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Coolant technology of water cooled reactors

***Volume 1:
Chemistry of primary coolant
in water cooled reactors***



INTERNATIONAL ATOMIC ENERGY AGENCY

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**COOLANT TECHNOLOGY OF WATER COOLED REACTORS
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FOREWORD

More than 95% of the nuclear power in the world is derived from water cooled reactors. In nuclear power plants water is used in primary circuits, secondary circuits (PWRs and PHWRs) and in a number of auxiliary systems. Water is an aggressive medium at high temperature when in contact with structural materials. This means that the reliability of many nuclear power plant systems (fuel, steam generators, etc.) is dependent on the water chemistry during normal operations, startups, shutdowns and abnormal operations. Reliable water chemistry specifications have been developed for the existing water cooled reactors; however, there is still room for improvement. Water cooled power reactor experience shows that even under normal operating conditions some undesirable effects can occur: corrosion, erosion or deposition of corrosion products on heat transfer surfaces.

Moreover, beyond the adverse effect of corrosion on the mechanical properties of components and of corrosion product deposits on heat transfer, the migration and transfer of activated corrosion products lead to the formation of highly radioactive deposits on some out-of-core surfaces of the primary circuit. This is the main cause of radiation exposure during repair and maintenance, and could require decontamination of some equipment or of the primary circuit as a whole. This is of particular importance when the level of the maximum average permissible dose is under discussion and will probably be decreased to 20 mSv over a year.

The need to decrease radiation levels is now supported by greater management interest, and efforts are being made to improve, for instance, the understanding of fundamental processes and to develop the on-line monitoring technique. Understanding the chemistry is now a major task in the improvement of the operating performance especially with the increase in burnup levels, higher coolant temperatures and with the possibility of nucleate boiling in PWRs.

This report is a summary of the work performed within the framework of the Co-ordinated Research Programme on Investigations on Water Chemistry Control and Coolant Interaction with Fuel and Primary Circuit Materials in Water Cooled Power Reactors (WACOLIN) organized by the IAEA and carried out from 1987 to 1991. It is the continuation of a programme entitled Reactor Water Chemistry Relevant to Coolant-Cladding Interaction (IAEA-TECDOC-429), which ran from 1981 to 1986. Subsequent meetings resulted in the title of the programme being changed to Coolant Technology of Water Cooled Reactors.

The results of this Co-ordinated Research Programme are published in four volumes with an overview in the Technical Reports Series.

The titles of the four volumes are as follows:

Volume 1: Chemistry of Primary Coolant in Water Cooled Reactors

Volume 2: Corrosion in the Primary Coolant Systems of Water Cooled Reactors

Volume 3: Activity Transport Mechanisms in Water Cooled Reactors

Volume 4: Decontamination of Water Cooled Reactors.

These publications should be of interest to experts in water chemistry at nuclear power plants, experts in engineering, fuel designers, R&D institutes active in the field and to consultants to these organizations.

EDITORIAL NOTE

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This text was compiled before the recent changes in the former Union of Soviet Socialist Republics.

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OVERVIEW

CHEMISTRY OF PRIMARY COOLANT IN WATER COOLED NUCLEAR REACTORS

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Abstract

Primary coolant system water chemistry technology in nuclear reactors is quite complex as it deals with high temperature chemistry, radiation induced reactions, materials methodology and corrosion and erosion phenomena. An efficient water chemistry control is quite important from the consideration of material integrity, plant radiation levels and safety. Chemical control technical specifications evolved earlier based on plant operational experiences, have been under continuous revision as a result of the enormous amount of basic and applied work that is presently being pursued world over for understanding material compatibility, mass transport and contamination mechanisms. Keeping this in view, specific features of the primary coolant chemistry in BWRs, PWRs and PHWRs are described and the existing primary circuit chemical control specifications for these type of units both with respect to control and diagnostic parameters under cold shut down, start-up, normal operation and off normal mode conditions are presented. Details of primary coolant sample manipulations for representative sampling, measurement methodology of various key control parameters and the constraints involving the use of chemical and volume control systems, particularly in PWRs are described. Integrity considerations for core (fuel) materials, structural materials and steam generator tube materials are discussed. Plant radiation level reduction considerations both with respect to (a) source term control (choice of materials with lesser cobalt inventory and lesser corrosion/release rates under transient water chemistry conditions and (b) recipient term control (prefilming, optimisation of Ni/Fe ratio, zinc injection passivation and improvement of CPU performance) are presented. Penalty of primary coolant chemistry violations, particularly with respect to harmful effects, viz, (a) increased corrosion rates; specific/incipient corrosion attacks; primary boundary and fuel clad failures and (b) build-up of radiation levels on out-of-core surfaces has been described. Necessity of (a) carrying out long term experimentation under controlled and simulated conditions, (b) in-situ monitoring of important parameters such as high temperature pH, ECP and dissolved hydrogen and (c) carrying out basic research work in high temperature radiation chemistry is emphasised.

1.0 Introduction

Chemistry control in nuclear reactors is important at least from three different angles, viz (a) material integrity (b) plant radiation levels and (c) safety. The basis of chemistry control is operational experience, corrosion and release data and the transport and deposition of crud/corrosion

products under operating conditions. The chemical control in nuclear reactors consists of two essential parts:

a) Chemicals added to counteract the harmful effects of products generated by radiolysis and the corrosion of constructional materials and also to counteract the acidity excursions due to chemical shim.

b) Minimisation of the concentration of chemical impurities which catalyse the degradation of material, coolant and protective oxide coatings.

Water chemistry strongly influences the operational safety of reactors in the following ways:

(i) By affecting the integrity of the barriers containing radioactivity such as fuel clad and primary circuit materials.

(ii) By affecting the out-of-core radiation fields which in turn influence man rem budgeting.

Good control of water chemistry can significantly reduce both above mentioned problems and consequently improve the plant safety.

The zirconium alloy cladding, used to contain the fuel pellets within the fuel rod, forms the first barrier against the release of fission products formed during power operation. Cladding integrity, therefore, is a major objective for plant operational safety.

The primary circuit forms the second barrier against release of corrosion products. The integrity of the reactor pressure vessel is not significantly influenced by water chemistry, but water quality has a major impact on the integrity of piping in BWRs and steam generators in PWRs.

Intergranular stress corrosion cracking has been a major problem in BWRs, affecting almost the entire reactor system and particularly the primary recirculation piping systems and reactor water clean-up systems. A correlation between extent of cracking and poor water quality has been demonstrated and further improvements have been shown from hydrogen addition.

The goal of all plant operators must be to keep radiation doses to the workers as low as reasonably achievable (ALARA) in order to minimise health hazards. Radiation exposure is a combination of the time spent by the worker in a radiation area and the intensity of radiation, or radiation field to which the workers are exposed. The time of exposure can be reduced by using remotely controlled equipment and by reducing the need for extensive maintenance and repair work, which is strongly influenced by chemistry, as discussed above [1].

One is concerned with reducing the out-of-core radiation fields, particularly in PWR steam generators, BWR recirculation piping and reactor clean-up systems, PHWR feeder cabinets and boiler cabinets which are responsible for much of the doses experienced during inspection and maintenance work. These radiation fields are the result of fission products released from failed fuel and activated corrosion products. Under normal operating conditions with little or no failed fuel, activated corrosion

products are responsible for over 90% of out-of-core radiation fields. These corrosion products come from either in-core components or are released from corroding and wearing surfaces in the coolant system, transported by the water to the reactor core where they become activated and are subsequently deposited on out-of-core surfaces. Cobalt isotopes (cobalt-58 and cobalt-60) are responsible for most of the fields, and much is being done in new plants to reduce cobalt sources, by controlling cobalt impurity concentration in constructional materials and minimising as far as possible the use of cobalt-based hardfacing alloys. However once a plant is built, the operator has only limited opportunity to further reduce the sources. Chemistry control is the main technique available to the operator to reduce the rate of build-up of radiation fields. Preconditioning surfaces before and during initial start-up is important, involving careful water chemistry control during this period. Good control of water chemistry during operation and at shut-down is essential to minimise the release, transport and deposition of the radio isotopes and also to control iron input from the feedwater in BWRs, which can result in high radiation fields in crud traps. Worldwide plant operating experience shows that plants with poor water chemistry control generally have higher radiation fields. Many PWRs and BWRs operating with good water chemistry have annual collective doses in the 100 - 200 man-rem range, compared to 5 times that dose for plants operated with poorer water chemistry control.

Although effective chemical decontamination techniques have been developed and demonstrated for both PWR and BWR applications, the cost and downtime needed for decontamination require that the use of decontamination technology should be minimised by controlling radiation field build-up rates through good water chemistry.

1.1 Specific Features of the Primary Coolant Chemistry in Nuclear Reactors

To achieve high water quality requires a good make-up water demineraliser system, a high degree of condenser integrity, attention to leaks to avoid oxygen ingress and effective primary coolant and condensate polishing systems. These are general principles applying to both BWR and PWR systems.

BWRs

Each plant design presents its own potential problems. For instance, ingress of resins, organics and inorganic impurities are of particular concern in BWRs because of boiling conditions in the core. Control of reactor feedwater quality is essential in a BWR, since the combination of impurities and oxygen (formed by radiolysis of the coolant water in the core) can be very aggressive towards materials.

PWRs

PWR primary system chemistry is complicated by the requirements to use a decreasing concentration of boric acid throughout the fuel cycle to control the nucleonics of the core. This requires an alkalisng agent, generally lithium hydroxide or potassium hydroxide, whose concentration must also vary if pH is to be stabilised. A hydrogen overpressure must be maintained to suppress radiolytic oxygen formation, which would otherwise lead to localized corrosion and heavy crud deposits on fuel.

PHWRs

The simplicity of primary heat transport system of PHWRs is due to the separation of the moderator system. The complications arising from the use of chemical shim in the primary coolant system and consequently coordinated lithium-boron chemistry do not exist at all. Hence two major chemistry requirements namely dissolved oxygen (<5 ppb) and lithium in the range of 0.35 to 1.4 mg/kg of water could be very efficiently maintained. Hydrogen over pressure (3 -10 ml/kg) of D₂O is maintained to suppress radiolytic oxygen formation.

The operational specifications, material integrity, man-rem considerations and hazards of violations of chemistry limits are discussed in the following Sections:

2.0 Existing Chemical Control Specifications

2.1 Definition of Terms

The water chemistry specifications of the primary coolant system are dependent on the plant design, plant status and the available justifications for treating a particular parameter as a plant controlling one. Special features of various types of water cooled nuclear reactors have already been described in Section 1.

Three states have been defined for a nuclear power plant for the purpose of framing limiting values for the control and diagnostic parameters. The reactor is said to be under cold shut-down if it is subcritical and the coolant temperature is < 120°C. Start-up state is when the reactor is subcritical but the coolant temperature is > 120°C. The third viz., the operational state is the one when the reactor is critical and is approaching or is at full power. The off normal mode is defined with respect to this state. During the off normal state the control parameters remain outside the limiting values at different action levels when suitable remedial measures are initiated [1].

Control parameters are those, whose limiting value when exceeded, may lead to lowering of the system reliability, fuel corrosion and increased radiation field build-up. Hence actions have to be initiated either to bring the control parameter value within the limiting value or resort to an orderly shut down of the plant.

Diagnostic parameters are useful for determining the cause of a problem but do not directly affect operational safety. Hence they do not have action levels.

The value of the parameter at Action level 1 represents the range outside of which the available data or engineering judgement indicates that long term system reliability will be affected. An improvement of operating practice is warranted so as to bring the parameter below the appropriate limit within 7 days.

Action level 2 represents the value of a parameter beyond which a significant damage could be caused to the system in relatively short time.

Corrective actions should be undertaken to bring the value of the parameter within the limiting value in 24 hours time.

Action level 3 requires orderly unit shut down to be initiated immediately so that conditions of subcriticality and coolant temperature below 120°C are reached as rapidly as possible, keeping in view other engineering constraints. Value of the parameter in Action level 3 represents a limit beyond which it is not advisable to operate the plant.

2.2 Pressurised Water Reactors

There are two main objectives which must be attained by chemical conditioning of primary circuit water.

1. minimisation of the general corrosion to protect the barrier's integrity
2. control of dose rates by minimising production and transport of corrosion products.

In addition to boric acid, the primary coolant is treated with lithium hydroxide (PWR) or potassium hydroxide (VVER), to minimise general corrosion of materials of primary system. This treatment is monitored by means of Li^+ or K^+ (more exactly the sum of $\text{K}^+ + \text{Na}^+ + \text{Li}^+$) measurements, and has a direct influence on the pH.

Other provisions are made to minimise corrosion by reducing the levels of aggressive ions like F^- or Cl^- .

The concentration of oxygen, arising from water radiolysis, is limited by excess of hydrogen, which is injected into primary water (in PWRs) or by ammonia (continuously or periodically dosed in VVERs).

Stringent control of chemical elements capable of forming zeolites (calcium, magnesium, aluminium, silica) is mandatory, especially in make-up water.

The logic of coolant chemistry management with B-Li is shown in Fig 1.

The second objective could be attained by maintaining during operation a constant pHr in the primary system. For some time a pH of 6.8 (at operating temperature) has been recommended in the absence of solubility data on nickel ferrite, since this corresponds to the zero temperature coefficient of solubility of magnetite, which was used to model the behaviour of fuel crud. Comparative testing at two PWR plants showed that a pH of 6.9 gave significantly less crud on the fuel than lower pHs, and that radiation fields on piping and steam generators built up more slowly. Moreover, when the low pH plant changed to a pH of 6.9 for the second and subsequent fuel cycles, the increase in radiation fields ceased, and new fuel remained clean even though the initial, heavily crudded fuel retained its deposits. There is, therefore, strong practical evidence to support a chemistry regime with a pH of 6.9 or higher, rather than a lower pH. More recent work involving the analysis of fuel crud removed from discharged fuel assemblies showed a nickel ferrite structure of varying stoichiometry. Subsequent measurements indicate that solubilities tend to increase at higher pHs and the temperature of

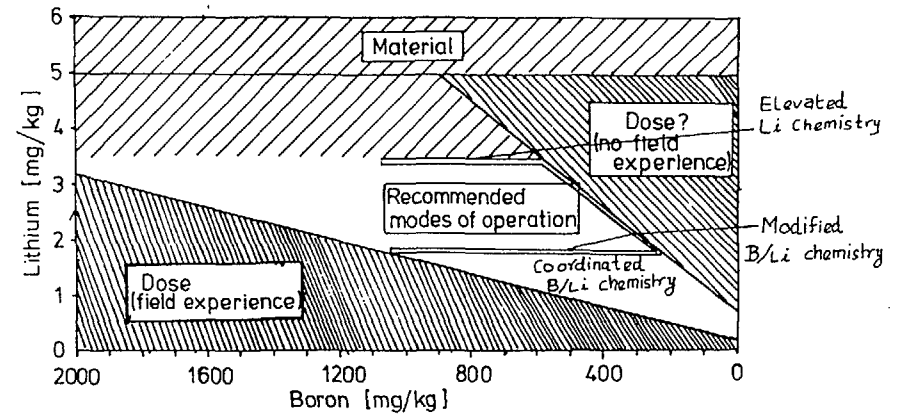


FIG. 1. Options for coolant chemistry.

minimum solubility decreases, which means that corrosion products will tend to precipitate on out-of-core surfaces, rather than on the fuel. These data lead to a prediction that raising the pH from 6.9 to 7.4 would reduce out-of-core radiation fields.

The state of art of the coolant specification is summarized in Table.I. It contains a comparison of relevant data from various vendors and institutions. Within the framework of the specifications, three options for coolant chemistry can be identified:

- a) Coordinated B/Li-chemistry with a pH_{aoo} of 6.9 ± 0.2
- b) Modified B/Li-chemistry where the Li-concentration is kept constant at 2 ppm Li till reaching a boron concentration of 350 ppm and then following the line $\text{pH}_{\text{aoo}} = 7.4$.
- c) Elevated B/Li-chemistry which is representative for 3.5 ppm Li in the early cycle and then following the curve $\text{pH}_{\text{aoo}} = 7.4$.

The theoretical basis for shifting the pHr value to 7.4 can be seen from Fig.2. Tables.IIa - IIe summarize the mode of operation in all Light-water PWRs and Fig.3a - 3d illustrate this by using lithium-boron-curves. In addition to the comparison of coolant specifications (Table.I), it seems necessary to look into more details under the following aspects:

- Sample frequencies,
- Action levels and
- Shut-down, start-up conditions.

These aspects are documented in Tables IIIa - IIIc for PWRs and Table. IV for VVER-440 and VVER-1000.

Table I Coolant Specifications for Power Operation

Parameter	EPR (US)	Westing-house (US)	VGB (FRG)	Siemens-KWU (FRG)	J-PWR (Japan)	EdF (France)	WWER 440/1000 (SU)	WWER 440 (Finland)
Lithium hydroxide	0.2-2.2*	0.7-2.2*	0.2-2.2*	0.2-2*	0.2-2.2*	0.6-2.2* 0.45-2.2	2-16.5#	2 - 22 #
Potassium hydroxide	-	-	-	-	-	-	> 5	> 5
Ammonia	-	-	-	-	-	-	-	-
Hydrogen	2.2-4.5	2.2-4.4	1 - 4	2 - 4	2.2-3.15	2.2-4.4	2.7-4.5	2.2-4.5
Oxygen	< 0.01	< 0.005	< 0.005	< 0.005	< 0.005	< 0.1	< 0.01	< 0.01
Chloride	< 0.15	< 0.15	< 0.2	< 0.2	< 0.05	< 0.15	< 0.1	< 0.1
Fluoride	< 0.15	< 0.15	-	-	< 0.1	< 0.15	< 0.05	< 0.1
Conductivity(25°C)	*	*	-	< 30	-	1-40	4-80*	-
pH (25°C)	*	4.2-10.5*	-	5-8.5	4.2-10.5	5.4-10.5	> 6	> 6
Dissolved Iron	-	-	-	(< 0.05)	-	-	-	-
Total Iron	-	-	(< 0.01)	-	-	-	< 0.2	-
Sulphate	0.1	-	-	-	-	-	-	-
Silica	-	< 0.2	-	(< 0.5)	-	< 0.2	-	-
Suspended solids	0.35	< 1	-	(< 0.1)	< 0.5	< 1	-	-
Aluminium	-	< 0.05	-	-	-	< 0.1	-	-
Calcium	-	< 0.05	-	-	-	< 0.1	-	-
Magnesium	-	< 0.05	-	-	-	< 0.1	-	-

() = normal operating value
 - = not applicable/specified
 * = According to LI and B concentration
 ** = According to LI & B concentration, new treatment
 # = Calculated taking into account K+Na+Li

Concentrations in mg/kg (ppm)
 Conductivities in µS/cm (µmhos/cm)

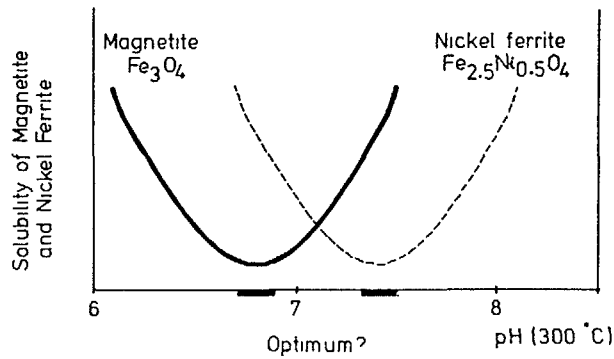


FIG. 2. Operational pH value with respect to dose rate buildup

Table IIa. PWR Coolant Chemistry Mode of Operation

Plants	LI/B-coord.	Elevated/modified	Others
Germany:			
Obrigheim			X
Stade	X		
Biblis-A	(X) →		X
Biblis-B	(X) →		X
Neckarwestheim-1			X
Underwester	X		
Grafenheinfeld	(X) →		X
Grohnde			X
Philippsburg-2			X
Brokdorf	X		
Mulheim-Karllich	X		
Isar-2			X
Emsland			X
Neckarwestheim-2			X
Switzerland:			
Beznau-1			Li 1-2 ppm
Beznau-2			Li 1-2 ppm
Gosgen		X	
Sweden:			
Ringhals-2	(X) →		X
Ringhals-3	(X) →		X
Ringhals-4			X
Belgium:			
Doel-1	X		
Doel-2	X		
Doel-3	(X) →		X
Doel-4			X
Tihange-1	X		
Tihange-2	X		
Tihange-3	X		
Netherlands:			
Borssele	X		

Table IIb.

Plants	Li/B-coord. pH(T) = 6.9	Elevated/modified pH(T) = 6.9-7.4	Others
France			
Chinon-A3	X		
Chooz	X		
St. Laurent-A1	X		
St. Laurent-B1	X		
St. Laurent-B2	X		
Bugey-1	X		
Bugey-2	X		
Bugey-3	X		
Bugey-4	X		
Bugey-5	X		
Fessenheim-1	X		
Fessenheim-2	X		
Dampierre-1	X		
Dampierre-2	X		
Dampierre-3	X		
Dampierre-4	X		
Gravelines-B1	X		
Gravelines-B2	X		
Gravelines-B3	X		
Gravelines-B4	X		
Gravelines-CS	X		
Gravelines-C6	X		
Tricastin-1	X		
Tricastin-2	X		
Tricastin-3	X		
Tricastin-4	X		
Le Blayais-1	X		
Le Blayais-2	X		
Le Blayais-3	X		
Le Blayais-4	X		

Table IIc.

Plants	Li/B-coord. pH(T) = 6.9	Elevated/modified pH(T) = 6.9-7.4	Others
France			
Chinon-B1		X	
Chinon-B2		X	
Chinon-B3		X	
Chinon-B4		X	
Cruas-1		X	
Cruas-2		X	
Cruas-3	X		
Cruas-4	X		
Paluel-1	X		
Paluel-2	X		
Paluel-3	X		
Paluel-4	X		
Saint-Alban-1	X		
saint-Alban-2	X		
Flamanville-1	X		
Flamanville-2	X		
Cattenom-1	X		
Cattenom-2	X		
Nogent-1	X		
Nogent-2	X		
Belleville-1	X		
Belleville-2	X		

Table II d.

Plants	Li/B-coord.	Elevated/modified	Others
Spain:			
Almaraz-1	X		
Almaraz-2	X		
Asco-1	X		
Asco-2	(X) →		
Vandellos-2		X	
Trillo-1		X	
Zorita	X		
Finland:			
Loviisa-1			KOH/NH ₃ pH(τ) = 7.2-7.6
Loviisa-2			
Japan:			
Mihama-1	X		
Mihama-2	X		
Mihama-3	X		
Takahama-1	X		
Takahama-2	X		
Takahama-3	X		
Takahama-4	X		
Ohi-1	X		
Ohi-2	X		
Ohi-3	X		
Genkai-1	X		
Genkai-2	X		
Sendai-1		X	
Sendai-2		X	
Ikata-1	X		
Ikata-2	X		
Tsuruga-2		X	
Taiwan:			
Maanshan-1	X		
Maanshan-2	X		

Table IIe

Plants	Li/B --Coord. pH(T) = 6.9	Elevated/modified pH(T) = 6.9-7.4	Others
South Africa:			
Koeberg-1	X		
Koeberg-2	X		
South Korea:			
Kori-1	X		
Kori-2	X		
Kori-3	X		
Kori-4	X		
Wolsung-1	X		
Yongkwang-1	X		
Yongkwang-2	X		
Ulgin-1	X		
USA:			
Milstone-3		X	
Calvert Cliffs		X	
St. Lucie-1		X	
St. Lucie-2		X	
H. P. Robbins		X	
Ginna		X	
Other PWRs	X		

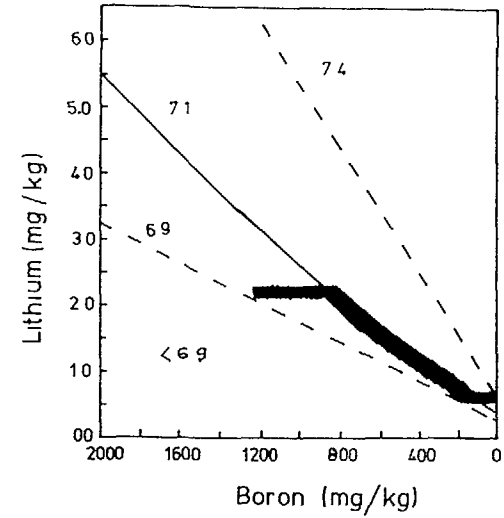


FIG. 3b. Reactor coolant chemistry in France (Ref. GEBCO Eng, Inc)

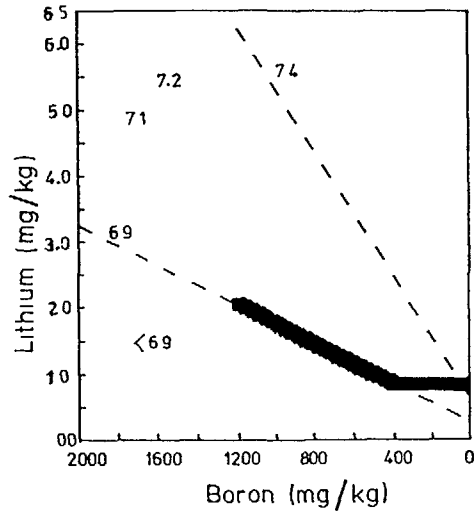


FIG. 3a. Reactor coolant chemistry in France (Ref. GEBCO Eng, Inc)

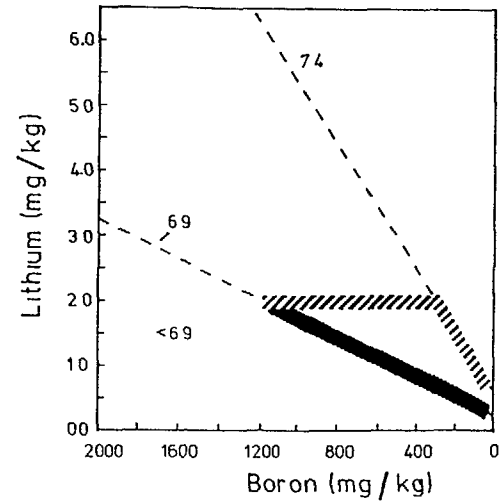


FIG. 3c. Reactor coolant chemistry in Germany (Ref. GEBCO Eng, Inc)

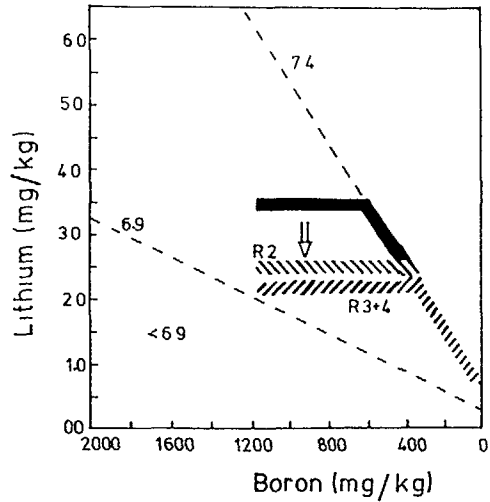


FIG 3d Reactor coolant chemistry in Sweden (Ref GEBCO Eng , Inc)

The following tables give the chemical control specifications for PWRs and VVERs [1]

Table IIIa. PWRs - Normal Operation
Primary Circuit Control and Diagnostic Parameters

Parameter	Units	Limiting value/Range	Sample frequency	Action level 1	Action level 2	Action level 3
Control						
Lithium	ng/kg	0.2 - 2.2	3/week	-	-	-
Diss O ₂	ng/kg	<0.005	1/day	-	>0.1	>1
Diss H ₂	ml(STP)/kg	25 - 50	3/week	<50, >25	≤15	≤5
Chloride	ng/kg	<0.05	1/day	-	>0.15	>1.5
Fluoride	ng/kg	<0.05	1/day	-	>0.15	>1.5
Diagnostic						
pH	-	see text below *	1/day			
Spcond	μs/cm at 25°C	see text below *	1/day			
Crud	ng/kg	<0.35	1/week			
Boron	ng/kg	0-1200	1/day			
Silica	ng/kg	<0.2	1/month			
Calcium	ng/kg	<0.5	1/month			
Magnesium	ng/kg	<0.1	1/month			
Aluminium	ng/kg	<0.1	1/month			
Sulfur (as SO ₄ ⁼)	ng/kg	<0.005	1/week			

* The specific conductivity and pH of the primary system water are dependant on the concentration of lithium, boron and other constituents of the medium. Lithium alone has been treated as a chemical control parameter. Based on the physical chemistry principles a quantitative relationship has been derived between the pH and specific conductivity and boron and lithium concentrations [2]. Detailed tabulated values at 25 and 300°C are reproduced in Tables 1 - 5 of Appendix - I for ready reference. For efficient radiation field control on SG channel heads, maintenance of a specific pH₃₀₀ value becomes essential. It can be seen from the solubility data of the magnetite, nickel ferrite and cobalt ferrite reported by different authors that there is a sharp minimum at pH₃₀₀ 6.9 - 7.0 [3 - 5]. Different plants have employed values between 6.9 and 7.4 while the tolerated variations around this value have been kept within ± 0.2 units. In view of the reported better performance characteristics in terms of low radiation levels by resorting to pH₃₀₀ between 6.9 and 7.4, the choice of the absolute value should be left to the specific operator depending on the design and other engineering considerations. Nevertheless the allowed tolerances should be either ± 0.2 units or lower based on ALARA considerations.

Table IIIb. PWRs - Cold Shut Down Conditions
Primary Circuit Control and Diagnostic Parameters

Parameter	Units	Limiting value/ Range	Sample frequency	Action level 1	Value prior to exceeding 120°C
Control					
Chloride	ng/kg	<0.05	3/week	>0.15	≤0.15
Fluoride	ng/kg	<0.05	3/week	>0.15	<0.15
Oxygen	ng/kg	NA	NA	NA	≤0.1
Diagnostic					
Lithium	ng/kg	-	-	NA	Consistent with Station's lithium program
Boron	ng/kg	As per reactor physics considerations	As per technical specifi- cations	NA	-
Sulfur	ng/kg	≤0.1	1/week	NA	-

Table IIIc. PWRs - Start-up Conditions
Primary Circuit Control and Diagnostic Parameters

Parameter	Units	Limiting value/ range	Sample frequency	Action level 1	Action level 2	Action level 3	Value prior to criticality
Control							
Chloride	ng/kg	<0.05	Consistent with Station's chemistry Management Programme	-	>0.15	>1.5	≤0.15
Fluoride	ng/kg	<0.05	-	-	>0.15	>1.5	≤0.15
Dissolved hydrogen	ml(STP)/ kg	-	-	-	-	-	≥15
Dissolved Oxygen	ng/kg	<0.01	-	>0.1	>1.0	-	≤0.1
Diagnostic							
Lithium	ng/kg	Consistent with Station's Li program	-	-	-	-	-
Boron	ng/kg	As required by reactor physics con- siderations	-	-	-	-	-
TDS	ng/kg	≤0.35	-	-	-	-	-
Sulfur (as SO ₄ ⁼)	ng/kg	<0.05	-	-	-	-	-

Note For pH and Sp conductivity refer to the discussions under Table IIIa

Table IV. VVER's Primary Circuit
Control and Diagnostic Parameters

Parameter	Units	VVER-440		VVER-1000	
		Limiting value/ range	Sample frequency	Limiting value/ range	Sample frequency
Control					
Potassium	ng/kg	2-12	1/day	-	-
K+Li+Na	mmol/kg	-	-	0.05-0.35	1/day
Dissolved Oxygen	ng/kg	<0.01	1/2 days	<0.01	1/2 days
Dissolved Hydrogen	ml(STP) /kg	25-50	1/day	30-60	1/day
Chloride	ng/kg	<0.20	1/day	<0.10	1/day
Fluoride	ng/kg	-	-	<0.10	1/3 weeks
Diagnostic					
pH 25°C	-	7.0-9.4	1/day or continuous	5.7-10.2	1/day or continuous
Boron	ng/kg	0-1200	1/day	0-1200	1/day
Ammonia	ng/kg	3-20	3/day	>5	3/day
Crud(as Fe)	ng/kg	<0.20	1/week	<0.10	1/week
Copper	ng/kg	-	-	<0.02	1/week

2.3 Pressurised Heavy Water Reactors

The primary coolant is treated with lithium in PHWRs to minimise general corrosion of system constructional materials. Provisions are also made to minimise corrosion by reducing the levels of aggressive chemicals like chlorides and fluorides. As the reactivity control system is separated out from the primary heat transport system, control of primary system pH is very much simplified. As it is possible to maintain pH at a reasonably constant value, the second objective of radiation level control on out-of-core surfaces is easily met. The concentration of dissolved O₂ arising from radiolysis is limited by excess hydrogen injected into the PHT system. The primary coolant specifications for PHWRs are given in Table V.

2.4 Boiling Water Reactors

The primary objectives for Water Chemistry Control in BWR primary circuits is to ensure that ingress of impurities into the reactor coolant are kept to a practical and achievable minimum. Another objective is to reduce

Table V. PHWRs - Normal Operation
Primary Circuit Chemical Control and Diagnostic Parameters

Parameter	Units	Limiting Value/range	Sample frequency
Control			
pH 25°C *	-	10.2-10.8	1/day or continuous
Dissolved Oxygen	mg/kg	<0.01	1/day
Dissolved Hydrogen	ml(STP)/kg	3-10	1/day
Chloride	mg/kg	<0.2	1/day
Fluoride	mg/kg	<0.1	
Diagnostic			
Lithium	mg/kg	1-2	
Spcond at 25°C	μs/cm	20-25	
Crud**	mg/kg	<0.1	
Iodine-131***	Bq/kg	<3.7x10 ⁶	

* Refers to pD in heavy water systems. Since measuring instrument is calibrated with light water, the following correction is applied:

$$pD = pH (\text{measured}) + 0.4$$

** Under cold shut down and start-up conditions, limiting crud valve is < 1 mg/kg

*** In PHWRs where on-line refuelling is a part of the design, iodine measurement is used as an indicator for fuel failure.

the radioactivity release from the fuel both through the leakage of fission products and the release of the activated crud from the fuel surfaces. The third objective (under HWC) is the control of injection rate of H₂ based on O₂ measurements or electrochemical potential in the recirculating water. The chemical control guidelines for BWRs are given in Tables VIa - VIc.

The primary water chemistry in a BWR is highly related to the quality of the feedwater. Therefore many of the actions that must be taken as a result of primary water chemistry excursions have to be taken in the clean-up systems. Among these the condensate polishing and the make-up water treatment are of special importance for the mitigation of impurity ingress to the primary water. To be able to minimise the consequences of an eventual ingress of impurities to the primary system the reactor water clean-up system should operate at sufficient capacity.

The reactor water clean-up system in BWRs normally are specified for flow-rates between 1 and 2 percent of the feedwater flow rate. This figure will determine the concentration factor for impurities that are introduced to the primary system. Unfortunately this is only valid for dissolved species. Due to the very efficient deposition of suspended particles on the core surface, the clean-up system is not very efficient for reducing the concentration of suspended corrosion products in the reactor water.

The specifications for chloride and conductivity are of special importance for the primary system. Excursions of these parameters are often the result of inleakage of cooling water to the condenser hot-well. For BWRs without deep-bed demineralizers for condensate polishing, the specification limits will soon be exceeded and therefore it is important to be able to quickly locate and plug leaky tubes. Conductivity measurements at the individual condenser hot-wells are good indicators of tube leaks.

Conductivity measurements downstream of the filter units are normally used to determine the need for filter demineralizer exchange or eventual regenerating of deep-bed demineralizers for the condensate polishing system. To be able to keep the specified values for corrosion products in the feedwater of a BWR it is essential to keep erosion-corrosion in the turbine systems at acceptable levels. The problem with erosion-corrosion on carbon-steel piping is related to the oxygen concentration and pH of the condensate. At concentrations lower than 20 ppb, an accelerated corrosion on carbon steel piping can arise. If forward pumping of condensate is used, the oxygen content in the preheater drains will normally be sufficient to provide the condensate line with oxygen in excess of 20 ppb.

Start-up deaeration techniques are generally adopted by several BWR utilities. The procedures are to be site and design specific but the general aim is to suppress the oxygen content (e.g. below 300 ppb) before the temperature increases above 100 - 150°C.

In some BWRs, where all the preheater condensates are cascaded to the condenser hot-well, the oxygen can be too low due to the deaeration that takes place in the condenser. For these stations, injection of oxygen to levels between 20 - 100 ppb, may provide the condensate lines with sufficient oxygen to prevent excessive corrosion.

3.0 Chemistry in Auxiliary Systems and Chemical Analysis Methods

This section deals with recommended analysis and continuous monitoring techniques for measurement of chemistry parameters, identified in Section.2.

3.1 Sampling

The size and length of the sample line and the design of the sample probes are given in ASTM standards (D-1066; D-1192; D-3370)[6]. There are, however, deviations from the above standards due to the following reasons:

- i) Sample line delay coils are used to allow decay of short half life radionuclides.
- ii) Continuous line purging is discouraged to minimise rad waste.
- iii) Sample bombs are employed to prevent degassing of the samples.

Table VIa. BWRs - Normal Operation
Reactor Water Chemical Control and Diagnostic Guidelines

Parameter	Units	Limiting Value/Range	Sample frequency	Action levels		
				1	2	3
Control						
Spcond at 25°C	µs/cm	<0.2	Continuous	>0.3	>1.0	>5.0
Chloride	µg/kg	<20	1/day	>20	>100	>200
Silica	µg/kg	<100	1/day	>200	-	-
Total Metal (Fe, Cr, Cu)	µg/kg	<5	1/day	-	-	-
Diagnostic						
Dissolved Oxygen*	µg/kg	200-400	1/day			
Dissolved Hydrogen*	µg/kg	25	1/day			
pH at 25°C**	-	7	Continuous			

* In hydrogen water chemistry, 1 mg/kg of hydrogen is maintained in feed water to reduce dissolved oxygen in the recirculation system by a factor of 100

** pH is indicative of chemistry transients. Not very representative when specific conductivity is less than 10 µs/cm because of the inherent uncertainties in measurement under these conditions

Table VIb. BWRs - Normal Operation
Condensate, Feed Water and Control Rod Drive Water
Chemical Control Guidelines

Parameter	Units	Limiting value/Range	Sample frequency	Action levels		
				1	2	3
Control						
Spcond at 25°C	µs/cm					
a) Condensate		≤0.15	Continuous	-	-	>10
b) Feed water		≤0.06		>0.07	-	-
c) Control rod drive water		≤0.10		>0.3	-	-
Dissolved Oxygen	µg/kg					
a) Condensate		-	-	-	-	-
b) Feed water		20-50	Continuous	<10	-	-
c) Control rod drive water		<50	1/day	>200	-	-
Total iron (feed water)	µg/kg	≤1	weekly, integrated	>5	-	-
		≤2*		>5	-	-
Total copper (feed water)	µg/kg	≤0.1	weekly, integrated	>0.5	-	-
		≤0.3**	weekly, integrated	>0.5	-	-

* Plants with forward pumped heater drains

** Plants with copper alloy condensers and powdex filter demineralisers

Table VIc. BWRs = Start-up/Cold Shut Down Conditions
Reactor Water Chemical Control Guidelines

Parameter	Units	Limiting value/Range	Sample frequency	Action levels		
				1	2	3
Control						
Spcond at 25°C	µs/cm					
a) Cold shut down		<2	Continuous	>2	-	-
b) Start-up		<0.5	Continuous	-	>1	>5
Chloride	µg/kg					
a) Cold shut down		<50	1/day	>500	-	-
b) Start-up		<20	8/day	-	>100	>200
Dissolved Oxygen	µg/kg					
a) Cold shut down		-	-	-	-	-
b) Start-up		<200 (when temperature >105°C)				

Table VIId. BWRs = Start-up Conditions Condensate and Feed Water Chemical Control Guidelines

Parameter	Units	Limiting value/range	Sample frequency	Action levels		
				1	2	3
Control						
Spcond at 25°C	µs/cm					
a) Condensate		<0.15	Continuous	-	-	>10
b) Feed water		<0.10	Continuous	>0.15	-	-
Suspended crud (Feed water)	µg/kg	<15	-	>100	-	-

No standard sample manipulation panel design presently exists, and a wide variety of designs are encountered. A schematic of representative design of a sampling system is given in Figure 4. Other techniques for obtaining samples for nonvolatile species are: samples collection in polyethylene bottles, gas samples collection by employing a low-pressure water displacement apparatus,

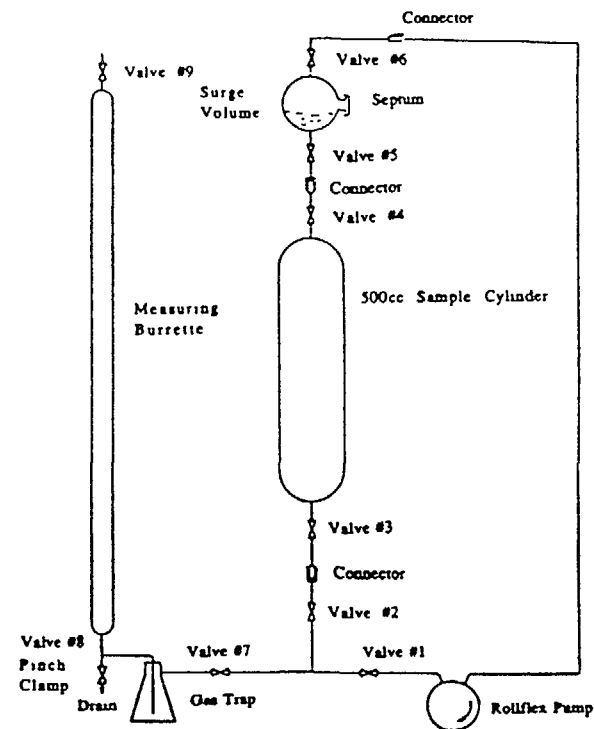


FIG. 4. Primary coolant sample manipulation apparatus.

etc. Relative to these guidelines, several techniques are considered acceptable for obtaining a liquid sample for analysis of nonvolatiles. Specifically, the sample could be obtained in an open bottle following recognized good practices. As an alternate, the sample could be obtained from the sample manipulation panel in the laboratory following degassing in a high-pressure sample cylinder. The latter approach will allow a sample to be obtained for total gas, hydrogen, oxygen, and radiolytic gas analyses. Use of the high-pressure cylinder approach for obtaining the gas phase sample is considered the preferred technique.

3.2 Measurement Methodologies for Key Parameters

Methodologies recommended for measuring key chemistry parameters are discussed below. Whenever possible, references to specific analytical procedures presented in accepted industry sources such as ASTM [6] or Standard Methods [7] are given. Reference also should be made to procedures supplied by the nuclear steam supply system vendor or instrument manufacturer. Other laboratory analytical procedures also can provide

accuracy and sensitivity levels similar to those given in such sources. However, these procedures must be qualified for reactor application prior to adoption. In all cases, procedures should be demonstrated to be applicable in the normal reactor primary coolant matrix which may contain significant amounts of chemical control additives.

3.2.1 Boron

Conventional wet chemistry procedures (ASTM D3082-79) [6] are generally applicable. The mannitol potentiometric technique (method B) is the method recommended for routine analyses. The carminic acid colorimetric method can be applied in the range of 1 to 10 ppm; below 1 ppm, the curcumin colorimetric extraction method is the only standard method available. Plasma emission spectroscopy has been successfully utilized below 50 ppb with a reported precision of approximately 20% at 10 ppb level. An ion chromatography procedure also is available. In the mannitol method used for the routine analyses of Boron the absorption of acidic or alkaline gases from laboratory air during the course of titration may cause a drift in the solution pH and result in error. Use of concentrated hydrochloric acid or concentrated ammonia solutions should not be permitted outside of a fume hood while boron titrations are being performed. The error from atmospheric carbon dioxide can be minimized by titrating rapidly. Titration of the blanks and standards, if carried out under conditions as similar as possible to those of the sample titrations, will compensate for any carbon dioxide error. Automatic titration equipment can also be employed so as to avoid these errors.

3.2.2 Chloride

The normally employed wet chemical procedure based on ASTM D512-81 [6] is limited to chloride concentrations above approximately 50 ppb. Laboratory specific ion electrode (SIE) techniques are accurate at levels near 10 ppb. Ion chromatographic equipment allows accurate determination of chloride concentrations at levels below 1 ppb. Wet chemical laboratory procedures should parallel ASTM D512-81 [6]. The calibration procedures for the SIE technique vary significantly from those normally employed for other species, since calibration curves in the range of interest are linear rather than semilogarithmic. In addition, calibration curves vary significantly with temperature thereby requiring temperature control within approximately $\pm 3^\circ\text{C}$ during analysis. The calibration procedures furnished by the SIE supplier should be used but with full cognizance of the variability in response characteristics of those electrodes in the range of interest.

3.2.3 Fluoride

Method B of ASTM D1179-80 [6] employs an ion selective electrode for measurement of fluoride. Procedures should include a caution to assure that response of the electrode remains Nernstian, i.e., approximately a 59 mV change in potential for a decade change in fluoride concentration. The extent of non-Nernstian behaviour, if any, should be verified as a function of fluoride concentration for each apparatus. Fluoride analyses also may be performed by ion chromatography.

3.2.4 Hydrogen

Until recently, the only technique employed for quantifying the hydrogen concentration in the primary coolant was chromatographic analysis of a gas phase sample. However, several commercial hydrogen analyzers for on-line analysis of primary coolant recently have become available and have been evaluated. These units, which employ electrochemical cells, have been reported to be accurate between 5 and 50 cc (STP)/kg hydrogen.

3.2.5 Lithium

The lithium concentration in the primary coolant can be determined by flame atomic absorption, flame emission, or direct current plasma emission. Assuming the effect of boric acid on instrument response has been considered, each of these procedures may yield results of acceptable accuracy over the range of interest.

The ASTM atomic absorption procedure for lithium (D3561-77) [6] has been evaluated in multiple laboratories only at high concentrations. Accuracy or precision pertinent to 1 ppm lithium have yet not been fully estimated. However, it has been indicated that an accuracy of ± 0.1 ppm can be achieved at the 1 ppm level with such a technique. Standard Methods [7] gives the accuracy of the flame emission technique as 0.1 to 0.2 ppm at a lithium concentration of 0.7 to 1.2 ppm.

3.2.6 Oxygen

Reliable manual and instrumental techniques for oxygen measurements exist. In-line techniques would be preferred, for primary coolant analysis. In manual procedures, such as ASTM D888-81 [6] based on indigo carmine, thorough rinsing of sample bottles and elimination of air contamination during sampling and chemical injection must be performed to eliminate extraneous sources of oxygen.

3.2.7 pH

Although pH instrumentation is employed commonly, caution should be exercised in measuring and interpreting variations in pH, since the instrument reading can be dependent on the total ionic strength of the sample solution. The pH - pD relationship also should be taken into consideration. Recommended measurement and calibration procedures are discussed in ASTM D1283-78 [6]. Daily verification of pH instrument performance is recommended. At least, a two-point calibration may be carried out.

3.2.8 Silica

Only reactive silica is measured by conventional laboratory or instrumental procedures based on ammonium molybdate. As such significant fraction of the silica in some samples may not be detected. In the primary coolant, however, it is expected that silica will be reactive, although evidence substantiating this premise is not available. A major fraction of the silica present in primary makeup water may be nonreactive and thus go undetected.

ASTM procedure D859-80 [6] is used as a basis for plant colorimetric procedures. Graphite furnace atomic absorption procedures allow total silica levels near approximately 20 ppb to be quantified. It is understood that an ASTM procedure on this approach is being developed.

3.2.9 Specific conductivity

Conductivity is a reliable technique for estimating the total concentration of ionic species in a water solution, although no information is furnished relative to the specific ions in solution. Samples should be at $25 \pm 3^\circ\text{C}$ to facilitate reference to curves or tables relating ionic concentrations to conductivity.

The most common problem in obtaining accurate primary coolant conductivity data is reliance on temperature compensation circuitry of commercial conductivity instruments when sample temperature is not controlled within the indicated range. Specifically, compensation circuitry of conventional instruments employed for grab sample analysis compensate only for the average variation with temperature of the equivalent conductance of common ions. Such equipment does not compensate for variations in ionization constants of water or boric acid with temperature. Such variations can lead to significant changes in solution conductivity with temperature. As such, all measurements should be made with the sample temperature within the recommended range.

It should also be noted that laboratory conductivity measurements of grab samples with a conductivity of $< 1 \mu\text{S}/\text{cm}$, e.g., primary makeup water, should not be expected to be accurate since absorption of carbon dioxide by the sample will rapidly increase its conductivity. In-line flow cell measurement techniques are recommended for such analyses. A procedure for cell calibration can be obtained from ASTM D1125-82 [6]. Monthly calibration of in-line and laboratory cells against known standards is recommended.

3.2.10 Sulfate and Sulfur-Bearing Compounds

Conventional wet chemical analysis procedures do not allow sulfate to be measured accurately at the ppb level. The only available technique with good sensitivity and accuracy is ion chromatography (IC). Although the IC sulfate peak generally is considerably broader than that for chloride, reasonable accuracy and reproducibility can be achieved at levels near 3 ppb. Oxidation of sulfur compounds by heating the sample for 20 minutes near boiling in a 20-ppm hydrogen peroxide solution at pH 10 has been suggested. Comparison of sulfate values of treated and untreated samples will give an indication of the magnitude of other sulfur compound concentrations.

3.2.11 Ammonia

Ammonia concentrations can be determined employing Nesslerization procedures. Results using this technique are affected if there is a significant amount of hydrazine in solution. ASTM D1416-79 [6] discusses the Nesslerization procedure. More recently, application of SLE techniques has increased because of the relative ease and reliability.

3.2.12 Hydrazine

During start-up, hydrazine may be employed in the primary system to reduce oxygen concentrations. The procedure for hydrazine may be similar to that based on p-dimethylaminobenzaldehyde (described in ASTM D1318-78).

3.2.13 Radionuclide Analyses

Information on fission and activation product levels in the primary coolant and at various locations in the purification system can be of considerable value in assessing fuel integrity and purification system component performance. Such data also provide a basis for plant-to-plant comparisons relative to activated corrosion-product behaviour.

Aliquots of primary coolant and dissolved gases can be counted to obtain detailed isotopic lists of gamma emitters employing high resolution gamma spectroscopy. For accurate analysis of pure beta emitters, radiochemical separation and purification are necessary. However, estimates of pure beta emitter concentrations can also be obtained by measuring the concentration of related gamma emitting isotopes. For tritium analysis, radiochemical separation and purification are required. Alpha concentrations can be estimated using windowless gas proportional counters employing corrections for sample self-absorption. Alpha-emitting isotopes can be identified using silicon surface barrier detectors.

3.2.14 Total Dissolved Gas

In the preferred approach, a primary coolant sample collected in a high-pressure cylinder is degassed in the sample manipulation panel. Total dissolved gas values are obtained directly from burette readings with appropriate attention to temperature, pressure, sample size and gas solubility.

Procedures for degassing the primary coolant sample and calculating total dissolved gas concentrations are specific to each individual sample panel design, sample cylinder size, etc. Recirculation of the gas phase is required to achieve equilibrium.

3.3 Chemical and Volume Control Systems (CVCS)

In PWRs, CVCS assumes major importance because of the coordinated B-Li chemistry. The system calls for innumerable number of pumps, valves, etc. involving hardfacing alloys which are potential sources of cobalt. Since the coolant has to essentially flow through this circuit for both purification and chemistry control, release of cobalt from CVCS could be a potential hazard. Yet, cobalt input from such a system has been found to be less than 0.003 mg/tonne of water, a feature not of very great concern. However, improved hardfacing alloys such as Fox Antinit Dur - 300, listed in Table VII under Section 4.0 could be usefully employed.

The crud particles and associated radioactivity picked up by the ion exchanger and physical filtration systems might get dislodged and carried over by the primary coolant. It has been estimated that the particulate

contribution due to pressure, flow and bed change over perturbations were of the order of 0.2 - 20 mg/tonne of water. This aspect could be overcome if precautions are taken to bypass the system:

a) When there are excessive particulate level periods at reactor shut down and start-up and

b) By employing finer filtration (0.45 μm) at IX bed outlet under steady operational conditions.

4.0 Material Integrity Considerations

The materials of construction used in the primary systems of nuclear reactors are given below in Table VII. In general multiple metals are made use of in reactors due to neutron economy, material strength, heat transfer and corrosion rate considerations, depending upon the zone where they are employed.

4.1 Core (Fuel) Materials

From consideration of neutron economy and mechanical stability at high temperature, hafnium free zirconium alloys are being used as fuel cladding material since late forties. The alloy development work has been carried out to overcome the deleterious effects of the impurities, to meet the desired mechanical strength and to prevent the oxide against cracking. The choice and proportion of the alloying elements were dictated by the following [8]:

- (i) the alloying elements should not unduly increase the absorption of thermal neutrons.
- (ii) they should stabilize the corrosion resistance and reduce the tendency to pick-up hydrogen.
- (iii) they should have an out-of-pile post transition corrosion rate of 1 mg/dm²/day or less and the oxide should be adherent.
- (iv) they should improve the mechanical properties, and
- (v) they should not make the metal more difficult to process.

With regard to the status of the zirconium alloy corrosion, problem areas related to hydriding, pellet-clad interaction and fretting have already been overcome by implementation of corrective measures during fabrication/operation. Fuel performance in water cooled reactors has shown failure incidence lower than 0.2%. Waterside corrosion has also not been substantially contributing to failures. However, PLEX may warrant investigations with respect to compatibility for higher burn-ups than designed.

Under normal operating conditions of LWRs, the external corrosion of zircaloy is not considered to be life limiting as proved by the large number of intact fuel rods which have met design burn-up. However, general

Table VII. Materials of construction in the Primary system of Reactors

Material	Location	Nominal composition	Critical cobalt level
Zircaloy-2	In core (fuel clad, coolant tubes)	Zr, Sn 1.5%	---
Zircaloy-4		Fe 0.07%, Ni 0.05%, Cr 0.05%	
Zirc-Niobium alloy		Zr, Sn 1.5%	
		Fe 0.18%, Ni 0.007%, Cr 0.07%	
		Zr, Nb 2.5%	
Carbon steel	System piping headers and feeders	Fe, C 0.2%, Si 0.15%, Mn 0.6% S 0.05%, P 0.4%	0.006% (max)
Stainless/High alloy steels	pumps	Fe, Cr 5-20%, Ni 0-10%, C 0.03-0.1%, Si 0.3-0.8% Mn 0-15%, S 0-0.02%, P 0-0.2%	---
SS 400 series	End fittings	Fe, Cr 4-18%, Ni 2.5% (max) C 0.15-0.2%	---
Monel - 400	Steam generator tubes	Fe 2.5%, Ni 63-70% Cu (bal)	0.005% (max)
Inconel - 600		Fe 6-10%, Ni 72%, Cr 14-17%	
Incoloy - 800		Fe (bal), Ni 30-35%, Cr 19-23% Co 50-60%, Cr 20-33%, W 5-20%	
Stellites	Valve seats	Ni 0-13%, Mo 0-6%, C 0-2.5%	being replaced by non cobalt based alloy
Fox Antinit Dur- 300	Core internals	Cr 21%, Ni 8%, Si 5% Mn 65%, Fe (bal)	

corrosion rates, hydriding, modular corrosion, enhanced oxide growth and spalling are various aspects that have attracted the attention of water chemists globally.

Since PWR coolant temperatures generally exceed those of BWR by 30-50°C, the PWR thermal corrosion rates are higher. However, since dissolved hydrogen is maintained in PWRs/PHWRs to suppress radiolytically produced dissolved O₂, radiation enhanced corrosion of the clad is minimised.

Dissolved hydrogen in the coolant can attack zircaloy to form hydride precipitates. During the pre-transition period, hydrogen pick-up is low due to protective nature of the oxide. During the post-transition period, however, it depends on temperature, environment and alloying conditions. The hydrogen pick-up rates on the cladding material in oxygenated environments (BWRs) are well within design limits. In PWRs/PHWRs, though the hydrogen pick-up is high, it is still lower than the design limit. It has also been observed [9,10] that increased percentage of heavy water (98%) causes reduced hydrogen pick-up for zircaloy-2 even though the general corrosion rates increase by a factor of 3-8 in high heavy water content medium. Improved alloys such as Zircaloy-4 and Zr-2.5% Nb after proper heat treatment provide better alternatives.

Specifically in oxygenated BWR coolant environment, uniform zircaloy corrosion gets accelerated by radiation flux [8]. Presence of threshold fast neutron flux and dissolved oxygen environment, specially at zones of thicker oxide have caused nodular corrosion of Zircaloy. Nodular corrosion is a localized attack characterised by discreet coalesced patches (nodules) of thicker white oxide against a background of uniform thinner oxide. This phenomena is much lower in PWRs/ PHWRs as compared to that in BWRs. Heat treatment in the phase region followed by quenching could be an effective palliative to reduce nodular corrosion.

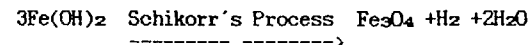
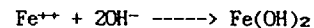
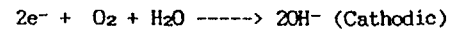
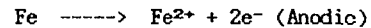
Oxide film grown in irradiated oxygenated water has given evidence of enhanced porosity in the oxide, reflecting the enhanced oxide growth. The creep of zirconia [8] in the presence of oxygen and irradiation could affect the stoichiometry of the surface layers causing local oxide break down and becoming a source of nodule nucleation.

Thus it is evident that uniform corrosion of zircaloy may not pose a serious problem under current operating conditions of water cooled reactors. If it is required to expose the fuel to high burn-ups, apart from other factors like improved fabrication procedures and alloy composition, careful control of water chemistry with respect to dissolved H₂ and O₂ would be essential.

4.2 Structural Materials

4.2.1 Carbon Steel

The high tensile strength of carbon steel makes it useful as a reactor structural material. When protected by an adherent oxide film, carbon steel is useful as primary system constructional material where reducing and alkaline environments prevail. The use of carbon steel for feeders, headers, system piping and vessel shells is an inherent feature of PHWRs. General long term corrosion rate of carbon steel is about 10-25 mg/dm²/month and the release rate is less than 10 mg/dm²/month (pH 10.2 - 10.8 at 25°C and dissolved O₂ < 10 ug/kg). The protective coating which is formed initially during PHT system hot conditioning is according to the following solution mechanism.



The last reaction is instantaneous at temperatures above 215°C. During the course of the operation of the reactor, the protective coating refurbishment takes place continuously. In addition to protecting the surface from successive corrosion and release, this film growth mechanism also limits the radioactivity build-up on that surface. After an adherent

and protective magnetite coating is formed on carbon steel surfaces, water chemistry control with respect to Cl⁻, NO₃⁻, etc. is not very critical as under these conditions, the material is not sensitive to any specific type of corrosion attack.

4.2.2 Stainless Steel

Austenitic stainless steels, used extensively in BWRs and PWRs, are generally more resistant to corrosion (2.5 - 5 mg/dm²/month) and release (0.6 - 1.5 mg/dm²/month). A thin protective film of chromium oxide present over stainless steel surface makes it passive under ambient conditions. The oxides formed under high temperature conditions contain Fe, Cr and Ni spinels with varying percentages of metals as a function of time and thickness. In contrast to carbon steel, chloride nitrate and sulfate ions are deleterious to stainless steel especially in oxygenated environments (> 100 ppb). Localised pitting attack and crevice corrosion are controlled by dissolved oxygen reduction which otherwise will lead to intergranular stress corrosion cracking through brittle fracture propagation at relatively low stress levels. Effective residual stress removal, reduction of carbon level in steel to avoid chromium segregation as carbide along the grain boundaries, utilisation of special alloying elements such as Mo, Nb and Ta and maintenance of optimum electrochemical potential (<-325 mV vs SHE) by hydrogen injection in the coolant are some of the important and useful palliatives for avoiding stress corrosion cracking failures in SS. Low corrosion rates at high temperatures, high tensile strength and adequate hardness in the rolled joint areas determine the use of 400 series stainless steels for the end fittings of the fuel channels in PHWRs.

4.3 Steam Generator Tube Materials

Monel-400 has been used as SG tube material in several operating first generation PHWRs. It is less expensive than Inconel-600 and is felt to be generally free from stress corrosion cracking. However, it can corrode significantly under oxygenating conditions (localised boiling conditions permitted in the recent designs of PHWR core where it is more difficult to suppress the radiolytically produced dissolved oxygen). The service performance of Monel-400 in PHWRs has been excellent.

Inconel-600 was chosen as SG tube material mainly in PWRs, primarily because of its excellent resistance to chloride induced transgranular stress corrosion cracking and because it has low corrosion rates even in oxygenated water. However, Inconel-600 with its high nickel content is susceptible to intergranular stress corrosion cracking.

Incoloy 800 has been chosen as SG tube material in some PWRs and in advanced PHWRs mainly because of the following reasons:

- a. Better resistance to stress corrosion cracking in high purity water.
- b. Better resistance to intergranular corrosion caused by acid excursions
- c. Less contribution to radiation fields
- d. Resistance to localised corrosion in concentrated caustic.

Experience with Incoloy-800 steam generator tube material has been generally very good. However, there is a slight disadvantage in using Incoloy-800, as its thermal conductivity is lower than that of Inconel-600 [11].

5.0 Plant Radiation Level Reduction Considerations

Contribution to the plant radiation levels depends on the deposition of radioactivity on the surfaces of components in the primary heat transport circuit. Those activities that are deposited on the normally inaccessible areas do not concern, while the deposition on out-of-core surfaces directly controls the man-rem budgeting. A survey of the radionuclides involved in the radiation build-up has revealed that ^{60}Co and ^{58}Co contribute more than 90%. Over the years the contribution from fission product radioactivity has gone down with improved clad performance or with decreasing fuel pin failure rate although some first generation plants remain as exceptions. The dominant corrosion products activity is generated from the very minor chemical constituent of the constructional material namely cobalt (^{58}Co). Cobalt is an impurity in Nickel, one of the alloying elements of steam generator tubes (large surface area) and it is a major constituent of the hardfacing alloys used in the primary system, whose area of exposure is minimal. The source term for radioactive cobalt nuclides will be controlled by both surface area exposed to the coolant and the percentage of cobalt and nickel in the material. The receipt term dealing with build-up of out-of-core surface activity and generation of radioactivity within the core will depend on coolant chemistry preconditioning/ prefilming, in situ passivation and decontamination.

5.1 Source Term Control

In BWRs, the hardfacing alloy stellite and core internals like control rod blades and fuel spacer springs are being effectively replaced with iron based hardfacing alloys and low cobalt containing (<0.05%) steels. In fact recent operational experience from PWRs has shown that despite the use of Incoloy 800 for SG tubes, radiation levels have not come down effectively. This is being attributed to the high cobalt inventory present in the in-core materials as in BWRs. Materials like $\text{Cr}_2\text{C}_3/\text{Cr-Ni}$ and Fox Antinit Dur 300 (59% Fe, 21% Cr, 8% Ni, 5% Si and 6.5% Mn) have been used as substitutes or coating for some of the core internals [12].

Considering the sensitivity of the general corrosion rates of SG tubes materials used in PWRs and PHWRs to the dissolved oxygen levels in the primary coolant a change in SG tube material has been effected from Monel 400 to Inconel 600 and then to Incoloy 800 (Table.6). Although Inconel and Incoloy have comparable corrosion rates at relatively higher dissolved oxygen levels (> 100 ppb), the cobalt source term is considerably lower for Incoloy - 800 due to its lower nickel content.

In VVERs, resorting to stainless steel (with 10% nickel) SG tubes itself has reduced the total quantity of nickel exposed to the coolant. Hence the cobalt impurity source term also gets considerably lowered [13].

5.2 Receipt Term Control

The capacity of the out-of-core surfaces to pick-up radioactivity depends on many factors. The variation of the release rates of different metals and the dependence of the solubility of various types of oxides formed with the chemistry of the coolant will constitute the two major parameters. It is evident from Table VIII that the surface areas of different materials exposed to the primary coolant differ considerably based on the reactor type.

Table VIII. Alloys used in Coolant Circuits

Material	% Surface Area of Coolant Circuit			
	BWR	PWR	VVER	PHWR
Stainless steel	44	5	79	-
Inconel 600 ; Incoloy 800 ; Monel 400 ;	-	75	-	77
Carbon steel	8	-	21	10
Zircaloy/ Zr Nb (Fuel cladding, coolant tubes)	48	20	-	13

In BWRs, oxygenated boiling environment excludes the use of material other than stainless steel and zircaloy for primary circuit. In the absence of SSGs in BWRs, the redistribution of corrosion product materials between the core and SG tube surfaces does not exist and hence coolant chemistry variations do not significantly contribute to such a phenomena. However, the contamination of recirculation system piping does exist and is dominated by suspended corrosion products. In PWRs, the release rates of corrosion products from SG tubes contribute to the receipt term significantly. The release rates from carbon steel, being much higher than that of any of the SG tubes used, become preponderant in PHWRs. As a result of the above mentioned differences in surface areas and release rates, the nature of the suspended and deposited oxides (which act as carriers for radioactivity) is different between the three reactor types.

BWRs : Magnetite, $\text{r Fe}_2\text{O}_3$ and chromium ferrite
 PWRs : Nickel ferrite, Chromium ferrite and Magnetite
 PHWRs : Magnetite (major), Nickel and Chromium ferrite (minor)

Suppression of the transport of ionic corrosion products from in-core to out-of-core surfaces and vice versa is controlled only by the solubility of the corrosion products as a function of system pH and temperature. Thus in order to minimise the receipt term, coolant chemistry that would ensure minimum release rates and specifically pH that would ensure minimum

solubility of the corrosion products have to be maintained [14]. Operational experience from VVERs has shown that dose rates at SG channel heads were lowest when the average pH_{300} was equal to 7.2 [13]. This is different from that expected for an oxide composition of $Ni_{0.5}Fe_{2.5}O_4$ whose pH_{300} of minimum solubility lies at 7.4. Canadian experience with PHWRs using lithium (upto 2 ppm) and pH_{300} in the range 7.4 - 7.8 has shown very low radiation levels. This pH is clearly in the positive temperature coefficient of solubility region, which is the basis of CANDU philosophy of minimum residence time in core. In PWRs, as a result of the coordinated B-Li chemistry and varying SG tube materials, optimisation of pH based on operational experience is rather difficult. Thus the recommended pH_{300} value ranges between 6.9 and 7.2. The role of the temperature differential across the core in conjunction with pH on the solubility of corrosion products is discussed in detail in Section.6.

Prefilming/ hot conditioning (Refer Section 4.1 for details) has been established to suppress activity accumulation on out-of-core surfaces. This effectively reduces the metal release rates by passivation and also keeps down the ionised nuclide intake as a function of time. While hot conditioning in PWRs/ PHWRs is usually carried out before nuclear run, Prefilming is done in BWRs before or during the nuclear heat-up, varying the chemistry conditions (variation of dissolved O_2 levels) suitably.

Optimisation of Ni/Fe ratio to <0.2 by iron injection (5 to 10 g/hour as iron crud) at the feed water inlet in BWRs has been shown to decrease the out-of-core radiation levels by a factor of 2 to 3 [15].

Improvement of CPU performance by utilizing hollow fibre filters and increasing the reactor water clean-up system flow rates in BWRs have also reduced the crud input to the reactor core and hence resulted in lower radiation levels [16].

Zinc injection passivation (5 - 15 ppb Zn in reactor water) has been found to function as a good radiation control measure in BWRs and the reduction in radiation field levels has been observed to be by a factor of 5-10 [17, 18].

Despite the above mentioned measures to control both the source and recipient terms, there is some build-up of radioactivity on out-of-core surfaces. Since this becomes a cause for additional burden on man-rem budgeting, resorting to chemical decontamination periodically may become essential.

6.0 Penalty of Primary Coolant Chemistry Violations

Deviations from the Technical Specifications during the normal reactor operation lead to two types of harmful effects viz, (a) increased corrosion rates; specific/ incipient corrosion attacks; primary boundary failures and fuel clad failures and b) build-up of radiation levels on out-of-core surfaces. The effects of violation of the technical specifications regarding the control parameters given in Section 2 are discussed below:

6.1 Chloride in association with dissolved O_2 has been the cause of intergranular stress corrosion cracking [1] of SS 304 SS used in BWRs. The electrochemical potentials fall in the range of 0 to + 100 mV vs SHE for BWRs

operating with normal water chemistry without additives. Even in the absence of harmful impurities like chloride and sulfate, IGSCC could occur in BWRs because of the unavoidable presence of the sensitized (HAZ) pipe welds. However, in the presence of chloride IGSCC could also transform into the transgranular mode. In addition, as a result of the increased thermal movements in the structure during start-up, initiation of SCC is more probable during this period because of oxide layer disruptions that locally expose the base metal to the coolant [1]. The cumulative incorporation of chloride in the oxide layer decreases its electrochemical resistance resulting in rapid attack of the base metal. Thus resorting to hydrogen water chemistry ensures the establishment of an electrochemical potential of -300 mV vs SHE which is beyond the IGSCC region. However, presence of oxidising impurities like nitrate in the coolant can effectively nullify the advantage provided by hydrogen water chemistry.

6.2 In PWR primary systems, IGSCC has been generally a less serious problem due to hydrogen injection carried out to maintain minimum oxidant concentrations and to minimise primary system corrosion. IGSCC failures seen in some of the PWRs have been attributed to impurity levels such as chloride, sulfate and other anions which alter the electrochemical potential. Excessive fluoride enhances zircaloy corrosion. Zeolite forming minerals such as Ca, Mg, Al and Si in the coolant can lead to the formation of dense tenacious low thermal conductivity deposits on fuel surface resulting in high clad surface temperature and hence enhanced corrosion. Silica has an additional capability of getting carried over with steam and affecting turbine performance.

6.3 In the absence of significant concentrations of the impurities a well defined relationship exist between the pH, lithium/boron concentrations and specific conductivity of the coolant. At room temperature, complying with this relationship will show that impurities which contribute either to pH or conductivity are not present. As a result of the stringent requirement of tolerable pH variation from the point of view of solubility of corrosion product oxides, currently allowable pH_{300} variation remains at ± 0.2 units. However it is known that uncertainties in the equilibrium constants of various equilibria involved in the computation of high temperature pH would compound to result in a value with errors larger than the allowed variation. In the presence of impurities of unknown quantity, which can happen during transients or under boiling conditions, exact definition of ionic strength will not be possible. Equilibria involving hydrogen ions but not related to lithium or boron may also come into play. As a result of these ambiguities in computation of pH_{300} from the currently measured pHs, it is recommended that pH_{300} is measured with suitable probes in situ in the primary coolant system. The high temperature pH measurements are currently being attempted by installation of yttria stabilised zirconia (YSZ) membrane based indicator electrodes with Ag-AgCl reference electrodes [19, 20]. If the high temperature pH monitoring is not implemented, there is a possibility that the pH variation seen by the system will be more than the allowed value of ± 0.2 .

6.4 Elevated lithium (upto 3.5 ppm) chemistry in the primary coolant system has been resorted to in some of the PWRs for the purpose of radiation field control on out-of-core surfaces. As a result of enhanced lithium, two problems are foreseen:

- a) Enhanced fuel cladding (zircaloy) corrosion
- b) Primary side cracking of steam generator tubes (Inconel- 600)

Though some of the results on the effect of lithium on zircaloy corrosion have shown that under the working concentration ranges it will not be of much concern [21], careful justifications for the use of high lithium concentrations in the primary coolant are however, needed, considering the observed lithium hide out problems. The reported enhanced corrosion of zircaloy in the presence of LiOH vis a vis KOH need not be of any great concern as the data is restricted to short term exposure and it may not be simple to extrapolate the same to long durations. The reported observations that the failure of mill annealed Inconel 600 SG tubes within the tube sheet and in the short bend regions through IGSCC were because of the use of high lithium, have prompted intensive research work in this field. Since the results of these test runs have not been conclusive [22], it is not possible presently to decide in favour or against the use of high lithium. The use of $^7\text{LiOH}$ and $\text{H}_3^{10}\text{BO}_3$ has safety and economic relevance. In PWRs, tritium problem gets totally overcome by the use of $^7\text{LiOH}$. Reduction in the required lithium concentration and also the reduced consumption of ion exchangers for boron removal are some of the gains if one uses ^{10}B .

VVER reactors have been using KOH in place of LiOH for pH control probably because of better compatibility with the fuel clad surfaces. Ammonia injection has been the practice for dissolved O_2 control presumably through the radiolytic production of hydrogen. Hydrazine in the coolant has been thought to give reduced corrosion rates as compared to the standard KOH - H_3BO_3 coordinated chemistry and some loop experiments have been in progress to test its performance for its ultimate use in the reactor systems [23].

7.0 Conclusions

Water Chemistry technology is quite complex since it deals with high temperature chemistry, radiation induced reactions, surface phenomenon, corrosion, material morphology, etc. Despite the complexity, in the past the chemical control technical specifications have been based on plant operational experience rather than on long term experimentation under controlled and simulated conditions. However, the enormous amount of basic and applied research work, that is presently being pursued all over the world in order to understand material compatibility, mass transport and contamination mechanisms, has caused revision of these specifications. It has also emphasized the need to classify the chemical parameters into the control and diagnostic parameters. Subsequent to understanding of the deleterious effects caused by violation of the technical specification, control of the reactor operation could be more systematically carried out through resorting to various action levels. The importance that is attached to the monitoring of control and diagnostic parameters gets substantiated only when the sampling procedures and the analytical methods are not prone to the systematic and statistical errors.

On line monitoring of chemical parameters is usually not implemented because the rate of change in the chemical parameters is rather slow and the measurement times involved are rather large thereby making any corrective action also a slow process. On the contrary, if high temperature pH, electrochemical corrosion potentials and dissolved hydrogen could be monitored in-situ, it would be possible to initiate corrective actions instantaneously through computerised additions. The present chapter deals with justifications for the above from the points of view of material

compatibility and man rem problems. The radiation levels continue to be dominated by ^{60}Co and ^{58}Co excepting that the origin of the parent nuclide is in doubt. Since presently the emphasis is on the total replacement of cobalt bearing materials from the primary coolant systems, contribution to radiation levels due to cobalt will be minimised in due course of time. In such an event the choice of SG tube material and the associated water chemistry control will depend more on material compatibility aspects rather than on cobalt content of the alloy.

Most of the Technical Specifications drawn have been based on out-of-pile tests. The overtone due to radiation is not fully understood as very few experiments have been carried out in-pile and that too not at system temperature. The discrepancies due to extrapolation of the results of these experiments to real systems were evident when primary system water chemistry modelling was done in BWRs. A recent review [24] has emphasised the need for carrying out basic research work in high temperature radiation chemistry. This may explain some of the radiation induced corrosion phenomena and also some of the observed effects in the radiation chemistry of aqueous solutions of interest to reactor coolant technology.

Appendix 1

TABULATED VALUES FOR pH AND CONDUCTIVITY OF BORIC ACID LITHIUM HYDROXIDE-AMMONIA SOLUTIONS AT 25°C/300°C

TABLE 1. pH OF BORIC ACID-LITHIUM HYDROXIDE SOLUTIONS AT 25°C

B, ppm	LITHIUM CONCENTRATION, ppm																
	0.0	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0	2.25	2.5	2.75	3.0	3.25	3.5	3.75	4.0
0	7.00	9.55	9.85	10.02	10.15	10.25	10.33	10.39	10.45	10.50	10.55	10.59	10.63	10.66	10.69	10.72	10.75
50	5.78	7.12	7.43	7.61	7.74	7.84	7.92	7.99	8.05	8.11	8.16	8.20	8.24	8.28	8.32	8.35	8.38
100	5.63	6.82	7.12	7.30	7.42	7.52	7.60	7.67	7.73	7.79	7.83	7.88	7.92	7.95	7.99	8.02	8.05
150	5.54	6.64	6.94	7.11	7.24	7.34	7.42	7.49	7.55	7.60	7.64	7.69	7.73	7.76	7.80	7.83	7.86
200	5.47	6.50	6.80	6.98	7.10	7.20	7.28	7.35	7.41	7.46	7.51	7.55	7.59	7.63	7.66	7.69	7.72
300	5.37	6.31	6.60	6.78	6.91	7.00	7.08	7.15	7.21	7.26	7.31	7.35	7.39	7.42	7.46	7.49	7.52
400	5.30	6.15	6.45	6.63	6.75	6.85	6.93	7.00	7.05	7.11	7.15	7.19	7.23	7.27	7.30	7.33	7.36
500	5.23	6.03	6.32	6.49	6.62	6.72	6.80	6.86	6.92	6.97	7.02	7.06	7.10	7.14	7.17	7.20	7.23
600	5.17	5.91	6.20	6.38	6.50	6.60	6.68	6.75	6.81	6.86	6.90	6.95	6.98	7.02	7.05	7.08	7.11
700	5.12	5.81	6.10	6.27	6.40	6.49	6.57	6.64	6.70	6.75	6.80	6.84	6.88	6.91	6.94	6.98	7.00
800	5.07	5.71	6.00	6.17	6.30	6.39	6.47	6.54	6.60	6.65	6.70	6.74	6.78	6.81	6.84	6.88	6.90
900	5.02	5.62	5.91	6.08	6.20	6.30	6.38	6.45	6.50	6.56	6.60	6.64	6.68	6.72	6.75	6.78	6.81
1000	4.98	5.54	5.82	5.99	6.11	6.21	6.29	6.36	6.42	6.47	6.51	6.56	6.59	6.63	6.66	6.69	6.72
1100	4.94	5.46	5.74	5.91	6.03	6.13	6.21	6.27	6.33	6.38	6.43	6.47	6.51	6.54	6.58	6.61	6.64
1200	4.89	5.39	5.66	5.83	5.95	6.05	6.13	6.19	6.25	6.30	6.35	6.39	6.43	6.46	6.50	6.53	6.56
1300	4.86	5.32	5.58	5.75	5.87	5.97	6.05	6.12	6.17	6.23	6.27	6.31	6.35	6.39	6.42	6.45	6.48
1400	4.82	5.26	5.51	5.68	5.80	5.90	5.98	6.04	6.10	6.15	6.20	6.24	6.28	6.31	6.35	6.38	6.41
1500	4.78	5.19	5.45	5.61	5.73	5.83	5.91	5.97	6.03	6.08	6.13	6.17	6.21	6.24	6.28	6.31	6.34
1600	4.75	5.14	5.38	5.55	5.67	5.76	5.84	5.91	5.96	6.02	6.06	6.10	6.14	6.18	6.21	6.24	6.27
1700	4.72	5.08	5.32	5.48	5.60	5.70	5.78	5.84	5.90	5.95	6.00	6.04	6.08	6.11	6.15	6.18	6.20
1800	4.69	5.03	5.26	5.42	5.54	5.64	5.71	5.78	5.84	5.89	5.94	5.98	6.02	6.05	6.08	6.11	6.14
1900	4.66	4.98	5.21	5.37	5.48	5.58	5.66	5.72	5.78	5.83	5.88	5.92	5.96	5.99	6.02	6.05	6.08
2000	4.63	4.94	5.16	5.31	5.43	5.52	5.60	5.67	5.72	5.77	5.82	5.86	5.90	5.93	5.97	6.00	6.03

TABLE 2. CONDUCTIVITY OF BORIC ACID-LITHIUM HYDROXIDE SOLUTIONS AT 25°C

B, ppm	LITHIUM CONCENTRATION, ppm																
	0.0	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0	2.25	2.5	2.75	3.0	3.25	3.5	3.75	4.0
0	.05	8.2	16.5	24.7	32.9	41.2	49.4	57.6	65.8	74.0	82.2	90.5	98.7	106.9	115.1	123.3	131.4
50	.64	2.8	5.6	8.4	11.2	14.0	16.8	19.6	22.4	25.2	28.0	30.8	33.6	36.4	39.2	42.0	44.9
100	.91	2.8	5.6	8.4	11.2	13.9	16.7	19.5	22.3	25.1	27.9	30.7	33.4	36.2	39.0	41.8	44.6
150	1.12	2.9	5.6	8.4	11.1	13.9	16.7	19.5	22.2	25.0	27.8	30.6	33.3	36.1	38.9	41.7	44.4
200	1.31	2.9	5.6	8.3	11.1	13.9	16.6	19.4	22.2	24.9	27.7	30.5	33.2	36.0	38.8	41.5	44.3
300	1.64	2.9	5.6	8.3	11.0	13.8	16.5	19.2	22.0	24.7	27.5	30.2	33.0	35.7	38.5	41.2	43.9
400	1.96	3.0	5.6	8.3	11.0	13.7	16.4	19.1	21.8	24.5	27.2	30.0	32.7	35.4	38.1	40.8	43.6
500	2.27	3.1	5.6	8.2	10.9	13.5	16.2	18.9	21.6	24.3	27.0	29.7	32.4	35.0	37.7	40.4	43.1
600	2.60	3.1	5.6	8.2	10.8	13.4	16.1	18.7	21.4	24.0	26.7	29.4	32.0	34.7	37.4	40.0	42.7
700	2.93	3.2	5.6	8.1	10.7	13.3	15.9	18.6	21.2	23.8	26.5	29.1	31.7	34.4	37.0	39.6	42.3
800	3.28	3.4	5.6	8.1	10.6	13.2	15.8	18.4	21.0	23.6	26.2	28.8	31.4	34.0	36.6	39.2	41.9
900	3.65	3.5	5.7	8.1	10.6	13.1	15.7	18.3	20.8	23.4	26.0	28.6	31.1	33.7	36.3	38.9	41.5
1000	4.04	3.7	5.7	8.1	10.6	13.1	15.6	18.1	20.7	23.2	25.8	28.3	30.9	33.5	36.0	38.6	41.1
1100	4.44	3.9	5.8	8.1	10.5	13.0	15.5	18.0	20.6	23.1	25.6	28.2	30.7	33.2	35.8	38.3	40.8
1200	4.87	4.1	5.9	8.2	10.5	13.0	15.5	18.0	20.5	23.0	25.5	28.0	30.5	33.0	35.5	38.1	40.6
1300	5.31	4.3	6.0	8.2	10.6	13.0	15.4	17.9	20.4	22.9	25.3	27.8	30.3	32.8	35.3	37.8	40.3
1400	5.77	4.6	6.2	8.3	10.6	13.0	15.4	17.8	20.3	22.8	25.2	27.7	30.2	32.7	35.2	37.7	40.1
1500	6.25	4.9	6.3	8.4	10.7	13.0	15.4	17.8	20.3	22.7	25.2	27.6	30.1	32.5	35.0	37.5	40.0
1600	6.75	5.3	6.5	8.5	10.7	13.0	15.4	17.8	20.2	22.7	25.1	27.5	30.0	32.4	34.9	37.4	39.8
1700	7.26	5.6	6.7	8.6	10.8	13.1	15.4	17.8	20.2	22.6	25.0	27.5	29.9	32.3	34.8	37.2	39.7
1800	7.79	6.0	7.0	8.8	10.9	13.2	15.5	17.8	20.2	22.6	25.0	27.4	29.8	32.3	34.7	37.1	39.6
1900	8.33	6.4	7.2	9.0	11.0	13.2	15.5	17.9	20.2	22.6	25.0	27.4	29.8	32.2	34.6	37.1	39.5
2000	8.90	6.8	7.5	9.2	11.2	13.4	15.6	17.9	20.3	22.6	25.0	27.4	29.8	32.2	34.6	37.0	39.4

TABLE 3. pH OF BORIC ACID-LITHIUM HYDROXIDE SOLUTIONS AT 25°C IN THE PRESENCE OF 0.5 ppm AMMONIA

B, ppm	LITHIUM CONCENTRATION, ppm																
	0.0	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0	2.25	2.5	2.75	3.0	3.25	3.5	3.75	4.0
0	9.19	9.64	9.88	10.04	10.16	10.25	10.33	10.40	10.45	10.50	10.55	10.59	10.63	10.66	10.69	10.72	10.75
50	7.04	7.39	7.58	7.71	7.82	7.90	7.98	8.04	8.09	8.14	8.19	8.23	8.27	8.31	8.34	8.37	8.40
100	6.73	7.08	7.27	7.40	7.51	7.59	7.66	7.72	7.78	7.82	7.87	7.91	7.94	7.98	8.01	8.04	8.07
150	6.55	6.90	7.09	7.22	7.32	7.40	7.47	7.53	7.59	7.64	7.68	7.72	7.76	7.79	7.82	7.85	7.88
200	6.42	6.76	6.95	7.08	7.19	7.27	7.34	7.40	7.45	7.50	7.54	7.58	7.62	7.65	7.68	7.71	7.74
300	6.22	6.56	6.75	6.88	6.99	7.07	7.14	7.20	7.25	7.30	7.34	7.38	7.42	7.45	7.48	7.51	7.54
400	6.07	6.41	6.60	6.73	6.83	6.91	6.98	7.04	7.10	7.14	7.19	7.23	7.26	7.29	7.33	7.35	7.38
500	5.95	6.28	6.47	6.60	6.70	6.78	6.85	6.91	6.97	7.01	7.06	7.09	7.13	7.16	7.19	7.22	7.25
600	5.83	6.16	6.35	6.48	6.58	6.67	6.74	6.80	6.85	6.90	6.94	6.98	7.01	7.05	7.08	7.11	7.13
700	5.73	6.06	6.24	6.38	6.48	6.56	6.63	6.69	6.74	6.79	6.83	6.87	6.91	6.94	6.97	7.00	7.03
800	5.64	5.96	6.15	6.28	6.38	6.46	6.53	6.59	6.64	6.69	6.73	6.77	6.81	6.84	6.87	6.90	6.93
900	5.55	5.87	6.05	6.18	6.28	6.37	6.43	6.49	6.55	6.59	6.64	6.68	6.71	6.74	6.78	6.80	6.83
1000	5.47	5.78	5.96	6.09	6.19	6.28	6.35	6.41	6.46	6.51	6.55	6.59	6.62	6.66	6.69	6.72	6.74
1100	5.39	5.70	5.88	6.01	6.11	6.19	6.26	6.32	6.37	6.42	6.46	6.50	6.54	6.57	6.60	6.63	6.66
1200	5.32	5.62	5.80	5.93	6.03	6.11	6.18	6.24	6.29	6.34	6.38	6.42	6.46	6.49	6.52	6.55	6.58
1300	5.26	5.55	5.73	5.85	5.95	6.04	6.10	6.16	6.22	6.26	6.31	6.35	6.38	6.41	6.45	6.47	6.50
1400	5.19	5.48	5.65	5.78	5.88	5.96	6.03	6.09	6.14	6.19	6.23	6.27	6.31	6.34	6.37	6.40	6.43
1500	5.14	5.41	5.59	5.71	5.81	5.89	5.96	6.02	6.07	6.12	6.16	6.20	6.24	6.27	6.30	6.33	6.36
1600	5.08	5.35	5.52	5.65	5.75	5.83	5.90	5.95	6.01	6.05	6.10	6.14	6.17	6.20	6.23	6.26	6.29
1700	5.03	5.29	5.46	5.58	5.68	5.76	5.83	5.89	5.94	5.99	6.03	6.07	6.11	6.14	6.17	6.20	6.23
1800	4.98	5.23	5.40	5.52	5.62	5.70	5.77	5.83	5.88	5.93	5.97	6.01	6.04	6.08	6.11	6.14	6.16
1900	4.93	5.17	5.34	5.47	5.56	5.64	5.71	5.77	5.82	5.87	5.91	5.95	5.99	6.02	6.05	6.08	6.11
2000	4.89	5.12	5.29	5.41	5.51	5.59	5.65	5.71	5.77	5.81	5.85	5.89	5.93	5.96	5.99	6.02	6.05

TABLE 4. CONDUCTIVITY OF BORIC ACID-LITHIUM HYDROXIDE SOLUTIONS AT 25°C IN THE PRESENCE OF 0.5 ppm AMMONIA

B, ppm	LITHIUM CONCENTRATION, ppm																
	0.0	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0	2.25	2.5	2.75	3.0	3.25	3.5	3.75	4.0
0	4.14	10.5	17.9	25.8	33.8	41.8	50.0	58.1	66.3	74.4	82.6	90.8	99.0	107.1	115.3	123.5	131.7
50	3.37	6.1	8.9	11.7	14.4	17.2	20.0	22.8	25.6	28.3	31.1	33.9	36.7	39.4	42.2	45.0	47.8
100	3.41	6.1	8.9	11.7	14.4	17.2	20.0	22.8	25.5	28.3	31.1	33.9	36.6	39.4	42.2	45.0	47.7
150	3.44	6.2	8.9	11.7	14.4	17.2	20.0	22.7	25.5	28.3	31.0	33.8	36.6	39.3	42.1	44.9	47.6
200	3.47	6.2	8.9	11.6	14.4	17.2	19.9	22.7	25.4	28.2	31.0	33.7	36.5	39.2	42.0	44.8	47.5
300	3.54	6.2	8.9	11.6	14.3	17.1	19.8	22.5	25.3	28.0	30.7	33.5	36.2	39.0	41.7	44.5	47.2
400	3.62	6.2	8.8	11.5	14.2	16.9	19.6	22.4	25.1	27.8	30.5	33.2	35.9	38.6	41.4	44.1	46.8
500	3.71	6.2	8.8	11.4	14.1	16.8	19.5	22.2	24.8	27.5	30.2	32.9	35.6	38.3	41.0	43.7	46.4
600	3.81	6.2	8.7	11.4	14.0	16.7	19.3	22.0	24.6	27.3	29.9	32.6	35.3	37.9	40.6	43.2	45.9
700	3.94	6.2	8.7	11.3	13.9	16.5	19.1	21.8	24.4	27.0	29.7	32.3	34.9	37.6	40.2	42.8	45.5
800	4.09	6.2	8.7	11.2	13.8	16.4	19.0	21.6	24.2	26.8	29.4	32.0	34.6	37.2	39.8	42.4	45.0
900	4.26	6.3	8.7	11.2	13.7	16.3	18.9	21.4	24.0	26.6	29.2	31.7	34.3	36.9	39.5	42.1	44.7
1000	4.46	6.4	8.7	11.2	13.7	16.2	18.7	21.3	23.8	26.4	28.9	31.5	34.1	36.6	39.2	41.7	44.3
1100	4.69	6.5	8.7	11.2	13.6	16.1	18.6	21.2	23.7	26.2	28.8	31.3	33.8	36.4	38.9	41.4	44.0
1200	4.95	6.6	8.8	11.2	13.6	16.1	18.6	21.1	23.6	26.1	28.6	31.1	33.6	36.1	38.7	41.2	43.7
1300	5.24	6.7	8.9	11.2	13.6	16.0	18.5	21.0	23.5	26.0	28.4	30.9	33.4	35.9	38.4	40.9	43.5
1400	5.55	6.9	9.0	11.2	13.6	16.0	18.5	20.9	23.4	25.9	28.3	30.8	33.3	35.8	38.3	40.7	43.2
1500	5.89	7.1	9.1	11.3	13.6	16.0	18.4	20.9	23.3	25.8	28.2	30.7	33.2	35.6	38.1	40.6	43.1
1600	6.26	7.3	9.2	11.4	13.7	16.0	18.4	20.8	23.3	25.7	28.2	30.6	33.1	35.5	38.0	40.4	42.9
1700	6.65	7.5	9.3	11.5	13.7	16.1	18.4	20.8	23.2	25.7	28.1	30.5	33.0	35.4	37.9	40.3	42.8
1800	7.07	7.8	9.5	11.6	13.8	16.1	18.5	20.8	23.2	25.6	28.0	30.5	32.9	35.3	37.8	40.2	42.6
1900	7.51	8.1	9.7	11.7	13.9	16.2	18.5	20.9	23.2	25.6	28.0	30.4	32.8	35.3	37.7	40.1	42.5
2000	7.98	8.4	9.9	11.9	14.0	16.3	18.6	20.9	23.2	25.6	28.0	30.4	32.8	35.2	37.6	40.0	42.5

TABLE 5. RELATION OF pH AT 300°C TO LITHIUM AND BORON CONCENTRATIONS

pH	6.30	6.90	7.00	7.10	7.20	7.30	7.40	7.50
B, ppm	Li, ppm							
0	.17	.22	.27	.35	.44	.55	.69	.87
50	.22	.28	.35	.45	.56	.71	.89	1.13
100	.27	.34	.43	.55	.69	.87	1.10	1.38
150	.32	.41	.52	.65	.82	1.03	1.30	1.64
200	.38	.48	.60	.75	.95	1.20	1.51	1.90
250	.43	.54	.68	.86	1.06	1.36	1.72	2.16
300	.48	.61	.77	.97	1.22	1.53	1.93	2.43
400	.59	.75	.94	1.18	1.49	1.88	2.36	2.97
500	.70	.89	1.12	1.41	1.77	2.23	2.81	3.53
600	.80	1.03	1.30	1.63	2.06	2.59	3.26	4.11
700	.94	1.18	1.48	1.87	2.35	2.96	3.73	4.69
800	1.06	1.33	1.68	2.11	2.66	3.34	4.21	5.29
900	1.18	1.49	1.87	2.36	2.97	3.73	4.70	5.91
1000	1.31	1.65	2.07	2.61	3.28	4.13	5.20	6.54
1100	1.44	1.81	2.28	2.87	3.61	4.54	5.71	7.19
1200	1.57	1.98	2.49	3.13	3.94	4.96	6.24	7.85
1300	1.71	2.15	2.70	3.40	4.28	5.39	6.78	8.53
1400	1.85	2.32	2.93	3.68	4.63	5.83	7.33	9.22
1500	1.99	2.50	3.15	3.97	4.99	6.28	7.90	9.93
1600	2.14	2.69	3.38	4.26	5.36	6.74	8.48	10.66
1700	2.29	2.88	3.62	4.56	5.73	7.21	9.07	11.40
1800	2.44	3.07	3.86	4.86	6.12	7.69	9.68	12.17
1900	2.60	3.27	4.11	5.18	6.51	8.19	10.30	12.94
2000	2.76	3.47	4.37	5.50	6.91	8.69	10.93	13.74

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NATIONAL CONTRIBUTIONS

PRIMARY CIRCUIT CHEMISTRY OF PRESSURE VESSEL PHWRs

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Abstract

Pressure vessel PHWR's based on natural uranium fuel use heavy water as primary heat transport fluid ("coolant") and as moderator. Both systems comprise different loops but they are effectively communicated with each other.

The water chemical specifications are determined by material selection: zirconium alloys in fuel elements cladding, Incoloy 800 and Inconel 600 in steam generators and moderator heat exchangers tubes and tube-sheets and stainless chrome nickel steels in components and pipelines.

The generalized metal release of the steels presents a minimum in the moderately alkaline pH range associated with the properties of the film grown on the metal surface, mainly magnetite and nickel ferrites. Although the release rates are low, it is important to control selective forms of corrosion like pitting, crevice corrosion and stress corrosion cracking through an adequate control of oxygen and impurities levels.

Zirconium alloys suffer an oxidation mechanism that leads to hydrogen uptake into the metal and this may cause the degradation of their properties. The rate of corrosion depends on the temperature, the oxidative condition of the media, the thickness of the oxide layer and neutron flux.

The main objective of chemical control is to optimize water quality thus minimizing general metal release rate and the probability of selective corrosion occurrence. These requirements are fulfilled through appropriate ⁷LiOD dosage, D₂ conditioning and specific operational procedures. Operational experience and the state of the art play an important role in the evolution of the chemical control criteria of nuclear plants. In that sense the limiting values for the primary media of Atucha 1 NPP are:

(LiOD) 1-2 mg ⁷Li/ kg
(D₂) 6 mg D₂/ kg
(O₂) <0.05 mg O₂/ kg
(Cl⁻) <0.2 mg Cl⁻/ kg,

while the recommended values for the future Atucha 2 are:

(LiOD) 0.2-0.7 mg ⁷Li/ kg
(D₂) 0.6-2 mg D₂/ kg
(U₂) <0.005 mg U₂/ kg
(Cl⁻) <0.2 mg Cl⁻/ kg

The criterion related with man-rem reduction requires the minimization of the sources of radionuclides and their transport and deposition along the entire circuit. These are fission products released from fuel elements, activated products from water and additives and activated corrosion products, these last the major contributors to man-rem inventory, reduced in the future plants by the absence of cobalt alloys in the neutron flux zones.

Another relevant feature of PHWR's is the possibility of refuelling during operation, which allows the removal of damaged fuel elements once they are localized.

1 MATERIAL CHARACTERISTICS MATERIAL INTEGRITY CONSIDERATIONS

1.1 Introduction

Only two heavy water pressure vessel reactors have been built in the world: MZFR is a German multi-purpose research 57 MWe reactor, and Atucha 1 NPP is an Argentine 375 MWe pressure vessel PHWR that is commercially operating since 1974. Another unit, Atucha 2 NPP, is being built at the same site in Lima, a small town near Buenos Aires city. Its design characteristics are included in Table I.

These reactors use natural uranium fuel and heavy water as primary heat transport fluid ("coolant") and as moderator. Coolant and moderator comprise different loops, but they are communicated with each other and there is an effective flow rate of mixing. A typical flow sheet is shown in Figure 1.

Table I
Thermodynamic, Design and General Data

	Atucha 1 NPP	Atucha 2 NPP
Capacity (MWth)	1179	2161
Effective full power (MWe)	370	700
Commissioning	1974	(1933)
Coolant		
Flow rate (t/h)	20000	37200
Type of circulation	forced	forced
Number of loops	2	2
Pressure (MPa)	11.5	11.9
Temperature (°C) inlet	265	278
medium	282	296
outlet	300	314
Moderator		
Flow rate (T/h)	1400	3200
Type of circulation	forced	forced
Pressure (MPa)	11.5	11.9
Temperature (°C)	180	170
Number of loops	2	4
Inventory (Mg)	120	235
Secondary coolant		
Flow rate (T/h)	1856	3450
Steam generators	2	2
Pressure (MPa)	4.4	5.6
Temperature (°C)	255	271

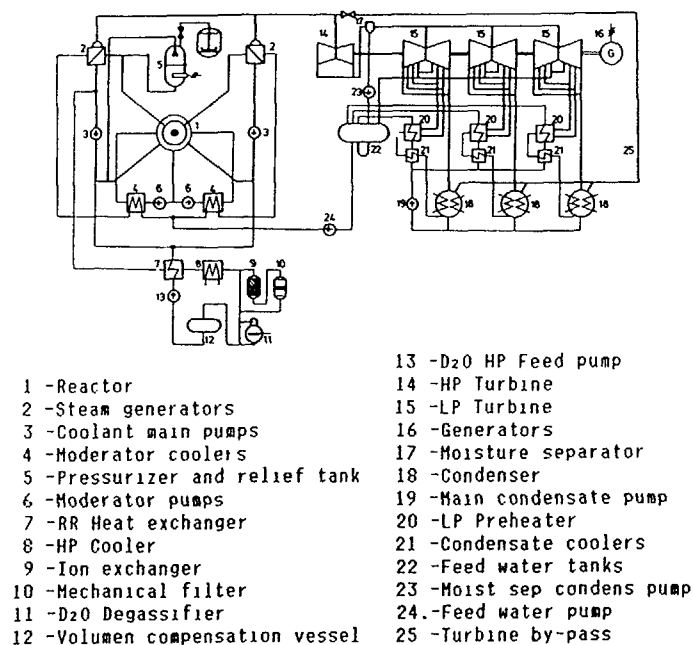


Figure 1

Pressure Vessel NPP flow sheet

1.2 Material characteristics

The water chemical specifications are determined by material selection. Table II summarizes primary circuit base materials and corresponding surface areas. Stainless chrome-nickel steel is used in components and pipe-lines of main heat transport system, Zircaloy 4 in fuel elements cladding, and Incolloy 800 and Inconel 600 in steam generators and moderator heat exchangers tubes and tube-sheets. High alloys and chrome steels complete the scope.

A real advance from the point of view of radiation fields generation is the elimination of cobalt alloys, especially from zones under neutron flux, as discussed later.

1.3 Materials considerations

The generalized metal release at work temperature of austenitic steels and high nickel alloys, presents a minimum in the moderately alkaline pH range due to the properties of the film grown on the metal surface, mainly magnetite and nickel ferrites that include compounds of non stoichiometric composition, typically Ni_{0.5}Fe_{2.5}O₄.

Table II
Base Materials

Component	Atucha 1 NPP	Atucha 2 NPP
Pressure vessel base material	Carbon steel	Carbon steel
Pressure vessel cladding	x5CrNiNb19 9	20MnMoNi55
Main tubing system (>200 mm)	22NiMoCr37	x10CrNiNb18 9
Tubing cladding	x10CrNiNb18 9	x10CrNiNb18 9
General piping	x10CrNiNb18 9	x10CrNiNb18 9
Upper filling	x10CrNiNb18 9	x5CrNi13 4
SG tubing	Incolloy 800	Incolloy 800
SG tube-sheet	Inconel 600	Inconel 600
Moderator vessel	x10CrNiNb18 9	x10CrNiNb18 9
Moderator heat exchanger tub	Incolloy 800	Incolloy 800
Fuel rod cladding	Zry-4	Zry-4
Refrigeration channel	Zry-4	Zry-4
Guide tubes of control rods	Zry-4	Zry-4
Areas in contact with primary media (m ²)		
x10CrNiNb18 9 (DIN 1 4550)	3700	5000
Incolloy 800	8000	16000
Zry-4	3300	5800
Stellite	25	--

Minimization of the solubility of metal oxides leads to different operational practices. To minimize magnetite solubility, as seen in Figure 2⁽¹⁾ the optimum pH is 6.9 at 300°C. If nickel ferrites behaviour is considered the optimum pH is 7.5. There are not enough data to support the choice of either one.

Samples of films on steam generator⁽²⁾ walls of Atucha I NPP indicate a very thin coverage, thicker at the outlet zone in accordance with the increase of magnetite solubility as the temperature decreases (from 300 to 275°C) at the working pH.

Oxides on Incolloy 800 present a typical double layer structure. The inner layers are compositionally related to the base material, the outer layer is enriched in chromium. This is indicative of "in situ" generation instead of crud deposition origin.

Deposits of the NiCr₂O₄ type are usually found on austenitic steels, for instance in the main pumps seals. These oxides play an important role in the passivation of stainless steels and are not sensitive to reductive attack, characteristics that are taken into account in decontamination procedures.

Austenitic CrNi-steels have similar, and very low, metal release rates at the operating condition of a PHWR. The occurrence of selective forms of corrosion must be minimized through the adequate chemical control. The most important forms are pitting, crevice corrosion and stress corrosion cracking. Disturbances or lack of the passive layer are involved in these undesirable phenomena. Design characteristics (crevice corrosion) and

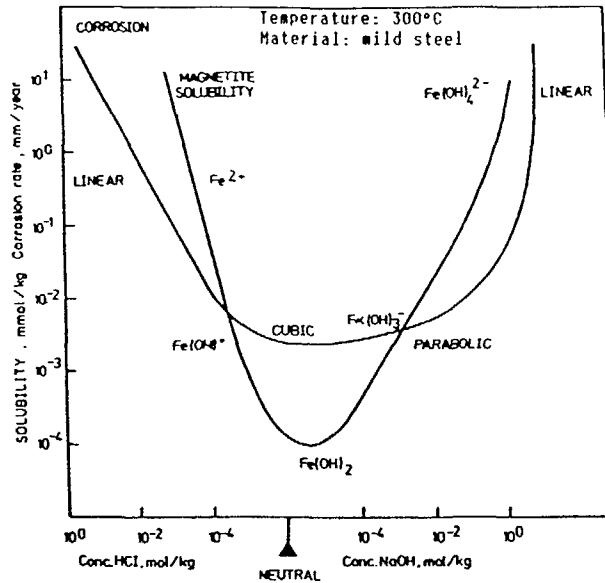
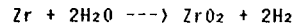


Figure 2
Generalized metal release and magnetite solubility

mechanical stress (SCC) are also important. In every case the presence of corrosive agents is required, mainly the simultaneous presence of oxygen and chloride ion.

Zircaloy 4 (Sn 1.5%; Fe 0.18%; Ni 0.007%; Cr 0.07%; Zr) is the zirconium alloy used in pressure vessel fuel rod cladding.

The oxidation of the zirconium alloys is as follows:



A fraction of this cathodically released hydrogen is then uptaken into the metal.

The rate of the corrosion depends on the temperature, the oxidative condition of the media, the thickness of the oxide layer and the neutron flux. Above a critical thickness value, the oxidation rate strongly increases. Hydrogen content in the water controls the growth of the oxide, reaction rate and hydrogen production.

Under certain conditions, hydrides can precipitate as a result of the hydrogen pick-up by zircaloy, giving rise to embrittlement.

2. FUEL CLADDING INTEGRITY

The fuel elements in pressure vessel PHWR contain natural uranium UO₂ pellets (0.7% ²³⁵U; major ²³⁸U). Fission products are confined within the

Table III

Activity values in Atucha 1 NPP primary circuit without and with damaged fuel rods

	without damaged fuel rods	with damaged fuel rods
¹³¹ I	2.5 E2 Bq/ml	6.5 E3 Bq/ml
¹³² I	1.0 E3 Bq/ml	6.3 E3 Bq/ml
¹³³ I	3.7 E4 Bq/ml	4.0 E4 Bq/ml
¹³⁴ I	3.4 E3 Bq/ml	7.8 E3 Bq/ml
¹³⁵ I	3.3 E3 Bq/ml	6.7 E4 Bq/ml
¹³¹ I/ ¹³³ I	0.064	1.59

sheath made of Zircaloy 4. In spite of this, the fission products are released to the fluid through small defects in cladding.

Diffusion through the intact zircaloy barrier, as a possible source of tritium, is negligible in a heavy water reactor.

The processes involved in the release of the fission products from the pellets to the coolant are extremely complicated. As a first step, radiation produces physical and chemical changes in the uranium dioxide structure. Chemical changes are related with oxygen pressure and composition and are increased with fuel burning. Volatile products can dissolve into the oxide matrix, generate bubbles or diffuse through the solid to the plenum. This is the typical behaviour of noble gases, Kr and Xe, and halogens. Heavy water penetrates into the fuel element through defects, promotes corrosion and hydriding and transports fission products back to the medium. Release rate would be proportional to the nuclide concentration within the fuel. At steady state this rate is equal to the elimination rate through the purification system plus the decay rate.

An actual leakage of the fuel sheath generates a release of nuclides that modifies steady state relations.

Examples of normal figures at Atucha 1 NPP are shown in Table III.

In pressure vessel reactors, the detection and identification of leaking fuels is easy, depending on their location within the geometric arrangement. Routine measurements of the primary coolant activity are performed and evaluated for the presence of leaks. In addition, a defective fuel location system is installed for this purpose. Two sets of sampling lines each one associated with a multiway valve allow to draw sequential water samples from pairs of coolant channels and measure the activity of the contained gaseous fission products. In the detection mode a long life radionuclide (¹³⁵Xe for instance) is continuously monitored. In the location mode a relative shortlived nuclide is determined (¹³⁷Xe or ⁸⁹Kr). The ratio between its decay period and transport time to multichannel detector is important for a proper identification. The time lag between sampling and measurement, and the multiway valve material behaviour have been the cause of some problems in Atucha 1.

Fuel rod integrity is determined by the chemical conditions of the coolant, the design and manufacture of the element and the operation of the reactor.

Table IV
Pressure vessel fuel rod design characteristics

	MZFR	A-1NPP	A-2NPP
Gross Electric Power (MWe)	57	367	750
Ner. Coolant Channels	121	253	451
Ner. Fuel Assemblies	242	253	451
Coolant Pressure (bar)	88	115	115
Coolant Inlet Temperature (°C)	252	262	278
Ner. Fuel Rods per Fuel Assembly	37	36	37
Active Length (mm)	1800	5300	5300
Fuel Rod Diameter (mm)	11.7	11.9	12.9
Clad Wall Thickness (mm)	0.4	0.55	0.57
Ner. Spacer Grids per Fuel Assembly	6	15	13
Ner. Tie Plates per Fuel Assembly	2	1	1
UO ₂ Weight per Fuel Assembly (kg)	63	173	214
Diameter of Coolant Channel (mm)	97.0	108.2	108.2
Max. Channel Power (MW)	3.0	7.0	7.2
Ave. Linear H. Generation Rate (W/cm)	117	232	232
Max. Linear H. Generation Rate (W/cm)	430	600	600
Fuel Rod Internal Pressure (bar)	1	18	pre-press.
Plenum Length (% Active Length)	-	4	4
Fuel Pellet Diameter (mm)	10.8	10.62	11.57
Diametrical Clearance (µm)	100	180	190
Fuel Density (g/cm ³)	10.55	10.55	10.55
²³⁵ U Content (weight %)	1	natural uranium	
Eq. Average Discharge Burnup (GWd/tU)	16	6	7.5

In comparison with light water reactors, pressure vessel reactors fuel rods design requirements present the following boundary conditions:

- relatively low burn-up
- relatively short insertion time
- high average linear heat generation rate
- power ramps during refuelling at full power

Design characteristics⁽³⁾ are summarized in Table IV. The maximum fuel temperature has to be below the uranium dioxide melting point of about 2800°C, even for the maximum values of linear heat generation rate.

Fission gas release is of little importance due to the low burn-up. The full-length rod design allows a plenum at the upper end to keep internal pressure below coolant pressure.

In the burn-up range, the allowable strain is limited by the pellet-cladding mechanical interaction that produces stress corrosion cracking (different from fission product assisted SCC, which is observed at higher burn-ups in light water reactors).

Water chemistry control limits corrosion and deuterium pick-up. Due to the short fuel residence time and the lower coolant temperature, the uniform oxide layer on the rod surface remains in a few microns range.

The vertical arrangement of the fuel bundles with refuelling from the top of the pressure vessel requires that the fuel assemblies must be radially supported inside the coolant channels to prevent damage due to flow induced vibration. The design has been modified from the early experimental MZFR concept.

Atucha 1 started into operation with a very low failure rate but it suffered an unexpected increase in the period 1978-80. Nearly all defective rods deteriorated quickly with white rings or in a more advanced stage, cracks at the axial positions of zircaloy washers due to a localized secondary hydriding mechanism leading to an early discharge of the suspected fuel elements and the development and test of designs without washers.

More recently some fuel failures have been associated with asymmetric power ramps during daily operation cycles.

3. MAN-REM REDUCTION CONSIDERATIONS

The ALARA criterion requires the minimization of the sources of radionuclides and their transport and deposition along the entire primary circuit.

3.1. Sources of radionuclides

Main radionuclides are fission products released from fuel elements, activated products from water and additives and activated corrosion products. These last, which are the major contributors to man-rem inventory, are generated by two mechanisms:

-In-situ activation of the structural materials of the core components and their following release to the media. Fuel assemblies and incore reactor internals are made of zircaloy and special steels. The radionuclide production by neutron activation depends on the concentration of the activable nuclides in the metal and the local neutron flux. The release rate depends on the area in contact with the coolant and the respective radionuclide content.

-Activation of corrosion products deposited on fuel surfaces and their subsequent release. Mass transport between the fuel element and the coolant is the result of two first order processes: deposition on the surface, the velocity of which depends on crud concentration, essentially colloidal particles; and release from the surface, the velocity of which depends on the deposited mass, considering the fraction of covered area to be far from unity.

There are experimental indications of a great mobility of the activated products. The released particles circulate through the circuit and deposit on surfaces where hydraulic, thermal and chemical conditions favour their reprecipitation. The few available data show that less than 10% activity is eliminated by purification and less than 1% when fuel elements are extracted. Most of the activated products remain on metal surfaces generating the radiation fields in the components.

The primary long-term contributor to radiation fields in PHWR is ⁶⁰Co formed by neutron capture of ⁵⁹Co.

For pressure vessel reactors operating under continuous refueling, activation of deposited crud and release of activated materials are both important; in certain cases, the latter may represent a sizable fraction of

Table V
Activation of corrosion products

Nuclear reaction	Source
$^{54}\text{Fe} (n, \gamma) ^{55}\text{Fe}$ $^{58}\text{Fe} (n, \gamma) ^{59}\text{Fe}$ $^{54}\text{Fe} (n, p) ^{54}\text{Mn}$ $^{56}\text{Fe} (n, p) ^{56}\text{Mn}$ $^{50}\text{Cr} (n, \gamma) ^{51}\text{Cr}$	Incolloy 800, austenitic steels
$^{62}\text{Ni} (n, \gamma) ^{63}\text{Ni}$ $^{64}\text{Ni} (n, \gamma) ^{65}\text{Ni}$ $^{58}\text{Ni} (n, p) ^{58}\text{Co}$ $^{59}\text{Co} (n, \gamma) ^{60}\text{Co}$	Incolloy 800, austenitic steels Stellite
$^{94}\text{Zr} (n, \gamma) ^{95}\text{Zr}$ β^- ^{95}Nb $^{96}\text{Zr} (n, \gamma) ^{97}\text{Zr}$ β^- ^{97}Nb	Zircaloy; fission products
$^{98}\text{Mo} (n, p) ^{99}\text{Mo}$ β^- $^{99\text{m}}\text{Tc}$	vessel mat.; fission products
$^{109}\text{Ag} (n, \gamma) ^{110\text{m}}\text{Ag}$	Silver seals
$^{121}\text{Sb} (n, \gamma) ^{122}\text{Sb}$ $^{123}\text{Sb} (n, \gamma) ^{124}\text{Sb}$	Antimony seals Antimony bearings

the total cobalt activity. In Atucha 1 NPP the in situ activation cobalt rich alloys⁽⁴⁾ in the neutron flux zone, is the principal source of ^{60}Co .

The relevance of each mechanism may be independently assessed. The nuclides ^{59}Fe and ^{54}Mn are both produced from natural iron isotopes, the first essentially by thermal neutron capture, and the latter by fast neutron activation. Consequently, the activity ratio $A(^{59}\text{Fe})/A(^{54}\text{Mn})$ should be larger if activation of structural materials is important, and lowest when only deposited crud can be activated. Experimentally, the ratio $A(^{59}\text{Fe})/A(^{54}\text{Mn})$ is around 1-3 in pressure tube PHWR, where in situ activation is negligible, 4-8 in the experimental pressure vessel MZFR and 5-10 in Atucha 1 NPP.

In future plants the absence of cobalt in the neutron flux zone (substitution of stellites, low residual cobalt of all incore parts), should be mandatory.

The adequate selection of materials is then the first factor affecting man-rem reduction. The more important activation products formed from the constituents of usual alloys are summarized in Table V.

The contribution of the nuclides other than ^{60}Co to radiation fields is less significant because of their particular characteristics: low generation rate in the case of ^{54}Mn and ^{59}Fe , weak gamma emission in the case of ^{51}Cr , short half-life period of ^{56}Mn and ^{65}Ni or gamma free decay of ^{55}Fe and ^{63}Ni .

Zirconium and molybdenum isotopes are originated both from structural materials activation and from fuel fission products release. The latter is the usual source of ^{95}Zr .

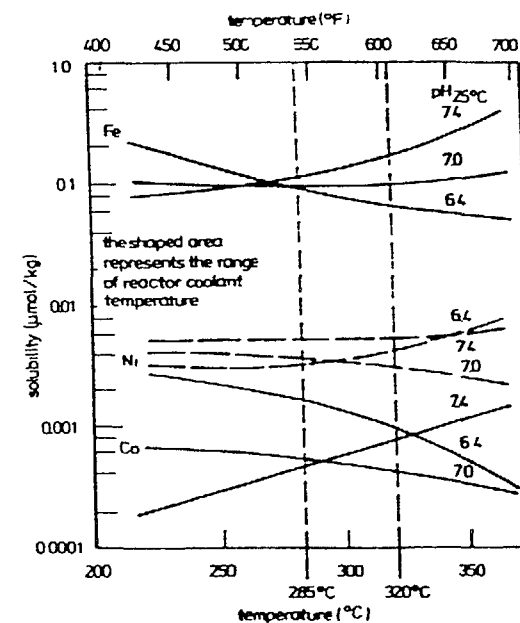
3.2 Transport of activated corrosion products

The activated corrosion products migrate throughout the coolant system in soluble, insoluble and colloidal forms. The incorporation of these activated species into the out of core surface oxide layers is responsible for the build up of radiation fields.

The chemistry of the medium, particularly the pH, exerts a large impact on the transport of the corrosion products: on ionic transport through solubility effects, on colloidal transport through changes in zeta potential and on particulate transport through the influence on particle size and composition.

Magnetite and nickel cobalt ferrites are the main corrosion products. Solubility data as a function of temperature⁽⁵⁾ are shown in Figure 3. The minimum solubility pH values at 300°C are 7.5 for nickel ferrite and 6.9 for magnetite.

The different operational pH and B/L1 concentration strategies can be used. These are shown in Figure 4.



(L1) 0.7 ppm	pH(25°C) 6.4
2.8 ppm	7.0
7.0 ppm	7.4
(B) 600 ppm	(H2) 25ml NPT/kgH ₂ O

Figure 3
Solubility data at the operation temperature range
Solubility of Fe, Ni and Co from Ni-Co-ferrites

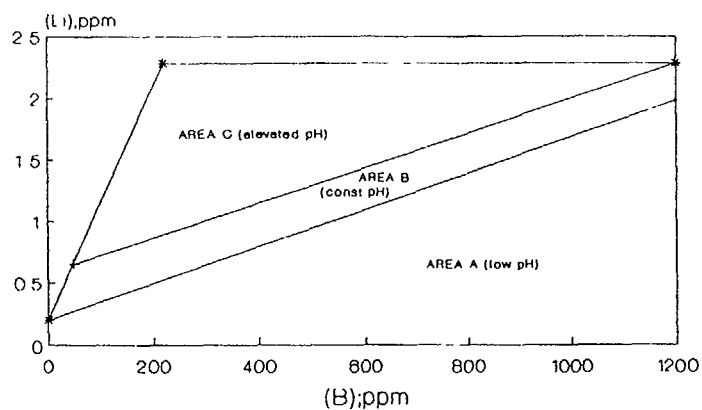


Figure 4
Lithium-boron: modes of operation

Current specifications for almost all PHWR's are similar, but chemical parameters can chose either to maintain high alkalinity at high temperature (Area A in Figure) or to keep high temperature constant pD coordinated boron-lithium treatment (Area B).

Atucha 1 operates close to the high almost constant pD range, in order to minimize base materials release and out of core dose rate build up by reducing the in core residence time of magnetite and corrosion products. However, this is not the major contribution to radiation fields (see above).

In Atucha 2 NPPP the constant pD mode will be adopted during normal operation, with slightly acidic condition during cold shutdown because of lithium removal.

Coordinated boron-lithium control aims to a high temperature pD of about 7 based on corrosion products solubility considerations.

Transport of radionuclides as particulate matter has been demonstrated in Atucha 1⁽²⁾. Magnetite and nickel ferrites seems to be the ⁶⁰Co carriers.

The adsorption of Co(II) on magnetite is highly dependent on pD and is almost complete in the neutral and alkaline range at all the concentrations likely to be found.

Radiochemical determinations in Atucha 1 NPP show that ⁵¹Cr is associated with smaller particles than ⁵⁹Fe and ⁶⁰Co; these latter nuclides are almost quantitatively retained by 0.1 μ m membrane filters.

Typical crud concentrations in Atucha 1 NPP are about 1-2 ug.kg⁻¹.

3.3. Operational procedures

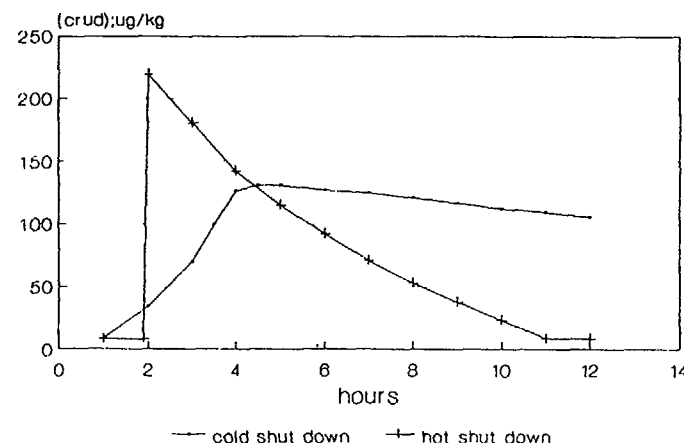
To keep chemical parameters within specifications and maximum purification flow rates to control fission and activated corrosion products are basic operational procedures aiming to man-rem reduction. Decontamination procedures are occasionally required.

The Physico-chemical Cyclic Method for operational decontamination of the primary circuit⁽²⁾ in a pressure vessel reactor takes advantage of crud bursts brought about by chemical and physical perturbations, especially shutdown and startups. Crud evolution during these transients are plotted in Figures 5 and 6.

The change from reductive (normal) to oxidative conditions by injection of oxygen (up to 50 ppb) also produces an increase of crud level, from ca. 6 up to 3500 ppb. Subsequent hydrazine addition produces an additional (smaller) crud burst.

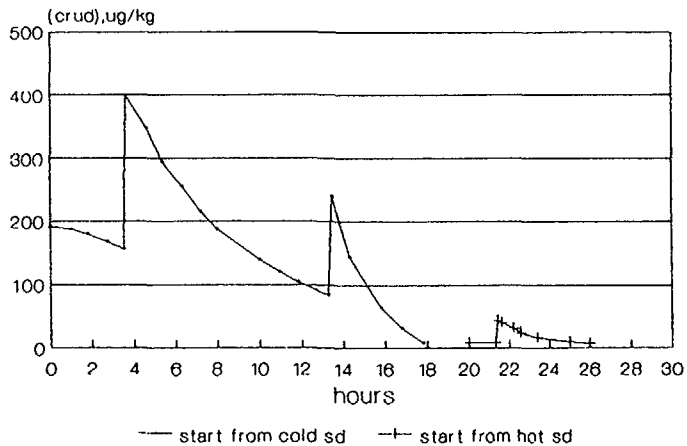
The effect of varying pD in the range from 6 to 10 is less significative; crud level increase by a factor 5-10.

Characterization of the crud release during transients demonstrates the existence of several groups of particles characterized by different size and composition. ⁶⁰Co is associated with larger (magnetite or nickel ferrite) particles, and ⁵¹Cr is related to smaller ones (NiCr₂O₄). Accordingly, the filtration efficiency is different, as accurately illustrated in Figures 7 and 8. Mechanical filters are adequate enough to remove radioactive crud bursts during PCC method application. PCC does not provide a means to achieve large DF's. It is recommended however as a simple operational procedure to reduce radiation fields in some crud traps that collect loose particles and impacts collective dose significantly because of their location.



SHUT-DOWNS

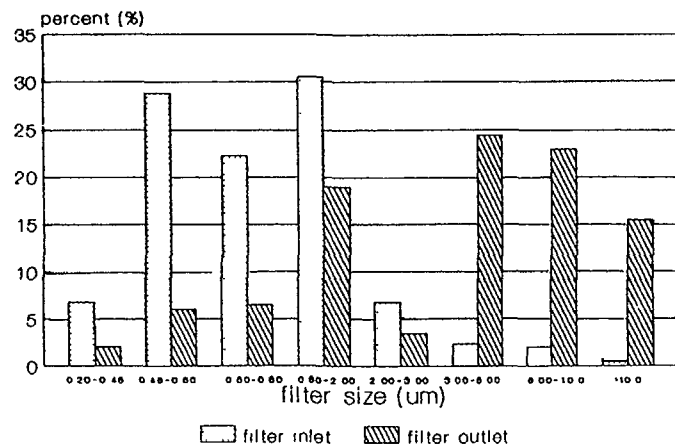
Figure 5
Evolution of crud concentration in A-1 NPP during shut-downs



START-UPS

Figure 6

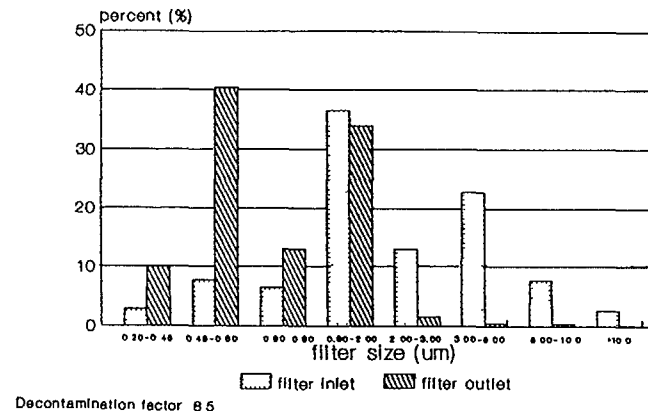
Evolution of crud concentration in A-1 NPP during start-ups



Decontamination factor: 13.9

Figure 7

⁶⁰Co filtration efficiency in A-1 NPP TC filters



Decontamination factor: 8.5

Figure 8

⁵¹Cr filtration efficiency in A-1 NPP TC filters

3.4. Tritium

Possible tritium sources in a heavy water reactor are:

- Diffusion of tritium produced from ternary fission in the fuel, through the fuel cladding.
- Neutron capture by ⁷Li.
- Neutron activation of deuterium from heavy water.

Literature gives a value of tritium within the fuel between 0.1 and 1% which diffuses through the zircaloy cladding and enters the coolant. Likewise, the additional leakage of tritium out of fuel rods having cladding defects is not significant in this type of reactors.

The principal source is the activation of deuterium from heavy water. The amount of tritium generated is essentially a function of the total generated energy. In Atucha 1 tritium concentration has evolved to a value of 14.7 Ci.kg⁻¹ in August 1988 with a rate about 1-2 Ci.kg⁻¹ full power year⁻¹ as shown in Figure 9.

The upper concentration at the end of 30 years in service is expected to be around 40 Ci.kg⁻¹.

Newer designs allow for the use of the heavy water upgrading system the column to detritiate the coolant. The management of highly active tritiated water residues poses several problems of difficult solutions.

4. SPECIFICATIONS

4.1. Considerations

The main objective of chemical control is to optimize water quality thus minimizing general metal release rate and the probability of selective corrosion occurrence, to avoid deposition of corrosion products on heat transfer surfaces, to limit chemistry related dose rate build-up and to suppress oxygen formation by radiolysis.

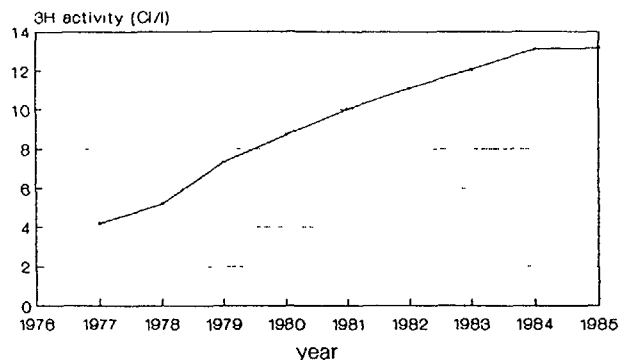


Figure 9

Evolution of tritium activity in Atucha 1 NPP

The basic premises to fulfill these requirements are alkalization through appropriate ⁷LiOD dosage, D₂ conditioning and specific operational procedures.

In pressure vessel PHWR, an effective mixing coolant-moderator takes place, so that reactivity and chemical control are strongly related to each other.

In the first stage of plant operation when a fully fresh nucleus is loaded, excess of reactivity is compensated usually with boric acid until burn up steady state is reached. After the first working year, Atucha 1 reactivity characteristics allow for free of boron normal operation and shut downs. On the other hand, in Atucha 2, boron dosification will be used to secure negative reactivity during cold shut downs along its whole useful life.

The presence of boric acid has to be considered in pD control, because of its tendency to suffer polycondensation reactions and the possibility of adsorption on crud.

Most recent trends favor strategies to keep a high constant pD in primary circuit. The increased solubility of corrosion products with increasing temperature, yields high solubility in the core and consequently low residence times of oxide particles on the surface of the fuel elements.

The additive commonly adopted for pD control is ⁷LiOD. Lithium-7 has a small neutron absorption cross-section, does not produce harmful activation products and is normally present in the media through the nuclear reaction ¹⁰B(n,α)⁷Li. In spite of this, neutron economy using ⁷Li isotope is sometimes not important and the formation of tritium through the reaction ⁶Li(n,α)³H, is negligible in heavy water reactors. The use of KOD as alkalizing agent is a possibility that has not been explored.

If lithium concentration drops below 0.2 mg/kg D₂O, an increase in metal release rate is expected, with greater deposition of corrosion products on fuel surfaces. If it is larger than 2 mg/kg, the probability of selective attack to zircaloy is increased.

Redox conditioning is achieved through deuterium injection. Concentrations within 2 and 4 mg/kg heavy water are recommended. Values below 0.5 mg/kg are insufficient to counteract radiolytic generation of molecular oxygen and values below 2 mg/kg has a negative influence in magnetite solubility since it depends on cubic root of hydrogen pressure. High concentrations, above 5 mg/kg result in embrittlement of the zircaloy cladding tubes.

As selective forms of corrosion in Incoloy 800 and austenitic steels are promoted by the simultaneous presence of oxygen and impurities of the type of chloride ion, special care must be taken with impurities control. In Atucha 1 part of the volume inventory control system operates at subatmospheric pressure, with the possibility of air in leakage. This perturbation is easily detected by ⁴¹Ar monitoring.

4.2. Chemical specifications

4.2.1. Steady-state

Chemical specifications are summarized in Table VI, with indication of limiting and recommended values.

Limiting values determine the permissible range of the given parameters for any plant operational mode. Deviations imply the possibility of material corrosion and its consequences. They must be controlled and counter-measures must be immediately carried up when deviations occurs. There is an estimated permissible time lapse, usually of some hours to a day from the moment of disfunction detection until limits are reached.

Deviation from recommended values do not necessarily mean damage to the materials, but they are indicative of an operational disturbance. Error source identification and correlative counter-measures should be immediately initiated.

Normal values obtained in routinary procedures in Atucha 1 NPP operation are included.

4.2.2. Start-up

The following chemical criteria must be fulfilled during start up from the operational state "sub critical cold":

- Control oxygen concentration below 0.1 mg/kg D₂O before coolant temperature reaches 170°C.
- Dose LiOD to 1-2 mg/kg.
- Add D₂ to about 2 mg/kg before reaching criticality.
- Manage boron removal according with physics requirements.

Atucha 1 operates without boron since after its first year work, whilst Atucha 2 will require boric acid dosage along its whole useful life. Boron removal is illustrated in Figure 10.

4.2.3. Shut-downs

The minimization of contamination and radiation exposure during maintenance in the components of primary circuit requires:

- Noble gas and iodine activity reduction.
- Deuterium concentration lowering.

The normal operational procedure included continuous purifying and degassing of primary media.

Table VI
Chemical specifications
High constant pD operational procedure (Atucha 1 NPP)

Primary System	
Limiting values	
(LiOD)	1-2 mg ⁷ Li/kg
(D ₂)	6 mg D ₂ /kg
(O ₂)	0.05 mg O ₂ /kg
(Cl ⁻)	0.2 mg Cl ⁻ /kg
Recommended values	
pD (25°C)	10.5-10.9
Conductivity (25°C)	30 uS/cm
(SiO ₂)	4 mg SiO ₂ /kg
Crud content	1 mg crud/kg
(B ₀₃ D ₃)	reactivity requirements
Operational values	
(LiOD)	1.1 mg ⁷ Li/kg
(D ₂)	1-2 mg D ₂ /kg
(O ₂)	5-20 ug O ₂ /kg
pD	10.7
Conductivity (25°C)	10-15 uS/cm
Crud content	6 ugcrud/kg
Congruent boron-lithium operational mode	
Recommended values	
(LiOD)	0.2-0.7 mg ⁷ Li/kg
(O ₂)	0.005 mg O ₂ /kg
(Cl ⁻)	0.2 mg Cl ⁻ /kg
(D ₂)	0.6-2.0 mg D ₂ /kg

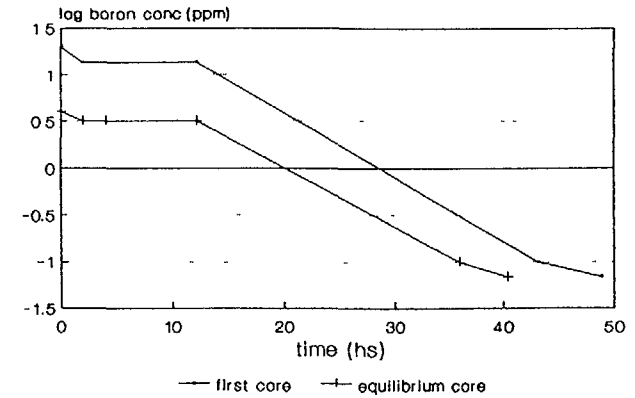


Figure 10
Boron concentration during start-ups

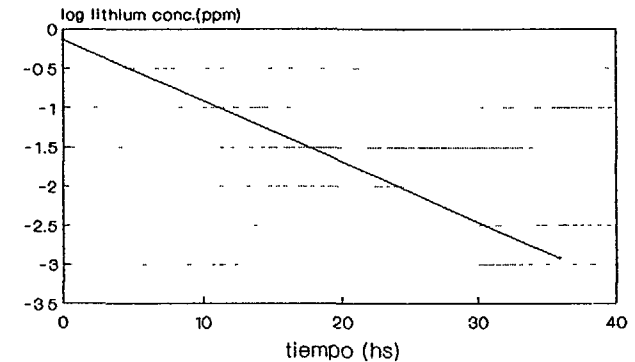


Figure 11
A-2 NPP: Lithium concentration decrease during shutdowns

In Atucha 2 the boron concentration at shut-downs will be about 5 ppm (equilibrium core) or more than 13.7 (first core).

Lithium, which is added to coolant and moderator during normal operation for alkaline conditioning is extracted during shut-downs to permit cesium removal. Decrease of lithium concentration is plotted in Figure 11.

4.3. Heavy water as process fluid

Heavy water is required as main heat transport fluid and as moderator when the fuel is natural uranium because of the advantageous smaller capture cross section of ²H as compared to ¹H.

Although there are many similarities between H₂O and D₂O, there are some chemical and physical differences. Some of them are compiled in Table VII.

Acidity is determined in heavy water solutions using glass electrodes previously calibrated with aqueous standards and is related to the corresponding light water value through the expression pD = d + pH, where d = 0.45 if concentrations are expressed in mol.kg⁻¹ and d = 0.41 if concentrations are expressed in mol.liter⁻¹.

Table VII
H₂O and D₂O physico chemical properties

Property	Unity	H ₂ O	D ₂ O
Molecular weight	12C scale	18.015	20.028
Fusion temperature	°C	0.00	3.813
Triple point temperature	°C	3.98	11.23
Boiling temperature	°C	100.00	101.431
Max density	g cm ⁻³	1.00000	1.10596
Density (25°C)	g cm ⁻³	0.99701	1.1044
Fusion entalpy (fus temp)	Kcal mol ⁻¹	1.436	1.515
Vapour pressure (25°C)	mm Hg	23.75	20.51
Dielectric constant(25°C)	Debyes	78.39	78.06
Viscosity (25°C)	cpoises	0.8903	1.107
Ionization constant (25°C)		1.10 ⁻¹⁴	1.95.10 ⁻¹⁵
Critical temperature	°C	374.2	371.5
Critical pressure	atm	218.53	218.6
Critical density	g cm ⁻³	0.325	0.363
Refractive index (20°C)		1.33300	1.32828
Vibrational frecuencies	cm ⁻¹	3657.05	2671.69
Vibrational frecuencies	cm ⁻¹	1594.59	1178.33
Vibrational frecuencies	cm ⁻¹	3755.79	2788.02

If heavy water standards are used, pD can be directly read in the meter without any correction. Table VIII summarizes the heavy water references recommended by the National Bureau of Standards.

The isotopes effect on the ionization of water is accurately known up to 300°C. The experimentally determined constants are shown in Table IX, together with the values of log (K(D₂O)/K(H₂O)).

Ionization constants⁽⁷⁾ of weak acids are also affected by solvation effects for practical purposes, a good correlation between log (K(HA)/K(DA)) and log K(HA) applies for certain monobasic acids, see Figure 12. The correlation RT log (K(HA)/K(DA)) vs RT log K(HA) seems to be temperature independent.

5 AUXILIARY SYSTEMS

5.1. Inventory and Pressure Control System

This system connects the hot and pressurized main heat transport system and the cold and depressurized auxiliary systems. Its functions are related with operation and security of the reactor, storage of the inventory of heavy water, filling of primary and auxiliary systems, compensation of volume variations due to density changes, particularly during start-ups and shut-downs and small leakages, and derivation of a fraction of coolant to the purification and degassing system.

Table VIII
pD Standards

t(°C)	KD ₂ Citrate (0.05M)	KD ₂ PO ₄ (0.025M) Na ₂ DPO ₄ (0.025M)	NaDCO ₃ (0.025M) Na ₂ CO ₃ (0.025M)
10	4.352	7.504	10.924
20	4.310	7.449	10.793
25	4.293	7.428	10.736
30	4.279	7.411	10.685
40	4.260	7.387	10.597
50	4.250	7.377	10.527
KD ₂ Citrate	0.05M	0.01151gKH ₂ Citrate / g D ₂ O	
KD ₂ PO ₄	0.025M	0.003402gKH ₂ PO ₄ / g D ₂ O	
Na ₂ HPO ₄	0.025M	0.003549gNa ₂ HPO ₄ / g D ₂ O	
NaHCO ₃	0.025M	0.002100gNaHCO ₃ / g D ₂ O	
Na ₂ CO ₃	0.025M	0.002650gNa ₂ CO ₃ / g D ₂ O	

Table IX

Thermodynamic Quantities for the Ionization of D₂O

t(°C)	log Q*	neutral pD	log (KD ₂ O/CH ₂ O)
0	-15.972	7.986	-1.031
25	-14.951	7.475	-0.958
50	-14.176	7.088	-0.904
75	-13.574	6.787	-0.865
100	-13.099	6.549	-0.835
125	-12.725	6.362	-0.811
150	-12.434	6.217	-0.792
175	-12.215	6.107	-0.774
200	-12.060	6.030	-0.758
225	-11.964	5.982	-0.742
250	-11.923	5.961	-0.727
275	-11.933	5.966	-0.709
300	-11.992	5.996	-0.69

* Q is referred to concentration rates

From the chemical point of view, pressure and temperature changes affect precipitation, dissolution and phase transformations equilibria of the transported species. These parameters vary from ca. 270°C and 112 bar in the extraction line to 50°C and 2-3 bars in the purification system. Some fission and activation products, principally iodine, noble gases and tritium, concentrate in the storage and volume regulation tanks.

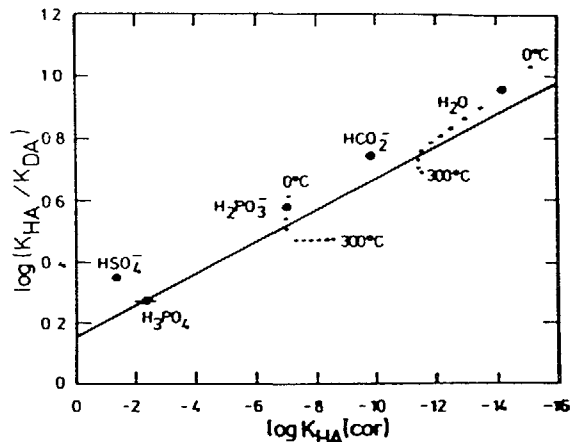


Figure 12

Correlation between acidic constants of deuterated and hydrogenated forms of monobasic acids

The colloidal and ionic impurities are removed when the primary fluid passes through the purification system. This system consists of several subsystems with mechanical filters and resin beds. During normal operation, corrosion and activation products are removed without altering LiOD concentration, using a mixed bed filter loaded with lithiated cationic resin and hydroxylated anionic resin.

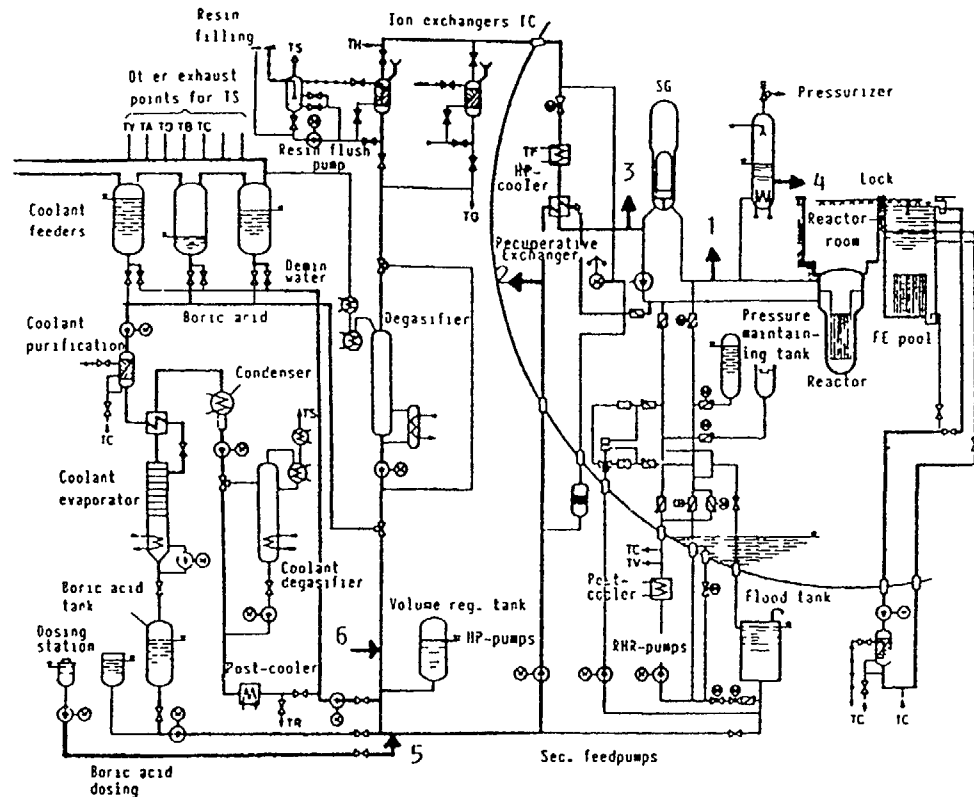
Atucha 2 will also operate a resin filter to remove cesium during start-ups and a filter to remove boron according to reactivity requirements. This anionic bed is to be regenerated for reuse. The other spent resins are disposed through the solid waste processing systems.

The coolant degassing system removes noble fission gases during continuous operation taking into account the permissible limits of activity release in the exhaust air. Before start-ups it removes dissolved nitrogen and oxygen; during shut-downs hydrogen and noble gases.

5.2. Sampling points. Sampling system

The nuclear sampling systems in pressure vessel reactors are designed for monitoring the quality of the reactor coolant and the associated systems. Furthermore, gases can be sampled from various circuits for chemical and radiochemical measurement.

The principal sampling points are located in each primary and moderator loop, volume control system and pressurizer. The various samples are fed to a common sampling line, adequately valved to prevent simultaneous sampling, that leads to a central sampling box. During plant operation, the system samples coolant from the injection and extraction lines upstream of the recuperative heat exchanger, as shown in Figure 13. Water is then returned into the extraction line upstream of the branch off to the coolant purification system.



- 1 - Boron monitoring Sampling point for Li, Cl; D₂, crud; pD; conductivity
- 2 - Oxygen monitoring Sampling point for returning water control
- 3 - Alternative sampling point
- 4 - Sampling point for B, Li, O₂, H₂
- 5 - Dosing point for Li, N₂H₄ and B
- 6 - Dosing point for H₂

Figure 13

Operational chemistry aspects

Some chemical values are monitored and registered continuously: e.g. nuclear poission and oxygen concentration. Gases can be discontinuously analyzed by gas chromatography. Special sampling devices are used for laboratory measurements and to filter corrosion products for analysis.

The samples of auxiliary systems are led to local sampling boxes, according to process requirements. Boxes are made in stainless steel and depressurized.

5.3. Analytical methods

On-line oxygen determination is performed with a polarographic device of the Oxyflux type.

Boron monitoring is not easy in the ppb range; plasma induced atomic emission spectrometry seems to be the most promising method. Spectrofluorimetric techniques with chromotropic acid and colorimetric techniques with azomethine H are also recommended down to 10 ppb.

Gases can be measured by gas chromatography, whether in the gaseous phase or dissolved in the liquid medium.

Heavy water downgrading is determined by ir spectrometry. General properties are measured by standard instrumental methods: conductivity, pD, gamma scan and turbidity.

In addition to visible uv spectrophotometry, AAS is recommended for cations analysis and ionic chromatography for anions.

Membrane filters in stainless steels support are used to collect colloidal and particulate corrosion products. The quantification can be made by gravimetry or disgregation and subsequent analysis, by AAS or uv-visible spectrophotometry.

5.4. Operational chemistry aspects

During normal operation, lithium concentration is continuously adjusted: if it exceeds the upper limit it is removed with an acidic cationic resin bed; if the concentration is too low, the adequate solution is dosed.

Water conditioning is completed with continuous H₂ or D₂ dosage. The dosage point is in the volume control system, on the suction side of the HP charging pump. A scheme of the operational chemistry aspects is seen in Figure 13.

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PRIMARY CIRCUIT CHEMISTRY OF PRESSURE TUBE PHWRs

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Abstract

Pressure tube PHWRs are natural uranium fuelling power stations. They use heavy water as primary heat transport fluid and as moderator, which comprise two separate loops with different temperature, pressure and chemical condition according with structural materials. Surfaces "in core" are made of zirconium alloys, steam generators and moderator exchangers tubes of Incolloy 800 and tube sheets plated with Inconel 600.

The main characteristic related with material selection stands in the use of carbon steel for "out of core" piping and some components of primary circuit and stainless steel for the moderator circuit. As a consequence, chemical specifications of the water in both systems differ each other.

Meanwhile pD value in primary cycle is adjusted to 10⁻³-10⁻⁸ through L10D dosage, moderator cycle operates at pD values within the neutral range.

Limiting values at normal operation are

	Main heat transport sy	Moderator
(L10D)	0.7-2 mg Li/kg	
(D ₂)	0.5-4 mg D ₂ /kg	
(O ₂)	< 0.10 mg O ₂ /kg	
(Cl ⁻)	< 0.20 mg Cl/kg	< 0.20 mg Cl/kg

Moderator chemical control is easier to perform and is related with reactor reactivity requirements, heavy water radiolysis prevention and gaseous products production.

An adequate material selection minimizes active corrosion products generation. Operational procedures such as fuel management and water purification contribute to man rem reduction.

1 SPECIFICATIONS

1.1 Considerations

Corrosion of the structural materials, radioactive crud production and fission product release, are reduced by careful selection and control of the chemistry of the medium. Because the moderator in pressure tube PHWRs is separated from the primary coolant, the chemistries of the two systems, related with the respective materials and conditions, are independently controlled. The characteristics of each system are shown in Table I which summarizes design data of a 600 MWe station. Figure 1 shows the corresponding flowsheet.

This arrangement avoids the addition of reactivity poisons, such as boric acid, to the heat transport medium and permits the use of carbon steel for primary circuit piping, valve bodies, pump bowls, feeders and

Table I

Design data of 600 MWe Embalse (Cordoba)NPP

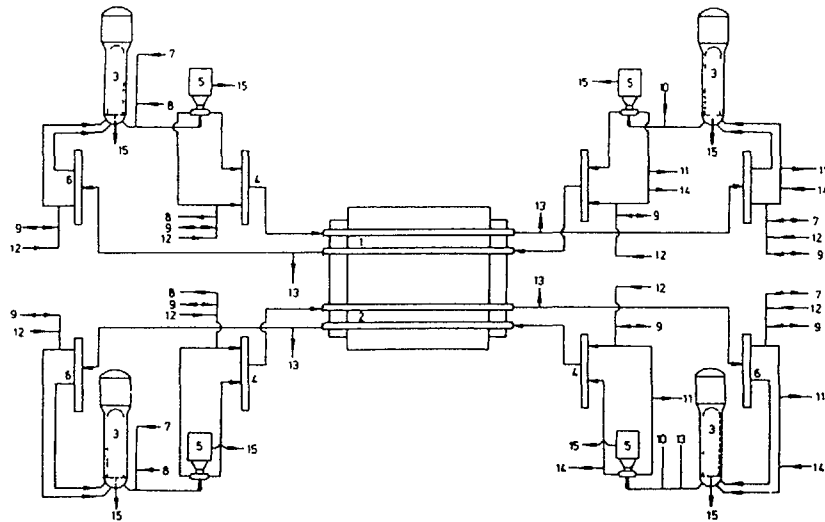
Component		Material	
Calandria		x5CrNi189	
Calandria tubing		Zircaloy-4	
Pressure tubing		Zr-2.5Nb	
Fuel rod cladding		Zircaloy-4	
End fittings		SS-403	
Moderator vessel		ASTM 106	
Mod heat exchanger tubes		Incolloy 800	
Mod heat exchanger tube sheet		Carbon steel/Inconel 600	
Steam generator tubing		ASME A 669	
Steam generator tube sheet		Inconel 600	
Operational parameters			
		Coolant	Moderator
Flow rate		30,900 T/h	1,033 T/h
Number of loops		2	1
Pressure		10.1 MPa	0.165 MPa
Temperature	inlet	266°C	58°C
	medium	290°C	
	outlet	312°C	
D ₂ O purity		95%	99.75%

headers, i.e., the bulk of the system outside the core excluding heat transfer surfaces.

The pD value in primary cycle is adjusted to minimized corrosion through the addition of lithium deuterioxide of natural isotopic composition. The small volume of PHTS fluid under neutron flux does not make mandatory the use of the isotope ⁷Li for neutron economy.

In the fuel channels boiling can occur up to 4%, a likely concern is therefore the possibility that concentration of the salt on the fuel sheaths may lead to rapid corrosion of the zirconium alloy, consequently it is important to maintain lithium content within the limits.

A correct management of O₂ content can drastically reduce the aqueous attack of carbon steel⁽¹⁾ in high temperature water, as seen in Figure 2. A small amount of oxygen in the medium decreases the iron release rate and this effect changes to acceleration if 10 ppm are exceeded. The inhibiting phenomena is associated with a gradual change in the film grown on the surface of the alloy, formed mainly by black magnetite. At relatively high oxygen, it transforms to non protecting hematite and the corrosion rate becomes very high. In spite of this, concentration of oxygen is limited to an extremely low level to avoid localized corrosion if the chloride ion, mainly from resin bed disfunction or degradation, is present. Attack to mild steel and solubility of magnetite⁽²⁾ at 300°C are strongly related, as seen in Figure 3. Pressurization of the entire primary circuit prevents accidental oxygen entrance in pressure tube PHWRs.



- | | |
|---------------------------------|-----------------------------|
| 1 -Loop 1 | 8 -Purification System |
| 2 -Loop 2 | 9 -Shutdown Cooling System |
| 3 -Steam generators | 10 -Hydrogen Addition Sys |
| 4 -Inlet headers | 11 -Sampling |
| 5 -Pumps | 12 -Emergency Cooling Sys |
| 6 -Outlet headers | 13 -Delayed neutron monitor |
| 7 -Press and Invent Control Sys | 14 -Fission product monitor |
| | 15 -D2O Collection tank |

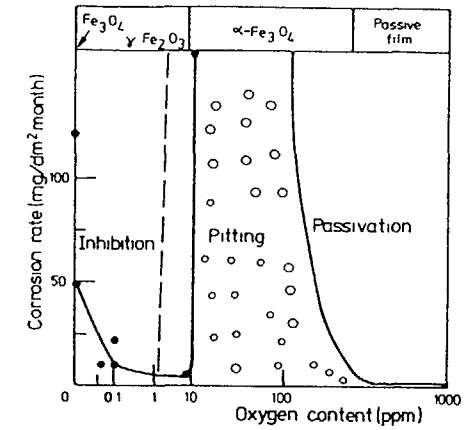
Figure 1
Pressure tube NPP flow sheet

Chemical control is completed with active corrosion products and fission products control. An adequate material selection minimizes both productions. Ionic species are removed by mixed bed resin filters. Recent designs eliminate cobalt containing alloys which are the source of ⁶⁰Co, hard gamma emitter.

Carbon steels does not contain chromium and nickel, the major alloying elements of austenitic stainless which give rise to the radioactive ⁵¹Cr and ⁵⁸Co, then reducing radionuclides generated through activation of crud deposits on fuel surfaces.

Moderator chemical control is easier to perform. Stainless steel as circuit material and mild temperature conditions determine low corrosion rates, and high fluid quality is achieved with minimum purification flow rate.

Chemical conditioning in this case is needed to - control reactor reactivity through the use of soluble neutron poisons (boron and gadolinium)



Time 1 month
Temp 240-315°C

Figure 2

Effect of oxygen concentration in the water on the corrosion rate of mild steel

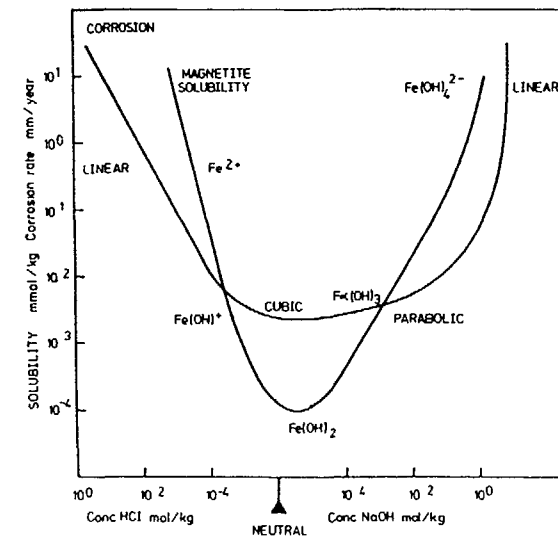


Figure 3

Corrosion of mild steel and solubility of magnetite at 300°C

prevent heavy water radiolysis and control their products concentration in the cover gas, specially the formation of flammable gaseous mixtures minimize the corrosion of the components and hence the contamination of the circuit by radioactive crud

Boron is used for long term reactivity control. Its concentration decreases from 4 mg/kg to about 0.1 mg/kg D₂O during the first year operation and is added as a solution of boric oxide in heavy water.

Gadolinium is used as a substitute for ¹³⁵Xe during reactor startups and as the poison to be injected by the second shut down system. It is handled as a solution of gadolinium nitrate in heavy water.

Oxygen and deuterium gases are the main products of moderator water radiolysis, they are transferred to the cover gas, through their respective solubility equilibria. Deuterium peroxide is another important product which remains quite stable in the liquid phase and can be responsible of resins degradation.

Factors that affect water radiolysis and must be controlled are reactor power, ionic and non-ionic impurities concentration and dissolved gases, particularly O₂ and N₂.

To control the corrosion of the moderator system it is needed to reduce aggressiveness of the neutral oxygenated heavy water to the structural materials, namely zircaloy and stainless steel. The control parameters are:

- impurity level, particularly chloride and fluoride ions
- nitrogen in the cover gas, that forms nitric acid under irradiation (expectedly not in dangerous amounts)
- dissolved oxygen and deuterium, that can increase corrosion on stainless steel and hydriding on zircaloy, respectively

1.2 Steady state operation specifications

The limits of the chemical parameters during normal operation, based on the previously discussed concepts, are summarized in Table II, together with the desirable values for the best available conditioning.

Normal crud concentration around 5 ug/kg D₂O

Maximum purification flow rate and the addition of lithium deuterioxide or hydrogen are the usual procedures to maintain parameters within the recommended range.

1.3 Start ups

After a short outage, less than a few days, no special controls are needed for start up. After a prolonged shut down, for example, a scheduled maintenance period, some requirements must be fulfilled:

The repaired equipment should be properly inspected, tested, conditioned, cleaned and flushed, in agreement with the state of the art.

All systems should be fully operative.

The special shut down chemical controls have to be turned off, drained or vented, as it corresponds.

Thermohydraulic perturbances during operative transients disturb suspended and deposited oxides promoting intense crud bursts. This phenomenon happens specially during start up and shutdown. A high primary purification flowrate, generally about 70 kg/sec in 600 MWe pressure tube PHWRs, is recommended to control crud concentration.

Table II
Chemical specifications

	Main Heat Transport Sy.	Moderator
Limiting values		
(LiOD)	0.7-2 mg Li/kg	
(D ₂)	0.5-4 mg D ₂ /kg	
(O ₂)	0.10 mg O ₂ /kg	
(Cl ⁻)	0.20 mg Cl/kg	0.20 mg Cl/kg
Recommended values		
pD (25°C)	10.3-10.8	
Conductivity (25°C) (BO ₃ D ₃) (GaNO ₃)	20-60 uS/cm	5 uS/cm 10 mg B/kg 10 mg Ga/kg
Operational values*		
(LiOD)	1 mg Li/kg	
(D ₂)	0.5-1.5 mg D ₂ /kg	
(O ₂)	70 mg O ₂ /kg	
pD	10.3	
Conductivity (25°C)	25-30 uS/cm	
Crud content	5 ug/kg	

* Embalse N P P

Moderator water must be conditioned after a long shutdown to eliminate soluble poisons. The removal of boron, when it is the only additive used to achieve safe shutdown condition, is made through the corresponding ion exchange columns working in series, filled with mixed bed resin with an excess of anionic type. When boron and gadolinium were used together for reactivity control, the removal is completed with two additional cationic resin beds.

In every case, reactivity requirements determine purification flow rates.

1.4 Shutdowns

Proper chemical control of primary system during shutdowns is required to:

- minimize components corrosion, particularly localized attack.
- decrease the generation, release and transport of radioactive crud
- lower fission product level

In a general way the heat transport system can be considered as composed of two separated subsystems, the main HT and the shutdown cooling system.

As stated in the previous paragraph large quantities of radioactive crud are released and transported through the circuit during cooldown and warmup and following pressure changes.

Removal of crud by using the maximum purification flow rate (35 or 70 kg/sec) is an effective mean of controlling the transport of radioactive material around the circuit.

Significant quantities of fission products are also released through defective fuel sheats following shutdown depressurization. The use of the purification system reduces radiation fields buildup.

Chemical specifications for PHTS are applied to the shut down cooling system. Oxygen level during maintenance outages is 50 ug/kg. Higher values, up to 500 ug/kg, can be accepted for a maximum of one day.

During a short shutdown, hydrogen addition may be made and control achieved as during normal operation.

The maximum purification flow rate available is 70 kg/sec, using both filters and both ion exchange columns, when the main heat transport pumps are operating, and half this value if the shut down cooling system pumps are operating, using only one filter and one exchange resin column.

High purification flow rate should be maintained until ^{60}Co activity is less than 10^{-2} Sv/kg or for a definite time, usually 8 hours, whichever is longer.

During short shutdowns, moderator chemical control is the same as for normal operation. Special care must be taken to prevent deuterium excursions.

2. AUXILIARY SYSTEMS

2.1. Pressure and Inventory Control System

Pressure and Inventory Control System plays several important functions:

- pressurize and limit coolant pressure increases due to transients.
- compensate volume variations related to power changes.
- supply heavy water at appropriate pressure and temperature to main coolant pumps seals.
- provide enough relief capability for eventual over pressurizations of the coolant system.
- degassify heat transport system

This system consists of a pressurizer, a condenser-degasifier, a heat exchanger, two feeder pumps, and valves. Even though it is possible to release continuously the gaseous fission products through the expansion tank, this operation is performed discontinually. Primary system degasification is usually carried out before a shut down to decrease exposure of the personnel. The whole circuit, including pressure and inventory control system components acts as a gaseous radionuclides decay tank, minimizing the emission to the atmosphere during normal operation.

2.2. Sampling points. Sampling system

A correct control of the chemical condition of primary and moderator systems begins with a sampling procedure which ensures that the sample is representative of the stream and that no foreign matter contaminates it.

The parameters to be measured include isotopic purity of heavy water, dissolved gases and solids concentrations, colloidal matter and chemical

Table III

Sampling points and related sampling procedures

System	Grab	On-line	Hyp.syr.	Cartridge	Filter
Moderator system		+	+	+	
Mod. purification sys.		+	+		
Deut. and dedeuteration		+	+		
D ₂ O collection			+		
Cover gas		+			
Soluble poison			+		
MHTS		+	+	+	+
Main pumps seals cooling			+		+
MHTS purification			+		+
MHTS D ₂ O collection			+		+
Degassifier		+			
Shield cooling sys.	+				
Spent fuel bay				+	
Liquid shut down sys.			+		
Liquid zone control	+				
D ₂ O vapour rec.			+		
D ₂ O cleaning		+	+		

impurities, as well as physicochemical properties, pH and conductivity. Radioactive impurities are quite important from the point of view of process control and radiological protection.

Basically there are three types of sampling procedures: "grab-samples", from light water ancillary systems; sealed samples, from heavy water systems and "on-line" samples.

Grab samples are taken into clean plastic or glass containers, after draining in order to flush the line and remove stagnant water.

Sampling of heavy water is done via rubber diaphragms or cartridges. Samples of that kind are carefully transferred to the laboratory.

The last procedure consists in a line where process media flows through a continuous analyzer.

A membrane filter device is used to determine crud level. It is able to operate on line even at high pressure.

Table III summarizes sampling points and techniques used in a typical 600 MWe station.

2.3. Analytical methods

General properties are measured by standard instrumental methods: conductivity; pH; gamma scan and turbidity. Crud level is determined through filtration and gravimetry, sometimes the latter is replaced by membrane disgregation and spectrometry or A.A.S. analysis.

Inorganic elementary analysis is performed by A.A.S., specially in the case of cations lithium, sodium, magnesium, iron, copper and other metals. Ionic chromatography is specially recommended for anionic species: nitrate, carbonate, silicate, chloride and fluoride.

The most common method for organic compounds determinations is visible-uv spectrometry.

Special assemblies measure dissolved gases on line, like oxygen and hydrogen. They are generally based on separation by diffusion and electrical potential measurements. Gas chromatography can be used to determine gases in liquids or gases.

2.4. Operational chemistry aspects

An important operational aspect in PHWR is radionuclide determination. Each 600 MWe pressure-tube reactor is supplied with a gaseous fission product (GFP) monitor and a delayed neutron (DN) monitor. The GFP monitor is a gross radioactivity measurement system that can detect the presence of defective fuel in the core by monitoring the bulk coolant activity in each of the two reactors loops. Two sample lines, one for each half of the primary heat transport system, are leaded to a gamma spectrometer to measure ^{131}I , ^{133}Xe , ^{135}Xe , ^{88}Kr and total gamma. The activity levels are transmitted to the station control computers and can be displayed on operator demand.

The DN monitor is used to identify the channel containing the defective fuel. The monitor sensitivity permits to detect defects that expose only 200 to 500 mm² of UO₂ surface inside the sheat without the need for power cycling, (which enhances the sensitivity), and the operation at low reactor power during the scan. A carriage which holds the detectors scans the sample holders, one for each fuel channel, for delayed neutrons emitted by ^{131}I and ^{87}Br that are released into the coolant. When used during the re-fuelling, the system can identify the defective bundle. The prompt extraction of defective bundles can be made without affecting normal operation.

Four autoclaves are installed in both hot and cold branches of each coolant loop in most of pressure-tube nuclear stations, to house specimens of the structural materials.

Accurate examinations of the specimens are used to evaluate the efficiency of the primary circuit preconditioning, to monitor the corrosion of base materials during operation, shutdown, start-up and decontamination processes, to investigate the corrosion resistance of alternate materials under the same in service conditions and to assess the effect of anomalous events.

Several techniques, scanning electron microscopy and EDAX (Energy Dispersive Analysis of X-ray), are used for probe inspection, after the adequate decontamination procedure.

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SPECIATION IN AQUEOUS BORIC-BORATE SOLUTIONS AT HIGH TEMPERATURE

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Abstract

Speciation in aqueous solutions containing boric acid and lithium hydroxide has been studied using all the available information in the literature on the ionic equilibria in this system.

The temperature dependence of the equilibrium constant was used to estimate the pH of the solutions at temperatures relevant to the PWR chemistry.

Ionic association and polyborate formation have been considered in the calculation. The incomplete dissociation of lithium hydroxide has a small effect on the results, while lithium borate association and polyborate formation are only significant at high boron concentration.

Comparison with other calculations and experimental data show that the thermodynamic data and the procedure used in this work are very reliable to assess speciation in light and heavy water over a wide range of temperature and concentration.

The effect of pressure on the results has not been analyzed since it is not expected to be important under PWR coolant chemistry conditions.

1. FOREWORD

The chemistry of the primary loops in nuclear power stations is controlled by the addition of boric acid and lithium hydroxide.

Both substances take part in a number of ionic equilibria in aqueous solutions, so the calculation of the concentration of a given species (*i.e.* pH) is not trivial. On the other hand, the equilibrium constants related to these processes change with temperature and, in some cases, they are not directly known but they must be estimated from experimental information on similar systems.

In this work we have calculated the concentration of the species in the system $B(OH)_3$ - $LiOH$ - H_2O at concentrations and temperatures similar to those present in the primary loop. From this information it is possible to obtain basic properties of the system such as pH and electrical conductivity.

2. PREVIOUS RESULTS

Some results have been reported for this system concerning with pH estimation. McDonald *et al.* [1] have calculated activity coefficients and pH of solutions containing $B(OH)_3$

and $LiOH$ between 25° and 275°C in order to compare them with experimental values obtained with palladium hydride electrodes. The author [2] found good agreement between calculated and experimental pH and redox potential up to 200°C.

Later, McDonald [3] used ceramic electrodes (yttria-zirconia) for measuring pH in aqueous systems at high temperature and he concluded that these electrodes have a Nernstian behaviour over the entire range of temperature. The deviations with respect to calculated potential values do not exceed 0.1-0.15 pH units at temperatures above 200°C.

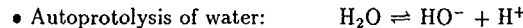
These measurements can be considered as a qualitative experimental validation of the pH calculation because it was difficult to estimate errors due to liquid junction potential.

More recently, Thornton and Polly [4] have performed pH calculation for this system under conditions of a PWR primary loop, in relation with the study of solubility of corrosion products. These authors also reported experimental results by Chaudon *et al* [5] at 250° and 300°C.

McDonald assumed in his calculation that boron polymeric species $(B_n(OH)_{3n+1}^-)$ with $n > 1$ do not contribute to the pH. Thornton and Polly, on the other hand, assumed that $LiOH$ is completely dissociated in aqueous solutions.

3. SPECIATION IN THE PRIMARY MEDIA

In this work all the ionic equilibria in solution are taken into account:



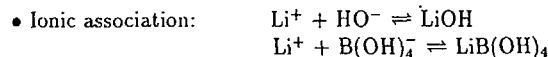
$$Q_w = [HO^-][H^+] \quad (1)$$



$$Q_{11} = \frac{[B(OH)_4^-]}{[B(OH)_3][HO^-]} \quad (2)$$

$$Q_{21} = \frac{[B_2(OH)_7^-]}{[B(OH)_3]^2[HO^-]} \quad (3)$$

$$Q_{31} = \frac{[B_3(OH)_{10}^-]}{[B(OH)_3]^3[HO^-]} \quad (4)$$



$$Q_{LiOH} = \frac{[LiOH]}{[Li^+][HO^-]} \quad (5)$$

$$Q_{LiB} = \frac{[LiB(OH)_4]}{[Li^+][B(OH)_4^-]} \quad (6)$$

We can add the mass and charge balance equations

$$[Li^+] + [H^+] = [HO^-] + [B_1^-] + [B_2^-] + [B_3^-] \quad (7)$$

$$[Li]_{total} = [Li^+] + [LiOH] + [LiB_1] \quad (8)$$

$$[B]_{total} = [BH] + [B_1^-] + 2[B_2^-] + 3[B_3^-] + [LiB_1] \quad (9)$$

where we have simplified the notation for the boron species

We have finally a set of nine equations with nine unknown concentrations, corresponding to the species H^+ , HO^- , Li^+ , B_1^- , B_2^- , B_3^- , BH , $LiOH$ and LiB_1

The set of equations can be linearized by taking logarithm in the concentration quotients, Q_i . The set is then solved by an iterative Newton Raphson procedure with a program developed for any multicomponent equilibria system which is able to run in IBM compatible PC. Generally, convergence is reached before 15 iterations

3.1 Equilibrium constants and their temperature dependence

The equilibrium constant of autoprotolysis of water has been measured by Sweeton *et al* [6]

Marshall and Franck [7] have formulated an equation which describes pK_w over a wide range of pressure and temperature. In this work we have used the results of reference 6 because they came from direct measurements in the range of temperature we are interested for the PWR chemistry

The concentration quotient, Q_w , is expressed as a function of the temperature and ionic strength, by the equation

$$\log Q_w = \log K_w + \log \frac{\gamma_+ \gamma_-}{a_w} \quad (10)$$

where

$$\log K_w = \frac{31286.0}{T} + 94.9734 \ln T - 0.0097611T - \frac{2170870.0}{T^2} - 606.522 \quad (11)$$

and

$$\log \frac{\gamma_+ \gamma_-}{a_w} = \frac{2AI^{1/2}}{1 + (5.28289 - 0.00700806T)AI^{1/2}} - 0.0860725I - 0.000779432IT - 0.0947686I^{3/2} + 0.000522999I^{3/2}T \quad (12)$$

where I is the ionic strength, T is in Kelvin, and

$$A = -2.97627 + 0.0480688T - 2.6980 \cdot 10^{-4}T^2 + 7.49524 \cdot 10^{-7}T^3 - 1.02352 \cdot 10^{-9}T^4 + 5.58004 \cdot 10^{-13}T^5 \quad (13)$$

$$A' = 0.4125A^{1/3} \quad (14)$$

The formation constant of borate, diborate and triborate have been determined by Mesmer *et al* [8]. The following equations give their temperature dependence

$$\log Q_{11} = \frac{1573.21}{T} + 28.8397 + 0.0011748T - 13.2258 \log T \quad (15)$$

$$\log Q_{21} = \frac{2576.1}{T} - 18.966 + 5.835 \log T \quad (16)$$

$$\log Q_{31} = \frac{3339.5}{T} - 8.084 + 1.497 \log T \quad (17)$$

The association constant of Li^+ with HO^- and $B(OH)_4^-$ have been analyzed elsewhere [9], and the temperature dependence have been fitted with the equations

$$Q_{LiOH} = 6120.376 - \frac{169084.6}{T} - 1067.556 \ln T + 1.784478T \quad (18)$$

$$Q_{LiB} = -862.0372 - \frac{37623.67}{T} + 136.9755 \ln T - 0.1272792T \quad (19)$$

The values of these constants as a function of temperature are shown in Figure 1. A small effect of the lithium borate association is expected at the concentrations involved in the primary loop.

Our estimations of the $LiOH$ association are based on the conductivity measurements of aqueous solutions of this electrolyte at low [10] and high [11] temperature.

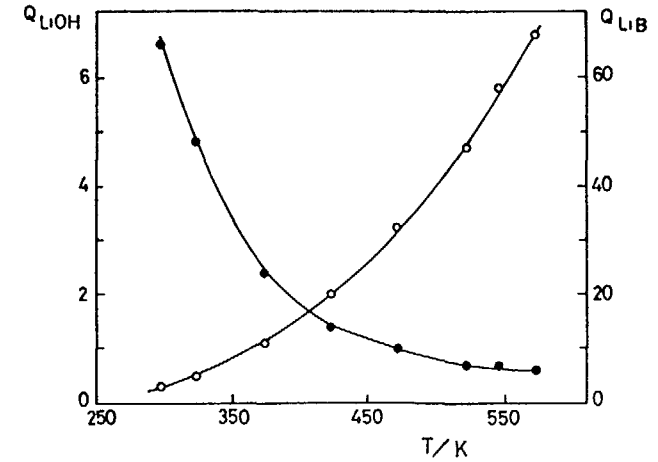


Figure 1 Concentration quotients for ion association as a function of temperature (●) $LiOH$ (○) $LiB(OH)_4$

TABLE I pH AT 250°C AS A FUNCTION OF BORON AND LITHIUM CONCENTRATIONS

boron (ppm)	lithium (ppm)	This work	Cal (Ref 4)	Exp (Ref 5)
0	1.5	7.49	7.53	7.5
100	2.0	7.31	7.38	
250	1.5	6.94	7.02	6.9
250	5.0	7.44	7.52	7.5
500	1.5	6.69	6.77	6.6
1000	0.0	5.04	5.08	5.0
1000	0.4	5.84	5.92	
1000	1.0	6.23	6.31	6.1
1000	3.0	6.69	6.77	6.7

4 RESULTS

4.1 Speciation in H₂O

As an example, we show in Table I some results obtained for the system B(OH)₃-LiOH-H₂O at 250°C for boron and lithium concentrations relevant to the operation of nuclear power stations

It is worthy to note that

$$\begin{aligned} 1m \text{ B} &= 10800 \text{ ppm B} \\ 1m \text{ Li} &= 7000 \text{ ppm Li} \end{aligned}$$

In Table I we also reported the pH values calculated by Thornton and Polley [4]. It is clear that the LiOH association does not modify the concentration of the species in solution with respect to the calculation assuming complete dissociation. The agreement with the experimental data [5] is very satisfactory.

4.2 Speciation in D₂O

Our knowledge of the equilibria constants in D₂O is scarce. However, K_w for D₂O is known [12] and $\Delta pK = pK_{D_2O} - pK_{H_2O}$ have been studied for several acids.

It was concluded that for boric acid $\Delta pK = 0.63$ [13]. Moreover, we know that ΔpK for acids is independent of temperature [12]. Thus, Q₁₁ in D₂O was calculated using the relation

$$\log Q_d^{D_2O} = \log Q_d^{H_2O} - 0.630 \quad (20)$$

where

$$Q_d = Q_{11} Q_w \quad (21)$$

TABLE II pH AT VARIOUS TEMPERATURES AS A FUNCTION OF BORON AND LITHIUM CONCENTRATIONS

B(ppm)	Li(ppm)	pH 25°C	pH 250°C	pH 300°C	pD 25°C	pD 250°C	pD 300°C
0	0	7.02	5.60	5.65	7.54	5.96	6.00
5	0	6.21	5.58	5.64	6.53	5.94	5.98
10	0	6.06	5.57	5.63	6.38	5.92	5.97
20	0	5.91	5.56	5.62	6.23	5.88	5.89
50	0	5.71	5.51	5.59	6.03	5.80	5.88
100	0	5.56	5.44	5.54	5.88	5.71	5.81
0	0.5	9.83	7.03	7.13	10.79	7.76	7.83
5	0.5	8.32	7.01	7.12	8.96	7.71	7.80
10	0.5	7.99	6.99	7.11	8.63	7.67	7.77
20	0.5	7.68	6.95	7.08	8.31	7.60	7.72
50	0.5	7.27	6.85	7.01	7.90	7.44	7.60
100	0.5	6.96	6.72	6.92	7.60	7.26	7.45
0	1.0	10.12	7.32	7.43	11.08	8.05	8.12
5	1.0	8.69	7.30	7.41	9.34	8.01	8.09
10	1.0	8.32	7.28	7.40	8.96	7.97	8.06
20	1.0	7.99	7.24	7.37	8.62	7.90	8.02
50	1.0	7.57	7.14	7.31	8.20	7.74	7.90
100	1.0	7.26	7.02	7.21	7.90	7.55	7.75
0	1.5	10.29	7.49	7.59	11.25	8.22	8.29
5	1.5	8.96	7.47	7.58	9.60	8.17	8.26
10	1.5	8.53	7.45	7.57	9.17	8.14	8.23
20	1.5	8.18	7.41	7.54	8.81	8.09	8.19
50	1.5	7.75	7.31	7.48	8.38	7.91	8.07
100	1.5	7.43	7.19	7.38	8.07	7.72	7.92
0	2.0	10.41	7.61	7.71	11.37	8.34	8.41
5	2.0	9.20	7.59	7.70	9.87	8.30	8.38
10	2.0	8.70	7.57	7.69	9.34	8.26	8.35
20	2.0	8.32	7.53	7.66	8.95	8.19	8.31
50	2.0	7.87	7.44	7.60	8.51	8.03	8.19
100	2.0	7.56	7.31	7.50	8.19	7.85	8.04

and

$$\Delta Q_w = pQ_w^{D_2O} - pQ_w^{H_2O} = 0.958 \quad (22)$$

The results obtained in D₂O are summarized in Table II. It can be observed that the change of pH or pD with boron concentration is quite small at high temperature due to the low dissociation constant of the boric acid.

Figures 2 and 3 show the change in pH and pD with the concentration of B(OH)₃ and LiOH at 25°C.

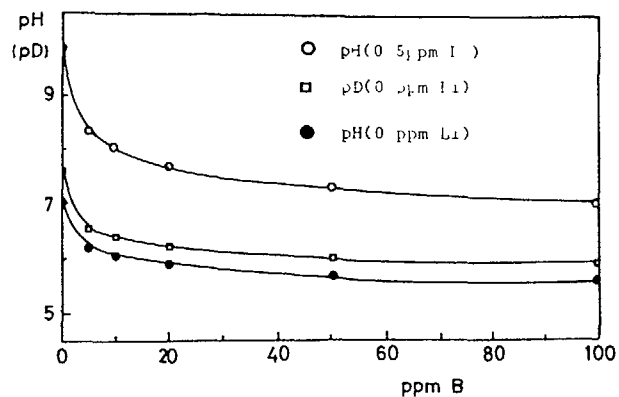


Figure 2 pH (pD) for LiOH B(OH)_3 solutions at 25°C as a function of the boron concentration

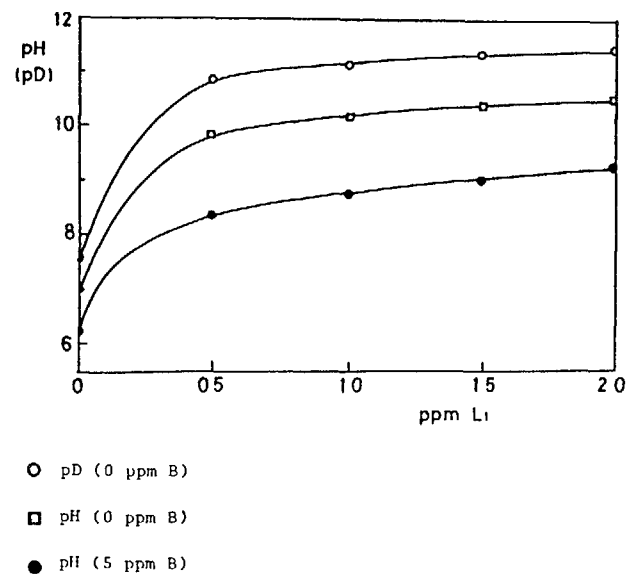


Figure 3 pH (pD) for LiOH B(OH)_3 solutions at 25°C as a function of the lithium concentration

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WATER CHEMISTRY OF NPS CORROSION PRODUCT CHARACTERISTICS

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Abstract

In this report on VVER 1000 primary circuit chemistry in Bulgaria recommendations on usage of VVER 1000 specifications are given. It is advised to operate the reactor on the pH value adjusted on KOH concentration.

The primary coolant filtration system is briefly described. Analysis of corrosion product sampled in the secondary circuit are given.

In Bulgaria now are operated two types NPS with PWR VVER-440 (440 MWe) and VVER-1000 (1000 MWe). This units are imported from Soviet Union. The design are after Novovoroneg NNP's prototype.

The coolant temperature is from 289 °C to 322 °C for VVER-1000 and from 268 °C to 301 °C for VVER-440 . The pressure in VVER-1000 is 16 MPa and in VVER-440 is 12.5 MPa.

The materials in reactor circuits for VVER-1000 and VVER-440 are:

- | | |
|---------------------------|---------------------------------|
| a) Reactor vessel: | perlite C-steel , 48 TC |
| b) Vessel cladding: | CrNiTi.18.12. (stainless steel) |
| c) Circuit pipes: | CrNiTi.18.10. (stainless steel) |
| d) Steam generators tubes | CrNiTi.18.9. (stainless steel) |
| e) Fuel element cladding | ZrNb1 (H-1) (zircaloy, 1% Nb) |

The specification of the impurities and additives in reactor coolant of VVER-1000 and VVER-440 units are compared in a separated table given in the part "Coolant chemistry specifications"

The first Bulgarian units VVER-440 started in September 1974 and now in Bulgaria operated 4 units VVER-440.

We have carried out large study on water chemistry problems of these units (1,2). The attention is shaped to the change of quality characteristics of steam generator blow down water in secondary circuit coolant by transient operation conditions. We have observed the Hide-out and Hide-out return effects in SG water and in reactor coolant in VVER-440.

The Hide-out phenomena shows that at normal good quality of water in secondary and primary circuits determined by steady-state conditions is not enough guaranty for an optimal chemical environment of the materials used in SG and reactor circuits.

The first operation period of VVER-1000 unit (from December 1987 to May 1989) shows that the specific quality of reactor coolant are in limited values (under steady state condition at 500 MWe , 700 MWe and 980 MWe).

The second operation period of 1000 MW unit began at 15 November 1989 and the investigation continue during the 1990 .

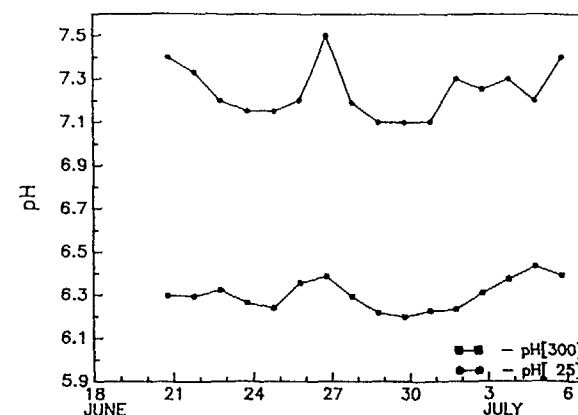


Figure 1

By these studies we have found that during the second operating period the concentration of KOH , NH₃ , H₃BO₃ and H₂ are in the specification limits.

It is worth to be noted that in spite of this , during the definite periods of operating , the calculated values of pH₃₀₀ are lower than the permitted level - Fig.1 . That is why , it is recommended the operating control of pH to be based on the data of pH₃₀₀ . Consequently , we recommended the dosage of KOH to be on the data of pH₃₀₀ .

The VVER-1000 has 2 different bypass purification systems (BPS):

BPS N 1 consist of 4 mechanical filters with special support material - porous titan . Filter's volume is 1.45 m³ . The volume of filter material/per filter unit is 0.7 m³ .

The volume flow rate of every filter is about 80 m³/h and the total volume flow rate of the BPS N 1 is about 400 m³/h.

In BPS N 1 the coolant water is treated without reduction of the coolant water temperature (the working temperature is about 290 °C) . The pressure in the filter is 16.0 MPa.

The obtained data for the efficiency of these mechanical filters show some variations. The removed part of suspended solids is from 40-60% .

BPS N 2 is with ion-exchange units for control of the K and Cl concentrations in coolant water.

By the filtration of water coolant through ion-exchange filters the suspended solids and the activity of coolant water are reduced. At steady state condition the concentration of corrosion products in reactor coolant is below 0.1 mg/l and the activity evaluated the basis of iodine isotopes are lower as the specified value.

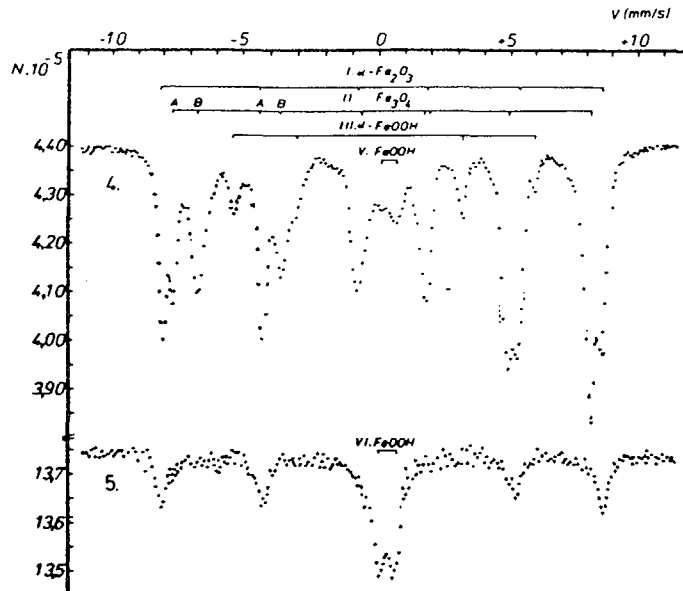


Figure 2

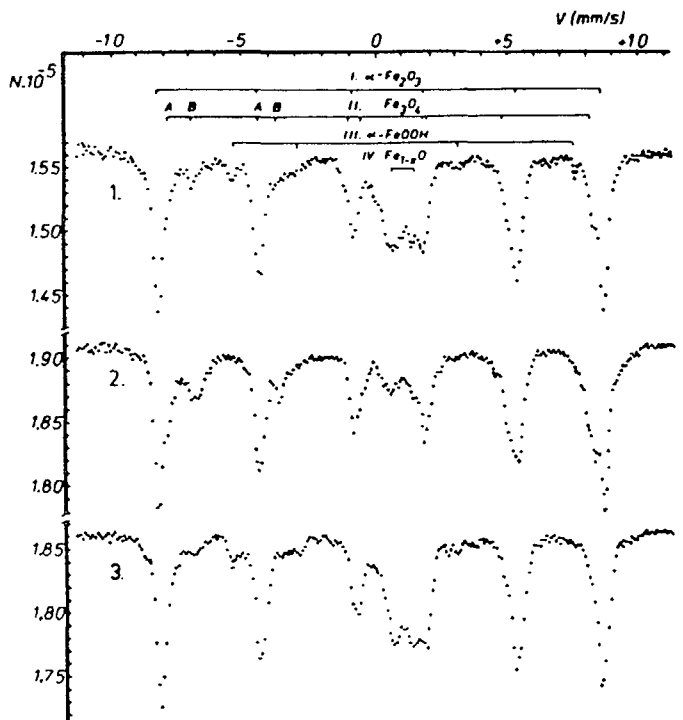


Figure 3

In this research program the characteristics of corrosion products in secondary circuits by Moessbauer spectroscopy are investigated. Object of this study are corrosion products from HP-tubes :

- corrosion products from steam side - Fig. 2
- corrosion products from water side - Fig. 3

The components of water side corrosion products are :

δ - Fe_3O_4 58% , δ - $FeOOH$, Fe_3O_4 12% , $Fe_{1-x}O$.

The component of steam side corrosion products are :

α - $Fe_{3-x}O_4$ 47% , α - Fe_2O_3 30%

In the corrosion products of steam side we have found an absence of $Fe_{1-x}O$ and a new component, namely γ - $FeOOH$. With this investigation we have tried to obtain more information about morphology of corrosion products and to use this information as an indication of local corrosion - environmental conditions.

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A NEW POINT OF VIEW ON THE DRASTIC CHANGE IN COOLANT ACTIVITY BY POWER TRANSIENTS IN PWRs

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Abstract

In this report is described a new mechanism explaining the increase of corrosion product release during power transient.

It is an established fact that coolant transients which occur under specific operating conditions in PWR (power change shutdown or trip situation), are accompanied by significant (order of magnitude) change of concentration of activation products (Fig. 1) (1).

Normally initiating factors for this phenomena are variations of thermal, hydrodynamical conditions in the systems. (In any cases, like the change of boric acid concentration, the role of chemical effects, is very important).

According to the recently developed main hypothesis, because of the solubility consideration, these transients are accompanied by change of concentration of activation product species in the coolant.

The thermal gradient is highest at the fuel surface, hence the crude and soluble products release will favor in-core deposits and these may be of higher specific activity than under steady operational conditions.

As a significant ground of the idea that the solubility of corrosion products in coolant was a very important factor in PWR-transport phenomena, is the founding that the solubility of Fe_3O_4 or nickel ferrite is strongly dependent on the temperature and pH of coolant.

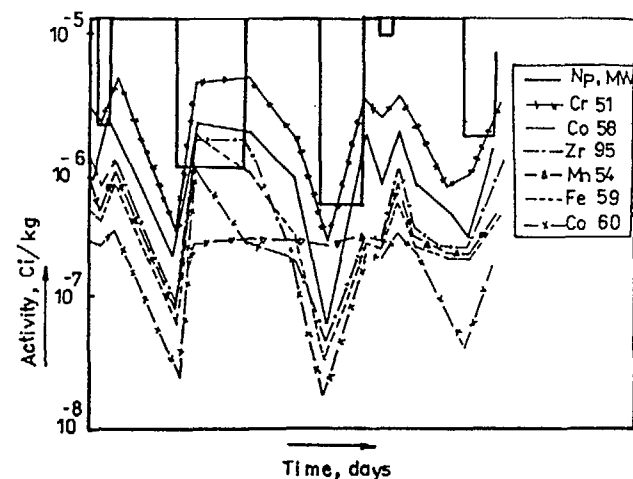


FIG. 1.

For example the experience in French PWR's shows that excessive crude build-up in the core can usually be avoided by a well adopted carefully operated coolant chemistry : Optimisation of the lithium (pH) hydrogen treatment combines the objectives of reducing the sources of radiation fields and crude build-up.

These requirements, after Beslu (2) can be ensured (since crude deposition in the core and its activation) by maintaining the pH in the desired range to maintain a positive temperature coefficient of solubility for nickel ferrite in the core.

Independence of practical confirmation of the hypothesis that the solubility of corrosion products on coolant conditions is the main factor determining the mechanism of transport phenomena in the core, and influences the activity build-up in the primary circuit herein we try to explain the transport phenomena during the power change in PWR with another mechanism of location of soluble and colloidal species in the core.

After our interpretation the drastically change of coolant activity during the power change of PWR is an excellent example of Hideout - Return effects, like Hideout effects in steam generators (3,4).

In our opinion (4) Hideout effect is connected with specific phenomenon existing in non-equilibrium systems, described in irreversible thermodynamic. In particular case, Hideout effect is connected with self - organization phenomena (formation of dissipative structures) in non-equilibrium systems.

According to our hypothesis the main part of charged colloidal products in PWR coolant is dynamically located near to the core heat transfer surfaces. The formation of these dynamic layer from suspension of charged colloidal products near to the heat transfer surfaces is effected from great heat flux and (electrical) electrophoretical forces. Normally between that layer and metallic surface a hydrodynamic boundary layer is located.

By our opinion the soluble charged species (ions) are located mainly as ions layers around the charged colloidal particles (corrosion products).

Also not solid deposition on the heat transfer surfaces of fuel elements, but this dynamic layer of corrosion products suspension, located near to the heat transfer surface determine the length residence time of corrosion products in core, necessary for its activations. Also the soluble species (ions) are not be due to formation of solid phase (of insoluble products) located at the fuel cladding surface for ensuring sufficient residence time in core. (Alternative of this is the location of ions around of charged colloidal particles, formed the dynamic layer).

The change of steady operational conditions, accompanied with change of thermal (heat flux) and hydrodynamical conditions in core has as consequent the destroying of dynamic layer and dispersion of its colloidal particles in bulk coolant. We observe the drastic increase of activity, resp. of the concentration of colloidal and soluble corrosion products in coolant stream - Hideout - Return effect.

By restoration of steady operational conditions we observe the Hideout of activity from coolant bulk. By this conditions the dynamic layer near to the fuel surface is again restored.

With correspondence of this mechanism is the observations at WSGHWR (5) suggest that activity levels on out of core pipe work are not largely affected by "crude bursts" during cooling.

According to the Hideout and Hideout - Return mechanism, based at the formation of dynamic layer from colloidal particles suspension near to the heat transfer surface of fuel elements is possible to explain the relatively quick release the activity in the bulk coolant.

The very important influence are pH (OH ions concentration) in water chemistry of primary circuit (6,7), and especially the positive results of Hydrazine - hydrate water chemistry (1) in primary circuits of PWR (WWER 440) are possible to be interpreted, as factors influencing the charge of colloidal particles in the coolant and as initiating factors for change of the conditions influencing the formation and characteristics of dynamic layer of charged colloidal particles near to the core heat transfer surfaces.

Namely the dynamic layer from suspension of corrosion products plays important role for the colloidal particle transport through the hydrodynamic boundary layer towards the wall of fuel elements cladding, ensuring the necessary high gradient of particles concentration (bulk concentration is very low to "feed" this transport process). The charge characteristic parameters of wall surfaces and colloidal particles in dynamic layer are important factors for formation of cladding depositions.

The over explained hypothesis create the possibility for new argumentation of the rational water chemistry for primary circuit in PWR, with respect of knowledge in the field of self - organization in non-equilibrium systems (8) and at the ground of properties of colloidal corrosion products in PWR's (9, 10, 11, 12).

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RESEARCH WORK ON COOLANT TECHNOLOGY IN CHINA

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Abstract

In the Peoples Republic of China, research is being carried out in order to provide water chemistry data for design, construction and operation of small and medium size NPS in China. Nuclear Program in China have some national features, the projects to study the water chemistry aspects reflects the requirements of China's NPS engineering and design. The structural materials made in China such as fuel cladding materials, steam generator heat transfer tubes and ion exchange resins are not the same as those made in other countries we have learnt from other countries and we have actively adopted their successful experiences in all aspects, besides, we have carried out a series of experiments on water chemistry problems concerning design and operation of NPS in China. The preparation of nuclear grade resins, control of boron and lithium in dynamic water loop, determination of impurities (O₂, Cl, F and other metallic species) in primary circuit and monitoring on line the thermal breakdown of resins in high temperature, high pressure water loop, study of decontamination processes and study on Zircalloy and steam generator heat transfer tubes corrosion are some of the studies being carried out in the field of water chemistry. The project 'Investigation on water chemistry of primary circuit for PWR unit' is essentially a fundamental study on water chemistry which are related to the three tasks of "WACOLIN"

The Description of our Research Work

As all known, although there is on-going nuclear power programme in our country, but our nuclear power stations are yet under construction and design, so that the aim of our research is to conduct the preliminary fundamental experiments and offers water chemistry data for design, construction and operation of small and medium size NPS in China

Because the structural materials made in China, such as fuel cladding materials, steam generator heat transfer tubes, ion exchange resins etc, are not all the same to those made in other country, and also because design and construction of NPS in China have some national feature, therefore our projects of water chemistry are necessarily biased towards China's nowadays state and are based on necessities of China's NPS engineering design. Probably, these research works will arouse the interest of other countries

Our SWCR has set up the business with many countries and nuclear organizations all over the world, we have learnt from other countries and have adopted actively their successful experiences in all aspects, besides these, we have carried out a series of experiments on water chemistry problems concerning design, construction and operation of NPS in China, for example, the preparation of domestic nuclear-grade resins, controlling concentrations of boron and lithium in dynamic water loop, determination of impurities (O₂, B, Cl, F, metallic species etc) in primary circuit and monitoring in line (or on line), thermal breakdown of resins in high temperature high pressure water loop, study of decontamination processes, study of corrosion of zircalloy and heat transfer tubes of steam generator etc

Work done

1 Purification of Water and Control of Water Quality

1 1 Controlling Concentrations of Boron and Lithium in Dynamic Water Corrosion Loop

This paper describes various methods for control of the boron concentration and the lithium concentration in the high temperature and high-pressure dynamic water corrosion loop. The boron concentration is controlled using the temperature effect of the borate-form resin. A hydrogen-form cation exchanger is installed to remove the excessive lithium in water, by means of feed and bleed operations, both boron concentration and lithium concentration are diluted with boron-free and lithium free pure water. The results show that borate form resin prepared from the strong base anion resin made in our country is capable of boron concentration regulation with temperature variation, as a major means of regulating boron concentration, it is simple and easy. The use of the hydrogen-form of ion exchanger is able to reduce the lithium concentration rapidly and efficiently in water. Feed and bleed procedure is a necessary supplementary method during the loop operation.

1 2 Ion Exchange Statical Equilibrium of Borate-Form Resin

This paper describes ion exchange statical equilibrium of strong anion resin in boric acid system, and confirms the formula of Fletcher for calculating boron content in resin. The calculation method has been proposed for the determination of components of resin under various equilibrium conditions. Ion exchange constants of Kc_1 and Kc_3 are determined and the influence of various factors on these constants are also observed.

Results of experiments show that experimental data of boron content in resin is coincident with calculated values, boron exchange constant of domestic anion resin is more lower than that of foreign resins, and the conversion rate and temperature also exhibit significant influence on exchange constants.

This work was performed in the years 1970, a further study is being conducted for modification.

1 3 The Preparation of Nuclear Grade Ion Exchange Resins

This paper describes novel conversion processes and related technical conditions for preparation of nuclear grade resin from Chinese domestic commercial resin. Low residual chloride nuclear grade anion and cation resin have been prepared with these novel conversion processes. Results of tests show that these nuclear grade resins exhibiting good performances, can be satisfactorily used in water treatment for nuclear power stations.

1 4 A Study on residual Chloride Release from Anion Exchange Resin under Operating Conditions of Primary Circuit

This paper describes the behaviour of residual chloride released from anion exchange resin under normal and transient operating conditions of primary circuit PWR. Results of experiments show that release of chloride from resin is significantly increased, during the start up of the reactor, therefore the nuclear grade anion resin with low residual chloride should be the most satisfactory water treatment agent for NPS.

2 Study of Chemical Decontamination Methods

2 1 Study of Chemical Decontamination Methods and Effects of Decontamination Condition on Corrosion Behaviour of Structural Materials

Some experiences gained in decontamination under the laboratory conditions and actual operation are useful to reduce man rem exposures for both personnel and public safety. The high concentration AP Solution applied as preoxidizing reagent in POD process is used successfully. Monitoring of the concentration and temperature of cleaning solutions, and also the cleaning time might reduce undesirable corrosion of base metal, higher level of radioactive accumulation on the surface of the material would occur if intergranular corrosion happens.

2 2 Decontamination with NP and AP based POD Processes for PWR Materials

Experiments consisting of three parts have been performed. Available formulation of NP (nitric acid permanganate) and AP (alkaline permanganate), as preoxidizing conditions for PWR decontamination have been selected on a number of prefilmed specimens (18-8 ss and alloy No. 13). The behavior of chromium release from the prefilmed specimens (18-8 ss and alloy No. 13 and Incoloy 800) in various formulations of NP and AP solutions have been observed. Decontamination tests performed on the radioactive 18-8 ss specimens using NP and AP based processes are described.

3 Analytical Techniques for Monitoring Water Chemistry

Study of various analytical methods for determination of impurities in water coolant and in resin has been performed in our division. These methods are used to confirm that the water chemistry of coolant and prepared resins are either within or outside specified ranges, and also to give quantitative data for research work of water chemistry in our division.

Work in Future

1 Ion Exchange Resin Thermal Breakdown Experiment in PWR's Primary Circuit Conditions

1 1 Thermal Breakdown Experiments in Static Autoclave Containing the Resin

1 2 Adding the Resin into High Temperature and High Pressure Water Loop

1 3 Determination of Major Thermal Degradation Products

2 Water Chemistry Control in High-Temperature and High Pressure Water Loop

3 Heat Regeneration of Boron in Resin

4 Determination of Chloride and Fluoride in Water Coolant with Ion Chromatographic Method

5 Development of Neutron Absorption Boron Concentration Meter. This Meter may Monitor Two Samples which are Situated at Different Places Simultaneously

6 Electrochemical Experiments of the Decontamination Processes

7 Study of NP-LOMI Decontamination Process

PREPARATION OF NUCLEAR GRADE ION EXCHANGE RESINS

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Abstract

This paper describes novel conversion processes and related technical conditions for preparation of nuclear grade resin from Chinese domestic commercial resin. Low residual chloride nuclear grade anion and cation resin have been prepared with these novel conversion processes. Results of tests show that these nuclear grade resins having good performances can be satisfactorily used in water treatment for nuclear power stations.

1 Introduction

The nuclear grade ion exchange resins have been applied in water treatment for light water reactors in China. These ion exchange resins are different from those which are being used in conventional water treatment plant. It requires less impurity, high conversion rate, high uniformity of particle size and good mechanical strength etc.

According to the requirements of water quality for nuclear power plant, nuclear grade cation resins of H⁺-form and Li⁺-form, and nuclear grade anion resins of OH⁻-form containing different contents of residual chloride have been prepared by processes described in this paper.

This paper emphatically describes the novel conversion processes and the related laboratory experiments for preparing nuclear grade ion exchange resins from commercial resins made in China. Based on the characteristics of these commercial resins, using novel methods of preparation accomplished in this work, the purity is increased and the broken percent is reduced for cation resin, the content of residual chloride is reduced for anion resin, and also good performances for both cation resin and anion resin are demonstrated.

2 The Preparation of Nuclear Grade Cation Exchange Resin

Nuclear grade cation resin (H form and Li form) are still the most frequently used types of ionic exchangers in water treatment for NPS. The experiments for preparation of these resins from Chinese domestic resin are as follows.

2.1 The Preparation of Nuclear Grade H Form Resin

Nuclear grade H-form cation resin are prepared by two steps: pretreatment and conversion with acid. The original cation resin used is the commercial cation exchange resin 001 x 7 (Na-form).

* Author of section on cation resin

** Author of section on anion resin

2.1.1 Comparative Tests for Pretreatment Methods

General procedures are described as follows: the commercial cation resin are to be sieved and immersed in 10% sodium chloride solution for a short period of time, then filled in ion exchange column, with acid and alkali solution cleaning in turn. The purpose of alkali cleaning is to remove organic impurities from the resins, while the acid can remove high-valent heavy metal ions. In order to prepare chloride free nuclear grade cation resin, it is necessary to prevent breaking of commercial resin during preparation later on, for this reason the comparative experiments of three pretreatment methods have been conducted.

Method 1 Na-form resin should first be treated with 1N NaOH, followed by 2N HCl⁽²⁾
Method 2 Na-form resin should first be treated with 2N HCl, followed by 1N NaOH
Method 3 Na-form resin should be treated with improved pretreatment procedure⁽³⁾

The results of comparative experiments are listed in table 1.

Table 1 The effect of pretreatment method on the content of metal impurities in resin and broken percentage

Pretreatment method	Content of iron impurities mg/L	Extractable impurities mg/L	Broken percentage %
Method 1	< 5	74	1 ~ 2
Method 2	< 5	46	> 50
Method 3	1.9	/	1

Table 1 shows that method 1 and method 3 are more available, because of less broken percentage. However, results⁽³⁾ of tests indicate that for preparing conventional nuclear grade cation resin method 1 is preferred and for preparing chloride free nuclear grade cation resin method 3 is preferred.

2.1.2 The Effect of Acid Amount on the Iron Content in Resin

It has already been pointed out by Fan Junfu⁽¹⁾ that using 2N HCl is better than using 1N HCl for removing iron from the resin. In order to find available amount of 2N HCl, tests were carried out and the results are listed in Table 2.

Table 2 The effect of HCl amount on iron content in resin

Resin sample	Amount of 2N HCl (resin Bed volume)	Equivalent ratio HCl to resin	Iron content in resin mg/L
1//	3	3.9:1	< 5
2//	4	5.2:1	< 5
3//	5	6.5:1	< 5

The results show that using three resin bed volume of 2N HCl, iron content in resin has been reduced to less than 5 mg per liter of resin.

2 1 3 The Effect of Acid Amount and Conversion Reagent on Conversion Rate of Resin

The results of experiments are listed in table 3 and table 4

Table 3 The effect of acid amount on conversion rate

Resin sample	Amount of 1N HCl (resin Bed volume)	Equivalent ratio HNO ₃ to resin	Strong acid capacity meq/gwet	Conversion rate* %
1//	4	2 6 1	2 0	98
2//	6	3 9 1	2 0	99
3//	8	5 2 1	2 0	99
4//	10	6 5 1	2 0	99

* Expressed in equivalent percentage of H-form resin

Table 4 The effect of conversion reagent on conversion rate of resin

Resin sample	Conversion reagent	Acid amount (resin Bed volume)	Strong acid capacity meq/gwet	Conversion rate %	Broken percentage %
1//	1N HNO ₃	6	2 0	99	1
2//	1N H ₂ SO ₄	6	2 0	99	1
3//	1N HCl	6	2 0	99	1

Experiments show that the following conversion conditions are suitable 1N H₂SO₄ (or 1N HNO₃) and 6 resin Bed volume The conversion rate of H-form can be up to 99 %

2 1 4 The Main Characteristic Parameters of Nuclear Grade H-Form Resin (4)

Using the conversion conditions mentioned above, two batches of nuclear grade H-form resin has been prepared The results of measurements and examinations are listed in table 5

The characteristic parameters listed in table 5 show that the main characteristic properties of these ion exchangers prepared with the process in this paper have met the requirements of nuclear grade resin specifications From these experimental results it can be seen that the processes accomplished in this paper combines the advantages of higher conversion rate, less impurity in resin and less broken percentage of resin

Table 5 Properties of nuclear grade H form cation exchange resin

Properties		General nuclear grade	Chloride free nuclear grade
Specific Bed volume	ml/g	1 3	1 3
Moisture content	%	60	60
Strong acid capacity	meq/gwet	2 0	2 0
	meq/gdry	5 0	5 0
Conversion rate	%	99	99
Metallic impurities mg/L	Na	61	58
	Fe	2 2	1 9
	Cu	0 7	0 5
	Pb	0 6	0 5
Extractable Impurities	mg/L	74	/
Chloride content	mg/L	< 90	< 20
Broken percentage	%	1 ~ 2	1
Particle size	mesh	20 - 40	20 - 40

2 2 The Preparation of Nuclear Grade ⁷Li-Form Resin

The preparation of Nuclear grade ⁷Li-form cation resin has been performed, converting directly from nuclear grade H-form cation resin into ⁷Li-form using ⁷LiOH solution, in which ⁷Li abundance is 99 98 %. Tests indicate that conversion rate can be up to 99 % It is easy to recover expensive reagent of ⁷LiOH In general, the consumption rate of ⁷Li is less than 0 6 %

3 Preparation of Nuclear Grade Anion Exchange Resin

Commercial anion exchange resin used in this research is quaternary ammonium Type I strong base anion exchange resin 201 x 7 Some important parameters of this resin are shown in Table 6

Table 6 Parameters of 201 x 7 anion exchange resin

Type	Initial form	Exchange capacity	Water Retention %	Particle size mm	Active group
Strong base 201 x 7	Cl ⁻	> 3 0	40 - 50	0 3 - 1 2	-N(CH ₃) ₃

The Method of Preparation

The nuclear grade strong base anion exchange resins containing different contents of residual chloride have been prepared by a novel process which comprises pretreating a commercial anion exchange resin (Type I 201 x 7 in this paper) with an aqueous medium followed by a two-step conversion of the resin to hydroxide form. Properties of various nuclear grade anion resins prepared by this novel processes are summarized in Table 7 (method 2 and method 3), properties of general nuclear grade anion resin are also listed in Table 7 (method 1)

Table 7 Properties of different nuclear grade anion exchange resins

Method	1	2			3	
Description	Normal nuclear grade anion exchange resin (Residual chloride < 5 %)	Nuclear grade anion exchange resin with lower residual chloride (Residual chloride < 1 %)			Nuclear grade anion exchange resin with low residual chloride (Residual chloride < 0.5 %)	
Particle size (mesh)	20 - 40	20 - 40			20 - 40	
OH ⁻	89.7	93.1	93.4	92.4	95.5	95.3
E % CO ₃ ²⁻	8.1	6.1	6.0	7.1	4.3	4.5
Cl ⁻	2.2	0.8	0.6	0.5	0.2	0.2
Exchange capacity meq/ml	1.1	1.0	1.0	1.0	1.0	1.0

4 % -- means equivalent percent based on the total ion exchange capacity of the resin

3.1 Pretreatment of Resin

Generally, acidic solution is used as pretreating agent. An improvement has been made in pretreatment process⁽⁵⁾. The comparison between the improved pretreatment process and acid pretreatment process is shown in Table 8

Table 8 Comparison between two pretreatment methods

Pretreatment process	The improved process of pretreatment				Acid pretreatment process			
Exchange capacity meq/ml	1.1	1.1	1.0	1.0	1.1	1.1	1.1	1.1
OH ⁻	91.3	93.1	92.4	95.5	89.8	90.6	89.7	90.0
E % CO ₃ ²⁻	7.9	6.1	7.3	4.3	8.4	7.7	7.9	8.9
Cl ⁻	0.8	0.8	0.3	0.2	1.8	1.7	2.4	1.1

According to the experimental results, it is indicated that the improved process is quite effective to reduce residual chloride in anion resin. Compared with acid pretreatment, residual chloride in resin pretreated with improved process can be decreased by 50 % under normal condition. In addition, if the pretreatment temperature is different, the conversion effect will be different.

3.2 Selection of Intermediate Conversion Agent

A two-step conversion process for preparing nuclear grade anion resin have been summarized early⁽⁶⁾. In this paper, we take an interest in selection of the best intermediate conversion agent which is used to reduce the chloride content to a level unachievable by hydroxide, when the anion resin is converted from the chloride form to hydroxide form by means of a two-step ion exchange. Generally, those salts which have intermediate selectivity between chloride and hydroxide can be used as the so-called intermediate selective agent, more preferred are Na₂CO₃, NaHCO₃, (NH₄)₂SO₄ and NaHSO₄. For comparative purposes, a number of experiments have been done. The results listed in Table 9 show that NaHCO₃ is the best of all four compounds. The experiments concerning the effect of NaHCO₃ amount on E % of residual chloride in OH-form resin have been carried out and these results are shown in Table 10.

Table 9 The effect of different intermediate selective agent on properties of resin

Intermediate conversion agent	OH ⁻	E % CO ₃ ²⁻ Cl ⁻		Exchange capacity meq/ml
Na ₂ CO ₃	88.2	9.6	2.2	1.0
NaHCO ₃	90.0	8.9	1.1	1.1
(NH ₄) ₂ SO ₄	88.1	10.4	1.5	0.8
NaHSO ₄	93.2	5.7	1.1	0.9

Table 10 The effect of NaHCO₃ amount on residual chloride of OH-form resin

Amount of NaHCO ₃ (Multiplication factor corresponding to total exchange capacity of resin)	Residual chloride of OH-form resin E %
1.3	12.2
1.8	6.1
2.0	4.0
2.5	2.1
3.8	2.0
4.0	1.3
5.0	1.2
6.0	1.1
7.0	1.1

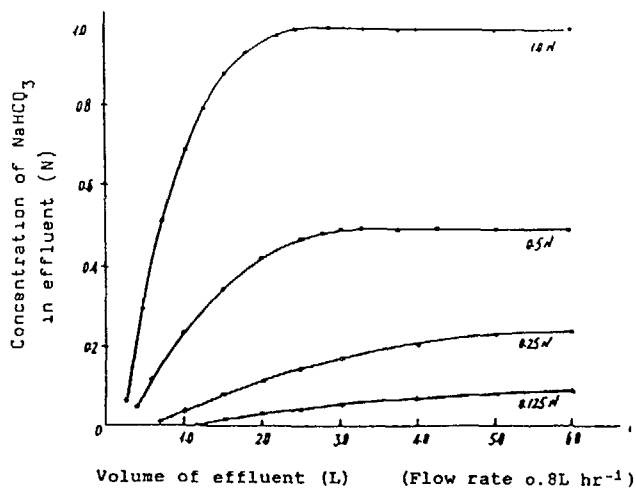


Figure 1 Elution curves with different concentrations of NaHCO₃

In Figure 1 are plotted curves of the NaHCO₃ concentration in effluent versus the effluent volume of NaHCO₃ solution for various concentrations of influent solution (NaHCO₃ 1.0N, 0.5N, 0.25N, 0.125N) with 0.8L/hr flow rate. It is obvious from these results, the lower concentration of NaHCO₃ solution, the less of NaHCO₃ amount, the longer elution time are required to reach equilibrium state.

However, it appears that considerable effect on conversion rate and residual chloride content on resin with different concentrations of NaHCO₃ has not been observed (0.25N, 0.5N, and 1N). Thus, using 0.5N NaHCO₃ solution as an eluting reagent, the relationship between the concentrations of Cl⁻ and HCO₃⁻ in effluent and effluent volume are shown in Figure 2.

Based on the above data of laboratory experiments, evidently, as an intermediate conversion agent, 0.5N NaHCO₃ solution having 10-12 resin bed volume has been preferred to others, because of higher conversion rate, less residual chloride in resin, less time-consumption and less agent consumption.

3.3 The Selection of Concentration and Amount of Basic Solution

More suitable compounds for conversion from intermediate ion form (HCO₃⁻ is selected in this paper) to hydroxide form are inorganic bases, such as the alkaline metal hydroxides and the like. NaOH solution has been selected as the conversion agent in this work.

There are different opinions concerning which of concentrations of NaOH solution is more available, some authors confirmed that 2.5N and 1.75N are preferred, whereas other authors recommended that it must be no more than 1N. In respect of more available amount of NaOH, the opinions are the same, that is 10 resin bed volumes.

Using domestic anion resin Type I, a number of experiments were performed and these results are shown in Table 11 and Table 12. From results listed in Table 11, 1.0N or 1.5N NaOH solution may be selected as the conversion agent, according to requirements of various nuclear grade anion exchange resins, and from results listed in Table 12, it can be seen that 6-8 resin bed volumes of NaOH solution are preferable to the others.

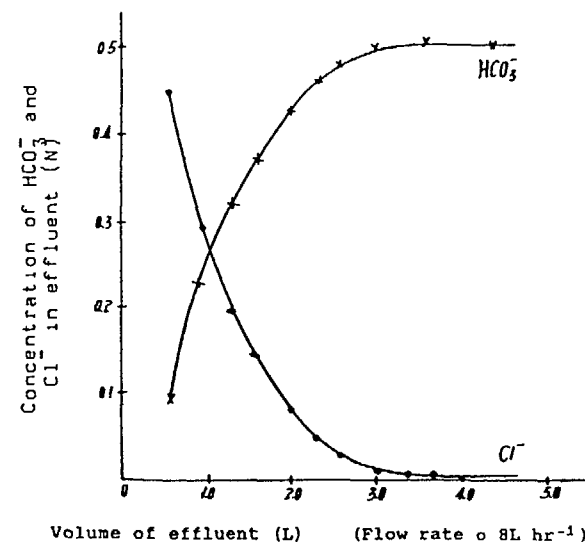


Figure 2 Elution curves with 0.5N NaHCO₃

Table 11 The effect of various concentrations of NaOH solution on chemical properties of anion exchange resin Type-I

Concentration of NaOH solution		1.0N	1.5N	2.0N
Amount of NaOH solution (Resin bed volume)		8	7	6
E %	OH ⁻	93.1	95.4	95.2
	CO ₃ ²⁻	6.1	4.0	4.1
	Cl ⁻	0.8	0.6	0.7
Exchange capacity meq/ml		1.1	1.1	1.1

Table 12 The effect of various amounts of 1N NaOH solution on chemical properties of anion exchange resin

Amount of NaOH solution (Resin bed volumes)		5	6	8	10	14
Exchange capacity meq/ml		1 0	1 0	1 0	1 0	1 0
E %	OH ⁻	91 5	92 4	93 6	92 8	93 7
	CO ₃ ²⁻	8 1	7 3	6 0	6 9	6 0
	Cl ⁻	0 4	0 3	0 3	0 3	0 3

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4 Conclusion

The nuclear grade cation and anion resins prepared with these conversion processes in this paper have been applied for water treatment in LWR. Results of tests have demonstrated that the performances of these resins are very good.

Compared with general conversion processes, the novel conversion processes developed in this paper combine the advantages of less impurity, higher conversion rate, lower residual chloride content etc.

These nuclear grade resins prepared with novel processes, especially the low residual chloride anion resin and cation resin are expected to be the most satisfactory water treatment agents for nuclear power station

Acknowledgement

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ACTIVITIES OF THE NUCLEAR RESEARCH INSTITUTE IN WATER COOLANT INTERACTION WITH FUEL AND PRIMARY CIRCUIT MATERIALS

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Abstract

The development of nuclear power in Czechoslovakia is based on pressurized water reactors of VVER type. There are at present eight reactors in commercial operation. Main characteristics of VVER-440 and VVER-1000 MW reactor systems are described. Operational experience of these reactors is presented. Experimental loops in Nuclear Research Institute is presented. Loops model the conditions of primary circuit of PWR. The results of coolant chemistry influence on corrosion and activity build-up, environmental degradation of primary systems materials is resulted.

1. INTRODUCTION

The development of nuclear power in Czechoslovakia is based on pressurized water reactors of VVER type. There are at present eight reactors in commercial operation. All of them are 440 MW PWR of soviet design, located in Bohunice and Dukovany. Date of the start-up of these power stations and next power stations are in the Fig.1. Under construction there are 4 x 440 MW units in Mochovce and 4 x 1000 MW units in Temelín.

2. PRIMARY SYSTEMS TECHNOLOGY

In Table 1 main characteristics and parameters of VVER-440 and VVER-1000 MW reactor systems are described. The most of the primary system including horizontal steam generators components are made of stainless-steel. Fuel cladding is

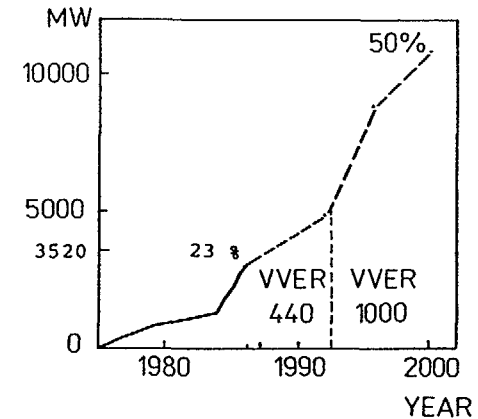


Fig. 1 Nuclear power plant development in Czechoslovakia

Table 1
Characteristics and Parameters of Reactor Systems

PARAMETER	Unit	VVER-440	VVER-1000
Thermal capacity	MW	1375	3000
Electrical capacity	MW	440	1000
Number of loops		6	4
Pressure	MPa	12.25	15.7
Inlet/outlet temperature	°C	264/299	289/322
Flow rate	m ³ .h ⁻¹	39 000	76 000
Fuel element linear heat flux	kW.m ⁻¹	13.1	17.6
Number of fuel assemblies		349	151

made of Zr-1% Nb alloy. Material characteristics of primary systems of VVER-440 are at the Table 2. Purification system of 440 MW reactor is based on ion-exchange technology operated at high pressure and temperature below 60°C. The first filtration unit is composed of two columns; cation exchanger and anion exchanger. Cation column is used for pH control and

Table 2
Material Characteristics of Primary Systems of VVER-440 MW

SURFACE	MATERIAL	SURFACE /m ² /
Fuel Cladding	Zr-Nb	4007
Steam generator, piping	stainless steel 08CH18N10T	15000
In-core structures	stainless steel 08CH19N10G	140

Table 3
Reactor Water Quality Specifications for VVER Reactors Types

PARAMETER	Unit	VVER-440	VVER-1000
H ₃ BO ₃	g.kg ⁻¹	0 - 6	0 - 13.5
pH (25°C)	6	6	6
KOH	mg.kg ⁻¹	2.5 - 16	2.5 - 30
NH ₃	mg.kg ⁻¹	5	5
H ₂	Nml.kg ⁻¹	30 - 60	30 - 60
O ₂	mg.kg ⁻¹	0.01	0.01
Cl ⁻	mg.kg ⁻¹	0.1	-
Cl ⁻ + F ⁻	mg.kg ⁻¹	-	0.1
Fe	mg.kg ⁻¹	0.2	0.2
Cu	mg.kg ⁻¹	-	0.02

anion column for boric acid removal at the end of fuel cycle. Second filtration unit is composed of mix-bed filter for chloride and iodide removal. The flow rate is 20 t/h that is 0.05% of total primary loops flow rate.

Purification at 1000 MW PWR operates at low pressure and is similar to that of 440 MW reactor. In addition, 1000 MW reactor has high pressure, high temperature mechanical filtration, which is used for radioactive corrosion product build-up reduction. Mechanical filtration is provided in 100 t/h column on each of the four primary loops. 400 t/h are so filtrated which is 0.5% of primary loops flow rate.

Primary water specifications are given in Table 3. Today, all of the VVER type reactors use KOH and NH₃ to alka-

lize the primary coolant. The standards for water chemistry of the reactors prescribes that the concentration of the alkalinizing agent must be dependent on boric acid concentration in the reactor coolant. Concentration of hydrogen which is necessary for oxygen suppression is formed by the radiolytic decomposition of ammonia.

3. OPERATIONAL EXPERIENCE

3.1. Radiation field control

The radiation control strategy for VVER reactor is based on the following:

- limits of cobalt concentration in construction materials, 0.05% for 440 MW reactor, 0.025% for 1000 MW reactor,
- avoiding the cobalt-base alloys (like Stellite) in primary system application,
- water chemistry control of primary coolant, correlation between potassium and boric acid concentration during fuel cycle,
- high pressure ion-exchange purification of primary coolant at 440 MW reactor,
- high pressure, high temperature purification of primary coolant of 1000 MW reactors.

At present the highest dose rate for personnel is at steam generator maintenance work. On Bohunice nuclear power plant the highest dose rate is from 1 to 3 mGy/h (100-300 mR/h) and middle dose rate is from 0.2 to 1 mGy/h /1/.

Occupational radiation exposure per unit at Czechoslovakian nuclear power plants is in Fig.2.

Fig.3 shows the occupational radiation exposure per unit electricity generated by Czech. PWR (Bohunice Power Station) in comparison with exposures in other countries, that were published in BNES Conference, 1986 /2/.

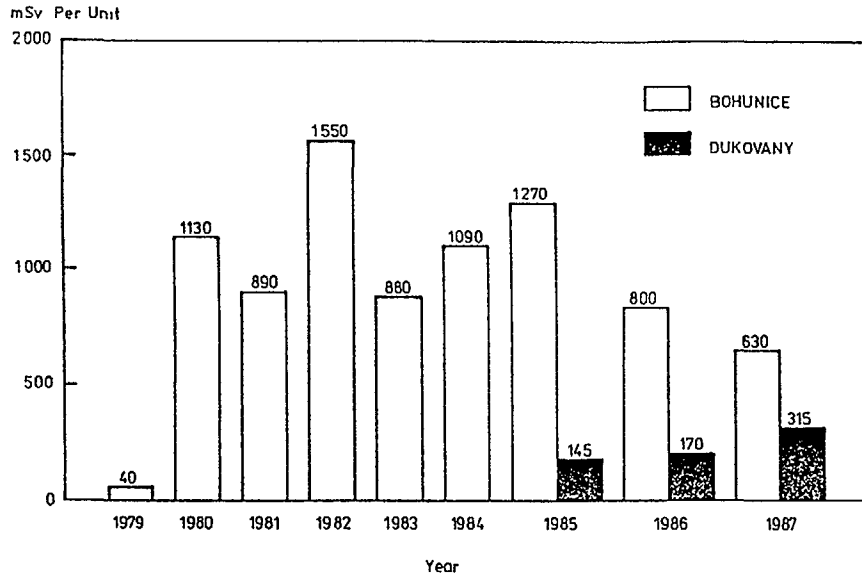


Fig. 2 Occupational radiation exposure per unit at Czechoslovakian Nuclear power plants

3.2. pH control and corrosion

Primary water chemistry specifications for VVER 440 MW is given in Fig.4. This figure prescribes the relation between potassium concentration and boric acid concentration during fuel cycle. This concept allows rather small variation of the pH values of the reactor water. (The potassium and ammonium hydroxide is used to alkalize the reactor water.)

The high temperature pH (pH_T) is one of the best parameters characterizing the primary water chemistry and this is widely used. According to the Meek calculations the pH_T (260°C) = 7.1 - 7.3 for 440 MW reactor coolant specifications. This corresponds according to Sweeton, Baes (1971) the pH_T (300°C) = 6.7 - 6.9.

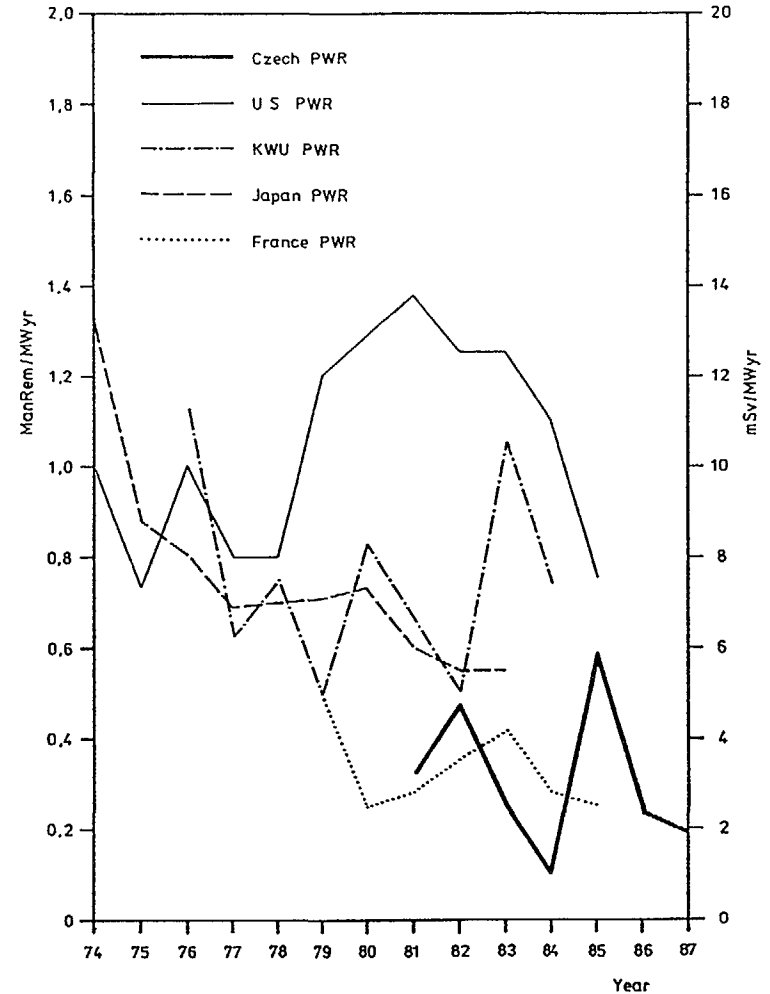


Fig. 3 Occupational radiation exposure per unit electricity generated by PWR nuclear power plants

Up to present in the Czechoslovakian PWR's there have been no serious corrosion problems in the primary system component. This state is achieved by pregnant water chemistry control during the operation /3/.

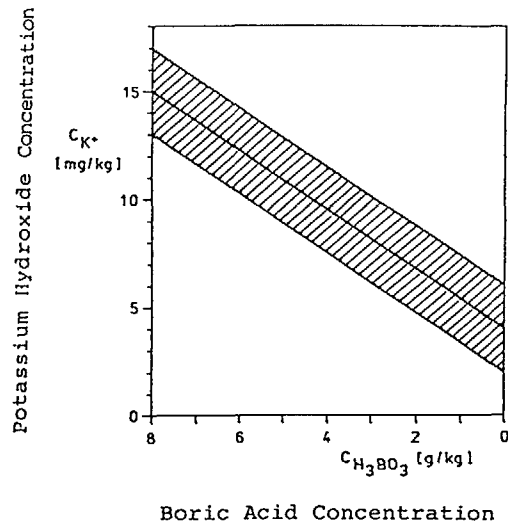


Fig. 4 Potassium hydroxide - boric acid mode of operation for VVER-440 MW unit

4. RESEARCH AND DEVELOPMENT

Experimental loops were built on the base of nuclear power development. In-pile loop and out-of-pile loop operated for the research in the field of corrosion and activity transport. Loops model the conditions of primary circuit of pressurized water reactors including pressure, temperature, water chemistry and radiation. The out-of-pile loop works at the temperature 350°C, pressure 19 MPa, circulation 20 kg/h, The high pressure in-pile water loop works with the coolant flow rate 10 000 kg/h, neutron flux in active channel $7 \cdot 10^{13}$ n/cm².s, 16 MPa, 330°C; high temperature electromagnetic filter is connected with the loop /4/.

Research carried out involves:

- a) In-pile loop experiments in different modes of water chemistry (standard, higher pH and hydrazine chemistry) directed towards implementation in plant operation.

- b) Preconditioning and passivation technology for minimizing corrosion product deposition, involving electropolishing and prefilming.
- c) Development of high pressure, high temperature sensors for water chemistry and environment control.
- d) Study of environment sensitive cracking in pressure boundary materials including stresses and irradiation.

4.1. Description of experimental facilities and methodics

4.1.1. Out-of-pile loop

The scheme of the loop is in Fig.5. The loop comprises two mutually interconnected flow autoclaves with volumes of 450 cm³ each, regulated electrical heating with power of 1500 W, sensors for measurement of temperature and pressure of the environment, degassing valves and a relief valve. The rig operates without a steam or gas bubble, both autoclaves are entirely filled by compressed water environment. The required pressure is obtained by means of dilatation of the liquid during heating and by regulation of the amount of

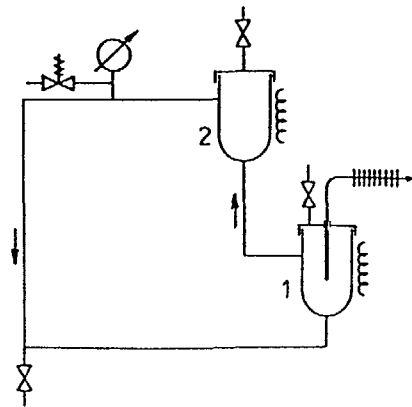


Fig. 5 Schematic diagram of the experimental facility

liquid in the rig. Natural circulation, caused by heating of autoclaves and cooling of return piping leads to flowrate at about 30 l/hr, so that the environment in each autoclave is renovated approximately every minute. It is possible to build in a ceramic passage in the removable head of each autoclave for outlet of cooled electrical signal route /5/.

4.1.2. In-pile high pressure reactor loop

The loop RVS-3 comprises a closed pressurized-water circuit with forced circulation and has a test section located in the core of the VVR-S type reactor, and filtration and measuring circuits /5/. The loop is so equipped that it is possible to operate the loop with the following nominal parameters:

allowable overpressure	16.67 MPa
working overpressure	15.70 MPa
working medium	deionized chemically treated water
flowrate	10.000 t/hr.

The diagram of the loop may be seen in Fig. 6.

The equipment of the loop enables to carry out experiments in wide range of these operational parameters. In these experiments the following facilities can be used:

1. Test sections in reactor core and comparative test sections in the main, filtration, and measuring circuits;
2. hot and cold measuring circuits;
3. filtration circuit;
4. sampling of liquid and gaseous samples from all circuits;
5. dosing equipment;
6. a possibility to operate only the in-pile circuit with natural circulation, or only the in-pile circuit with forced circulation, or all loop with forced circulation;
7. delaying vessel;
8. numerical information and evaluation system.

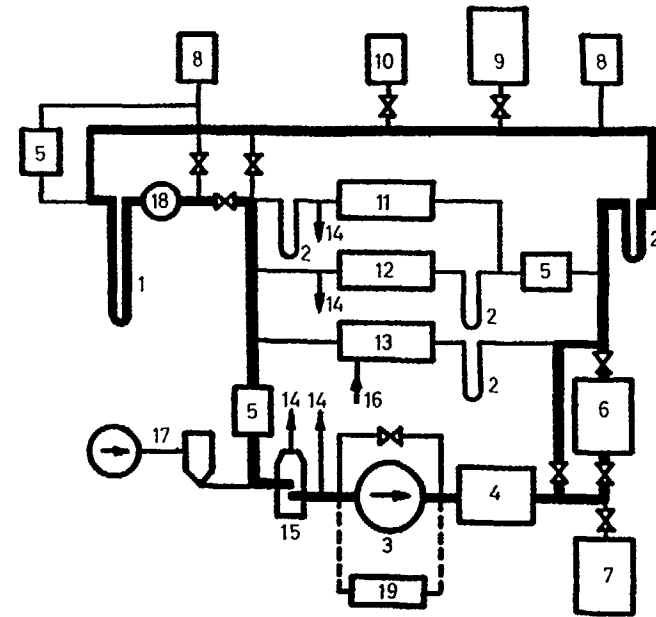


Fig. 6 Schematic Diagram of the High Pressure Reactor Water Loop RVS-3.
 (1 - radio-active channel, 2 - comparative channel, 3 - circulating pump, 4 - heater, 5 - cooler, 6 - auxiliary vessel, 7 - drain vessel, 8 - pressurizer, 9 - pressurizer, 10 - treatment of water, 11 - filtration circuit, 12 - cold measuring circuit, 13 - hot measuring circuit, 14 - laboratory - sampling, 15 - degasing, 16 - gas inlet, 17 - dosing plant, 18 - dosimetric sensors, 19 - attached experimental facilities

Fig. 6 Schematic Diagram of the High Pressure Reactor Water Loop RVS-3.

Monitoring of radiation parameters during irradiation the active channel is provided with two monitoring probes with self-powered detectors and calorimeters. The probe with the self-powered detectors for monitoring the thermal neutron fluence rate includes 7 Soviet self-powered detectors DPZ-1 (with emitter diameter and length of 0.4 mm and 50 mm, respectively). The probe with calorimeters for gamma radiation exposure rate monitoring includes 5 calorimeters with tungsten bodies and one compensating calorimeter.

4.2. Coolant chemistry influence on corrosion and activity build-up

Coolant chemistry has been recognized as the major factor which influences radiation fields around primary systems. We suppose that there are two possibilities to modify the primary coolant chemistry at the VVER reactors: higher pH and hydrazine water chemistry. The results of plant tests were recently published and the experience achieved was the base for decision to start experimental program. We joined our efforts with GDR (German Democratic Republic)* institute ZfK Rossendorf and KKW Rheinsberg NPP. The experiments of pressurized water loops were decided as a first step in the program before the implementation on Rheinsberg power plant and then on reactors VVER 440.

The main objective was to compare three loops experiments with different coolant chemistry: standard water chemistry, high pH and hydrazine. Data and measurements were collected during and after each experiment and were divided into: coolant analysis, corrosion and activity measurements on metal samples, dose measurements. Before each of experiments the RVS-3 loop was decontaminated and thus the same initial conditions were maintained. The decontamination procedure has two steps and was developed in the KKW Rheinsberg /7/.

The conditions of experimental runs and results of corrosion rates measurements are summarized in Tables 4, 5, 6 and in Fig. 7. The activity measurements evaluation is still in progress. The corrosion rate measurement from metal samples shows no differences between the experiments (Table 6). Corrosion rates from decontamination of the loop internal surfaces increase as follows: hydrazine < standard water chemistry < high pH. The first decontamination of the loop was not fully successful so the procedure had to be repeated (see Table 7). Possible explanation of this fact is the oxide layer formed at high pH chemistry is more resistant to decontamination.

* This text was compiled before the unification of Germany in October 1990.

Table 4. Thermohydraulic parameters in the loop during activity build-up experiments

	Main Circuit	Heater	Samples		
			Active channel	Measuring Circuit	Comparative channel
Temperature °C	274-294	274-294	290	270-285	294
Pressure MPa	12	12	12	12	12
Flow Rate t.h ⁻¹	2.5	2.5	2.5	0.14	2.5
Linear Velocity m.s ⁻¹	0.97	0.025	4.6	0.25	4.6
Reynolds Number	274 000	22 200	189 000	10 300	189 000
Internal Surface m ²	18,2				
Volume dm ³	240				

Table 5. Water chemistry parameters in the loop during activity build-up experiments

Parameter	Experiment		
	Standard	Higher pH	Hydrazine
H ₃ BO ₃ g.kg ⁻¹	6.4 ± 0.4	6.1 ± 0.2	6.1 ± 0.3
KOH mg.kg ⁻¹	17.7 ± 3.8	72.3 ± 3.0	16.5 ± 2.7
NH ₃ mg.kg ⁻¹	15.0 ± 2.0	15.0 ± 2.3	0 - 120
N ₂ H ₄ μg.kg ⁻¹	-	-	30 - 100
pH 25°C	6.6 ± 0.3	7.3 ± 0.1	7.1 ± 0.4
pH 270°C (MESMER)	6.65	7.20	6.65
pH 300°C (MESMER)	6.80	7.40	6.80
H ₂ Nml/kg	0.2 - 0.4	0.2 - 0.4	23 ± 4

Table 6. Corrosion rate of metal samples during experiments

Experiment	Corrosion rate [kg.m ⁻² .s ⁻¹]			
	Blank samples		Preoxidized samples	
	Comparative channel	Measuring circuit	Comparative channel	Measuring circuit
Standard	6.9 E-10	9.4 E-10	4.5 E-10	4.5 E-10
High pH	1.5 E-9	1.2 E-9	3.9 E-10	4.4 E-10
Hydrazine	1.2 E-9	8.9 E-10	3.5 E-10	4.4 E-10

Remark: Corrosion rate during preoxidizing step was 9.2 E-10

The steam generator tubes with different surface treatment were exposed during experiments with different coolant chemistry. Tube samples were placed in hot measuring circuit of the RVS-3 loop. The tubes with standard blasted surface and the tubes which have electropolished surface were exposed. The results of corrosion layer measurement and parameters of roughness are summarized in Table 8. Corrosion layer was distinguished in outer and inner oxide layer by procedure which consists of two dissolution steps: first step is dissolution with EDTA and the second step is dissolution with permanganate. Content of iron, chromium and nickel in outer and inner oxide layers (Fig.8) shows the differences between these layers. It was found that the outer oxide layer is Fe-rich and the inner oxide layer is Cr-rich. The differences between mass of the outer layers (see Table 8) on blasted and electropolished tubes can be explained by the fact that electropolished surfaces is less susceptible to crystallite deposition.

4.3. Environmental degradation of primary systems materials

The experimental loops are utilized for the study of environmental degradation of pressure boundary materials.

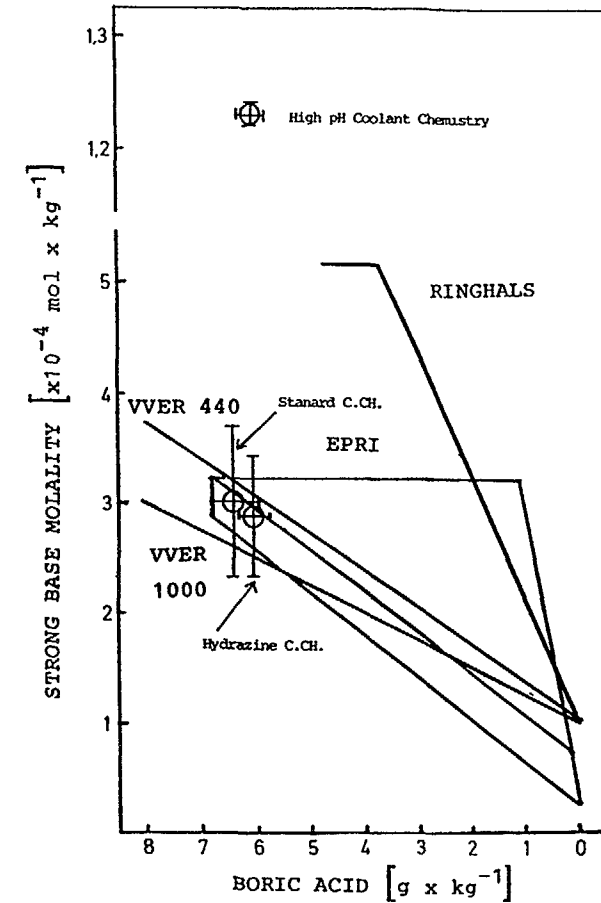


Fig.7. Coolant Chemistry during Experiments versus recommendations for VVER 440, VVER 1000, EPRI and Ringhals

Sensitivity to cracking of steam generators material is studied in the out-of-pile loop. The tubes of steam generators in VVER reactors are made of titanium-stabilized austenitic stainless steel. Stress corrosion cracking (SCC) is studied on material samples which are mechanically stressed. An example of stressed tube can be seen on Fig.9. A structure with

Table 7. Corrosion rate of the loop surface calculated from decontamination data

Parameter	Standard	Higher pH [†]			Hydrazine
		I.	II.	I.+II.	
Gained metals g					
Fe	58.08	63.25	29.25	92.50	35.02
Cr	2.40	8.63	4.18	12.81	4.37
Ni	5.86	6.63	2.09	8.72	2.49
Σ metals	66.34	78.51	35.52	114.03	41.88
Corrosion rate kg.m ⁻² .s ⁻¹	1.56 E-9	1.72 E-9	7.78E-10	2.5 E-9	9.88 E-10
Remarks: I. - first decontamination II.- second decontamination					

Table 8. Oxide layer on steam generator tubes

EXPERIMENT	Mass of layer mg/cm ²			
	blasted surface		electropolished surface	
	outer layer	inner layer	outer layer	inner layer
Standard	0.32	0.08	0.13	0.04
High pH	0.52	0.07	0.04	0.01
Hydrazine	0.01	0.13	0.01	0.11
Roughness, R _a	0.34		0.086	

spring enables to achieve the same strength during the whole experimental runs.

The behaviour of the in-core materials is influenced also by radiation. If we exclude fuel cladding there remain two different materials in the core: carbon steel of pressure vessel, stainless steel of internal structures and welded stainless steel cladding. The study of stress corrosion cracking and corrosion fatigue of these materials is very important for the program of plant life extension. Recently

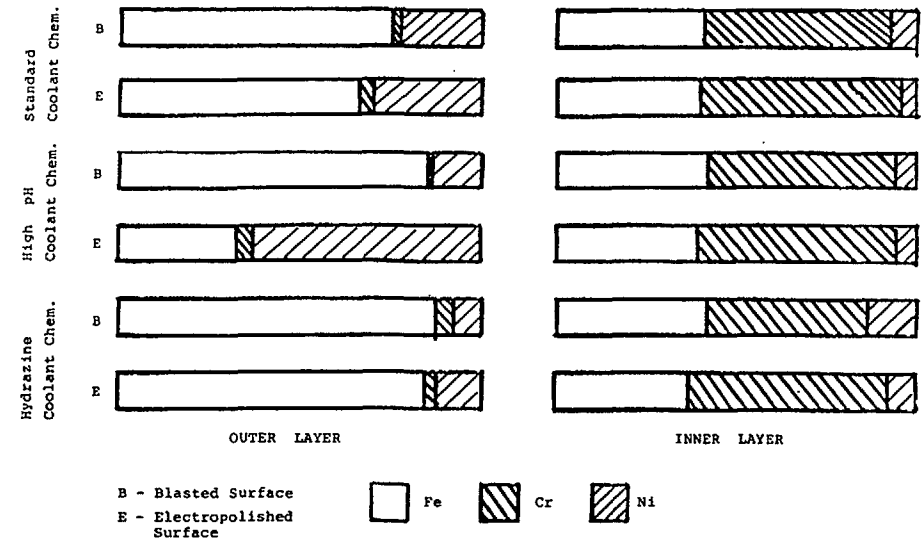


Fig.8 Relative Content of Iron, Chromium and Nickel in Oxide Layers

irradiation-assisted stress corrosion cracking (IASCC) has been defined as the form of cracking that would not have occurred in the absence of radiation /6/. Water chemistry has an important place in the study of this phenomenon. It is assumed that water chemistry influences two relevant crack growth mechanisms - film rupture/slip dissolution and hydrogen induced cracking. In the case of IASCC the radiolysis of water leads to radiolytic species - radicals and peroxides. The behaviour of these species in crevices may be quite different from the behaviour in the bulk coolant. Radiation affects passive film and electrochemical potential of materials.

In the active channel of the reactor loop some experiments were carried out that enable the estimation of radiation influence on water radiolysis under PWR coolant conditions and influence of radiation on hydrogen behaviour in carbon steel.

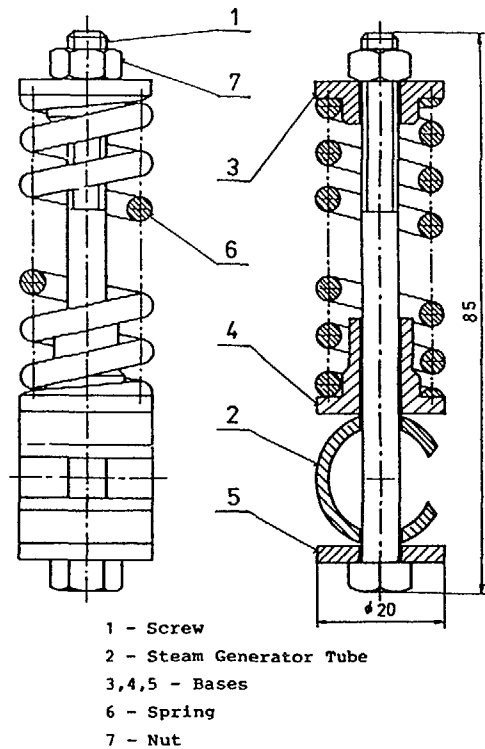


Fig. 9 Test Specimen of Steam Generator Tube

An redox electrode with gold active surface was placed in irradiation channel. Potential was measured at temperature of 287°C and pressure of 13 MPa. The electrode potential changes with reactor start-up and shut down (see Fig.10). It was found that measurement of the electrode potential of surface which is simultaneously irradiated is technically possible.

Radiation influences the behaviour of hydrogen in carbon steel. Comparison between the hydrogen behaviour in irradiated and non-irradiated carbon steel samples is in the Fig.11.

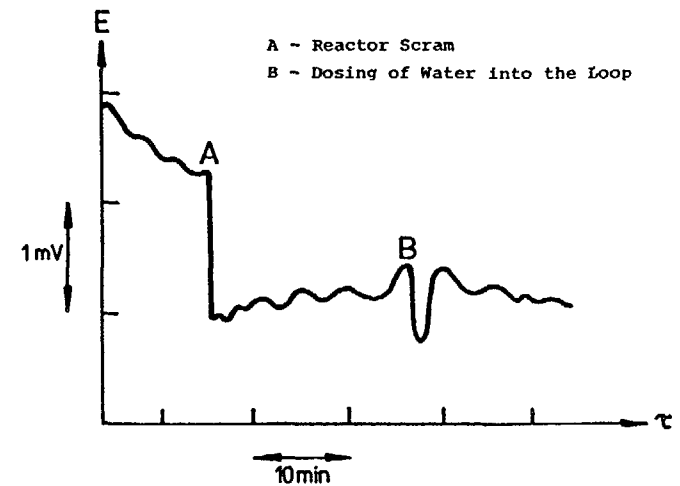
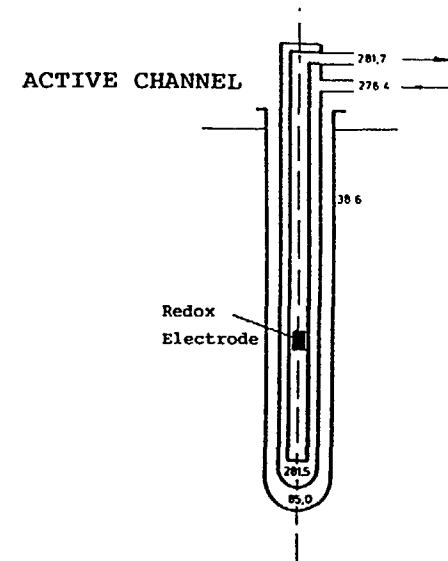


Fig.10 Potential of Redox Electrode in Active Channel of the Loop

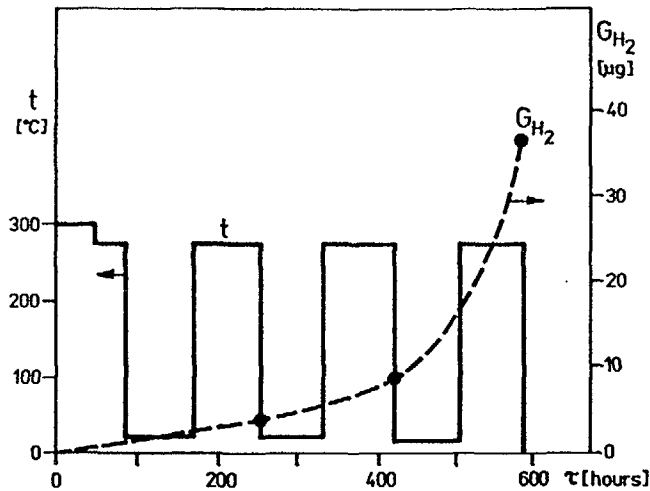


Fig. 11 The Dependence of Hydrogen Development in Steel Sample on Irradiation Time in the Reactor Loop

5. SUMMARY

An attempt has been made to touch briefly on water chemistry experience of pressurized water reactors in Czechoslovakia. Many of problems have been resolved for plant operation by joined effort of plant staff and research institutes. The major problem in primary coolant technology today is the exposure of personnel due to radioactivation of corrosion products.

The next program involves reduction of radiation exposure, assurance of material compatibility, improvement of utilization of nuclear fuel and extension of plant life.

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WATER COOLANT INTERACTION WITH FUEL AND PRIMARY CIRCUIT MATERIALS

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Abstract

Activated corrosion products transported in nuclear power plant primary circuit depend on type of reactor and water chemistry. The analysis of reactor water showed that the pH value for VVER's reactors in practically all the fuel cycle lower than 7.2. The experimental determination of optimum pH value in high pressure water loop is proposed. For this the model of fuel element is prepared. The development of computer model for mass transfer is also involved.

1. Introduction

Type of the nuclear power plant primary circuit water chemistry is decisive for corrosion rate and for the amount of activated corrosion products transported in the system. Growing knowledge of physical and chemical phenomena taking place in water systems under high pressures and temperatures and, simultaneously, an effort to suppress corrosion phenomena and, in this way, to reduce the amount of radioactive nuclides in the system have led to experiments with other, different water régimes than the current ones.

Changes in corrosion behaviour of components, deposition, transport and time of residence of corrosion products in reactor core and, as a consequence of this, activation of corrosion products can be caused by both the pH value and the redox potential. As the temperature gradient of solubility of austenitic steel corrosion products depends strongly on pH and the major part of corrosion products - magnetite -

exhibits a solubility minimum for the presently used water chemistry, the value of pH used would have to ensure positive temperature gradient of solubility and therefore time of residence of corrosion products in reactor core. This change of pH must not adversely affect the fuel assemblies and components of primary circuit. The value of pH can be changed only to such extent that the total mass of corrosion products remains unchanged. It corresponds only to minor changes of pH with $\Delta \text{pH} \leq 1$ as compared with the presently used régime.

2. Reactor water chemistry at VVER's

In Table 1 main characteristics and parameters of VVER-440 and VVER-1000 MW reactor systems are described. The most of the primary system including horizontal steam generators components are made of stainless-steel. Fuel cladding is made of Zr-1% Nb alloy. Material characteristics of primary systems of VVER-440 MW are at the Table 2. Purification system of 440 MW reactor is based on ion-exchange technology operated at high pressure and temperature below 60°C. The

Table 1
Characteristics and Parameters of Reactor Systems

PARAMETER	Unit	VVER-440	VVER-1000
Thermal capacity	MW	1375	3000
Electrical capacity	MW	440	1000
Number of loops		6	4
Pressure	MPa	12.25	15.7
Inlet/outlet temperature	°C	264/299	289/322
Flow rate	m ³ .h ⁻¹	39 000	76 000
Fuel element linear heat flux	kW.m ⁻¹	13.1	17.6
Number of fuel assemblies		349	151

Table 2
Material Characteristics of Primary Systems of VVER-440 MW

SURFACE	MATERIAL	SURFACE /m ² /
Fuel Cladding	Zr-Nb	4007
Steam generator, piping	stainless steel 08CH1810T	15000
In-core structures	stainless steel 08CH19N10G	140

first filtration unit is composed of two columns; cation exchanger and anion exchanger. Cation column is used for pH control and anion column for boric acid removal at the back of fuel cycle. Second filtration unit is composed of mix-bed filter for chloride and iodide removal. The flow rate is 20 t/h that is 0.05% of total primary loops flow rate.

Purification at 1000 PWR operates at low pressure and is similar to that of 440 MW reactor. In addition, 1000 MW reactor has high pressure, high temperature mechanical filtration, which is used for radioactive corrosion product build-up reduction. Mechanical filtration is provided in 100 t/h column on each of the four primary loops. 400 t/h is so filtrated which is 0.5% of primary loops flow rate.

3. Reactor water chemistry

Primary water specifications are given in Table 3. Today, all of the VVER type reactors use KOH and NH₃ to alkalize the primary coolant. The standards for water chemistry of the reactors prescribes that the concentration of the alkalizing agent must be dependent on boric acid concentration in the reactor coolant. Concentration of hydrogen which is necessary for oxygen suppression is formed by the radiolytic decomposition of ammonia.

Primary water chemistry specifications for VVER-440 MW and VVER-1000 MW prescribe the relation between potassium

Table 3
Reactor Water Quality Specifications for VVER Reactors Types

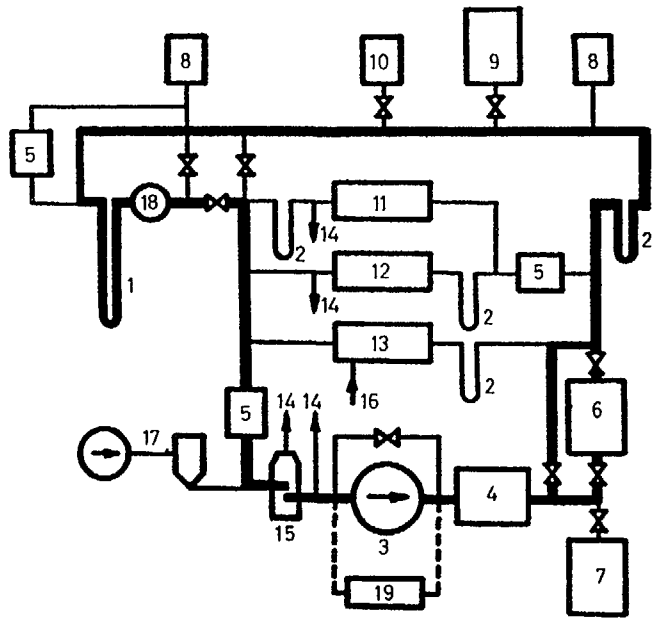
PARAMETER	Unit	VVER-440	VVER-1000
H ₃ BO ₃	g.kg ⁻¹	0 - 6	0 - 13.5
pH (25°C)	6	6	6
KOH	mg.kg ⁻¹	2.5 - 16	2.5 - 30
NH ₃	mg.kg ⁻¹	5	5
H ₂	Nml.kg ⁻¹	30 - 60	30 - 60
O ₂	mg.kg ⁻¹	0.01	0.01
Cl ⁻	mg.kg ⁻¹	0.1	-
Cl ⁻ + F ⁻	mg.kg ⁻¹	-	0.1
Fe	mg.kg ⁻¹	0.2	0.2
Cu	mg.kg ⁻¹	-	0.02

concentration and boric acid concentration during fuel cycle. This concept allows rather small variation of the pH values of the reactor water. (The potassium and ammonium hydroxide is used to alkalize the reactor water.)

The high temperature pH (pH_T) is one of the best parameters characterizing the primary water chemistry and this is widely used. According the Meek calculations the pH_T (260°C) = 7.1 - 7.3 for 440 MW reactor coolant specifications. This corresponds according Sweeton, Baes 1971 the pH_T (300°C) = 6.5 - 6.7.

4. Technical preparation of the experimental facility

A part of the experimental work on the RVS-3 in-pile water loop will be represented also by a research on deposition of corrosion products on a model of the VVER-1000 pressurized water reactor fuel assembly. As the required standard model of the fuel assembly has not been supplied yet, an electrically heated model of the fuel pin with O.D. of 8.5 mm and with 08CH18N105 steel cladding will be used in the first stage of the experiments, where the basic characteristics



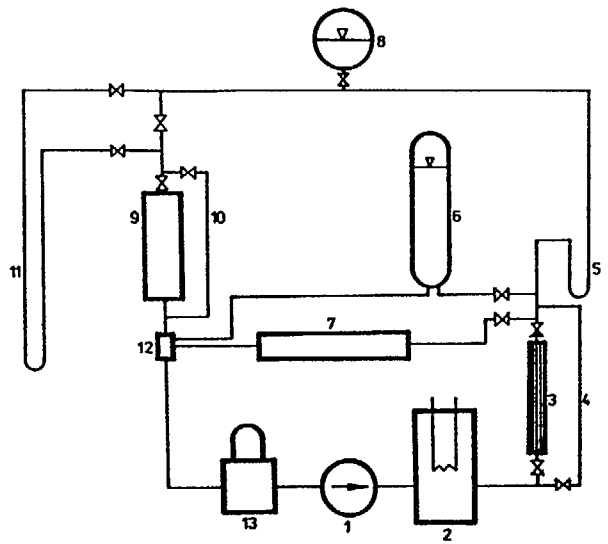
(1 - radio-active channel, 2 - comparative channel, 3 - circulating pump, 4 - heater, 5 - cooler, 6 - auxiliary vessel, 7 - drain vessel, 8 - pressurizer, 9 - pressurizer, 10 - treatment of water, 11 - filtration circuit, 12 - cold measuring circuit, 13 - hot measuring circuit, 14 - laboratory - sampling, 15 - degasing, 16 - gas inlet, 17 - dosing plant, 18 - dosimetric sensors, 19 - attached experimental facilities

Fig.1 Schematic diagram of the high-pressure reactor water loop RVS-3

will be verified. In the second stage, the use of a pin with O.D. of 11 mm and Zr..Nb alloy cladding is envisaged.

The test section - a channel with imitators of fuel pins - is incorporated into the water loop primary circuit (see Figs. 1, 2). The source of radioactive products will be represented by either the RVS-3 loop active channel, or an inserted defined source of the radioactive products. A scheme of the sectional view of the channel with fuel pin imitators is in Fig. 3. The U-shaped fuel pin has O.D. of 8.5 mm and is electrically heated with supposed power of 70 W/cm². The heated length is 200 cm.

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- 1 circulating pump
- 2 heater
- 3 test-section
- 4 by-pass
- 5 comparative channel
- 6 pressurizer
- 7 hot measuring circuit
- 8 volume-compensator
- 9 cooler
- 10 by-pass
- 11 active channel
- 12 mixture chamber
- 13 degasser

Fig. 2

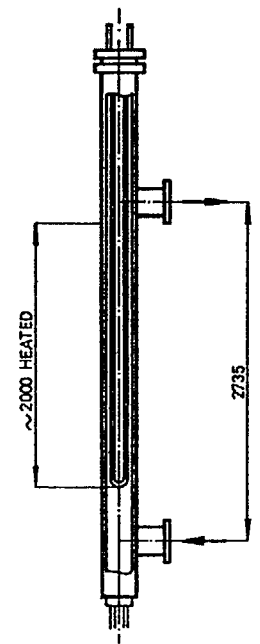


Fig. 3 Sectional view of the channel with fuel pin imitators

Cross-sectional views of the channel and fuel pin are in Figs. 4 and 5.

The parameters of the model of fuel assembly and their comparison with the parameters of similar loops worldwide are presented in Table 4.

The imitators of fuel pins used in our experiments are represented by rods with an indirect electrical heating, that is, the resisting material is insulated from the coolant. A sectional view is in Fig. 3.

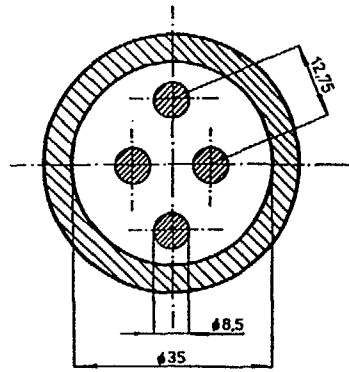


Fig. 4 Cross-sectional view of the channel

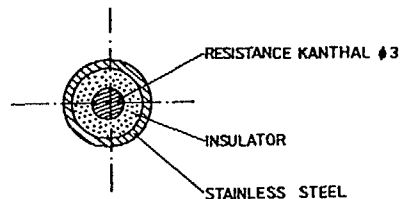


Fig. 5 Cross-sectional view of fuel pin

Table 4

Comparison of thermohydraulic parameters of fuel imitators of RVS-3 loop with reactor VVER-1000 and other loops

PARAMETER	RVS-3	VVER-1000	X-3	CIRENE
P MPa	15.7	15,7	9.64	15
t_{outlet} °C	322	322	268	342 max
t_{inlet} °C	290	290	250	290
Q_{kp} $\frac{\text{W}}{\text{cm}^2}$	70	58.2	114 max	125 max
Q_{s} $\frac{\text{m}^3}{\text{max}}$	10	88000	5	6
Re	3×10^5	4×10^5	1.3×10^5	-
t_{surface} °C	350	350	-	350
ϕ_{rod} mm	8.5	9.1	15.2	9.2
length cm	200	353	200	310

X-3 loop at NRX Reactor, Chalk River Canada

CIRENE ... loop in CEA, Cadarache, France

Materials of the heated rod:

- cladding: steel 17246
- core: KANTHAL "A"
- filling material: oxides of aluminium and magnesium

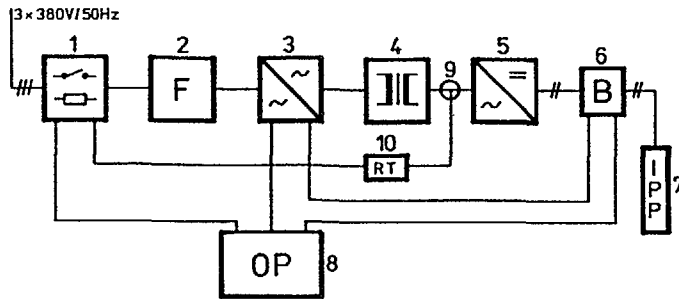
Dimensions of the heated rod:

- length: 2600 mm
- outer cladding diameter: 8.5 mm
- cladding wall thickness: 1 mm
- core diameter: 2.8 mm

Electrical resistance:

- $R = 0.57$ at 20°C.

The lead-in wires are represented by two pieces of copper conductor with diameter of 3 mm and length of 1500 mm, located in a pipe with O.D. of 10 mm. For the reason of thermal dilatation of the assembly at higher temperatures, the U-shape imitators and one-sided lead-out from the test section have been chosen.



- | | |
|----|-------------------------------|
| 1 | switch with protection |
| 2 | filter |
| 3 | alternating voltage changer |
| 4 | transformer |
| 5 | rectifier |
| 6 | shunt box |
| 7 | fuel pin imitator |
| 8 | control panel |
| 9 | current measuring transformer |
| 10 | over-current protection |

Fig. 6 Block diagram of direct-current power source

The electrically heated imitators of fuel pins are supplied from a direct-current power source with galvanic isolation of the imitators from the power supply grid and continuous control of power from zero to maximum. A block conception has been chosen and the source consists of a bridge-type rectifier, transformer and an alternating voltage transformer. A block diagram of the source is in Fig. 6. The source enables to achieve the imitator specific load as high as 150 W/cm².

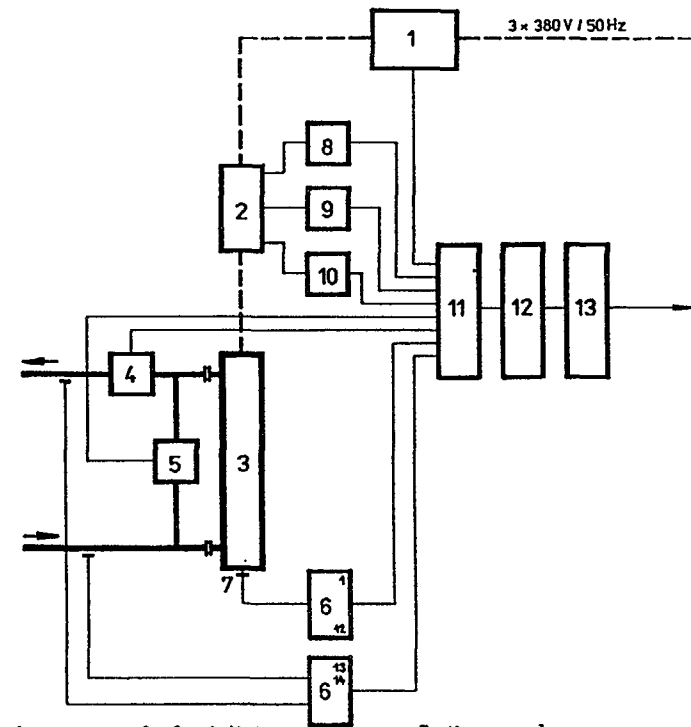
Measurement of basic electrical and physical parameters of the test section with fuel pin imitators

The following physical quantities and electrical parameters will be measured:

- temperature and fourteen points of the test section,
- coolant flowrate in the test section,
- pressure drop on the test section,

- current through the imitator,
- voltage,
- power of the imitator.

All measured quantities are transformed into electrical signals and treated to form an input of the measuring unit. Processing and evaluation of the measured values will be ensured by the measuring unit ADT 4700. A block diagram of the measurement is in Fig. 7.



- | | | | |
|---|--|----|-------------------------|
| 1 | power supply for imitators | 7 | thermocouples |
| 2 | shunt box | 8 | current converter |
| 3 | test section with fuel pin imitators | 9 | voltage converter |
| 4 | flowmeter | 10 | power converter |
| 5 | pressure difference sensor | 11 | diplex box |
| 6 | thermostats of the thermocouple comparison junctions | 12 | unification box |
| | | 13 | measuring unit ADT 4700 |

Fig. 7 Block diagram of the measurement

5. Experience of mass and activity transfer in RVS-3 loop

On the basis of a joint working programme of experiments on a test facility, work on a change or optimization of water chemistry of the VVER-type NPP primary circuit has been carried out in CSSR and GDR with the aim to improve the NPP safety and availability and to decrease the radiation loads of the operating personnel. The experiments are a necessary step before the test on a nuclear power plant.

For the purpose of comparison, three experiments have been chosen. The water chemistry usual at present was compared with water chemistry with higher pH and with the hydrazine water chemistry (Exp. I - standard chemistry, Exp. II - higher pH, Exp. III - Hydrazine chemistry).

An important factor for evaluation of the effect of water chemistry on mass transport in the loop has been represented by removal of corrosion layers from the whole loop inner surface. In the experiment with higher pH value it was necessary to repeat the procedure of decontamination owing to more resistant corrosion layer. The total corrosion rate in the experiments II, I and III was decreasing. The hydrazine water chemistry exhibited besides lower corrosion rate also the lowest presence of nickel in the corrosion layer.

From the distribution of activities it is evident that higher presence in the outer layer is exhibited by the nuclides ^{51}Cr , ^{59}Fe and ^{124}Sb . Extreme difference in behaviour of antimony and manganese can be explained by different diffusion of these nuclides through the corrosion layer. Whereas manganese diffuses more deeply into the inner layer, antimony, possibly owing to formation of voluminous polyanions, is more concentrated in the outer region. Different distribution of radionuclides between the outer and inner corrosion layer is also affected by flow velocity and the degree of preoxidization. Higher flow velocity ($\text{Re} = 2 \times 10^5$) on the sample surface in the loop main channel than that in the loop by-pass

($\text{Re} = 1 \times 10^4$) causes higher presence of nuclides in the outer layer. The same holds also for the preoxidized samples. It is obvious that there is no substantial difference in composition of the corrosion layers in the individual experiments with the exception of presence of nickel in the inner corrosion layer where the relative amounts of Ni have the following tendency: $\text{I} > \text{III} > \text{II}$. Also the relation between the relative amounts of an element in the corrosion layer and the type of surface treatment of the material tested is characteristic. Whereas the relative content of Fe and Ni in the inner layer of the preoxidized samples is always lower than in the samples treated mechanically (and higher in the case of Cr), the outer layer exhibits inverse behaviour. These differences are a consequence of different time of build-up of the corrosion layers of these samples and not the long-term exposition (1000 hr) can be taken as sufficient for establishment of permanent relative presence of the individual metallic elements in the corrosion layers.

The ratio of area masses of the outer and inner corrosion layers enables deeper understanding of general laws of formation of the oxidic layer. Liquid flow velocity has a demonstrable effect on the process: increased flow velocity increases this ratio for the preoxidized samples. In the case of mechanically treated sample surfaces such tendency can be found only for the hydrazine water chemistry. With the time period of exposition increased also the ratio of the outer and inner corrosion layer is increased, with the principal part in the formation of corrosion layer taken over by the outer layer. The share of the individual processes (crystallization at the amorphous surface of the outer layer or deposition of particles from the solution) in formation of the outer layer remains an open issue.

6. Modelling of mass and activity transport

An important role in prediction of occupational radiation exposure and radiation level is played by mathematical

modelling of transport and activation of corrosion products in primary systems /1/.

In the past period of the contract the following progress in model's development was performed.

Corrosion of structural materials and release of corrosion products into coolant

The parabolic law of corrosion is assumed. The corrosion rate of structural materials for a given nuclide k^{COR} and the rate of release of corrosion products into coolant k^{TR} are given by the relations:

$$k^{COR} = p_1 \cdot p_2 \cdot \frac{P}{\sqrt{t}} \quad (\text{kg/m}^2 \cdot \text{s}) \quad (1a)$$

$$k^{TR} = p_3 \cdot k^{COR} \quad (\text{kg/m}^2 \cdot \text{s}) \quad (1b)$$

where: p_1 - fraction of an element in structural material, (-)
 p_2 - fraction of a nuclide in the natural mixture, (-)
 p_3 - fraction of CP released from the total amount of the CP formed, (-)
 P - constant of corrosion rate, ($\text{kg/m}^2 \cdot \text{s}^{1/2}$)
 t - time, (s).

Deposition of particles

The deposition of particles is described by the model of Beal /2/ based on the relation (2) for mass flow towards the wall caused by pulsations of concentration in turbulent wind and by molecular diffusion.

$$N = D \cdot \frac{dc}{dy} + \overline{v' \cdot c'} \quad (2)$$

where: N - mass flux towards the wall, ($\text{kg/m}^2 \cdot \text{s}$)
 D - Brownian diffusion coefficient, (m^2/s)
 v' - velocity pulsations in the direction towards the wall, (m/s)
 c' - concentration pulsations, (kg/m^3)

Deposition coefficient is given by the relation:

$$k^P = \frac{K \cdot p \cdot v}{K + p \cdot v} \quad (\text{m/s}) \quad (3)$$

where: K - transport coefficient, (m/s)
 p - sticking probability, (-)
 v - radial component of particles velocity (m/s).

Erosion of particles

In the computer programme the erosion coefficient and fraction of CP released from the total amount of CP formed are selected as a free parameters the system used for as close as possible approximation of experimental data. The values of erosion coefficient are within the interval from 10^{-7} to 10^{-6} (1/s).

Dissolution of the oxidic layer

The process of dissolution of oxidic layer takes place when the concentration of corrosion products dissolved in the coolant is lower than the concentration near the wall (in boundary layer).

Dissolution of corrosion products from the surface and their transfer into the bulk of coolant is considered as a two-stage process. The first stage is molecular dissolution of deposits in some microlayer of coolant, the second stage is mass transport through boundary layer.

The mass flux of the dissolved corrosion products will be expressed by means of dissolution coefficient:

$$Q^{SOL} = k^{SOL} \cdot F \cdot S \quad (\text{kg/s}) \quad (4)$$

$$\text{where: } k^{SOL} = \chi \cdot (c_w - c_b) / (s(\chi \cdot F / 2G + 1)), \quad (1/s) \quad (5)$$

$$\chi = 1 / (1/k \cdot \rho_w + 1/\alpha \cdot h \cdot s), \quad (\text{kg/m}^2 \cdot \text{s}) \quad (6)$$

- c_w - solubility of corrosion products near the surface, (kg/kg)
 c_b - concentration of corrosion products in the bulk of coolant, (kg/kg)
 s - surface concentration of corrosion products, (kg/m²)
 F - surface considered (m²)
 G - coolant flow rate (, (kg/m³)
 k - coefficient of mass transfer through the boundary layer, (m/s)
 ρ_w - coolant density, (kg/m³)
 α - surface area of deposits, (m²/kg)
 h - rate of molecular dissolution, (kg/m².s).

Precipitation of corrosion products

Precipitation of corrosion products on primary circuit surfaces takes place when concentration of CP in bulk of flow exceeds the solubility in boundary layer. The flux of mass precipitated on a surface is limited by the rate of transfer through the coolant boundary layer:

$$Q^{CR} = k.F. \rho_w (c_b - c_w) = k^{CR}.F \quad (\text{kg/s}) \quad (7)$$

The coefficient of mass transfer through the boundary layer is given by the relation:

$$Sh = 0.0165.Re^{0.86}.Sc^{0.33} \quad (8)$$

where: $Sh = k.d/D$ - Sherwood's number (9)

$Re = U.d/\nu$ - Reynold's number (10)

$Sc = \nu/D$ - Schmidt number (11)

d - hydraulic diameter, (m)

U - coolant flow velocity, (m/s)

ν - kinetic viscosity, (m²/s)

k^{CR} - coefficient of precipitation, (kg/m².s)

Determination of pH_T solubility

For determination of pH_T , the concentration of chemical reagents (B(OH)₃, KOH, LiOH, NaOH, NH₃) and coolant temperature is taken into consideration. In the computer code CPPWR, it is possible to use the following data on solubility:

- solubility of Fe from magnetite determined by the fit model of Tremaine and LeBlanc /3/;
- solubility of Fe from mixed ferrites (Ni_xFe_{3-x}O₄) determined by the fit model of Lindsay /4/;
- solubility of Fe, Ni, Co from mixed ferrites determined on the basis of experimental data of Kunig and Sandler /5/.

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HIGH TEMPERATURE WATER CHEMISTRY MONITORING

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Abstract

Almost all corrosion phenomena in nuclear power plants can be prevented or at least damped by water chemistry control or by the change of water chemistry control or by the change of water chemistry. Successful water chemistry control needs regular and continuous monitoring of such water chemistry parameters like dissolved oxygen content, pH, conductivity and impurity contents. Conventionally the monitoring is carried out at low pressures and temperatures, which method, however, has some shortcomings. Recently electrodes have been developed which enables the direct monitoring at operating pressures and temperatures.

1. INTRODUCTION

In order to extend the operating life of the nuclear power plants and to avoid corrosion related degradation it is important to establish and maintain appropriate water chemistry conditions. This includes at least continuous monitoring of pH, conductivity and impurity levels, oxygen content and related corrosion potentials of construction materials at operating temperatures. Due to the complexity of the corrosion phenomena and the wide variations between plants, it is difficult to define one appropriate environment for all plants. Therefore water chemistry monitoring should incorporate the field experiments and the laboratory test results to extend the operating time of components.

The purpose of this paper is to describe the water chemistry monitoring system developed at the Technical Research Centre of Finland (VTT).

2. NEED FOR WATER CHEMISTRY MONITORING IN PREVENTION OF CORROSION

The reliable operation of components in nuclear power plants needs evaluation and understanding of long-term deterioration mechanisms of potentially critical components. Since the environment has an influence on the degradation of materials through corrosion it is necessary to use and further develop environment monitoring systems, Fig. 1.

In power plants extensive instrumentation and laboratory analysis programmes are applied to provide rapid and reliable diagnosis of water chemistry. However, at the moment chemical monitoring is applied mainly at low temperature, low pressure conditions or by using grab

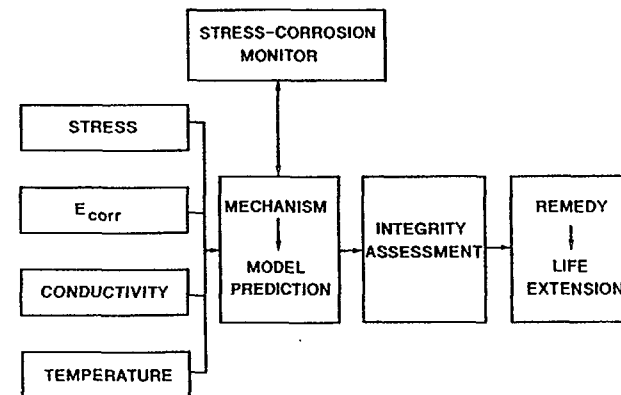


Fig. 1. Interaction of environment monitoring and the deterioration model to give an assessment of plant integrity and life extension /Ford et al. 1987/.

samples. More relevant information concerning the chemical environment could be obtained by using a flow-through cell for high temperature, high pressure measurements of pH, conductivity and electrochemical potentials, which indicate the presence of oxidizing elements in the water, Fig. 2.

2.1. pH-Measurements at High Temperatures

pH i.e. the activity of hydrogen ions is highly influenced by the temperature. Due to the nature of pure water, pH usually shifts towards neutral values at higher temperatures. Generally the pH of base solutions is decreased and pH of acid solutions is increased when temperature increases. This neutralizing effect is caused by the interaction between the water and the dissolved species. The resulting pH of the solution is highly dependent on the buffering capacity of the dissolved species. However, the pH-shift and its direction is difficult to predict or calculate in complicated, dilute solutions at higher temperatures. Therefore it is particularly useful to be able to measure pH.

2.2. Conductivity at High Temperatures

The conductivity of pure water increases with temperature. The reason for this is partly due to the dissociation of pure water itself and partly due to the increase in impurities dissolved at higher temperatures. Additionally the deposition of dissolved ions changes the conductivity of the solutions to some extent if the temperature decreases. These are the reasons why the conductivity in pure water at high temperatures cannot be evaluated reliably by using low temperature conductivity measurements.

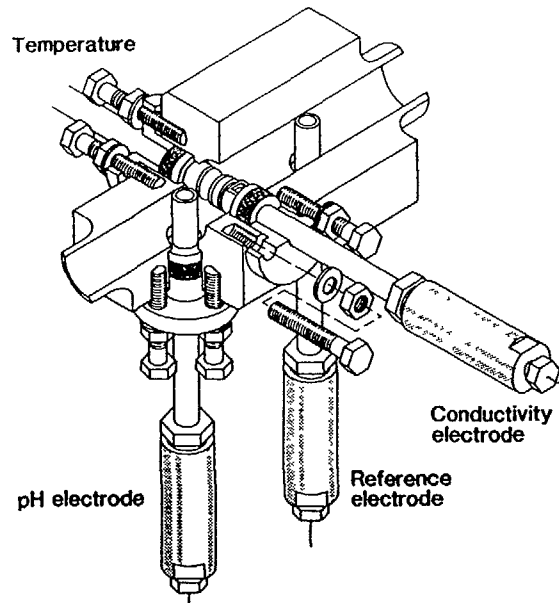


Fig. 2. Flow-through cell and electrodes for water chemistry monitoring.

2.3. Electrochemical Potentials at High Temperature

The electrochemical potential of a metal is a measure of the equilibrium reaction obtained between the surface and the environment. Because most metals form some kind of oxide layer on its surface in water containing solutions, the electrochemical potentials are mainly controlled by the oxygen content and the temperature of the environment.

3. HIGH TEMPERATURE MONITORING SYSTEMS

The major area of interest in material water reactions monitoring systems for high temperature and pressure environments is corrosion reactions. Most metals are unstable with respect to water and their utilization in water containing environments depends on the kinetics of their corrosion reactions. In many cases the reaction rates are so small that they permit practical application of the materials. However, corrosion reactions are dominating when the long term stability and integrity of energy and process plants are considered. In order to better predict the reliability of materials, the real service conditions should be known.

For the most common metals and alloys critical potentials for different corrosion processes has been determined by experimental laboratory tests. Thus pitting, crevice corrosion, stress corrosion and hydrogen embrittlement can be avoided if the metals potential is higher or lower than this critical potential in the specific environment. The methods to control corrosion potentials are twofold; either the chemical environment i.e. the redox-potential can be controlled, or the corrosion potential of the material can be controlled by external current supply i.e. anodic or cathodic protection.

External reference electrode systems, in which the electrodes themselves are housed in separate compartments maintained at ambient temperature but in operation pressure via solution bridges, have made the measurement of corrosion potentials in high temperature aqueous environments possible. However, the temperature gradient between the high temperature environment and the reference electrode at ambient temperature gives rise to a thermal liquid junction potential, which can be numerically corrected /MacDonald et al. 1979/.

Technical Research Centre of Finland (VTT) and Imatran Voima Oy (IVO) have jointly developed the on-line monitoring system for the power plant water chemistry monitoring under actual operating conditions, without pressure reduction or cooling of the sample flow. These flow-through measurement cells with electrodes have been in operation in the OECD Halden reactor since March 1987, Fig. 3, and in Loviisa PWR plants since June 1988, Fig. 4. At the end of 1989 monitoring of the water chemistry parameters in HDR-test reactor in Germany was started.

3.1. Structure of the Monitoring System

High temperature pH electrode

The body of the pH sensor is made of stainless steel and is designed to withstand high operation pressures and temperatures. A

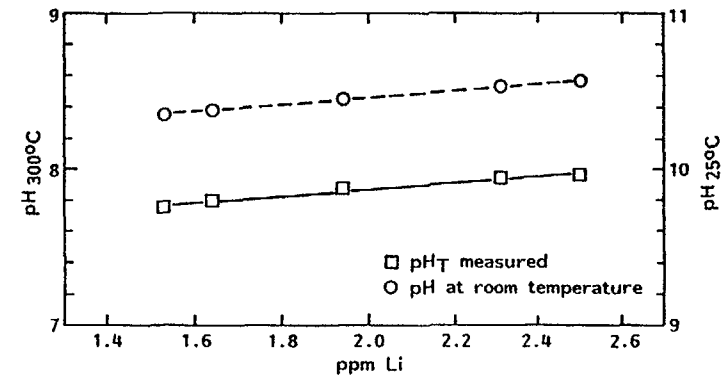
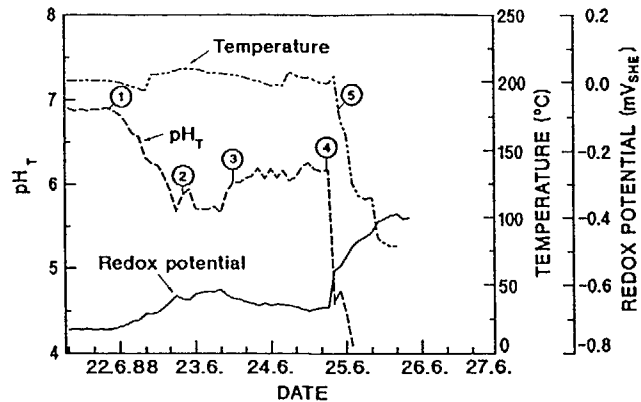


Fig. 3. Measurements at OECD Halden reactor. The effect of Li concentration on the pH at 300°C and at 25°C.



- 1 Ammonia supply stopped, the removal of cations with the primary water clean-up system and the degasification of the primary circuit water is started.
- 2 An equilibrium of 5 ml/kg H₂ is established.
- 3 The degasification of the primary circuit water is stopped and small amounts of ammonia is supplied to the primary circuit every three hours.
- 4 The reactor is subcritical and the boration of the primary circuit is started.
- 5 The cooling down of the primary circuit is started.

Fig. 4. The data from the monitoring system during shutdown at Loviisa 1.

classic pH-electrode, the glass electrode, is suitable for pH_T detection up to 120 °C. The use of stabilized zirconium oxide as a sensing membrane instead of the glass allows the pH detection up to 300 °C. The pH_T sensing with zirconia membrane is based on the selective diffusion of oxygen ions through the membrane and this limits the lowest operation temperature to about 150 °C. The pH_T measurement technique also needs, in addition the pH_T electrode, a stable, high temperature reference electrode.

High temperature reference electrode

The body of the silver/silver chloride reference electrode is made of stainless steel and is designed to withstand high operation pressures and temperatures. The salt bridge connecting the sensor with

the test solution is made of oxide powder saturated with the internal electrolyte. The internal electrolyte is usually a potassium chloride solution with a defined concentration. The entry of the internal electrolyte to the test solution is prevented by using porous ceramic plug, which separates the test solution from the salt bridge.

Conductivity electrode

The body of the conductivity electrode is made of stainless steel, and it can be used in high temperatures and pressures. The electrolytic conductivity is measured by the electrodes which are in contact with the test solution in such a way that the measured electrical conductance between the platinum plates can be related to the conductivity of the test solution. The cell constant of the electrode system can be changed allowing measurements in various test solutions.

3.2 Data Logging System

The data logging system consists of the following main parts seen in Fig. 5.

- measurement amplifiers
- personal computer with AD-converter
- hardcopy device (printer, plotter)
- software.

The pH, redox, conductivity, cell temperature and external temperature transmitters are included in the measurement electronics.

The measurement amplifiers usually are located near the flow-through cell, and the signals are transferred via triaxial cables from the electrodes to the electronics. The standard signals 4 - 20 mA are transferred from the measurement electronics via coaxial cables to the AD-converter, which is situated in the extension slot of the personal computer.

The software gathers and analyzes the data coming from the measurement electronics. The software runs on AT or compatible micro-computers under MS DOS -operation system and user interface. The software measures pH_T, redox, conductivity and temperature continuously and displays measured signals graphically on the screen, stores data on the hard disc, and, if necessary, outputs data to the printer.

4. CONCLUSIONS

The on-line water chemistry monitoring system has proven to give reliable and useful information over a very long measurement periods. The results obtained in PWR environments are used to study the differences in the water chemistry conditions during the steady state operation and transients like shutdowns. The water chemistry has shown to be important in order to control the activity buildup, especially during the chemical changes in the primary circuit water. In BWR

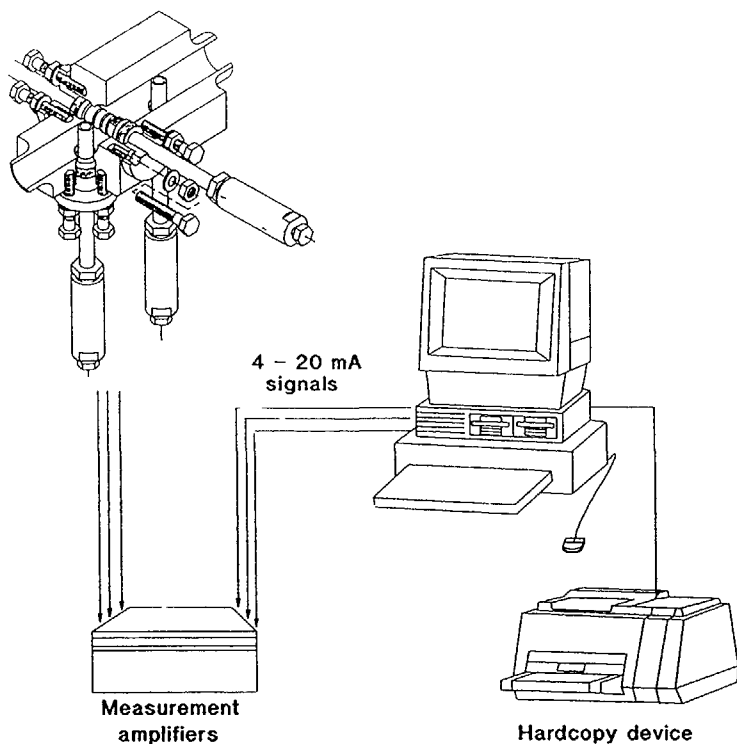


Fig. 5a. Data logging system.

environments the continuous monitoring of the redox potential and the conductivity of the coolant are important to avoid the stress corrosion incidents of sensitized materials.

Material testing in simulated reactor environments is necessary for further improvement of nuclear materials. Simulation of reactor environments can be difficult, especially when tests are carried out in small scale laboratory test loops where the coolant volume to the internal metal surface area ratio is different from that in real power reactors. In order to be able to simulate the reactor conditions, the local water chemistry conditions in specific locations of the reactor should be estimated or experimentally measured. Based on these parameters the simulation can be carried out.



Fig. 5b. The on-line monitoring system in operation in the sample line of the primary circuit in the Loviisa Power plant.

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COOLANT CHEMISTRY IN PRESSURIZED HEAVY WATER REACTORS—THE INDIAN EXPERIENCE

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Abstract

Salient features of the design of Indian PHWRs and the philosophy behind the primary coolant chemistry are described. Usefulness of carrying out PHT system hot conditioning during its light water commissioning is discussed. The three major aspects of chemical control viz (a) maintenance of a constant and higher coolant pH, (b) strict control of dissolved oxygen content by hydrogen injection during operation and (c) efficient bleed purification by passing through a filter and a mixed bed are described and their role in achieving satisfactory performance, particularly with reference to minimisation of corrosion and erosion of heat transfer surfaces resulting in fairly low boiler cabinet radiation fields is elaborated.

1 Introduction

There are four operating pressurised heavy water reactors (200 -235 MWe) in India (until 1988), while several others are under different stages of construction and commissioning. An advanced version of these reactors forms the basis of current design of 500 MWe PHWRs. All these units are of the pressure tube type, employing zircaloy-2 clad natural uranium dioxide fuel, using heavy water as the moderator as well as the coolant, but in separate circulating systems, which operate under different conditions of temperature, pressure and chemistry. The primary heat transport system comprises of multi metal surfaces, the major components being Carbon Steel, Zircaloy-2 and Monel-400. The philosophy behind coolant system chemistry is the same as in all other nuclear power reactors, viz, to minimise the out-of-core radiation fields by minimising the processes of corrosion and erosion of the heat transfer surfaces.

2 Hotconditioning

A pre-requisite for achieving this objective is Hot conditioning, of the primary heat transport system during its light water commissioning stage. After cleaning and degreasing the system surfaces, water maintained at pH 10 (by LiOH) and deoxygenated (by hydrazine) is circulated in the system in the temperature range of 220 - 240°C for about 10 to 15 days. Such a procedure results in the formation of a protective layer of magnetite (Fe_3O_4) especially on carbon steel surfaces. This minimises the further corrosion of the structural materials and acts as a check on crud inventory. The steady state crud concentration values have been observed to be < 0.01 ppm, with

some transient values during start up and cool down operations. The integrity of the magnetite film is due to a well regulated coolant chemistry and consequently results in a reduction of the activity transport to a low value and this contributes to lower levels of out-of-core radiation fields.

3 pH

As compared to PWRs or WWERs, the advantage in PHWRs stem from their separate moderator system to which boron is added and not to the coolant. This simplifies the coolant chemistry and in general permits a constant and higher pH of operation, which is mostly kept at 10 (25°C) by the addition of LiOH. The specific conductivity of the coolant normally ranges between 15 to 30 $\mu\text{s}/\text{cm}$. A pH of 10 at 25°C due to LiOH addition alone means a pH of 7.4 to 7.6 at 270 - 280°C, which generally is the operating temperature in our PHWRs. In terms of magnetite solubility, the pH and the temperature regimes ensure that the solubility of magnetite is nearly at its minimum (actually a little towards the right hand side of the minimum in the solubility Vs pH at 280°C curve for Fe_3O_4). With a positive temperature coefficient, the magnetite solubility increases in the coolant channel from the inlet to the outlet, thus reducing the chance of deposition on the fuel clad surface. It may be mentioned that the adsorption of Co(II) on magnetite is maximum and constant in the pH range. This would mean that the Co adsorbed by the magnetite layer on the fuel clad surfaces has a chance to get activated. On the other hand with the solubility gradient of magnetite in a fuel channel, Co(II) is expected to be in the suspended or soluble form in the coolant. In short, the operating pH takes care of the integrity of the magnetite film formed during hot conditioning/normal operation, keeping the magnetite solubility in an appropriate direction and ensures a lower residence time for Co(II) in the core.

4 Dissolved oxygen

Another chemical control that is strictly adhered to is that of dissolved oxygen in the coolant. In a closed system, water radiolysis leads to generation of OH radicals which end up as dissolved oxygen. As mentioned earlier, the PHT system in our operating PHWRs have a large surface area of Monel-400 (Steam generator tubes) in contact with coolant D_2O . The corrosion of this alloy at high temperatures is adversely influenced by dissolved oxygen. In view of the high Ni content of this alloy, Monel surfaces are one of the major sources of cobalt in the system. Thus it is essential to maintain a low level of dissolved oxygen (10 ppb) so as to minimise the corrosion of Monel and hence the input of cobalt. OH radicals can be scavenged by increasing the partial pressure of dissolved hydrogen in the coolant. In other words by injecting hydrogen, the recombination reaction with the dissolved oxygen can be promoted. In our PHWRs, hydrogen injection to the level of 10 to 15 ml at STP/Kg of D_2O has been found to keep dissolved oxygen at 10 ppb. Following the development and good performance of Incoloy-800 as the steam generator tube material, it has been decided that in all our future reactors under construction, Monel-400 will be replaced with this alloy. Incoloy-800 is not all that susceptible to dissolved oxygen transients at high temperatures and with a lower Ni content, will have less cobalt. It is also to be noted that hydrogen addition at the levels mentioned to the coolant does not influence the solubility of magnetite, since it has been shown that the solubility is dependent on cube root of hydrogen partial pressure.

The third aspect of the coolant chemistry in our PHWRs relates to its purification. A part of the coolant (<1% of coolant inventory) is withdrawn from the circuit, is cooled and then passed through a filter and mixed resin bed. In order to keep the pH of the coolant constant, Li^+ form of the cation exchanger is employed, while OD^- form of the anionic resin ensures no degradation of isotopic purity. The use of organic ion exchangers is one cause for a chemical transient, since the intrusion of any of the resin fines into the system will upset the chemistry due to thermal and radiation degradation.

5 Indian Experience

Against the above background, the experience of coolant chemistry in our PHWRs has been very satisfactory. Chemical transients are rare with respect to pH, dissolved oxygen and resin intrusion. More important is the fact that the radiation fields around the steam generator cabinets, measured 24 hours after a shut down, are fairly low and constant (300 to 500 mr/hr). On-line monitoring of the outer surfaces (over the insulation) of the PHT piping indicates that the major contributing radionuclide to the activity is ^{60}Co and occasionally fission products, as in other reactor types. Typical specifications for chemical control of the coolant are given in Table I.

Given the same Coolant Chemistry, it is expected that the radiation field build up on the out-of-core surfaces will be less than what is currently observed subsequent to the replacement of Monel-400 by Incoloy-800 in all our future reactors.

Typical chemical composition of crud samples from Indian PHWRs is given in Table II.

In PHWRs, one might envisage a leaky fuel channel in an accident situation. High pH of the coolant ensures a lower partition factor for radio iodines, between the liquid phase and the ambient environment into which the leak might percolate.

TABLE I CHEMICAL CONTROL SPECIFICATIONS FOR PHT SYSTEM

Parameter/ Constituent	Sampling point	Sampling frequency	Range/limit	Remarks
Isotopic purity % W/W D_2O)	Main System	3/week**	95% minimum	From reactivity consi- derations
Specific conductivity at 25°C	-do-	3/week	30 micro Siemens/cm maximum	Specific conductivity limited by the concentration of lithium hydroxide (LiOH) maintained in the coolant for keeping its (pH) within specified limits)
pH	-do-	1/day	Between 10.0-10.5*	Adjusted with lithium hydroxide (LiOH). This is the optimum pH range for least corrosion of the carbon steel in the system.
Ammonia	-do-	3/week	0.5 mg/l maximum	To minimise corrosion of monel boiler tubes in the presence of oxygen.
Chloride	-do-	3/week	0.3 mg/l maximum	To minimise possible stress corrosion.
Fluoride	-do-	1/month	0.05 mg/l maximum	Higher concentrations of fluoride can have a corrosive effect on zircaloy tubes and fuel cladding.
Crud	-do-	1/week	0.1 mg/l maximum for steady operation	Circulating crud gets activated in the core and will get deposited on the fuel bundles and on the PHT system surface.
			1.0 mg/l maximum before applying nuclear heat during start-ups	The former affects heat transfer efficiency and the latter leads to higher radiation field in shut-down and accessible areas.

TABLE I (cont)

Parameter/ Constituent	Sampling point	Sampling frequency	Range/limit	Remarks
Dissolved oxygen	-do-	3/week	10 micro grams/l during steady operation*	Higher values of oxygen damages the protective magnetite layer and increases the corrosion rate of monel boiler tubes. Both will lead to problems of activity transport
Dissolved deuterium	-do-	1/week	Between 3-20 ml/l of D ₂ O at S T P	Maintained by injecting hydrogen to the system when pressurised. The purpose is to maintain the equilibrium concentration of dissolved oxygen within specifications
Total dissolved gases excluding helium	-do-	1/week	50 ml/l of D ₂ O maximum	Higher concentrations of dissolved gases can cause cavitation of pumps. Degassing system will be operated when the dissolved gas concentration exceeds 30 ml/l D ₂ O
Gross Beta-Gamma	Outlet of ion exchange column	1/week	Activity in main system Activity in ion exchange outlet = 10 (minimum)	This ratio gives a measure of the efficiency of removal of radioactivity by ion exchange purification

* If the limit exceeds the value, it shall be brought back below the limit in 72 hours, failing which the reactor shall be shut-down

** This is applicable for equilibrium core only. For fresh core the number is higher and would have to be assessed

TABLE II CHEMICAL COMPOSITION OF CRUD SAMPLES FROM AN INDIAN PHWR

S NO	Source	% of total metals in oxides	% of metals in oxides			
			Fe	Ni	Cu	Co
1	Circulating	70.4	53.3	8.0	6.9	2.2
2	In core	63.0	41.2	8.6	12.7	0.5
3	In core	73.4	38.7	13.2	20.9	0.6
4	Out of core	66.7	33.1	9.1	24.1	0.4
1	Reactor power steady at 180 MWe for 44 days prior to this sampling					
2	Sampled immediately after the reactor trip as scheduled from the power level of 180 MWe					
3	Sampled 2 hrs after the reactor trip					
4	Sampled 25 hrs after the reactor trip					
a)	Presence of Ni _x Fe _{3-x} O ₄ is indicated where x varies from 0.3 to 0.65					
b)	Presence of Cu is significant					

GOOD WATER CHEMISTRY PRACTICES FOR PHWRs

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Abstract

Due to its close relationship to man-rem problems, primary coolant chemistry control plays a dominant role in the economic and efficient operation of a PHWR. Good water chemistry practices are therefore tuned currently towards the goal of (a) reducing man-rem for occupational personnel, (b) achieving plant life extension (PLEX) for avoiding capital cost of new plant constructions and (c) reducing radiolytic gas generation and escape of fission products under accident conditions. Keeping this in view, water chemistry regimes compatible with the core, steam generator tube and structural materials are described in details. Various palliatives for an effective control of the source and receipt terms for radioactivity, viz (a) selection of the proper coolant system structural materials, (b) PHT system hot conditioning prior to commissioning, (c) water chemistry dependence through a high and narrow range pH control ($\text{pH}_{\text{ZSO}} 10.4 \pm 0.2$), (d) increased coolant purification and (e) occasional dilute chemical decontamination are discussed.

1 Introduction

The economic and efficient operation of a PHWR is principally dependent on the water chemistry practices. Though Engineering, Physics, Metallurgy and other related disciplines do contribute towards the operation, Chemistry is dominant because of its close relationship to Man-rem problems. Current water chemistry practices are thus tuned towards this goal of reduction of man-rem for occupational personnel. Plant life extension (PLEX) is sought after by reactor operators to reduce capital costs of new reactor constructions. Chemistry is the only solution to PLEX. Radiolytic gas generation and escape of fission gases under accident conditions seem to be related to water chemistry practices⁽¹⁾. Hence the balancing of water chemistry with reactor operation should also consider the factors such as preoperational, operational and LOCA conditions.

The materials that go to make up a reactor should meet the criteria of corrosion resistance, neutron economy, high tensile strength and hardness under heat transfer and radiation environments. A typical list of the materials is given in Table I and can be further classified as core, SG and structural materials. The water chemistry regimes compatible with each of the three types of reactor materials are discussed below.

TABLE I Materials of construction in PHT system of PHWRs

Material	Location	Nominal compositions	Desirable low impurity levels
Zircaloy 2)	Zr Sn 1.5%	Nitrogen 20-45 ppm
Zircaloy-4) In core) (fuel clad,) coolant) tubes)	Zr Sn 1.5% (Fe 0.18% Ni 0.007%, Cr 0.07%	
Zirc Niobium alloy)	Zr, Nb 2.5%	
Carbon steel	System piping headers and feeders	Fe, C 0.2%, Si 0.15%, Mn 0.6%, S 0.05%, P 0.04%	Cobalt 0.006% (max)
Stainless/High alloy steels	Pumps	Fe, Cr 5-20%, Ni 0-10%, C 0.03-0.1%, Si 0.3-0.8%, Mn 0-15%, S 0-0.02%, P 0-0.2%	-
SS 400 series	End fittings	Fe, Cr 4-18%, Ni 2.5% (max), C 0.15-0.2%	-
Monel-400)) Steam Gene-	Fe 2.5%, Ni 63-70% Cu (bal)	
Inconel-600) rator tubes))	Fe 6-10%, Ni 72%, Cr 14-17%	Cobalt 0.05% (max)
Incoloy-800))	Fe (bal), Ni 30-35% Cr 19-23%	
Stellites	Valve seats	Co 50-60%, Cr 20-33%, W 5-20%, Ni 0-13%, Mo 0-6%, C 0-2.5%	being replaced by non cobalt based alloys

2 Water chemistry regime compatible with core material

PHWRs use Zry-2, Zry-4 and Zr-Nb alloys because they are highly corrosion resistant due to the formation of thin protective oxide films ZrO_2 ($n < 0.05$) layer following cubic rate law in the pre-transition and linear rate law in the post transition periods. Dissolved O_2 in the presence of radiation is known to enhance Zircaloy corrosion by disrupting the protective film. Radiolysis enhanced by local boiling could provide this oxidizing environment. Radiolytically produced D_2 and H_2/D_2 injected to suppress radiolysis (3-10 cc/kg D_2O) can result in increased hydrogen absorption resulting in the formulation of radially oriented zirconium hydride ($\text{ZrH}_1.5$) platelets thereby affecting the mechanical integrity.

Chemical impurities like Al and N in zircaloy are kept at very low levels to ensure that enhanced corrosion due to them is kept within acceptable limits.

PHWR design feature allows on-line refuelling. It has facility for failed fuel detection and removal of fuel bundles as soon as the clad leak occurs. The fuel failures could be caused because of clad-coolant interaction; pellet-clad interaction, mechanical and power ramp factors apart from manufacturing defects. Strict hydrogenous material control in the fuel and low burn-up of PHWR fuel has alleviated hydride problem from the fuel side and PCI failures. The absence of correlation between bundle power and the defective fuel bundle has not established overstraining of fuel sheaths due to high bundle power⁽²⁾. Thus the chemistry with respect to the core materials in PHWRs should look at only the long term compatibility of the coolant tubes with the coolant and the integrity of the clad with respect to clad-coolant interaction. Failed fuel in a PHWR core has a direct bearing on man-rem problem if it is not detected and removed. Gaseous fission product and radio iodine monitoring are used for detection while DNM is used for location of the failed fuel. While the efficiency of delayed neutron monitoring (DNM) versus channel r monitoring of fission gas iodines is under debate, one should keep in mind that man-rem problem is directly proportional to the time of existence of failed fuel in the core. This issue has no relationship to good water chemistry practices but it can contribute to the build-up of fission product radioactivity on out-of-core oxide films.

The good water chemistry practices to meet the above requirements are:

- * controlled dissolved O₂ <10 ppb.
- * Dissolved H₂ in the range 3-10 cc/kg D₂O, pH < 10.7 (25° C) (higher pH may result in thicker oxide film, problem of lithium hide out and generation of differential chemistry regimes) and
- * pH control over a narrow range of 10.3 - 10.7 to minimise corrosion product residence time in the core.

3. Water chemistry regime compatible with steam generator tube materials

It is worthwhile to discuss on the corrosion characteristics of steam generator tube materials because their integrity is very important for the efficient operation of the plant. Monel-400 has been used in several operating PHWRs. It is felt to be generally free from stress corrosion cracking. However, it can corrode significantly under oxygenating conditions or under localised boiling conditions permitted in the recent designs of PHWR core, where it is more difficult to suppress the radiolytically produced dissolved oxygen. The service performance of Monel-400 in commercial PHWRs has been excellent. Inconel-600 was chosen as SG tube material, primarily because of its excellent resistance to chloride induced transgranular stress corrosion cracking and because it has low corrosion rates even in oxygenated water. However, Inconel-600 with its high Ni content is susceptible to intergranular stress corrosion cracking. Incoloy-800 has been chosen as SG tube material in the later and advanced PHWRs mainly because of the following reasons: a) better resistance to stress corrosion cracking in high purity

water, b) better resistance to intergranular corrosion caused by pH excursions on the acidic side during regular operation or to the acidic chemical cleaning solutions, c) less contribution to radiation fields and d) resistance to localised corrosion in concentrated caustic or phosphate solutions as good as that of Inconel-600. Experience with Incoloy-800 steam generator tube material has been generally very good. However, there is a slight disadvantage in using Incoloy-800. Its thermal conductivity is lower than that of Inconel-600.

Tubesheets are either carbon steel or low alloy steel overlaid with a nickel alloy on the primary side. Tube supports in the operating steam generators are all made of carbon steel for fresh water cooled stations and type 410 stainless steel and Inconel-600 for sea water cooled stations. Carbon steel is used for the shell and head of all PHWR steam generators.

The choice of nickel based steam generator tube materials requires greater attention with respect to cobalt content because of the very large surface areas exposed and the long lived gamma emitting radioactive isotopes getting generated. Thus it turns out that low dissolved oxygen with pH₂ in the range 10 should be compatible with the SG tube material on the primary side.

4. Water chemistry regime compatible with structural materials

Plant radiation levels are mainly borne by the carbon steel piping feeders, headers etc. They come in the way of shut down maintenance⁽⁴⁾. The radiation field itself is due mainly to ⁶⁰Co and ⁵⁸Co though fission products and ⁶⁵Zn have significantly contributed in some specific reactors.

Carbon steel, being the major out-of-core constructional material of a PHWR, produces two-layer oxide in a chemically reducing environment. The inner layer contains crystals of precipitated magnetite. The radioactive corrosion products arriving at the out-of-core surfaces diffuse down the pores of the inner layer and are incorporated firmly. Coprecipitation along with the inactive corrosion products and surface crud deposition tend to build up activated corrosion product radioactivity in the outer layers; the source of radioactive corrosion product being that released from the fuel surface. The source term can be effectively controlled by a suitable structural material selection and by revising the concentration of cobalt (⁵⁸Co).

1. Carbon steel	0.015% reduced to 0.006%
2. Ni alloys	0.15% reduced to 0.005%
3. Stellite- 6	replace with Colmonoy - 4 Colmonoy - 5 Colmonoy - 440 C Deloro - 50

4.1 Increased coolant purification

Another mode of source term control is by increased coolant purification. The general reduction in the inventory of dissolved corrosion product and crud occurs due to increased PHT purification circuit flow. While

this factor assists in reducing the radiation fields by minimising the basic inventory of metals in the coolant, it does not eliminate the generation of metals in coolant. Hot filtration using magnetic and graphite filters are only different technologies employed besides the conventional Ion exchange filtration.

4.2 Dependence on chemistry

In the temperature range 250 - 315°C and pH₂s region 10.3 - 10.7, the solubility of magnetite shows a strong positive temperature coefficient. Hence the core resident time of the crud is minimised by reducing the fuel deposit thickness to a region of 10 - 40 mg/m². Hence, pH control over this narrow range is mandatory. The importance of pH control from the point of view of general corrosion and release of corrosion product is only of secondary nature. However, the high pH excursion is deleterious to the zirconium oxide film and also causes oxidising radiolysis. Hence pH > 10.7 should be avoided.

4.3 Dissolved O₂ effects

The oxygen excursion has a direct influence on CS pitting and corrosion apart from the effects mentioned under the other materials. Its effect will only be in the form of increase in circulating crud concentration leading to an addition of source term. Hence, dissolved oxygen must be restricted to 5 µg O₂/kg D₂O by H₂ injection.

The source term and recipient term for the radioactivity are further controlled by exercises like preconditioning/prefilming, metal ion injection passivation (MIP) and cyclic decontamination.

4.4 Preconditioning

Hot conditioning has been one of the regular exercises to build up oxide layers on CS surfaces without the incorporation of radioactive atoms prior to startup. It is believed to reduce radiation build up during actual operation. An improvement in the quality of magnetite layer is achieved by carrying out hot conditioning under controlled chemistry conditions and system parametric conditions as given below.

pH (at 25°C)	10 - 10.5 using LiOH
Dissolved oxygen	<5 ppb (achieved by addition of required amount of hydrazine)
Chloride	< 0.3 ppm
Temperature	235 - 240°C

A comparison of adherent magnetite thickness obtained during PHT system hot conditioning of Indian PHWRs is given in Table II. Introduction of EDTA hotconditioning and/or Zinc injection passivation (ZIP) could provide

TABLE II COMPARISON OF ADHERENT MAGNETITE THICKNESS OBTAINED DURING PHT SYSTEM HOTCONDITIONING OF INDIAN PHWRs

Station	Average Temperature during hot conditioning (°C)	Duration of hot conditioning (days)	Adherent magnetite thickness (micron)
RAPS-1	ca 185	17	0.17
RAPS-2	ca 200	20	4.3
MAPS-1	ca 230	13	0.71
MAPS-2	ca 230	11	1.33
NAPP-1	ca 240	10	1.65

a solution for reduction of radioactivity on out-of-core surfaces. A conditioning step may also become mandatory subsequent to each decontamination before going to power.

4.5 Decontamination

Frequent decontamination removes the deposited radioactive corrosion products from out of core surfaces enabling

i. Low radiation penalty to personnel to carry out maintenance activities.

ii. Reduced radiation exposure to O/M personnel during subsequent regular plant operations.

iii. As a result of increase in the efficiency of preventive maintenance of critical components, plant life extension is achieved.

iv. In systems where fuel failures have been dominating the radiation levels, decontamination is the only solution.

In order to develop decontaminants for various surfaces systematically, a regenerating system was investigated at Water and Steam Chemistry Laboratory, Kalpakkam. This system, based on ion exchange (IX), could effectively remove Iron and other cations while regenerating the complexants and organic acids. Dissolution of oxides formed on inactive carbon steel coupons (90%) was carried out by the dilute chemicals with IX system within a time span of 6 to 24 hours.

TABLE III CHEMICAL CONTROL PARAMETERS FOR THE PRIMARY HEAT TRANSPORT SYSTEM OF INDIAN PHWRs

Chemical Parameter	Steady state operation
1 Specific conductivity ($\mu\text{s}/\text{cm}$) at 25°C	< 30
2 Dissolved oxygen* ($\mu\text{g}/\text{kg}$) of D_2O	< 10
3 pH at 25°C*	10 - 10.5
4 ^{131}I (Bq/kg)*	< 3.7×10^6
5 Crud (mg/l)	< 0.1
6 Chloride (mg/l)*	< 0.3
7 Dissolved deuterium (ml/l of D_2O)	2.0 - 10.0
8 Dissolved gases ($\text{D}_2 + \text{N}_2$), ml/l of D_2O	< 50

* Mandatory specifications

Active coupons (CS and Monel) and cut portions of SS pipe exposed to the PHT system of an Indian PHWR were decontaminated in laboratory experiments in a dynamic glass loop with various formulations as shown below

DF(FP/ACP)	CS	Monel	SS
Dilute chemical with IX	6-10 40	4-6 10	-
Reducing agent & complexing agent with make up	20 30	1.5-2.0 2.0	-
AP (H^+) OX	-	2-2.5	2.5-3.0

As the table indicates, the dilute chemical decontaminants worked satisfactorily for both CS and Monel surfaces. The activities and the metals dissolved could be completely held on the IX column. The formulation chemicals could also be removed by an IX system thereby eliminating the washing step. The decontamination procedures of this type could be periodically employed to lower radiation levels in the PHT system.

5 Conclusions

Water chemistry regimes, dealt with earlier to suit various constructional materials converge into a unified Technical Specification as shown in Table III. While Table III deals with operational technical specification limits, the action levels set on pH is given as ± 0.2 units around an average of 10.4 (pH 25°C) to ensure better control of activity transport. The effects of nuclear radiations, principally neutrons and gamma photons on corrosion products, water and water additives has to be assessed so that the chosen water chemistry and materials of construction results in a system in which the corrosion of materials and the activated corrosion product are both minimised.

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PRECONDITIONING OF PRIMARY HEAT TRANSPORT SYSTEMS OF PHWRs – THE INDIAN EXPERIENCE

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Abstract

With a view to obtain an adherent, uniform and protective coating of magnetite (Fe_3O_4) on carbon steel surfaces and to reduce the crud inventory in the primary coolant system for minimising activity transport and man-rem problems during subsequent post operational periods, PHT systems of PHWRs are pre-conditioned by circulating demineralised light water under controlled temperature (~ 235 - 240°C) and water chemistry environment conditions (pH 9.5-10.5; Dissolved Oxygen < 5 ppb; $\text{Cl}^- < 0.3$ ppm.) Results of the hot conditioning evaluation for magnetite coating thickness during a typical process followed at MAPS-2 are discussed and compared with those obtained earlier at MAPS-1 and later at NAPP-1.

1. Introduction

The Primary Heat Transport Systems of PHWRs are preconditioned by circulating demineralised light water under controlled chemistry environment as a first step towards commissioning of the reactor. This process called 'hot conditioning' is carried out with the following objectives from water chemistry point of view.

- a) To obtain an adherent, uniform and protective coating of magnetite (Fe_3O_4) on the carbon steel surfaces, which minimises its further corrosion. Other structural materials of the primary system are also exposed to high temperature and high pressure water for the first time.
- b) To reduce the inventory of crud in the PHT system, thus minimising activity transport problem during subsequent reactor operations after criticality and man-rem problems during shut-down maintenance.

The PHT systems in Indian PHWRs have been provided with dynamic bypass autoclaves with stringers containing CS coupons for monitoring the progress in the build-up of magnetite coating. Hot conditioning evaluations were carried out on the basis of such studies.

2. Chemistry

The optimum water chemistry and system parametric conditions required for PHT system preconditioning are given as under:

pH (at 25°C)	: 10 - 10.5 using LiOH
Dissolved oxygen	: < 5 ppb (achieved by addition of required amount of hydrazine)
Chloride	: < 0.3 ppm
Temperature*	: $235 - 240^\circ\text{C}$

* Preconditioning operation's zero time is when the PHT system temperature goes above 185°C .

The alkaline pH and low dissolved oxygen reduce the rate of corrosion of carbon steel surfaces. Chloride control is to prevent the pitting corrosion of carbon steel. System temperature is a critical parameter and it needs to be as close to 235 - 240°C as possible for optimum formation of magnetite layer in a reasonable period of time. Higher thickness of the coating is expected to render better protection. Its characteristics are uniformity and fine grain size. Work from USSR indicates that the presence of EDTA in the operation is helpful in this regard. This has not been employed during five preconditioning operations carried out in India.

3. Preconditioning process

A typical preconditioning process followed in Unit # 2 of Madras Atomic Power Station (MAPS) is described below. An adherent uniform and protective magnetite film of $1.3 \mu\text{m}$ thickness was formed on the CS coupons surfaces, which is taken as an indicator for CS system surface.

During the first attempt at hot conditioning run and when the system was above 185°C for 12 hrs, there was a trip of all the eight primary coolant pumps due to the system leaks and the temperature remained between 185°C and 36°C for 69 hrs. Hot conditioning run was attempted for the second time and then during the entire period of hot conditioning of 11 days the temperature remained at 235°C . The pH was between 10 and 10.2 except for the initial 19h when it was at 9.8. Dissolved oxygen was always below 5 ppb and the crud values as measured by sampling were low and below 0.5 ppm except at the beginning of the run. Due to system leaks in the initial stages, hydrazine addition and removal by ion-exchangers was required frequently. However, the concentration of ammonia in the system could not be brought below 5 ppm during the entire period even though a mixed bed ion exchanger was in service throughout the period. The magnetite film thickness reached $68 \text{ mg}/\text{dm}^2$ ($1.3 \mu\text{m}$) just in 100 h and did not increase very significantly thereafter. Photomicrographic examinations showed that the surface coverage of the magnetite film increased progressively during hot conditioning.

4. Indian experience

A comparison of adherent magnetite thickness obtained during PHT system hot conditioning of Indian PHWRs is given in Table I. As compared to MAPS-2, preconditioning earlier in MAPS-1 gave a magnetite coating thickness of $0.7 \mu\text{m}$ while recently in Unit # 1 of Narora Atomic Power Project, a coating thickness of $1.5 \mu\text{m}$ was obtained.

In addition to carbon steel surfaces, coupons of other constructional materials, viz., Monel-400/Incoloy-800, Zircaloy-2, Stainless steel 304,

TABLE I COMPARISON OF ADHERENT MAGNETITE THICKNESS OBTAINED DURING PHT SYSTEM HOTCONDITIONING OF INDIAN PHWRs

Station	Av Temperature during hot conditioning(C)	Duration of hot conditioning (days)	Adherent magnetite thickness (micron)
RAPS-1	ca. 185	17	0.17
RAPS-2	ca. 200	20	4.3
MAPS-1	ca. 230	13	0.71
MAPS-2	ca. 230	11	1.33
NAPP-1	ca. 240	10	1.85

Stainless steel 403 and Zr-2.5% Nb were also exposed to PHT system environments during the above mentioned hot conditioning processes. Metallographic and microstructural investigations on exposed coupons of all the above materials indicated that there were no undesirable traits and deleterious structural changes due to exposure to the PHT system environment during hot conditioning.

5. Conclusions

It has been the experience, in Indian PHWRs, that if the temperature is 200°C, the preconditioning run will be prolonged and the magnetite layer will be thin. This is not advisable. If a higher level of dissolved oxygen is present under such non-optimum conditions, the base metal loss will be comparatively high and considerable loose deposit will result.

Preconditioning of the PHT system in PHWRs carried out under optimum temperature and chemistry conditions mentioned earlier will be very beneficial to system during reactor operation from corrosion and activity transport points of view.

COOLANT CHEMISTRY IN NUCLEAR POWER PLANTS IN THE REPUBLIC OF KOREA

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Abstract

The primary coolant radioactivity control of the operating power reactor core is an essential countermeasure for radiation exposure reduction.

We have presented the crud analysis results of the spent fuel rod cladding surface, analysis results of the defected fuel element and the amount of tramp uranium, and the analysis results of sipping tests.

As we have compared the our analyses results with the coolant histories of the end of cycles, we can see that the amount of crud materials and the number of defected fuel elements are closely related to the reactor water control.

1. Introduction

The reliability of many system materials at nuclear power plants depends on primary coolant control.

The reliability and safety are achieved by using proper cladding and structure materials and special measures are taken to prevent dangerous corrosion products, fission products release and other processes.

The primary coolant radioactivity control is an essential countermeasure for radiation exposure reduction.

We have measured the radioactivity of primary coolant to analyze the radiation source.

The crud samples have been taken from the spent fuel rod cladding surface of Korea Nuclear Unit 1 and analyzed the radioactivities of isotopes.

The measurement and analysis of fission products in the primary coolant of nuclear power reactor have been carried

out at full power operating condition of pressurized water reactor. We have analyzed the defective fuel element and tramp uranium.

We have analyzed the sipping test results of spent fuel elements and discussed on the water quality control record.

2 Coolant chemistry

2.1 Crud analysis

The crud samples have been taken from the spent fuel rod cladding surfaces of Korea Nuclear Unit 1 and analyzed the radioactivities of isotopes by using computerized multichannel analyzer. The summary of the analysis results have been shown in the Table 1. The one of analysis results of each crud sample has been shown in Table 2.

The radioactive materials of the corrosion products are mainly the Co-60, Mn-54, Co-58, and Cr-51 isotopes. The fission products are Zn-95, Nb-95, Ru-103, Cs-137, Cs-134, Sn-113, and Sb-124 isotopes.

The crud analyses of Korea Nuclear Unit 7 and 8 have been carried out and the analyses results have been shown in Table 3 and 4.

The radioactive materials of the corrosion products are also Co-58, Co-60, Fe-59, Mn-54, Cr-51, and Zr-95 isotopes.

2.2. Analysis of defected fuel and tramp uranium

The measurement and analysis of fission products in the primary coolant of nuclear power reactor have been carried out at the Korea Nuclear Unit 1. The selected results of measured activity have been shown in Table 5.

The analysis results [1] of defected fuel and tramp uranium deduced from comparison of the calculated activity with measured activity have been shown in Table 5.

The average value of defected fuel for cycle 3 of Korea Nuclear Unit 1 is 9.7 ± 0.8 elements.

Table 1. SPENT FUEL CRUD ANALYSIS RESULT

Sample	Sample Location		CRUD			Corrosion Products		
			Weight (g)	Surface Concentration (mg/dm ²)	Thickness (mil)	Co-58	Mn-54	Co-60
BKG	SFT water	-	0.0003	-	-	1.56E-4	2.40E-5	1.53E-4
1	C-3	5-6	-	-	-	1.78E-4	3.18E-5	2.20E-4
2	C-32	4-5	-	-	-	2.25E-4	4.34E-5	3.11E-4
3	A-08	3-4	0.0009	1.09	0.0036	1.14E-4	1.11E-4	7.94E-4
4	A-08	2-3	0.0015	2.18	0.0072	1.09E-4	7.16E-5	6.07E-4
5	A-03	2-3	0.0010	1.27	0.0042	1.18E-4	9.47E-5	8.23E-4
6	A-03	1-2	0.0011	1.45	0.0048	1.34E-4	7.43E-5	7.84E-4
7	A-04	4-5	0.0009	1.09	0.0036	1.24E-4	1.13E-4	1.13E-3
8	A-04	3-4	0.0006	0.54	0.0018	1.33E-4	9.15E-5	8.68E-4
9	A-10	3-4	0.0004	0.18	0.0006	1.34E-4	9.54E-5	1.46E-4
10	A-10	2-3	0.0003	0.54	0.0018	1.30E-4	6.11E-5	5.09E-4
11	A-18	3-4	0.0003	0.18	0.0006	1.52E-4	1.15E-4	4.56E-4
12	A-18	2-3	0.0007	.	.	1.45E-4	1.63E-4	5.77E-4
13	A-36	2-3	0.0004	.	.	1.27E-4	9.20E-5	4.65E-4
14	A-36	1-2	0.0004	0.73	0.0024	1.29E-4	1.38E-4	6.60E-4
15	B-10	2-3	0.0003	0.18	0.0006	1.83E-4	4.00E-4	1.40E-3
16	B-10	1-2	0.0004	0.18	0.0006	1.25E-4	1.05E-4	3.23E-4
17	B-21	2-3	0.0003	.	.	1.45E-4	2.00E-4	8.55E-4
18	B-21	1-2	0.0007	0.18	0.0006	1.40E-5	9.40E-5	5.48E-4
19	B-27	6-7	0.0004	.	.	1.36E-4	7.48E-5	3.76E-4
20	B-27	1-2	0.0003	0.73	0.0024	1.99E-4	5.44E-4	2.15E-3
21	B-28	6-7	0.0419	11.07	0.0364	2.98E-4	5.61E-4	3.01E-3
22	B-28	1-2	0.0003	.	.	1.46E-4	1.26E-4	5.68E-4
23	B-33	6-7	0.0003	75.64	0.2481	8.91E-4	7.56E-4	5.78E-3
24	B-33	4-5	0.0003	.	.	1.84E-4	1.21E-4	4.69E-4
25	D-01	4-5	0.0004	.	.	3.2 E-4	2.23E-4	7.10E-4
26	D-01	2-3	0.0003	.	.	3.15E-4	3.27E-4	9.70E-4
27	D-18	5-6	0.0004	0.18	0.0006	2.15E-4	1.23E-4	3.39E-4
28	D-18	3-4	0.0003	.	.	2.95E-4	1.83E-4	6.0 E-4
29	D-29	6-7	0.0007	0.73	0.0024	2.65E-4	1.30E-4	3.9 E-4
30	D-29	3-4	0.0005	0.36	0.0012	3.0 E-4	1.45E-4	5.0 E-4
31	C-36	5-6	0.0005	0.36	0.0012	4.25E-4	1.60E-4	6.58E-4
32	C-06	4-5	0.0003	.	.	3.98E-4	1.25E-4	4.78E-4

Table 1 Continued

Sample	Fission Products							Remark
	No	Ce-144	Ce-141	Sn-113	Ru-103	Sb-124	Zr-95	
BKG	1.40E-3	4.87E-5	1.30E-5	7.15E-5	3.28E-5	5.17E-4	1.00E-3	-
1	1.40E-3	4.83E-5	1.40E-5	7.53E-5	3.35E-5	5.06E-4	1.02E-3	Cycle 1
2	1.51E-3	5.04E-5	1.64E-5	9.34E-5	4.40E-5	5.63E-4	1.14E-3	//
3	1.01E-3	2.65E-5	9.14E-6	4.72E-5	2.65E-5	3.57E-4	7.69E-4	//
4	1.01E-3	2.53E-5	8.83E-6	4.79E-5	2.19E-5	3.62E-4	7.79E-4	//
5	1.06E-3	2.74E-5	8.82E-6	5.30E-5	2.05E-5	3.75E-4	8.23E-4	//
6	1.25E-3	3.28E-5	1.11E-5	6.43E-5	2.46E-5	4.34E-4	9.57E-4	//
7	1.10E-3	3.02E-5	8.78E-6	5.51E-5	2.36E-5	3.82E-4	8.54E-4	//
8	1.16E-3	3.12E-5	1.19E-5	5.23E-5	2.20E-5	4.19E-4	9.26E-4	//
9	1.13E-3	3.24E-5	1.09E-5	5.27E-5	2.58E-5	4.04E-4	8.72E-4	//
10	1.23E-3	3.28E-5	2.14E-5	5.79E-5	2.76E-5	4.36E-4	9.50E-4	//
11	1.25E-3	3.30E-5	2.34E-5	5.63E-5	2.62E-5	6.76E-4	1.48E-3	//
12	1.14E-3	2.79E-5	2.33E-5	5.18E-5	2.36E-5	5.03E-4	1.33E-3	//
13	1.19E-3	3.26E-5	1.30E-5	5.51E-5	2.52E-5	3.79E-4	8.54E-4	// & Cycle 2
14	1.10E-3	2.85E-5	1.25E-5	4.74E-5	2.25E-5	3.89E-4	8.19E-4	// & //
15	1.61E-3	4.35E-5	4.20E-5	7.67E-5	3.79E-5	1.17E-4	2.55E-3	// & //
16	6.28E-4	1.76E-5	1.91E-5	3.23E-5	1.48E-5	4.97E-4	1.08E-3	// & //
17	1.34E-4	3.68E-5	1.07E-5	6.24E-5	3.23E-5	4.63E-4	9.33E-4	// & //
18	1.31E-4	3.38E-5	1.24E-5	6.17E-5	3.01E-5	4.49E-4	9.80E-4	// & //
19	1.22E-3	3.37E-5	1.06E-5	5.50E-5	2.90E-5	4.29E-4	9.37E-4	// & //
20	1.31E-3	3.54E-5	1.80E-5	1.83E-5	3.73E-5	5.28E-4	1.37E-3	// & //
21	3.56E-3	8.38E-5	5.04E-5	9.28E-5	5.27E-5	1.08E-3	1.12E-3	// & //
22	1.36E-3	3.75E-5	1.35E-5	6.25E-5	3.25E-5	4.95E-4	1.34E-3	// & //
23	5.21E-3	1.01E-4	9.21E-5	2.03E-4	9.16E-5	5.21E-3	7.25E-3	// & //
24	1.52E-3	4.10E-5	2.55E-5	7.00E-5	3.70E-5	7.63E-4	1.60E-3	// & //
25	1.69E-3	4.58E-5	4.69E-5	7.87E-5	4.46E-5	1.33E-3	2.7 E-3	Cycle 2 & Cycle 3
26	1.80E-3	4.86E-5	7.2 E-5	8.5 E-5	-	1.8 E-3	3.3 E-3	// & //
27	1.49E-3	4.18E-5	2.37E-5	6.75E-5	3.80E-5	8.13E-4	1.70E-3	// & //
28	1.56E-3	4.03E-5	3.3 E-5	7.80E-5	3.97E-5	1.08E-3	2.33E-3	// & //
29	1.66E-3	4.68E-5	2.65E-5	7.75E-5	3.60E-5	8.45E-4	1.74E-3	// & //
30	1.56E-3	4.4 E-5	3.0 E-5	7.65E-5	3.25E-5	9.0 E-4	1.85E-3	// & //
31	1.38E-3	4.25E-5	3.15E-5	7.48E-5	2.85E-5	8.33E-4	1.69E-3	Cycle 1 & Cycle 3
32	1.25E-3	4.70E-5	2.90E-5	8.85E-5	3.70E-5	9.0 E-4	1.85E-3	// & //

Table 2. Radionuclides Analysis of Crud Sample

GAMMA 1 <02.3 > 19-JAN-82 14:33:15 PAGE 1

SPECTRUM ACQUISITION STARTED LIVE REAL
0010066.SPC 27-DEC-82 17:11:00 120 126

SAMPLE
THE DATA ARE ANALYZED BY DR. JAE CHOON YANG
AND WITH GELIGAM PROGRAM.

DETECTOR SYSTEM
GE(L1) DETECTOR OF CENTRAL LABORATORY.
KOREA ADVANCED ENERGY RESEARCH INSTITUTE

CALIBRATION ES.CLB
EFFICIENCY OF
5TH POSITION

LIBRARY L20
START STOP 50. 4050 SENS(%) 10 MULTIPLIER 1.000000
DECAY CORRECTED TO 09-DEC-82 00:00:00

***** SUMMARY OF NUCLIDES IN SAMPLE *****

NUCLIDE	TIME OF COUNT ACTIVITY UCI	TIME CORRECTED ACTIVITY UCI	PERCENT UNCERTAINTY COUNTING 2 S
CS-137	2.4E-02	2.4E-02	
CO-60	1.485E+00	1.495E+00	4.1
MN-54	3.431E-01	3.576E-01	#
CO-57	2.366E-02	3.007E-02	#
BA-133	2.138E-01	2.148E-01	#
ZR-95	1.927E+00	2.360E+00	6.6
NB-95	3.873E+00	5.601E+00	3.6
CE-141	1.051E-01	1.566E-01	#
RU-103	1.238E-01	1.719E-01	#
FE-59	8.538E+00	1.135E+01	#
CO-58	6.566E-01	7.876E-01	8.6
CR-51	1.6E-01	2.5E-01	#
CS-134	4.7E-03	4.8E-03	#
SN-113	8.5E-01	9.5E-01	#
SB-124	1.024E-01	1.270E-01	#

***** UNUSED PEAKS *****

ELAPSED TIME: 26.6 SECONDS
LP: NS

Table 3. Crud Analysis Result of Korea Nuclear Unit 7
(µci/cc)

Element	Date	'88. 6. 6	'88. 6. 13	'88. 6. 20	'88. 6. 27
⁵⁰ Co		1.79 × 10 ⁻⁶	9.11 × 10 ⁻⁶	4.11 × 10 ⁻⁶	1.20 × 10 ⁻⁶
⁶⁰ Co		9.80 × 10 ⁻⁷	1.01 × 10 ⁻⁶	1.74 × 10 ⁻⁶	-
⁶⁵ Zn		-	-	-	-
⁶⁴ Ni		3.21 × 10 ⁻⁶	4.07 × 10 ⁻⁶	5.47 × 10 ⁻⁶	3.70 × 10 ⁻⁶
⁶¹ Co		6.27 × 10 ⁻⁶	2.13 × 10 ⁻⁶	1.22 × 10 ⁻⁶	-
⁹⁰ Zr		8.83 × 10 ⁻⁷	3.11 × 10 ⁻⁶	-	-

Table 4 Crud Analysis Result of Korea Nuclear Unit 8
($\mu\text{Ci}/\text{cc}$)

Element	Date	'88. 6. 10	'88. 6. 17	'88. 6. 24
^{58}Co		3.3×10^{-4}	3.13×10^{-3}	3.27×10^{-3}
^{60}Co		1.3×10^{-5}	1.19×10^{-4}	1.37×10^{-4}
^{59}Fe		1.0×10^{-5}	7.54×10^{-5}	7.56×10^{-5}
^{54}Mn		1.4×10^{-5}	8.62×10^{-5}	1.11×10^{-4}
^{51}Cr		2.3×10^{-5}	1.65×10^{-4}	1.94×10^{-4}
^{95}Zr		7.9×10^{-6}	5.62×10^{-5}	6.28×10^{-5}

Table 5 Analysis Result of Defected Fuel and Tramp Uranium

Date	Measured Activity ($\mu\text{Ci}/\text{g}$)		Number of Failed Fuel	Tramp Uranium (kg)
	^{131}I	^{133}I		
1981. 6. 12	0.22	0.48	11.1	0.6
1981. 6. 25	0.22	0.60	10.2	0.8
1981. 7. 24	0.23	0.72	10.1	1.1
1981. 9. 17	0.23	0.96	8.9	1.5
1981. 9. 24	0.23	0.87	9.3	1.4
1981. 10. 1	0.24	0.93	9.5	1.5
1981. 10. 15	0.24	0.95	9.4	1.5
1981. 10. 22	0.27	1.00	11.1	1.6
1981. 12. 10	0.25	1.10	9.0	1.8
1982. 1. 7	0.27	1.30	9.2	2.1
1982. 1. 14	0.29	1.30	10.6	2.1
1982. 1. 28	0.30	1.40	10.3	2.3
1982. 2. 4	0.31	1.40	11.2	2.3
1982. 2. 11	0.28	1.30	9.7	2.2
1982. 2. 25	0.27	1.40	9.0	2.3
1982. 3. 5	0.27	1.20	9.7	2.0
1982. 3. 11	0.27	1.30	9.2	2.1
1982. 3. 18	0.26	1.30	8.7	2.2
1982. 3. 26	0.27	1.30	9.2	2.4
1982. 4. 1	0.28	1.40	9.1	2.4
Average Value			9.7 ± 0.8	1.8 ± 0.5

2.3 Sipping test

We have analyzed the sipping test results of spent fuel elements for the cycle 3 of Korea Nuclear Unit 1. The detectors used to measure are NaI(Tl) and Ge(Li).

The detecting isotopes are I-131 and Cs-137. The number of sipping tested fuel assemblies are 81 spent fuels.

The sipping test results have been shown in Table 6. The cumulative distribution of sipping test result of D-region [2] has been shown in Fig.1. The detecting isotope is I-131 and the detector is NaI(Tl).

The cumulative distribution of sipping test results of D-region, Cs-137 for detecting isotope, NaI(Tl) for detector, has been shown in Fig.2.

The cumulative distribution of sipping test results of D-region, I-131 for detecting isotope, Ge(Li) for detector, has been shown in Fig.3.

2.4. Coolant history of reactor

The coolant histories for the Korea Nuclear Unit 1 reactor from cycle 3 to cycle 4 have been shown in Fig.4.

The boron and lithium concentrations and PH values for Korea Nuclear Unit 7 have been shown in Table 7.

Table 6. Comparison of Defected Fuel Analysis Result with Sipping Test Result

Sipping Test Result			Analysis Result in this Work
Detector used to Measure	Isotope for Analysis	Number of Failed Fuel	Number of failed fuel
NaI (Tl)	^{131}I	10	9.7 ± 0.8
NaI (Tl)	^{137}Cs	11	
Ge (Li)	^{131}I	10	

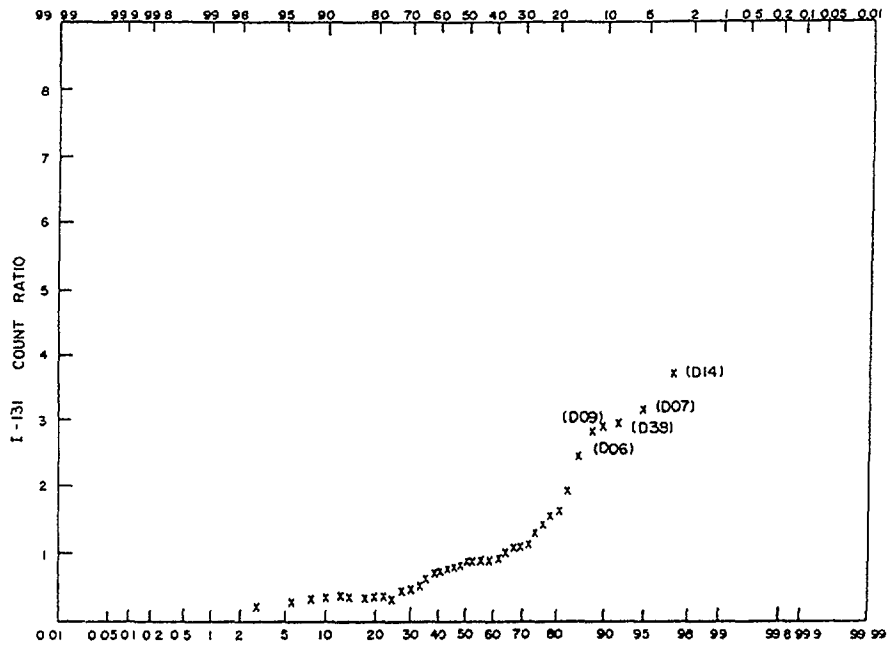


Fig.1 Cumulative Distribution of Sipping Test Result, D-Region, I-131, NaI(Tl).

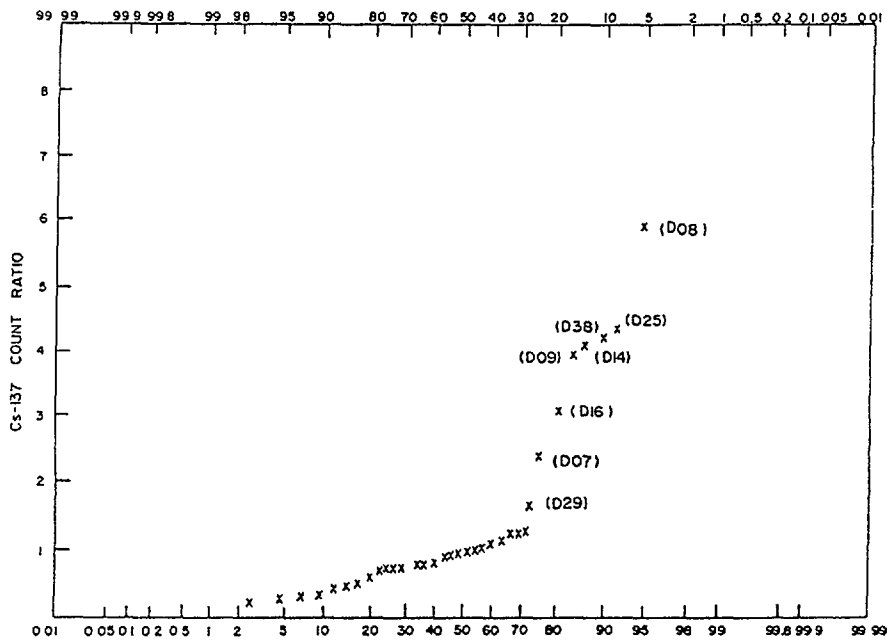


Fig 2 Cumulative Distribution of Sipping Test Results, D-Region, Cs-137, NaI(Tl).

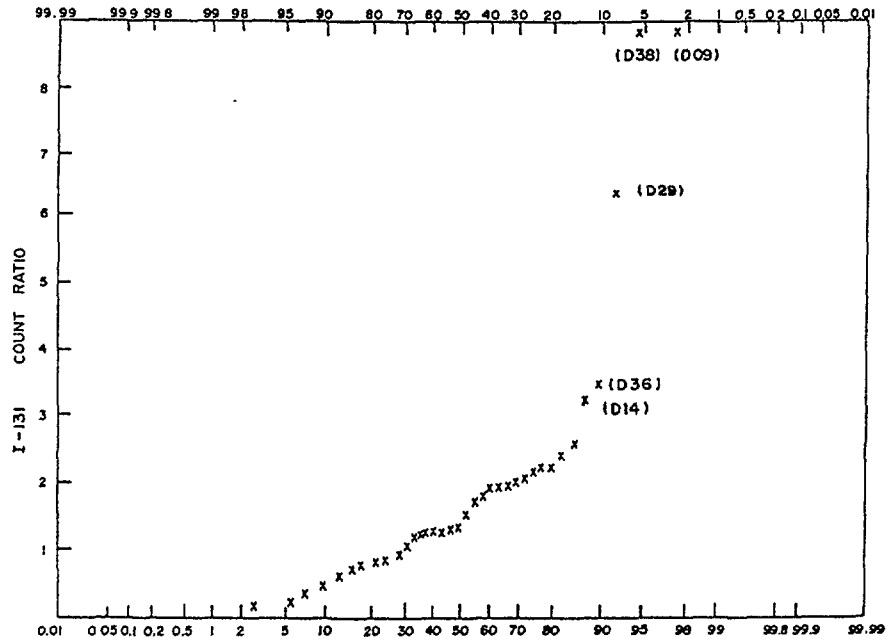


Fig.3. Cumulative Distribution of Sipping Test Results, D-Region, I-131, Ge(Li).

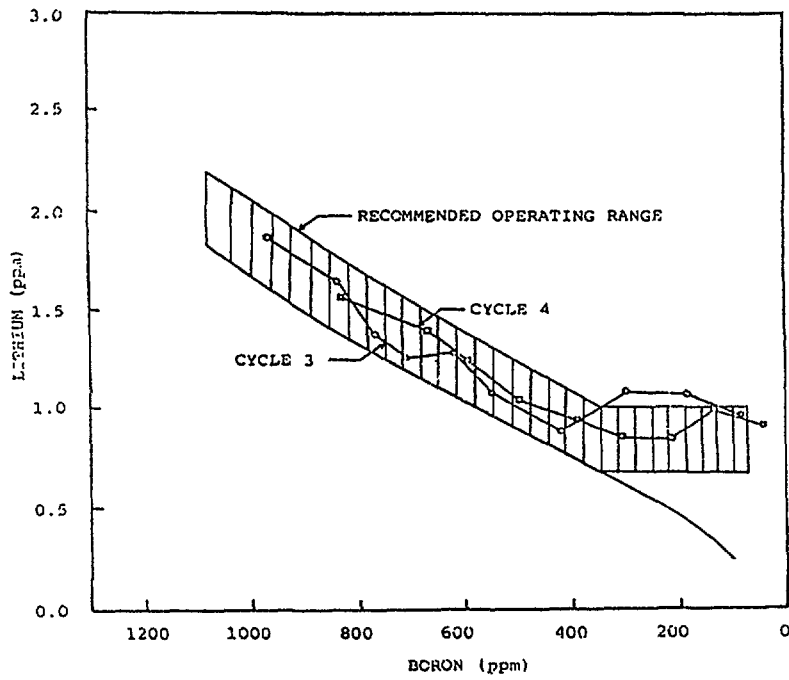


Fig.4. Boron versus Lithium Concentrations in the Kori Unit 1 Reactor Coolant During Cycle 3 and 4.

Table 1 / Coolant Chemistry Data for Korean Nuclear Unit 1

	Power (%)	B (ppm)	Li (ppm)	pH
6. 1	100	157	1.19	7.2
2	100	153	1.18	7.2
3	100	152	1.20	7.3
4	100	149	1.20	7.3
5	100	146	1.19	7.3
6	100	143	1.19	7.3
7	100	141	1.19	7.3
8	88	140	1.19	7.3
9	100	138	1.01	7.3
10	100	130	0.82	7.1
11	100	125	0.83	7.1
12	100	122	0.84	7.1
13	100	119	0.86	7.1
14	100	115	0.86	7.1
15	100	110	0.87	7.1
16	100	107	0.90	7.1
17	100	105	0.94	7.1
18	100	97	0.96	7.1
19	100	91	0.98	7.1
20	100	89	0.99	7.1
21	100	85	1.00	7.1
22	100	81	1.03	7.2
23	100	80	1.06	7.3
24	100	75	0.79	7.2
25	100	73	0.83	7.3
26	100	71	0.86	7.2
27	100	70	0.89	7.3
28	100	66	0.93	7.3
29	100	62	0.94	7.3
30	100	59	0.97	7.3

3. Conclusion

As the results of crud analysis, the radioactive materials of corrosion products are mainly the Co-60, Mn-54, Co-58, and Cr-51 isotopes. This results are well agreed with the results Solomon [3].

The analysis results of defected fuel and tramp uranium are in a fairly good agreement with the result of the sipping test during the refueling period for cycle 3 of Korea Nuclear Unit 1.

As we compare the crud analysis results with coolant histories of the end of cycles, we can see that the amount of crud materials are closely related to the water control.

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APPLICATION OF NEW COMPOSITE ION EXCHANGERS FOR THE REMOVAL OF RADIONUCLIDES FROM THE PRIMARY COOLANT OF WATER REACTORS. PART 1

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Abstract

The properties of a novel composite ion exchanger selective for caesium ions are described. The sorbent consists of titanium hexacyanoferrate incorporated into a matrix of phenolsulphonic resin, and has a form of spherical beads. The beads were examined by electron microscopy and tested as adsorbent of radiocaesium ions from aqueous solutions simulating the primary coolant of nuclear reactors (VVER). The composite material combines very high caesium selectivity of the inorganic component with good mechanical properties of the resin matrix. The sorption kinetics on the composite is much better than on the inorganic component. Radiocaesium is very efficiently adsorbed from acidic and neutral solutions containing potassium and ammonium ions at millimole concentrations and boric acid, as found in the column process under conditions simulating the real filtration. The decontamination factor after eluting 20,000 bed volumes exceeded 100.

Other composite ion exchangers containing hexacyanoferrates of cobalt, nickel and zinc, stable in a broader pH range, were also synthesized and temporarily tested as caesium adsorbents.

1. INTRODUCTION

The programme of this CRP¹ comprises the consideration of potassium chemistry as an alternative option in PWR primary water chemistry control from the point of view of corrosion problems [1]. Such an operation regime has been already practiced in VVER type reactors [2]. The presence of potassium ions in the coolant creates problems connected to radiocaesium removal from the coolant, because common ion exchangers become inefficient to caesium in the presence of strongly competing potassium cations. Large amounts of liquid wastes containing radiocaesium and boric acid, originated mainly from primary circuits of VVER-s, indicate

¹"Investigations on Water Chemistry Control and Coolant Interactions with Fuel and Primary Circuit Materials in Water Cooled Power Reactors" (WACOLIN).

the importance of this problem. Novel caesium-efficient ion exchange resins recently developed by DUOLITE have been tested only for lithium-containing coolants [3]. Our experience shows that similar phenolsulphonic resins are not sufficiently useful for radiocaesium removal from potassium-containing solutions.

Another reason for developing efficient methods for removing radiocaesium from PWR primary coolants is connected to the other part of this CRP, i.e. the use of boron-10 as chemical shim in PWRs [4]. To eliminate the losses of expensive enriched boron-10, boric acid free of accumulating long-lived radionuclides has to be recovered from the used coolant, and efficient recovery systems have to be developed.

2. RESULTS AND DISCUSSION

A composite ion exchanger consisting of specially prepared titanium hexacyanoferrate (the mole ratio of Ti to Fe being 8:1) referred to as TCF, firmly incorporated (ca 20 %) into a matrix of phenolsulphonic resin, especially selective to caesium even in the presence of potassium ions, has been manufactured in the form of spherical beads (0.3 - 1.5 mm in diameter) [5]. The novel adsorbent combines very high caesium selectivity of the inorganic component with good mechanical properties of the resin matrix.

The process of pearl polycondensation of the phenolsulphonic matrix, carried out in the presence of powdered titanium hexacyanoferrate, results in obtaining spherical beads of the composite species. Black beads containing ca 20 % titanium hexacyanoferrate were examined by means of a scanning electron microscope, BS-301 KUVO-TESLA (Brno), kindly rendered accessible to us by the Institute of Plasma Physics and Laser Microsynthesis in Warsaw (Fig.1). The images of the surface and fracture of the beads show that fine (0.5 to 4 μm) titanium hexacyanoferrate grains are uniformly dispersed within the bead and cause the roughness of the bead surface.

The tests on the efficiency of radiocaesium adsorption for the adsorbent were carried out under dynamic conditions simulating the process of purification of the coolant bled from the primary circuit of a VVER-440 reactor at nuclear power plants, i.e. at a temperature of 50°C and the flow rates up to 10 m/h. The column contained 1 cm³ of the swollen adsorbent, the bed height being 80 mm and the diameter 4 mm. The influent was a coolant simulating solution of the following composition: boric acid - 0.065 M (4 g/dm³), KOH - 2.5x10⁻⁴ M, NH₄OH - 2x10⁻³ M and a carrier-free ¹³⁷Cs⁺ tracer; the pH was 7.2. The flow was stopped for nights and started again the next day, so the efficient time of the experiment was only 20 to 30% of the total time. In the experiments carried out at room temperature the efficient time reached ca 60% of the total time.

The efficiency of the column process was expressed in terms of decontamination factor (DF) defined as the ratio of the specific radioactivity of the influent to that of the effluent, and plotted against the effluent volume expressed as a number of the bed volumes (BV) - Fig.2. The value DF = 100 has been arbitrarily

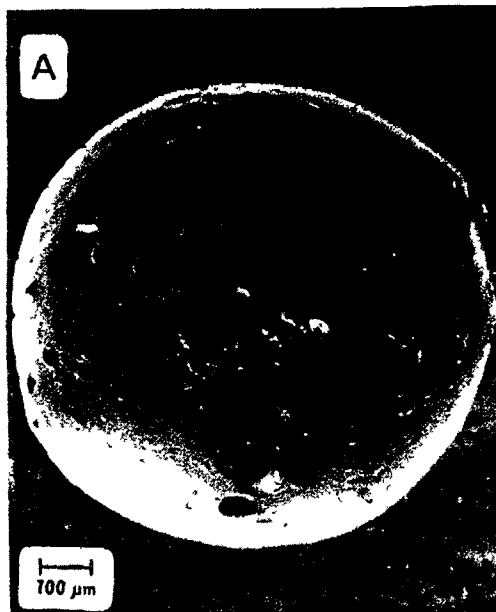


Fig.1. The SEM images of composite ion exchanger containing 20% titanium hexacyanoferrate in phenolsulphonic matrix: whole bead (A); bead surface (B); bead fracture (C).
(All Figures have been reproduced from ref.[5]).

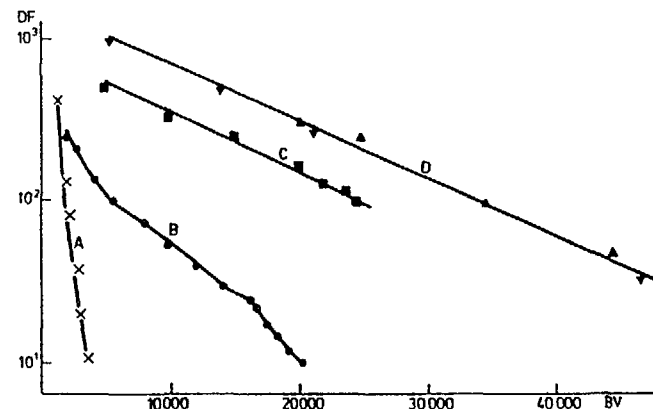
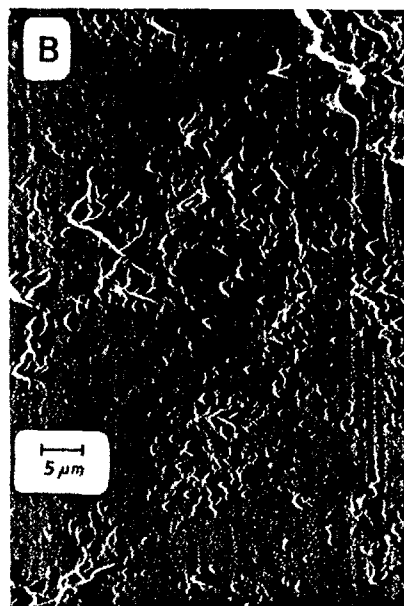


Fig. 2 Efficiency of discontinuous (see text) processes of $^{137}\text{Cs}^+$ fixation from the reactor-coolant-simulating solution on columns filled with beads (0.5–1.0 mm) of phenolsulphonic resin (A), grains (0.3–0.5 mm) of pure TCF (B) and beads (0.5–1.0 mm) of 20% TCF-composite adsorbent (C), at 50°C and at the flow rate 10 m · h⁻¹. Curve D corresponds to the same process as that described with curve C, but at lower flow rate 7–9 m · h⁻¹

chosen as the break-through point of the column. For the comparison both pure titanium hexacyanoferrate (0.3 – 0.5 mm grains) and pure phenolsulphonic resin (0.3 – 0.5 mm beads of the "empty matrix") were tested under the same conditions (Fig. 2, curves B and A, respectively). Curves C and D represent the process for the composite adsorbent at various flow rates: 10 m/h and 8 m/h, respectively. The results confirm that the break-through capacity of the column is a function of both affinity of the adsorbent to caesium ions and the dynamics of the column process. The latter depends on the flow rate, temperature, size of the sorbent grains, column dimensions, etc. A rapid drop of DF for the pure resin, resulting in the break-through of the column already after about 2×10^3 BV (curve A), is obviously due to the relatively low resin-to-caesium affinity, in spite of the highest rate of the ion exchange (Fig. 3). Very high caesium affinity to the composite adsorbent, combined with a satisfactory kinetics of the ion exchange, brings about the high efficiency of the column process, the bed being not broken-through until ca. 24,000 BV (Fig. 2, curve C). At this high flow rate through the column (10 m/h or 120 BV/h), the efficiency-controlling factor in the column process on both pure and composite titanium hexacyanoferrate is the kinetics of the ion exchange. The flow rate through the bed of the composite adsorbent strongly affects the efficiency of the process. At the flow rate decreased by only 20%, the other conditions remaining constant, the break-through point is shifted to 33,000 BV (curve D). Much slower rate of the ion exchange on pure titanium hexacyanoferrate causes much worse

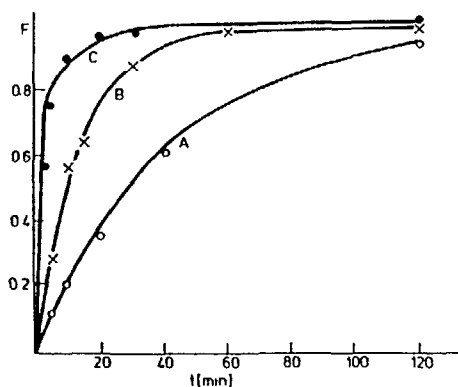


Fig. 3 Kinetics of caesium fixation on pure TCF (A), 20% TCF-composite adsorbent (B) and phenolsulphonic resin—the empty matrix (C) from the reactor-coolant-simulating solution at 50°C. The diameter of the adsorbent particles--from 0.5 to 1.0 mm

decontamination of the solution (curve B), in spite of the very high caesium distribution coefficients and smaller size of the adsorbent grains.

The changes of temperature affect the distribution coefficients and the kinetics of caesium fixation in the opposite directions, but under the conditions of this experiment (high flow rates), the net effect of the temperature rising is favourable for the efficiency. A decrease of the temperature to 20°C, the other parameters of the process remaining constant, results in lowering the break-through point of the column to 10,000 BV or less, depending on the bead size (the results are not shown in the Figure). On the other hand, an increase of the column length increases the efficiency of caesium fixation. The break through point of the column with doubled height of the sorbent bed (155 mm) at 20°C was found again at 25,000 BV (flow rate 10 m/h). Because the height of the sorbent bed in the real filters in NPP-s is expected to be ca 1 m, the flow rate remaining the same, one can expect a strong favourable effect on the efficiency of radiocaesium fixation.

The drawback of the composite ion exchanger with titanium hexacyanoferrate is its instability above pH 8 wherein the inorganic component decomposes to titanium oxide. To avoid this trouble, other composite adsorbents have also been synthesised, containing hexacyanoferrates of other transition metals: zinc, cobalt and nickel. All of them are more stable than the titanium compound and seem to be superior adsorbents of radiocaesium at higher pH (Fig.4). Further studies will be carried out on this problem.

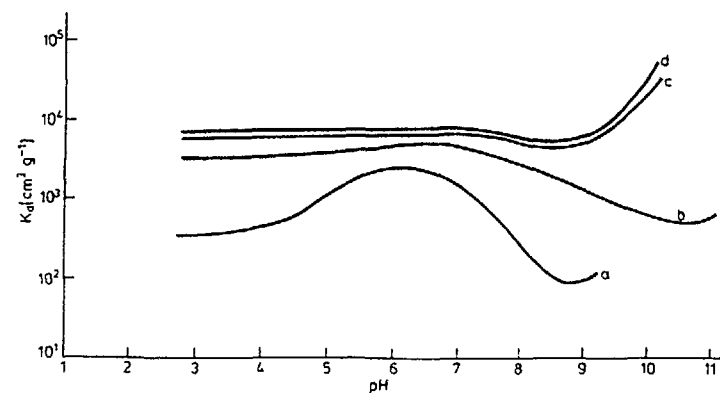


Fig.4 Distribution coefficients of caesium ions for composite ion exchangers containing hexacyanoferrates of various metals (20% each) in the phenolsulphonic matrix, plotted as a function of pH. Concentration of competing ions, $\text{NH}_4^+ + \text{K}^+$, $0.1 \text{ mol}\cdot\text{l}^{-1}$. Temperature 25°C a—composite sorbent with titanium hexacyanoferrate, b—composite sorbent with zinc hexacyanoferrate, c—composite sorbent with nickel hexacyanoferrate, d—composite sorbent with cobalt hexacyanoferrate

The composite ion exchanger can be manufactured not only in laboratories but also on an industrial scale. Attempts to develop the technology have resulted in obtaining a bulk of 170 kg of the product in one of the Polish chemical factories. Further efforts ought to be concentrated on a large scale testing the sorbent in a NPP, the test to be carried out with a real coolant bled from the primary circuit of the VVER-440 reactor. In the case of positive results the sorbent can be produced in large amounts and supplied on request.

3. CONCLUSIONS

A novel caesium-selective composite ion exchanger has been produced on both the laboratory and industrial scale, and tested as radiocaesium adsorbent from the simulated primary coolant of the power reactor (VVER-440) under laboratory conditions. The results indicate that the composite adsorbent can be successfully used to remove radiocaesium from the coolant bled from the primary VVER circuit. This problem is important not only from the point of view of rad-waste treatment; it can be significant for developing both potassium and boron-10 chemistry in PWRs as covered by WACOLIN CRF.

Further studies are required on other similar composite ion exchangers stable at higher pH. The adsorbent has also to be tested with real reactor coolants in a NPP.

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APPLICATION OF NEW COMPOSITE ION EXCHANGERS FOR THE REMOVAL OF RADIONUCLIDES FROM THE PRIMARY COOLANT OF WATER REACTORS. PART 2

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Abstract

Novel composite ion exchanger in the form of beads, selective for caesium ions, composed of titanium hexacyanoferrate (ca 20 %) incorporated into a matrix of phenolsulphonic resin, was tested as adsorbent of radiocaesium from the real primary coolant of power nuclear reactor (VVER) and from water of fuel pool in NPP. High decontamination factors for radiocaesium were found in both experiments: DF > 1000 after 6,000 BV, and DF = 100 after 25,000 BV, respectively. The DF values for other radionuclides detected in both solutions were much lower.

Other composite ion exchangers were prepared, containing nickel and cobalt hexacyanoferrates, titanium phosphate, hydrous titanium oxide, and mordenite. The composites with nickel and cobalt hexacyanoferrates appeared to be efficient radiocaesium adsorbents from alkaline concentrates of radioactive wastes from NPP-s. The composite with hydrous titanium oxide is a good adsorbent of radiocobalt from solutions simulating the water of NPP fuel pool. The break-through point (DF = 100) was observed at the effluent volumes reaching up to 22,000 BV, depending on pH.

1. INTRODUCTION

Part 1 of this report [1] concerned a novel composite ion exchanger consisting of powdered titanium hexacyanoferrate incorporated into a matrix of phenolsulphonic resin, in the form of spherical beads, selective to caesium ions, manufactured in our laboratory [2], and designed for radiocaesium removal from the primary coolant of VVER-type (PWR) reactors. Lab-scale tests carried out with simulating solutions proved the efficiency of this novel material in adsorbing radiocaesium even in the presence of competing potassium and ammonium ions at millimole concentrations.

In this work preliminary results are reported on testing the composite ion exchanger with real radioactive solutions at NPP-s. Some other composite ion exchangers are also presented, including those selective for ions of radioactive corrosion products of importance in the operation of PWR-s.

2. RESULTS AND DISCUSSION

2.1. Testing of the composite titanium hexacyanoferrate adsorbent

The first lab-scale test of the composite adsorbent with the real VVER coolant bled from the primary circuit was carried out at Bohunice V-1 NPP in Czechoslovakia. A glass column of internal diameter 6 mm was filled with 1 cm³ of the composite ion exchanger (20% titanium hexacyanoferrate) in the form of beads (0.3 - 0.5 mm in diameter), the bed height being 35 mm. The coolant composition varied in the course of the experiment (18 days) as follows: boric acid - 2.6 to 2.2 g/dm³, ammonia - 11.7 to 8.1 mg/dm³; potassium ions - 8.6 to 5.0 mg/dm³; sodium ions - 0.4 to 0.2 mg/dm³; the pH (at 25°C) being 7.3 to 7.4; specific conductivity - 82 to 63 μS/cm; and total radioactivity (after 2 - 3 day cooling time) - 6.1 to 8.1 MBq/dm³. The solution passed through the column (from the top to the bottom) with the flow rate 15 cm³/h (15 BV/h) at room temperature. The experiment was continued only to 6 dm³ (6000 bed volumes) of the coolant passed through the sorbent bed, because the column clogged. At that time the values of decontamination factor (DF) for ¹³⁷Cs and ¹³⁴Cs exceeded 1000. The respective values for other radionuclides found in the coolant appeared much lower: DF was ca 10 for ⁵⁴Mn; 5 for ²⁴Na; 2 for ¹²⁵Sb; and close to 1 for ⁹⁰Mo, ¹⁰⁷W and ¹³¹I.

The removal of radiocaesium from the real VVER coolant appeared thus very efficient, but that experiment gave no answer, to which extent. In the previous experiments with the simulated VVER coolant (at elevated temperature and increased flow rates) more than 20,000 - 30,000 bed volumes of the solution were efficiently purified from ¹³⁷Cs (DF > 100) [1,2].

In order to avoid the column clogging, the experiment with reversed flow direction was started at the Kozloduy NPP in Bulgaria. A glass column (15 mm in diameter) was filled with 20 cm³ of the same composite ion exchanger (bead diameter 0.3 to 1.0 mm), the bed height being ca 120 mm. As the first step of the experiment, not the primary coolant but another genuine radioactive water from the NPP was used: water of spent fuel pool, containing more concentrated boric acid, ca 12 g/dm³, the pH being 4 to 5, and the total radioactivity of the most important nuclides (¹³⁷Cs, ¹³⁴Cs, ⁵⁴Mn, and ⁹⁰Co) exceeding 40 kBq/dm³. The solution passed the column from the bottom to the top with the flow rate in the range of 0.4 to 0.6 dm³/h (20 - 30 BV/h) at ca 50°C. The 1% break-through of the column (DF = 100) for radiocaesium was observed only after passing over 500 dm³ (25,000 bed volumes) of the real radioactive water. This result is only slightly worse than that obtained in the previous lab-scale tests with simulated solutions. Further experiments with the real VVER primary coolant are in progress¹.

¹ Preliminary results of the experiment still going on with the real primary coolant of the VVER-1000 give DF > 150 after passing 17,000 BV (note added in proof).

2.2. Novel composite ion exchangers

A number of novel composite ion exchangers have been prepared using the procedure described earlier [2,3]. The exchangers contained various inorganic components (ca 15 to 35%) dispersed in a matrix of phenolsulphonic-formaldehyde resin, the inorganic components being hexacyanoferrates of nickel and cobalt, titanium phosphate, hydrous titanium oxide (HTO), and synthetic mordenite. A modified procedure was used in the case of HTO [4], including alkaline treatment of composite beads [5].

The composite sorbents have been manufactured in the form of small beads from which the fraction of the diameter from 0.3 to 1.0 mm was selected for the experiments. The mechanical stability of the composite beads was much greater than that of grains of their parent inorganic sorbents: ca 20 - 35 N per bead (1 mm in diameter) compared to ca 1 - 7 N per grain (ca 1 mm). The kinetics of radionuclide ions adsorption from dilute aqueous solutions on the composite adsorbents was much better than that on their parent inorganic components, the sizes of the respective beads and grains being comparable [2,3].

The composites containing nickel and cobalt hexacyanoferrates were tested as radiocaesium adsorbents from alkaline (pH 12) concentrated (salt content up to 200 g/dm³) radioactive wastes - both simulated and real evaporator bottoms from the NPP Lovisa. Good performance of both sorbents under such rough conditions was observed (DF = 100 after up to 5,000 BV) but at the expense of much slower kinetics (i.e. at the flow rate ca 0.7 m/h) [6,7]. The composite containing mordenite, although also efficient caesium sorbent, seems to be less applicable to primary coolants because of its chemical composition causing leakage of Na, Al and Si, and its lower selectivity to caesium than that of metal hexacyanoferrates. The latter conclusion refers also to the composite titanium phosphate sorbent. Only the composite sorbent containing HTO deserves more attention.

Hydrous titanium oxide is a well known inorganic adsorbent for transition metal ions, including radioactive corrosion products from primary coolants of nuclear reactors. The recent studies have confirmed the excellent sorptive properties of this compound against the most important corrosion products (^{58,60}Co, ⁶⁵Zn, ⁵⁴Mn) under high temperature conditions simulating those in the primary circuit of power reactors [8]. The composite HTO sorbent cannot be used directly in the primary circuit because of poor thermal stability of the resin matrix, but its application at low temperature resin filters is not excluded a priori.

The composite sorbent containing ca 20% HTO was tested as an adsorbent for radiocobalt (⁵⁸Co) from solutions simulating the water of NPP fuel pools (see § 2.1). A glass column of 4 mm in the diameter was filled with 1 cm³ of the sorbent (0.3 - 1.0 mm), the bed height being ca 80 mm. Solution containing ⁵⁸Co ions (0.3 MBq/dm³) passed the column at both room and elevated temperature, the flow rate being ca 6.4 m/h (80 BV/h). Retention of radiocobalt on the column depended on the pH of solution. No break-through of the bed (up to 20,000 bed volumes) was detected at pH 5.8 (t = 20°C). The 1% break-through was observed after 22,000 bed volumes at pH varying from 4.7 to 5.0 (t = 50°C). Much

worse column performance was found at pH 4.4 ($t = 20^{\circ}\text{C}$) with 1% break-through after ca 5,000 BV and 10% break-through after ca 19,000 BV [7].

It was found in the previous studies that high distribution coefficients for Zn^{2+} , Co^{2+} and Mn^{2+} on HTO were reached above pH 5.5 to 6 [9], so the composite HTO resin is an efficient adsorbent for ions of corrosion products from nearly neutral and slightly alkaline aqueous solutions. Thus, this composite ion exchanger can be used complementary to well known adsorbents selective for ions of transition metals - chelating resins containing imino-diacetic acid groups, e.g. Dowex A-1, Chelex-100 or Wofatit MC 50, exhibiting high efficiency for Co^{2+} ions in the narrow pH range from 4.5 to 6 [10].

3. CONCLUSIONS

Composite ion exchanger consisting of powdered titanium hexacyanoferrate dispersed in a solid matrix of phenolsulphonic-formaldehyde resin in the form of beads, is a very efficient and selective adsorbent for radiocaesium from real radioactive waters of NPP-s, including the VVER primary coolant. Novel composite ion exchangers have been prepared and studied, the most important being those containing nickel or cobalt hexacyanoferrates, selective for caesium in solutions from acidic to moderately alkaline, and those containing hydrous titanium oxide, efficient for transition metal ions, especially Co^{2+} , above pH 5. The composite adsorbents, apart from high affinity to ions of important fission and corrosion products, exhibit improved kinetics of sorption, high mechanical stability, and good hydraulic properties.

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WATER CHEMISTRY IN SOVIET NUCLEAR POWER PLANTS

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Abstract

WWER reactors operate with water coolant which is alkalinized by a mixture of ammonia and potassium hydroxide. Ammonia dissociates to give hydrogen which suppresses coolant radiolysis. The narrow range of pH maintained ensures low material corrosion. Corrosion product transport and deposition on fuel cladding surfaces are also suppressed. The specified water quality is controlled by a system of ion exchange demineralizers with mixed or separate beds of resins. The dose rate from the primary circuit equipment is mainly due to inner surface deposits of activated corrosion products. WWERs are equipped with horizontal steam generators with stainless steel 0x18H10T steam generator tubes. With this design of steam generator and choice of SG tube material satisfactory operation of the equipment achieved with less stringent water chemistry specifications.

RBMK reactors are cooled with demineralized water. In order to suppress the corrosion of coolant circuit, oxygen is injected in the feed water circuit downstream of the condensate polishing plant and then removed from the water in the deaerator. At present injection of hydrogen is proposed as the remedy for stainless steel piping IGSCC. Current R&D work is directed towards further optimization of the chemical system and to improve the NPP safety and reliability.

Introduction

Nuclear power program in the USSR is based on pressurized water-cooled reactors of vessel type (WWER) and boiling water-cooled graphite-moderated reactors of channel type (RBMK). Construction of heat generating nuclear power plants has also begun.

Water chemistry regime for each reactor type depends on the reactor design.

Experience has shown that the adopted water chemistries of WWER- and RBMK- reactors provided high corrosion resistance of the structural materials, safe and reliable operation of the equipment, and low radiation doses.

In view of the current trends towards higher fuel burnups, more flexible power regimes, and more stringent requirements for safety and reliability, water chemistry problems are considered to be very important, especially the influence of water chemistry on

- The corrosion behaviour of the structural materials
- Corrosion product transport and deposition
- Radiation doses from the plant's equipment

1 Water Chemistry at NPPs with WWER-Reactors

WWER-reactors operate with water coolant alkalinized by a mixture of ammonia and potassium hydroxide. Potassium hydroxide provides the required pH value to decrease corrosion products de-

position on fuel and reduce the corrosion itself. Under the core irradiation ammonia dissociates with formation of hydrogen and nitrogen. Excess of hydrogen (30 - 60 ml/kg) provides for profound suppression of coolant radiolysis, as a result of which oxygen content is kept below 5 $\mu\text{mg/kg}$. The alkali concentration is coordinated with the boric acid content.

This concept of water chemistry has the following features:

- High pH level is varied in a narrow range (Fig. 1). Under these conditions the rates of material corrosion and corrosion product transport and deposition on fuel cladding are suppressed, and the risk of excess accumulation of strong alkali in the coolant is excluded.
- High hydrogen concentrations required for suppression of water radiolysis is reached with very simple means (no H_2 gas).
- Injection of hydrazine during refuelling periods suppresses the oxidative effect of air, when reactor vessel is open.
- Reducing conditions of the coolant prevent the radiation induced corrosion of zirconium alloys.

Water chemistry specifications for WWER-1000 are given Table 1.

The specified coolant quality is controlled by a system of ion exchange demineralizers with mixed or separate beds of resins.

The filters are installed in the main pump by-pass lines. At some units high temperature mechanical filters are installed. Capacity of each filter is up to 100 t/h. Heating up and cooling down periods of the clean-up system coincide with those of the reactor circuits. Washing off, decontamina-

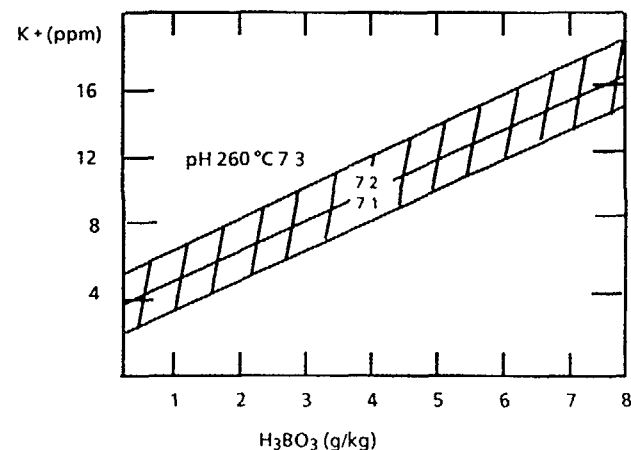


FIG. 1 (K^+) as function of boric acid concentration (pH calculations made on the basis of Meek data).

TABLE 1 SPECIFICATIONS FOR REACTOR WATER CHEMISTRY (WWER 1000)

Parameter	Value
pH (25 °C)	5.7 - 10.2
Halogens (Cl ⁻ + F ⁻) mg kg ⁻¹	<0.1
Dissolved oxygen, mg kg ⁻¹	<0.005
Dissolved hydrogen (NTP), ml kg ⁻¹	30 - 60
K ⁺ (tot) = (K ⁺) + (Na ⁺) + (Li ⁺) as function of H ₃ BO ₃ concentration mg eqv kg ⁻¹	0.05 - 0.45
NH ₃ , mg kg ⁻¹	>5.0
H ₃ BO ₃ g kg ⁻¹	0 - 13.5
Copper, mg kg ⁻¹	0.02
Corrosion product (as Fe), mg kg ⁻¹	<0.2

tion or unloading of spent resins are performed during reactor shut down periods for planned maintenance and repair

Normally a cation exchanger in potassium and ammonia form from the anion exchanger in BO₃-form are operating continuously. A cation exchanger in H-form is connected periodically, when potassium and ammonia concentrations in the coolant exceed the specified levels.

Two groups of filters are provided: one is in operation and the other is a standby. The capacity of each line is 40 t/h.

Long-term operation experience with fuel and post irradiation examinations in hot cells haven't revealed any case of fuel failure due to zirconium alloy corrosion. Oxide layers on fuel cladding are usually less than 3 μm thick, and internal hydrogen content on irradiated fuel cladding is about 0.008%. Number of leaking fuel elements doesn't exceed 0.02%.

The dose rate from the primary circuit equipment is mainly due to inner surface deposits of activated corrosion products (particularly, long-lived radionuclides), fission products are responsible only for a minor portion of the radiation dose. Radiation levels from WWER steam generator headers reach 1 - 2 R/h¹ for reactor operation period > 1 year.

The NPP's with WWERs are equipped with horizontal steam generators with vertical cylindrical collectors, headers and horizontal heat exchange tubing. This design prevents accumulation of slurry in the region of the tube expanded joints, and hence, the danger of tube corrosion damage. On these grounds austenitic stainless steel OX18H10T has been used for SG tube fabrication (compared to high nickel alloys in the foreign designs) and satisfactory operation of the equipment achieved with less stringent water chemistry specifications. The specifications of SG blowdown and feedwater are given in Table 2.

The secondary water chemistry of WWERs is corrected with hydrazine hydrate, continuously injected into the feedwater circuit before the LP-heaters. Injection is performed with a special facility which maintains the required hydrazine levels in all periods of reactor operation.

The NPPs with WWER reactors are provided with full flow condensate polishing plants, which consist of an (electromagnetic filter and a number of mixed bed demineralizers). The combination of

TABLE 2 SPECIFICATIONS FOR WATER CHEMISTRY OF STEAM GENERATORS (WWER)

Parameter	Value	
	Feed water	Blow down water
pH (25 °C)	7.5 - 8.5	7.8 - 8.8
Conductivity, μS cm ⁻¹	<0.3	<3
Hardness, μg eqv kg ⁻¹	<0.2	NS*)
Iron, μg kg ⁻¹	15	
Copper, μg kg ⁻¹	5(3)**)	NS
Oxygen, μg kg ⁻¹	10***)	NS
Sodium, μg kg ⁻¹	5	1000
N ₂ H ₄ , μg kg ⁻¹	40 - 70	NS
Oils, μg kg ⁻¹	100	NS
Chlorides, μg kg ⁻¹	NS	500
Electrochemical potential of Pt, E _{Pt} mV	100 ± 30****)	NS

- *) Not specified
- ***) With LP heaters having stainless steel piping
- ****) After deaerator
- *****) After the last LP heater

hydrazine injection with full flow condensate polishing ensures the specified quality of SG blow-down and feed-water.

Long-term experience shows, that normally the number of plugged tube in SG's does not exceed 0.08%.

In case of considerable deviations of water chemistry specifications corrosion failures of heat transfer tube were observed.

This depends not on duration of operation but on ingress of chlorides to the SG water.

2 Water Chemistry at NPPs with RBMK-Reactors

RBMK-reactors are cooled with demineralized water of high purity. No additives or inhibitors are dosed into recirculation or secondary circuits to prevent their accidental break through into the reactor water.

Operational experience has shown that the coolant quality in real systems corresponds to the specifications. For these see Table 3.

Considerable part of the NPP circuit (especially, that of the feedwater train) is made of pearlitic steels, which have higher corrosion rates compared to stainless steel OX18H10T. Corrosion products are released from these surfaces and can be carried out to the reactor core and activated there. In order to suppress these processes oxygen (up to 200 μg kg⁻¹) is injected into the feedwater circuit downstream the condensate polishing plant, and then removed from the water in the deaerator.

TABLE 3 SPECIFICATIONS FOR REACTOR WATER CHEMISTRY (RBMK-1000)

Parameter	Value
pH (25 °C)	6.5 - 8.0
Conductivity, $\mu\text{S cm}^{-1}$	1.0
Chlorides, $\mu\text{g kg}^{-1}$	<100
Iron, $\mu\text{g kg}^{-1}$	<200
Copper, $\mu\text{g kg}^{-1}$	<50
Salts, $\mu\text{g eqv kg}^{-1}$	<15

At present the injection of hydrogen into the system downstream the deaerator is proposed as the remedy for stainless steel piping IGSCC

With strict adherence of the adherence of the reactor and feedwater chemistries to the specifications, fuel deposits 40 - 60 μm thick are typical. These mainly consist of iron oxides (up to 90 %) and are the heaviest in the region of initial boiling.

The rate of (Zr + 1 % Nb) alloy corrosion in boiling water shows strong dependence on oxygen content and rather weak dependence on radiation. Internal hydriding of fuel cladding doesn't exceed 0.001 - 0.02 %, with hydrides oriented in a random or ring-like manner. On the corroding areas the hydrides have shown radial arrangement.

It is expected that radiolysis suppression may increase the operational reliability of both the fuel elements and (Zr + 2.5 % Nb) pressure tubes, the latter having much longer service life compared to that of the fuel elements.

Current R&D work is directed towards further optimization of the chemical system and increase of the NPP safety and reliability. Thus, much attention is paid to the physico-chemical processes in the NPP circuits and the development of new technologies for water chemistry control. Complex studies are also carried out in the direction of increasing material corrosion resistance, prevention of corrosion product deposition on the heating surfaces; designing systems for high-temperature clean-up of the coolant, new equipment for water preparation, and automatic systems for chemical and radiochemical monitoring.

HYDRAZINE REGIME FOR WWER-440 AND WWER-1000 PRIMARY CIRCUITS

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Abstract

Hydrazine regime in WWER type reactor primary circuit has been developed and proved in practice. This new water chemistry regime has been tested at Kolskaya, Rovenskaya and Pakash NPPs. With the use of hydrazine regime the corrosion product deposition constant is lowered in comparison to that of standard Ammonia-Boron-Potassium regime. This resulted in lower level of contamination stability. The use of Hydrazine regime immediately after standard regimes promotes peeling of corrosion products from fuel assemblies. Also its use during shut down conditions prevents pitting of vessels without stainless steel fusion cladding. Available data in the secondary circuit indicates that iron concentration exceeds the norm when hydrazine regime is used. The main source of iron entering the feed water is through steam and water of high pressure preheater and super heated steam separator. Analysis of corrosion product deposits formed in the secondary circuit after the introduction of hydrazine-ammonia water chemistry has been carried and the results given. The influence of hydrazine chemistry on the radiation chemical transformations of solution containing H_2BO_3 has been evaluated in this work.

Observation and discussion -

Water chemistry in WWER type reactor primary circuit with continuous hydrazine hydrate dosing of the coolant is developed and proved in practice. As a result of which the equipment surface contamination levels are reduced. When hydrazine hydrate water chemistry is adopted, the corrosion products from the primary circuit structural materials which are accumulated on fuel assemblies (FA) gets removed and the deposition rate of newly formed corrosion products is reduced significantly. Reduction in the amount of corrosion product in the intensive neutron zone reduces significantly the amount of radionuclides formed from corrosion products. Use of hydrazine water chemistry during shut down conditions (shut down, cooling, core refuelling and start up) prevents pitting of vessels without stainless steel fusion cladding.

New water chemistry regime was proved to be good when tested at two units of Kolskaya, two units of Rovenskaya NPP and Paksh NPP (Hungary). Research works on hydrazine hydrate dosing into the coolant of the reactor under operation were started in 1975 at Kolskaya NPP. When hydrazine was introduced into the coolant, increase in the concentration of ^{60}Co , ^{58}Co , ^{59}Fe , ^{51}Cr , ^{54}Mn , ^{56}Mn radionuclides were observed, which indicated that these radionuclides were washed off the FA surface.

Corrosion products formed under reactor operation conditions are found to deposit mainly on fuel assembly components (up to 85 - 90 %). Transport of corrosion products and radionuclides from fuel assemblies occurs mainly during fast power unit shut down (e.g. upon emergency protection system functioning). During this period the total activity of the coolant rises by 100 - 1000 times (Fig. 1).

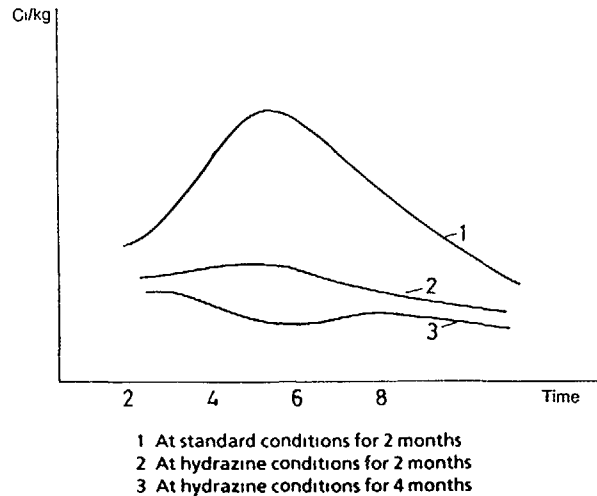
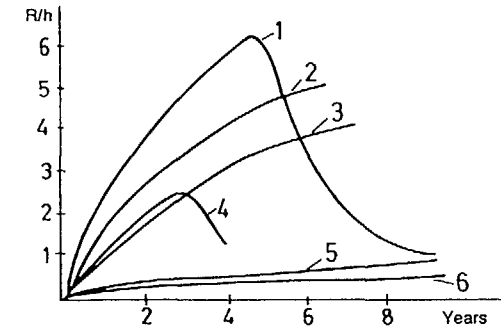


Fig 1 Change in radioactive contamination of the coolant of 20 min off load conditions

When standard boron ammonia potassium regime is used the constant for corrosion product deposition from the coolant was found to be $(1 - 5) \times 10^{-4} s^{-1}$. The product withdrawal factor of the special water treatment system (SVO 1) is $(1 - 2) \times 10^{-5} s^{-1}$. Activated corrosion products are deposited mainly on fuel assemblies. With the use of hydrazine hydrate regime, the corrosion product deposition constant decreased to $(1 - 5) \times 10^{-5} s^{-1}$. Comparable values of corrosion product deposition rate on fuel assemblies and their withdrawal to SVG-1 system leads to contamination stability at lower level, and in transient conditions the coolant activity increase doesn't take place (Fig 2)

The units 3&4 of Kolskaya NPP are operated with hydrazine regime from their very start up. Contamination of their primary circuits is much lower than that of Novovoronezhskaya NPP and Loviisa NPP for the same operation period (Fig 2)

The use of hydrazine regime at units 1&2 of Rovenska NPP after their long term operation under boron ammonia water chemistry conditions decreased the gamma dose rate on the surfaces of steam generator header by 6 - 7 times (Fig 2). The use of hydrazine ammonia water chemistry immediately after standard regimes promote peeling of corrosion products from fuel assemblies and their carry over to SVO 1 system. Also the use of hydrazine ammonia water chemistry in reactor shut down, off load periods and startup conditions prevented pitting of vessels without fusion on cladding. The second generation WWER 440 reactor vessels and pressurizers are manufactured from 48 TC and 22 K type pearlitic steels without stainless steel fusion cladding. Five such units were built in USSR. During reactor vessel inspection under operation conditions the cases of pitting were observed. Corrosion damage depth was found to be dependent on the time of operation of the respective power unit.



- | | | |
|-------------------------------|---------|-------------------------------|
| 1 Units 1&2 of Rovenskaya NPP | 5 KOLA3 | } Hydrogen from the beginning |
| 2 Unit 2 of Paksh NPP | 6 KOLA4 | |
| 3 Unit 1 of Loviisa NPP | | |
| 4 Unit 3 of Rovenskaya NPP | | |

Fig 2 Steam generator header radioactive contamination

The results of studies have shown that NO_2 and NO_3 ion concentration in reactor water increases. NO_2^- and NO_3^- ion formation reaction rates depend on residual gamma radiation dose rate after reactor setup (i.e. from time of fuel assembly operation to start up moment) and oxygen entering the reactor water.

Ionizing radiation and saturation with oxygen results in oxidation of ammonia dissolved in the coolant and the formation of nitrates and nitrites. When hydrazine water chemistry is used the nature of radiation and chemical transformations in solution consisting of 12 g/l of H_3BO_3 , 140 mg/l of NH_3 and 0.3 g/l of $N_2H_4 \cdot H_2O$ changes under the influence of radiation and free access to air. Residual radiation stimulates NO_2^- and NO_3^- ion reduction reactions in the presence of hydrazine and at temps 40 - 70°C. Pitting also stops at 1:3 mole ratio of NO_2^- and NO_3^- ion concentrations. With such concentration ratio maintained, reliable protection of reactor vessels manufactured from pearlitic steel is provided. Reactor vessel protection at Kolskaya NPP was achieved by this method.

The use of hydrazine water chemistry allowed to improve significantly the corrosion and radiation conditions in WWER 400 & 1000 primary circuits for the whole operation period. Results of longterm experience with hydrazine regime is available for WWER reactor secondary circuits.

Water quality specifications for WWER reactor secondary circuits are given in Table 1.

With the use of hydrazine the norm of iron could not be retained. The main source of iron entering the feed water is through steam and water of high pressure preheater (HPP) and super heated steam separator (SHSS). That is why iron concentration in feed water greatly exceeded the specified norm. The iron concentration values are given in Table 2.

Table 1

Water conditions of WWER 1 reactor secondary circuits

Specified index	Feed water at SG inlet	Turbine condenser		Condensate before deaerator	Saturated steam	Blowdown water	
		before condensate purification	after condensate purification			before bypass purification	after bypass purification
1	2	3	4	5	6	7	8
Hardness total g eq/kg		(0.5)	(0.5)				
Concentration Na $\mu\text{g/kg}$	5 (10)	10 (10)	5 (10)	-		1000 (200)	1000 (100)
$\mu\text{S/cm}$	0.3 (0.6)	2	0.3 -	- -	0.3 (0.4)	0.3 (0.6)	1.0 (1.0)
Concentration Fe $\mu\text{g/kg}$	15 (20)		-	-	-	-	-
Concentration Cu $\mu\text{g/kg}$				5 brass low pressure preheaters 3-steel			
Concentration O ₂ $\mu\text{g/kg}$	10 10	30 (30)	- (30)	- -	- -		-
Chloride concentration $\mu\text{g/kg}$						500 (500)	
Hydrazine concentration $\mu\text{g/kg}$	40 - 70 (20 - 60)						
pH at 25°C	7.5 - 8.5 (8.5 - 9.2)					7.8 - 8.8 (7.8 - 8.8)	
Ether extraction material $\mu\text{g/kg}$	100 100						
Conditional oxidored potential				100 ± 30 (100 ± 50)			

() without condensate purification

Table 2

Iron concentration in feed water of WWER reactor secondary circuits at NPPs

No	NPP	Iron Conc $\mu\text{g/kg}$
1	Khmel'nitskaya	50
2	Novo-Voronezhskaya	up to 40
3	Rovenskaya	up to 40
4	Zaporozhskaya	50
5	Kalininskaya	50

An increase in hydrazine concentration to 900 $\mu\text{g/kg}$ decreases iron concentration in feed water to 20 - 35 $\mu\text{g/kg}$ within 5 - 10 days, while hydrazine dosage increase to 80 - 100 $\mu\text{g/kg}$ did not lead to appreciably low iron concentration

The pH rise in secondary circuit should result in sharply decreasing pearlitic steel corrosion rate. The main difficulty with introduction of hydrazine ammonia water coolant chemistry is that copper containing alloys are present in secondary circuit and the NH_4^+ form cationite is absent in home industry H^+ cationite applied even at $\text{pH} = 9.1 \pm 0.1$ results in very small filter cycles

At Kalininskaya NPP for a period of one month hydrazine at a concentration of 40 - 50 $\mu\text{g/kg}$ and ammonium hydroxide at a conc. of 300 - 400 $\mu\text{g/kg}$ were dosed into feed water. Iron concentration in the steam generator feed water dropped to 10 $\mu\text{g/kg}$ level, copper concentration also did not exceed the norm. Hence hydrazine-ammonium water chemistry was introduced at Kalininskaya NPP, the iron concentration exceeded the norm only after high pressure preheater was put into operation, but even in this case it drops to the norm within 3 days. To examine the state of corrosion on equipment surfaces in the secondary circuit, the corrosion product deposits were sampled during repair periods, iron oxide chemical composition and phase content were determined. Results of the analysis are shown in Table 3. The deposits are mostly composed of iron oxides, with all known phases present where as under hydrazine regime the set of iron oxides is limited to 3 phases viz magnetite, hematite and lepidocrocite. Being predominantly made up of iron oxides, the deposits are common in their chemical composition, copper content is higher in steam generator and on mean-pressure cylinder stator blades. Considerable amounts of nickel present in the deposits are difficult to explain. In many cases nickel is found in larger amounts than copper.

To control the pearlitic steel and MHM-5-1 alloy corrosion rate, the samples were placed into the secondary circuit bypasses which are designed for taking representative samples. Bypasses layout is shown in Fig. 3. Studies showed that pearlitic steel is dangerous from the view point of corrosion during repairs, when equipment surfaces are affected by a damp atmosphere and are periodically wetted which results in the development of pitting corrosion. Average corrosion rates for representative samples are given in Table 4. Maximum corrosion rate is observed when pearlitic steel is kept after a unit purification system (UPS) in the bypass, minimum rate is in the condensate of super heated steam separator. It should be noted that corrosion rate of pearlitic steel under hydrazine regime is 3 - 4 times as high as under hydrazine ammonia regime. MHM-alloy corrosion rate is rather high under hydrazine-ammonia regime (Table 4), being almost double after corrective additive injection up to 0.14 g/m^2 per day. MHM-5-1 alloy resists corrosion when repairing equipment in the secondary circuit. Under hydrazine ammonia regime, corrosion rates remain within permissible limits. After the UPS, pearlitic steel corrosion rate is maximum. This fact as well as the difficulty in operating the UPS applying g cationite in the H^+ form make it possible to

Table 3
Analysis of WWER-1000 secondary circuit surfaces deposits

No	Site of sampling	Chemical analysis of sample mg/g						Phase analysis of iron oxides										
		iron oxide g/g	Cu	Fe	Cr	Ni	Si	δ FeOOH	α FeOOH	β FeOOH	γ FeOOH	Fe ₃ O ₄	α Fe	α Fe ₂ O ₃	γ Fe ₂ O ₃	α Fe ₂ O ₃ , V ₂ O ₅	A	B
1	Body of SHSS in shutter area (steel 20)	9	1.08	670	not determined	not determined	-	-	14	-	-	67	-	-	-	19	-	-
2	Steam pipe after SHSS in MPC (steel 20)	1	0.53	697	-	-	-	5	-	-	-	95	-	-	-	-	-	-
3	Slator blades of MPC (chrome steel)	65	9.07	260	12.6	-	-	-	-	-	28	28	15	-	-	16	13	
4	Upper part of MPC body	2	1.6	223	-	-	-	-	-	-	-	15	-	48	34	3	-	
5	LPP-2, condensate reversing chamber (steel 20)	0.6	0.9	642	-	-	-	-	-	10	64	-	-	-	26	-	-	
6	Triable deposits, down to the hole, from SG tubes (X18H10T)	70	72	385	1.04	43.4	-	-	-	-	55	-	9	-	31	5	-	
7	Bonded deposits	67	54	437	0.45	123	-	-	-	-	-	-	41	59	-	-	-	
8	Triable deposits from SG-4 bottom	30	23	402	1.02	40	-	-	10	-	64	-	26	-	-	-	-	

A, B - recurring non-identified phase

Table 4
Representative sample corrosion rate in WWER-1000 secondary circuit

No	Cassette location	Testing conditions	Surface preparation	Material	Deposit quantity g/m ²	Corrosion rate, g/m ² per day
1	Before UPS	P = 4.6 kgf/cm ² Q = 10 m ³ /h operation-215 days shutdown-20 days	grinding	MHM-5-1	0.4 ± 0.2	0.08 ± 0.01
2	After UPS condensate without corrective additives	- " - P = 2.5 kgf/cm ² Q = 5 m ³ /h	passivation	steel 20	225 ± 13	1.0 ± 0.1
3	Before LPP-3	- " - p = 13 kgf/cm ² Q = 13 m ³ /h	grinding	MHM-5-1	0.5 ± 0.1	0.14 ± 0.01
4	The bulk of condensate after LPP-4	P = 7.5 kgf/cm ² Q = 15 m ³ /h	grinding	MHM-5-1	1.2 ± 0.1	0.14 ± 0.01
5	Feed water after deaerator	P = 7 kgf/cm ² shutdown-235 days	passivation	steel 20	15 - 40	0.26 ± 0.3
6	Steam generator feed water after HPP	P = 70 kgf/cm ² operation-215 days shutdown-20 days	passivation	steel 20	10 ± 0.2	0.33 ± 0.10
7	Heating steam condensate	shutdown-235 days	passivation	steel 20	26 ± 5	0.16 ± 0.03
8	SHSS condensate after HPC	Q = 14 m ³ /h operation-215 days shutdown-20 days	passivation	steel 20	3.0 ± 0.5	0.20 ± 0.03
9	Heating steam condensate	shutdown-235 days	passivation	steel 20	22 ± 5	0.42 ± 0.08

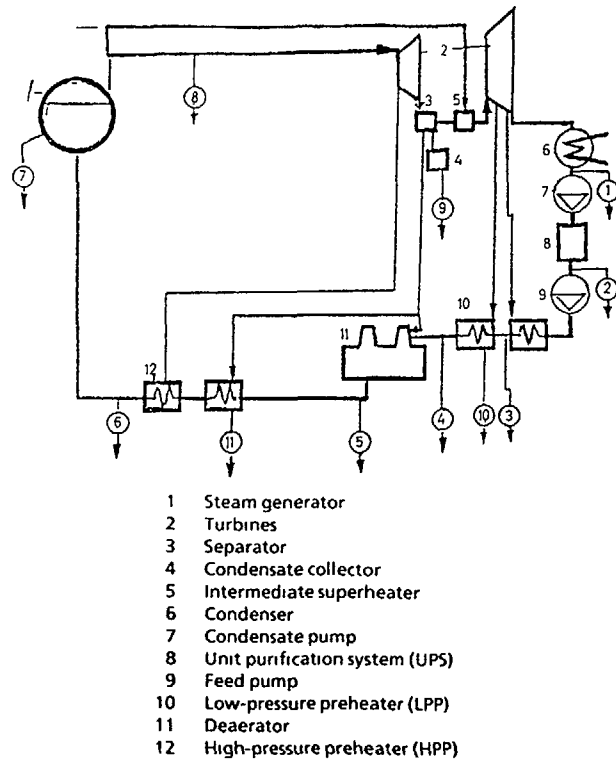


Fig 3 Diagram of representative samples arrangement in WWER-1000 second circuit
1 - 11 bypasses with samples cassettes

carry out experimental work when the secondary circuit purification system is shutdown for hydrazine ammonia regime to be established. This trend in studies supported by the fact that initially there were no unit purification systems in the second circuit, these were introduced with regard to non conditioned water chemistry.

Hydrazine regime used in WWER primary circuits was widely tested at operating NPPs and was found to have certain advantages of operation under the regime and in transient conditions. The use of hydrazine regime in the second circuit was developed further. At present hydrazine ammonia regime is considered to be more promising.

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Consultants Meeting on Decontamination

Berlin, Germany: 26-27 April 1990

Research Co-ordination Meetings

Heidelberg, Germany: 31 May - 3 June 1988
Vienna, Austria: 20-23 November 1989, 6-9 May 1991