Steam chemistry guidelines (SIT) versus high acid conductivity caused by organic additives or organic impurities

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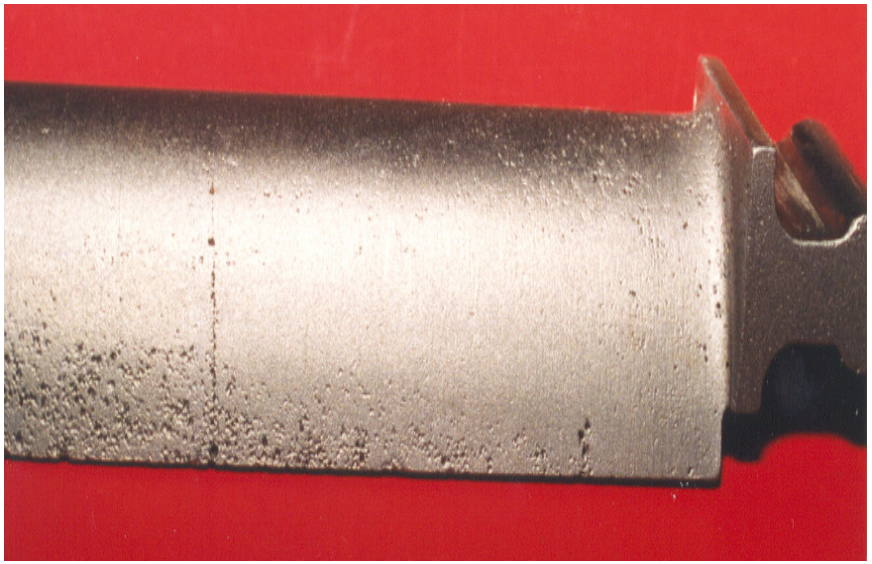

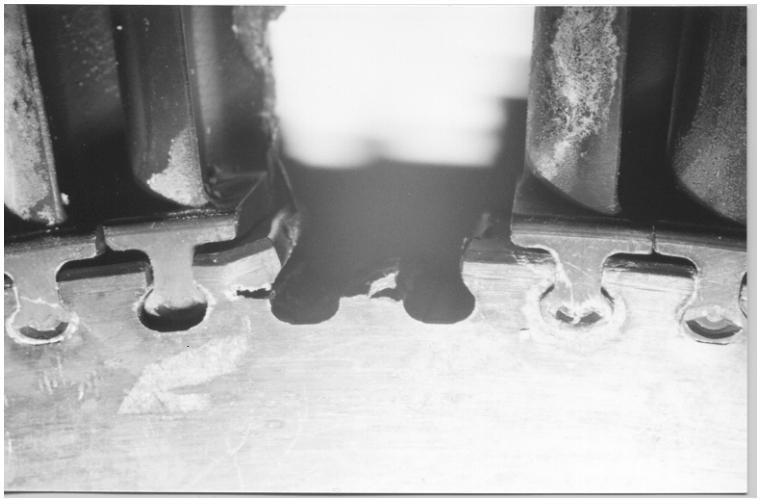

Additives - General recommendations (SIT)

- Ammonia as volatile alkalising agent
- Thermal deaeration, no oxygen scavenger

Customers (SIT)

- Industries – single cycle or combined cycle plants, many exporting steam with varying amounts of return condensate and make up water
- Small independent power producers
- Small to medium size utilities
  (often district heating units)

Organic additives are used in perhaps 50 % of the steam turbine units delivered by SIT (”Guestimate”)

Reasons:

- Requirements from industry using exported steam
- Insufficient in-house knowledge and/or outsourced cycle chemistry
- Local tradition
- (Remark: Different organic amines have been used for many years in nuclear PWR plants to reduce the rate of Flow Accelerated Corrosion)

Common potential disadvantages of organic additives and impurities

- Results in operation outside conventional guidelines for acid conductivity and often also for degassed acid conductivity (at least for “industrial” plants)
- Usually not possible to base supervision of steam chemistry on acid conductivity
- May also make it difficult to base supervision of steam chemistry on degassed acid conductivity

Dilemma (SIT)

- Many customers operating outside conventional guidelines for acid conductivity/degassed acid conductivity
- Many customers “forced” to use organic additives.
- We cannot abandon this market. Neither can we neglect the use of organic additives. (Not possible to reach the conventional targets for acid conductivity during the commissioning period).
- Customers are free to use what they want after end of warranty period
- Potential technical advantages of some organic amines

- **Conclusion – Adapt guidelines and requirements on supervision to reduce potential technical and commercial issues as far as possible**

Experiences of steam chemistry damages/failures (SIT)

- Our backyard is not filled with failed steam turbines although many customers operate with high acid conductivity due to organic decomposition products
- Severe failures in industrial units are usually due to steam contaminated with anions in sodium form like chloride, sulphate or hydroxide
- The most severe effect seems to be that the high background level for acid conductivity may mask ingress of aggressive sodium compounds in plants not supervising sodium online
- High acid conductivity may indicate increased risks for erosion corrosion/FAC in wet steam due to reduced pH.

Special features of SIT steam chemistry guidelines (2004)

- Na – online supervision required for all chemistries
- pH – requirements for steam, intermittent analyses
- Acid conductivity – Operation with values above “normal” limits allowed as long as it can be shown that Na is below limits and that pH is “high” enough
- Otherwise fairly conventional

- Experiences (“organics” for much more than 9 years)
- Debatable points
  - Consequences of halogenated organic compounds
  - “ammonium” chloride, “ammonium sulphate”

Acid conductivity in current and future guidelines
What is reasonable to expect?

- Increased acid conductivity due to carbon dioxide is today accepted by some guidelines up to a certain limit. Basis for this upper limit is unclear.
  - Opportunity for use of degassed acid conductivity
- Contribution from e.g. organic acids is usually not allowed
  - At least one major turbine manufacturer is considering to allow a moderate contribution from organic acids for PWR plants
- Indications of a some relaxation under the condition that it can be shown that high acid conductivity is not caused by ”traditional” aggressive impurities
- New types of online analytical instruments for aggressive anions may in the future be used as a complement to measurement of acid conductivity, allowing for contribution from less aggressive impurities to acid conductivity.

Fatigue limit ratio air/environment for 12% Cr steels (SIT 1975)

Environment	**pH**	**Fatigue limit ratio air/environment at 10^7 cycles**
Air	-	1
400 ppm NaOH	12	1.00
6% NaCl + NaOH + Na_2HPO_4	12	1.00
Distilled water	6-7	0.94
0.5% HAC* + NaOH	10	0.92
6% NaCl + NaOH	10	0.67
6% NaCl	7	0.47
35% NaOH	14	0.43
0.05% HAC	3.4	0.34
0.5% HAC	2.7	0.34
6% NaCl + HCl	3	0.30
6% NaCl + 0.5% HAC	2.7	0.29
6% NaCl + 0,05% HAC	3.4	0.26
6% NaCl + HCl	2	0.18

HAC seems less important than pH for corrosion fatigue of 12% Cr steels

SCC tests of rotor steels (SIT 1965-1990) in 6% NaCl + 0.5% HAC + H2S indicated long times to failure and no significant influence of HAC

Literature re Alternative Amines – industrial and conventional plants

- ETA (Field test at 140 bars/540 °C), VF* report 765
- ETA + MPA (Nalco 72310) at 780 MW triple pressure combined cycle plant (130 bar/35 bar/5 bar)
- ETA + MPA (Nalco 72310) used at combined cycle plant (100 bars/540 °C) for 10-12 years without significant problems. Condition – online monitoring of Na
- Thermal decomposition and alkalising effect of a number of organic amines have been investigated by tests in autoclaves (VF*-reports 655, 617, 503)
- Svoboda. R, The effect of Carbon dioxide and Organics in a Steam Turbine, PPChem 2009, 11(1), p 20-27

* VF = “Värmeforsk ≈ Swedish Thermal Research Assoc.