WATER CHEMISTRY AND CORROSION - MISSING KNOWLEDGE

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Abstract

This paper discusses the main water chemistry and corrosion processes and problems associated with steam generation which are not sufficiently understood. The discussion of missing knowledge is divided into four sections: 1. Root Cause and Failure Analysis, 2. Commissioning, Operation and Maintenance, 3. Water and Steam Chemistry, and 4. Corrosion.

Introduction

There have been major achievements in corrosion and water chemistry control [1 - 20] since the government initiated a study on the cost of corrosion published in 1978 by NBS (SP511-1) identified the cost of electric utility corrosion to be the highest of any U.S. industries. Ten cents of every dollar of gross production were spent on corrosion and the total cost to U.S. utilities was 9 billion dollars. This study, together with the utility recognition of the high forced outage and maintenance costs, resulted in increased R&D, formation of EPRI, and other corrective actions. In the subject area, achievable goals were formulated.

The best achievements of the corrective period (1978 to 2000), many of them through EPRI programs, but often in cooperation with other organizations [1 - 3], include:

- improved communication among designers, operators, water chemists, and researchers [1 - 8]
- transfer and use of knowledge
- reduction of boiler tube failures [5]
- formulation of cycle chemistry guidelines and improvement of cycle chemistry [1-3, ASME]
- better instrumentation and sampling practices [15 - 17]
- recognition that copper alloys should not be used [18, 19]
- better operation of condensate polishers
- better condenser tube materials and tighter condensers [4]

Remaining Problems

Besides the achievements of the previous decades, the cost of corrosion and scale is still high [21], total cost is 17.3 billion dollars per year, and efficiency and generating capacity losses due to scale and deposits persist [22 -24].

In our opinion, the main reasons for this high cost and losses are:
- unresolved cycle component design problems such as stress corrosion of turbine blade attachments and designs prone to flow-accelerated corrosion
- old uncorrected cycle design and material selection problems such as the use of copper alloy tubing in feedwater heaters and use of carbon steel in areas prone to flow-accelerated corrosion (FAC)
- equipment aging, cycling of units designed for base load
- insufficient commissioning of new units
- use of incorrect water chemistry control (some organic chemicals, phosphate hideout)
- insufficient transfer and use of existing knowledge

The lack of use of existing knowledge in cycle and component design often includes the absence of FAC and cavitation considerations, selection of wrong materials (copper alloys, high yield strength turbine disks, etc.), sampling systems with low velocity, no sampling nozzles for steam, and insufficient instrumentation. The current EPRI project on "Low-Temperature Corrosion Problems in Fossil Power Plants - State of Knowledge Report" [4] also addresses missing knowledge for major steam cycle components.

Missing Knowledge

The following tables briefly describe specific problems with knowledge of water chemistry and corrosion in the areas of root cause and failure analysis, operation and maintenance, water and steam chemistry, and corrosion. In each table, the items are in the order of priority. Discussion of selected problems follow.

Table 1

Root Cause and Failure Analysis

Problem	Missing Knowledge
Deaerator cracking	Source of stresses for corrosion fatigue, effects of welding [4, 22 - 24]
LP turbine blade corrosion fatigue (CF)	Stress amplitude, effects of mean stress, stress concentrations, pitting, sources of excitation, CF limits for service environments (EPRI BLADE) [4, 25]
Blade attachment stress corrosion cracking (SCC)	Effects of chemistry, crevice, galvanic, droplet charge, early condensate [4, 11]
L-0R blade failures	Effect of trailing edge erosion [4, 22]
Turbine SCC and CF	Effects of heater box and periodic overspeed, LCCF (low cycle corrosion fatigue)
Flow-accelerated corrosion	Effects of organic water treatment chemicals and their decomposition products [4, 22, 23]
CF of boiler tubes	Effect of high pH, NaOH [5]
Hydrogen damage	Effects of NaOH, acid phosphate [5, 26]
Boiler tube corrosion	Effects of "acid phosphates", maracite [5, 26, 27]
Water droplet erosion	Predictive equations, effects of chemistry [7, 28]
Corrosion in steam and water	Local, at surface environments [1, 2, 5, 7 - 14]
Forced-circulation boiler orifice plugging	Mechanism

Table 2

Commissioning, Operation and Maintenance

Problem	Missing Knowledge
Boiler carry-over	How to measure for AVT and EP (equilibrium phosphate)
Pre-operational chemical cleaning	When needed? Citric acid vs. high Cr steels in superheaters
Steam and air blows	Blow parameters for efficient blows, better monitoring [29]
Disposal of EDTA	How to dispose of used solutions, reduce cost
Oxide scale and deposits in feedwater systems of older fossil and nuclear units	How to clean
Removal of preservatives	Need, procedures
SF_6 for leak detection	Environmental impact
Sample tubing deposits	How to clean, criteria

Table 3

Water and Steam Chemistry

Problem	Missing Knowledge
Boiler carry-over	Effect of NaOH, EPT, EDTA, dispersants, suspended solids, organic acids
Turbine steam chemistry	Early condensate and liquid films in PWRs [7 - 14]
Steam chemistry	Hydrolysis of salts including sodium phosphate
Impurity concentration in boiler tubes	Chemistry, reaction with oxides, hideout, pH, concentration for AVT, EPT
Confusion with EPT	Is there acid phosphate corrosion during phosphate hideout? How can solid maracite, $NaFePO_4$ be corrosive? Nuances of opinions.
Boiler tube scale growth	Effects of water chemistry
Scale growth in liquid water	Effects of flow, surface finish, mixed oxides, suspended solids
At-temperature and on-surface pH measurement	Is it ready after 20 years of research?
Organics vs. environment	Long-term effects of discharges on aqueous systems [20]
Organic water treatment chemicals	Decomposition products, their transport around the cycle, carry-over, deposits, corrosion effects, surface reactions [20]
Hydrazine vs. substitutes	True environmental impact, effects of organic decomposition products [20]
Volatility	Basic model [30]
Condensation	Homogeneous or heterogeneous, nucleation seeds, Wilson line, electrical charges, effect of chemistry [12 - 14]

Table 4

Corrosion

Problem	Missing Knowledge
Corrosion data	Accessible pertinent corrosion, SCC, CF, pitting, crevice, and galvanic data
Design against SCC and CF	Design rules, allowable stresses, defects, interaction of SCC and CF, variable amplitude CF and fatigue [31]
SCC in PWR LP turbines	Steam and surface chemistry (amines, organic acids and salts, boric acid) [32]
Boiler tube corrosion vs. hideout	Corrosion data for maracite, direct measurement of acid phosphate corrosion (corrosion hydrogen) [26]
Boiler tube corrosion fatigue	Crack initiation and growth rate data for sodium phosphate, NaOH, EDTA, polymers [5]
Cavitation	Effects of water chemistry
Stress corrosion cracking	Crack initiation data for pertinent aqueous and steam environments
Corrosion of bolts, disk steeples	Effects of Loctite, graphite, etc.
Galvanic series	For steam cycle environments
Stress corrosion and corrosion fatigue	Basic mechanisms (see Epilogue) [33 - 37]
Turbine SCC and CF	Effects of droplet charges

Examples

Deaerator Cracking [24]

Stress corrosion and corrosion fatigue cracking of deaerator welds has been a major problem for several decades. It is also a safety issue because it has resulted in fatalities. Thirty to forty percent of inspected deaerators are found to have cracks and, depending on the local regulations, every indication may have to be repaired.

Root causes of this problem have not been identified and the only correlation found was that of the apparent crack propagation rate and the age of the deaerator (see Figure 1). While several deaerator users measured stresses, the source of alternating stresses causing corrosion fatigue has not been found. The only source of high-cycle stresses reported in literature is called "water piston" which can occur in horizontal vessels with a water level as an instability which depends on the storage tank geometry, viscosity, and location of the water level (see Figure 2).

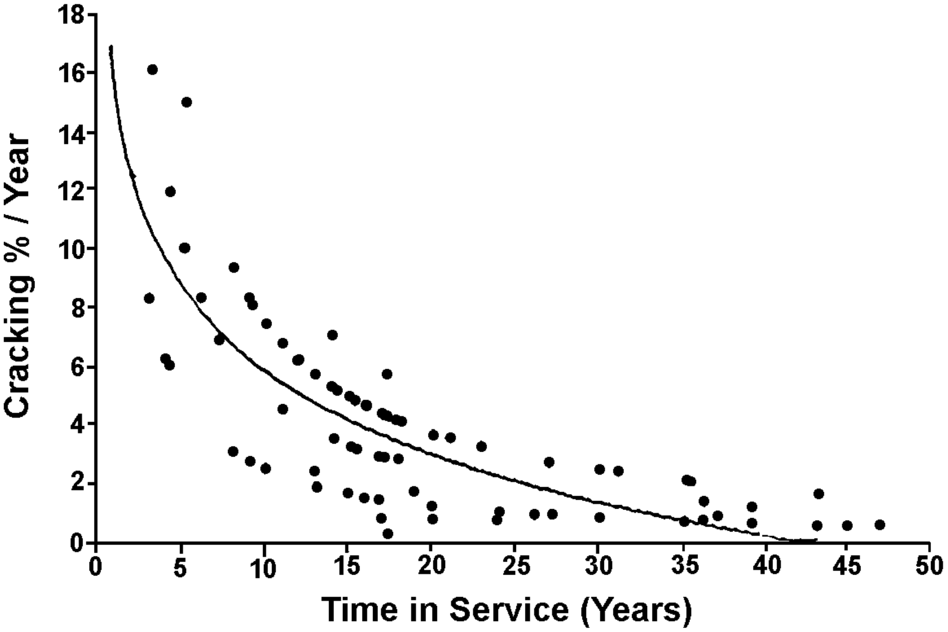

Figure 1
Deaerator Storage Tank Weld Cracking: % of Wall Thickness per Year vs. Time in Service

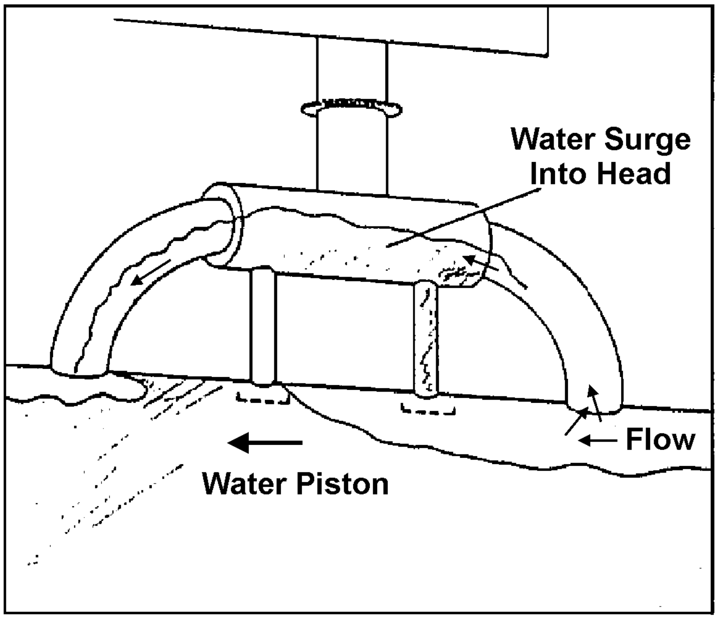

Figure 2
Water Piston

Steam and Air Blow

These costly pre-commissioning procedures are an art which is solely based on experience. An online monitoring of a steam blow [29] indicates that there could be extended periods of time wasted when there is no removal of impurities from the steam piping and that certain steam blow conditions, such as the length of the blows, are more effective than others (Figure 3). The most common, infrequent monitoring is with impact targets which does not allow for timely blow condition adjustment. Similar situations exist for air blows.

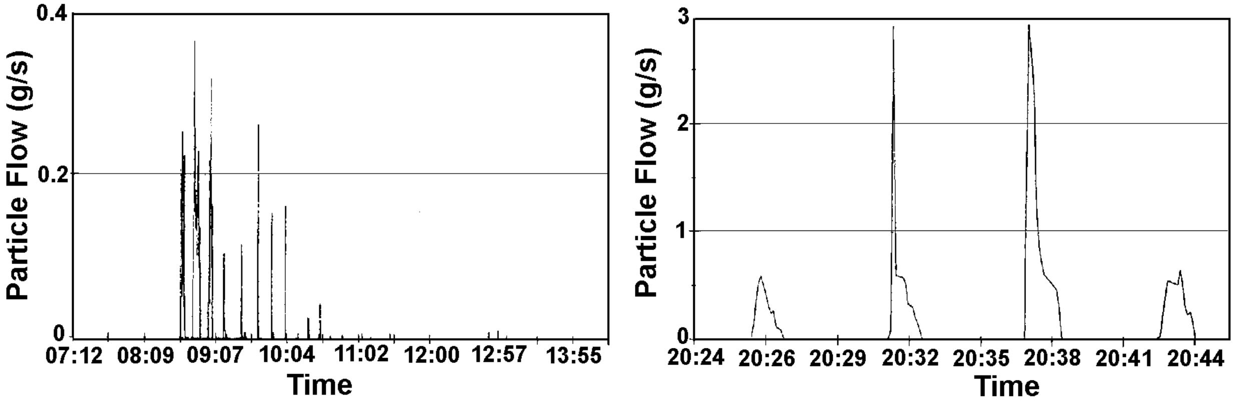

Figure 3
Steam Blows vs. Removal of Particulate Matter

Impurity Concentration on Boiler Tubes

It is assumed that soluble impurities such as $NaOH$ and $NaCl$ concentrate at the hot tube surfaces in the liquid because of the temperature gradient - vapor pressure of the solution, thermodynamic relationships. The second impurity concentration speculative model is the "wick boiling" model for the surface oxide. While these models may reflect reality, they have never been experimentally confirmed and the effects of boiling, water treatment, flow, and solid phases have not been determined.

Confusion with Equilibrium Phosphate Treatment - EPT [26, 27]

The concepts of not exceeding the equilibrium (acceptable) concentration of sodium phosphate in boiler water and of increasing pH at low phosphate concentrations required for high pressure high and heat flux boilers with low concentrations of $NaOH$ are sound. However, the speculative conclusions on corrosion by $NaFePO_4$ (a solid under boiler conditions) need to be experimentally evaluated. In the international survey [3], several participants reported phosphate hideout and pH swings without any tube corrosion consequences. It should also be emphasized that for EPT, the limits of corrosive impurities in the boiler water are as low as those for AVT and that, for many applications, condensate polishing may be required.

Carry-over of a Dispersant and Turbine MW Loss

There have been multiple cases of polymeric dispersant carry-over from the boiler water into the turbine and a consequent buildup of hard organic deposits in turbine control valves and on turbine blades. In one case, the deposit prevented valve closure, resulting in a turbine wreck due to overspeed. Figure 4 shows heavy deposits on turbine blades caused by carry-over of a polymeric dispersant, which resulted in loss of MW and overloading of the thrust bearing.

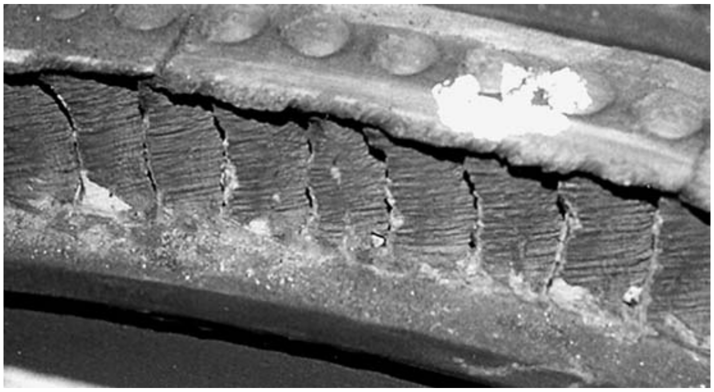

Figure 4
Turbine Deposits Caused by Carry-over of a Polymeric Dispersant

Conclusions and Recommendations

1. A significant amount of knowledge is not available, costing the steam generation industry millions of dollars annually. Included is the knowledge needed to solve some of the costliest generic corrosion problems, such as deaerator cracking and steam turbine blade attachment SCC.

2. Application of existing knowledge needs to be improved and better used in root cause analysis and problem solving. With the current staffing at utility and industrial companies, the transfer and application of the existing knowledge is often provided by consultants. This is OK as long as the management of the owners/operator companies is aware that this knowledge exists.

3. The best application of existing knowledge is in the cycle and component design phase. However, design reviews of water chemistry and corrosion are still rare (FAC, SCC and CF in turbines, etc.)

Epilogue

On Stress Corrosion - S. P. Rideout (Savannah River Laboratory), 1969 [33]

The image of stress corrosion I see
Is that of a huge unwanted tree,
Against whose trunk we chop and chop,
But which outgrows the chips that drop;

And from each gash made in its bark
A new branch grows to make more dark
The shade of ignorance around its base,
Where scientists toil with puzzled face.

Chemists and metallographers,
Technicians and philosophers,
Though struggling individually,
Their common goal: to fell the tree.

At intervals researchers gather,
And on mechanisms all palaver;
Each to his own work will refer,
Ignoring those who don't concur,

But as we speculate and ponder,
Those who run the mills out yonder
To us with anxious voices wail,
"Please help us lengthen 'time to fail!'

For us to pay your research bills
By sale of products from our mills,
Wheels must turn and planes must fly,
And on high-strength alloys we rely."

Thus, as we argue with each other,
Let us not forget our brother
Our Siamese twin, the engineer,
Whose working profits sent us here.

The Conference ended, let us pledge
To go again with sharpened edge,
And with redoubled energy
To pit ourselves against this tree.

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