CONTROL OF WATER CHEMISTRY IN OPERATING REACTORS

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Water chemistry plays a major role in fuel cladding corrosion and hydriding. Although a full understanding of all mechanismus involved in cladding corrosion does not exist, controlling the water chemistry has achieved quite some progress in recent years. An an example, in PWRs the activity transport is controlled by operating the coolant under higher pH-values (i.e. the "modified" B/Li-Chemistry).

On the other hand, the lithium concentration is limited to a maximum value of 2 ppm in order to avoid an acceleration of the fuel cladding corrosion. In BWR plants, for example, the industry has learned on how to limit the copper concentration in the feedwater in order to limit CILC (Copper Induced Localized Corrosion) on the fuel cladding.

However, economic pressures are leading to more rigorous operating conditions in power reactors. Fuel burnups are to be increased, higher efficiencies are to be achieved, by running at higher temperatures, plant lifetimes are to be extended.

In summary, this paper will describe the state of the art in controlling water chemistry in operating reactors and it will give an outlook on potential problems that will arise when going to more severe operating conditions.

1. Introduction

The IAEA Technical Reports series No. 347 summarizes the work within the framework of a co-ordinated research programme entitled "Investigations on

Water Chemistry Control and Coolant Interation with Fuel and Primary Circuit Materials in Water Cooled Power Reactors (WACOLIN)". This programme was organized by the IAEA and carried out from 1987 to 1991. This reports concludes:

"Good reactor coolant chemistry, corrosion control and minimization of activity buildup are indispensable for the optimum performance of nuclear power plants. Without these the systems integrity may be jeopardized, the activity transport may create various problems for heat transfer.

The corrosion control and activity buildup depend upon the physicochemical parameters of the coolant. As the nuclear industry has progressed, knowledge of corrosion control and activity buildup through its chemistry has also progressed. With regard to the objectives of the WACOLIN pogramme it can be stated that progress has been made in the following areas:

(a) Man-sievert reduction
  (i) Activity transport is controlled in PWRs and PHWRs by operating the coolant in a narrow range of high pH values.
  (ii) In BWRs the activity buildup is controlled; for example, by lowering the impurity levels and/or by injecting metal ions (Zn and Fe).

(b) Plant life extension
  (i) In PWRs and PHWRs the selection of an optimized pH contributes to the minimization of primary water SCC phenomena.
  (ii) Oxidizing conditions that promote SCC in BWRs are being counteracted by low conductivities or by hydrogen dosing.

(c) Fuel life extension
  (i) Limiting the lithium concentration in PWRs is a contribution to limiting the zirconium oxide formation and therefore to extending the fuel life.

(ii) The exclusion of copper from the steam-water cycle of BWRs has greatly reduced the copper induced localized corrosion phenomenon.

(iii) The hydriding of zirconium alloy components in cores is minimized by the adjustment of the dissolved hydrogen concentrations.

(d) General safety, materials reliability. For all of the different reactor systems (PWRs, BWRs and PHWRs) there have been no shutdowns in recent years due to violations of chemical parameters in the primary system. This is an excellent indication that with regard to this item (general safety and materials reliability) the coolant chemistry has become mature.

Nevertheless, there is no room for complacency, as corrosion problems and activity buildup continue to occur. Economic pressure are leading to more demanding operating conditions in power reactors. Examples of these conditions are: fuel burnup is to be increased, higher efficiencies are to be achieved by running at higher temperatures, plant lifetime is to be extended, and more and more reactor sytems are load following. Therefore, in order to maintain adequate levels of safety and reliability, it is recommended to implement the improvements that are elaborated within this programme."

Possible actions with regard to man-sievert reduction and plant life extension are:

(1) Avoid the use of cobalt based alloys:
   - as in-core material,
   - as out-of-core RCS material,
   - as material in the CVCS.

(2) Replace the cobalt based alloys in older plants (if possible).

(3) Reduce the residual cobalt content of structural materials to a minimum.

(4) Operate the primary coolant chemistry in the modified lithium-boron version or maintain the co-ordinated potassium-boron chemistry.

(5) Ensure the smoothest possible surface finish (i.e. electropolishing).

(6) Carry out prefilming during the first startup.

(7) Perform system decontamination as and when required (full or partial system decontamination).

(8) Reduce the corrosion product input in BWR reactor systems.

(9) Use Inconel 690 or alloy 800 in steam generators of new plants and in replacement steam generators.

(10) Ensure smooth operation to avoid thermal transients in all systems and components.

(11) Use HWC in BWR systems.

Despite the fact that all these recommendations are made as a result of this programme, it is felt that in the future several problems will have to be investigated and resolved. These areas are outlined in Table VI of the Technical Reports Series No. 347.

Now, nearly three years later it should be checked what happened to the recommended actions and the areas of future development. With this question in the background, the present paper will handle two areas:

° Review the water chemistry specifications and indicate recent developments.

° Evaluate the recommended actions of 1991.

2. Chemistry of Primary Coolant in Water Cooled Reactors

2.1 PWRs with LiOH as pH control agent

Typical water chemistry specifications are shown in Table I and Figure 1.

The three options being consistent with the guidelines are:

° Elevated Li-B-Chemistry

- Modified Li-B-Chemistry
- Co-ordinated Li-B-Chemistry.

TABLE I. EPRI GUIDELINES FOR PRIMARY COOLANT

Hydrogen (cm^3 (STP)/kg H_2O)[a]	25 - 50
Chlorides (mg/kg)	< 0.15
Fluorides (mg/kg)	< 0.15
Dissolved oxygen (mg/kg)	< 0.01
Lithium (mg/kg)	Consistent with station lithium programme

[a] STP, standard temperature and pressure (0°C, 1 atm).

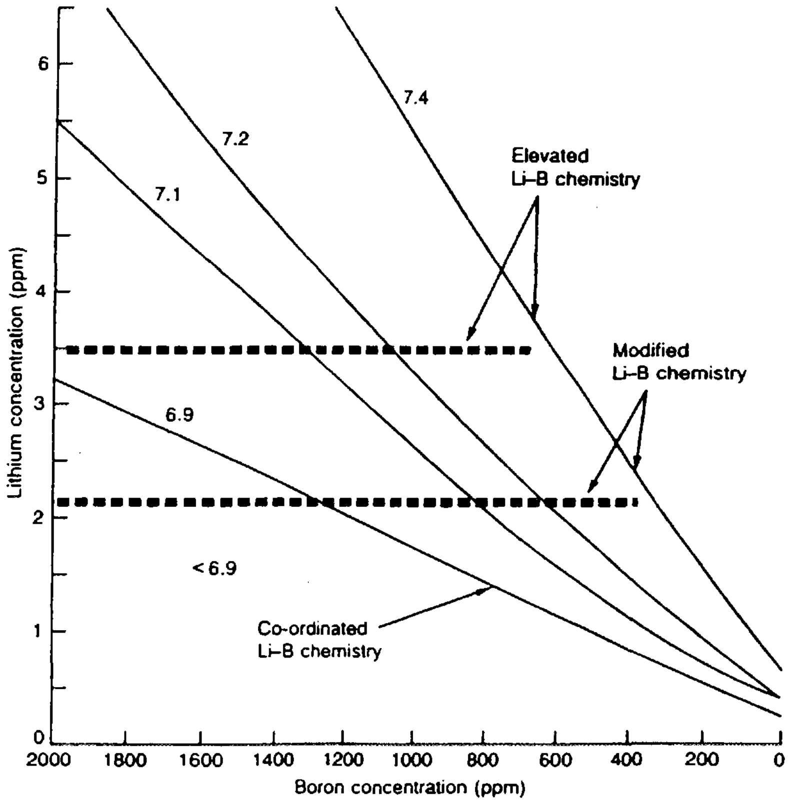


Fig. 1: Various lithium-boron modes of operation

Here, the operational experience of the last three years has clearly shown that the modified Li-B-Chemistry should be preferred over the other two options. All trial operations with "Elevated Li-B-Chemistry" were stopped by one reason or the other. Examples for that are:

° Ringhals:	Concerns on Inconel-600 PWSCC
° Millstone-3:	Concerns both on I-600 PWSCC and Fuel Corrosion for high burnup
° North Anna:	

2.2 PWRs with KOH as pH Control Agent

The specifications are shown in Table II.

The only trend that became known recently is to avoid NH_3-injection for the H_2 production. A direct and continuious hydrogen injection is considered in order to avoid fluctuation of the pH value. All reported fuel cladding corrosion data are extremely low, i.e. there are no concerns.

2.3 Pressurized Heavy Water Reactors (PHWRs)

The specification for this type of reactor is summarized in Table III.

New trends to modify coolant control are not known.

2.4 Boiling Water Reactors

As an example for BWR water chemistry specifications, the EPRI guidelines are listed in Table IV.

TABLE II. SPECIFICATIONS OF REACTOR WATER QUALITY FOR PWRs OF TYPE WWER-440 and WWER-1000

Indicator (with reactor 'on load')	Values	
	WWER-440	WWER-1000
pH (25°C)	6.0-10.2	5.7-10.2
K^+, Li^+, Na^+ (mmol/kg) (depending on H_3BO_3 concentration)	0.05-0.45	0.05-0.45
NH3 (mg/kg)	> 5.0	> 5.0
Hydrogen (cm^3/kg)	30-60	30-60
Chlorides and fluorides (µg/kg)	≤100	≤100
H_3BO_3 (g/kg)	0-9.0	0-13.5
Oxygen (µ/kg)	≤5	≤5
Copper (ng/kg)	<20	<20
Iron (ng/kg)	<200	<200

TABLE III. SPECIFICATION OF PRIMARY COOLANT QUALITY FOR PHWRs

PWR	
LiOH (ppm)	1-2
Dissolved deuterium (ppm)	6
Dissolved oxygen (ppm)	0.05
Chloride (ppm)	0.2
pH (25°C)	10.5-10.9
Silica (ppm)	≤4 SiO_2
Dissolved iron (ppm)	0.5
Crud (ppm)	1
Pressure tube reactor	
pH (25°C, controlled with Li)	10.2-10.8
Dissolved hydrogen ml/kg	3-10
Dissolved oxygen ppb	< 10
Chloride ppm	< 0.2
Fluoride ppm	< 0.1
Crud ppb	< 10

TABLE IV. EPRI CHEMISTRY GUIDELINES FOR BWRs

Control parameter	Frequency of measurement	Achievable value	Action levels		
			1	2	3
Reactor water - power operation					
Conductivity (μS/cm at 25°C)	Continuously	≤0.20	>0.30	>1.0	>5.0
Chloride (ppb)	Daily	≤15	>20	>100	>200
Sulphate (ppb)	Daily	≤15	>20	>100	>200
Diagnostic parameter, silica (ppb)	Daily	≤100			
Reactor feedwater / condensate - power operation					
Feedwater conductivity (μS/cm at 25°C)	Continuously	≤0.06	>0.07		
Condensate conductivity (μS/cm)	Continuously	≤0.08	>0.10		>10.0
Feedwater total	Weekly	≤0.10	>0.50		
copper (ppb)	integrated	≤0.30	>0.50		
Feedwater total iron (ppb)	Weekly integrated	≤2.0	>5.0		
Feedwater dissolved oxygen (ppb)	Continuously	20-50	<10	>200	

These and corresponding guidelines are now worldwide under review. The existing operational problems, specially the IGSCC problem, require more stringent values.

For example, it is currently discussed to fix the chloride and sulphate values for the reactor water and action level 1 at 5 ppb. Also, the iron level for the feedwater seems to be to high. There are even considerations to establish much more stringent chemistry values. Such considerations are made with the following objectives as background:

° Avoid IGSCC

° Man-Rem < 1 Man-Sievert

- ° Radwaste volume < 110 m^3
- ° No other corrosion problems like fuel cladding corrosion.

These objectives require for example

- Reactor water conditions (µS/cm) < 0.08
- Feedwater iron level (ppb) 0.1 - 0.5

To fulfill these requirements the following operational options have to be considered:

- ° Improve cleanup of the steam water cycle.
- ° Hydrogen water chemistry (ECP < 230 mV)
- ° Noble metal coating
- ° Zinc-injection

3. Status of Recommended Actions

In this section, an update of the recommended actions of the IAEA-Roport "Coolant Technology of Water Cooled Reactors" will be given. The number of actions is indicated with ( ) and the current status with "Comment".

(1) Avoid the use of cobalt base alloys

- as in core material
- as out-of-core RCS material
- as material in the CVCS

Comment:

EPRI is currently working on Revision 1 of its Cobalt Reduction Guidelines. This guideline contains information that exceeds the current guideline in two aspects:

a) Test results from various qualification experiments of cobalt replacement materials like NOREM, EB5183 and Everit 50 compared to Sellite 6.

b) Utility Experience with Co-Hardfacing Alloys.

Despite such activities, it became evident at the last EPRI Radiation Control Seminar in Seattle (August 1993) that there is no consensus that the major step forward in reducing radiation fields is the replacement of the cobalt-base alloys.

However, Siemens believes to be in a position to be able to provide the data base for the statement that Stellite-replacement is the key action for reducing occupational radiation exposure. The new standard for occupational radiation exposure in PWRs of western design is < 50 Man-Rem/year and plant (see Figures 2). The surface areas of stellites in older and newer plants designed by Siemens/KWU can be seen in Tables V and VI.

(2) Replace the cobalt based alloys in older plants (if possible).

Comment:

Locations for Stellite in older Siemens-designed plants are shown in Figure 3. The replacement of these components is technically feasible. However, licensing and cost-benefit-aspects are very high barriers to take this action.

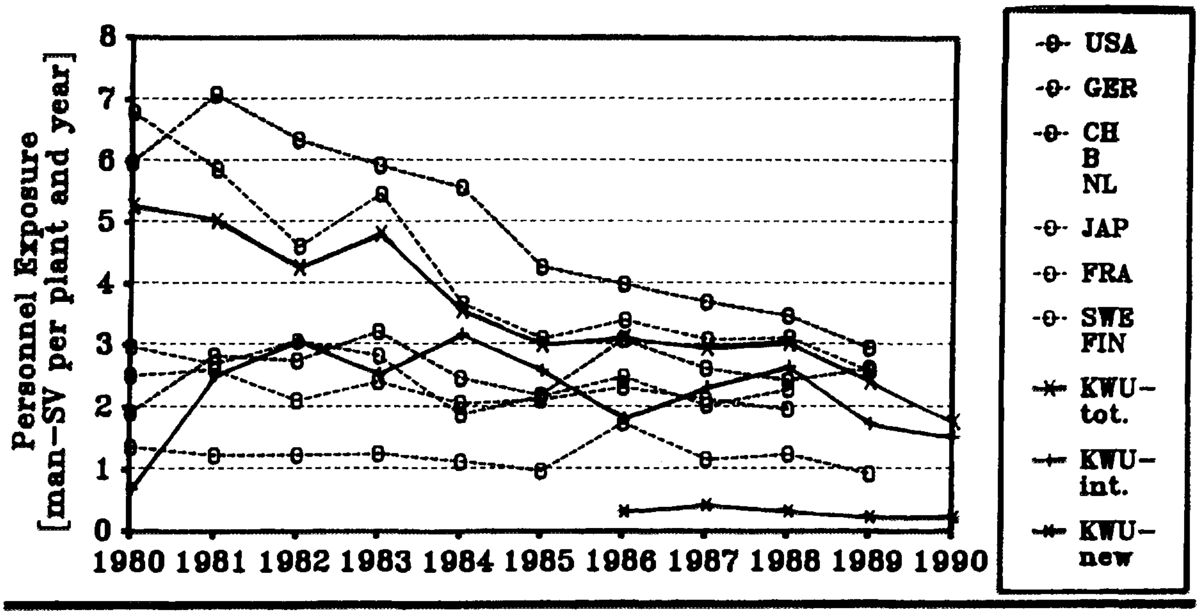


Fig. 2 Average annual personnel radiation exposure of PWRs

TABLE V: Materials Inventory of "Older" 1300 MWe Siemens-designed PWRs

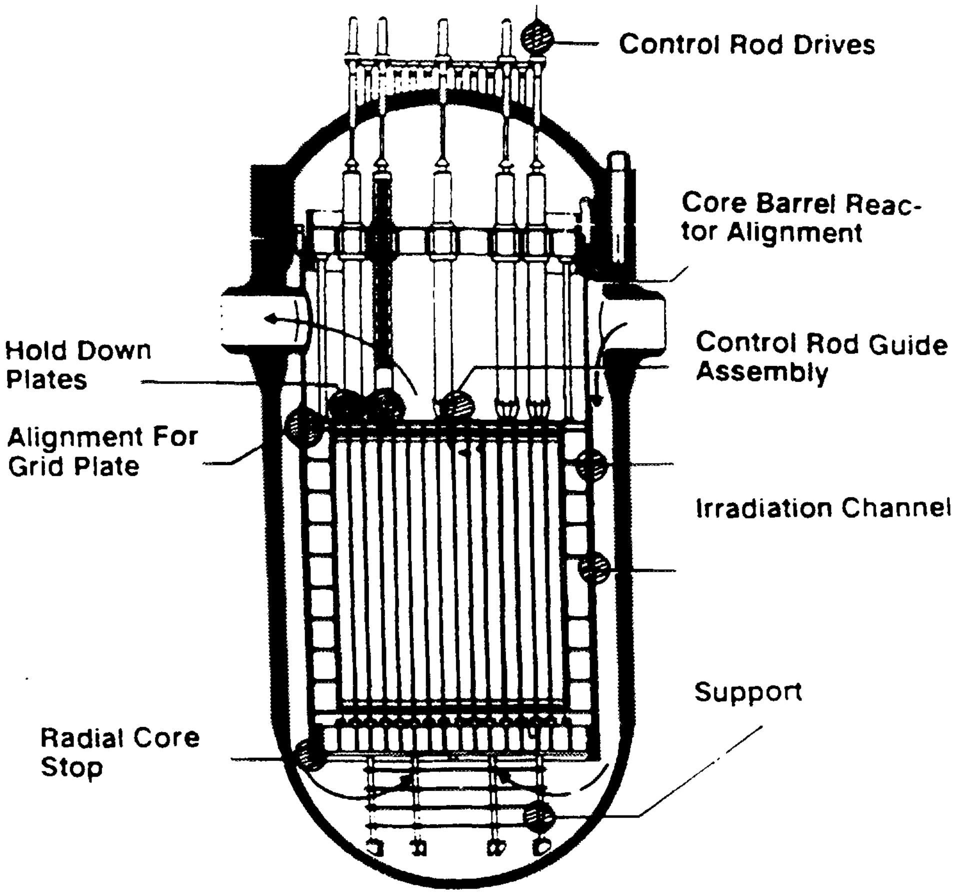
Group	Component	Material	Surface [m^2]	Co-59 Specification [%]
1	Fuel*)	Zircaloy 4	9660	~ 0
		Inconel 718	1220	< 0.1
		Stainless steel	220	< 0.1
	RPV-Internals	Stainless steel	1124	< 0.1
		Co-base alloys	1.1	63
2	Control rod assemblies	Stainless steel	340	< 0.1
	Control rod drive	Stainless steel	220	< 0.2
		Co-base alloys	1.54	≤ 67
	Steam generator	Incoloy 800	16276	< 0.1
	RPV, Loops	Stainless steel	719	< 0.2
	Main Coolant Pump	Stainless steel	155	< 0.2
		Co-base alloys	1.5	63
3	Auxiliary systems	Stainless steel	~ 500	< 0.2
		Co-base alloys	6.5	63
	Total	Zircaloy	9660	
		Stainless steel	19554	
		Inconel	1220	
		Co-base alloys	10.64	

*) Material composition used before 1985, modifications per fuel cycle possible

TABLE VI: Materials Inventory of "Recent" 1300 MWe Siemens-designed PWRs

Group	Component	Material	Surface [m^2]	Co-59 Specification [%]
1	Fuel*)	Zircaloy 4	~ 10660	~ 0
		Inconel 718	394	< 0.1
		Stainless steel	220	< 0.1
	RPV-Internals	Stainless steel	1126	< 0.1
		Co-base alloys	0.026	63
2	Control rod assemblies	Stainless steel	340	< 0.1
	Control rod drive	Stainless steel	220	< 0.2
		Co-base alloys	1.54	≤67
	Steam generator	Incoloy 800	16276	< 0.1
	RPV, Loops	Stainless steel	719	< 0.2
	Main Coolant Pump	Stainless steel	156	< 0.2
		Co-base alloys	0	63
	Auxiliary systems	Stainless steel	506	< 0.2
		Co-base alloys	0.79	63
	Total	Zircaloy	10660	
		Stainless steel	19563	
		Inconel	394	
		Co-base alloys	2.36	

*) Modification per fuel cycle possible



ENTIRE HARDFACED AREA : Co-BASE ALLOY
Control Rod Drives : 1.46 m^2
Core Area : 1.59 m^2

Fig. 3: Stellites in Siemens-designed PWRs

(3) Reduce the cobalt content of structural materials to a minimum.

Comment:

This is an ongoing action item if structural materials are replaced. An example was described at the 1993 EPRI Radiation Control Seminar in Seattle by Niagara Mohawk.

(4) Operate the primary coolant chemistry on the modified lithium-boron version or maintain the co-ordinated potassium-boron chemistry.

Comment:

see section 2.1 and 2.2 of this paper.

(5) Ensure the smoothest possible surface finish (i.e. electropolishing).

Comment:

The enthusiasm existing two or three years ago has gone. Framatome/EdF are doing no electropolishing of the channel heads of new steam generators. This decission was made on cost-benefit considerations. EPRI is still in proposing this surface finish for new steam generators.

(6) Carry out prefilming during the first startup.

Comment:

Prefilming has been demonstratet to have a beneficial effect on activity buildup. Especially the experiments in Doel have shown that chromating results in lowest radiation fields.

The other chromating technology that shuld be followed very closely was qualified in Rossendorf and Rez for plant application.

(7) Perform system decontaminations as and when required (full or partial system decontamination).

Comment:

Decontamination has been accepted by industry as a tool for Man-Rem-Reduction. However, the waste problem is an area of great concern. The most updated status of the decontamination technology can be seen in the Proceedings of the EPRI Decontamination Seminar held in June, 1993, in Charlotte, North Carolina.

(8) Reduce the corrosion product input in BWR reactor systems.

Comment:

This is an ongoing effort. However, the objective is not to reduce the iron level to the lowest possible values. An optimum range of 0.1 to 0.5 ppb Fe in the feedwater of BWRs seems to be desirable. The cleaning facilities have to be adjusted to meet this objective.

(9) Use Inconel 690 or alloy 800 in steam generators of new plants and in replacement steam generators.

Comment:

This recommended action is fully accepted worldwide in all new projects and used for replacement of steam generators.

(10) Ensure smooth operation to avoid thermal transients in all systems and components.

Comment:

This is recognized by many utilities and it is integrated in their operational procedures. However, this remains an area of future activities.

(11) Use HWC in BWR systems.

Comment:

The benefits of HWC regarding IGSCC are questionable. In addition, HWC has caused a steep increase in the radiation levels in several BWRs. Therefore, OWC (Optimum Water Chemistry) a mixture of HWC and Zinc seems to be the new panacea on the horizon.

4. Conclusion

The conclusions and recommendations of the WACOLIN programme have been re-evaluated here. Based on this review, it can be stated that:

- All conclusions and recommendations are still valid.
- Priorities have changed in the last three years.
- Fuel life extension is still a major area for future development.
- Alternatives to current water chemistry are still desirable.
- On-line monitoring as a tool for better controlling the corrosion processes is a very reliable recommendation for the continuation of the WACOLIN programme.