

COPPER DEPOSITION AND MW LOSS: PROBLEM AND ITS SOLUTIONS

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Summary: This paper gives background information on the problem of copper deposition leading to MW *and* efficiency loss occurring in utility steam cycles, reviews experience, copper alloy corrosion behavior, and the effects of water chemistry, cycle design and operation, and turbine design. Conclusions for all the above areas are presented and recommendations are given which can lead to a reduction or elimination of the problem.

INTRODUCTION

There are hundreds of high pressure utility drum boiler cycles which are experiencing MW and efficiency losses due to deposition of copper in the high pressure turbines (1-4). The presence of copper alloy corrosion products has additional negative effects such as more difficult boiler cleaning, copper interference with weld repairs of waterwall tubes, shortened feedwater heater life, copper effects on corrosion in LP turbines and elsewhere, nickel effects on boiler tube corrosion, and zinc effects on phosphate hideout.

Thousands of lower pressure utility and industrial drum boilers are experiencing copper deposition on waterwall tubes. Only a few once-through boiler units have these problems today.

There is no technical reason why copper alloys should be used in utility heat exchanger applications. The only (weak) argument is the biocidal property of condenser tubes. The use of copper alloys has cost U.S. utilities hundreds of millions of dollars in forced outages and maintenance.

The copper deposition problem seems to be most frequent in forced circulation drum boiler units at pressures above 2600 psi with copper alloy LP and HP feedwater heater tubing and no condensate polishers. The problem is often combined with iron and phosphate

deposition in the HP turbine. In the once-through boiler units, the problem is less frequent (5, 6) because of its early recognition (6) and cycle design without copper alloys.

While the understanding of corrosion and transport behavior of copper and its oxides is yet incomplete, solutions to the copper deposition problem exist and have been successfully applied.

These solutions include optimization of water chemistry, modification of cycle design and operation (retrofit of polishers, replacement of copper alloys, reduction of maximum pressure when copper concentration is high, etc.), modification of turbine design, and periodic turbine washing.

Elimination of the copper deposit related problems by any available means is a cost effective measure with return in 1 to 5 years and with many less obvious benefits, such as a reduction of the number of shut-downs, elimination of effects of copper and its oxides on corrosion elsewhere in the system, elimination of the need to wash or chemically clean the turbine, etc. It is possible to operate without copper related problems with copper alloy condenser tubing and copper in some auxiliary heat exchangers and LP heaters, but without replacement of the HP feedwater heater tubing, these problems cannot be entirely eliminated.

The cost of 30 MW loss of capacity for a large coal-fired unit at 3 cents per kWh is about \$700,000 per year, plus the cost of extra fuel, emissions, turbine washing, boiler chemical cleaning, maintenance, and life reduction.

EXPERIENCE

While copper alloy corrosion is frequent in all kinds of steam cycles, the MW loss is a problem mostly in the highest pressure drum boiler units. Similar MW loss can be experienced within a broad range of copper concentrations in the feedwater; 20 to 20,000 ppb.

The experience with six high pressure drum boiler units is summarized as an illustration of typical situations. Table 1 presents the cycle and cycle material characteristics of these units, represented by the co-authors of this technical paper. These units are in different stages of copper deposition analysis and application of engineering solutions.

Table 1
Steam Cycle Characteristics and Materials

Unit	Max. MW	Boiler Type Pressure	Copper in	Treatment	Cond. Polish	Operation	MW Loss
CP&L Roxboro 2	690	Forced Circul. 2850 psi	LPFWH	AVT	No	Load Follow	60
Tri-State Craig 2	447	Natural Circul. 2820	Condenser LPFWH HP-Monel	AVT	Powdex	Coord. Follow	18
WP&L Columbia 1, 2	549	Forced Circul. 2800 psi	Condenser LPFWH HPFWH	EPT	No	Load Follow	29
Montana P. Colstrip 3, 4	776	Forced Circul. 2850 psi	Condenser, All FWHs	PO ₄	Startup Powdex	Base Load	30

The preboiler cycle of one of the above units is shown in Figure 1.

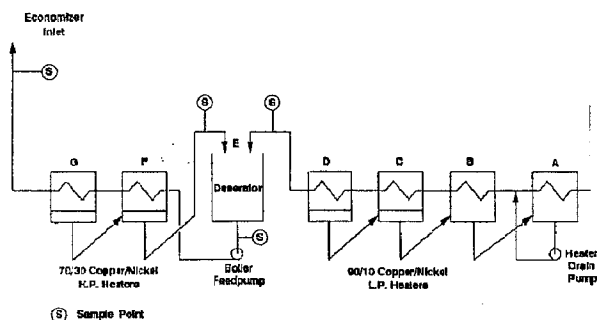


Figure 1. Columbia Unit Preboiler Cycle

Also shown are sample locations for monitoring of copper concentration. The loss of generating capacity in the same unit and the benefits of chemical cleaning of the HP turbine are illustrated in Figure 2. Table 2 gives information on copper, nickel, and iron transport; Table 2a during normal operation, Table 2b after a cold startup.

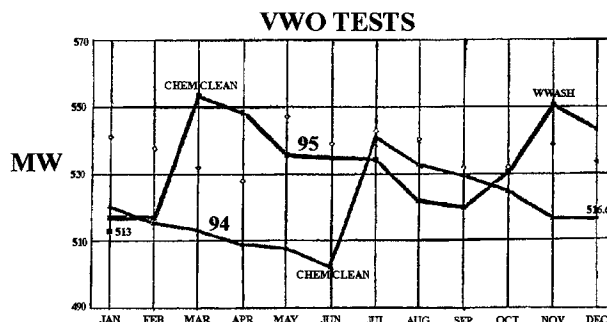


Figure 2. Megawatt Loss with Time and Effects of HP Turbine Cleaning

Table 2
Average Transport Rates at Columbia Generating Station, Unit-1

Table 2a - Normal Cycling Operation

Sample Location	Average Transport, lb./month		
	Copper	Nickel	Iron
Economizer Inlet	2.5	11.	12.
Boiler Feedpump	1.6	3.0	9.7
High Pressure Heater Drains	1.1	3.0	0.22
D-Heater Outlet	5.2	1.2	9.5

Table 2b - After a Cold Startup

Sample Location	Average Transport, lb./month		
	Copper	Nickel	Iron
Economizer Inlet	23.	11.	64.
Boiler Feedpump	12.	4.3	62.
High Pressure Heater Drains	5.6	3.9	1.7
D-Heater Outlet	11.	1.7	57.

As can be seen in Figure 2, there are rapid changes of the MW generating capacity in all units. The capacity can be recovered by chemical cleaning of the turbine or by abrasive cleaning after disassembly. Turbine washing can partially remove the lost MWs.

COPPER ALLOY CORROSION

The experience with the use of copper alloys in condensers and feedwater heaters and the corrosion mechanisms have been investigated for several decades (8, 9). The pH-potential diagram in Figure 3 shows the stability regions for different water chemistry conditions. Depending on the material, water chemistry, temperature, and flow velocity, the corrosion mechanisms include: oxidation, exfoliation, crevice corrosion, and erosion-corrosion. Corrosion behavior of copper alloys has been recently reviewed at an ENEL-EPRI-VGB conference (2, 10, 11, 12).

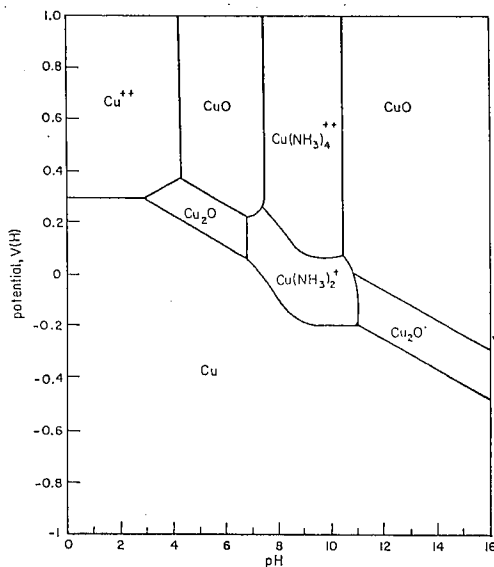


Figure 3. pH - Potential Diagram for Copper

During unprotected layup, copper alloys and deposited copper oxidize due to presence of air and high humidity or aerated water. Besides the feedwater heater and condensate tubing, the major reservoirs of copper are boiler waterwall and superheater tubes.

During operation, copper alloys corrode due to synergistic action of ammonium hydroxide and oxygen but also by ammonium carbonate, ammonium acetate, acids, and even hot water. Reducing conditions (N_2H_4) are necessary to minimize corrosion during operation.

The water treatment dilemma is to simultaneously protect copper alloys and carbon and low alloy steels; each of which have different pH and N_2H_4 - O_2 range for best corrosion protection. Under the high temperature conditions in the HP feedwater heaters, all currently

used copper alloys corrode. In marginally designed feedwater heaters, erosion-corrosion is often the main corrosion mechanism, particularly at the tube inlets.

EFFECTS OF WATER CHEMISTRY

It has been recognized for several decades, that in the utility drum boiler cycles with mixed metallurgy (steels and copper alloys), the control of preboiler cycle corrosion by chemical additives is difficult (13, 14). This is because the optimum pH for prevention of carbon and low alloy steel corrosion is higher than the optimum pH for copper alloys used in condensers and feedwater heaters. In these high pressure units, ammonium and hydrazine are usually the only chemicals used in the feedwater. Ammonium hydroxide, particularly in a synergism with oxygen and carbonate, is very aggressive to copper alloys used in steam generation. There are other volatile bases and oxygen scavengers used in steam generation, however, in the high pressure cycles, all these chemicals decompose, forming organic acids and CO_2 , which can further aggravate the corrosion situation for copper alloys and also cause corrosion and erosion-corrosion of carbon steels.

Many possible combinations and concentrations of the feedwater treatment chemicals and oxygen scavengers have been used without much success in controlling copper alloy condenser and feedwater heater tubing corrosion. It can be concluded that a purely chemical solution to copper alloy corrosion has not been found yet.

The most common situation is that in these problem units, only hydrazine is used in the feedwater cycle, pH is elevated by the ammonia produced by the decomposition of hydrazine and the MW loss control is by periodic washing or chemical cleaning of the high pressure turbine.

CYCLE CHEMICAL TRANSPORT

The major amount of copper is transported as CuO and Cu_2O from the corrosion sites in the condenser, feedwater heaters, and boiler and superheater deposits into the turbine during cold startups. Feedwater copper concentrations in the ppm range have been experienced. As the boiler pH and oxidation-reduction potential change during startup, dissolved copper oxides precipitate in the boiler water and are, together with the

dissolved copper, carried downstream by mechanical and vaporous carry-over (at high pressures, carry-over is ~ 30%). A smaller amount of copper is transported into the turbine through superheater attemperating sprays.

Investigation of copper deposition in superheaters revealed inventories of over a thousand pounds of copper. The superheater scale is a mixture of copper species with magnetite with the proportion of copper increasing towards the superheater outlet.

It is not clear how the water treatment (AVT, PO₄, EPT [OH foaming?], OT) affects the boiler carry-over. Cu and Fe oxides are also jointly transported as exfoliated particles from the superheater. Condensate polishers and magnetic filters can remove large quantities of copper from the cycle. Prior to cold startup, copper can also be removed by draining, side stream condensate filtration, washing condenser with LP turbine hood sprays in blowing down boiler mud drums or lower headers.

Main features of the copper transport are shown in Figure 4. Mechanical and vaporous carry-overs for boiler water contaminants, including copper oxides, are given in Figure 5 (13, 14). Volatility of copper species is still under investigation (15, 16). Some work has been done on copper-bearing colloids (17), and sorption, deposition, and crystal growth of copper, nickel, and zinc need to be considered (18-20).

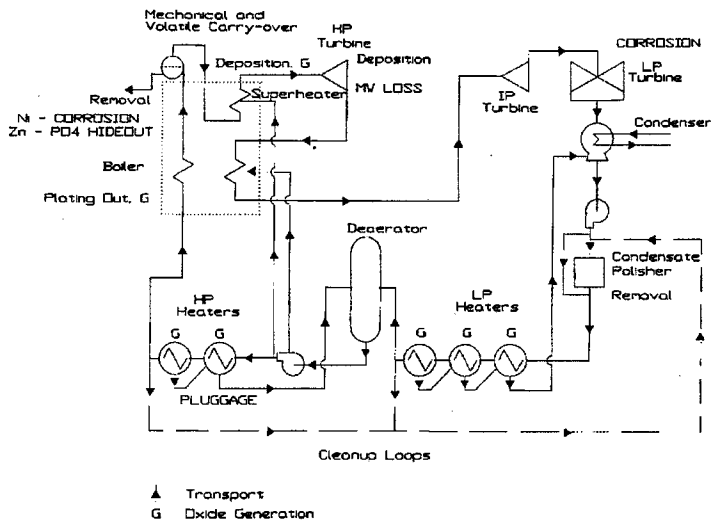


Figure 4. Copper, Nickel and Zinc Generation, Transport, and Effects

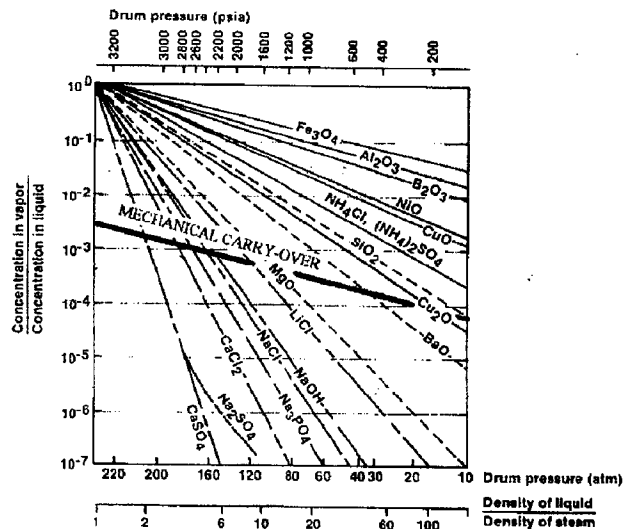


Figure 5. Distribution Ratios for Boiler Water Contaminants and Mechanical Carry-over

Solubility in water has been studied quite extensively (21, 26) and solubility in steam has also been measured (7, 27).

Deposition in the HP turbine is governed by:

- 1) sharp drop of the solubility of copper species in superheated steam as the steam expands (25, 27)
- 2) impact and adhesion of soft particles carried from the drum (dried drops) and the superheater

Boiler Mechanical Carry-over

There are many cycle operating transients and operating modes which can temporarily increase mechanical carry-over by increasing drum water level. Examples include:

- rapid load drops, particularly with sliding pressure operation
- under-frequency events - turbine valves open
- not all circulating pumps running - forced circulation boilers.

Transport of copper-related species has been studied for a long time (28-31), but there is still a limited understanding. In particular, the effects of turbine design, deposition in superheater, boiler carry-over, layup, sorption, and transport as particulates used to be recognized.

EFFECTS OF TURBINE DESIGN

The impact of deposits on turbine performance depends on their thickness, their location and the resulting

surface roughness (32-36). The effects of change in the blade nozzle area on flow capacity are shown in Figure 6. Small nozzle area blades are more sensitive to deposition. Deposits will change the basic profile of the nozzle partitions resulting in losses caused by changes in energy distribution and aerodynamic profiles as well as by surface roughness effects (see Figure 7). Experience on "impulse" units has shown that when deposits are present, they occur predominantly on the stationary nozzles with only minor deposits on the rotating buckets (usually under the bucket covers).

The major effect of deposits, which can be easily recognized, is the reduction in the maximum capacity of the turbine. Figure 4 shows the maximum capacity change that can be expected for changes in nozzle area. For example, a 10% reduction in nozzle area of the first stage, because of deposits, would reduce the maximum capacity of the unit by 3%. The values in Figure 4 are approximately additive, i.e., an additional 10% reduction in the second-stage nozzle area would result in a total maximum capacity reduction of 5.2%.

Reference (6) gives two examples of the effects of deposits on both efficiency and capacity. A 16.5% reduction in the maximum capacity of a unit and a 12.2% drop in HP turbine efficiency were attributed to severe deposits throughout the entire HP turbine section. Deposit thickness on the nozzles was found to vary from 41 mils on the first stage to 93 mils on the last HP stage. Bucket deposits varied from 10 mils on the first stage to 60 mils on the fourth stage and 29 mils on the seventh stage.

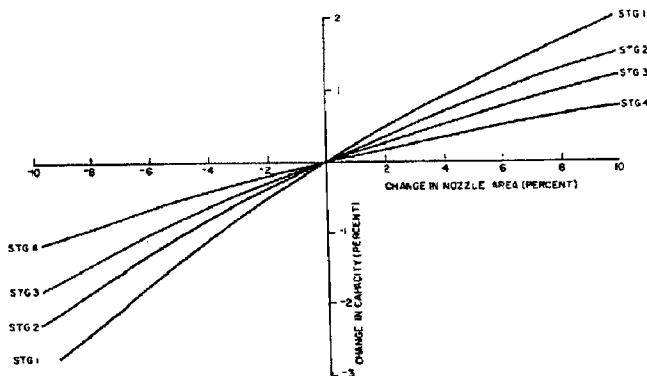


Figure 6. Effect of Change in Nozzle Area on Flow Capacity

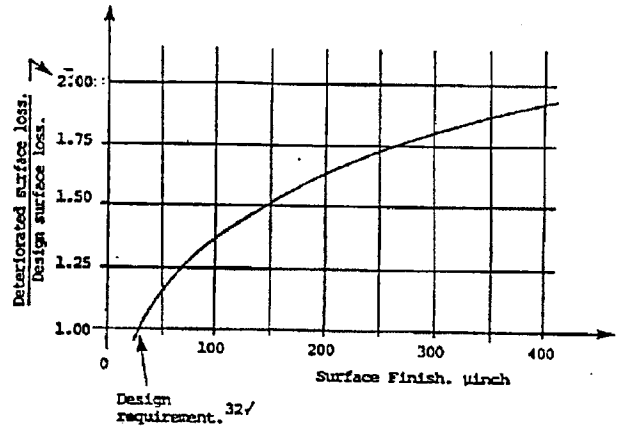


Figure 7. Increase in Frictional Losses as a Function of Surface Finish Deterioration

COPPER PROBLEM CORRECTION

Before expensive corrective actions are implemented, field verification of the copper alloy corrosion and transport mechanisms and a cost/benefit analysis should be performed. What needs to be known is:

1. How much iron, copper, nickel, and zinc?
2. From what components do corrosion products originate?
3. What is the inventory of copper and other oxides in the boiler, superheater, and elsewhere?
4. Quantitative effects of Cu and Fe oxide deposits on turbine flow capacity (MW) and efficiency, deposit weight density and heat transfer in boiler and superheater?
5. What is the remaining life of condenser and feedwater heater tubing?
6. What are the inspection results?
7. Is there exfoliation in superheater, reheater, and steam pipes and solid particle erosion in turbine?

Field verification steps:

1. Verify that the sampling and analytical methods are correct (37, 38).
2. Besides normal chemical parameters, monitor iron, copper, nickel, and zinc in the main steam, condensate, after condensate polishers (if used), in feedwater heater drains, deaerator outlet, final feedwater, and in boiler water - during all modes of operation.
3. Determine boiler mechanical carry-over vs. load and boiler pressure and during transients (average and local).

4. Review all inspection, turbine deposit, boiler and superheater tube scale analysis, and NDT records.
5. Install EPRI Isokinetic Steam Sampling Nozzle (19) and Turbine Deposit Collector (39) on main steam and determine at what mode of operation is copper depositing in the HP turbine. Determine other deposit components such as Fe, Ni, Zn oxides, Na, and PO₄.
6. Perform a Flow Path Audit.

Corrective Actions

The following are corrective actions which typically lead to the amelioration or elimination of the copper deposition problem and its consequences. They are collated from relatively easy solutions to the more expensive ones.

1. Optimization of feedwater chemistry: optimize concentration of ammonia and hydrazine, mini-mize condenser and air inleakage, maximize use of condensate polishers, pre-startup cleanup, etc.
2. Reduce boiler carry-over by operating at reduced boiler pressure when copper concentration in the boiler water is high (above 50 ppb) and by other carry-over control measures.
3. Implement proper layup practices (wet layup, dry air, nitrogen blanketing).
4. System filling with deaerated water (deaerator storage tank and boiler).
5. Implement periodic turbine washing to restore steam flow and MW.
6. Replace copper alloy HP feedwater heater tubing.
7. Replace copper alloy LP feedwater heater tubing (when water chemistry cannot be optimized due to erosion-corrosion of C-steels).
8. Retrofit better preboiler cycle cleanup loop and turbine by-pass system.
9. Retrofit condensate polishers.
10. Chemically clean boiler and superheater.

Feedwater heater tubing replacement options include: all austenitic stainless steel, ferritic or austenitic stainless for LP and carbon steel for HP heaters, and all carbon steel.

CONCLUSIONS

1. There are hundreds of high pressure utility drum boiler cycles which are experiencing MW and efficiency losses due to deposition of copper in the high pressure turbines. The copper deposition has additional negative

effects such as more difficult boiler cleaning, copper interference with weld repairs of waterwall tubes, shortened feedwater heater life, copper effects on corrosion in LP turbines and elsewhere, nickel effects on boiler tube corrosion, and zinc effects on phosphate hideout.

Thousands of lower pressure utility and industrial drum boilers are experiencing copper deposition on waterwall tubes. Only a few once-through boiler units have these problems.

The copper deposition problem seems to be most frequent in forced circulation drum boiler units at pressures above 2600 psi with copper alloy LP and HP feedwater heater tubing and no condensate polishers. The problem is often combined with iron and phosphate deposition in the HP turbine.

2. While the understanding of corrosion and transport behavior of copper and its oxides is yet incomplete, solutions to the copper deposition problem exist and have been successfully applied. These solutions include optimization of water chemistry, modification of cycle design and operation (retrofit of polishers, replacement of copper alloys, reduction of maximum pressure when copper concentration is high, etc.), modification of turbine design, and periodic turbine washing.

3. Elimination of the copper deposit related problems by any available means is a cost effective measure with return in 1 to 5 years and with many less obvious benefits, such as a reduction of the number of shutdowns, elimination of effects of copper and its oxides on corrosion elsewhere in the system, elimination of the need to wash or chemically clean the turbine, and elimination of the effects of zinc on phosphate hideout. It is possible to operate without copper related problems with copper alloy condenser tubing and copper in some auxiliary heat exchangers and LP heaters, but without replacement of the HP feedwater heater tubing, these problems cannot be entirely eliminated.

Feedwater heater tubing replacement options include: all austenitic stainless steel, ferritic or austenitic stainless for LP and carbon steel for HP heaters, and all carbon steel.

4. There are no water chemistry solutions when copper alloy tubing is in high pressure feedwater heaters. With

copper in the LP feedwater heaters, the problems can be minimized by optimization of water chemistry. The most common and practical feedwater chemistry optimization is a reduction of ammonia concentration and feeding of such concentrations of hydrazine which results in a good compromise in the protection of copper alloys and carbon and low alloy steels. Reducing conditions in feedwater are necessary.

5. Operation with morpholine, cyclohexylamine, and other volatile bases (except ammonia) always results in the thermal decomposition of these chemicals, formation of organic and carbonic acids, and a danger of corrosion to other cycle components, such as the LP turbine.

Similar problems arise with the use of alternate oxygen scavengers (besides hydrazine). Use of hydroquinone and DEHA results in increase of copper pickup and more deposits.

Control of the decomposition products resulting from the use of these alternate chemicals is better in units with full flow condensate polishers used all the time because the polishers can remove most of these decomposition products.

6. Air inleakage and the presence of organic impurities can accelerate corrosion of copper alloy feedwater heater tubing due to formation of ammonium carbonate and organic acids which are poorly neutralized at the elevated temperatures in feedwater.

7. Significant copper deposits can be caused by corrosion of auxiliary heat exchangers and transport of copper bearing anti-seize lubricating compounds used on bolt threads.

8. Copper alloy tubing can be corroding both on the tube side and shell side of feedwater heaters by general corrosion and oxidation and erosion-corrosion in the areas of high flow velocity and turbulence, such as at tube inlets at the tube sheet.

9. The copper and its alloying elements, i.e., nickel and zinc, are transported from the corroding feedwater heater and condenser tubing with feedwater into the boiler where some deposit on the generating tubes, some are removed by blowdown, and the rest is transported by boiler carry-over (volatile and mechanical) into the superheater and the turbine.

High mechanical carry-over is often caused by elevated drum water level; locally or along the drum, during some transients and high load.

Usually, a small quantity of copper is transported by superheater and reheater attemperating water.

10. A major quantity of copper alloy corrosion products is generated during unprotected layup of feedwater heaters and boilers and transported during cold startups. Copper, nickel, and zinc concentrations during cold startups can reach 10-30 ppm.

11. During unprotected layups, copper alloy feedwater heater and condenser tubing and the copper deposited in the boiler and superheater are exposed to moisture and oxygen, forming oxides which are picked up during the following cold startups.

12. In some units, the practice of boiling off the boiler or PWR nuclear steam generator layup water dosed with up to 100 ppm of ammonia and 200 ppm of hydrazine, together with the addition of aerated makeup and fill water, results in very high concentrations of ammonia, oxygen, and ammonium carbonate - all good copper solvents.

13. During startup and operation, copper is transported into the turbine as small (0.05 to 1 micron) particles eroded from the superheater surfaces and formed by evaporation of droplets of mechanical carry-over, and as copper oxides dissolved in superheated steam.

The soft particles deposit on impact with the HP turbine blade surfaces. The dissolved copper and copper oxides precipitate and deposit as the steam expands through the nozzle block and control stage because of the rapid decrease of the solubility of copper oxides in superheated steam under the HP turbine steam expansion conditions.

14. Turbine deposits up to 0.2 inch thick have been found on the HP turbine inlet stages. These deposits restrict steam flow causing up to 15% reduction of the MW generating capacity and 2% reduction of the HP turbine efficiency. Depending on the mode of operation, water chemistry, and cycle and turbine design, these losses can occur in less than 2,000 operating hours after a turbine copper removal.

15. Turbine design plays a major role in the sensitivity of a unit to copper deposits. In some units, rapid MW loss occurs with concentrations of copper from steam in the range of 3 to 10 ppb, in other units, the same MW loss occurred with startup concentration of more than 10,000 ppb.

The turbine features which are critical for deposition of copper include:

- steam density at stages with deposits
- size of the flow areas through stationary and rotating blades (height x throat)
- design and operation with proper inlet angle and blade shape minimizing turbulence and thickness of the boundary layer
- pressure and temperature drop across one stage
- surface finish

In different turbines, the critical flow restriction can be in different inlet stages of the HP turbine. This results in a different distribution of copper-bearing deposits in the inlet stages. It has been determined experimentally that only 3 mills of deposits can reduce the thermodynamic efficiency of HP blades by 3%.

16. Morphology of superheater deposits and the ratio of iron to copper change throughout the superheater. In the cooler sections of the superheater, there is a higher ratio of iron to copper and the copper is partially adsorbed on magnetite and partially present as small particles. Towards the finishing section of the superheater, there is high concentration of copper, and copper can be present as a metallic foil with crystals and particles intermixed. Surprisingly, there is often a decrease of copper concentration in the superheater section after the attemperating sprays.

The chemical compounds found in superheaters include: Fe_3O_4 , Fe_2O_3 , FeO , Cu , Cu_2O , Fe , FeZn .

17. The peak of copper deposition and the thickest copper-bearing deposits in the turbine are on the control stages of the HP turbines. Morphology of the deposits is a mixture of small particles and crystals. The chemical compounds found in these HP turbine deposits include: Cu , CuO , Cu_2O , Na_3PO_4 , NaOH , Fe_3O_4 , $\alpha\text{Fe}_2\text{O}_3$, $\gamma\text{Fe}_2\text{O}_3$, αFe , FeCuO_2 , Al_2O_3 , and SiO_2 .

18. EPRI limits for copper and iron in feedwater are adequate for prevention of turbine deposits. However,

there still could be a deposit buildup during cold startups due to oxidation of copper deposits in the boiler and superheater and transport of these oxides into the turbine.

EPRI limit for sodium in steam is currently being investigated and may be lowered, which would further reduce deposition of sodium phosphate in the turbine.

RECOMMENDATIONS

1. The use of mixed metallurgy, i.e., steels and copper alloys, is not recommended for any unit. To completely eliminate the negative effects of copper alloys on steam cycle components (deposits in boiler, superheater, and HP turbine, effects on corrosion) in high pressure drum boiler units, copper alloy tubing in HP and LP feedwater heaters should be replaced with carbon or stainless steel.

2. A reduction of the copper related problems can be achieved by a combination of maintenance, operation, and water chemistry actions, including:

- replacement of the HP heater tube bundles
- periodic turbine washing
- minimizing air leakage
- elimination of erosion-corrosion of the feedwater heater tube inlets by flow guides or inserts
- layup protection
- control of mechanical carry-over
- proper cold startup procedures operating at lower boiler pressures during startups and when feedwater and boiler copper concentration is high
- optimization of the ammonia - hydrazine treatment

In optimization of water chemistry, i.e., concentration of the alkalizing agent and oxygen scavenger, attention must be paid to the effects on the whole cycle; in particular on:

- iron concentration in feedwater and steam
- decomposition of water treatment chemicals, transport of the decomposition products, and their effect on corrosion and condensate polishers

The most common practical optimization of the feedwater chemistry is by minimizing ammonia feed and adjustment of pH by hydrazine. The effectiveness of this optimization is measured by iron and copper concentration in feedwater.

3. The choice of the unit-specific corrective actions depends on the complex cost and benefit relationships given by the:

- fuel and electricity prices
- cost of money
- age of the unit and reliability of individual cycle components
- cost and benefits of chemical cleaning of the turbine and superheater

4. Before and during cold startups when large quantities of copper, nickel, and zinc are often transported into the boiler and turbine, all copper removal and transport control measures should be employed, including:

- use of condensate polishers or filters
- steam and mud drum (lower header) blowdown
- filling with deaerated makeup water
- feedwater recirculation and cleanup
- use of turbine bypass
- washing of condenser by the LP turbine hood sprays
- operating at reduced boiler pressure and with minimum attemperation until the feedwater copper and iron concentrations are within the normal limits

5. During layups, avoid:

- exposure of copper alloys to oxidizing conditions (air, aerated water)
- exposure of deposited copper in the boiler and superheater to oxidizing conditions
- boiling out the boiler layup water dosed with ammonia and hydrazine
- filling heaters and other components with aerated water

6. The experimental investigation of copper alloy corrosion and corrosion product transport and deposition should include:

- verification of water and steam sampling practices and correction of deficiencies
- determination of the sources of corrosion products
- determination of the times, type of operation, and types of layups during which the corrosion occurs
- determination of the corrosion product transport characteristics of each specific unit (boiler carry-over, effects of attemperation, rooting of drains)
- determination of the copper alloy corrosion product inventories in boiler, superheater, feedwater heaters, and elsewhere in the cycle

- quantitative determination of the effects of water chemistry on iron, copper, nickel, and zinc concentrations in feedwater, boiler water, and steam

7. The following corrosion and chemical items should be investigated for better understanding of the copper problems:

- copper alloy corrosion by carbonates and organic acids
- speciation and solubility in boiler water for AVT, phosphate, and oxygenated treatments
- boiler volatile carry-over for copper species for different water treatments
- effects of boiler water treatment in high pressure boilers on mechanical carry-over and foaming

REFERENCES

1. Turbine Copper Fouling Meeting, PacifiCorp, Ken Layton, Salt Lake City, April 15 - 16, 1996.
2. Intl. Conf. on Interaction of Non-Iron Based Materials with Water and Steam, Piacenza, Italy, June 1996.
3. Lawrence, G., "Chemical Cleaning of HP Turbines at Columbia Energy Center," 1995 Intl. Water Conference, Pittsburgh, PA IWC-95-68.
4. F. Gabrielli, "Copper Alloy Corrosion and Transport in Power Plant Cycles," in Ref. 2.
5. R.G. Axley et al, "Turbine Copper Deposits in a Supercritical Once-Through Unit," Proceedings: Intl. Conf. on Fossil Plant Cycle Chemistry, EPRI, TR.100195, Dec. 1991.
6. K.N. Thomsen and K. Daucik, "Deposits in Turbines in Relation to the Use of Copper Alloys in the Water/Steam Cycle," in Ref. 2.
7. F.J. Pocock and J.F. Stewart, "The Solubility of Copper and its Oxides in Supercritical Steam," Journal of Engineering for Power, 1963.
8. "Corrosion-Related Failures in Power Plant Condensers", EPRI NP-1468, August 1980.
9. "Corrosion-Related Failures in Feedwater Heaters", EPRI CS-3184, July 1983.
10. B. Syrett, "A Review of Corrosion of Copper Alloys Exposed to High Purity Waters," in Ref. 2.
11. V.G. Kritskij and P.S. Skyazhkin, "Copper Corrosion in Cooling Circuits of Nuclear Power Plants," in Ref. 2.
12. D. Macdonald, "The Electrochemistry of Copper-Base Alloys in Power Plant Environments," in Ref. 2.

13. "Interim Consensus Guidelines on Fossil Plant Cycle Chemistry," EPRI GS-4629, June 1986.
14. "Cycle Chemistry Guidelines for Fossil Plants: All-Volatile Treatment," EPRI TR-10541, April 1996.
15. D. Palmer et al, "Volatility of Copper Species," in Ref. 2.
16. T. Petrova and O. Martynova, "Behaviour of Copper Corrosion Products in the Two-Phase Region," in Ref. 2.
17. P. Belouschek, "Colloids in Water-Steam Cycle," in Ref. 2.
18. O. Jonas and N.F. Rieger, "Turbine Steam, Chemistry, and Corrosion," EPRI TR-103738, August 1994.
19. O. Jonas, "Development of a Steam Sampling System," EPRI TR-100196, December 1991.
20. D.P. Laxen, "Adsorption of Lead, Cadmium, Copper, and Nickel onto Hydrous Iron Oxides under Realistic Conditions," Heavy Met. Environ., Intl. Conf., 4th, Vol. 2, pp. 1082-5, Univ. Edinburgh, UK, 1983.
21. B. Hearn et al, "Solubility of Cupric Oxide in Pure Subcritical and Supercritical Water," Journal of Chemical and Eng. Data, Vol. 14, 1969.
22. A. J. Paulson and D.R. Kester, "Copper (II) Ion Hydrolysis in Aqueous Solution," Journal of Solution Chemistry, Vol. 9, 1980.
23. S.E. Ziemniak et al, "Copper (II) Oxide Solubility Behavior in Aqueous Sodium Phosphate Solutions at Elevated Temperatures," Journal of Solution Chemistry, Vol. 21, 1992.
24. S.E. Ziemniak, "Metal Oxide Solubility Behaviour in High Temperature Aqueous Solutions," Journal of Solution Chemistry, Vol. 21, 1992.
25. M.A. Styrikovich et al, "Solubility of Copper Oxides in Boiling Water," Teploenergetika, Vol. 20, No. 11, 1973.
26. S. Ziemniak, "Zinc (II) Oxide Solubility and Phase Behaviour in Aqueous Sodium Phosphate Solutions at Elevated Temperatures," Journal of Solution Chemistry, Vol. 21, 1992.
27. O.I. Martynova, "Solubility of Inorganic Compounds in Subcritical and Supercritical Water," presented at the High Temperature High Pressure Electrochemistry in Aqueous Solutions Conf., Univ. of Surrey, England, 1974.
28. O. Smith, "A Program to Locate Copper Pickup in a High-Pressure Utility System," Vol. XXIX, Proceedings of the American Power. Conf., 1967.
29. T. Mizumo et al, "Corrosion Products Transport in Steam-Water Cycle during Startup," Properties of Water and Steam, Proceedings of the 11th Intl. Conf., Prague, September 1989.
30. D. Gunn et al, "COHAC and Copper Transport Through the Unit Cycle," in Ref. 2.
31. R. Bisogni et al, "Copper Behaviour in Thermal Cycle Fluid with CWT Conditioning," in Ref. 2.
32. J. Angelo and K.C. Cotton, "Observed Effects of Deposits on Steam Turbine Efficiency," Paper No. 57-A--116, ASME, December 1957.
33. V.T. Forster, "Performance Loss of Modern Steam-Turbine Plant due to Surface Roughness," Proc. Inst. Mech. Engr., Vol. 181, 1966-67.
34. K. Bammert and H. Sandstede, "Influences of Manufacturing Tolerances and Surface Roughness of Blades on the Performance of Turbines," Journal of Engineering for Power, January 1976.
35. P. Schofield, "Maintaining Optimum Steam Turbine-Generator Thermal Performance," presented at EPRI Fossil Plant Heat Rate Improvement Workshop, Charlotte, NC, August 1981.
36. K.C. Cotton, Evaluating and Improving Steam Turbine Performance, Cotton Fact Inc., New York, 1993.
37. Yu-Sen Chen et al, "Sampling and Analysis of Copper in Power Generation Systems," 1990 Intl. Conf. on Measuring Waterborne Trace Substances, EPRI-NIST, Baltimore, Aug. 1990.
38. K. Maeda et al, "Improvements of Metal Impurities Sampling and Measurement," 1990 Intl. Conf. on Measuring Waterborne Trace Substances, EPRI-NIST, Baltimore, Aug. 1990.
39. O. Jonas, "On-Line Diagnosis of Turbine Deposits and First Condensate," 55th Annual Intl. Water Conf., Pittsburgh, PA, Oct. 31-Nov. 1-2, 1994.