FR0301273
INIS-FR-1661

COMPARISON OF FRENCH AND GERMAN NPP WATER CHEMISTRY PROGRAMS

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1. INTRODUCTION

PWRs in the western hemisphere obey basically the same rules concerning design, choice of material and operational mode.

In spite of these basic similarities, the manufacturers of PWRs in different countries developed different solutions in respect to single components in the steam/water cycle.

Looking specifically at France and Germany, the difference in the tubing material of the steam generators (Inconel 600/690 chosen by Framatome and Incoloy 800 chosen by the former Siemens KWU) led to specific differences in the respective chemistry programs and in some respect to different 'philosophies' in operating the water/steam cycle.

Compared to this, basic differences in operating the reactor coolant system cannot be observed. Nevertheless specific solutions as zinc injection and the use of enriched B-10 are applied in German PWRs. The application of such measures arises from a specific dose rate situation in older PWRs (zinc injection) or from economic reasons mainly (B-10).

2. REACTOR COOLANT SYSTEM

2.1 Reactor Coolant System of French PWRs

2.1.1 EDF design and material concept

The materials used in the primary circuit are mainly composed of stainless steels (reactor vessel, internal structures), nickel based alloys (Inconel 600 or 690 for SG tubes) and Zirconium alloys (fuel cladding).

2.1.2 EDF water Chemistry Guidelines

The EDF primary water chemistry specifications are very similar to other ones in western countries [1].

The most crucial limit is related to lithium concentration in order to get the desired pH all along the fuel cycle as the boron content decreases. Figure 1 shows the technical specification limits required by the French Safety Authority and the target value for lower dose rates.

The target of lithium corresponds to a range of 0.1 above and 0.1 below 2.1 mg/kg of enriched ^{7}Li. The lithium is kept constant up to reaching 570 mg/kg of boron, corresponding to a $pH_{300°C}$ of 7.2. Then, lithium decreases down to 0.5 ± 0.1 mg/kg, accordingly with boron, at this constant pH.

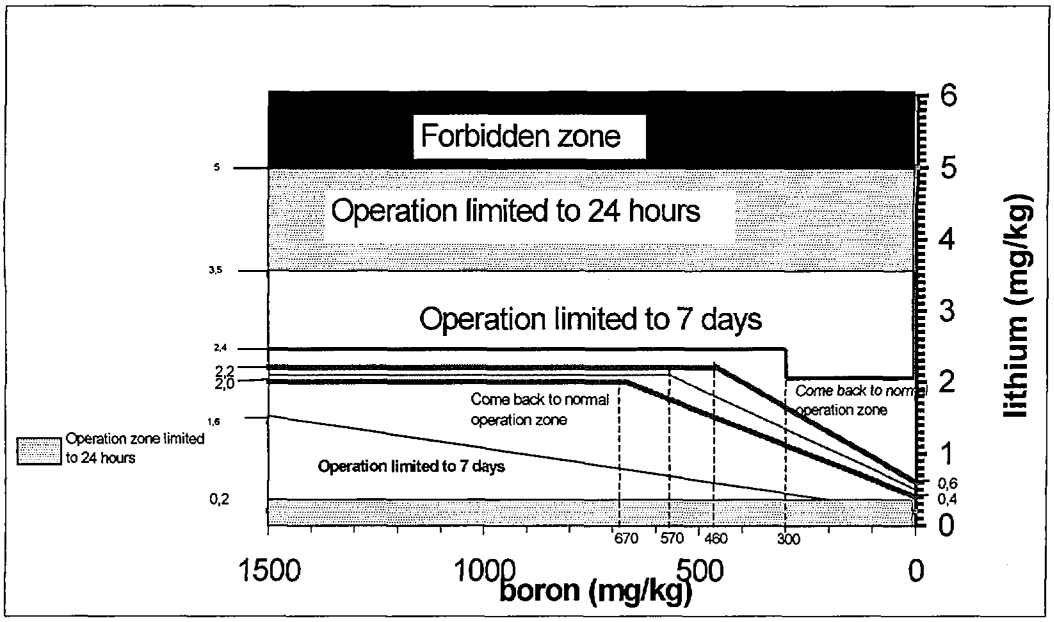


Figure 1: Lithium target and technical specifications limits

The target band of lithium value ± 0.1 mg/kg is not a technical specification but an internal EDF objective for minimising dose rates associated with corrosion products transport requiring an optimum and constant $pH_{300°C}$ of about 7.2. Other organisations prefer a pH of 7.3 or 7.4. EDF has decided to select 7.2 for various reasons. Past experience with a pH of 7.0 compared to 7.2 did not show a significant difference in operating units. A higher pH will unlikely induce important benefit and may have inconveniences in French plants.

The pH of 7.2 instead of the previous value of 7.0 has been selected based only on international experience and code calculations from French Commissariat à l'Energie Atomique [2].

Lithium concentration is limited to 2.2 mg/kg by fuel vendors to prevent the cladding from general corrosion, particularly with high duty fuel, high heat flux, high temperature, when nucleate boiling may occur under deposits, creating local overconcentration of lithium. Thus, the corresponding pH at the beginning of the fuel cycle is close to 7.0 and far below 7.2 or 7.4. Consequently, it will be impossible to reach 7.4 before the last part of the fuel cycle. Keeping the pH at 7.2 will give a more constant pH during the overall fuel cycle.

The upper limits with operation limited to 7 days or 24 hours have been established in agreement with Safety Authority in order to avoid a too high pH which would be deleterious for the fuel cladding generalised corrosion mainly with nucleate boiling and Alloy Inconel 600 Stress Corrosion Cracking which increases with lithium concentration and pH.

The lower limits with operation limited to 7 days or 24 hours have been also established in agreement with Safety Authority in order to avoid a too low pH which would be deleterious for the generalised corrosion of stainless steels in the primary coolant system. There is no reason and no need to operate under such low values of pH and lithium even if no unacceptable degradation is expected, on a safety.aspect.

Only one unit (Cattenom 2) applies a modified chemistry in the frame of DUO experimentation, as shown on Figure 3 [3].

The use of ^{10}B is not yet decided in France. Its advantage would be clearly established in two cases:

- if it would avoid modifying existing tanks to take into account fuel or core management modifications,
- if the present operation or with the intended modifications (beginning of fuel cycle with a high lithium content for extended fuel cycles [3]) during fuel management modification, could not be maintained because of unacceptable consequences on corrosion, fuel deposits or dose rates.

Another reason could also be a great decrease in the authorized released amounts of boron in the environment.

EDF strategy for the shutdown and start up RCS chemistry optimization are described in this conference [4].

2.1.3 EDF operational practice

The operational results of French NPPs are gathered by the Central Laboratories through a chemistry data base (MERLIN) which gives the results from all the units, the trends and evolutions of performances, problems ; the data bank also allows to check the potential impact of a specification modification on availability and relation between chemistry and corrosion or dose rates.

Figures 2 and 3 give the B/Li results for Golfech 1, which follows the classic coordinated chemistry and Cattenom 2, which follows the modified chemistry [3], during the third conversion cycle.

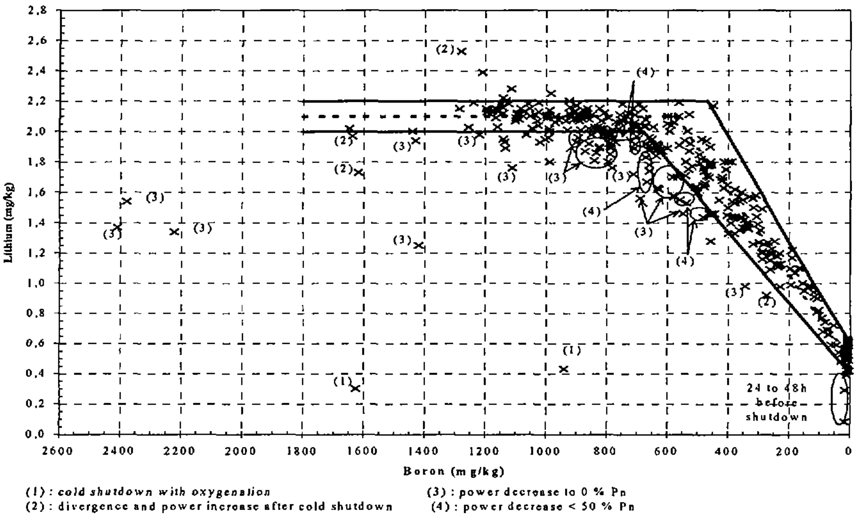


Figure 2: B/Li results during Golfech 108

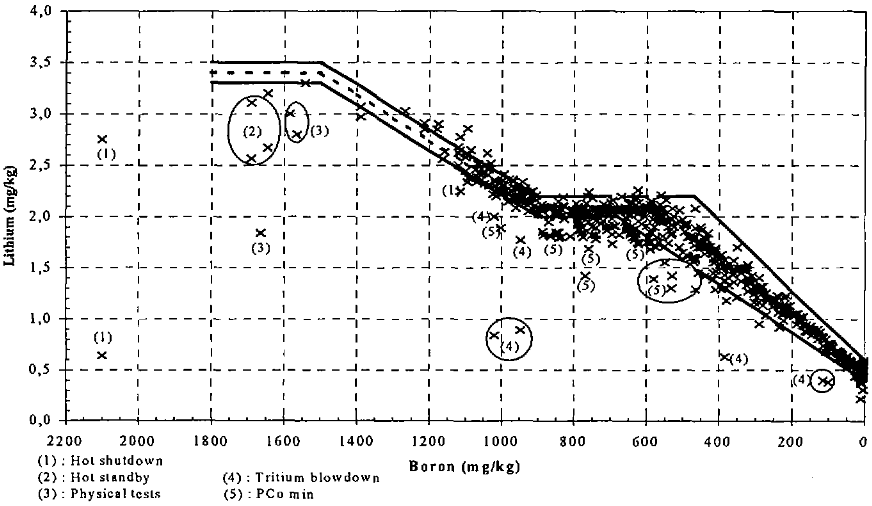


Figure 3: B/Li results during Cattenom 210

2.2 Reactor Coolant System of German PWRs

2.2.1 Design and material concept

The materials used in the reactor coolant system of German PWRs are mainly composed of stainless steel (reactor pressure vessel, RPV internal structures, pressurizer, loop piping cladding, auxiliary systems), Incoloy 800 for SG tubing and Zirconium alloys (fuel cladding). With respect to the dose rate development, it is important to mention, that in the new Siemens plants, Pre-Convoy (Philippsburg-2 and Brokdorf) and Convoy plants (Isar-2, Emsland and Neckarwestheim-2) a Cobalt Replacement Program was applied, whereas all the other plants contain cobalt base materials in RPV internals, valves and pumps.

Regarding the system design, Siemens plants have very similar design if compared with the EdF plants, except in all Siemens plants there is a degazifier in their let down line down stream the coolant purification mixed bed filters. This degasifier enables to remove oxygen fast from the coolant during start-up of the plant.

2.2.2 Coolant chemistry program

The main objectives of the coolant chemistry control program is to maintain the primary system and fuel integrity and in addition to reduce ex-core radiation fields. To fulfill these objectives, coolant chemistry parameters were specified by VGB in cooperation with Siemens (KWU) in the early seventies as given in the Table 1:

Parameters	Specifications
Lithium [mg/kg]	0.2 – 2.2
Hydrogen [mg/kg]	1 - 4
Oxygen [mg/kg]	< 0.005
Chloride [mg/kg]	< 0.2

Table 1: VGB coolant chemistry specifications

Based on the request and need of several plants, these coolant specifications were modified by Siemens in the late nineties with the introduction of action levels (see Table 2).

Parameters	Operating range	AL 1	AL 2	AL 3
Lithium [mg/kg]	< 2.1	> 2.1	> 2.5	> 5
Hydrogen [mg/kg]	2 - 4	< 2 / > 4	< 1	< 0.5 / > 5
Oxygen [µg/kg]	< 5	> 5	> 20	> 50
Chloride [mg/kg]	< 0.1	-	> 0.2	> 1

AL 1: Action level 1, 4 weeks operation
AL2: Action level 2, 1 week operation
AL3: Action level 3, plant shutdown within 12 hours

Table 2: Siemens power operation control parameters

The limitation of the chemistry parameter concentrations addresses material compatibility issues, especially to maintain the compatibility of the fuel cladding. To achieve a reduction of the ex-core radiation field, a "Lithium-Boron Operation Strategy" was established and improved, based on the achieved field results. In addition to the improvements of the coolant chemistry, cobalt replacement programs in new plants are applied and other measures like Zinc injection in some old plants are introduced. The coolant chemistry changes and the improvements of the plant materials with the aim to reduce the ex-core radiation field in Siemens plants can be chronologically summarized as follows.

2.2.3 Coolant chemistry improvements

The materials and coolant chemistry of Siemens designed PWRs have been progressively modified in successive plants, in order to improve the dose rate situation. The early plants started operation between 1969 and 1984, contain cobalt-base alloys in their reactor pressure vessel internals, pumps and valves; accordingly they showed a rather poor radiation field performance, caused mainly by ^{60}Co. However some improvements were achieved by introducing reasonable coolant chemistry improvements. The cobalt replacement program, introduced in the latest plants (pre-convoy and convoy plants started operation between 1985 and 1989), was very successful with respect to radiation field reduction [5]. Besides this cobalt replacement program, coolant chemistry improvements were applied. These coolant chemistry improvements were performed in three stages as shown in Figure 4.

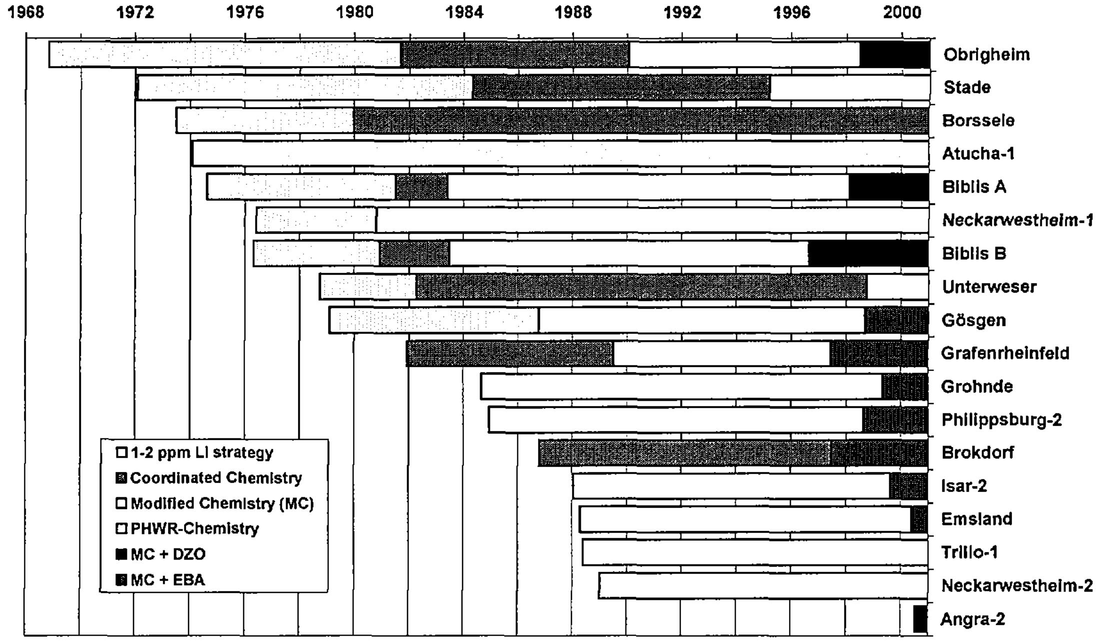


Figure 4: Applied coolant chemistry in Siemens designed PWRs as a function of time

a. "1-2 ppm Li strategy"

For this program, the achievement of a specific pH value by coordinating the lithium to boron concentration was not specified. The operating lithium concentration was between 1-2 ppm. Usually lithium was build up by boron-10 burnout and when 2 ppm was reached, it was removed down to 1 ppm by coolant purification system. During this stage several plants tried to control the lithium concentration according to the observed reduction of the coolant cobalt activities.

b. "Coordinated Chemistry"

This chemistry program with the assumption that the scales on the primary system surfaces consist mainly of magnetite, specifies a constant coolant pH value of 6.9 at 300 °C to achieve the minimum solubility of magnetite. The constant pH_{300} of 6.9 was achieved by coordinating the Lithium concentration according to boron concentration (Figure 5). This coolant chemistry strategy was applied in the eighties in most of the German plants (Figure 4).

c. "Modified Chemistry"

The modified chemistry targets to maintain a coolant pH_{300} of 7.4, conditions for a minimum of the nickel ferrite solubility. Because of the risk for fuel cladding corrosion, the lithium concentration in Siemens designed plants is limited to 2.2 ppm. Accordingly the desired pH_{300} of 7.4 can not be adjusted at the beginning of fuel cycles. The modified chemistry is applied by keeping the lithium concentration at ~ 2 ppm, until a pH_{300} of 7.4 is achieved. Then the lithium concentration will be reduced with reducing boron concentration keeping the pH_{300} at ~ 7.4 (Figure 5). The application of this chemistry in Siemens designed plants started mid of the eighties. Due to better results with respect to dose rate reduction, almost all Siemens designed plants are operating under modified coolant chemistry program.

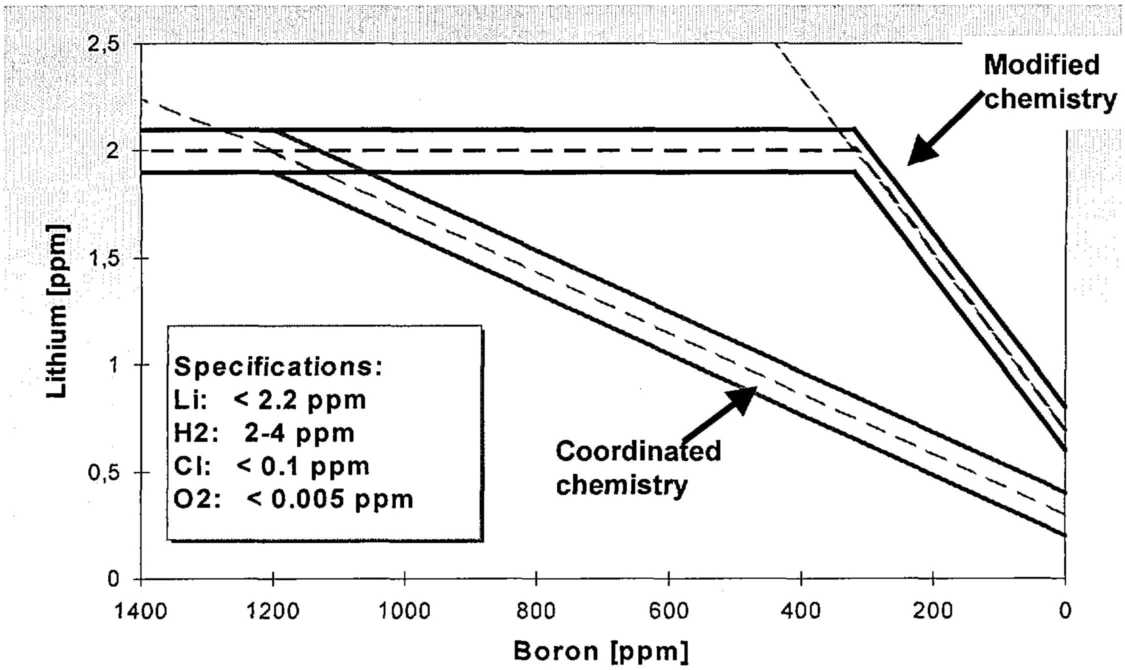
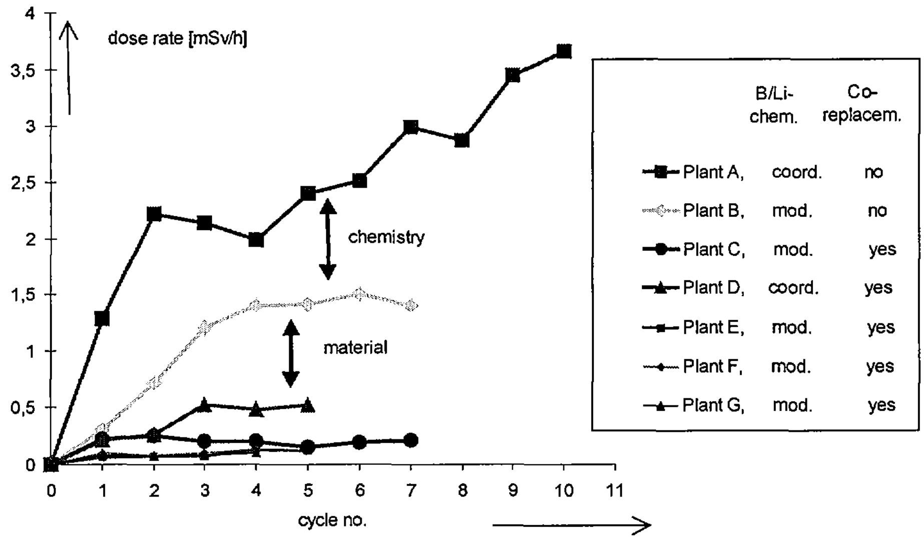


Figure 5: Coordinated and modified coolant chemistry in Siemens designed plants

The modified coolant chemistry was introduced first time in 1981 in NPP Neckarwestheim-1. Based on the field results regarding the dose rate development, this chemistry program was favored by almost all other plants later on. The dose rate field results of several plants operating under coordinated or modified chemistry are given in Figure 6. This figure illustrates the superiority of the modified chemistry:

- If the dose rate development is compared in the cobalt-base materials containing plant A and plant B, a pronounced higher dose rate development can be seen in the plant A operating with coordinated chemistry.
- Even in the cobalt replacement Plants C,D,E and F with very low radiation fields, higher dose rate development can be recognized in the plant F with modified chemistry if compared with the other modified chemistry plants.



Published in SFEN Conference, Apr. 1994 [4]

Figure 6: Influence of materials and coolant chemistry on dose rate evolution in the loop piping

The operating chemistry data regarding the measured coolant lithium concentrations and the calculated pH_{300} values are given for four plants in Figures 7 and 8 respectively as an example for the recent German plants coolant chemistry practice.

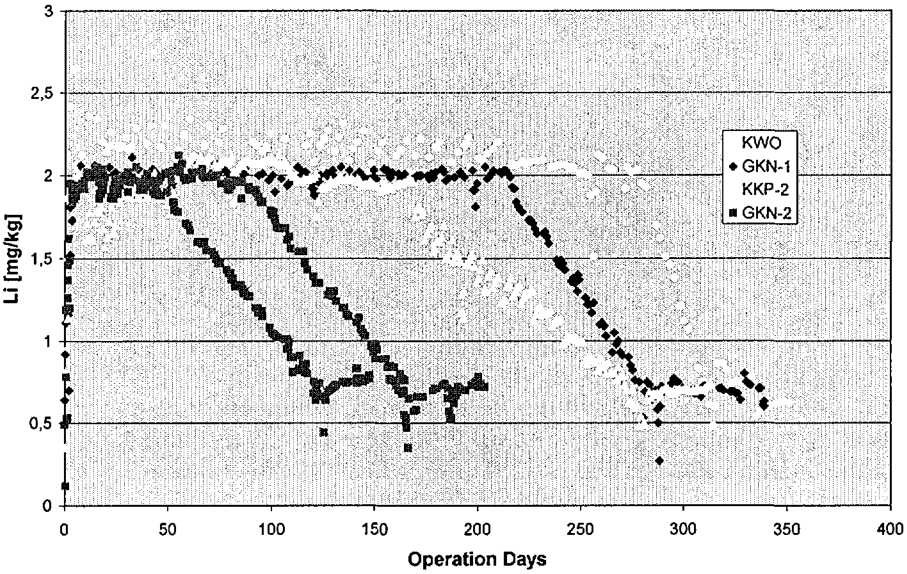


Figure 7: Applied modified chemistry (lithium concentrations)

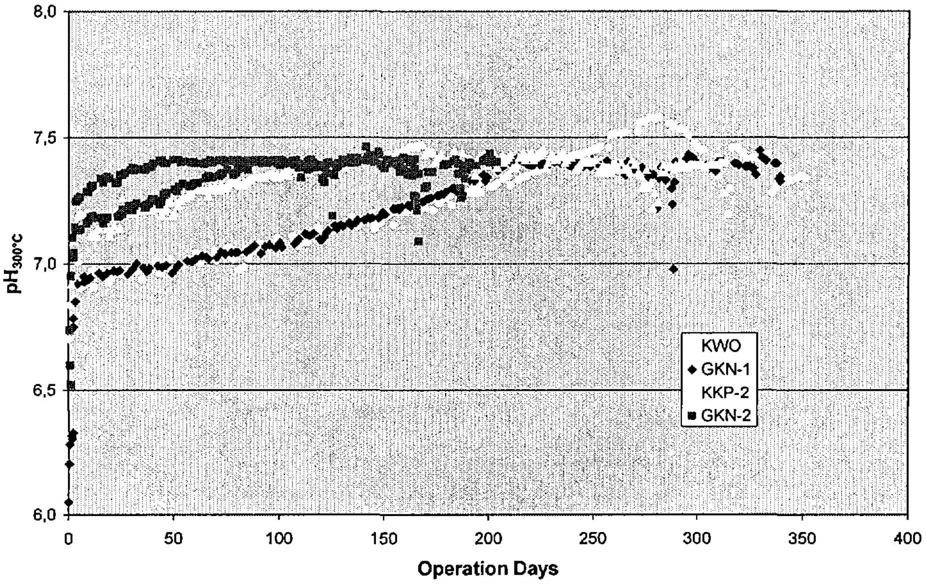


Figure 8: Applied modified chemistry (pH_{300} values)

In addition to the above described coolant chemistry modifications, two other dose rate reducing measures, Zinc injection and the use of Enriched Boric Acid, were introduced in the late nineties in several plants (Figure 4). The incentives for introducing these measures were different from each other:

Zinc injection

The purpose of zinc injection is to reduce dose rates in plants with older design, where the cobalt replacement program can't be applied because of technical and/or economical reasons. In order to confirm the effectiveness of the zinc injection and its compatibility with the overall plant, a comprehensive surveillance program was implemented in two lead plants, NPP Biblis B in 1996 and NPP Obrigheim in 1998. Based on good experience gained in Biblis B, the utility decided to start the zinc injection also in Biblis A in 1998. After five years of operating experience in three German PWRs, it can be concluded that the zinc injection is very effective to reduce the dose rates (in average more than 10% per cycle can be achieved), inexpensive and easy to apply [5,7]

Use of Enriched Boric Acid (EBA)

Recently (>1997) the use of ^{10}B enriched boric acid was introduced in seven Siemens designed PWRs using higher fuel burnups because of economical reasons. The plant operation with higher fuel burnup requires higher boron concentrations if natural boron (^{10}B content 20%) is used to control the core reactivity during shut-down and during power operation. This demand would lead to an increased volume of the borating system, which is associated with significant cost, and furthermore results in a decrease of operating coolant pH due to limitation of the lithium concentration. To take economical benefit of higher fuel burnups without having the above mentioned problems, seven plants decided to use EBA with ~30% (applied is 28-31%) enriched ^{10}B. The use of EBA reduces the required coolant boron concentrations and enables to reach the optimum pH_{300} of 7.4 earlier during the operating cycles. Therefore a positive influence of EBA on the radiation field development can be expected in the future.

Shut-down Chemistry

In Siemens designed PWRs, the shut-down chemistry consists in injecting H_2O_2 during the plant cool-down at a temperature <120 °C (actually ~ 80 °C). This procedure was developed in the past with the aim to remove antimony from the coolant before opening the reactor coolant system to avoid high antimony radiation fields during the outage activities. The source of the antimony was the main coolant pump seals. The replacement of these antimony sources led to reduced need for H_2O_2 injection. At the present this shutdown chemistry is applied not in every shutdown and not in every PWRs; it is applied only when necessary.

3. STEAM / WATER CYCLE

3.1 Steam / Water Cycle of French PWRs

3.1.1 EDF design and material concept

The design of French SG has changed with time : first CP0 units (Fessenheim and Bugey) are equipped with model 51A SGs, with carbon steel TSPs and no partition plate, then CP1 units were equipped with 51M SGs, with carbon steel TSPs and partition plate, CP2 units with 51BI/B SGs (broached carbon steel then 13 % Cr TSPs). All 1300MW units and RSGs are equipped with broached 13 % Cr TSPs.

There was also an evolution in the SG tubing material : Inconel 600MA for the old SGs, Inconel 600TT for 27 units and 690TT for the RSGs and the most recent plants.

No condensate demineralizing system is used on French plants; on some plants (those very sensitive to IGA/SCC of SG tubing), a mobile filtration-demineralisation system is used, only during start-up or after high pollution phases to eliminate more rapidly soluble impurities and corrosion products, which are in high quantities in these operation phases.

3.1.2 EDF water Chemistry Guidelines

The secondary water chemistry specifications have been established to cope with 3 main objectives [1] :

- low corrosion-erosion rate of carbon steels,
- limited stress corrosion cracking of SG tubing,
- low deposits on the tubes, which would decrease the heat transfer capability.

Corrosion-erosion rate of carbon steel remains acceptable in the water/steam system of French units thanks to a selection of sufficiently high pH at operating temperature. The selection of feedwater treatment is indicated in Table 3.

Parameter	Expected value	Limit value	Materials - Treatment
$pH_{25^\circ C}$	9.1 to 9.3	9.0 to 9.4	Copper Morpholine treatment
Morpholine, ppm	4 to 6	4 to 8	
Hydrazine, ppb	> 10	> 5	
$pH_{25^\circ C}$	9.5 to 9.6	9.2 to 9.8	No copper Morpholine treatment
Morpholine, ppm	6	4 to 8	
Hydrazine, ppb	100	> 50	
$pH_{25^\circ C}$	9.6 to 9.8	9.5 to 10.0	No copper Ammonia treatment
Ammonia, ppm	2 to 5	-	
Hydrazine, ppb	100	> 50	

Table 3: pH and reagent for feedwater in secondary system

For units with copper alloys in the secondary system (23 of the 58 French PWR units), the pH at low temperature in the condenser and the low-pressure heaters must not exceed 9.2 at 25 °C in order to avoid copper corrosion by solubilisation. In this case, a $pH_{25^\circ C}$ of 9.2, using morpholine (23 units) increases the high temperature pH in the secondary system. Ethanolamine could also be used, after tests performed in 1999 in Saint-Alban units, showing a protection against corrosion-erosion of carbon steel equivalent to morpholine, but for the moment no plant can use it, because this reagent is not yet included in the plant waste release decrees.

For units without copper alloys in the secondary system (35 units), the $pH_{25^\circ C}$ in the condenser and in the low-pressure heaters may be increased up to about 9.7. In this case, the high temperature pH in the secondary system may be obtained either by ammonia (8 units) or by morpholine (27 units) or potentially in the future by ethanolamine. The $pH_{25^\circ C}$ is limited to 9.7 for economical and environmental reasons. Above such a pH, the efficiency of resins for SG blowdown purification would quickly drop and the resin may not be operated a long time after exhaustion with the conditioning reagent ; their replacement would be too frequent.

Hydrazine concentration in feedwater for units without copper alloys is not increased above 100 ppb, because electrochemical potential measurements performed in Golfech 2 in 1996 [8] had shown that there was no significant influence either on the ECP or on the proportion of magnetite when increasing the hydrazine concentration up to 200 ppb.

Eleven units under morpholine treatment are also treated with boric acid addition in the secondary system to mitigate IGA/SCC of SG tubing (see below). In this case, the specified feedwater $pH_{25^\circ C}$ is lower than the values indicated in table 3, by about 0.3 pH unit to account for the influence of boric acid at room temperature pH. At high temperature, the boric acid (0.8 ppm boron in the feedwater and steam) is very slightly dissociated and has almost no impact on the high temperature pH and on the corrosion-erosion rate.

Secondary side corrosion of steam generator tubing is affecting many PWR units with Alloy Inconel 600, very sensitive to Stress Corrosion Cracking (SCC). Several remedies have been implemented in French units in order to mitigate IGA/SCC on the secondary side of steam generator [9]:

- selection of all volatile treatment (AVT),
- addition of boric acid to create a passive film and to neutralise caustic environment in crevices where concentration process occurs due to low flow,
- low electrochemical potential by adequate hydrazine addition and low oxygen concentration in the condenser (expected value : < 3 ppb – limit value : < 10 ppb),
- low corrosion product transport in order to avoid deposits where pollutants may easily concentrate,
- low level of pollution (sodium, oxygen, sulphate, chloride, lead, copper, etc...) through various improvements and good operation and maintenance practices. Thus, stringent chemistry specifications are applied for contaminants in condensate water and SG blowdown.

Chemical specifications for sodium and cation conductivity in steam generator blowdown are shown in Figures 9 and 10 respectively for units cooled by river water or sea/estuary water.

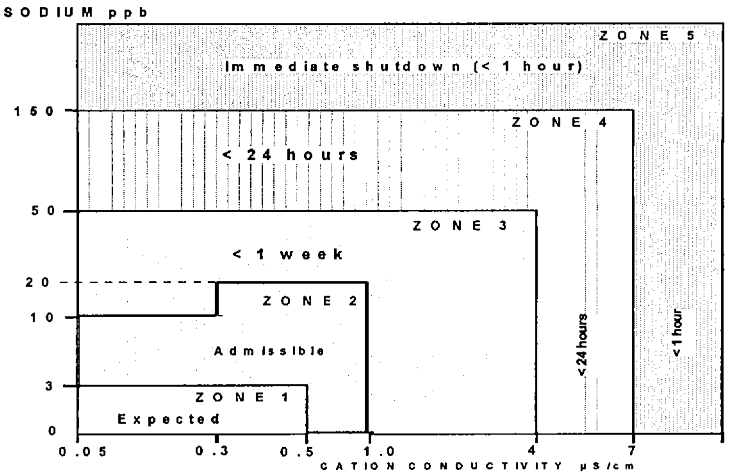


Figure 9: SG blowdown limits at P > 25 % NP for river water cooled units

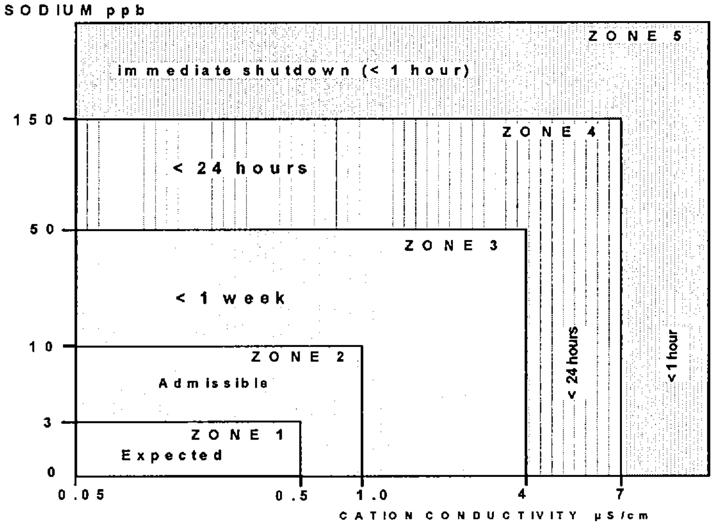


Figure 10: SG blowdown limits at P > 25 % NP for sea water cooled units

These limits apply when power is higher than 25 % nominal power that is when hideout of ionic pollution occurs in restricted flow areas. The allowed operating time decreases as the level of contamination increases.

Sodium and cation conductivity are the 2 parameters selected for deciding if the unit has to be shutdown when the steam generator is polluted.

They are measured on-line and the values are transmitted into the control room, with alarms associated to Zones 3, 4 and 5. In case of evolution of the cation conductivity (zone 2 or higher), grab sample analysis of chloride, sulphate, and organic acids is required to help the chemist to identify the exact type and origin of the pollution and then take the appropriate action. The expected values for chloride and sulphate are respectively < 5 and < 10 ppb.

The specification limits slightly differs for sea/estuary cooled water units (Figure 10) as compared to river water-cooled ones (Figure 9). The reason is the lower risk of IGA/SCC for sea water which induces an acidic environment instead of an alkaline one for river water under concentration at high temperature. This is why Zone 2 has been extended up to 20 ppb of sodium when the cation conductivity is between 0.3 and 1 µS/cm (small and non-alkaline pollution). Of course, the objective is to allow operation with very small sea water leaks, which cannot be localised, so as to maintain plant availability if there is no consequence on the material or the safety.

The differences in specification limits for the 11 units treated with boric acid addition for mitigating IGA/SCC of SG tubing is mainly concerning the upper values of cation conductivity for Zones 1 and 2, where the presence of about 8 mg/kg of boron induces an increase of no more than 0.3 µS/cm.

In this case, in order to compensate for the less sensitive detection of small anionic pollution, additional controls and limits have been established for chloride (expected value : < 5 ppb, limit value : < 10 ppb for river water and < 30 ppb for sea water cooled units) and sulphates (expected value : < 10 ppb, limit value : < 20 ppb) at SG blowdown (daily measurements).

Low amounts of deposits on the tube surface is important (i) to keep the heat flux at 100 % nominal power on the long term, (ii) to avoid concentration of deleterious compounds on tube surface and further SG corrosion.

This objective is achieved by the selection of an appropriate secondary water treatment. Morpholine with optimum hydrazine concentration has been demonstrated, by plant tests and feedback studies, to give low amounts of corrosion products in the feedwater train and in the steam generator (low amounts of sludge). The corresponding specification is the same as the one described above for erosion-corrosion limitation.

In addition to minimising pressure drop and corrosion consequences of deposits, a low quantity of corrosion products will allow to decrease operating costs by limitation of the number of sludge lancing and chemical cleaning to be done during shutdowns for refueling.

3.1.3 EDF operational practice

Table 4 gives the average results of French NPPs secondary chemistry during 2000, for the main parameters in FW (feedwater), CW (condensate water) and SGB (steam generator blowdown).

Unit power	900 MW 34 units	1300 MW 20 units	1450 MW 4 units
O_2 in CW	3 ppb	1.8 ppb	1.6 ppb
Na at SGB	1.6 ppb	1.4 ppb	2.3 ppb
Cl at SGB	5 ppb	4 ppb	3 ppb
SO_4 at SGB	5 ppb	4 ppb	4 ppb
Treatment	Ammonia w/o Cu	Morpholine with Cu	Morpholine w/o Cu
CC at SGB µS/cm	0.16	0.34	0.39
pH in FW	9.7	9.2	9.4

Table 4: Secondary chemistry operational results of French NPPs in 2000

3.2 Steam / Water Cycle in German PWRs

3.2.1 Design and material concept

Steam generators

Presently all Siemens designed PWRs have SGs with Incoloy 800 NG tubing material. In the past the first Siemens designed PWR Obrigheim had SGs with Inconel 600MA tubing, which had to be replaced due to Stress Corrosion Cracking (mainly PWSCC). For the tube support, egg crate construction is used. Whereas the general design of the SGs is remained almost unchanged, their size increased with the power of the plants. Some plants have SGs with preheaters (Grafenrheinfeld, Grohnde, Brokdorf and Trillo) and most of the plants constructed after Unterweser have Flow Distribution Baffles (Gösgen, Grafenrheinfeld, Grohnde, Brokdorf and Trillo).

Steam / water wycle

Presently all Siemens designed PWRs have "All Ferrous Secondary Side" systems. In the past (in all PWRs constructed before Grafenrheinfeld), copper alloys were used only in the condensers as tubing material. The copper replacement program was applied in those older PWRs before conversion from normal AVT to High-AVT chemistry (increasing the pH from < 9.5 to > 9.8). For the feedwater heaters and for the moisture separator reheater, carbon steel tubing are used. The use of chromium containing low alloyed steel, 10CrMo910 (P22), is limited only to several steam extraction lines, where two phase flows can't be avoided.

Regarding the condensate clean-up systems, only three PWRs (Unterweser, Grohnde and Brokdorf) have a condensate demineralizer system (CDS). In those plants, CDS is not considered to be operated during the normal power operation; they will be put in service only during the plant start-up operations and/or in case of condenser leaks. Several other PWRs have mechanical filters in their condensate system (30% partial flow in Philippsburg-2 and 100% full flow in Trillo, Isar-2, Emsland and Neckarwestheim-2). In addition to the mechanical filters in the condensate system, Trillo and the Convoy plants (Isar-2, Emsland and Neckarwestheim-2) have full flow Electro-mechanical filters (EMF) in their HP heater drain system. The Convoy and Trillo plants are using these filters not only during the plant start-up but also during the normal power operation. In the plants with condensate clean-up systems (either with mechanical filters or with CDS) a recirculation line of 30% flow capacity is considered for fast clean-up of the systems during the annual outages before plant start-up operation.

In all Siemens designed PWRs, the SG blow down is recovered to the main condenser by EMF and mixed bed filters in the blow down line.

To remove oxygen in the condensate, in all plants a feedwater tank is situated between condensate and feedwater systems as deaerator.

3.2.2 Water chemistry program

In the past, all Siemens designed PWRs, except Obrigheim with Inconel 600 SGs, were operating with a phosphate chemistry in their SGs and with normal AVT (feedwater pH < 9.5) in the entire secondary side. Because of the PO_4-wastage corrosion experienced beneath the SG tube deposits more or less in all plants, it was decided to change the SG chemistry from PO_4 to the High-AVT chemistry (a hydrazine ammonia based chemistry with high pH values and elevated hydrazine concentrations) [10]. In addition to maintaining the reducing conditions in the SGs, the main objective of this chemistry is to keep the SG deposit loading as low as possible by reducing the feedwater iron transportation. This goal is achieved by increasing the feedwater pH value to > 9.8 (actual values are above 10) , adjusted by ammonia which is produced by thermal decomposition of hydrazine. The hydrazine is the only chemical which is injected into the condensate system. The operating feedwater hydrazine concentration is in the range of 20 – 150 ppb. A copper free system is the prerequisite for this type of chemistry. Therefore in older plants a copper replacement program was applied in the eighties before converting the water chemistry, as shown in Figure 11.

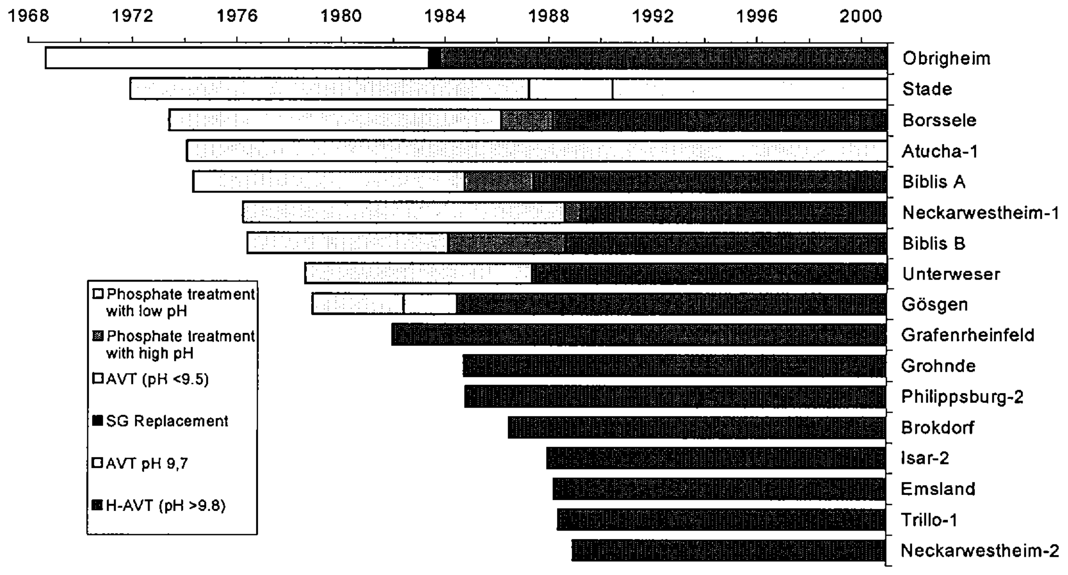


Figure 11: Secondary side water chemistry history of Siemens designed plants

VGB water chemistry specifications for the High-AVT chemistry for SG and feedwater is given in Table 5 and 6 respectively. According to the requirement and need of several plants, Siemens modified these VGB specifications later on by redefining the chemistry parameters and by adding action levels,

Parameters	Target value	Operating value	Limit value
Cation conductivity [µS/cm]	< 1.0	0.2 – 0.3	10
pH_{25} value	-	9.5 – 9.8	-
Sodium [µg/kg]	< 50	10	-
Chloride [µg/kg]	< 100	30	1000
Silicate [mg/kg]	< 4	20	-
Ammonia [mg/kg]	-	1.5 - 5	-

Table 5: VGB steam generator water chemistry specifications (1988)

Parameters	Target value	Operating value
Cation conductivity [µS/cm]	< 0.2	0.1 – 0.2
pH_{25} value	> 9.5	9.5 – 10.0
Hydrazine [µg/kg]	> 20	50 - 250
Oxygen [µg/kg]	< 20	< 5
Iron >0.45 µm [µg/kg]	< 20	1 - 3

Table 6: VGB feed water chemistry specifications (1988)

as given in Table 7. This power operation chemistry guidelines is not valid for the start-up ot the plant. For the start-up and the subsequent five days there are no chemistry conditions specified except reducing conditions. The chemistry control parameters specified with action level 1 - 3, i.e. cation conductivity, sodium and oxygen, are measured on-line with alarm indications in the control room in case of violations.

POWER OPERATION STEAM GENERATOR BLOWDOWN CONTROL PARAMETER						
Parameter	**Normal Frequency**	**Expected Value**	**Limit Value**	**Action Level**		
				1	**2**	**3**
Cation Conductivity [µS/cm]	**continuous**	**< 0,5**	**≤ 1,0 (1)**	**> 1,0**	**> 2**	**> 7**
Sodium [µg/kg]	**semi-continuous**	**< 10**	**≤ 50**	**> 50**	**> 100**	**> 500**

(1) Due to total strong anions. Theoretical conductivity to be calculated and compared with the measured values. Inconsistencies are to be investigated.

POWER OPERATION FEEDWATER CONTROL PARAMETERS						
Parameter	**Normal Frequency**	**Expected Value**	**Limit Value**	**Action Level**		
				1	**2**	**3**
pH	**continuous**		**≥ 9,8**	**< 9,8**		
Cation Conductivity [µS/cm]	**continuous**	**< 0,12**	**≤ 0,2 (1)**	**> 0,2**		
Oxygen [µg/kg]	***continuous***	**< 1**	**≤ 5**	**> 5**	**> 20**	**> 100**

(1) Due to strong anions.

Table 7: Siemens secondary side water chemistry guidelines

Parameters	SG Blowdown	Feedwater	Condensate
Cation conductivity [µS/cm]	0.07 - 0.18	0.07 - 0.12	0.06 - 0.11
Sodium [µg/kg]	0.1 - 4	-	0.1 – 0.5
Oxygen [µg/kg]	-	0.1 – 3.0	5 - 15
pH_{25} value	9.5 – 9.9	9.8 - 10.2	9.8 - 10.2
Fe [µg/kg]	-	0.1 – 1.3	-
Chloride [µg/kg]	1 – 5	-	-
Sulphate [µg/kg]	1 - 12	-	-

Table 8: The range of the average operating chemistry data in the secondary side of all Siemens PWRs

The range of the average chemistry data of all Siemens plants is given in Table 8. This chemistry was very successful to reduce the feedwater iron concentration, as shown in Figures 12 and 13 for the older plants after pH increase [11,12].

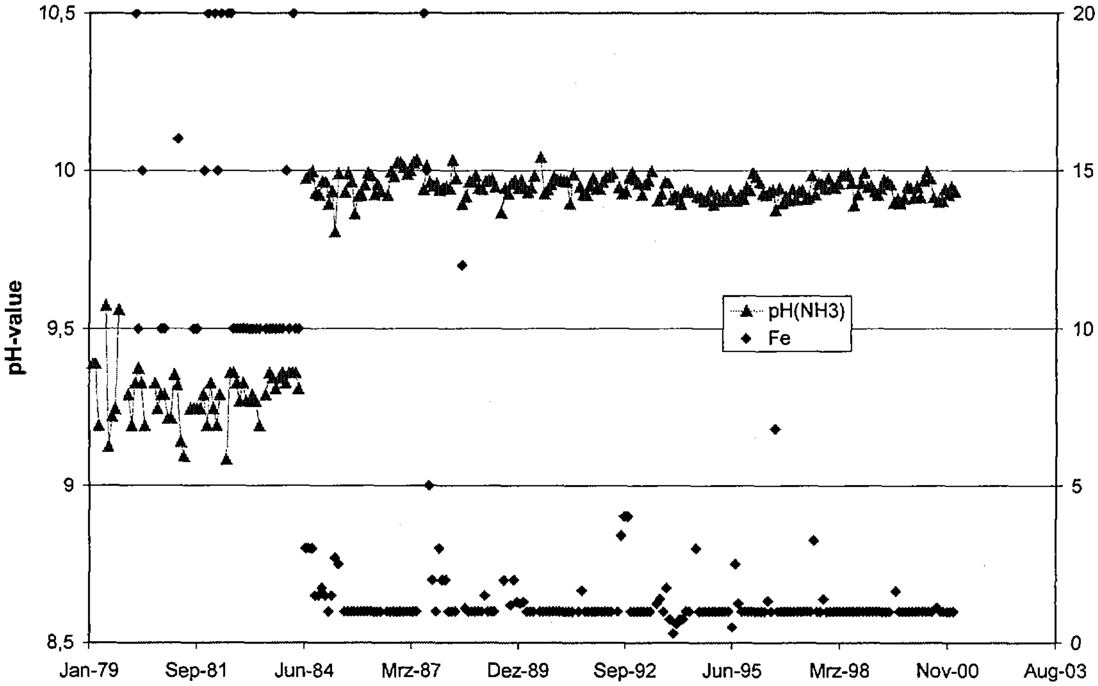


Figure 12: Feedwater iron concentration as a function of pH in Gösgen

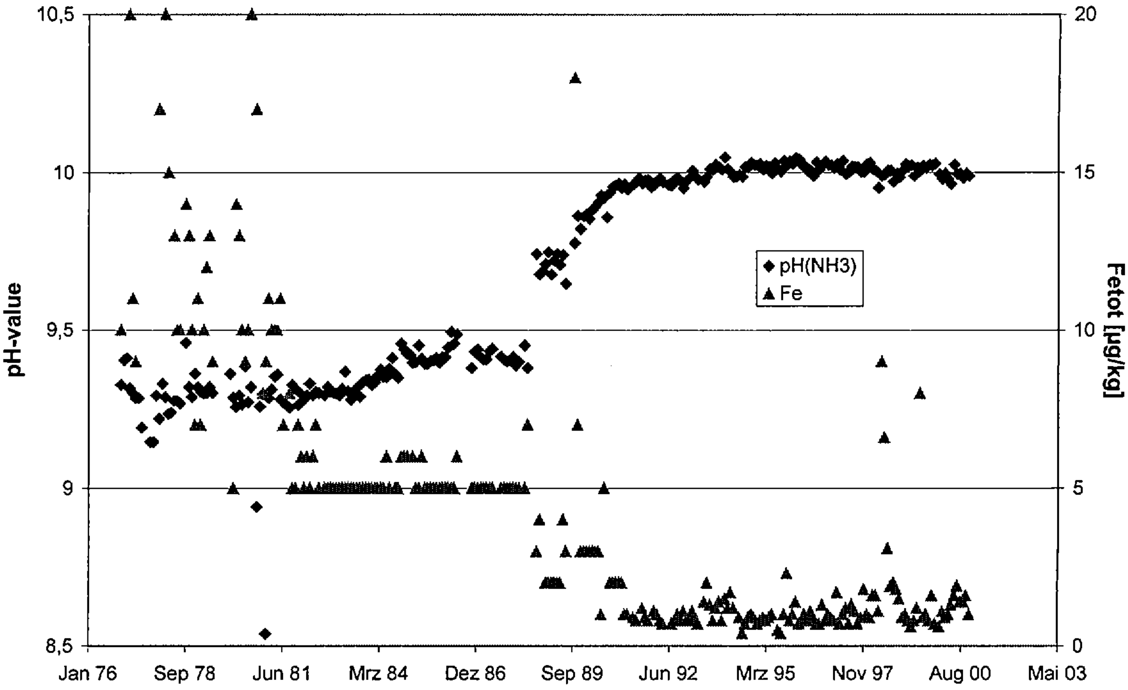


Figure 13: Feedwater iron concentration as a function of pH in Neckarwestheim-2

The operating feedwater iron concentrations in Siemens plants are presently in the range of ~ 1 ppb or even less in some plants (0.1 – 0.6 ppb). The reduction of the feedwater iron concentration was mainly due to a pH increase and resulted in lower SG sludge loading as confirmed by tube sheet lancing (TSL) results and fouling measurements. In the past with the old chemistry the amount of sludge removed by TSL was in the average ~30-40 kg per SG and cycle; this amount is reduced to ~ 2-6 kg per SG and per cleaning in average after each 2-3 cycles using an improved TSL technique (Figure 14). As it can be seen in Figure 15, also the SG tube fouling rate could be drastically reduced after increasing the feedwater pH.

Steam Generator Sludge Lancing Results (Dimension in kg/SG)

		Plants initially started with PO4								Plants started under H-AVT conditions							
No. of SGs	2	4	2	2	4	3	4	4	3	4	4	4	4	4	4	3	4
	Plant A	Plant B	Plant C	Plant HV	Plant D	Plant E	Plant F	Plant G	Plant H	Plant I	Plant K	Plant L	Plant M	Plant N	Plant O	Plant P	Plant Q
1969																	
1970																	
1971																	
1972																	
1973																	
1974																	
1975																	
1976																	
1977																	
1978																	
1979																	
1980							58										
1981		42,3	45,5		15,5	40	37,3	1,7	49								
1982		45,9	23,1	8,7	50,3	33,8	26,3	28,6		6							
1983		40,3	63,2		65,7	21	41,8	10,6	47	7,5							
1984		70,2	13,6		30,5	16,3		13	170	4,2	1,8						
1985		64,2	21,2		22,3	16,3	25,4	13	96	3,1		5,3					
1986		45,8	13,2		21,3	13,4	17,3	19	94,3		4,6	3,2					
1987		29	8,9		18,6	11	13,3	26	64,7	1,2			6,6				
1988		35,2	16,9		20,9	6,8	10,9	26	36,7			2,6				2,1	
1989		21,3	7,1			6,3	17,5	33	35,9					3,8		0,8	
1990		16,6	8,6		16,1			20,2	26,7		6,5		8,7				7,4
1991		23,9					9,9	35,7	32,2						3,8		
1992		30,3	12,3		28,2	11,4	15,8	29,1	18,7							2,7	
1993		26,7					22,3		18,3	5				3,5			
1994					14,1		16,9	91,5	5,7		6,7		5,8		4,1	2,7	
1995		29,3	17,2		16,7			5,9	36,1								
1996		12,7					30,7	8,9	18							1,1	
1997	41,1	6,9							18,7	8					4,8		
1998							42,1	6,3		12							11,9
1999									32,1								
2000		8,3			28,6			16,2						10,8			
Total per SG	41,1	548,9	250,8	8,7	348,8	176,3	327,5	384,7	800,1	47	19,6	11,1	21,1	18,1	12,7	9,4	19,3

▨	*) *moist sludge*	▨	start 1st cycle
▨	**) after comm. (80%)	▨	TSL not applied
☐	***) after comm. (100%)	▨	after CC

Figure 14: Tube sheet lancing results in Siemens plants

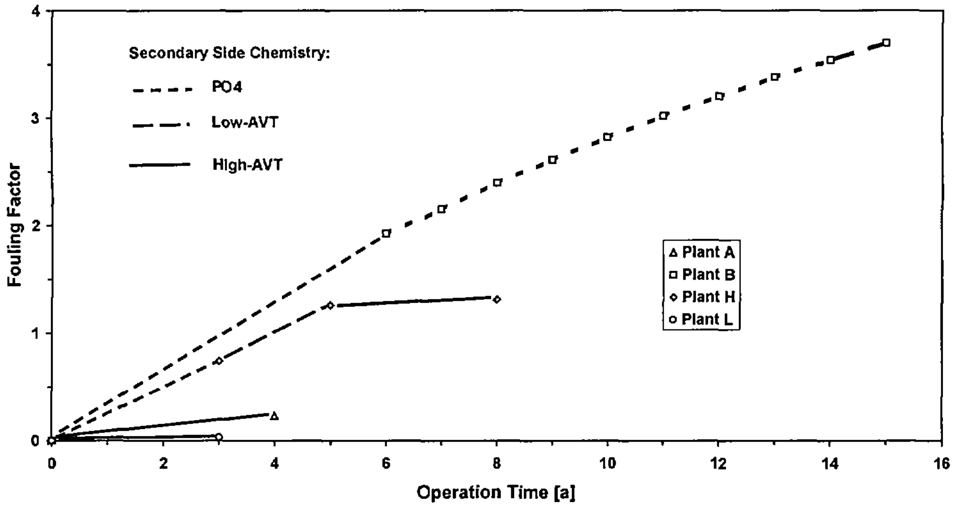


Figure 15: Influence of water chemistry on SG fouling data versus time (in years)

The change of the water chemistry to higher pH values was very favorable with respect to the corrosion performance of the entire secondary side including the SGs. Before operating with high pH in the secondary side, erosion corrosion (EC) in the steam systems was experienced more or less in all older plants, which led to extensive repair work and resulted in higher sludge loading in the SGs, which again caused SG tube wastage corrosion. After the pH increase, EC was stopped, accordingly the iron transport into SGs was drastically reduced and together with ending the PO_4 chemistry, wastage corrosion in the SGs was stopped.

The information regarding the SG corrosion performance in Siemens plants is summarized in Figure 16. Since about 30 years of SG operation the only corrosion mechanism, which caused tube plugging was wastage corrosion, with two exceptions found by ECT measurements: one tube was affected by SCC and two others had some pitting. All three tubes were pulled for examination.

PWR-Plant *)	Year of Start-up	No. of SG's	No. of Tubes	No. of Tube Leaks	No. of Plugged Tubes	No. of Plugged Tubes and Causes											
						Wastage		Fretting				P	SCC		D	Cav	Other
						large-surface	local 7)	AVB	LP	SCO	PB		OD	ID			
Stade	1972	4	11.972	1	329	314	8	2	-	-	-	-	-	-	-	-	5
Borssele	1973	2	8.468	1	126	113 / 2 2)	-	11	-	-	-	-	-	-	-	-	-
Atucha I	1974	2	7.890	5	180	3	3	165	2	-	-	-	-	-	-	-	7
Biblis A	1974	4	16.240	3	634	44 / 448 2)	5	56	1 **)	-	-	-	-	-	-	-	80 1)
Biblis B	1976	4	16.084	2 11)	94	7	1	51	2	-	-	2 5)	1 5)	-	-	29	1
Neckarwestheim 1	1976	3	12.063	2	24	4	-	6	10	-	-	-	-	-	-	-	4
Unterweser	1978	4	16.084	0	36	-	20 8)	-	5 10)	10	-	-	-	-	-	-	-
Goesgen	1979	3	12.318	0	15	1	-	-	13	-	-	-	-	-	-	-	1
Grafenrheinfeld	1981	4	16.344	1 11)	49	-	-	4	7	2 10)	-	-	-	-	-	18	18 9)
Obrigheim (new)	1983	2	6.020	0	0	-	-	-	-	-	-	-	-	-	-	-	-
Grohnde	1984	4	16.344	0	1	-	-	-	-	1	-	-	-	-	-	-	-
Philippsburg 2	1984	4	16.424	0	5	-	-	1	1; 3 10)	-	-	-	-	-	-	-	-
Brokdorf	1986	4	16.344	0	26	-	-	-	1	24 10)	-	-	-	-	-	-	-
Isar 2	1988	4	16.472	0	0	-	-	-	-	-	-	-	-	-	-	-	-
Emsland	1988	4	16.472	0	0	-	-	-	-	-	-	-	-	-	-	-	-
Trillo 1	1988	3	12.258	3	18	-	-	1	12	3	-	-	-	-	-	-	2 6)
Neckarwestheim 2	1989	4	16.472	0	9	-	-	-	-	1	-	-	-	-	-	8	-
*) Plants with Alloy 800 (mod.) tubed SGs, excluding 4)		59	234.269	18	1.544 = 0.42 %								SGs with Preheater				

Fretting:

AVB = Anti Vibration Bar
LP = Loose Part(s)
SCO = Structural Component
PB = Preheater Baffle

SCC = Stress Corrosion Cracking
OD = Outer Diameter (secondary side)
ID = Inner Diameter (primary side)

P = Pitting
D = Denting
Cav = Cavitation due to Tubeseet Lancing

1) 63 tubes plugged as precautional measure due to installation of additional AVB's
2) In: Wastage in the innermost U-bend area
3) Most of them not inspectable, excl. Biblis A
4) Tubing Alloy 690 TT
5) Pulled Tubes
6) 1 Tube Pulled for Fouling Investigations, 1 Tube precautionary plugged
7) Local corrosion due to inpurities at tube contacts of low and/or high grid bars, *attributed to legacies from initial* phosphate treatment of the SGs
8) From that 9 tubes precautionary plugged
9) Tubes precautionary plugged, from that 12 tubes LP-Fretting, 6 tubes with unclear indications
10) Precautionary plugged
11) One Leak due to tubesheet lancing (Cavitatio

Plant Status Summary of SIEMENS Steam Generators (SGs) as per 31.12.2000

Figure 16: Steam generator tube performance in Siemens plants

4. CONCLUSIONS

The differences in operating French and German PWRs deal mainly with the different design of the tube support structure and different tubing materials of the steam generators in the respective steam/water cycles. In most French steam generators, Inconel 600 is used and its propensity to stress corrosion cracking requires stringent SG blowdown specifications. An amine (morpholine), with a "better" distribution coefficient, is used in French PWRs to protect carbon steel from flow assisted corrosion, when copper alloys are present in the steam/water cycle, which limit the applicable upper pH.

In contrast to this, in German steam generators, only Incoloy 800 tubing is used and no copper alloys are present, so a "straightforward" chemistry regime, dosing only hydrazine and using the decomposition product ammonia as the only alkalising agent is applied (high AVT with an upper pH around 10).

The operational results in respect to iron concentration, sludge amount and integrity of the steam generator tubing are more than satisfying in both countries. Nevertheless there is a long term trend to replace Inconel 600MA by Inconel 690 in French PWRs. The operational results of Incoloy 800 under the high AVT regime are remarkably good.

The chemistry applied in the reactor coolant system is quite similar in both countries, differences in the final pH are within reasonable limits: at present 7.2 – 7.4, depending mostly upon the applied materials and especially the tubing material of the steam generators. Most important is the limitation of the lithium concentration for reasons of fuel integrity, which in turn limits the span of operation with a constant pH. One measure to overcome this restriction is the use of enriched B-10, applied in some German PWRs. This measure, applied mainly for economical reasons, as well as the injection of Zn-65 in the reactor coolant help reduce dose rates during outages to a large amount in the long run.

All in all, the chemistry programs in France (one operator, centralized structure) and Germany (eight operators in the past, nowadays four operators, federal structure, also in respect to authorities) show wide-ranging similarities and their operational results can stand any comparison.

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