

LCC₃ Annual Report

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Acronyms and explanations

5-AP	5-Aminopentanol
AECL	Atomic Energy of Canada
AkIGC	(Alkaline) Intergranular Corrosion
AkSCC	Alkaline (or caustic) SCC
ALARA	As Low As Reasonably Achievable
AM	Anion Membrane
ANT	Advanced Nuclear Technology
AOA	Axial Offset Anomaly
AR	Annual Report
ASSCC	SCC in alumino-silicate surface chemistry
ASTM	American Society for Testing and Materials
ATEM	Analytical Transmission Electron Microscope
AVT	All Volatile Treatment
B&W	Babcock & Wilcox
BAT	Boric Acid Treatment
BDD	Boron Doped Diamond
BMI	Bottom Mounted Instrumentation
BOP	Balance of Plant
BRAC	BWR Radiation Assessment and Control
BWR	Boiling Water Reactor
CANDU	Canadian Deuterium Uranium
CE	Combustion Engineering
CGR	Crack Growth Rate
CIPS	Crud Induced Power Shifts
ClSCC	Chloride Stress Corrosion Cracking
CM	Cation Membrane
COD	Chemical Oxygen Demand
COG	CANDU Owners Group
CPS	Condensate Polishing System
CRDM	Control Rod Drive Mechanism
CRUD	Chalk River Unidentified Deposits
CST	Condensate Storage Tank
CT	Compact Tension
CuSCC	Copper Acidic SCC
DH	Dissolved Hydrogen
DMA	Dimethylamine
DWST	Demineralised Water Storage Tank
DZO	Depleted Zinc Oxide
EAC	Environmentally Assisted Cracking
EBA	Enriched Boric Acid
EC	Erosion Corrosion
ECP	Electro Chemical Potential
ED	Electrodialysis
EDBM	Electrodialysis with Bipolar Membranes
EDI	Electro-Deionization
EDTA	Ethylene Diamine Tetra Acidic Acid
EPFY	Equivalent Full Power Years
EMF	Electro Magnetic Filter
EOC	End Of Cycle
EPRI	Electric Power Research Institute
ETA	Ethanolamine
FAC	Flow Accelerated Corrosion
FAD	Failure Assessment Diagram

FDE	Full Depth Explosive
FDH	Full Depth Hydraulic
FDR	Full Depth Roll
FOI	Factor of Improvement
FRED	Fuel Reliability Data Base
FRP	Fuel Reliability Program
FW	Feedwater
GC	General Corrosion
GE	General Electric
HAVT	High All Volatile Treatment
HHC	Hydrogen and Hydrazine Chemistry
HP	High Pressure
HPU	Hydrogen pickup
HPUF	Hydrogen PickUp Fraction
HPSCC	High Potential SCC
HWC	Hydrogen Water Chemistry
IGA	Intergranular Attack
IGC	Intergranular Corrosion
IGSCC	Intergranular Stress Corrosion Cracking
INPO	Institute of Nuclear Power Operations
JAPC	Japan Atomic Power Company
JNES	Japan Nuclear Energy Safety Organization
KKP	KernKraftwerk Philippsburg
KKM	KernKraftwerk Mühleberg
KR	Kiss Roll
KWU	KraftWerkUnion
LCC	LWR Coolant Chemistry
LOCA	Loss of Coolant Accident
LP	Low Pressure
LPSCC	Low Potential SCC
L-SIP	Laser Stress Improvement Process
LWR	Light Water Reactor
MA	Mill Annealed
MHI	Mitsubishi Heavy Industries
MOX	Mixed Oxide
MPA	Methoxypropylamine
MRC	Molar Ratio Control
MSLR	main steam line radiation
NDE	Non Destructive Examination
NG	Nuclear Grade
NMC	Noble Metal Chemistry
NMCA	Noble Metal Chemical Addition
NPP	Nuclear Power Plant
NSSS	Nuclear Steam Supply System
NWC	Normal Water Chemistry
OD	Outer Diameter
OEM	Original Equipment Manufacturer
OLNC	On Line NobelChem
OrSCC	Organic SCC
OTSG	Once Through Steam Generator
PAA	Polyacrylic Acid
PbSCC	Lead Induced Stress Corrosion Cracking
PDR	Part Depth Roll
PWR	Pressurized Water Reactor
PWSCC	Primary Water Stress Corrosion Cracking
RCP	Reactor Coolant Pumps

RCS	Reactor Coolant System
RFA	Robust Fuel Assembly
RFO	Refuelling Outage
RFQ	Request of Quotation
RSG	Re-circulating Steam Generator
RUB	Reversed U-Bend
RWCU	Reactor Water Clean-Up
SCC	Stress Corrosion Cracking
SG	Steam Generator
SGOG	Steam Generator Owners Group
SHE	Standard Hydrogen Electrode
SNOC	Southern Nuclear Operating Co.
SS	Stainless Steel
SSRT	Slow Strain Rate Test
STP	South Texas Project
Sy-SCC	Reduced Sulfur SCC
TEPCO	Tokyo Electric Power Company
TKS	Condensate Anode Cathode
TMI	Three Mile Island
T _p	Primary Side Temperature
TR	Technical Requirements
T _s	Secondary Side Temperature
TSP	Tube Support Plate
TT	Thermally Treated
TTS	Top of Tube Sheet
TXU	Texas Utilities Electric Co.
UFC	Ultrasonic Fuel Cleaning
USNRC	US Nuclear Regulatory Commission
USP	Ultrasonic Shot Peening
VEGP	Vogtle Electric Generating Plant
VCT	Volume Control Tank
VHN	Vickers Hardness Number
VVER	Voda Voda Energo Reactor (Russian type PWR)
WJP	Water Jet Peening
ZIRAT	Zirconium Alloy Technology
ZTF	Zero Tolerance for Failure

Unit conversion

TEMPERATURE		
$^{\circ}\text{C} + 273.15 = \text{K}$		
$^{\circ}\text{C} \times 1.8 + 32 = ^{\circ}\text{F}$		
T(K)	T($^{\circ}\text{C}$)	T($^{\circ}\text{F}$)
273	0	32
289	16	61
298	25	77
373	100	212
473	200	392
573	300	572
633	360	680
673	400	752
773	500	932
783	510	950
793	520	968
823	550	1022
833	560	1040
873	600	1112
878	605	1121
893	620	1148
923	650	1202
973	700	1292
1023	750	1382
1053	780	1436
1073	800	1472
1136	863	1585
1143	870	1598
1173	900	1652
1273	1000	1832
1343	1070	1958
1478	1204	2200

MASS	
kg	lbs
0.454	1
1	2.20

Radioactivity	
1 Sv	= 100 Rem
1 Ci	= 3.7×10^{10} Bq = 37 GBq
1 Bq	= 1 s^{-1}

DISTANCE	
x (μm)	x (mils)
0.6	0.02
1	0.04
5	0.20
10	0.39
20	0.79
25	0.98
25.4	1.00
100	3.94

PRESSURE		
bar	MPa	psi
1	0.1	14
10	1	142
70	7	995
70.4	7.04	1000
100	10	1421
130	13	1847
155	15.5	2203
704	70.4	10000
1000	100	14211

STRESS INTENSITY FACTOR	
MPa $\sqrt{\text{m}}$	ksi $\sqrt{\text{inch}}$
0.91	1
1	1.10

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I Introduction (Peter Rudling)

The overall objective of the *LWR Coolant Chemistry, LCC*, program is to enable the *LCC₃* Member to:

- Gain increased understanding of reactor water chemistry related to a successful plant operation and a continued integrity of Reactor Coolant System (RCS) materials while keeping radiation exposure low.
- Assist in the training and education of a new generation of chemistry and materials experts.
- Establish a new independent meeting point for experts to enable free and critical discussions and experience exchange.

The objective is met through critical review and evaluation of the most recent data related to reactor water chemistry, identification of the most important new information, and discussion of its significance in relation to water chemistry now and in the future.

The evaluations are based on the large amount of non-proprietary data presented at technical meetings and published in the literature.

The 2006/07 technical meetings covered include:

- Contribution of Materials Investigations to Improve the Safety and Performance of *LWRs*, Fontevraud 6, France, September 18-22, 2006.
- International Conference on Water Chemistry of Nuclear Reactor Systems, Jeju Island, Korea, October 23-26, 2006.
- Halden Enlarged meeting, March 11-16, 2007.
- Jahrestagung Kerntechnik, May 2007.
- EPRI 2007 Condensate Polishing Workshop, June 5 to 7, 2007; Palm Springs.
- Thirteenth International Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, Whistler, British Columbia, August 19-24, 2007.
- 7th International Conference on Voda Voda Energo Reactor (VVER) Fuel Performance, Modelling and Experimental Support, Albena near Varna, Bulgaria 17 - 21 Sep 2007.
- ANS *LWR* Fuel Performance Conference, San Francisco, Sept. 30- Oct. 3, 2007.
- PATRAM Conference, October 2007, Miami, Florida.

The extensive, continuous flow of journal publications is being monitored by several literature searches of worldwide publications and the important papers are summarised and critically evaluated. This includes the following journals:

- Nuclear Engineering and Design
- Kerntechnik
- Power Plant Chemistry
- Water Chemistry Guidelines of Vendors (if published)
- IAEA Documents

The open literature information have been collected throughout the last couple of years and the most relevant data are selected for the Annual Report (AR). The large collective experience gained by the Report authors in past and current projects is an important factor in making the evaluation, hence ensuring that the presented compiled information is put in perspective, and that the most important information is emphasized.

The following currently important issues are specifically addressed in this Report:

- Secondary side steam generator tube problems
- Material degradation management
- Cleanup system
- Fuel/chemistry interaction

The authors of the report are Dr. Rolf Riess, Dr. Peter Ford, Dr. Wilfried Rühle.

The work reported herein will be presented in one Seminar Valletta, Malta on February 21-22, 2008. The Term of LCC₃ started on February 1, 2007 and ended on January 31, 2008.

2 Secondary side steam generator tube problems (Rolf Riess)

2.1 Introduction

2.1.1 Background

Tubes for U-tube steam generators in nuclear power plants with Pressurized Water Reactors (PWR) are fabricated out of Inconel 600 Mill Annealed (MA) or Thermally Treated (TT), Incoloy 800 Nuclear Grade (NG), or Inconel 690 TT. Once Through Steam Generators (OTSG) use Alloy 600. The choice of the tubing material is a crucial factor in ensuring trouble-free Steam Generator (SG) operation. The design and operating modes selected for SGs and their associated water/steam cycles are equally important. SG tube performance is therefore determined by the complex interaction of such factors as design, choice of materials, and water chemistry.

This section of the Annual Report is actually concerned with the corrosion performance of steam generator tubing on the PWR secondary side. This discussion is appropriate now since many utilities are planning an extension of the lives of their steam generators beyond the designed life of about 40 years.

The discussion reviews also the chronology of steam generator corrosion together with the lessons learned for water chemistry. These lessons are relevant to the extension of life of steam generators. This review focuses primarily on the heat transfer crevices associated with tube supports, sludge piles, and tops of the tube sheet. Failures in steam generators have preferentially occurred at these locations. Also at these locations the effectiveness of Non Destructive Examination (NDE) like eddy current inspection is relatively low, owing to the complexity of geometries and presence of deposits associated with these locations. General Corrosion (GC), Stress Corrosion Cracking (SCC), Intergranular Corrosion (IGC), and pitting have also occurred on free spans. However, such corrosion is much less severe than the ones found in heat transfer crevices.

Typical steam generators of the Re-circulating Steam Generator (RSG) and OTSG types are shown in Figure 2-1(a) together with typical features that relate to subjects in this discussion. The Westinghouse model D 3 shown in Figure 2-1(a) is one typical example. However, the design of other manufacturers like Siemens, Babcock & Wilcox (B&W) and Combustion Engineering (CE) are similar in some ways and different in others. The Siemens design for example, shown in Figure 2-1(b), is generally like the Westinghouse design except that Siemens used different tube support designs and alloys from the beginning. These differences will be described later. However, it is important to recognise that the present designs of steam generators are vulnerable to corrosion damage. For example Alloy 690 can sustain extensive corrosion under certain conditions. Nevertheless, it can be assumed, that based on laboratory experiments and the existing field experience, Alloys 690 may not undergo the same experience like Alloy 600.

The reliability of steam generators as it depends on the PWR secondary side is influenced mainly by the characteristics of “heat transfer crevices”, in which dilute species from the secondary environment can be concentrated to produce highly corrosive environments operating close to the hot leg temperature.

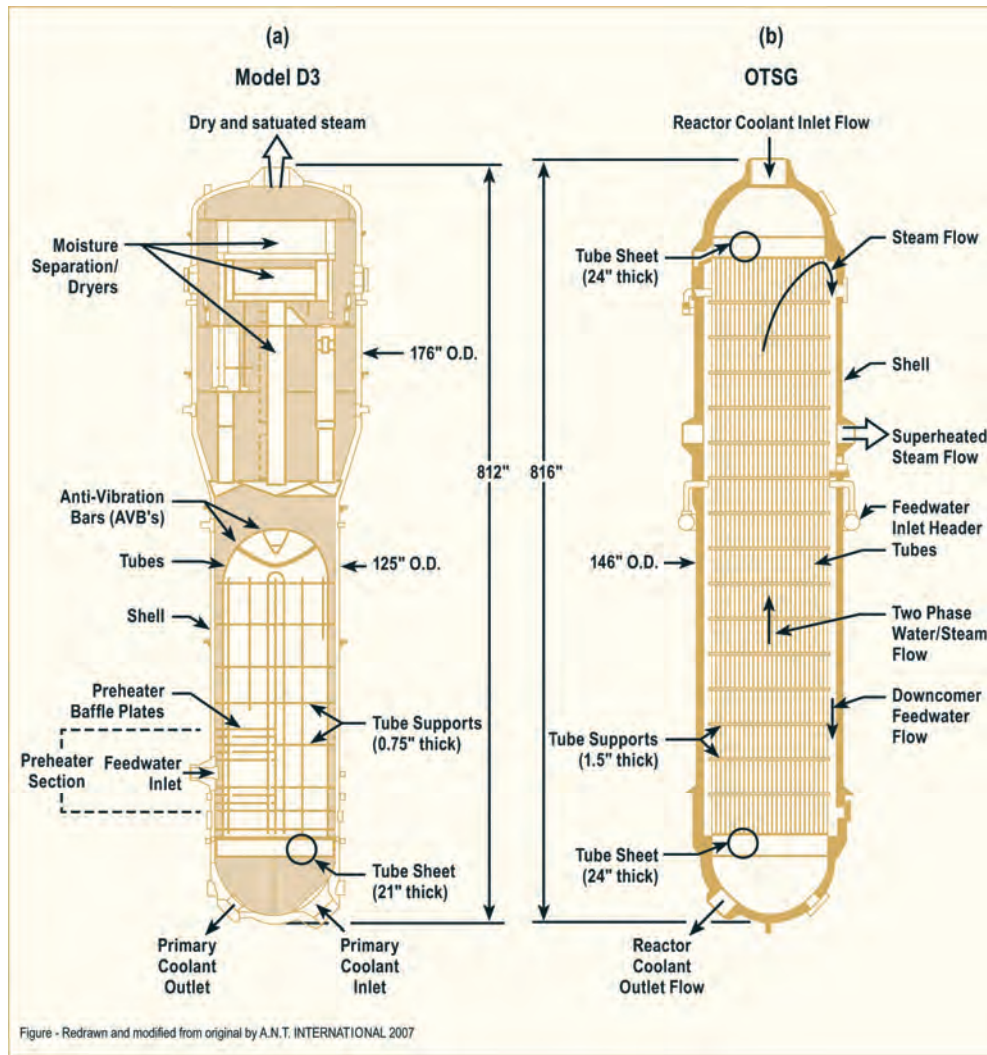


Figure 2-1(a): Schematic view of (a) *RSG* (Westinghouse Model D3) and (b) *OTSG* showing typical features. The *RSG* design is typical of that of Westinghouse, its licensees, *CE*, and Siemens. The *OTSG* design is typical of the *B&W SGs*, Staehle & Gorman, 2002.

A Siemens designed steam generator with economizer is shown in Figure 2-1(b). This figure contains some indications of typical regions where corrosion attack has occurred in steam generators of other manufacturers. This information is described in several documents released by Siemens, e.g. Schücktanzt et al., 1975; Riess, 1976; Riess et al., 1977; Schücktanzt et al., 1980; Riess et al., 1981; Riess, 1984; Riess et al., 1987; Stieding et al., 1990; Riess & Odar, 1991. These are few in comparison to those generated mainly in the United States, and reported in proceedings of conferences such as the International Symposia on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors or the Fontevraud Conferences. Many Electric Power Research Institute (EPRI) sponsored Workshops have been held and many Topical Reports issued. EPRI, for example, has published two revisions of a Handbook of Steam Generators and has sponsored the development and application of the MULTEQ-code for quantifying the problems in aqueous thermodynamics important for the resolution of issues in PWR secondary side components. A comprehensive list of References is given by Staehle & Gorman, 2002, and in their publications of 2003 and 2004 as well.

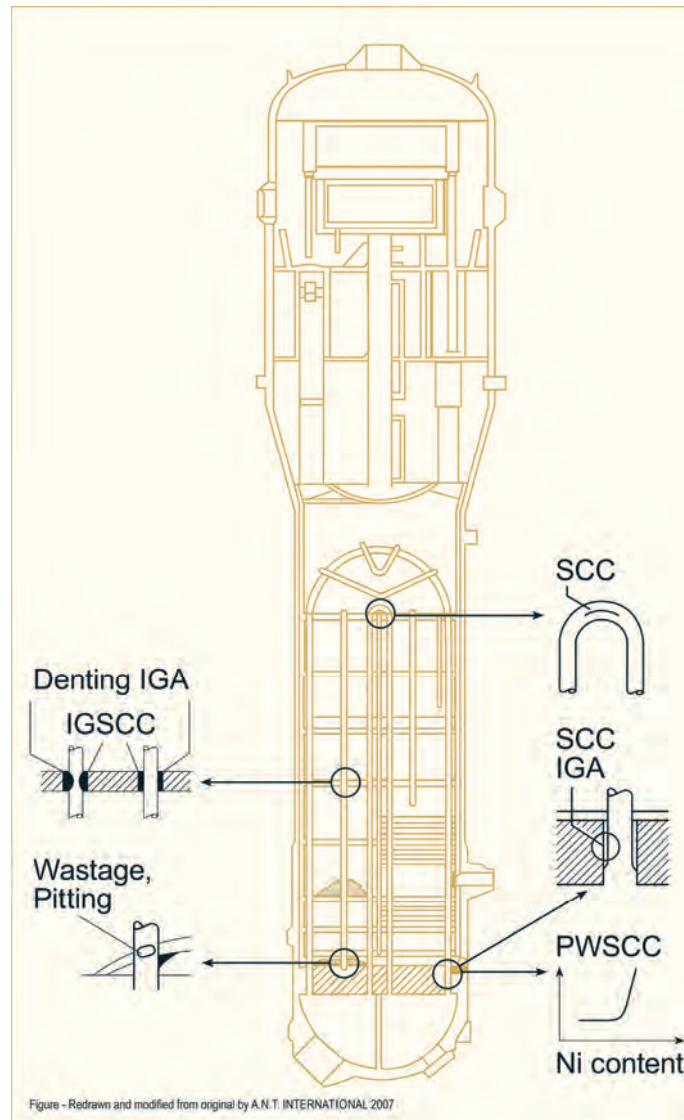


Figure 2-1(c): Siemens designed Steam Generator with Economizer showing typical regions of corrosion attack.

2.1.2 SG design features

For the discussion of heat transfer crevices it is necessary to identify and describe such crevices. Figure 2-2 shows the three types that are located at the steam generator tube sheet, in the sludge pile, and at the tube support plate. Regarding the tube support crevice there are three types: Drilled hole, broached hole, and egg crate, as illustrated in Figure 2-3. The tube sheet crevices itself can have three designs as shown in Figure 2-4. One of the early designs was a part-depth roll. This was replaced by full depth roll or explosive or hydraulic expansion in order to avoid possible corrosion in a long heat transfer crevice. Although a full depth expansion is now standard, there is always the 3 to 6 mm crevice near the top of the tube sheet in order to avoid “over-expansion”. In Figure 2-5 the evolution of the types of tube support design of the four manufacturers of steam generators are shown.

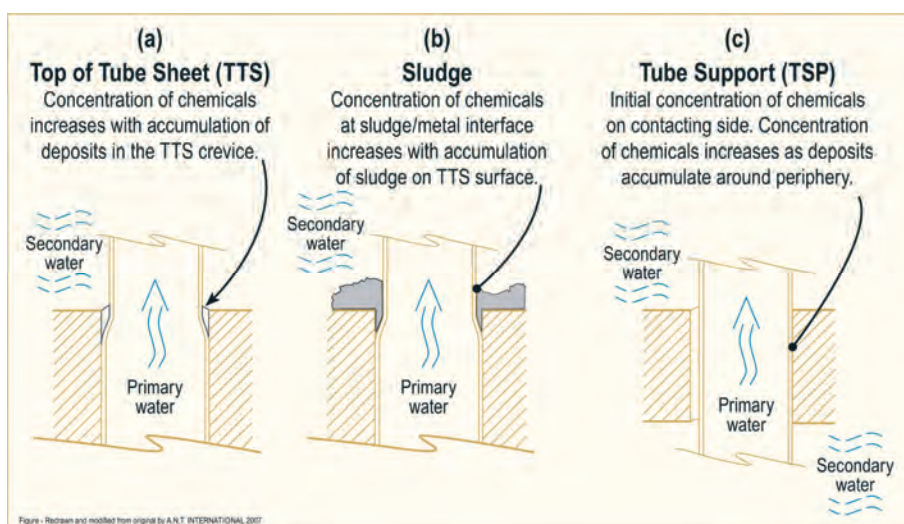


Figure 2-2: Geometries that produce heat transfer crevices involving tubing in steam generators: (a) top of the tube sheet; (b) sludge; (c) tube support, Staehle & Gorman, 2002.

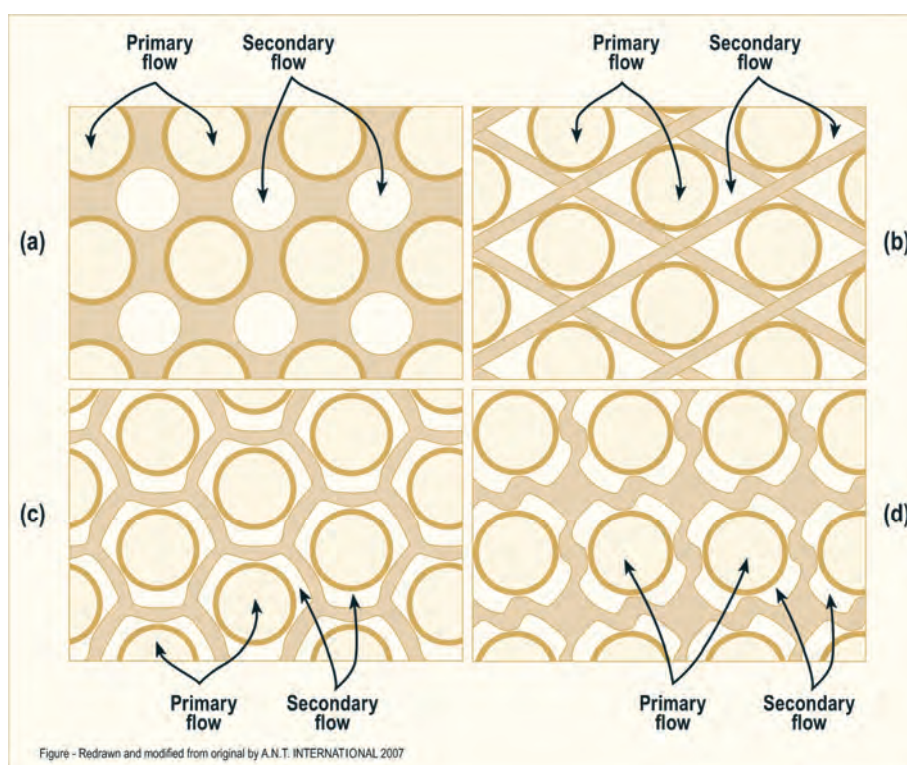


Figure 2-3: Geometries of tube supports: (a) Drilled hole typical of early Westinghouse designs; (b) egg crate typical of Siemens and CE; (c) broached trefoil typical of Babcock and Wilcox; (d) broached quatrefoil typical of later Westinghouse designs, Staehle & Gorman, 2002.

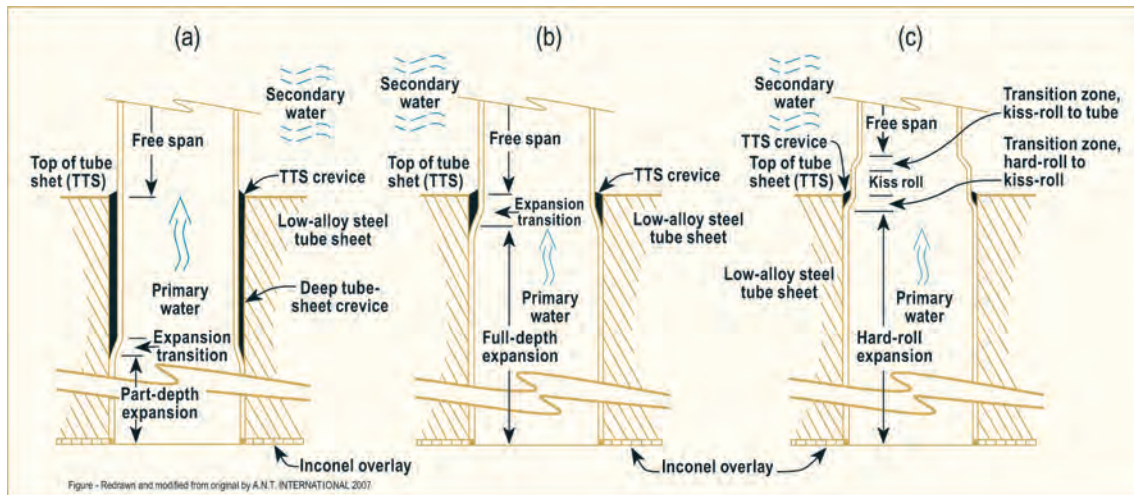


Figure 2-4: Tube sheet geometries. (a) Partially expanded. (b) Fully expanded. (c) Fully expanded with top "Kiss" roll, Staehle & Gorman, 2002.

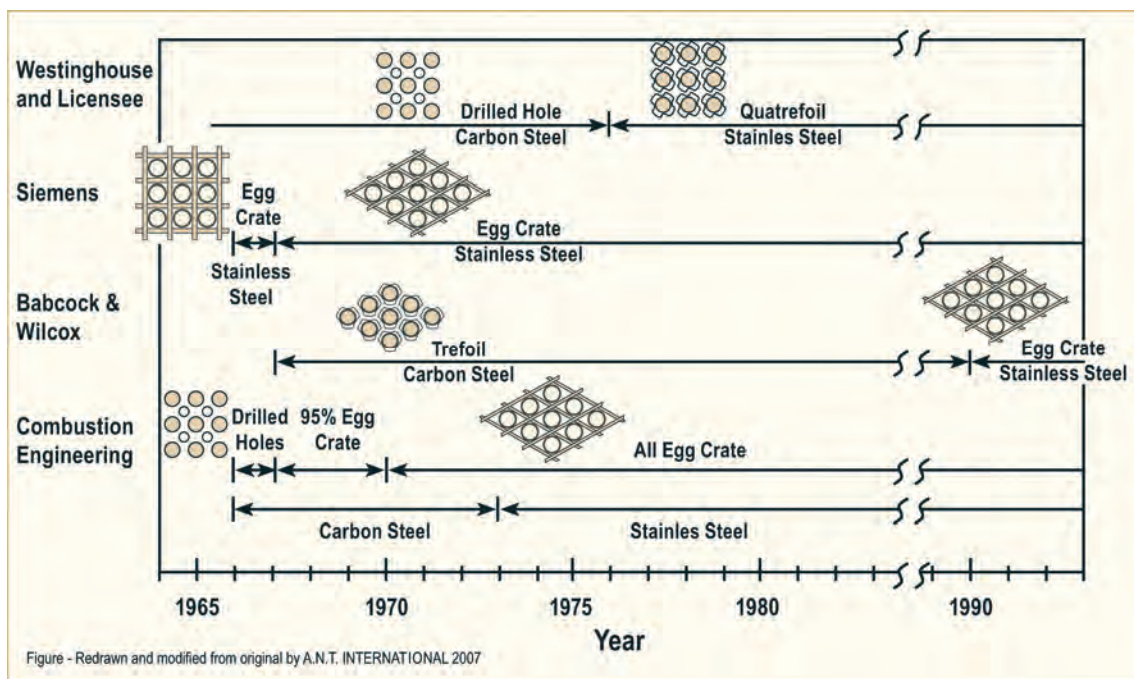


Figure 2-5: Evolution of tube support geometries and materials used by four Nuclear Steam Supply System (NSSS) vendors for steam generators. The geometries of tube supports are shown above the lines, and the materials of the tube supports are shown below. The arrows indicate approximately when manufacturing of the respective designs of tube supports started, Staehle & Gorman, 2002.

Heat transfer crevices are important for the fact that they concentrate impurities to high ratios of concentrations inside the crevice compared with the respective concentrations of species in the bulk solution. Thus the corrosion that occurs inside heat transfer crevices needs to be assessed in terms of these concentrated solutions rather than the dilute bulk solutions. Typical crevice geometries are shown in Figure 2-6 categorized in terms of the heat transfer characteristics.

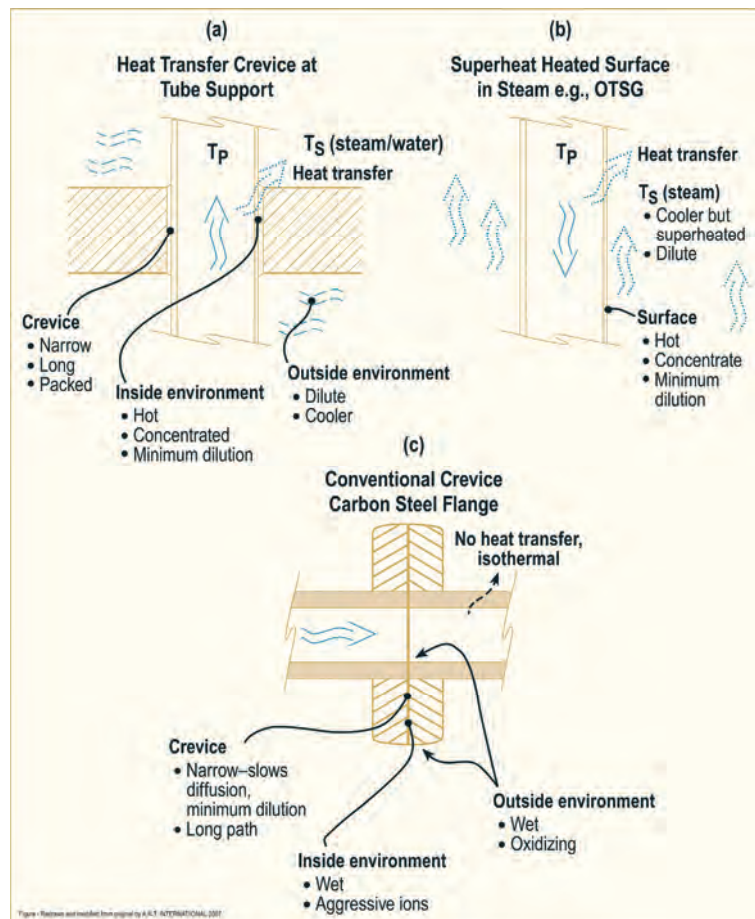


Figure 2-6: Three crevice geometries for producing corrosion: (a) Heat transfer crevice typical of those at tube supports, sludge piles, and top of tube sheet. (b) Heated surface where concentration occurs. (c) Non heat transfer crevice, Staehle & Gorman, 2002.

The terms Primary Side Temperature (T_p) and Secondary Side Temperature (T_s) in Figure 2-6 are used for the temperatures of the primary and secondary environments. The terms T_H and T_C are used for the outlet and inlet temperatures to the steam generator.

The important features of heated crevices in steam generators are:

- The Outer Diameter (OD) surface of the tube is close to the primary temperature of T_p .
- The temperature of the secondary water, T_s , is cooler. $T_p - T_s = \text{the superheat}$.
- The crevice fills with deposits, mainly iron oxide resulting from corrosion from iron based materials of construction in the secondary water; additional iron oxide is produced by corrosion of the tube support or tube sheet. Eventually, the crevice becomes fully packed with these deposits.
- Owing to the packing of the crevice, the region within the crevice tends to be steam with water at the edges with a water-steam interface.
- Various compounds and chemistries of deposits have been observed in the heated crevices. They may contain iron, aluminium, silicon and other species. Organic material may also be included.
- Sulphur is often present initially as sulphate that can be reduced by hydrazine to produce lower valence species.
- Inside the heat transfer crevices there are sharp gradients in electrochemical potential, temperature, concentration, and fluid density.

Deposits in heat transfer crevices accumulate with time although deposits at the top of the tube sheet are often removed at outages by sludge lancing and occasionally by chemical cleaning.

A typical heat transfer crevice is shown in Figure 2-7.

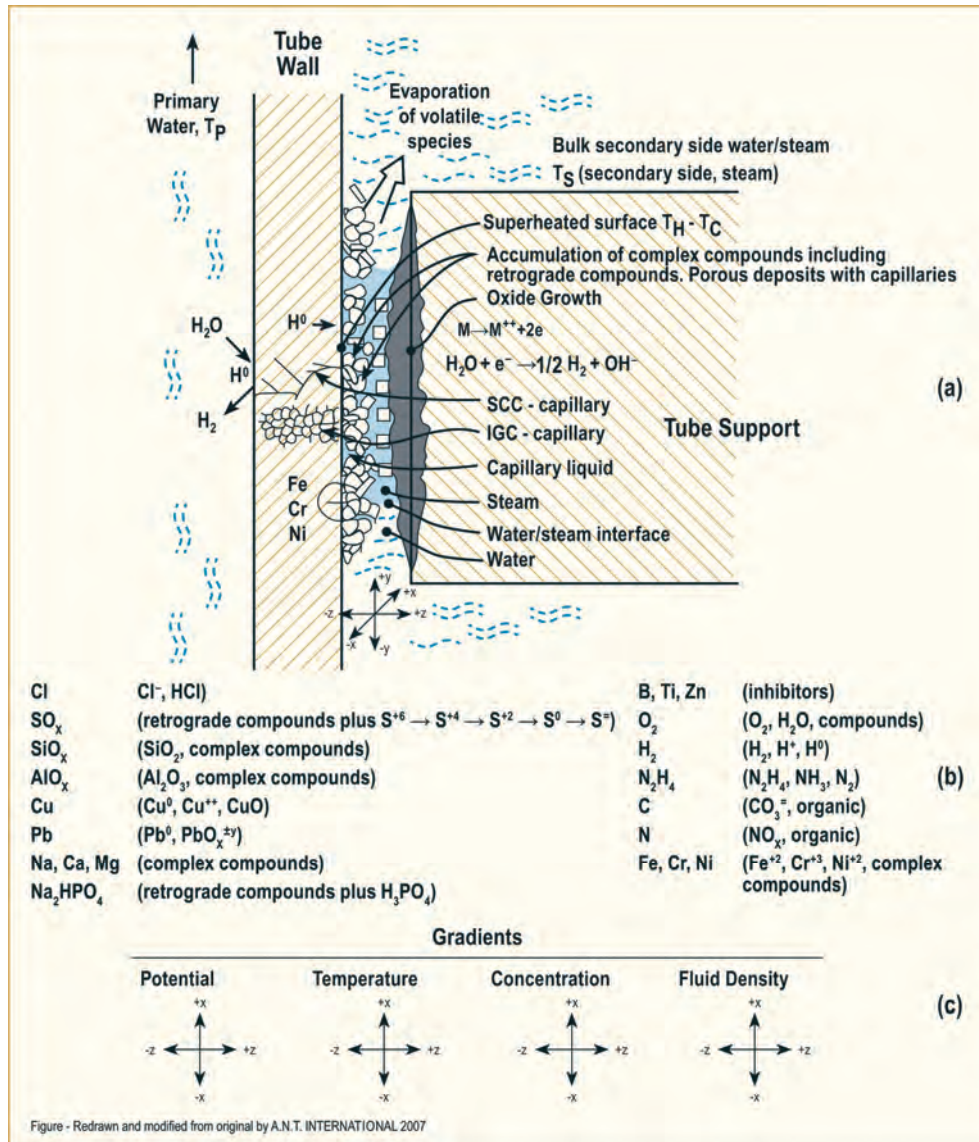


Figure 2-7: Schematic view of heat transfer crevice at a tube support. (a) Geometry. (b) Chemicals that accumulate and transform. (c) Types of gradients inside the heat transfer crevice, Staehle & Gorman, 2002.

The heat transfer crevice as shown in Figure 2-7 can generate a variety of environments depending on the impurities entering the steam generator with the feed water. The risk for generating an aggressive environment in heat transfer crevices is definitely higher in drilled support structures compared to structures with a line contact between heat transfer tube and support structure. Examples for line contact geometries are shown in Figure 2-8 and Figure 2-9.

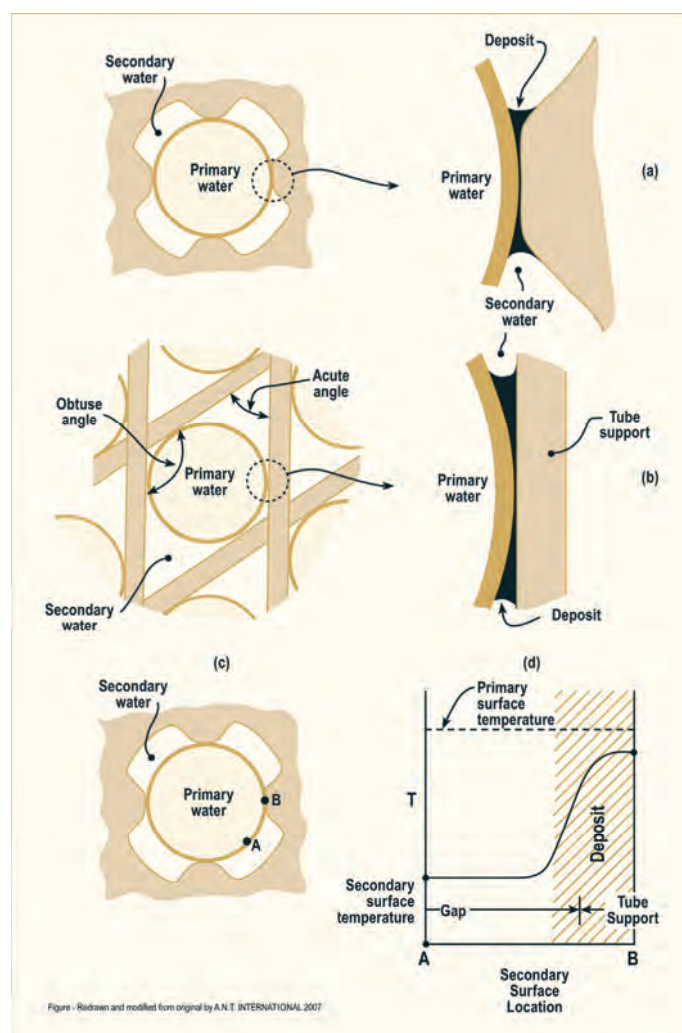


Figure 2-8: Schematic view of accumulation of deposits at line contact crevices associated with (a) broached holes and (b) egg crates. Example (c) of different temperatures (d) at open area and at deposit filled contact area, Staehle & Gorman, 2002.

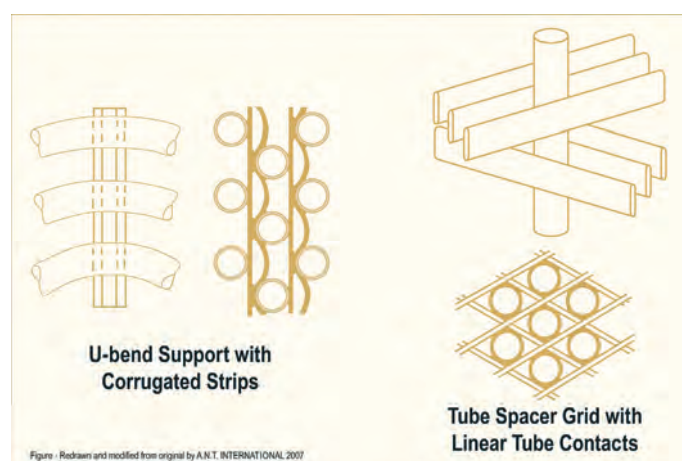


Figure 2-9: Design Features to avoid Tube Denting, Intergranular Attack (IGA), Intergranular Stress Corrosion Cracking (IGSCC) and Fretting, Riess & Odar, 1991.

Unique features of the Siemens steam generator design are the corrugated strips used as U-bend support. Regarding the spacer grids, these grids are running at a different level as shown in Figure 2-9. The operating experience has shown that these structures are giving enough structural stability to the tube bundle and on the other hand these designed elements are not prone to concentration of impurities. The worst case for a sensitive design element are the drilled holes.

2.1.3 Steam generator tubing materials

Regarding the steam generator tube degradation problems, the following chronology can be given. Austenitic stainless steel was used initially for tubing in several early PWRs but, as a result of corrosion problems with this material (such as caustic and chloride induced stress corrosion cracking) Alloy 600 was chosen. This was also stimulated by a decision of the Naval Reactors in the US to use Alloy 600 in the MA form instead of austenitic stainless steel.

Table 2-1, prepared by Staehle & Gorman, 2002, summarizes this development and reflects also the chronology which led to the development of Alloy 800 and Alloy 690 TT (Thermally Treated). The same indicates that the German Original Equipment Manufacturer (OEM) decided already in the 1960s to switch to a modified Alloy 800 NG, followed by its first application in 1972. The basis for this decision was on one hand the SCC findings of Coriou with Alloy 600 and the early experience in large PWRs where numerous corrosion problems occurred. The most important diagram of those days is shown in Figure 2-10. The OEMs in France and Japan were Licensees of Westinghouse and they strictly followed the US decision regarding the SG-Tubing Selection.

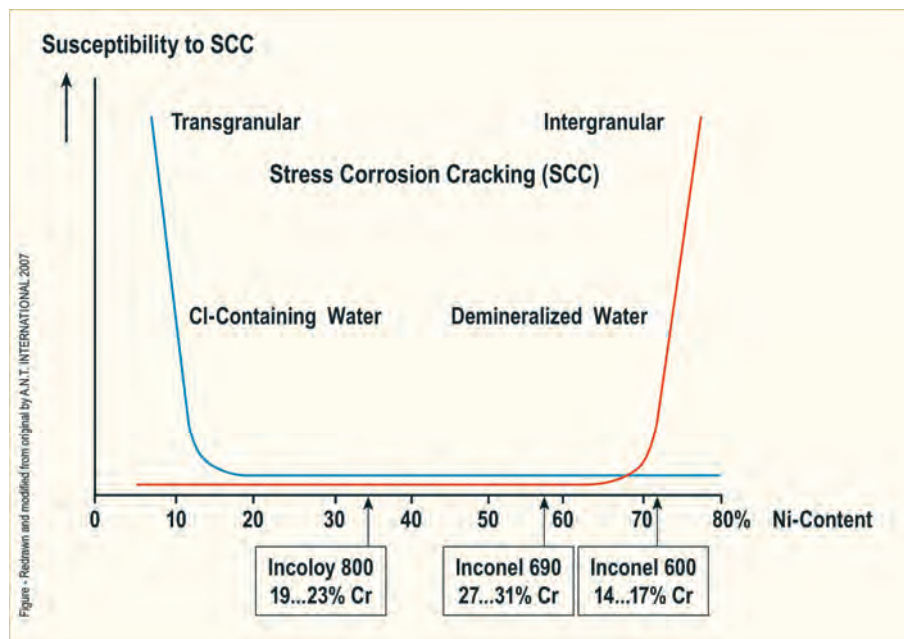


Figure 2-10: Stress Corrosion Cracking of austenitic alloys in 660 °F (350 °C) Water with 1000 ppm Chloride, (Debray & Stieding, 1972.) as a function of the alloys nickel content.

Table 2-1: PWR Steam Generator Design Evolution

Mode/lead plant (first commercial operation)	Typical design T _H (°C)	Hot leg heat flux Btu/hr/ft ²	Recirculating or once through	Tube orientation	Tube material*	Support type	Support material	Tube sheet expansion**	Flow distribution baffle (Y/N)	Preheater (Y/N)
Government laboratory designs										
Shippingport (1957)	283	29.000	Recirculating	Horizontal	SS then 600 MA	Hour-glass drilled holes	Carbon steel	PDR	Not applicable	N
N reactor (1965)	279	67.000	Recirculating	Horizontal	SS then 600 MA	Drilled holes	Carbon steel	PDR	Not applicable	N
Westinghouse and licensees designs										
Early SS designs (1961)	288-302	39.000	Recirculating	Vertical	304 SS	Drilled holes	Carbon steel	PDR	N	N
Early 600 MA designs (1968)	310-318	43.000	Recirculating	Vertical	600 MA	Drilled holes	Carbon steel	PDR	N	N
Intermediate 600 MA designs (1977)	317-322	44.000	Recirculating	Vertical	600 MA	Drilled holes	Carbon steel	FDE, FDR or FDR-KR	N	N
Later 600 MA designs (1981)	323-324	48.000	Recirculating	Vertical	600 MA	Drilled holes	Carbon steel	FDE, FDR or FDR-KR [†]	Y	N
Preheater 600 MA designs (1983)	326-330	49.000	Recirculating	Vertical	600 MA	Drilled holes	Carbon steel	FDE, FDR or FDR-KR	Y	Y
Model F type (1983)	326	53.000	Recirculating	Vertical	600 TT	Broached holes	405 SS	FDH or FDR-KR [†]	Y	N
Preheater 600 TT designs (1986)	326	49.000	Recirculating	Vertical	600 TT	Broached holes	405 SS	FDH or FDR-KR	Y	N
Latest replacement designs (1988)	See note	44.000	Recirculating	Vertical	690 TT	Broached holes	405 SS	FDH or FDR-KR [†]	Y	Y

Table 2-1: PWR Steam Generator Design Evolution, cont'd

Mode/lead plant (first commercial operation)	Typical design T _H (°C)	Hot leg heat flux Btu/hr/ft ²	Recirculating or once through	Tube orientation	Tube material*	Support type	Support material	Tube sheet expansion**	Flow distribution baffle (Y/N)	Preheater (Y/N)
<i>CE and licensee designs</i>										
First design (1971)	315	50.000	Recirculating	Vertical	600 MA	Drilled holes	Carbon steel	FDE	N	N
Intermediat designs (1973)	313	51.000	Recirculating	Vertical	600 MA	Eggcrates & drilled holes	Carbon steel	FDE	N	N
Later designs (1983)	321	56.000	Recirculating	Vertical	600 MA	Eggcrates	Carbon steel	FDE	N	N
Ekonomizer model (1986)	327	52.000	Recirculating	Vertical	600 MA	Eggcrates	409 SS	FDE	Y	Y
Latest Korean model	322	47.000	Recirculating	Vertical	690 TT	Eggcrates	409 SS	FDE	Y	Y
<i>B&W designs</i>										
Prototype plant design (1963)	271	-	Recirculating	Horizontal	304 SS	-	-	-	Not applicable	N
One-through design (1973 and later)	317-320	33.000	Once-through	Vertical	600 MA + sensitized	Broached holes	Carbon steel	PDR	N	N
Replacement RSGs (1992 and later)	See note ²	50.000	Recirculating	Vertical	690 TT	Lattice bar	410 SS	FDH	Y	N

Table 2-1: PWR Steam Generator Design Evolution, cont'd

Mode/lead plant (first commercial operation)	Typical design T_H (°C)	Hot leg heat flux Btu/hr/ft ²	Recirculating or once through	Tube orientation	Tube material*	Support type	Support material	Tube sheet expansion**	Flow distribution baffle (Y/N)	Preheater (Y/N)
Siemens										
Lead plant design (1969)	312	61.000	Recirculating	Vertical	600 <i>MA</i>	Lattice bar	<i>SS</i>	Rolled at top, mid and bottom	N	N
Second generation design (1972)	314-319	68.000	Recirculating	Vertical	800 <i>NG</i>	Lattice bar	<i>SS</i>	Rolled at top and bottom	N	N
Preheater design (~1983)	329	57.000	Recirculating	Vertical	800 <i>NG</i>	Lattice bar	<i>SS</i>	Rolled at top and bottom	Y	Y
Replacement design (1989)	See note ¹	51.000	Recirculating	Vertical	800 <i>NG</i> or 690 <i>TT</i>	Lattice bar	<i>SS</i>	<i>FDH</i> with roll at top and bottom	-	N

* *MA* = Mill annealed, *TT* = Thermal treated, *NG* = Nuclear grade

** *PDR* = Part depth roll, *FDR* = Full depth roll, *KR* = Kiss roll, *FDE* = Full depth explosive, *FDH* = full depth hydraulic

Notes:

¹ Variety of full depth tube sheet expansion designs used in Japan

² T_H of replacement *SGs* is usually lower than that of original *SGs*

The development of Alloy 690 *TT* started in the mid 70s after the occurrence of several severe problems with Alloy 600 *MA*, such as:

- IGA/SCC in the sludge pile region
- Phosphate wastage
- SCC in deep tube sheet crevices
- Denting

The first modification to Alloy 600 was a heat treatment at 704 °C for about 15 hours leading to Alloy 600 *TT*. However, the improvements were not large enough and SCC remained a material issue. As a consequence, a new material was developed by International Nickel, i.e. Alloy 690 *TT*. This material was qualified in the lab and then used from the mid 80s onwards and it is nowadays the favourite material for all new Westinghouse plants and the plants of previous Westinghouse Licensees (Siemens and Mitsubishi Heavy Industries (*MHI*)). The exception with respect to this case is Siemens as a former Westinghouse Licensee (now AREVA).

The status regarding the use of Alloy 690 *TT* has been described by Nordmann, 2004 and it is shown in Table 2-2.

Table 2-2: Ratio of Units with 690 *TT* 600 *MA*, Nordmann, 2004.

Units with	USA	France	Japan	Belgium Sweden, United Kingdom	China, Korea
690 <i>TT</i> (a)	21	18	15	7	5
600 <i>MA</i> (b)	34	13	0	3	4
R = a/b	0.62	1.4	-	2.3	1.2

The number of units with 690 *TT* is already greater than with 600 *MA*. According to Nordmann there should be almost no steam generator in 10 years with 600 *MA*.

The status regarding the use of Alloy 800 *NG* is that all German *PWRs* and some *PWRs* in other European countries and Canada are using this material.

As can be seen from the Table 2-1, the successful operating experience with both currently used materials is:

- 33 years with Alloy 800
- 15 years with Alloy 690.

Considering that both materials are susceptible to corrosion under some environmental conditions, the positive plant operating experience should be of great value for the selection of one of these materials.

Both materials can be characterized on the Fe-Cr-Ni ternary diagram of Pugh & Nisbet, 1950, for 400 °C. In addition, the composition of other materials, which are important for steam generator performance like support structure materials on the SG-secondary side or Reactor Coolant System (*RCS*) materials, can also be taken from this viewgraph (see Figure 2-11).

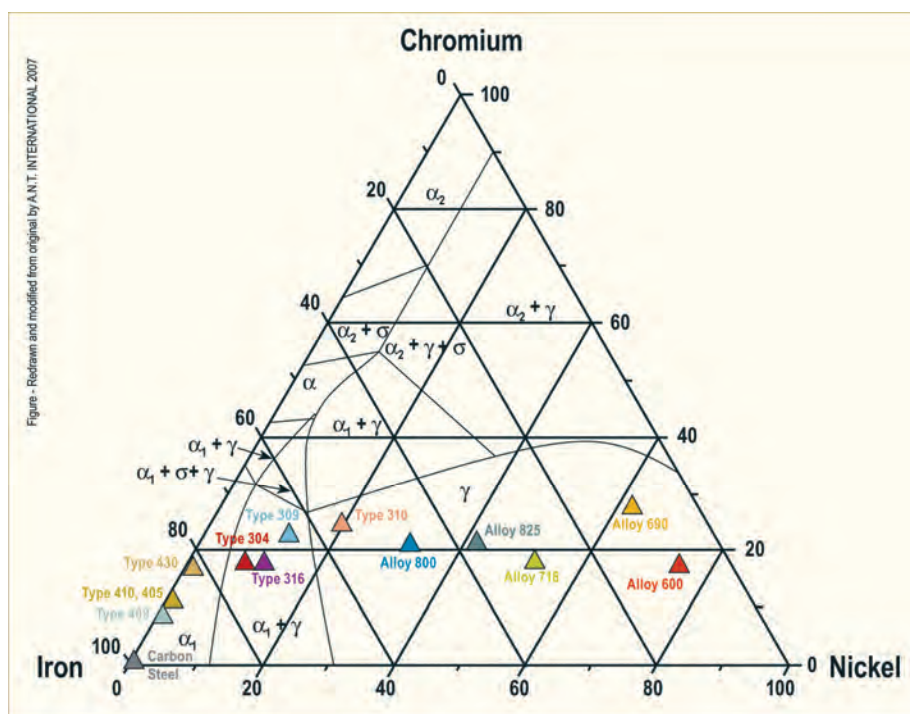


Figure 2-11: Fe-Cr-Ni diagram for 400°C, Pugh & Nisbet, 1950.

The detailed chemical composition of Alloy 690 *TT* and Alloy 800 *NG* can be taken from Stellwag et al., 1986, as it is shown in Table 2-3.

Table 2-3: Chemical Composition of the Alloys 690 *TT*, 800 *NG* and 600, Stellwag et al., 1986.

Element	Alloy 690 <i>TT</i>	Alloy 800 <i>NG</i>	Alloy 600
C	0.01-0.04	0.03	0.01-0.05
Mn	0.50	0.4-1.0	1.00
P	0.025	0.020	0.025
S	0.015	0.015	0.015
Si	0.50	0.3-0.7	0.50
Cr	28-31	20-23	14-17
Ni	Bal.(>58)	32-35	Bal.(>72)
Mo	-	-	-
Fe	7-11	Bal.	6-10
Cu	0.50	0.75	0.50
Co	0.10	0.10	0.10
Al	0.50	0.15-0.45	0.50
Ti	0.50	0.60	0.50
Other	-	Ti/C ≥ 12 ; Ti/(C+N) ≥ 8 N ≥ 0.03	-

Coming back to the chronology of Steam Generator Tube Degradation and the 1980s as Jones, 2004, summarized, several slower developing degradation forms emerged, such as:

- Pitting
- Vibration induced fretting and fatigue
- Primary side stress corrosion cracking and secondary side SCC and IGA

The last of these items has had the greatest impact on the rate of tube plugging, and the inability to control these forms of damage has resulted in major replacement activities.

A worldwide overview on the SG problems is shown in Figure 2-12.

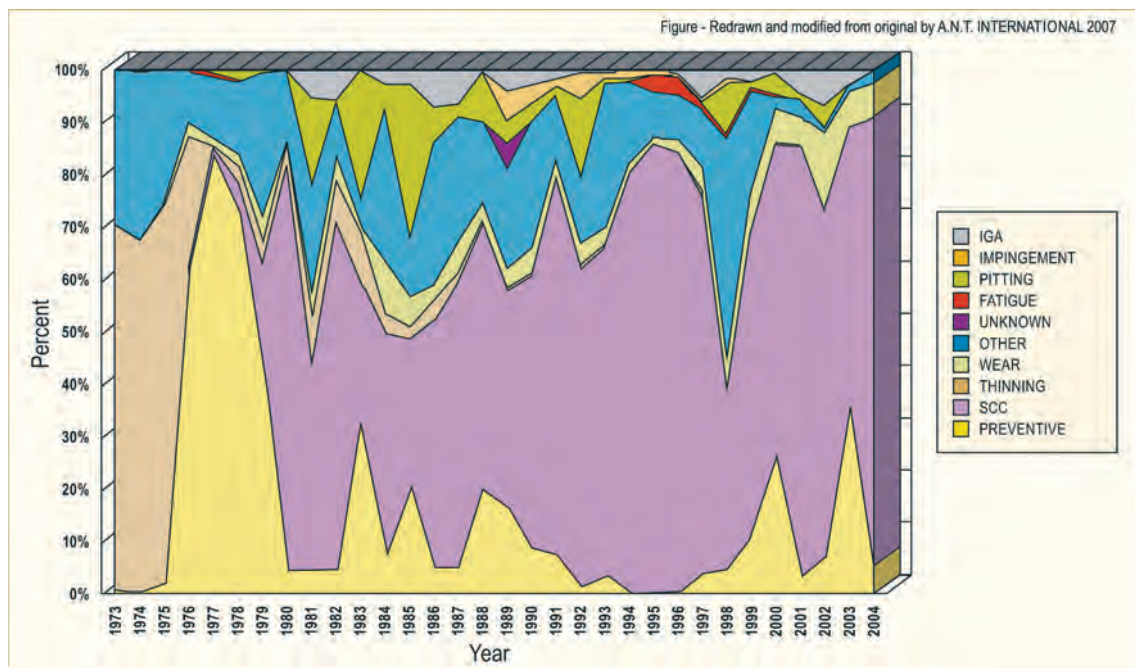


Figure 2-12: Worldwide Causes of Steam Generator Tube Repair, Jones, 2004.

From the corrosion issues especially in the US some conclusions were drawn by Jones, 2004:

- SCC proved to be the most difficult issue to be managed cost-effectively
- The management approach to SCC is to inspect, assess remaining life, and repair/replace. However, SCC is hard to detect and the Crack Growth Rate (CGR) can be rapid. Therefore, mitigation methods are desirable.
- In a SCC mitigation context the options are limited to stress reduction and/or water chemistry improvements. However, with respect to repair/replacement new more resistant materials are desirable.
- Water chemistry mitigation methods require extensive testing and qualifying and may become very expensive.

2.2 Temperatures and concentrations

Some corrosion phenomena occurring on the secondary side at tube support elevations are increasing with temperatures on the surface of the tube and the concentration of impurities in the crevices. This is verified with the decreasing occurrence of eddy current indication at successively higher tube supports. With increasing height the primary side temperature is reduced which reduces both the superheat and the surface temperature. Which of these effects is acting here is not clear. The experience regarding this phenomenon is shown in Figure 2-13 for three plants.

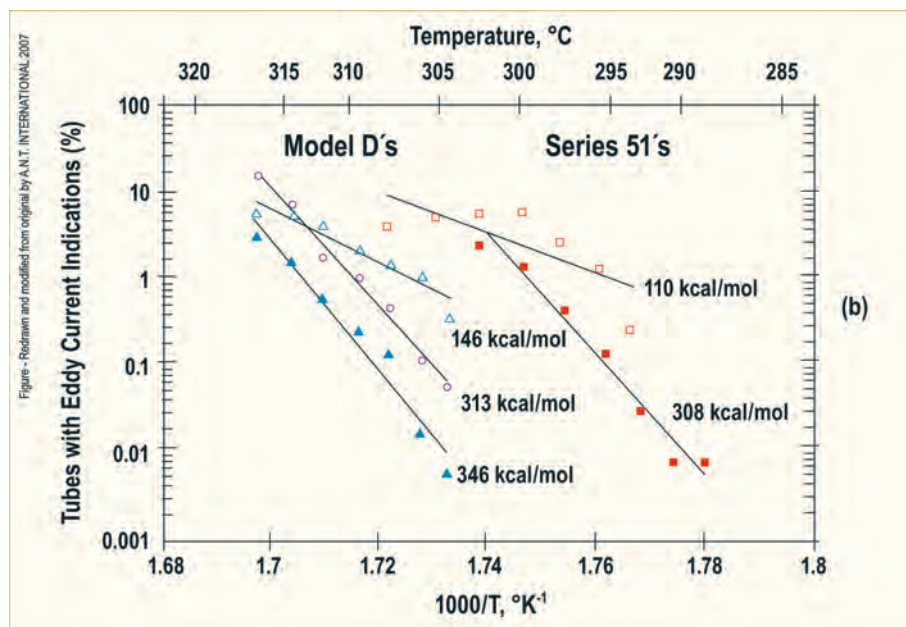


Figure 2-13: (a) Number of indications at successive tube support locations for three plants using Alloy 600 *MA* after about 12 to 15 years service. From Takamatsu et al., 1996. (b) Percentage of tubes with eddy current indications vs. $1000/T$ at successive tube supports for various Model D and Model 51 SGs. Activation energies shown. From Baum, 1999.

In addition to the influence of surface temperature the concentration of chemical species in crevices due to superheat contributes significantly to corrosion in heat transfer crevices. Figure 2-14 shows the magnitude of concentration that can occur in heat transfer crevices for various species as a function of concentration in the environment. Remarkable are the different concentration factors. Na and K concentrate more than Cl and F. Such differences are due to the different vapour pressures of these species.

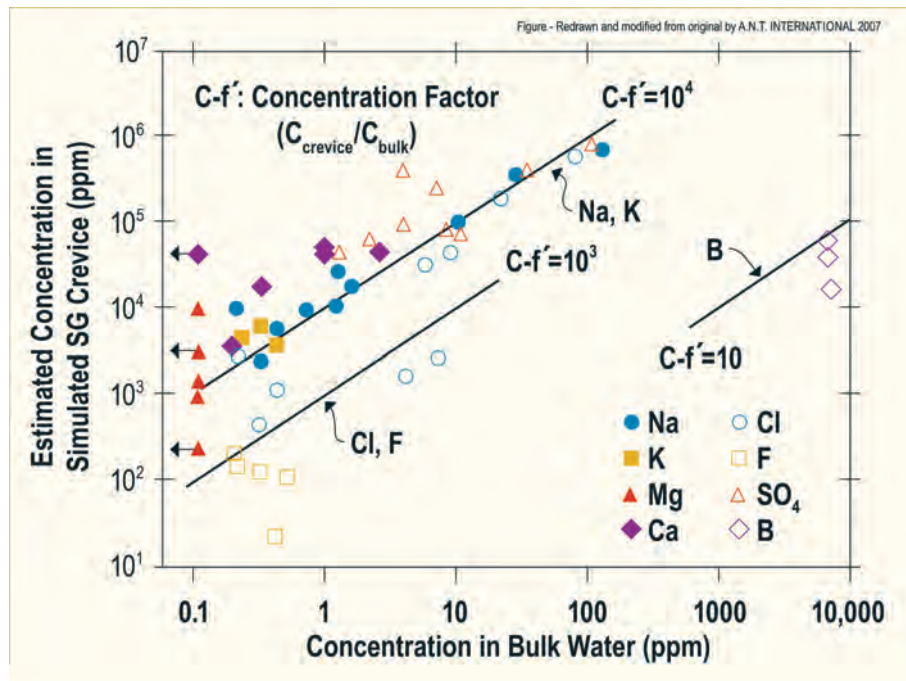


Figure 2-14: Estimated concentration of species in simulated SG crevices vs. concentration in the bulk water. Various concentration factors are shown. From Takamatsu et al., 1992.

2.3 PWR secondary side chemistry

2.3.1 Plant concepts

The secondary side chemistry has always been directed to avoid or minimize corrosion damage to the steam generator tubing. For US-plants it has always had priority compared to other secondary side equipments like turbines, condensers, feed water heaters, moisture separators and piping. This situation resulted in some conflicts which required compromises. The main problems and compromises for US-plants are according to Staehle & Gorman, 2002:

- A relatively high pH_T in the secondary system is desirable to protect the steam generators from corrosion and to minimize iron ingress into the steam generator from the secondary system. Corrosion of copper heat exchanger tubing increases as the pH is increased above about 8.8, while corrosion rates of carbon steel piping continued to decrease as pH is raised, at least to a pH of 10. Thus, if copper alloys are used in secondary systems pH has to be selected on a compromise basis at about 9.2.
- Protection of steam generators against corrosion requires that oxidizing conditions should be avoided. Achieving this goal is facilitated by maintaining low oxygen concentration in the feed-water and by using high concentrations of hydrazine. However, low oxygen and high hydrazine can increase rates of Flow Accelerated Corrosion (FAC) of carbon steel piping and steam generator internals. For this reason, hydrazine concentrations are selected considering both of these goals i.e. high enough to ensure protection of steam generators while not significantly aggravating tendencies towards FAC.

In order to describe the concerns of Staehle and Gorman, Figure 2-15 illustrates a concept of the secondary side of the US PWRs.

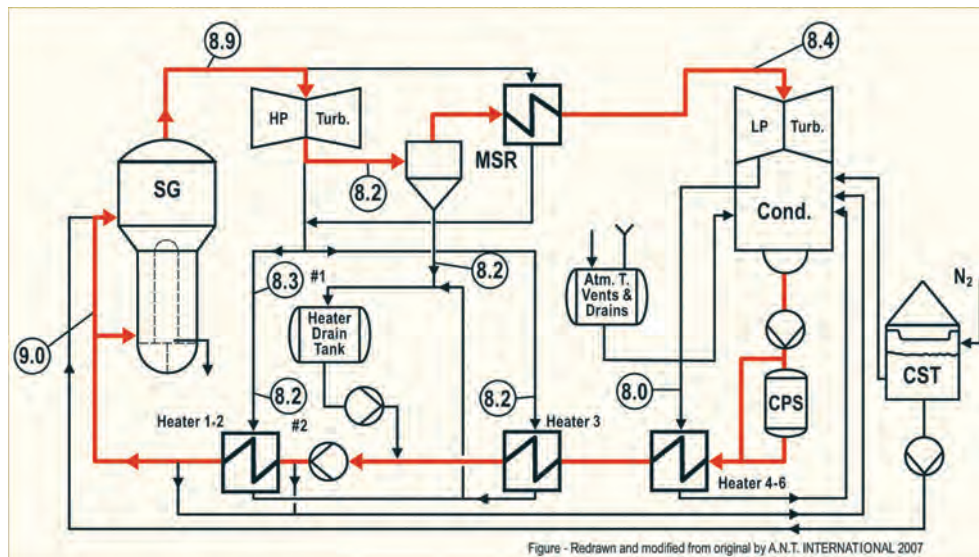


Figure 2-15: Secondary Side concept of a typical US PWR.

In order to practice the “standard” All Volatile Treatment (AVT) chemistry, ammonia is injected after the Condensate Polishing System (CPS), whereby the amount of this chemical is controlled by the pH in the final feed-water which is in Figure 2-15 at 9.0. In the steam generator itself the ammonia is distributed between steam and water by a factor of about 3 which means the ammonia concentration in the steam generator water is lower than in the re-circulating water. The next concern is related to the areas of the steam water cycle where steam is starting to condense. Calculations for several locations show that the pH in the water phase in areas where condensation occurs is below pH 9.0. At these low pH's the iron dissolution is enhanced. That means that more corrosion products are entering the steam generators with typical values of 10 to 15 ppb in the final feed-water. After condensation, the water of the heater drains is partially forward pumped. However, the water from the turbine condenser and the condensate coming from the low pressure (LP) heaters is passing the CPS where all the ammonia is taken out.

The second concern is the oxygen control because there are several locations in the cycle where oxygen can enter the system. Such locations are the turbine condenser, condensate storage tank and vents, and drain system. If the tightness of these systems is not good enough there remains only the option to inject some hydrazine downstream the CPS. However, hydrazine injection is limited because hydrazine decomposes partly to ammonia.

Such concerns do not exist in case of Siemens designed units as it is shown in Figure 2-16. The plant concept can be characterized by the following features:

- High integrity condenser which means the tubes are welded into the tube sheet
- Condenser tubing material is titanium or austenitic stainless steel
- No copper containing material in the entire secondary side
- Mechanical filtration downstream of the LP pre-heaters, and in the effluent of the high pressure (HP) pre-heater.
- No CPS (or no use of CPS)
- High-AVT Chemistry (feed water pH >9.8)

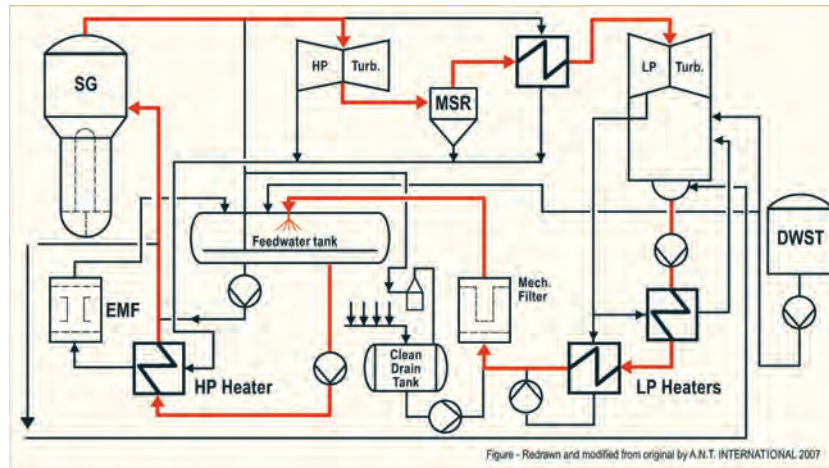


Figure 2-16: Simplified diagram of a Steam Water Cycle in Siemens designed *PWRs*-

In the case of the Siemens designed *PWRs* the iron transport to the steam generators is kept at a level of about 1 ppb, thus contributing to the cleanliness of the entire steam generator and specifically minimising the risk of the formation of heated crevices. A severe oxygen control at the cold end of the steam/water cycle is also not necessary. This is because sufficient hydrazine in the final feed water will scavenge the remaining oxygen that passes the oxygen removal system in the feed water tank. This physical O_2 - removal system alone keeps the O_2 -level within the specification limits of <5 ppb.

The concept of using high integrity condensers allows the operation of the plant without *CPS*. However, should a leak occur in the condenser area, it must be immediately identified and plugged.

2.3.2 Optimizations

In most cases, the plant concept is strongly influenced by the architect engineer, who has to design the plant with consideration of the economics of construction. The concepts, described in Section 2.1 are two extreme, but typical, examples.

Whatever plant concept is available for the actual operation, there are three parameters which strongly influence all the corrosion phenomena in the steam generators. They are:

- Corrosion products
- Impurities
- Oxygen.

In order to minimize the ingress of these species to the steam generator, the following optimizations were considered and implemented where required:

- Controlling iron transport e.g. by pH- and oxygen- optimization
- Adjusting water chemistry impurities by avoiding the formation of aggressive environments in heated crevice areas by As Low As Reasonably Achievable (*ALARA*) chemistry, Molar Ratio Control (*MRC*) and elevated hydrazine
- Minimizing corrosion accelerants
- Inhibitors for corrosion processes like:
 - Phosphate chemistry
 - Boric Acid Treatment
- Removing impurities from steam generators by chemical cleaning and/or sludge lancing
- Addition of Dispersants

3 Material degradation management (Peter Ford)

3.1 Situation at the conclusion of the *LCC2* report

Emphasis was placed in the *LCC2* annual report on the mechanisms and phenomenology of the various environmentally-assisted materials degradation modes. This approach was supplemented by a separate report entitled “Environmentally-Assisted Degradation of Structural Materials in Water Cooled Reactors” (Ford, 2006), which was aimed specifically at people who were relatively new to the subject, or needed a reminder of, for instance, the materials of construction, the basics of corrosion science, and the mechanisms of the various modes of degradation, including those (e.g. microbiologically-influenced corrosion) that they might not be concerned with during their normal day.

Materials degradation issues have presented economic and/or safety concerns to the water-cooled nuclear reactor industry for decades. The lack of adequate life-prediction capabilities, especially for environmentally assisted cracking, has forced the industry to manage these situations in a reactive manner, thereby allowing only a relatively short time for the prioritization of resources, the development of mitigation actions, the definition of inspection procedures, etc.. As mentioned in Section 2.4.1 there has been a concerted movement by the US utilities (Nuclear Energy Institute, 2003, Hickling & Jones, 2005, Riley, 2006) and by the *USNRC* (Muscara, 2007), to move from a reactive mode of managing materials degradation to a proactive mode. In other words, resource prioritization decisions and technical developments are made well before potential degradation modes present an economic or safety concern.

However, the development of a proactive management approach relies on predictions of future degradation, and that requires a quantitative understanding of the mechanisms of degradation that is in agreement with past plant and laboratory experience. It is for this reason that the discussions in the *ANT International* reports have emphasized a mechanisms-based understanding of the degradation modes.

The proactive management studies by both the US utilities and the NRC were conducted in two stages. First an *assessment* phase, which identified the *future* areas of concern, and second, a *management* phase, which involved prioritization of the future degradation issues and the development of appropriate mitigation actions, inspection procedures and the information required for “repair or replacement” decisions.

The findings of the two assessment studies were very similar. For brevity, the discussions in the *LCC2* report centered on the conclusions of the *USNRC* report (Muscara, 2007) which identified (a), existing materials degradation issues for specific *BWR* and *PWR* plant components that were likely to continue in the near future due to a lack of knowledge of the phenomenon, or (b), currently unidentified phenomena that were likely to emerge as issues in the longer term. In addition, discussion in the *LCC2* report touched upon generic problems that cut across these component-specific issues; an example of this would be the effect of cold work which can cause degradation in a wide range of normally resistant alloy/environment systems.

These preliminary discussions in the *LCC2* report were then expanded to cover specifically two topics highlighted in both the *USNRC* and utility assessments that needed continued attention.

Stress corrosion cracking of irradiated stainless steels in *BWRs*.

It was concluded that there was a sound mechanisms-based prediction methodology that gave reasonable predictions of irradiation-assisted stress corrosion cracking observations in the laboratory and in the plant. This methodology had evolved from that developed in the 1980's for stress corrosion cracking of non-irradiated components, such as stainless steel piping, carbon and low alloy steel pipes and pressure vessels, and nickel-base alloy safe ends and access hole covers. The main limitations to the use of these deterministic, mechanisms-based models for prediction of cracking in plant components were primarily related to the uncertainty in defining the actual system conditions (e.g. residual stress profiles, degrees of grain boundary sensitization, etc.). However this mechanistic knowledge certainly gave a strong basis for interpreting the cracking behavior as a function the interactions between the various material, environment and stress parameters, and gave a fundamental rationale for the quantification of, for example, water chemistry guidelines and the adoption of noble metal technology to mitigate irradiation-assisted stress corrosion cracking.

Stress corrosion cracking of nickel-base alloys in *PWR* primary environments

Intergranular stress corrosion cracking of Alloy 600 was observed in *PWR* primary side environments in the *laboratory* in the 1950s and '60s (Blanchet et al., 1977) and was initially observed in the early 1970s in recirculating steam generator (*RSG*) tubing on the primary side after, in some cases, extremely short operational times (e.g. 2 years at Obrigheim) (Schenk, 1976). The first observed cases of cracking leading to leakage in thicker section components occurred in 1986 at a pressurizer instrumentation nozzle in a *CE* plant (San Onofre-3) after 10,000 hours. The first incidence of cracking in the slightly lower temperature vessel head penetrations associated with the control rod drive mechanism occurred in France at the Bugey-3 plant in 1989. Further incidents (Shah et al., 1994) in France (Champigny et al., 2003), (Chartier et al., 2003), Sweden, Belgium and in the US (Hiser, 2003) indicated that cracking of the pressure vessel penetrations was not an isolated observation.

In spite of the fact that cracking has been observed in some nickel-base alloys in high temperature *PWR* primary side environments for more than 30 years, this phenomenon has been hard to predict and therefore manage. There are a number of reasons for this, including a large distribution in cracking data (e.g. "initiation" times, crack propagation rates). This distribution is associated with a high sensitivity of the cracking susceptibility to system parameters such as stress, material composition and microstructure, temperature and hydrogen fugacity. In many cases these parameters are either not known or are inadequately controlled. Moreover the time for failure of thin walled components, such as tubes, can be dominated by surface damage phenomena such as pitting, *IGA*, etc. These phenomena are stochastic in nature and, therefore, a distribution of failure times is to be *expected*, regardless of the accuracy of definition of the system.

In addition, unlike the situation for *BWRs* highlighted above, there has not been a mechanisms-based life prediction capability that has been qualified via comparison with the laboratory and plant experience. Thus there has been no basis for analyzing the complicated interactions between the various material, environment and stress parameters. It is only recently that the development of such a mechanisms-based understanding has been started.

The various system parameter interdependencies were discussed in the *LCC2* report, including the justification of mitigation actions associated with (a) the adoption of Alloy 690 *TT* as a replacement alloy for Alloy 600 *MA* and, (b) modifying the specifications for the dissolved hydrogen content in the coolant. This Section in the *LCC2* report concluded with a discussion of the empirically-based life prediction approaches that have been used for management of cracking (e.g. inspection, repair or replacement) in plant in Europe and the USA.

Future needs

At the conclusion of the *LCC2* report it was noted that there continued to be numerous concerns associated with stress corrosion cracking of structural materials in *LWR* components. Prioritization for future discussion in *ANT International* reports was given to the following topics either because they represented generic concerns to both *BWRs* and *PWRs*, or because there were concerns about the adequacy of the life prediction capabilities for specific plant components (and hence the adequacy of the mitigation actions);

- Stress corrosion cracking of *PWR* steam generator tubing in both the primary and secondary systems.
- Stress corrosion cracking of large section components in the *PWR* primary system manufactured with nickel-base alloys.
- Stress corrosion cracking of austenitic alloys associated with fuel assemblies.
- Effect of cold work on stress corrosion cracking of structural materials in both *BWRs* and *PWRs*.
- Effect of the environment on the fracture resistance of *LWR* structural materials.

These issues are addressed in current 2007/2008 *ANT International* reports. For instance, stress corrosion cracking of austenitic alloys associated with fuel assemblies is addressed in a Fuel Material Technology Report, and the issue of stress corrosion cracking of nickel-base alloys in *PWR* secondary environments is covered in Section 2.4 of this *LCC3* Annual Report.

In Section 3 of the *LCC3* Annual Report the following issues are discussed in the light of new information in 2006/2007.

- The effect of cold work on the stress corrosion cracking susceptibility of the materials of construction in *PWRs* and *BWRs*.
- The role of the environment on fracture resistance.
- The effect of hydrogen fugacity on stress corrosion cracking of nickel-base alloys in *PWR* primary systems.

3.2 Updates on materials degradation Issues

3.2.1 The effect of cold work on stress corrosion cracking of structural materials in *BWRs* and *PWRs*

It has been recognized for a long time that cold work may promote the initiation and propagation of stress corrosion cracks in structural alloys in *BWRs* and *PWRs*. This recognition started with observations in the 1960s of the effect of “abusive” grinding applied to welds in *BWR* stainless steel piping, and of the effect of cold work on the cracking of *PWR* tubing in the 1970s. More recently, similar deleterious effects have been noted for Type 304 stainless steel *BWR* core components that have been abusively ground and/or cold worked during fabrication (Medoff, 1996, Horn et al., 1997, Suzuki et al., 2004). In these more recent cases, however, the observations have been made on “resistant” L-grade stainless steels operating under strict water purity guidelines. Similarly cracking of stainless steels in *PWR* primary circuits has been observed under environmental conditions where cracking would not normally be expected and, again, this has been attributed to cold work effects.

It is apparent, therefore, that the beneficial effects vis a vis developing stress corrosion cracking resistance by modifying the alloy composition and microstructure, or controlling the water chemistry regime, may be negated if there is a significant degree of surface or bulk cold work in the structure.

4 Electrochemical membrane methods in *LWR* cleanup systems (Wilfried Rühle)

4.1 Introduction

Normally water treatment in Nuclear Power Plants consists of ion exchange, evaporation and mechanical filtration techniques. These technologies are used to control the chemical shim in *PWRs* and to clean the coolant in both light water reactor types from chemical pollutants and especially from radio nuclides.

Although these water treatment methods show excellent results, there are some areas for improvement. The equipment is spacious and consequently need much larger rooms. This is especially relevant for the control areas which have to be constructed at a high technological level connected to high costs. The most important disadvantage using traditional methods is producing a big amount of expensive radioactive waste. So there is a need for small and efficient equipment which doesn't produce much radioactive waste and doesn't require high investment costs.

Resulting of the experience from the chemical industry, electrochemical membrane techniques seemed to be the best choice as alternatives, Kupping et al., 1995. Although there is an old patent from 1979 in these fields, Grant, 1979 it lasted till the end of the nineties, when experiments with electrochemical membrane technologies in modern Nuclear Power Plants with *PWRs* and *BWRs* have been started, Paul, 1995.

In these experiments only electrochemical membrane techniques like “membrane electrolysis” and “electrodialysis” and similar techniques were used and only those are considered in this paper. All other membrane techniques used in chemical industry and in water purification, like reverse osmosis, ultra filtration, nano filtration, diffusion dialysis etc. were not tested as they are already implemented in the nuclear power plant industry for different areas of water treatment. However, based on *KKP* experience it can be concluded, that for radioactive contaminated waste water treatment, the electrochemical membrane techniques are the most promising methods.

4.2 Membrane techniques under consideration

As mentioned before, this paper covers only electrochemical membrane techniques like membrane electrolysis, electrodialysis, electrodialysis with bipolar membranes, electrodialysis with ion exchangers, and oxidation cells with boron doped electrodes.

4.2.1 Membrane electrolysis

Membrane electrolysis (Figure 4-1) is a process whereby both electrode reactions, i.e. the cathodic reduction as well as the anodic oxidation, are linked to the transport and transfer of charged ions.

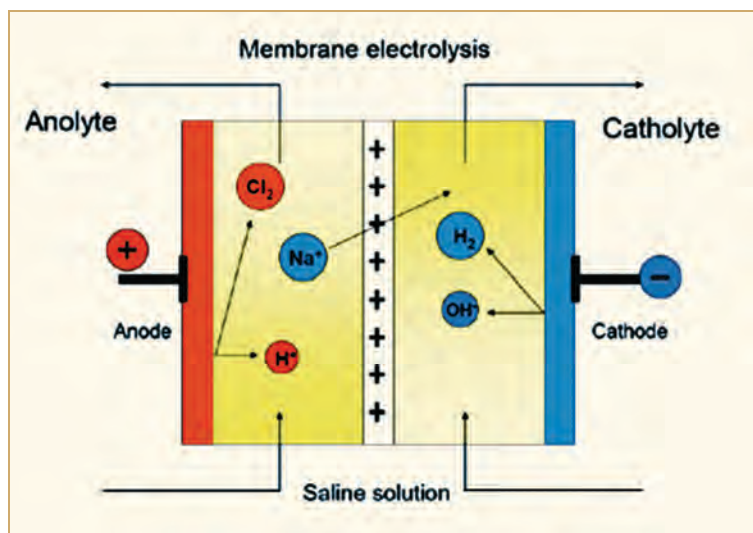


Figure 4-1: Schematic chart of membrane electrolysis (by courtesy of FuMA-Tech, a member of BWT AG, 2007).

In membrane electrolysis, the electrode reaction is essential to the actual separation process. The purpose of the membrane is to separate the anode loop (anolyte) from the cathode loop (catholyte) hydraulically, in order to avoid unwanted secondary reactions, so as to combine the electrode reaction with a separation step or to isolate separately the products formed on the electrode. In water electrolysis, such products may be in a gaseous form such as oxygen and hydrogen, as well as the acids (H^+) and bases (OH^-) formed on the electrode, or the combination of gaseous chlorine and caustic soda solution and hydrogen as in sodium chloride electrolysis.

Electrochemical reactions, that are frequently observed, include metal deposition as well as the formation of hydrogen on the cathode and the anodic oxidation of organic compounds but also of ions such as chloride, cyanide, nitrite and others.

Depending on the purpose of the separation process, both oxidative and reductive conversions are of interest to industry. The electrolysis of sodium chloride for the production of chlorine and caustic soda solution is the most important electro-membrane process worldwide. Nowadays, roughly 48 million tons of chlorine are produced each year, with more than 30% of this sum being converted by membrane electrolysis. Furthermore, membrane electrolysis is applied for the production of sodium hypochlorite for drinking water disinfection. Recently, electrolysis processes for the production of ozone, chlorine dioxide or hypochlorous acid have been increasingly applied in drinking water disinfection.

4.2.2 Electrodialysis (*ED*)

Electrodialysis is an electrochemical process whereby electrically charged particles, ions, are transported from a raw solution (retentate, diluate) into a more concentrated solution (permeate, concentrate) through ion-selective membranes by applying an electric field. When a salt solution is under the influence of an electric field, as is the case in an electrodialysis module, the charge carriers in the solution come into motion. This means that the negatively charged anions migrate towards the anode and the positively charged cations towards the cathode (Figure 4-2).

In order to separate salts from a solution, ion-selective membranes, through which in an ideal case only one type of ion can permeate, are arranged in the solution perpendicular to the electric field. Thus negatively charged particles (anions) can pass through an anion exchange membrane on their way to the anode but are selectively retained by the upstream cation exchange membrane. This separation stage results in a concentration of electrolytes in the so-called concentrate loop and a depletion of charge carriers in the so-called diluate loop.

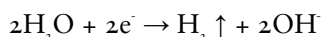
A special task is connected to the chambers containing the electrodes, Rautenbach, 1997. At the electrodes the electricity transport by electrons is switched to electricity transport by ions in the solution. This means exchanging electrons between ions and electrodes and so being a chemical reaction. The type of reaction at the electrodes depends on the composition of the solution. For example the following reactions can take place at the anodes:

For NaCl- solution, $\text{pH} > 7$: $\text{Cl}^- + 2\text{OH}^- - 2e^- \rightarrow \text{OCl}^- + \text{H}_2\text{O}$

For NaCl- solution, $\text{pH} < 7$: $2\text{Cl}^- - 2e^- \rightarrow \text{Cl}_2 \uparrow$

For Na_2SO_4 - solution: $2\text{H}_2\text{O} - 4e^- \rightarrow \text{O}_2 \uparrow + 4\text{H}^+$

At the cathode mostly hydrogen production occurs:



For extraction of the non condensable gases produced at the electrodes and other reaction products the electrode chambers are purged by a separate purging circuit. Normally a sodium sulphate solution is used for this purpose. It is useful to keep salt concentration and pH constant in this circuit.

For example, electrodialysis is applied on an industrial scale for the production of table salt from seawater, for the production of drinking water from brackish water, for the treatment of boiler-feed water and the desalination of whey (skimmed milk).

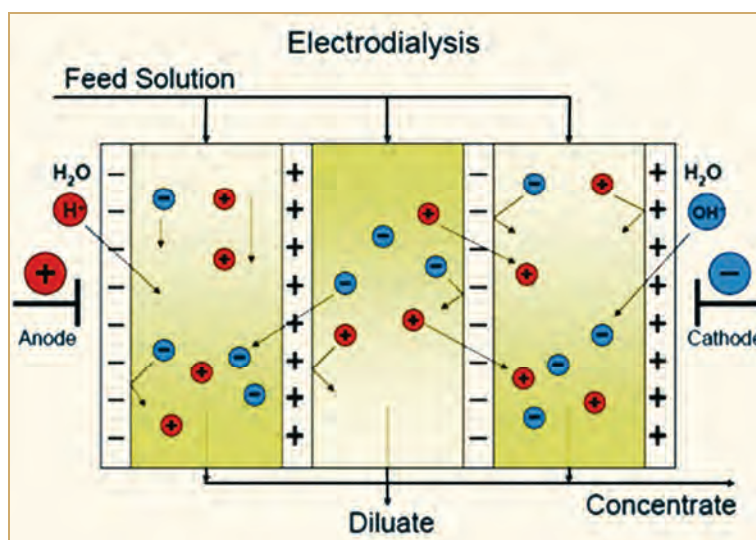


Figure 4-2: Schematic chart of electrodialysis (by courtesy of FuMA-Tech, a member of BWT AG, 2007).

However, the key advantages of electrodialysis come into effect particularly in applications for selective removed substance, as for example nitrogen removal from drinking water (nitrate, ammonium), desalination of organic substances, and concentration of salts, acids and bases.

4.2.3 Technical details of *ED* and other membrane techniques

4.2.3.1 Ion exchange membranes

Ion exchange membranes are ion exchangers formed as thin sheets. They consist of a matrix made of a polymer with charged chemical groups bound positively or negatively in this matrix (Figure 4-3).

5 Effect of water chemistry on fuel cladding

5.1 *PWR* water chemistry (Rolf Riess)

5.1.1 Introduction

The Primary Coolant serves as a moderator and is the medium for transporting heat from the core to the steam generators. Hence, it must not endanger plant operation by the corrosion of materials and consequences thereof. The task of water chemistry can be divided into the following main points:

- 1) Metal release rates of the structural materials should be minimal.
- 2) The occurrence of localized forms of corrosion should be counteracted.
- 3) The transport and deposition of corrosion products must be influenced in such a manner, that contamination of the primary coolant system is kept low.
- 4) The deposition of corrosion products on heat transfer surfaces, particularly on fuel assemblies, should be prevented as far as possible.
- 5) Radiolytic formation of oxygen should be suppressed.

The materials which are in contact with the primary coolant are:

- a) Austenitic stainless steels of components and piping of the primary system.
- b) Zirconium alloys for cladding of fuel assemblies.
- c) Incoloy 800, Inconel 690 *TT* or, Inconel 600 *MA* or *TT* for steam generator tubes. Stainless steel tubing is used in *VVER* SGs.
- d) High alloy materials (ferritic stainless steels) of low surface area for internals of the primary system.

The water chemistry conditions applied to these materials must fulfil the above mentioned requirements. Thus the primary coolant of *PWRs*, which contains boric acid (900-1800 ppm B at BOC) as a neutron absorber, is chemically conditioned by the addition of isotopically pure lithium (Li-7) hydroxide (2-5 ppm Li at BOC) as a non volatile pH-control agent and of hydrogen.

Recently, an increasing number of *PWRs* are adding zinc (5-40 ppb) in order to (1) reduce plant activation by reducing the metal release and by replacing cobalt isotopes in the oxide layer and (2) minimize the initiation of stress corrosion cracking of Inconel 600 material.

In *VVER* plants NH_3 is added, which decays to H_2 by radiolysis. Instead of LiOH , KOH is added, so that the pH-control is accomplished by $\text{K} + \text{Li} + \text{Na}$ (Li-7 is formed by the B-10 (n, α) Li-7 reaction) and NH_3 . None of the *VVER* plants are adding zinc like the *PWRs*.

5.1.1.1 Concerns regarding fuel elements

From today's perspective it is most important to evaluate the factors which are of greatest concern for the fuel element corrosion, and define the driving forces (problems) for water chemistry in the last 10 to 15 years.

These driving forces are improvements to plant availability and fuel economics which can be characterized by:

- Changing to 18 and 24 month cycle.
- Core up-rating.
- Higher enrichment fuel with increased burn-up.
- Low leakage cores combined with increased sub-cooled nucleate boiling.

These moves - based on operational experience - caused concerns over coolant additives and uncontrolled impurities because the fuel elements in the operating plants (specially in the US) experienced heavy *CRUD* deposition at positions where sub-cooled boiling created two negative effects, namely (1) accelerated corrosion effects and (2) Axial Offset Anomaly (AOA).

The corrective actions believed to be effective, are:

- Higher pH Primary Water Chemistry
- Zinc Addition

For the pH strategy the pH_T -values must be > 6.9 by increasing the LiOH concentration above the long time accepted value of 2-2.2 ppm Li. However, such an increase in the lithium concentration may present a risk regarding the corrosion resistance of the Zirconium Alloys.

Specifically one environmental factor may be emphasized which is the corrosion product deposition on fuel surfaces, which can lead to increased cladding temperatures and increased corrosion rates. Such deposits have been identified as non-stoichiometric Ni-ferrites ($\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$), Ni oxide or metallic nickel. Such *CRUD* deposition is occurring specifically at positions with sub-cooled boiling and may cause accelerated corrosion defects locally and an axial power shift by boron precipitation (AOA).

Zinc addition may also lead to a more degrading *CRUD* at positions with high steaming rates. Thus, surveillance programs after introduction of zinc are highly recommended, especially for *PWRs* with high duty cores. On the other hand, zinc reduces the corrosion product release from system surfaces.

5.1.1.2 Higher pH primary water chemistry; lithium/B-strategy

As described above, LiOH is used in Western *PWRs* as the pH control agent whereas KOH is used in *VVERs*. These compounds together with boric acid fix the pH at all temperatures. In order to explain all the Li/B-ratio changes, it is convenient to use the information shown in Figure 5-1 for the US case by Turnage, 2004. Further details can be found in a review of the *EPRI* Water Chemistry Guidelines by Fruzzetti et al., 2004.

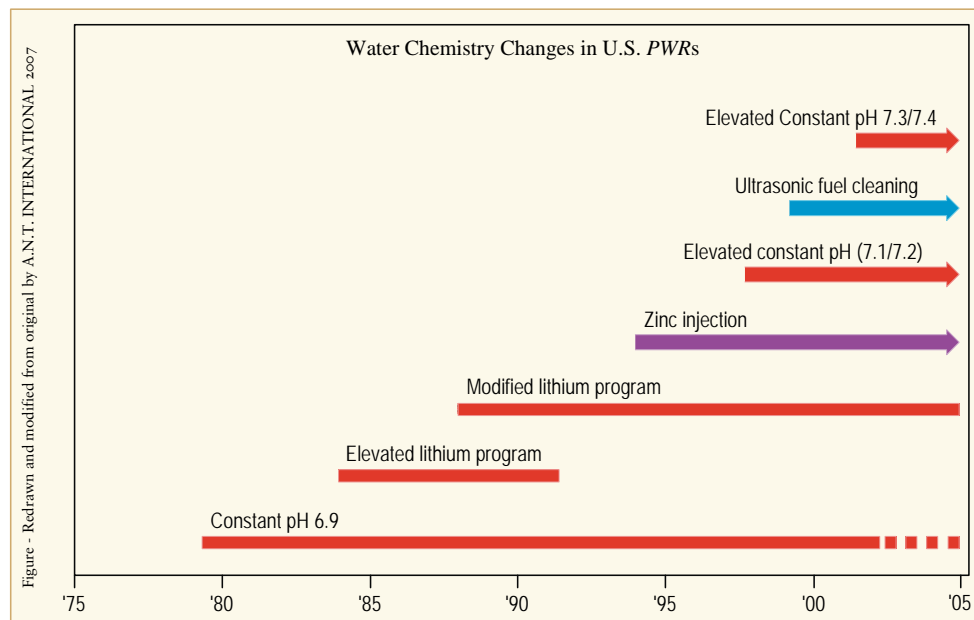


Figure 5-1: Water Chemistry Changes in U.S. *PWRs*, Turnage, 2004.

Regarding the application of all the Li/B-chemistries in operating *PWRs* there are major differences when applied in the various countries. These are discussed in detail in *LCC2* Annual Report (AR), Section 6.

The German *PWRs* for example are still operating today with the modified B/Li-program and therefore the specification, given by AREVA NP and VGB respectively, have an upper lithium limit of 2.2 ppm. Only in very specific cases, can utilities apply lithium values higher than 2.2 with the consent of the fuel manufacturer.

Bretelle et al., 2004 and Nordmann, 2005 described the actual situation in France regarding the optimum pH in the primary circuit of *PWRs*. According to their explanation, the $\text{pH}_{300^\circ\text{C}}$ of 7.2 ± 0.2 is applied because this value seems to be a good optimum for French *PWRs*. A typical French primary water chemistry for older EDF-stations is shown in Figure 5-2.

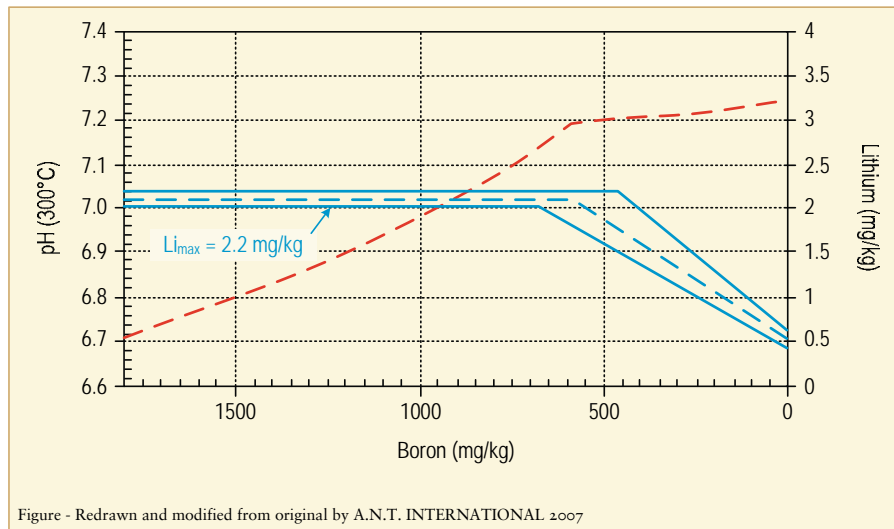


Figure - Redrawn and modified from original by A.N.T. INTERNATIONAL 2007

Figure 5-2: Typical French Primary Water Chemistry, Bretelle et al., 2004.

In case of longer fuel cycles it has to be considered to start operation with 3.5 ppm lithium up to a $\text{pH}_{300^\circ\text{C}}$ of 6.9, which is then kept constant till reaching 2 ppm Li. For the rest of the cycle Li remains constant till reaching a $\text{pH}_{300^\circ\text{C}}$ of 7.2.

As summarized by Yurmanov, 2005 and confirmed by Martikan, 2005 the general practice in VVER-plants is a coordination between boron and the pH control agents K+Li+Na in such a way that the $\text{pH}_{300^\circ\text{C}}$ is coordinated in the range between 7.0 and 7.2 over the entire cycle.

5.1.1.3 *PWR* zinc injection

In the late 1980s zinc injection in *BWRs* provided evidence that radiation fields could be reduced with the controlled addition of Zinc to the coolant. Some years later experimental studies and plant demonstrations in *PWRs* have also confirmed beneficial effects.

Based on these findings, the following expectations were developed, regarding the application in commercial power stations:

- Zinc affects the corrosion product films on the inner surface of the coolant system; it makes the oxide film thinner and more protective. This situation should therefore reduce the in-core deposits by reducing the *CRUD* production term.
- Zinc reduces the solubility of corrosion product films on coolant system surfaces. It should therefore affect the composition of *CRUD* deposits.
- Zinc should replace Co-60 in the oxide film.

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