proved to be hitherto unprecedented phenomenon in the regular power engineering sector in Poland (Table 4). The images of metallographic structures of the internal surfaces of tubes revealed large amounts of metallic copper built into deposit layers.

The amount of copper on the tubes from the boiler roof side was so large that even after chemical cleaning of the tubes their internal surfaces exhibited ample remainders of undissolved copper in the form of oblong flakes (Figure 5).

## Case 4

In 2008 the water wall tubes of the fluidised bed boiler were protected by overlay welding but due to the cracks occurring on the tubes these latter had to be replaced. The cracks

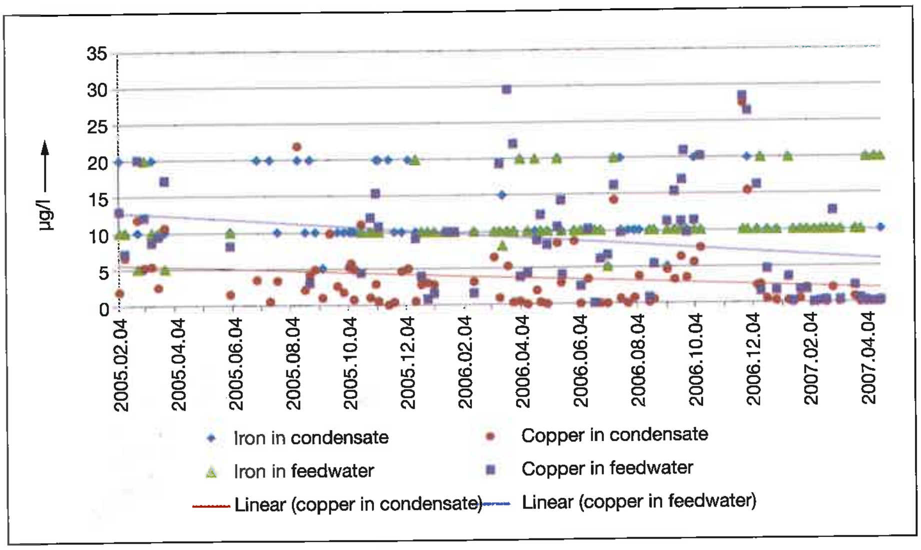

*Figure 1. Iron and copper contents in condensate and feedwater*

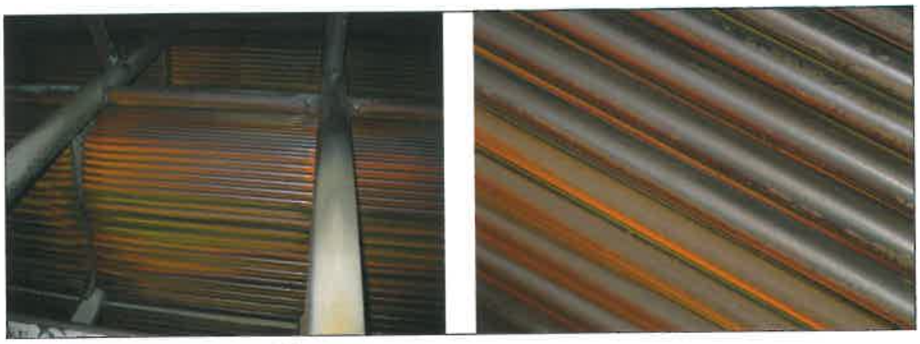

*Figure 2. Condenser steam side*

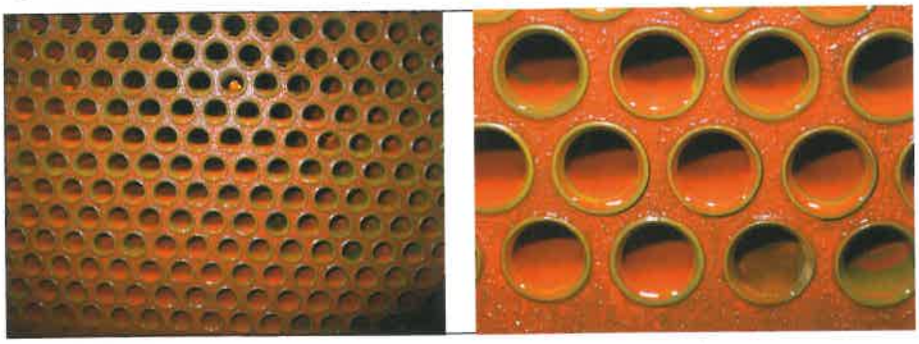

*Figure 3. Cooling water side of LP regenerative heaters*

*Figure 4. Boiler waterwall tube – flaky deposits on the internal surface*

*Figure 5. Flaky, copper deposits after chemical cleaning.*

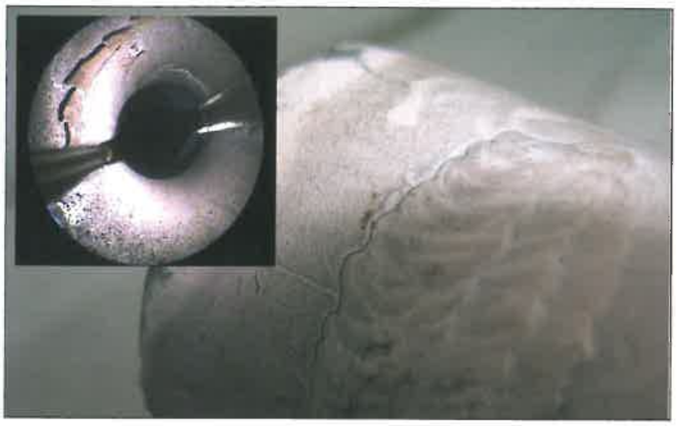

*Figure 6. Flaky deposits on the internal surfaces of the tubes. Concentrations of molten copper on the perforation areas (a/b).*

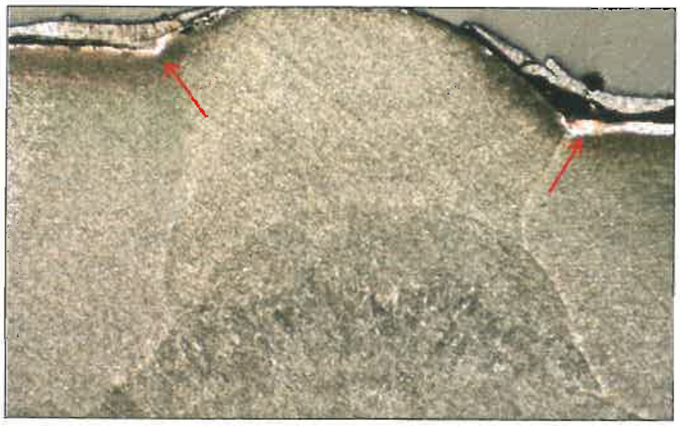

*Figure 7. Copper fused into the surface layer of metal*

were oriented either circumferentially, along the overlay weld, or radially. Considerable amounts of flaky deposits were found on the internal surfaces of the tubes, showing well-marked clusters in the area of welds performed. Noticeable concentrations of molten copper were found within the perforation areas as well (Figure 6a and 6b). The deposits from the internal surfaces of the tubes were checked for chemical composition which indicated the contents of copper compounds ranging from 44 % to 66 % (Table 5). The surface of the weld was found to be covered with large amount of copper occurring not only in the deposit itself but also fused into the surface layer of metal (Figure 7).

The welding problems and consequent damage to the tubes subjected to the overlay welding were caused by copper contained in the deposits covering internal tube surfaces. Due to high temperatures during welding, copper diffused into the tube wall metal along grain boundaries thus reducing the ductility of the heat affected zone, which resulted in brittle fractures. A similar phenomenon of precipitation hardening may occur with the steels in which copper contents exceeds 0.3%.

### Case 5

In the course of the boiler operation in 2008 a failure occurred at the live steam second degree platen superheater. The tube connecting

the platens via orifice with the superheater outlet header, was damaged.

The objective of the orifices is to change the velocity of steam flow through the platens whereby its temperature on the superheater outlet drops thus improving the operating conditions of the tubes interconnecting the platens and outlet steam header. The damaged tube exhibited a narrow crack accompanied by "bulging" deformation. The crack was localised on the extrados of the bend and was accompanied by numerous small cracks running in parallel with it. A longitudinal polished section was prepared from the orifice showing the deposit layers up to 2.2 mm thick on the edges of the orifice bore whose nominal size was 11 mm (Figure 8).
Metallographic specimens taken from both longitudinal and transverse cross sections of the damaged tube showed totally degraded microstructure wherein the fracture was surrounded by ferrite with spheroidised carbides abounding in micro cracks and creep-induced micro voids.

The samples of deposits taken from the internal surface of the orifice contained considerable amounts of copper (14 %), zinc (7 %) as well as sodium and phosphate compounds (Table 6).

The failure of the tube was caused by the overheating of its material due to the orifice bore being partly clogged by the deposits. The high degree of material degradation resulted from the operation at elevated temperatures, due to an insufficient heat transfer by steam.

According to the results of the measurements of oxide layer thickness temperature of the metal was 545 °C, however, having in mind a short period of boiler operation the working temperature might have been considerably higher being periodically as high as 600 °C.

## Case 6

The problems connected with the high-copper compound deposits have been gradually growing. The main problem, however, was the dropping target power of the turbine caused by an increased resistance to steam flow through the turbine due to deposits built up on the components of its flow system.

In 2009 during an overhaul of the unit, the turbine was opened and enormous amounts of deposits were found inside. The major part of the deposits appeared on the HP rotor stages although the IP and LP sections also showed deposits. The deposits were also precipitated

*Table 6. Elemental analysis of the deposits from the internal surface of the orifice.*

| Constituent % (by weight) | | | | | |
|---|---|---|---|---|---|
| O | Na | P | Fe | Cu | Zn |
| 61.5 | 10.9 | 3.1 | 3.2 | 14.5 | 6.7 |

*Table 4. Chemical composition of the deposits from the boiler waterwall tube.*

| Constituent | Unit | Result of analysis | | |
|---|---|---|---|---|
| | | Tubes from fluidised bed area | | Tubes from boiler roof |
| Iron – in terms of $Fe_2O_3$ | % (b.w.) | 68.71 | 66.52 | 32.93 |
| Copper – in terms of CuO | % (b.w.) | 29.04 | 31.62 | 64.73 |
| Calcium – in terms of CaO | % (b.w.) | 0.43 | 0.56 | 0.74 |
| Silica – in terms of $SiO_2$ | % (b.w.) | traces | traces | traces |
| Phosphates – in terms of $P_2O_5$ | % (b.w.) | 1.82 | 1.30 | 1.60 |
| Amount of deposits per internal surface unit | g/m$^2$ | 131.08 | 159.38 | 260.75 |

*Table 5. Elemental analysis of the deposits from the internal surface of the damaged boiler waterwall tube.*

| Tube | Constituent % (by weight) | | | | |
|---|---|---|---|---|---|
| | O | Fe | Cu | Zn | C |
| Water wall tube | 20.6 | 3.8 | 65.9 | 9.1 | – |
| Perforated tube | 15.0 | 7.0 | 51.1 | 21.3 | 4.2 |
| Weld areas | 25.8 | 10.0 | 44.2 | 12.0 | 8.1 |

*Table 7. Elemental analysis of the deposits from the turbine rotor.*

| % by weight | HP cylinder pitch plane | HP section | | | | | IP section | | LP section | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 6th stage | 8th stage | 12th stage | 14th stage | 18th stage | 13th stage | 14th stage | 4th stage (inlet) | 4th stage (output) |
| O | 29.74 | 32.20 | 25.84 | 29.21 | 29.88 | 25.70 | 43.62 | 21.82 | 21.25 | 55.95 |
| Na | – | – | – | – | – | – | 26.51 | 23.29 | 5.58 | 4.23 |
| Si | 0.28 | – | – | – | – | – | 7.40 | 8.27 | 24.56 | 33.77 |
| P | 0.77 | 5.58 | 2.76 | 5.10 | 3.30 | 3.43 | 0.18 | 0.31 | – | – |
| S | 0.25 | 2.45 | 1.99 | 1.82 | 3.43 | 1.47 | 1.02 | 1.19 | 0.29 | 0.14 |
| V | 0.23 | – | – | – | – | – | – | – | – | – |
| Cl | – | – | – | – | – | – | – | – | 0.92 | 0.45 |
| K | – | – | – | – | – | – | – | – | 0.20 | 0.36 |
| Ca | – | – | – | – | – | – | 0.19 | – | 0.17 | – |
| Cr | 1.11 | – | – | – | – | – | – | 0.33 | 0.31 | – |
| Mn | 0.24 | 0.28 | – | – | – | – | 0.23 | 0.43 | 0.25 | – |
| Fe | 45.01 | 6.07 | 5.60 | 2.76 | 1.80 | 1.88 | 6.47 | 17.36 | 19.14 | 1.21 |
| Ni | – | – | – | – | – | – | – | – | 0.36 | – |
| Cu | 22.37 | 43.76 | 59.12 | 57.32 | 60.11 | 65.60 | 12.04 | 22.61 | 23.28 | 5.83 |
| Zn | – | 9.66 | 4.68 | 3.80 | 1.49 | 1.92 | 2.35 | 4.39 | 3.67 | 1.06 |

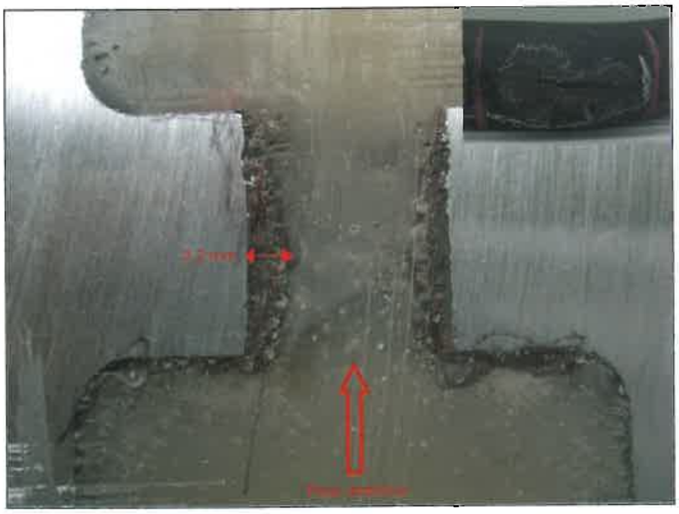

*Figure 8. Deposit layers on the edges of the orifice bore.*

on the guide vanes installed in the turbine cylinder and on the parting surfaces of the turbine cylinders. The results of the elemental analysis of the deposits from the turbine rotor are presented in Table 7 with the indication of growth/drop tendencies in the contents of their main constituents.

The deposits in the HP turbine section contained mainly copper and iron compounds. The fraction of copper compounds in the HP section was growing with the subsequent turbine stages and steam expansion degree. This is connected with an abrupt drop in the solubility of copper in superheated steam following its expansion.

The fraction of iron was decreasing following the subsequent stages of HP section. The deposits in the HP section were found to contain zinc as well. Zinc, as a constituent of copper alloys used in the construction of heat exchangers, was transported along with copper to the boiler and further to the turbine.

The deposits in the IP turbine section contained mainly sodium and silicium components, however, large amounts of copper compounds were found as well, which indicated that copper was present in the resuperheater coils where from, taking advantage of its solubility in steam and mechanical carryover, it was transported to the turbine. The presence of copper compounds in the deposits on internal surfaces of resuperheater coils is confirmed by considerably high contamination of live steam with copper which either was not precipitated in the HP turbine section or was redetached from the components of that section and then was carried over towards the resuperheaters. The deposits in the LP section constituted a mixture of sodium and silicium compounds (in the form of silica) accompanied by large amounts of copper and iron compounds. Such a large amount of copper and iron is not attributable to their theoretical solubility in steam and is probably connected with their mechanical exfoliation and transport from the preceding stages of the turbine flow system.

The effect of deposits, inclusive of copper compounds, on the turbine efficiency depends mainly upon their thickness, area of occurrence and roughness they produce on the surface of the flow system components. The changes in blading profile caused by the presence of deposits adversely influence the distribution of energy and in the case of still increasing roughness they can result in a considerable drop in turbine efficiency.

## Summary

Yet no theory has been developed coherently explaining the phenomena connected to the corrosion and copper transport in the water-steam cycle, nonetheless an increased fraction of copper in the deposits is closely linked to corrosion as well as corrosion-erosion processes occurring with brass tubing installed in condensers, regenerative heaters, district heat exchangers, etc. Damage to brass tubing due to corrosion and corrosion-erosion frequently results from the application of inadequate procedures for chemistry correction in the water-steam cycle or from an inobservance of predetermined chemistry specifications, all this being accompanied by inadequate hydraulic and thermal service conditions of such equipment.

Having in view the scale of the problem on the one hand and a limited possibility of controlling the processes connected with the emission and transport of the contaminants on the other hand, the only effective method to control these phenomena is the systemic integration of knowledge coming from both monitoring of current operation and maintenance diagnostics of the equipment. Taking advantage of these two sources in combination with the state-of-the-art data processing system makes it possible to quickly respond to any abnormal situation likely to happen and to schedule corrective and repair work to be performed during operation and maintenance with the selection of an optimum time periods from the standpoint of both service reliability and minimum costs of possible repairs.

## References

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