

***Consultancy Meeting on Update and Upgrade of IAEA-
TECDOC on Ageing Management of Steam Generators***

***The AREVA NP Strategy on
SG Design, Materials and
Secondary Side Chemistry of PWR Plants***

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The present lecture intends to give the fundamentals following the AREVA NP GmbH (ex-Siemens-KWU) philosophy for

SG aging management

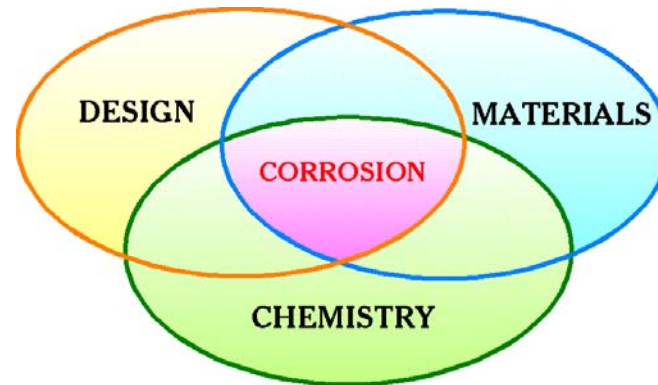
focusing on the chemistry aspects in correlation with

- ✓ *The SG design and material concept*
- ✓ *The balance of plant (BOP) design*

It includes

- ✓ *Features to prevent /minimize SG degradation*
- ✓ *Control of the SG condition to enable a situation-oriented maintenance*

> *The SG tubing corrosion depends of three factors, which must be simultaneously present:*

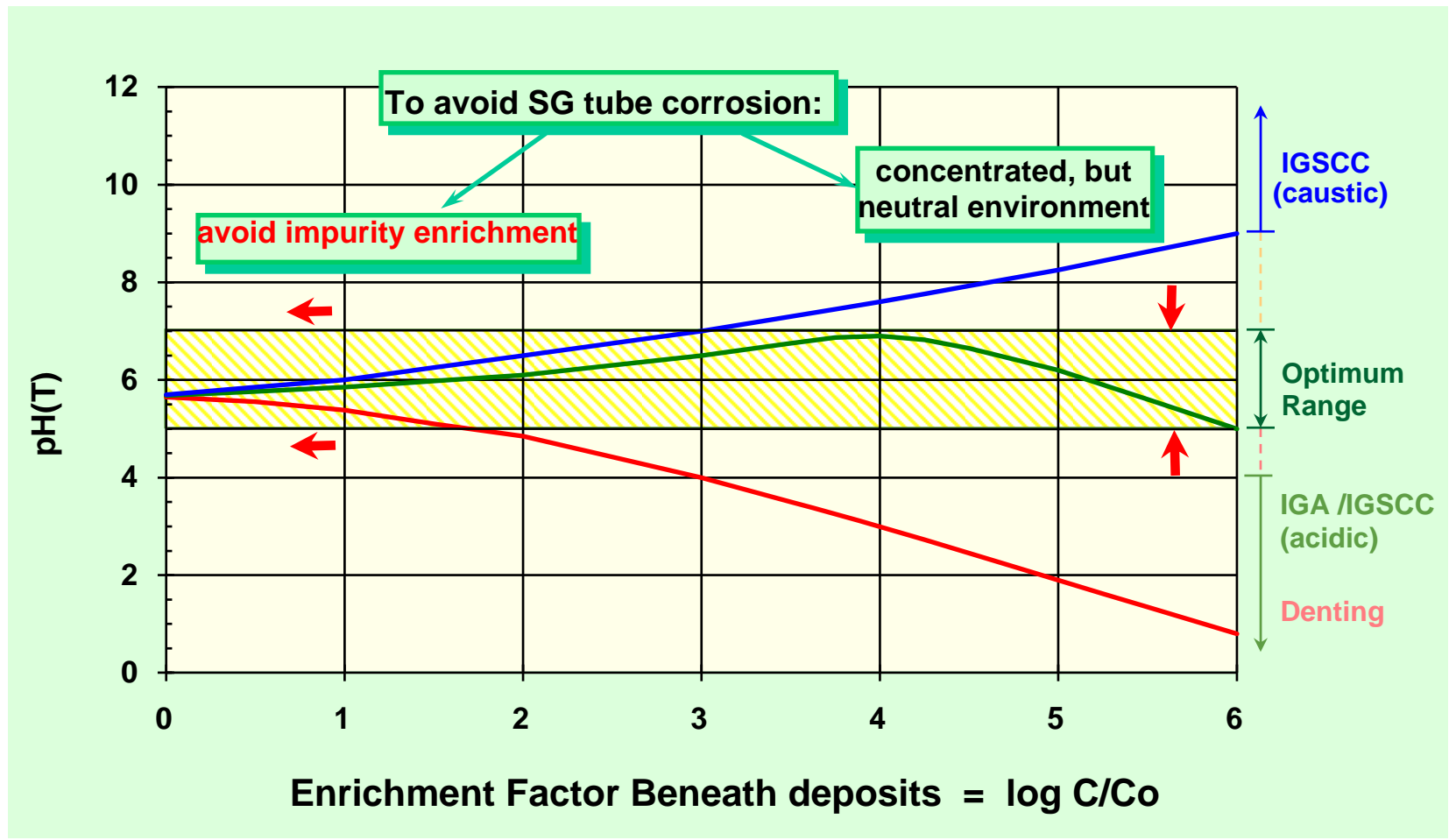


- *A good SG design and material concept reduces the SG tube corrosion risk even for different tube materials.*
 - *It enables a great relaxation of the chemistry operation conditions*
- *A good chemistry reduces the risk of corrosion if the design and materials is inadequate, but this alone cannot be effective to control corrosion processes.*

- > *The pre-requisite for the occurrence of SG tube corrosion is the accumulation of impurities in local points in contact with the tubes, associated with high temperatures.*
- > *An inadequate SG design will cause **corrosion products** to accumulate (mainly in TSPs),*
- > *Where corrosion products accumulate, local overheating may occur,*
 - *increasing the local temperature and*
 - *causing enrichment of the impurities dissolved in the SG bulk water up to unacceptable levels.*
- ➔ *Corrosion is likely to occur, almost independently of the tube material.*

Chemistry

Impurity Enrichment Beneath Deposits



Co: Impurity concentration in SG bulk water
C: Impurity concentration beneath deposits

- > *First priority: to reduce the **corrosion product** transport into the SGs*
 - *Pre-requisite for formation of aggressive environments*
- > *Second priority: to ensure **reducing conditions** in the SGs*
- > *Third priority: to minimize the ingress of **impurities** into the SGs*

In this order of importance

- > *This basic philosophy has been applied in German PWR NPPs,*
- > *Resulting in the **lowest SG tube corrosion history worldwide** among all plants operating with similar operation conditions (temperature been an important factor)*
 - *Wastage in the 70s (phosphate chemistry)*
 - *From then (AVT, high AVT): almost no corrosion-related SG tube damage*
 - *Negligible or no SCC, IGA, in 35 years*
 - *No denting at tube supports*
 - *Isolated cases of few tube sheet denting*

> The areas where deposit accumulation and subsequent impurity concentration may occur are mainly three:

- a) tube to tube separator intersections*
- b) tube sheet,*
- c) U-bend area, anti-vibration bars.*

in this order of importance.

> Tube to tube separator intersections

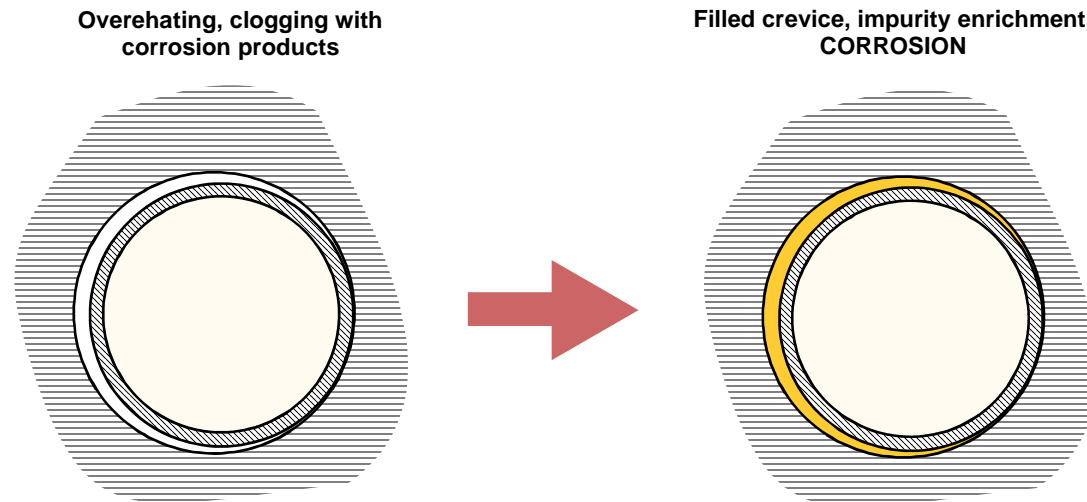
- Drilled hole plates*
- Broached hole plates*
- Egg crate-type grids*

> **Drilled hole tube supports**

- *Corrosion product deposition*
- *Strong increase of the local temperature due to lack of water circulation outside the tube.*
- *Local boiling conditions leading to dry-out of the area and enrichment of impurities in there.*

➔ **Corrosion**

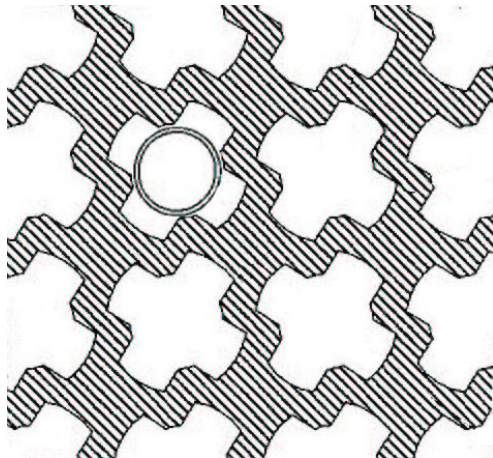
Main cause of tube degradation at tube support levels



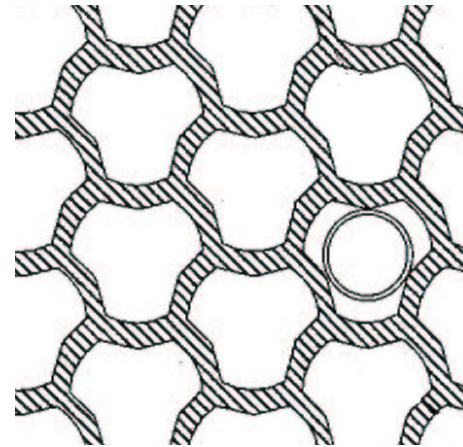
> **Broached hole tube supports**

- *No local overheating*
- *Less or no enrichment of impurities*
 - *Better corrosion behaviour*
- *Depending on the design, more or less susceptibility to deposit accumulation and eventually **clogging of the broached holes***
 - *Predominantly hot leg clogging (experience)*
 - *Perturbation of the SG internal hydrodynamics*
 - *Change of the recirculation rate*
 - *Increase of local flow velocities*
 - *Flow-induced fretting*
 - *Flow-assisted corrosion (C-steel plates)*
- *Design:*
 - *Quatrefoil or trefoil*
 - *Concave, straight or convex surfaces in contact with the tube*
 - *Square or triangular pitch*

Quatrefoil, square pitch



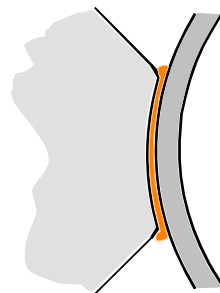
Trefoil, triangular pitch



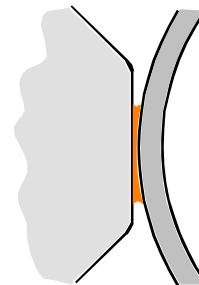
CP accumulation



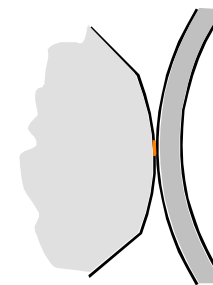
Good design



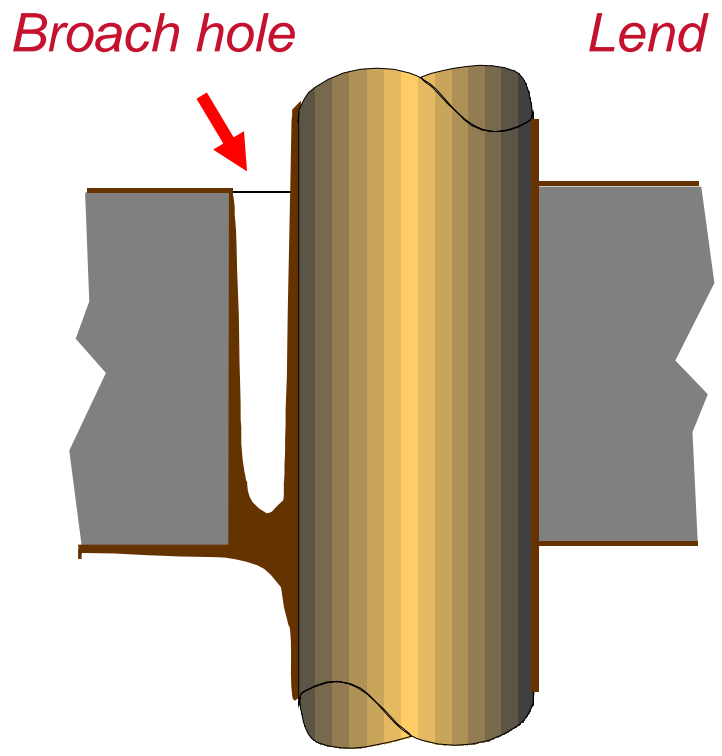
Concave lend



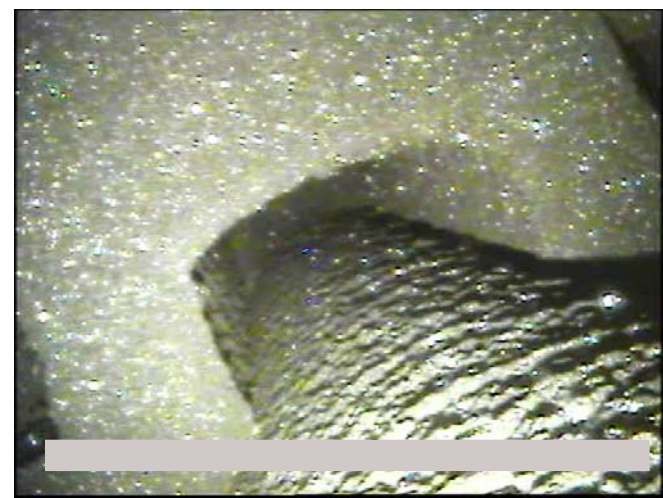
Straight lend



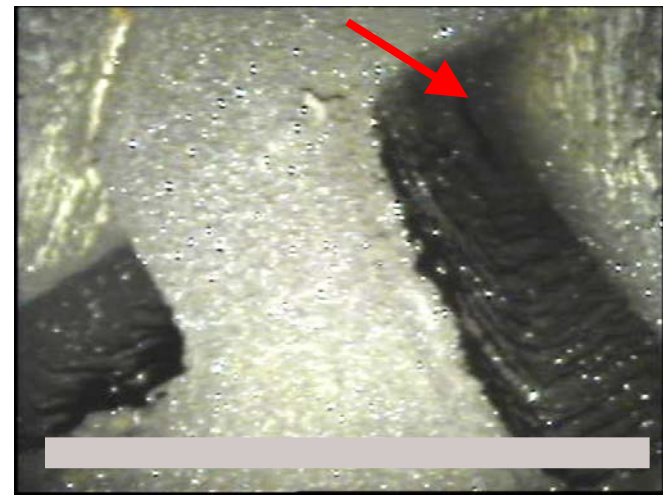
Convex lend



Clogged broach upper view

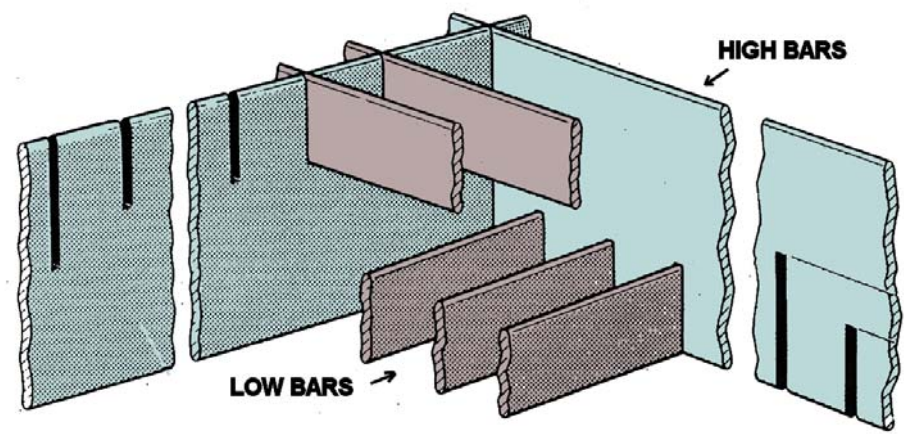
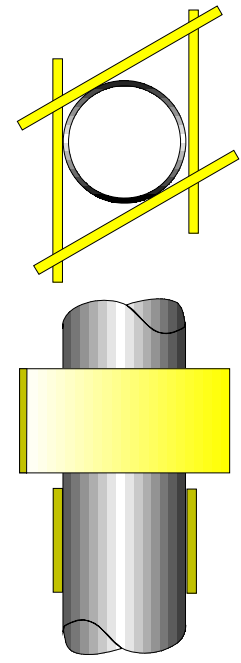


Partially clogged broach



> Egg crate-type grid supports

- From the chemistry point of view, the best choice.
- Reasons:
 - There are only two points in contact with the tube at a given level
 - The tube surfaces are better exposed to the SG bulk water, no overheating and/or deposit accumulation.
- ➔ No or negligible corrosion damage in more than 30 operation years

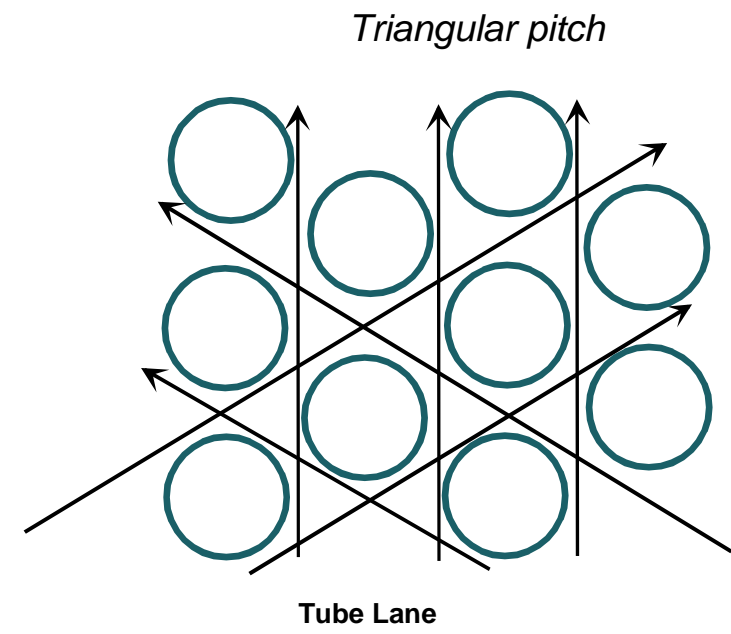
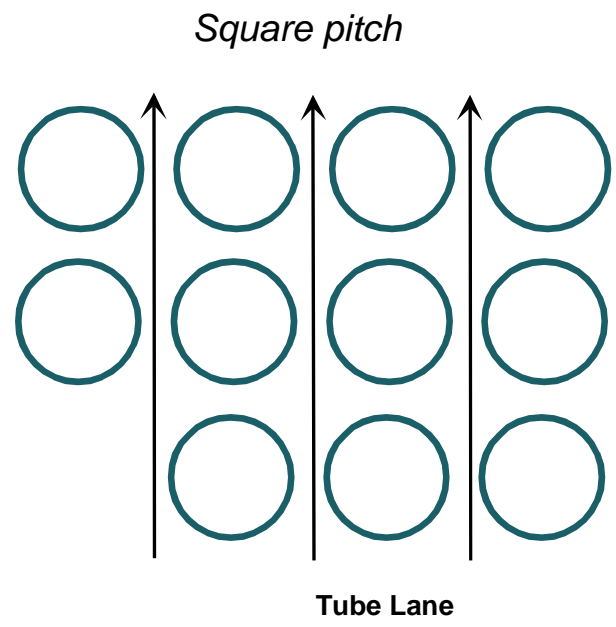


> **Tubesheet – the weakest point**

- *Accumulation of corrosion products on the tube sheet can be minimized by design by adequate design of the SG*
 - *Maximize the radial flow velocity to reduce deposition of corrosion products at the maximum extent.*
 - *Tube arrangement enabling efficient tube sheet cleaning*
- *Anyway, the main ways to reduce the accumulation of deposits on the TS are:*
 - *operate at a high feedwater pH.*
 - *minimize the corrosion product ingress during start-up transients*
 - *adequate SG and BoP system layout during outages*
 - *Tube sheet lancing*

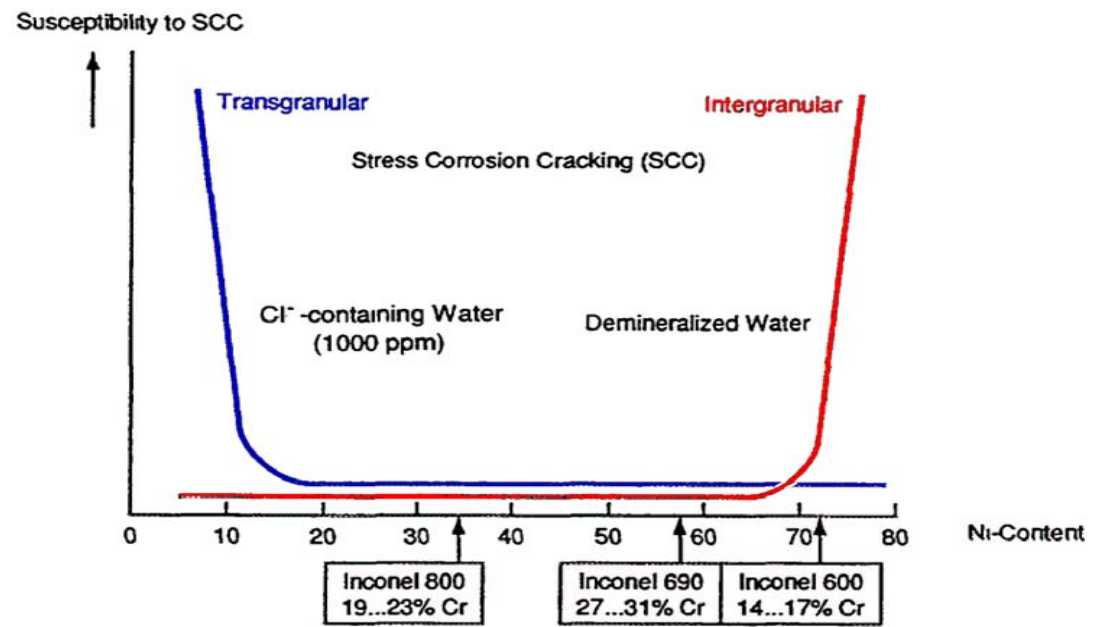
Tubesheet (cont'd)

- Once deposited, the corrosion products must be removed by TS lancing each shutdown.
- A tube arrangement with square pitch cannot be cleaned as thoroughly as those arranged with triangular pitch. In the later case, with an adequate cleaning tool the perimeter of the tube can be cleaned almost completely.



> Tube Material:

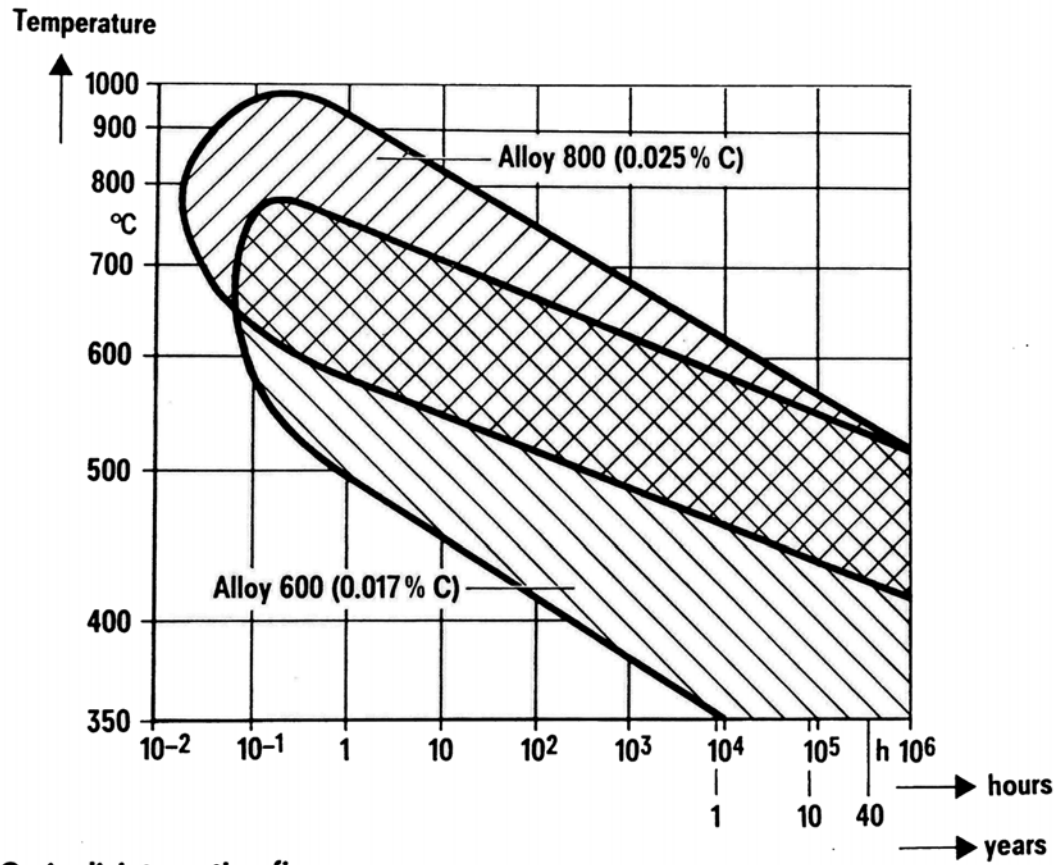
- Based on the negative results observed with 1600 other alloys were selected: 1800 and later 1690 as candidate materials.
- Both of them are in the region where the probability of either chloride-induced transgranular SCC or caustic-induced intergranular SCC is low. Both materials have to now a good operative experience.



From Coriou 1971, as reported by Berge 1993.

Comparison of Candidate Materials for SG Tubes

Sensitization Behaviour

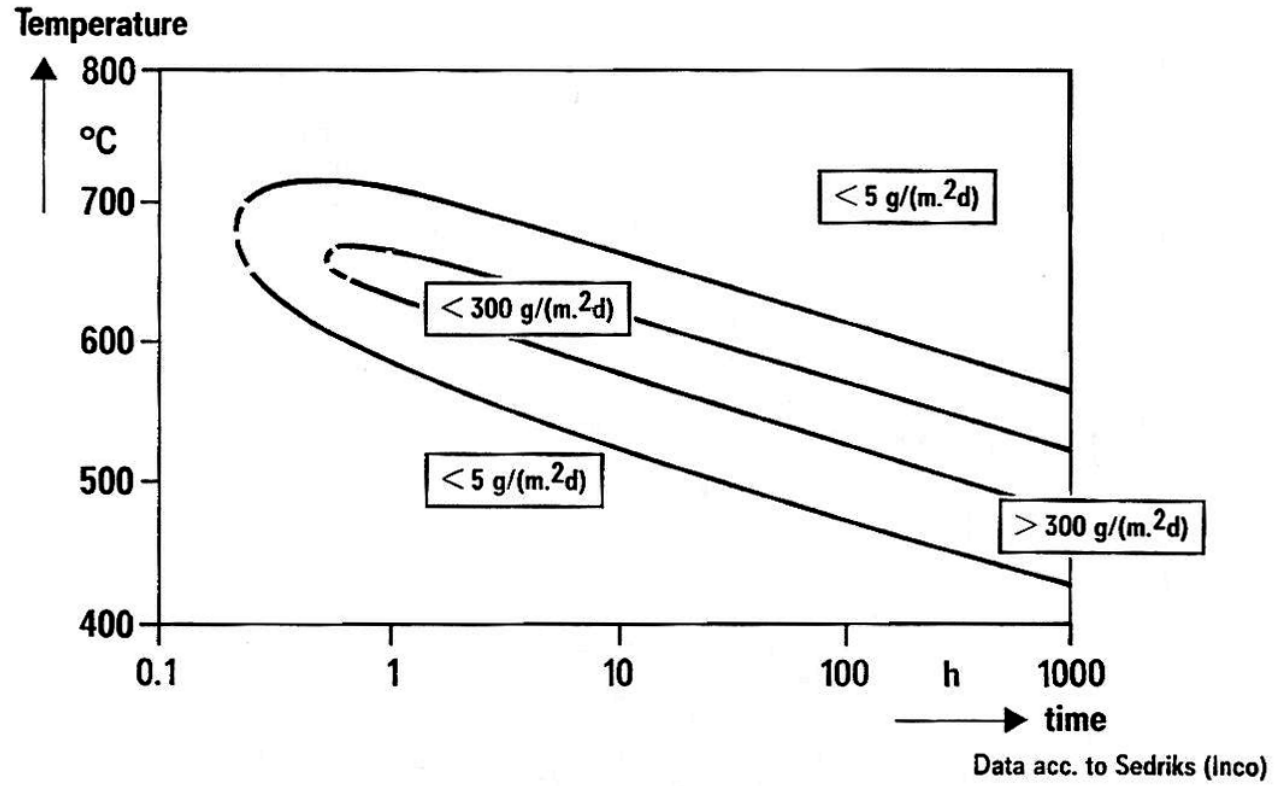


Grain disintegration figure

Alloy 800 (test in copper-sulfate sulfuric-acid-solution)
 Alloy 600 (test in iron [III]-sulfate sulfuric-acid-solution)

Alloy 600 can sensitize at PWR operating temperature.
No in-service sensitization in Alloy 800

Sensitization Behaviour



Time-Temperature-Sensitization diagram for Alloy 690

(Heat T-57177, 0.05% C in boiling 65 percent nitric acid material solution annealed 1h @ 1150°C/WQ)

Alloy 690 TT is desensitized

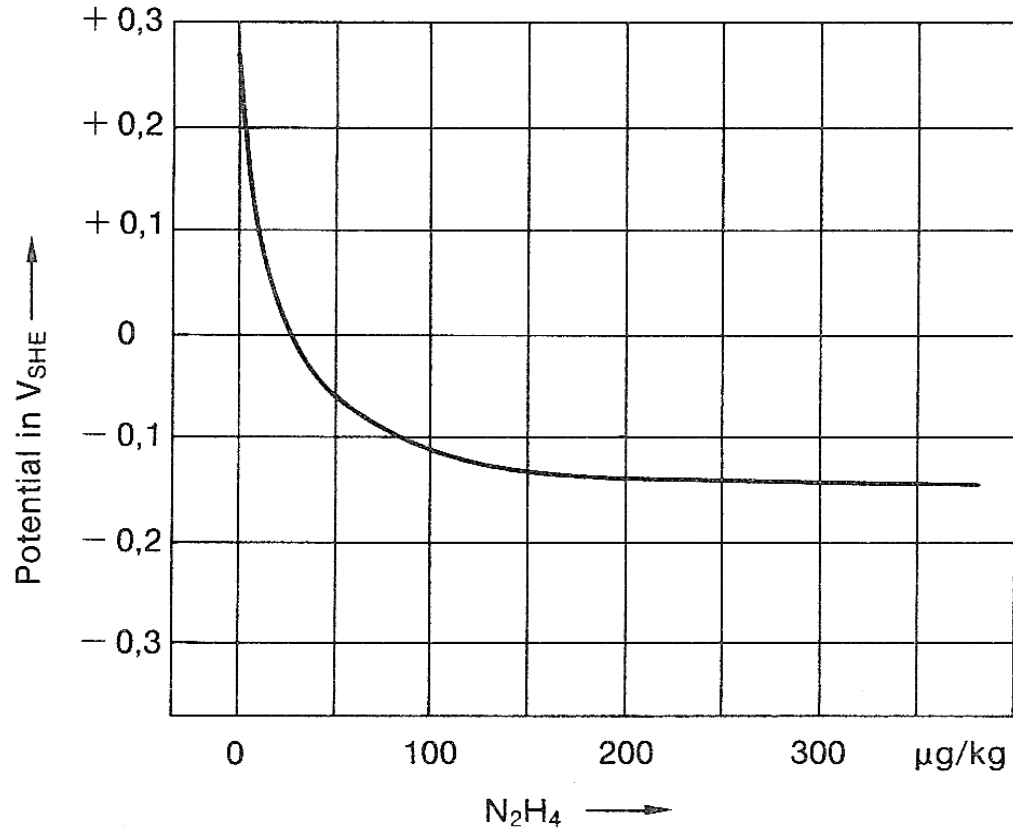
Minimization of corrosion product transport

- > *Main sources of corrosion products during operation:*
 - *General corrosion of C-steels*
 - *FAC*
- > *Answer: high pH by conditioning with an alkalizing agent*

Assurance of reducing conditions

- > *High hydrazine*
- > *Since hydrazine decomposes thermally at operation temperature, both objectives are bonded together*
 - *To maintain sufficient reducing conditions, considerable amounts of ammonia will be generated*

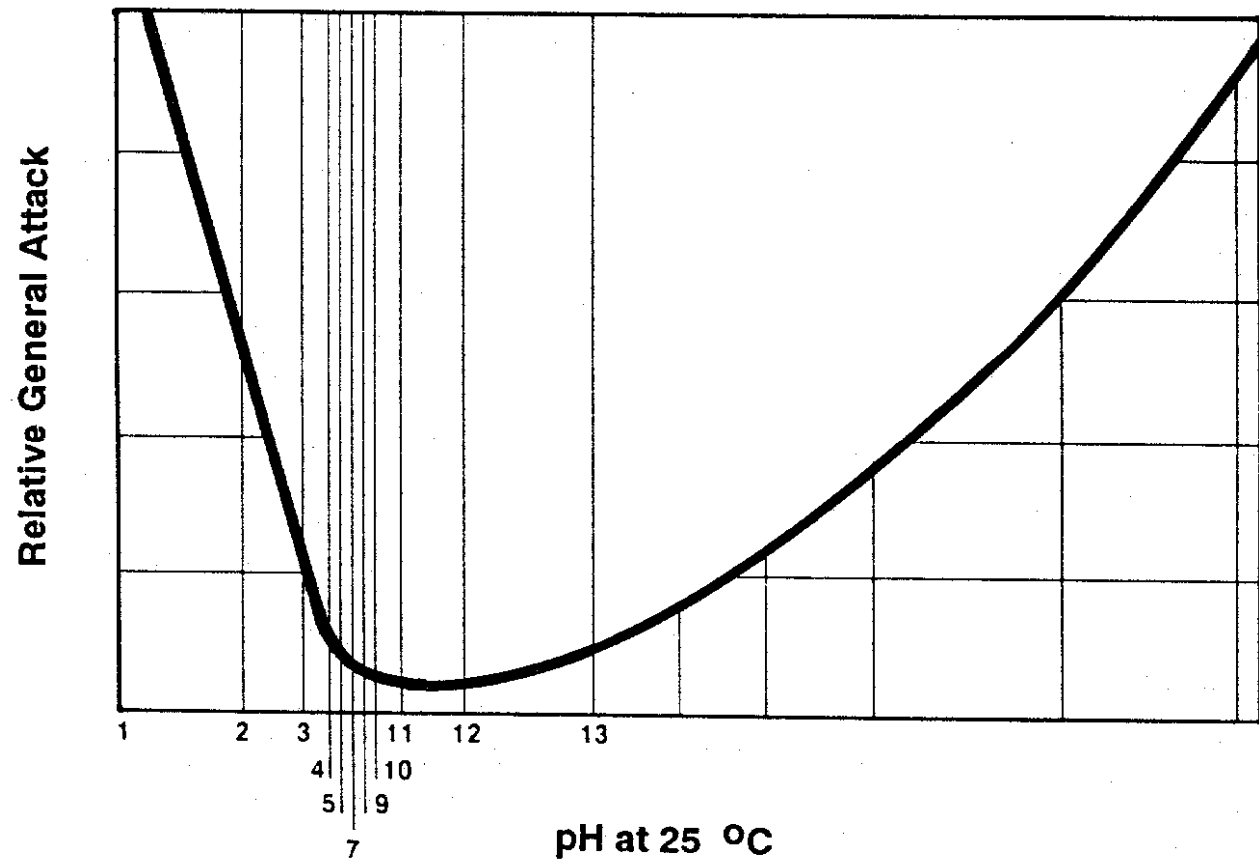
> 80 -120 $\mu\text{g N}_2\text{H}_4$ /kg are required



J. Haag et al.: On-line-Messung von Redox- und Korrosionspotentialen in Wasser für DWR-Dampferzeuger
Sammelband VGB-Konferenz „Chemie im Kraftwerk 1988“

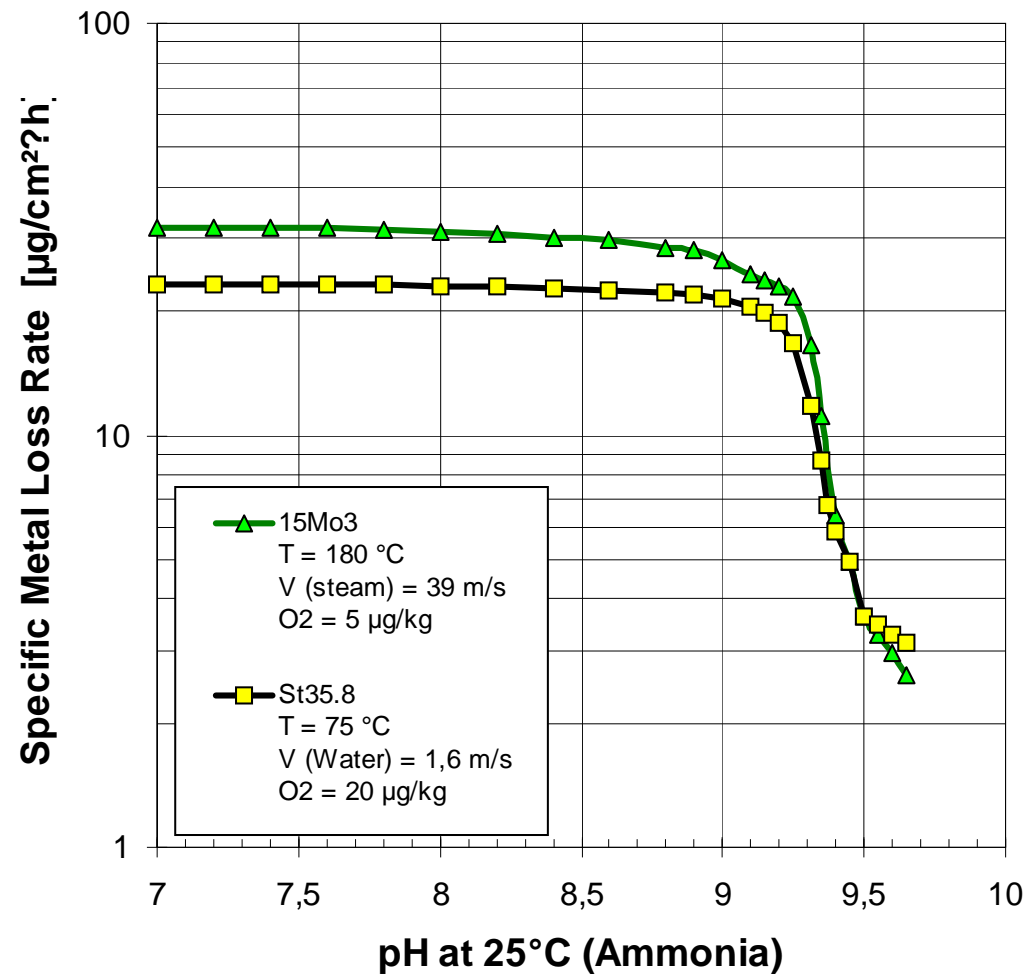
> Which pH is necessary?

General Corrosion of Carbon Steel as Function of pH



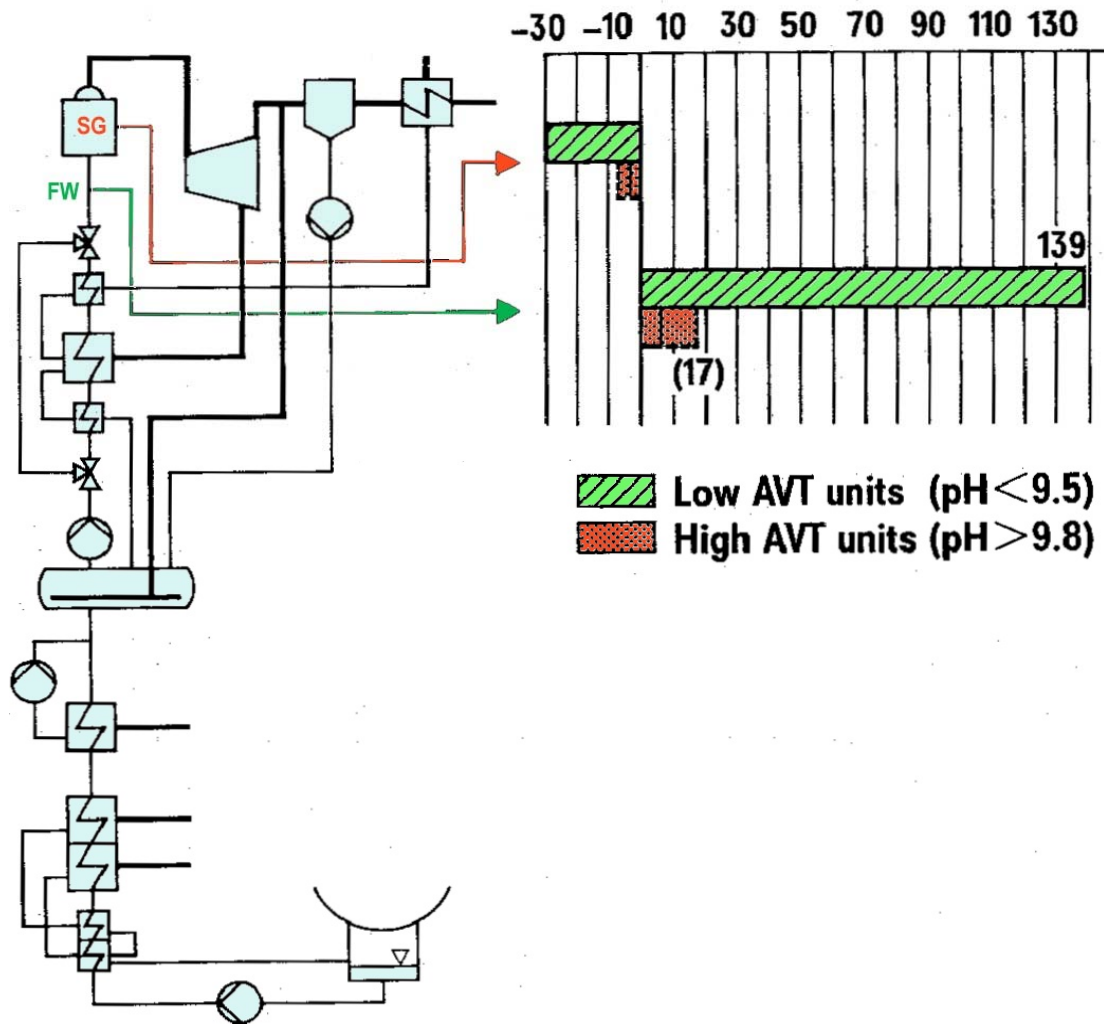
> Which pH is necessary?

Influence of pH in the FAC rate (Benson tests, Siemens-KWU)



- > *To minimize FAC, a pH (190°C) > 6,45 in the water film in contact with the C-steel surfaces is necessary*
 - *190°C being a typical temperature at the wet steam areas (T_{ws}) of the secondary circuit*
 - > *If ammonia is the alkalizing agent, this corresponds with a pH (25°C) > 9,45 in the water film*
 - > *The ammonia concentration corresponding with this pH is ~1,5 ppm.*
 - > *Making an ammonia mass balance in the circuit, it results that the ammonia concentration in feed water must be close to 10 µg/kg*
- $pH_{FW} > 9,8$**

Measured corrosion product rates in g/h



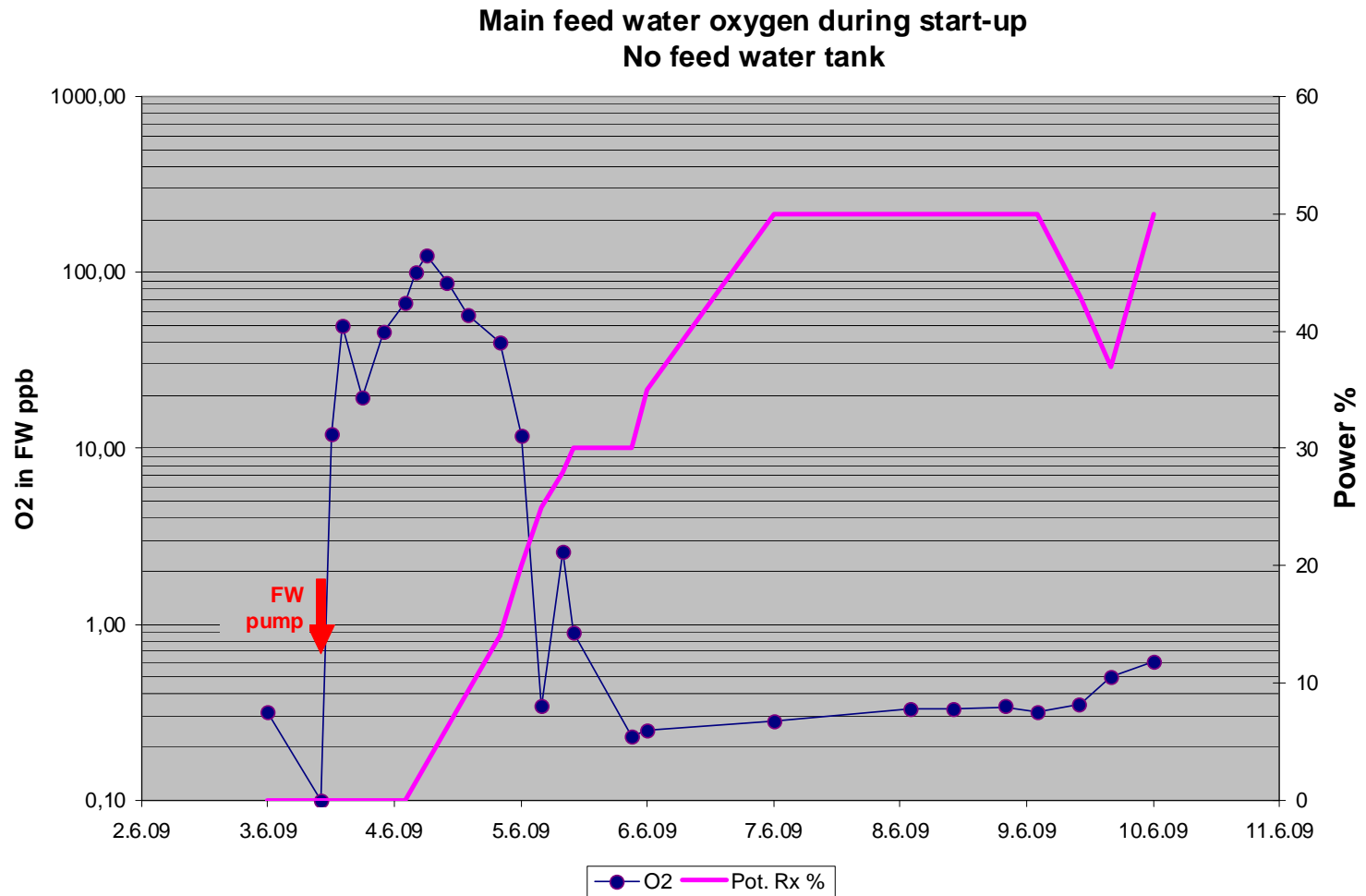
- > *The presence of ammonia cannot be avoided, since there is always a need of keeping a high hydrazine concentration in feedwater close to 80-120 µg/kg to ensure reducing conditions.*
- > *This will necessarily produce ammonia in a considerable extent, high enough to achieve the target pH.*
 - ➔ ***Ammonia cannot be replaced by an “alternative” amine***
- > *Anyway, in the case that it would not be possible to keep pH by only the ammonia generated by thermal decomposition of hydrazine, then either*
 - *additional ammonia, or*
 - *another amine (morpholine, ETA)*

shall be dosed
- > *Drawback of alternative amines: Increase of the cation conductivity in the system, masking the chemistry supervision.*

- > The need of maintaining reducing conditions using hydrazine obliges to adapt the BOP system design
 - **Absence of Cu alloys**
- > The use of low alloyed **Cr Mo carbon steels** is advisable for FAC minimization.
- > To ensure reducing conditions during the start-up transient: **Feed water de-aerator**
 - If not available: **condenser hotwell steam sparging** to reduce O₂ solubility during start-up
- > For impurity reduction:
- > **Tight condenser**
- > **Minimization of the make-up water** amount through SG blowdown recuperation
- > **No condenser polishers!**
 - Or very careful CPS design and operation

Balance of Plant Design Absence of FW Deareator Tank

> Oxygen at start-up when the FW pumps are started (water from condenser)



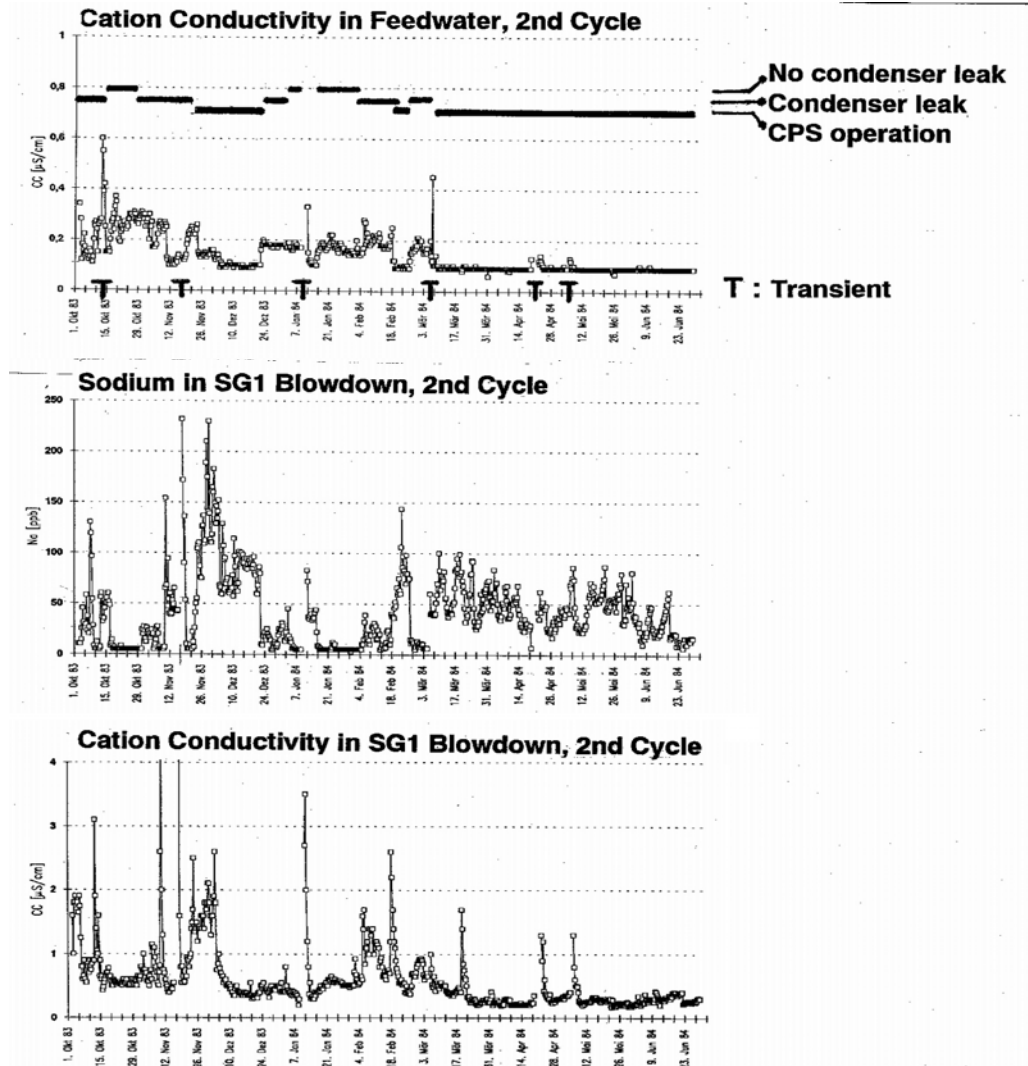
> Condenser polishing operation experience:

Elution of free caustic from the CPS.

- Low cation conductivity

but

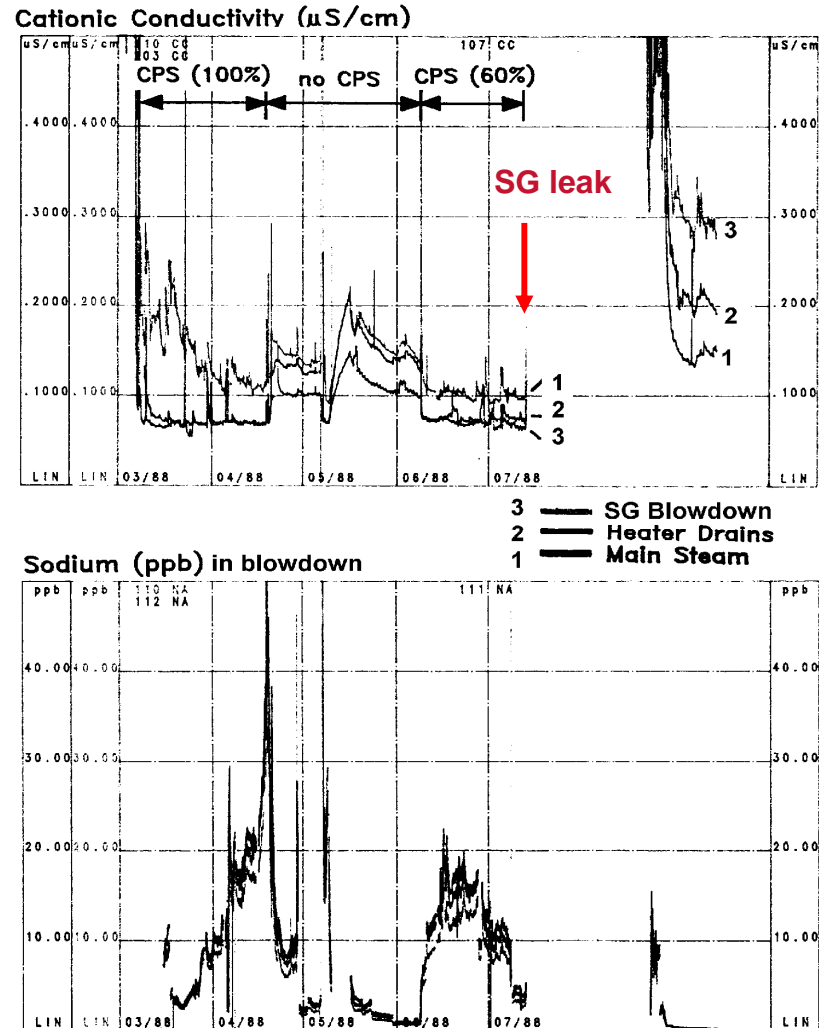
- Increase of Na concentration



> Faulty operation of the condenser polishing

Elution of free caustic from the CPS caused a SG leak. Consequence:

- ~ 500 SCC indications,
- ~ **350 tubes plugged!**
- Low cat. Cond. but
- Increase of Na concentration



When There is Good Harmonization with Design

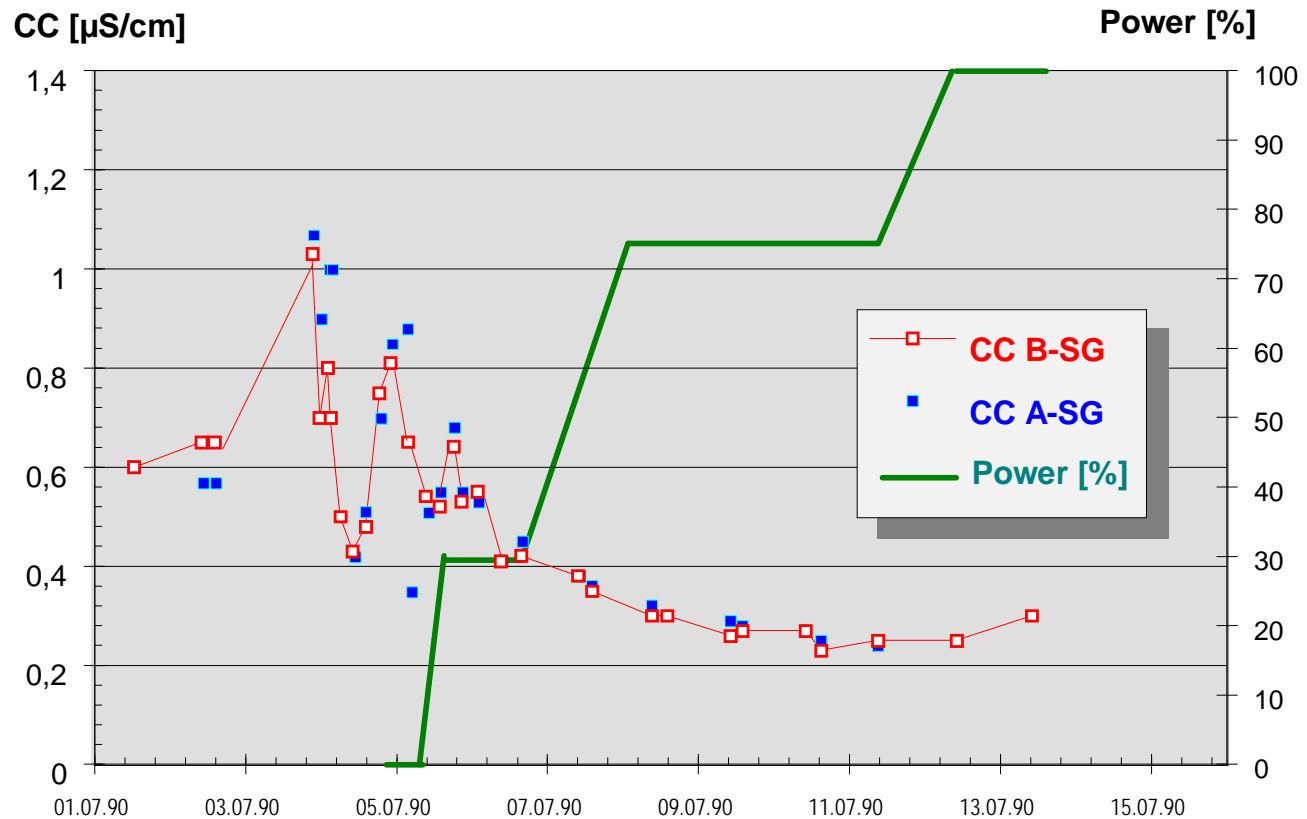
- > A good SG and BOP design will result in positive changes of the chemical behaviour of the plant
- > Hideout will almost not occur.
 - Ingress via feedwater = Removal via blowdown, or

$$\mathbf{CFW \cdot FFW = CBD \cdot FBD}$$
 (if FFW increases and FBD ; CFW are constant, then CBD increases)
- > The *incoming impurities are quantitatively eliminated by blowdown.*
- > The impurity concentration in SG blowdown will be in general higher than before, at the same feedwater quality.
- > Limitations of impurity concentration at start-up, like the usual limitation of SG blowdown cation conductivity to power >30%, doesn't make sense anymore. Higher CC at start-up may become usual.

Dependence of chemistry Behaviour with SG Design

Plants having SGs susceptible to hideout: a clear decrease of impurities with power increase is observed, indicative of strong hideout.

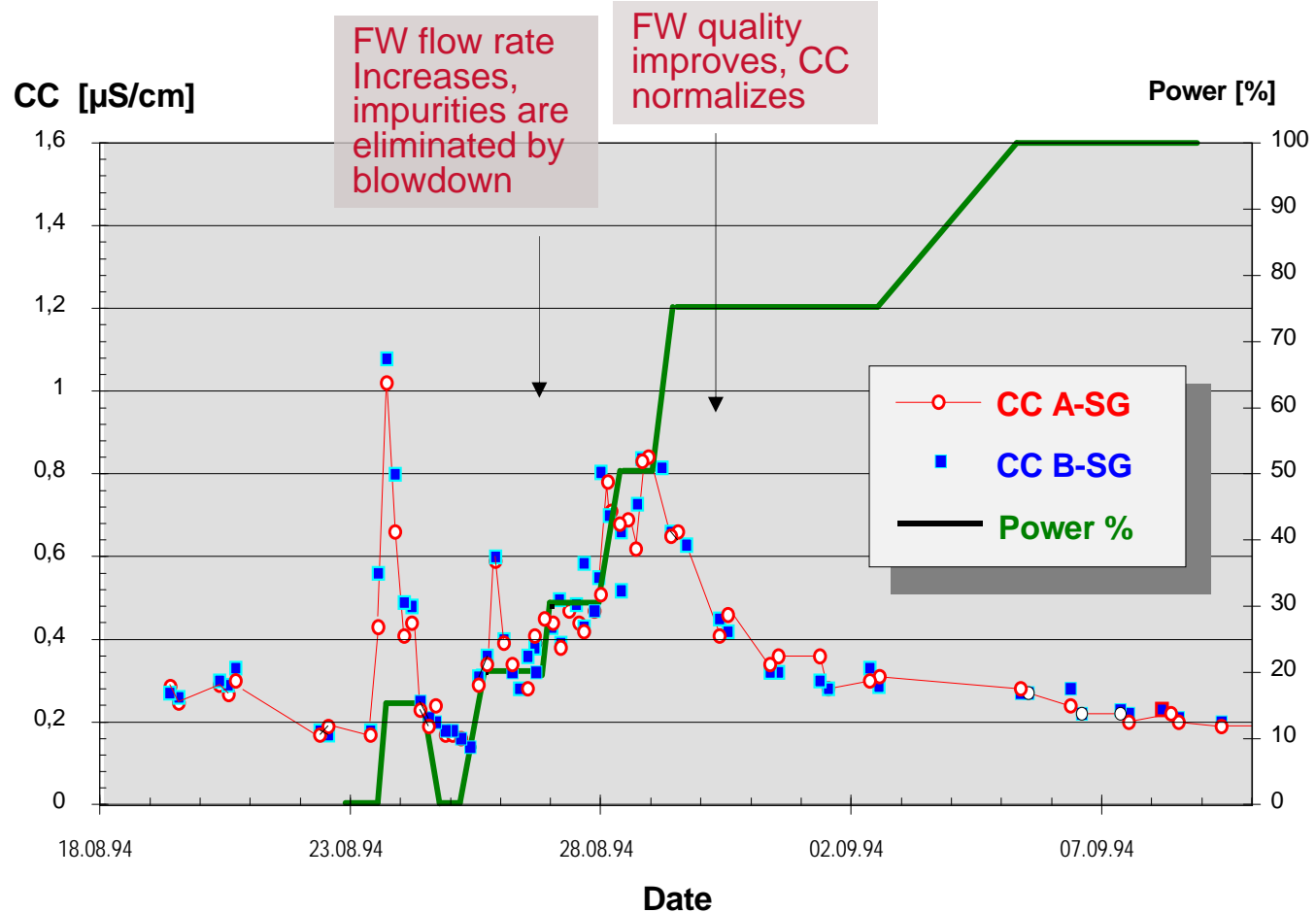
Plant with SG of the old type (CC decreases with power-up → hideout)



Dependence of chemistry Behaviour with SG Design

During plant power-up, when the FW flow rate increases, an increase of the impurity concentration in SG blowdown will occur.

Plant with SG of the new type (CC increases with power-up, → no hideout)



Dependence of Chemistry Control with SG Design

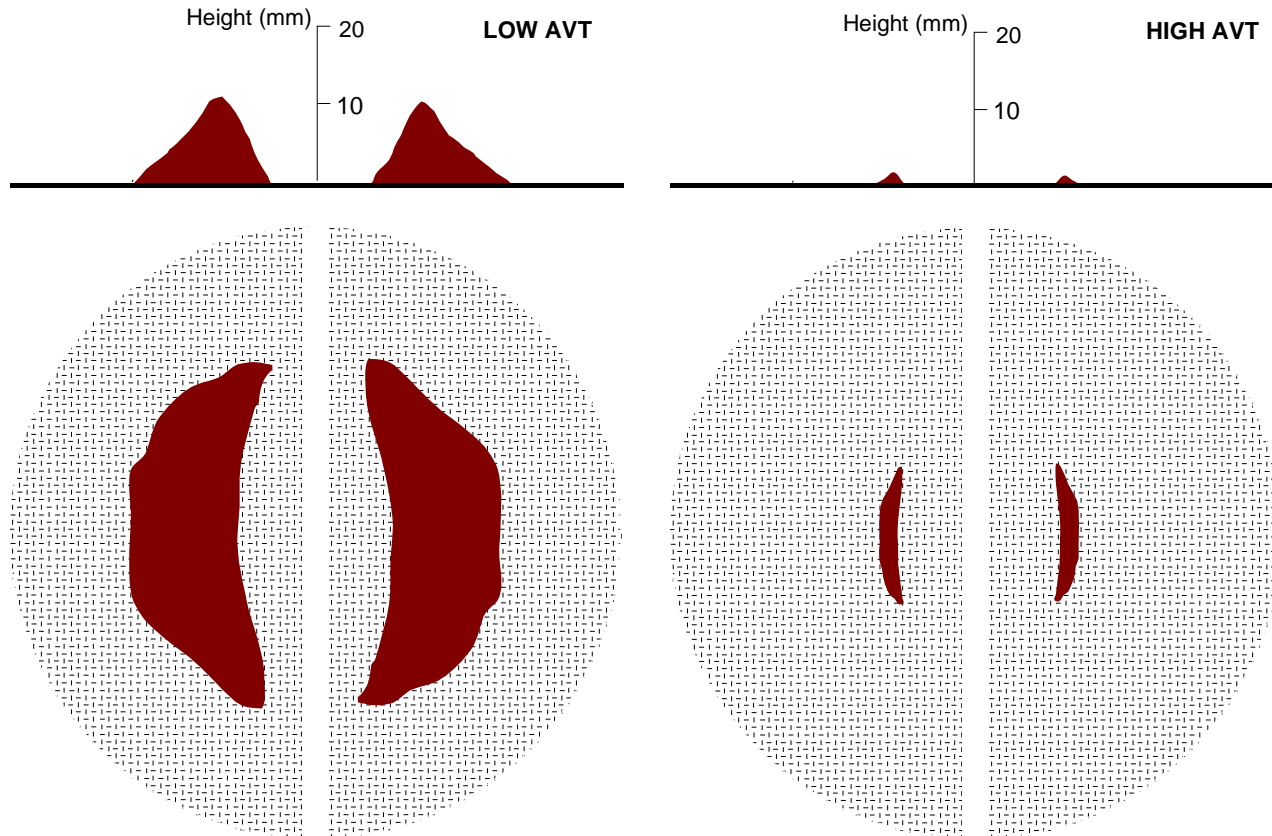
For plants with adequate SG and BOP design, the following can be concluded regarding chemistry:

- > The only location still having some SG tube corrosion risk is the tube sheet*
 - *Accumulation of deposits*
 - *Enrichment of impurities beneath deposits*
- > The first priority of the chemistry supervision must be the minimization of corrosion product transport to the SGs.*
- > The possible degradation mechanisms at the tube sheet level are:*
 - *Tube sheet denting*
 - *Stress corrosion cracking*

in the zones of deposit accumulation.
- > The corrosion product transport occurs not only during power operation (effectively controlled by high pH), but also during start-up transients*
 - *Careful cleanup of the feedwater train before start operation of the FW pumps*

High AVT and clean start-up transients

- ➔ *Less deposits*
- ➔ *Less tubes involved*

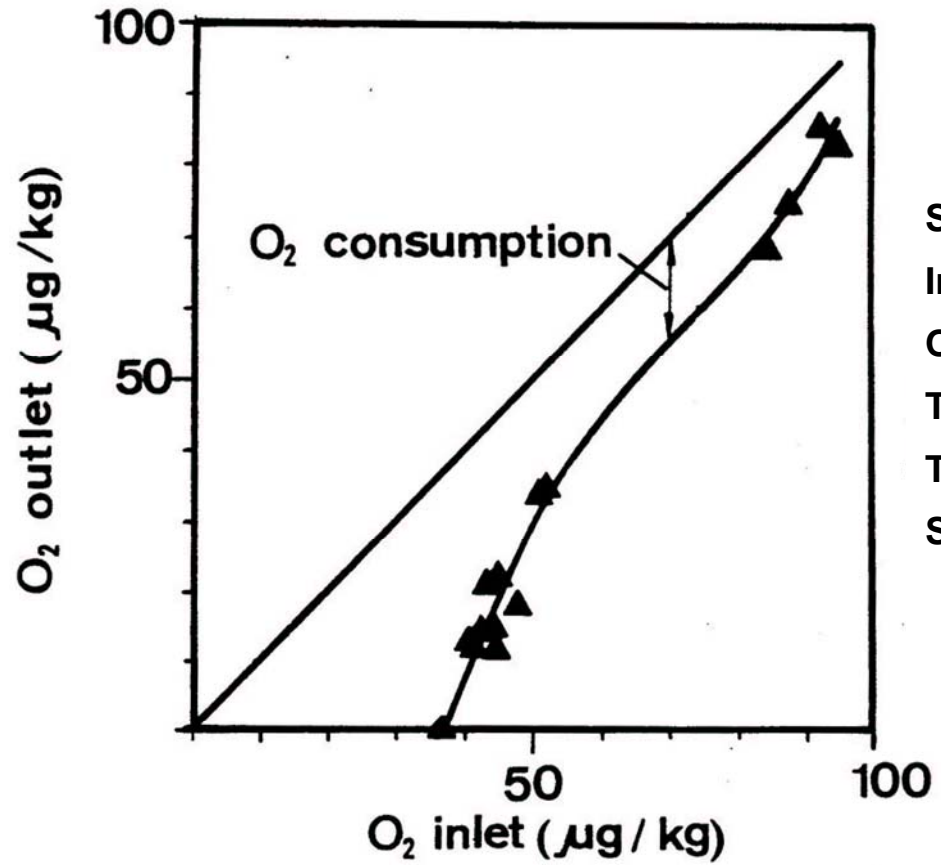


- > *The **second high priority** is the maintenance of **reducing conditions** in the SGs*
 - *Power operation*
 - *Shutdown condition*
 - *Start-up transients*
- > *Power operation: high hydrazine*
- > *Shutdown condition. Wet layup with hydrazine*
- > *Start-up transients: this requires special care since the absence of FW de-aeration tank and difficulty for maintaining O₂ concentration in the condenser hotwells causes O₂ peaking when the FW pumps are started. Improvements are advisable.*
 - *Redox potential measurement*
 - *Hardware. Hotwell steam sparging*
 - *Operational measures ?(adaptation of operation procedures)*

- > *Hotwell steam sparging*
 - *Main cause of high O₂ in condenser hotwells prior to power operation is the sub-cooled condition of the water.*
 - *By steam sparging the hotwell can be brought to saturated condition where the solubility of gases is zero*

- > *Redox potential measurement in final feed water*
 - *The O₂ measurement in final feedwater may not be sufficient*
 - *Oxygen consumption in the sampling line may lead to an underestimation of the measured value*
 - *Redox potential measurement makes visible variations due to changes of the O₂ concentration in condenser which are not detected by measurement of O₂ in feedwater*
 - *RP measurement will permit an optimization of the hydrazine dosing*

O₂ measurement in feedwater is normally affected by a defect error



- Sampling tube material: SS
- Inlet sample Temp.: 220 °C
- Outlet sample Temp.: 195 °C
- Tube length: 60 m
- Tube inner diameter: 8 mm
- Sample linear flow rate: 0,13 m/s