

# ***Coolant technology of water cooled reactors***

## ***Volume 3: Activity transport mechanisms in water cooled reactors***



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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.



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## CONTENTS

### OVERVIEW

Activity transport mechanisms in water cooled reactors .....	9
<i>E.W. Thornton</i>	

### NATIONAL CONTRIBUTIONS

#### Czechoslovakia

Comparison of standard and hydrazine water chemistry of VVER 440 units .....	55
<i>M. Burclova</i>	

#### France

Observations on recent application of high coolant pH in French PWRs and optimization of chemistry during shutdown .....	61
<i>P. Beslu</i>	

#### Germany

Lowering the corrosion rate to limit radioactive deposits .....	65
<i>R. Winkler</i>	
Behaviour of colloidal corrosion products .....	70
<i>F. Hüttner, R. Winkler</i>	

#### Hungary

Correlation of out-core surface activities and primary water chemistry in VVER-440 reactors .....	73
<i>G.L. Horváth</i>	
Influence of the primary circuit water chemistry on out-core surface activities .....	77
<i>G.L. Horváth, V. Civin, P. Ormai, T. Pintér</i>	

#### India

Good practices of man-rem reduction in PHWRs .....	89
<i>K.S. Venkateswarlu, P.K. Mathur, S.V. Narasimhan, G. Venkateswaran</i>	

#### Korea, Republic of

Assessment of failed fuel and tramp uranium based on the activity of fission products in the primary circuit .....	91
<i>Jae-Choon Yang</i>	

#### Switzerland

Corrosion products, activity transport and deposition in boiling water reactor recirculation systems .....	98
<i>H.P. Alder, D. Buckley, R. Grauer, K.H. Wiedemann</i>	
Corrosion products, activity transport and deposition in boiling water reactor recirculation systems: Review of the state of the art, May 1990 .....	124
<i>H.P. Alder</i>	

## **Union of Soviet Socialist Republics**

Main trends in investigations of corrosion products transfer processes in NPP circuits .....	132
<i>V.V. Versin, V.P. Brusakov, I.L. Rybalchenko, K.G. Kritskij, A.S. Korolev</i>	
Transfer of corrosion product particles in reactor circuits: Quantitative evaluation of corrosion product deposition on fuel elements .....	138
<i>V.P. Brusakov, Yu. A. Khitrov, V.N. Feofanov, V.V. Versin</i>	
Investigation on electromigration characteristics of corrosion products .....	144
<i>V.M. Sedov, V.A. Dojlnitsyn, A.I. Ovsyannikov, D.S. Gasanov, S.A. Medvedev</i>	
Technical-economic assessment of low cobalt content in structural materials .....	151
<i>Yu.N. Aniskin, Yu.A. Khitrov</i>	
Super-pure steel for nuclear power ( <i>Summary</i> ) .....	155
<i>Yu. A. Khitrov</i>	
USSR experience in decontamination and water chemistry of VVER type nuclear reactors .....	155
<i>V.I. Pashevich</i>	

## **United Kingdom**

PWR activity transport with reference to soluble and particulate corrosion products:	
Chemical and radiochemical analysis of PWR particulate material .....	175
<i>K.B. Butter</i>	
Method for pH calculation .....	183
<i>E.W. Thornton</i>	

Participants in the Co-ordinated Research Programme .....	186
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# ACTIVITY TRANSPORT MECHANISMS IN WATER COOLED REACTORS

E.W. THORNTON

Berkeley Nuclear Laboratories,  
Central Electricity Generating Board,  
Berkeley, Gloucestershire,  
United Kingdom

## Abstract

This paper is concerned with the identification of the mechanisms by which radioactivity is generated and subsequently deposited in reactor components and with identifying methods of minimising the resultant radiation dose rates. Emphasis is largely placed on the Pressurised Water Reactor with some discussion of its heavy water variants. A smaller part of the paper is devoted to the Boiling Water Reactor.

### (a) Pressurised Water Reactors

By far the major part of radiation dose rates is due to the activated corrosion or erosion products of the materials of construction of the main coolant circuit and of circuits which feed it. The corrosion of materials, movement of corrosion products and the magnitude of activity generation and deposition is the result of a very complex interaction between coolant chemistry and materials and is not understood well enough for predictive models to be reliable at present.

This document introduces the basic chemical concepts of solution and particulate chemistry and concludes that the role of particulate matter in activity transport is particularly poorly understood at this time.

The remainder of the document devoted to PWR investigates in detail the contributions of individual plant components to the formation of activated corrosion products and how these may be controlled by optimum selection of materials and coolant chemistry.

$^{60}\text{Co}$  is identified as the most important nuclide and an order of priority for reducing its precursor  $^{59}\text{Co}$  by selection of materials is established. Minimisation of activity generation and deposition is also discussed with respect to the types of surface finish and to the role of the preconditioning of surfaces before nuclear heat.

The chemistry of the coolant is primarily determined by the need to control corrosion and reactivity and these place the primary constraints on the composition of the coolant. The most significant parameter within the Chemist's day to day control is pH. The Document discusses in detail how pH varies with coolant composition and how it can affect the generation and deposition of activity through controlling crud solubility.

It is generally believed that the primary objective of pH control should be to select and maintain a pH which minimises deposition of corrosion products in

the core. Theories are based on the need to select a pH at which the temperature coefficient of solubility of the nominal iron spinel is zero at the core inlet temperature and positive across the core so that dissolving conditions are created in the core. The paper discusses the basis for concluding that the optimum pH is about 7.4 at 300°C. For most of a fuel cycle in reactors employing lithium hydroxide as alkalisng agent, this is higher than that achievable with the maximum concentration of alkalisng agent currently allowed by fuel vendors to prevent undue corrosion of fuel element cladding and results in various compromise chemistry regimes being employed.

There is extensive discussion of the practical results in many countries of applying various chemistry regimes, particular mention being made of the difference in chemical control methods employed in reactors of Russian design and those of other countries. In general, the correlation between the radiation dose rates and the predictions of theory are not particularly clear showing that many other factors influence dose rates.

Further sections are devoted to producing elevated pH in coolant without compromising the integrity of the fuel cladding and to the complications of pH control that can arise if load following or extended cycle operation is desired.

A final section summarises the principal findings and recommendations on materials choice and chemical control. Experience shows that control of materials, especially of cobalt hard facings, is instrumental in producing low dose rated. Conversely, the definition of an optimum chemical regime is less clear although the broad principles are agreed.

### (b) Boiling Water Reactors

$^{60}\text{Co}$  is identified as the most important contributor to radiation dose rates and, as in PWRs, cobalt hard facings are identified as the most probable major source of precursor cobalt.

The processes of activity buildup and the main chemical characteristics of the circulating and surface oxides are described. Most of the mass of crud is alpha Haematite although most activity appears to be associated with oxides having a Spinel structure.

Practical intervention to reduce activity generation is discussed primarily in terms of feedwater chemistry and feedwater material control. A list of other practical activity reduction measures is also given.

## 1. INTRODUCTION

This paper gives a summary of the current understanding of the mechanisms for corrosion product and radioactivity transport and deposition in the PWR primary circuit. The situation for the BWR system is to be found in the extensive reviews in the papers entitled "Corrosion products, activity transport and deposition in boiling water reactor recirculation systems" by H.P. Alder, D. Buckley, G. Grauer, K.H. Wiedemann and "Review of the state of the art", May 1990 by H.P. Alder. A summary of these papers will be given in

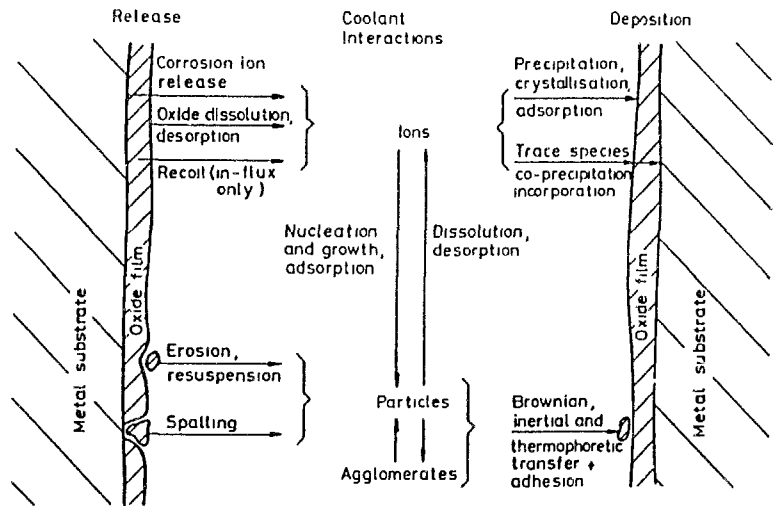


FIG. 1. PWR corrosion product formation, transport and deposition mechanisms [4]

2.1. Generation of Radioactivity

Material in the reactor core is neutron activated during power operation. There are two types of material in the core, the core components and corrosion products deposited temporarily in the core but released originally by corrosion of out-of-core components. Radioactive isotopes produced in both of these sources are available for release to the coolant, transport by it around the primary circuit and deposition in exactly the same manner as their non-radioactive counterparts.

For in-core materials, neutron activation in-situ leads to the release of radioactive corrosion product nuclides directly, whereas release from out-of-core materials must result in transport and deposition in-core before activation and re-release to the circuit can occur. This leads to a clear distinction regarding the relative importance of corrosion product sources in-core compared with those out-of-core. While in-core sources may contribute only a small proportion of the total elemental input of corrosion products, they could prove to be the major source of radioactive nuclides. As will be discussed, this has proved to be the case in some plants.

The following data give a summary of typical quantities of radioactivity contained in PWR primary circuit deposits:

Best Estimate Grud Inventory (TBq)

Radioactive Species	60Co			58Co
	4y	8y	40y	>1y
Out-of-Core Deposit	25	45	65	50
Core Crud	15	15	15	175
Refuelling	2	2	2	20
Shutdown Release				
Total	42	62	82	245

and the contribution of various radioisotopes to the lifetime collective station dose of PWRs:

Origin		Contribution to Dose (%) [2]	
Neutrons + 16N		5	)
Activated Core		5	) 15
Fission Products		5	)
Activated Corrosion Products		60Co	60 )
		58Co	15 ) 85
		Other	10 )

the main text of this volume. Other contributions representing detailed current views of particular aspects of corrosion product generation and transport are given as further National contributions. In some cases, use has been made of the information given in these National contributions to supplement the main text of this report.

Most of the processes involved in the broad subjects of PWR and BWR corrosion product and activity transport modelling were reviewed recently as part of an IAEA coordinated research programme on "Investigation of Fuel Element Cladding Interaction with Water Coolant in Power Reactors" and the results published as an IAEA technical document [1].

The PWR primary circuit and the BWR recirculation system are constructed principally from alloys of the first row transition elements: Cr, Mn, Fe, Co and Ni. The fuel is clad in a zirconium alloy and other elements are used in small quantities. All of these alloys corrode to a greater or lesser extent, becoming covered with corrosion product films. The films are composed of oxides of the elements, and the elements themselves are released to the coolant and transported by it both as soluble ions or molecules and as particles in which they are incorporated or on which they are absorbed. Material may also find its way into the coolant via make-up flows.

2. CORROSION PRODUCT AND ACTIVITY TRANSPORT MECHANISMS - PWR

Figure 1 summarises PWR corrosion product formation, transport and deposition mechanisms.

The production rate of an isotope by a given reaction may be determined from a knowledge of the parent abundance in the target material, the cross-section for the reaction and the relevant neutron flux. The radioactive corrosion products dominating shut down radiation fields are generally  $^{60}\text{Co}$  and  $^{58}\text{Co}$  with lesser contributions from  $^{59}\text{Fe}$ ,  $^{54}\text{Mn}$ ,  $^{51}\text{Cr}$  and others.

## 2.2. Coolant Chemistry

The PWR coolant contains boric acid, lithium or potassium hydroxide base and hydrogen dissolved in the water. The hydrogen may be dosed into the water directly or via the decomposition of ammonia. The most important solution parameter from the point of view of corrosion product transport is pH. This is the only parameter which can readily be altered since the hydrogen concentration which defines redox potential is specified within a fairly narrow band. pH is defined as  $-\log_{10}(\text{proton molality})$  and is controlled by the concentrations of boric acid and base. Since pH is an important parameter and there are a number of different treatments in the literature the paper entitled "Corrosion products, activity transport and deposition in boiling water reactor recirculation systems" by H.P. Alder, D. Buckley, G. Grauer, K.H. Wiedemann gives an account of pH calculation and recommends a standard calculation method involving use of the Marshall and Franck [3] correlation for the ionisation constant of water ( $K_w$ ). All pHs quoted in this Chapter use this correlation.

pH is sometimes used as a shorthand method of relating the behaviour of corrosion products in boric acid + lithium or potassium hydroxide solutions of different composition (but possessing the same proton concentration), for example oxide solubility or particle surface electrical potential. This is satisfactory for isothermal comparisons. However it must be remembered that:

1. The polymerisation of boric acid and the ionisation of both boric acid and water are temperature dependent. Consequently the pH of boric acid containing solutions is temperature dependent and pH at one temperature is not easily related to pH at another.
2. The variation of pH with temperature  $(dpH/dT)_{B, Li}$  differs slightly for boric acid + base solutions of different composition but having identical  $pH_T$ . This is due to the temperature dependent boric acid polymerisation reactions. It is important when considering temperature coefficients of oxide solubility, see below.

Caution should always be exercised in using pH as a parameter when different studies (say of oxide solubility or plant data) are compared. The pH calculated is always sensitive to the value of the water ionisation constant used in the data analysis.

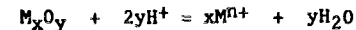
## 2.3. Corrosion Products

Corrosion products can conveniently be divided into soluble and particulate species. This section will discuss the natures of soluble and particulate species and their various transport mechanisms and interactions. A detailed discussion of the mechanisms is given by Rodliffe, Polley and Thornton [4].

### 2.3.1. Soluble species

The corrosion process releases dissolved metal cations to the coolant. Corrosion product oxides can also dissolve. The term "soluble species" refers to true dissolved molecular or ionic species. The usual practice of defining soluble species as that fraction passing through a 0.45 micron filter is quite arbitrary as it takes no account of colloidal material (see below).

In general, metal oxides dissolve to produce cations in solution and these will undergo hydrolysis thus:

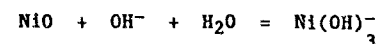


etc. In this case, dissolution of  $M_xO_y$  does not involve oxidation or reduction and  $y = nx/2$ .

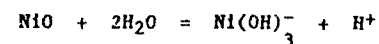
These hydrolysis reactions cause oxide solubility to be dependent upon solution pH. Extensive solubility studies of oxides containing only one metal (magnetite and nickel oxide) have resulted in estimates of thermodynamic parameters for the iron and nickel cations and their hydrolysis products up to 300°C without extrapolation. Data for all the other transition metals are sparse.

Two difficulties arise with data derived from oxide solubility studies - intercomparison and extrapolation outside the temperature range over which data were acquired, particularly above 300°C:

1. Before the results of different studies can be properly compared, it is essential that the data all be evaluated on exactly the same basis, using the same correlation for the ionisation constant for water. Nickel oxide and magnetite solubility data have been reanalysed by Thornton and Walker [5] resulting in a self-consistent set of parameters which can be extrapolated to above 300°C.
2. The temperature dependence of a thermodynamic equilibrium constant is most accurately accounted for when the heat capacity change for the reaction is small. However, the heat capacities of ionic solution species are large and strongly temperature dependent at high temperatures (above 250-300°C). This difficulty can be overcome by writing reactions in such a way that the net number of charged species in solution is conserved (an isoelectronic reaction):



instead of:



Thermodynamic calculations (as opposed to experimental studies) of oxide solubility rely on estimated, extrapolated thermodynamic parameters for ionic species and should be treated with caution. Many of the early studies used a procedure for extrapolating the necessary thermodynamic functions (the Criss-Cobble theory) which is probably not valid for the species involved. The means of extrapolating high temperature thermodynamic data has recently been well summarised by Cobble et al. [6]. These authors give estimates of the hydrolysis constants of the divalent cations of manganese to copper at temperatures up to 300°C, together with the thermodynamic properties of  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$  and  $Ni^{2+}$ . Thus there is still a lack of data for chromium and cobalt solution species at high temperature.

Experimental measurements have been made of the solubility of mixed metal oxides but in general the data are too sparse to allow good thermodynamic models to be fitted to the data. The results obtained by Westinghouse researchers on mixed spinel solubility have been summarised by Kunig and Sandler [7]. A correlation for iron solubility from some of the Westinghouse data over a limited range was made by Lindsay [8].

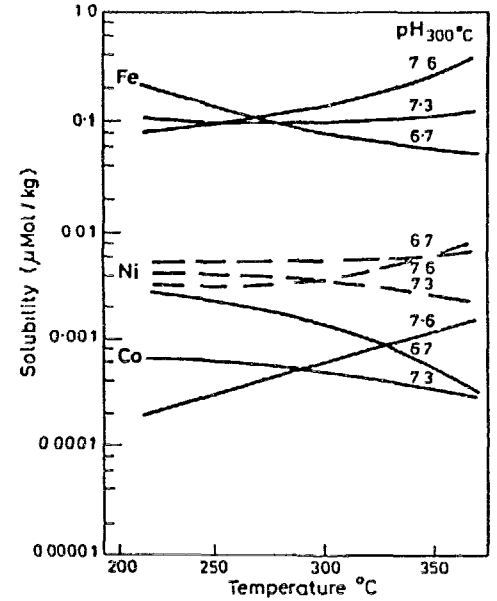
Oxide solubility depends upon solution chemistry and temperature. The important chemistry parameters are pH and redox potential (if dissolution involves reduction or oxidation). The latter is controlled in the PWR primary circuit by hydrogen addition. Two generalisations can be made:

1. At a given temperature, solubility has a minimum at some pH, with high solubility at the extremes of the pH scale.
2. The temperature coefficient of solubility can be positive, negative or zero depending upon temperature and solution chemistry.

These remarks apply both to the metals dissolved from "pure" oxides (i.e. containing a single metal) and to metals dissolved from mixed oxides such as corrosion product spinels.

Figure 2 shows Westinghouse results for Fe, Ni and Co equilibrium solubility from mixed spinels as a function of temperature and lithium hydroxide concentration in 650 ppm B boric acid. Iron and cobalt have clear negative temperature coefficients of solubility at a low lithium concentration (1.0 ppm Li), and positive temperature coefficients at a higher concentration (10 ppm Li). The results for Ni solubility are less clear cut. Fig.3 summarises temperature coefficients of solubility for iron dissolving from a nickel ferrite ( $x = 0.5$ ). The solid line shows the coolant compositions at which the temperature coefficient of iron solubility from the nickel ferrite is zero at 300°C (pH = approximately 7.4 at 300°C but altering from 7.39 at 1100 ppm B to 7.45 at 100 ppm B).

Points above the zero temperature coefficient of solubility line have positive temperature coefficient of solubility. This has important implications for choice of coolant chemistry since the sign of the temperature coefficient of solubility governs the tendency of corrosion products to precipitate on or dissolve from heat transfer surfaces such as fuel elements or steam generator tubing, i.e. in-core or out-of-core. It can be seen that a coolant chemistry specified to give zero or positive temperature coefficient of iron solubility over some temperature range will not necessarily correspond to an exactly constant pH at any given temperature.



Compound	Chemistry (LiOH)	pH <sub>300°C</sub>
$Ni_{0.22}Co_{0.24}Fe_{2.54}O_4$	$1.0 \times 10^{-4} M$	6.7
$Ni_{0.50}Co_{0.05}Fe_{2.45}O_4$	$4.0 \times 10^{-4} M$	7.3
$Ni_{0.50}Co_{0.05}Fe_{2.45}O_4$	$1.0 \times 10^{-3} M$	7.6

FIG. 2. Solubility of iron, nickel and cobalt from nickel-cobalt ferrites as a function of temperature and pH of 0.06 molal  $H_3BO_3$ , 25 cm<sup>3</sup>·kg<sup>-1</sup>  $H_2$  (redrawn from Ref [8]).

In summary, soluble species occur in the PWR primary coolant and are transported with it. Some of their thermodynamic properties are known but there are also gaps in these data. It is sufficient to note here that soluble species provide a pathway for corrosion product transport: following release by the corrosion reaction or dissolution from an oxide layer or particle, soluble species can participate in precipitation, dissolution and ion exchange with corrosion product oxides. After dealing with particulate material next we will return to soluble species to discuss their interactions with particles and oxide films via dissolution and precipitation.

### 2.3.2. Particulate material

Particles may be released from the precipitated outer layer of corrosion films by some process such as erosion and they may grow by heterogeneous nucleation in the bulk coolant to relieve supersaturation. It is possible that charging and make-up flows contain particulate impurity which could act as nucleation sites.

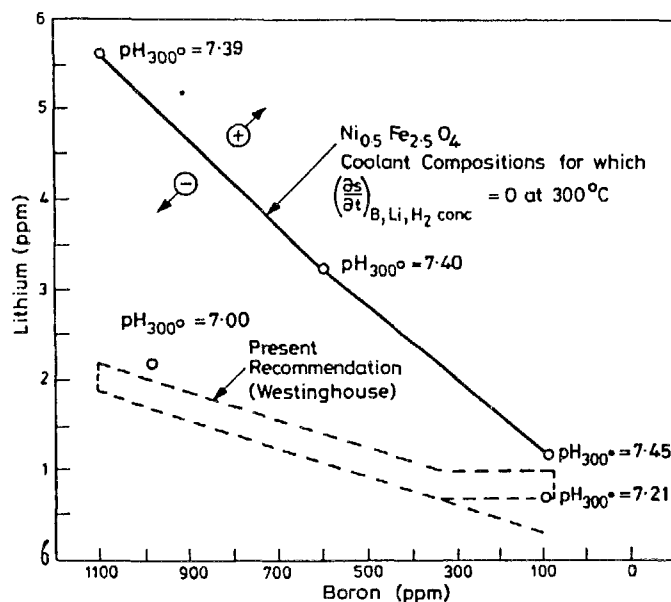


FIG. 3. Boundary between positive and negative coefficients of solubility for  $\text{Ni}_{0.5}\text{Fe}_{2.5}\text{O}_4$ , at  $300^\circ\text{C}$  and dissolved hydrogen concentration at 25 STP  $\text{cm}^3/\text{kg}$   $\text{H}_2\text{O}$ , compared with presently recommended Westinghouse control band for lithium boron co-ordination based on  $\text{Fe}_3\text{O}_4$  (redrawn from Ref. [8]).

Particulate material can usefully be divided into colloidal ( $<1\mu\text{m}$ ) and inertial ( $>1\mu\text{m}$ ) components since their transport to and from surfaces and their interactions with surfaces are governed by distinctly different mechanisms. We should also remember that the arbitrary distinction imposed by the conventional use of 0.45 micron membrane filters, mentioned above, takes no account of colloidal particles. Table 1 summarises the important properties of inertial and colloidal particles.

Colloidal studies may provide the link between the soluble and particulate phases of corrosion products.

Surveys [10] of colloidal studies done by Clarkson and others showed that the role of small size (colloidal) particles in activity transport may be important, because the rate of cobalt incorporation into adherent oxide deposits is limited by kinetic rates of oxide formation rather than by absolute concentration levels of radionuclides. The most important factors influencing the above kinetic rates are the temperature and "oxidation potential". Small size colloidal particles have also an important role in oxide formation.

Importance of potentials (zeta potential) is also acknowledged by Westinghouse researchers [10] who consider the zeta potential as the most important single

TABLE 1. PROPERTIES OF COLLOIDAL AND INERTIAL PARTICLES [9]

Particle Diameter	Colloidal Particles	Inertial Particles
	$<1\mu\text{m}$	$>1\mu\text{m}$
Boundary layer mass transfer mechanism	(i) Brownian diffusion (ii) Thermophoresis ( $0.1-1.0\mu\text{m}$ ) at heat transfer surfaces	(i) Inertial projection (ii) Gravitational settling ( $>100\mu\text{m}$ )
Dominant forces acting on particles	(i) van der Waals (ii) Electrical double layer (iii) Magnetic ( $0.1-1.0\mu\text{m}$ ) if substrate is magnetisable	(i) van der Waals (ii) Electrical double layer (iii) Gravity ( $>100\mu\text{m}$ ) (iv) Hydrodynamic drag
Surface interaction parameter	Surface reaction rate constant	Sticking probability

property for characterizing the oxide/solution interface and associated phenomena such as adsorption and electrokinetics. Evaluating the results of colloidal science these scientists suggest an activity transport model based on zeta potential, which provides a crucial link between dissolved ions and suspended particles and allows both to be included into the same model describing chemical behaviour of solution, colloids and large particles simultaneously.

The transport of colloidal particles between surfaces and the coolant bulk is described by well established empirical correlations. However the interactions of colloidal particles with surfaces cannot be said to be adequately understood. This is due to a lack of both plant and experimental data under the appropriate conditions and to inadequate understanding of electrical double layer forces. The latter has proven an intractable theoretical problem.

The transport of inertial particles between surfaces and the coolant bulk is well understood using correlations which have been validated for aerosol systems and are widely accepted. The interactions of inertial particles with surfaces during deposition or resuspension are largely understood.

Useful plant predictions have resulted from an understanding of the principles governing the behaviour of soluble species and the solubility measurements of synthetic corrosion product oxides (see 2.3.1. above). In contrast, lack of data has held up an understanding of the deposition and resuspension of particulate species [9][10] and consequently, reliable predictions concerning the impact of particulate species on radiation field build-up are really not possible at this time.

To summarise, inertial particles are found in PWR coolants and measurements can be made on reactor systems. Colloidal particles are difficult to measure



at the concentrations involved in reactor circuits. There are some gaps in our knowledge of the details of particle interactions with surfaces or with each other; however these gaps are more pertinent to corrosion product modelling than to the present review where it is sufficient to note that inertial particles certainly participate to a limited degree in corrosion product transport while colloidal particles play a conjectural but possibly important role. The source of particles is not known at present and plant measurements are required to resolve this; the source of particles is an important factor in choosing the optimum coolant purification strategy.

### 2.3.3. Dissolution and Precipitation

When the bulk coolant concentration is less than saturation solubility, net corrosion product oxide dissolution occurs; supersaturation is relieved by precipitation.

There are basically only two processes which occur at the solid/liquid interface: cations dissolved in the coolant can adsorb onto the surface and cations at the surface can desorb into the coolant bulk. There is a constant exchange flux between corrosion product oxides and cations dissolved in the coolant. These exchange processes occur by mass transfer through the fluid boundary layer and reaction at the surface. The mass transfer process is well understood and adequately described by empirical correlations with little extrapolation [4]. However, only limited measurements of adsorption and desorption rates have been made. Some of the measurements indicate that adsorption and desorption are limited by surface reaction rates rather than by mass transfer in the fluid [11][12]. However, there is evidence for precipitation at rates close to mass transfer limited rates in some corrosion experiments [13]. There is clear need for further addition to the limited experimental data base here.

When adsorption and desorption occur at equal rates at the surface of a soluble corrosion product oxide, the bulk coolant is saturated with dissolved corrosion product cations. However the exchange fluxes still occur even though there is no net dissolution or precipitation of corrosion product oxides.

When adsorption of a cation occurs on the surface of an oxide which already contains a substantial fraction of the same cation (e.g.  $\text{Fe}^{2+}$  on a spinel) then it is not possible or necessary to distinguish between adsorption and oxide growth. Similarly, when a cation leaves such a surface the processes of desorption and dissolution are synonymous.

Even though the radiologically significant cobalt species are trace species their adsorption and desorption behaviour should be describable by mechanisms similar to those used to describe the major species.

The mechanism by which cations are taken up by the in-core Zircaloy oxide corrosion film is generally taken to be adsorption at the oxide/coolant interface. Few measurements are available on the kinetics of the adsorption and desorption steps at high temperature and none have been made under in-core conditions. Lister, Kushneriuk, and Campbell [14] fitted deposition and release coefficients to an adsorption model applied to the results of a rig experiment under CANDU chemistry conditions. They also obtained some limited

evidence that a portion of the deposited  $^{60}\text{Co}$  had become incorporated in the oxide on the Zircaloy tubing in a bound form, which requires solid state diffusion for its removal.

The recognition of adsorption and the exchange fluxes on corrosion product oxides implies that adsorption of target nuclides (e.g.  $^{59}\text{Co}$ ) might occur on fuel pin Zircaloy oxide corrosion films even in the absence of any net deposition of corrosion product oxides on the fuel pins [15][14]. This pathway may limit the benefit to be gained from the use of coolant chemistry to control out-of-core radiation fields.

If a trace radioactive species adsorbs on a surface that is growing then it can be buried by further growth, in which case the term co-precipitation might be applied. Radioactive species can also diffuse into particles and oxide films subsequent to being adsorbed. The radioactive ion cannot now be released back to the coolant without first diffusing to the oxide/coolant interface. The mechanism by which radioactivity is incorporated into the inner corrosion layer on out-of-core surfaces is a contentious issue, in particular whether there is transport of metal ions in inner layer pores. Surprisingly, the mechanism of film growth is still not known with certainty. Camp ([16] measured cobalt profiles in pre-formed stainless steel oxide films on coupons exposed in a rig used to study Stellite corrosion. He found simple cobalt diffusion profiles with no evidence for enhanced incorporation deep in the oxide films, at the oxide/metal interface. Analysis of the diffusion profiles indicates that cobalt uptake was controlled by oxide grain boundary diffusion, with little or no contribution from bulk solid state diffusion or solution phase transport.

To summarise, the exchange fluxes provide a pathway for radioactive species to be transported around the circuit when net corrosion product movement is minimised and for the processes of activity and corrosion product transport to be decoupled. They provide a way for target nuclides such as  $^{59}\text{Co}$  to be adsorbed on fuel elements even in a core which is free from deposited corrosion product particles.

### 2.4. Summary

We have seen that corrosion products are released from construction materials and transported around the PWR primary circuit as both soluble and particulate species. We have also noted that exchange fluxes occur between soluble species and corrosion product oxides. Radioactive species can be released from corrosion products deposited in-core or adsorbed on fuel pins and directly from the corrosion of in-core components.

Activity transport occurs when radioactive species move around the circuit, from the core, to deposit on out-of-core surfaces. To account for all of the mechanisms leading to the build-up of out-of-core radiation fields we must account for:

1. the sources of neutron activatable isotopes,
2. their transport to and deposition in-core,
3. release of radioactive isotopes from in-core (both from deposited corrosion products and directly from in-core components) and
4. their transport out-of-core and deposition on out-of-core surfaces.

There are thus a number of transport paths to which both soluble and particulate species can contribute. The predominance of either soluble or particulate species to a given pathway cannot be predicted reliably under all conditions of temperature and chemistry, especially when transients occur. Hence neither soluble or particulate species can be safely neglected.

It will be seen in the following that low pH operation is correlated with high out-of-core radiation fields [17] and it will also be established that Stellite is a major source of  $^{59}\text{Co}$  (and hence  $^{60}\text{Co}$ ) in PWRs [18][19]. However these successes must not be taken as an indication that all of the mechanisms involved in corrosion product and activity transport are well understood and can be accounted for quantitatively. The state of understanding is that some mechanisms are established and plant data have confirmed qualitative trends or correlations.

The next section will give details of accepted approaches based on radiation field control in PWRs and indicate possible future approaches based on plausible transport mechanisms and sources of neutron activatable isotopes.

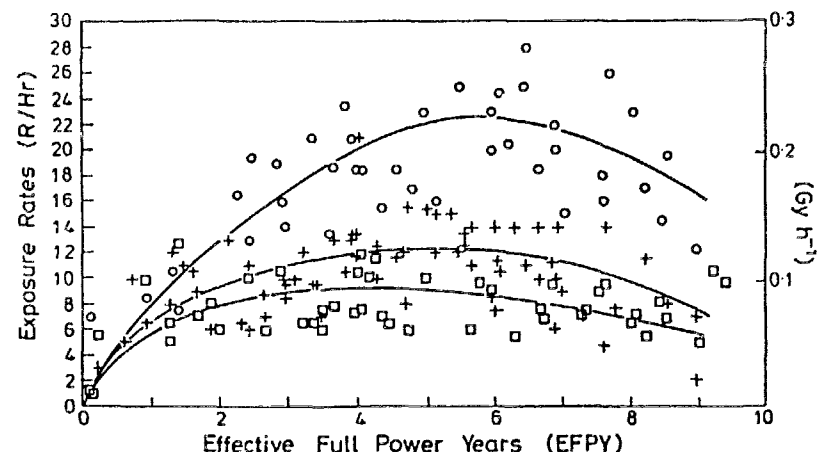
### 3. SCOPE FOR CONTROL AND INTERVENTION - PWR

#### 3.1. Introduction

The purpose of this section is to consider options which are potentially available for control of the development of radiation fields in PWRs and the scope for intervention. The formulation of these options is based on data concerning the processes of corrosion product generation and transport, together with worldwide experience of reactor operation. The processes of generation and transport of corrosion products have been considered above. Reactor operating experience shows that the build up of radiation fields varies very markedly from plant to plant. Bergmann has attempted to place individual Westinghouse plants into one of three categories, according to the radiation fields observed, with a view to identifying the factors involved (Figs 4 and 5) [20, 21]; this confirms that operational factors other than operating time are important. The general pattern of development of radiation exposure also seems to differ from one utility to another, as can be seen from Figs 6 to 8, which cover a typical range of world experience. This topic will be considered in more detail later in this Chapter.

Approaches to the control of radiation fields include controlling the input of corrosion products to the system, controlling the transport of these corrosion products during operation, and removal of corrosion products from the system. As indicated above the active species principally responsible for the development of out-of-core radiation fields in western PWRs are  $^{58}\text{Co}$  and  $^{60}\text{Co}$ , resulting from the activation of nickel and cobalt respectively. In the first year or two of operation  $^{58}\text{Co}$  is dominant, but through most of plant life  $^{60}\text{Co}$  is the most important radionuclide, as shown in Fig. 9.

Corrosion products enter the system either from the corrosion of primary circuit materials or from the CVCS. Options for the control of input from either source include selection of materials to reduce the rate of corrosion release, modification of the composition of materials (for example replacement of high cobalt alloys, reduction of permitted cobalt impurity levels in steels



□ Group 1	+ Group 2	○ Group 3
D.C. Cook Unit 1	Doel Unit 1	Indian Point Unit 2
Kewaunee	Doel Unit 2	Point Beach Unit 1
Prairie Island Unit 1	R.E. Ginna (S/G #1)	R.E. Ginna (S/G #2)
Prairie Island Unit 2	Beznau Unit 1	
Point Beach Unit 2	Beznau Unit 2	
San Onofre Unit 1	Ringhals Unit 2	
Yankee-Rowe	H.B. Robinson	

FIG. 4. Buildup of steam generator channel head dose rates (long term trends) (redrawn from Ref. [21]).

and Inconel), and modifications of the pre-treatment processes (including hot commissioning) to reduce corrosion release rates. Input from the CVCS might also be limited by some form of purification applied to the input system (for example high temperature ion exchange).

Control of the transport of inactive and activated corrosion products is an essential step in limiting the growth of radiation fields, and this control is exercised through the choice of coolant chemistry. Possible chemistry regimes which have been recommended include the adoption of a pH calculated to minimise iron solubility or the adoption of a pH to ensure a zero or positive temperature coefficient of solubility. The control of pH is complicated by the presence of boric acid in concentrations which vary according to the requirements for reactivity control. Since the chemistry regime must also be chosen to take account of its influence on corrosion release rates the selection of an appropriate alkaline solute and the choice of appropriate concentrations present a range of options. These include co-ordinated chemistry regimes and in particular the adoption of a higher pH regime. A

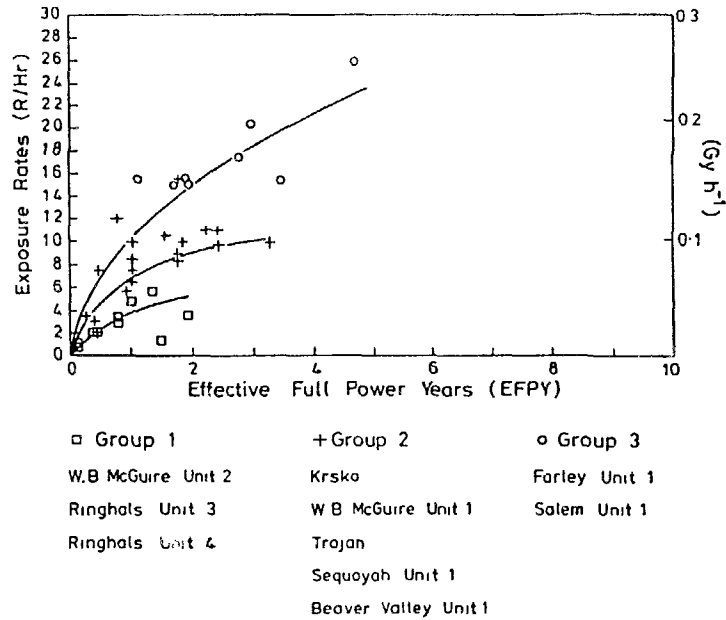


FIG. 5. Buildup of steam generator channel head dose rates (short term trends) (redrawn from Ref. [21]).

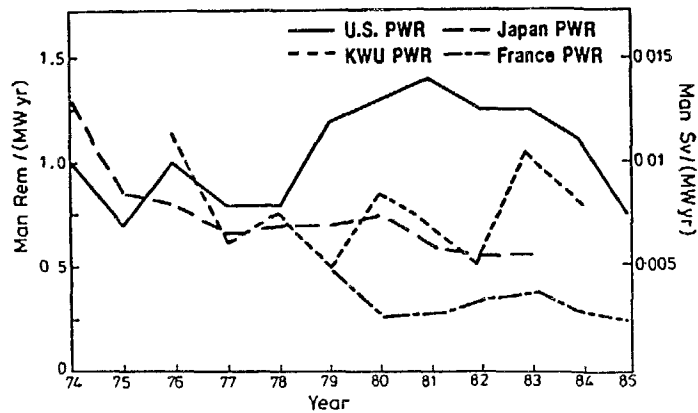


FIG. 6. Occupational radiation exposure per unit of electricity generated by PWR plants (redrawn from Ref. [101]).

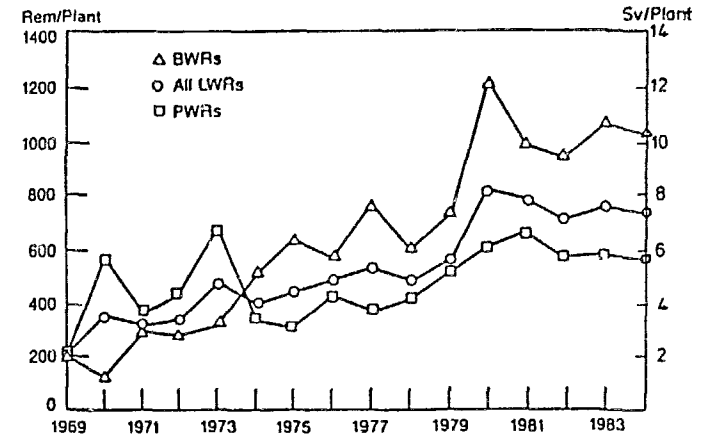


FIG. 7. Average occupational radiation exposure for US nuclear plants [102].

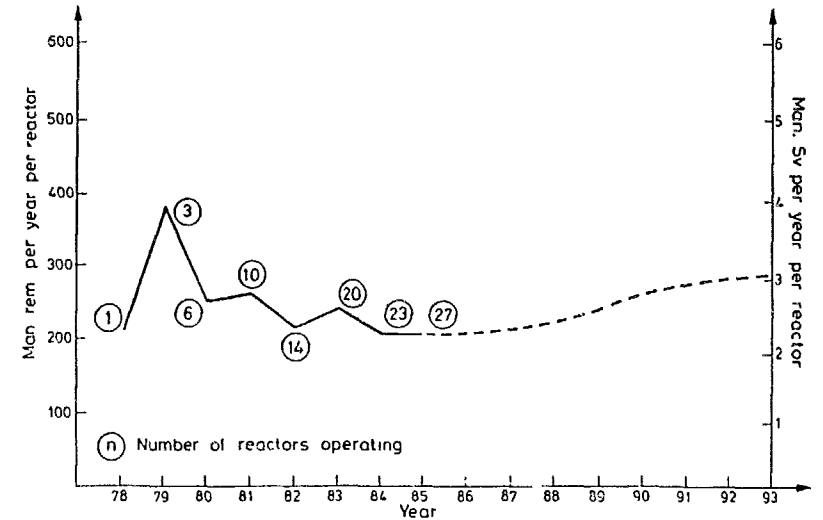


FIG. 8. Annual collective dose at French 900 MW PWRs (redrawn from Ref. [2]).

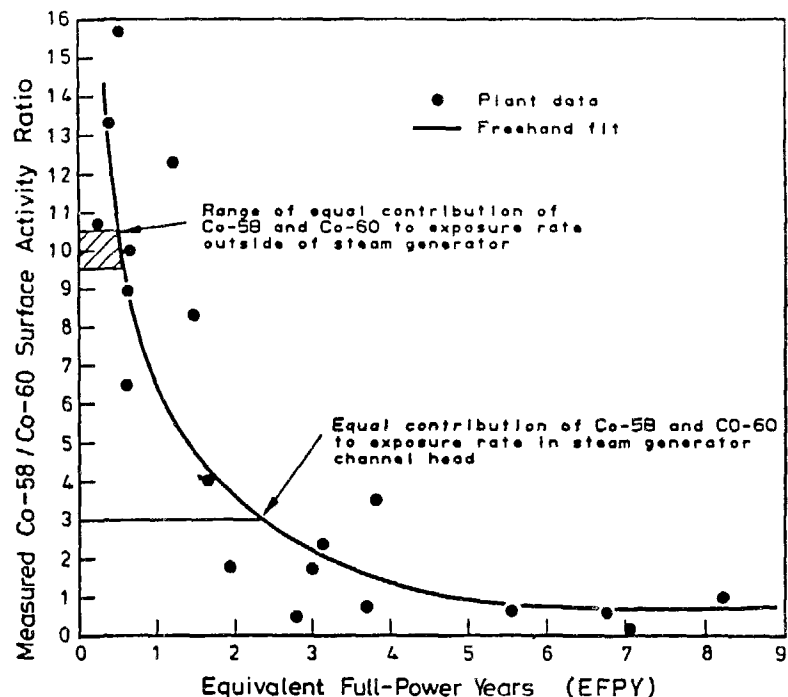


FIG. 9. Variation of Co-58/Co-60 ratio based on steam generator tube measurements [80].

higher pH regime can be achieved by using  $^7\text{LiOH}$ , potassium hydroxide and the use of boron enriched in  $^{10}\text{B}$ , which reduces the amount of boric acid required.

Removal of inactive and activated corrosion products from the coolant can be accomplished by a variety of purification processes which are effective for particulate and soluble species. However, the purification flow rates which are normally acceptable during operation have a very limited effect on the corrosion product inventory of the primary circuit. There may be more scope for removal during shut-down procedures when coolant corrosion product concentrations increase and higher purification flow rates can be achieved. Another approach to the removal of activated corrosion products is the application of decontamination to the primary circuit as a whole, or to individual components. Decontamination may be applied to control the build up of radiation fields generally or to reduce the fields locally in areas where access is required.

These various options will now be addressed in more detail.

### 3.2. Control of Activity Transport Through Materials Choice

This section discusses evidence for the relative importance of different corrosion product sources in contributing to primary circuit activity, and the merits of various materials choice options for minimising activity levels. The predominant source(s) may vary from plant to plant, depending on details of their construction and operation. The intention here, therefore is to identify an order of priority for tackling the corrosion product sources which is likely to be most beneficial in producing low circuit activity levels.

#### 3.2.1. Corrosion product source term analyses

Several corrosion product source term analyses have been conducted. The analyses of Bergmann, Landerman, Lorentz and Whyte [22] for Westinghouse plants concluded that Inconel 600 steam generator tubing is the main contributor of cobalt to the primary circuit for cobalt impurity levels around 0.05%, and the contribution from stainless steel surfaces is small for typical cobalt impurity levels (around 0.07%). Similarly CORA code calculations have indicated that reducing cobalt input by reducing the cobalt impurity levels in the Inconel 600 steam generator tubes from 0.1% to 0.015% would considerably reduce steam generator channel head dose rates in Westinghouse plants, since cobalt input from the steam generators was the dominant factor [23].

While this could be true when other contributions to cobalt input to the primary circuit are small, the evidence from examination of steam generator tube corrosion films from Westinghouse plants [19][24] is that this is not the case, since far too much cobalt is present in the oxide films for it to have been derived solely from corrosion of this material. Other sources must dominate the cobalt input in the plants whose SG tube oxide films have been studied, and therefore in all probability the majority of Westinghouse plants, rather than the SG tubes as concluded by the analyses indicated above.

A more informative approach to analyses of the type indicated above is that of Pinacci and Sejvar [25] who recognise that input terms may be inherently rather variable, and performed a limited sensitivity analysis using the CORA-II code. This showed the importance of contributions from Inconel 718 and stainless steel in-core materials when Inconel 600 steam generator tube cobalt impurity levels are low (0.015%), and the potential importance of contributions from CVCS stainless steel pipework if corrosion rates are high in these lower temperature parts of the system. The analysis probably still under-estimates the importance of input from Stellites and the CVCS, given the observations of cobalt enhancement in the SG tube oxide mentioned previously, but Fig. 10 summarises their analysis of the various contributors to plant activity levels for the materials compositions indicated in Table 2. The contribution from stainless steel is indicated to be relatively small, and the CVCS pipework contribution is only significant when corrosion release rates are 20 times higher than those associated with the primary coolant circuit.

Calculations by Metge, Beslu and Lalet [26] have indicated that Inconel 600 steam generator tubes are the main contributor of cobalt in French PWRs, contributing up to 46% of the total, as shown in Tables 3, 4, 5. Plant evidence in favour of this assessment has also been presented [26][27] principally correlations between activity levels and steam generator tubing

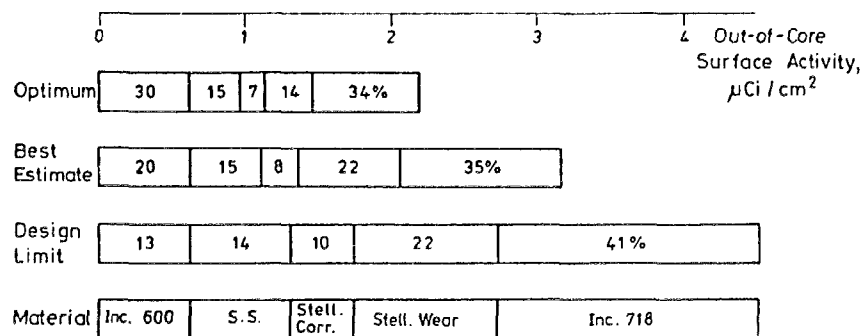


FIG. 10. Material percent contribution to out-of-core Co-60 activity — long term values (material parameters given in Table 2) [25].

TABLE 2. MATERIAL COBALT CONTENTS AND SURFACES USED IN CORA-II CALCULATIONS FOR THE PUN PLANT [25]

Material	Application	Surface (m <sup>2</sup> )	Cobalt Weight %		
			Design Limit	Best E.	Opt.
St. Steel	Fuel assembly	138	0.12	0.10	0.05
	R.V. Internals (peripheral parts)	286	0.12	0.10	0.10
	R.V. Internals (non per. parts)	648	0.20	0.10	0.10
	Reactor coolant piping	130	0.05	0.05	0.05
	Chemical and volume control system piping	66	0.20	0.13	0.13
Inc. 600	Steam generator tubes	14553	0.015	0.015	0.015
Inc. 718	Fuel grids	586	0.10	0.06	0.04
Stellite	Valves, pumps, control rod drive mechanisms, internals		Surface (m <sup>2</sup> )		
			6.75	4.54	3.22

cobalt contents. However, to obtain such correlations it was necessary to eliminate a number of plants (4 out of 12), whose 'cobalt input during hot functional tests may have been excessive (due to valve lapping and grinding)', or which 'suffered variable water chemistry'. Even then, the standard deviations for their correlations are relatively large.

TABLE 3. EDF REACTOR COOLANT SYSTEM CHARACTERISTICS FOR PACTOLE CALCULATIONS [26]

Material	Position	Surface Area m <sup>2</sup>	Cobalt Content %
Zircaloy under neutron flux	Fuel cladding	5,530	0.002
Stainless steel under neutron flux		1,185	0.04-0.08
Inconel 718 with nickel plating under neutron flux	Grids	514	0.08
Stainless steel	Primary piping	2,372	0.08
	CVCS pipe	206	0.08-0.15
Inconel 600	Steam generator	13,600	0.05
Stellite	CVCS after resins	0.12	60

TABLE 4. CORROSION RELEASE CALCULATED BY PACTOLE CODE FOR FIVE CYCLES OF OPERATION (4.6 EFPY) [26]

Material	Position	Temperature	Release Rate mg dm <sup>-2</sup> month <sup>-1</sup>	Release g m <sup>-2</sup>
S.S.	CRP	320°C-280°C	0.14-0.44	0.71-2.4
S.S.	CVCS	279°C-45°C	0.16-24.4	0.9 -130
Inconel 600	CRP	320°C-280°C	0.1-0.2	0.5 -1
Stellite	CVCS	45°C	0.28	1.5

TABLE 5 CALCULATED COBALT CONTRIBUTION IN EDF PWRs USING THE PACTOLE CODE [26]

Position/Component		Material	Total End First Cycle		Total End Fifth Cycle		Total End Tenth Cycle	
			g/yr	%	g/yr	%	g/yr	%
CRP under neutron flux	Grids	Inconel 718	1 30	3 5	0 70	4 2	0 55	4 5
	Internals	S S	2 30	6 2	1 00	6 0	0 75	6 1
	Control rods	Stellite	1 60	4 3	1 45	8 7	1 45	11 7
CRP out of neutron flux	SG tubes	Inconel 600	17 20	46 4	6 95	41 6	4 85	39 3
	Primary piping	S S	5 90	15 9	2 50	15 0	1 75	14 2
CVCS	Piping	S S	8 60	23 2	4 00	24 0	2 90	23 5
	Valves + charge pump	Stellite	0 15	0 4	0 10	0 6	0 10	0 8

The qualifying remarks noted above suggest that it is relatively easy to input additional cobalt from other sources, which may outweigh the influence of the steam generators. In other plants with higher  $^{60}\text{Co}$  radiation fields therefore, it could be concluded that Inconel 600 is not the main source of cobalt, as with Westinghouse plants.

### 3.2.2. Activity generated by in-core materials

There is good evidence from plant which demonstrates that when cobalt impurity levels in the nickel plating used on Inconel 718 fuel grids are high, the fuel grids can become the dominant contributor to out-of-core radiation fields. The earliest evidence of this was given by Kockx and Oljve [28] who correlated the  $^{60}\text{Co}/^{58}\text{Co}$  ratio in sipping tests on spent fuel with the level of cobalt in the nickel plating of the Inconel 718 grids in the Borssele plant. These proved to be as high as 1%, and possibly higher still for some fuel, compared with <0.06% for the grid material itself. The high level of in-core cobalt in the nickel plating of the grids was considered to be the main reason for the continuously rising steam generator channel head dose rate, which was approaching  $50 \text{ Rh}^{-1}$  after 8 cycles of operation. More recently Weitze et al. [29] have analysed the dose rate behaviour of the Goesgen and Neckarwestheim plants. They also concluded from the  $^{60}\text{Co}/^{58}\text{Co}$  ratios found in spent fuel sipping tests that high cobalt levels in the nickel

plating on the fuel grids was responsible for the continuing rise in radiation fields after 5 years operation at Goesgen. However, it was necessary to invoke water chemistry correction factors to obtain a satisfactory analysis of the difference in behaviour at the two plants, as well as differences in cobalt impurity levels in the grids (see Section 2.3.). Bergmann [20] has also indicated that Westinghouse plants operating with Inconel 718 grids have higher steam generator channel head dose rates than those operating with Zircaloy grids, or those which had changed to Zircaloy grids at some stage during their operation.

The analyses of Pinacci and Sejvar [25] indicate that the cobalt content of in-core stainless steel should be limited to around 0.05% to avoid this becoming a substantial contributor to out-of-core radiation fields, particularly in the case of fuel assembly components. Table 2 and Fig 10 indicate that an upper limit of Co concentration of 0.1% is necessary if this source is not to dominate  $^{60}\text{Co}$  production. When the cobalt impurity level of in-core stainless steel and Inconel 718 is low, around 0.05%, the materials are predicted to contribute a relatively small proportion of the total  $^{60}\text{Co}$  activity [25][26].

These studies indicate that Inconel 718 fuel grids, and in particular the Ni plating of them can be a major contributor to the out-of-core fields when the inherent cobalt impurity level in the material is not controlled to a very low value. At concentrations around 1% the plant measurements show it clearly to be the dominant source.

Oljve [30] has reported using Inconel 718 material with cobalt contents of 0.02%, and it seems desirable to adopt such low cobalt content materials if at all possible to conform to the ALARA principle.

Both Inconel and stainless steel corrosion films can take up cobalt from solution by adsorption so that their cobalt content is higher than would be expected from the base metal composition. Such a possibility has not received attention in any in-core activation analysis, but there seems no reason to assume that cobalt incorporation levels equivalent to those seen out-of-core could not occur on in-core surfaces as well. Effectively, this is equivalent to the in-core Inconel and stainless steel surfaces having a much higher cobalt concentration than the alloy itself would dictate. This would imply higher contributions to the  $^{60}\text{Co}$  activity from in-core materials via this indirect route, and provides an incentive to remove in-core Inconel and stainless steel, even though its direct contribution to activity levels may be relatively small. However, this would only apply in the case where cobalt was available in solution from other sources. In this case, the first step would be to remove the primary source, and only if this proves impossible would it be necessary to consider removing in-core stainless and Inconel materials to avoid activation by this secondary route. As indicated previously, every effort should be made to reduce the cobalt content of these in-core materials as much as possible, and switching to Zircaloy grids would be a very effective means of pursuing this goal.

In the special case of pressure vessel heavy water reactors, because of the continuous refuelling strategy used, Stellite surfaces are present in the core. The contribution to radiation fields from  $^{60}\text{Co}$  release after in situ activation has been estimated at Atucha I to be as high as 90% of the

long term out-of-core field. Urrutia et al [18] used an empirical model to make this estimate employing as parameters the specific release rates from Stellite and from other materials.

### 3.2.3. Cobalt input from Stellite and the CVCS

The high levels of cobalt observed in corrosion films formed on primary circuit surfaces in Westinghouse PWRs [24] can only be explained in one of two ways. Either the majority of cobalt observed is derived from Stellite surfaces within the primary circuit, or it enters the circuit from the CVCS or other auxiliary circuits. In the case of the CVCS and other auxiliary circuits, this could be during commissioning and start-up if measures are not taken to prevent cobalt input during that period. It is also true that if there is a substantial input from the CVCS and other auxiliary systems this could again be due to the use of high cobalt alloys (Stellites) in those circuits for valves and pumps. There is good reason to believe, therefore, that removing Stellite surfaces from PWR primary and auxiliary circuits will result in a marked reduction in cobalt input, and after ensuring minimum cobalt levels for all in-core materials, should be the next most effective method of ensuring low radiation fields out-of-core. Young et al [31] have concluded that Stellite hard facing surfaces are the main source of cobalt input in Combustion Engineering plants. Wear associated with the control element drive mechanisms was considered the most important process, contributing some 50 grams per year, just over 50% of the total. Other analyses have also indicated Stellite to be the main source of cobalt [32] but the detailed breakdowns of the Stellite surfaces responsible differ. Failure of a Stellite component can result in a massive injection of cobalt, giving rise to a large increase in radiation fields, as was seen during the third cycle of Biblis A [33]. Valve lapping during maintenance has also been considered to be a prime source of cobalt [34] but there is very limited direct evidence for this. Nevertheless, current evidence points strongly to Stellite surfaces being responsible for the major part of cobalt input. It is highly significant that Soviet reactors have extremely low  $^{60}\text{Co}$  radiation fields [35][36] presumably as a direct result of their avoidance of such high cobalt alloys. The oxide films on Loviisa 2 steam generator and cleanup circuit pipework have been examined by Pick [37]. Pick found that, in common with the oxide on stainless steel in Westinghouse PWRs, the corrosion films were enriched in nickel and chromium compared with the base metal and that the weight of metals in the oxide was very similar in the two reactor systems in comparable locations. However, there was no cobalt enrichment in the oxide on Loviisa 2 specimens compared with the base metal composition, which is in marked contrast to the cobalt enrichment factors of 4-30 found in Westinghouse PWRs. The  $^{60}\text{Co}$  levels on Loviisa 2 specimens were 60-100 times less than on Westinghouse specimens with similar EFPPY. CANDU reactors also exhibit low radiation fields, which are at least partly the result of avoiding the use of high cobalt alloys in the primary circuits.

Replacement of Stellite by other hard facing alloys cannot be undertaken without demonstrating the reliability of a suitable alternative. There is a very strong incentive to replace high cobalt alloys in both the primary and auxiliary circuits as far as is practicable.

In the case of valves, Bergmann and Landerman [38] concluded that the pressurizer spray valve and flow control valves in the CVCS downstream of the

demineralisers were the most important candidates for Stellite replacement. Wrought stainless steels such as 17-4PH and 440C have been used for flow control valves in some US and European PWRs with apparent success (Airey, [39]). However, while cobalt release from Stellite flow control valves has proved significant in some cases, particularly due to erosion-corrosion damage, the importance of cobalt release from other components (including other types of valve) still needs to be addressed thoroughly.

There are two other possible sources of cobalt input from the CVCS. One is from the CVCS pipework, and in particular from the stainless steel surfaces operating at intermediate temperatures, where release rates are likely to be much higher than for the main primary circuit surfaces. This is most relevant to the CVCS regenerative heat exchanger, and the most effective approach to reducing cobalt input from this source is to minimise the cobalt content of the stainless steel used for the heater.

A further source of cobalt input from the CVCS system may be the boric acid storage tank solutions and similar make up fluids, which may contain higher levels of cobalt than those in the main CVCS recirculation flow (for whatever reason). Fe, Mn and Ni concentrations have been reported in studies at Trojan and Beaver Valley [40] well over  $100 \mu\text{gkg}^{-1}$  on many occasions. Cobalt levels were not generally measured, but values up to  $43 \mu\text{gkg}^{-1}$  were determined when measurements were made, with an average value of  $26 \mu\text{gkg}^{-1}$  for the Beaver Valley plant. These high concentrations are not appropriate to the main CVCS injection flow to the reactor, but obviously some proportion of this material could enter the primary circuit via the CVCS.

The ultimate source of cobalt in these make up fluids is uncertain, but could be components such as the boron recycle evaporators which are typically fabricated from Incoloy 825, and which may have higher cobalt contents than is desirable, as well as Stellite valves. It appears pragmatic, therefore, to extend the policy of minimum cobalt content to most of the pipework and vessels associated with the CVCS, particularly those handling concentrated boric acid solutions.

Input of corrosion products from boric acid make-up solutions could be reduced by cation ion-exchange of the make-up solution prior to injection. This may be particularly effective during commissioning and initial operation and merits detailed consideration but such ion-exchange clean-up could be one of the most cost effective ways of reducing cobalt input to the plant. The CVCS as a whole is likely to provide an overall net input of corrosion products to the primary circuit unless measures are taken to prevent this: a concentration of  $0.1 \mu\text{gkg}^{-1}$  (100 ppt) cobalt in the CVCS injection flow would lead to the input of about 15 g of cobalt per year. This is not an inconsequential amount of material compared to the total cobalt inventory of primary circuit surfaces, and if concentrations of this order were to be demonstrated by plant measurements the incentive for further treatment of the CVCS injection flow would be considerably strengthened.

### 3.2.4. Reducing cobalt input from primary circuit surfaces

Reducing cobalt input from the main primary circuit surfaces, and the steam generator tubing in particular, is possible by reducing their cobalt content and/or reducing their inherent release rates. The data discussed previously

indicate that such measures are only likely to be effective after measures have been taken to minimise  $^{60}\text{Co}$  production by in-core sources, and cobalt input to the system from Stellite and more generally the CVCS system. Nevertheless, once these other measures have been pursued, reducing cobalt input from the main primary circuit surfaces becomes important. The lowest possible cobalt content is desirable if minimum cobalt input is to be achieved, and levels down to 0.015% can be obtained for steam generator tubing.

The stainless steel surfaces of the large diameter pipework in the primary circuit also contribute substantially to the total cobalt input. This seems likely to be due as much to the poorer surface finish of these components as an inherently higher corrosion release rate for stainless steel compared with Inconel. Improvements by obtaining as smooth a surface finish as possible for these components are therefore likely to be as effective as reducing their absolute cobalt contents. By comparison, production Inconel steam generator tube surfaces already give low release rates, although the reasons for this are not fully understood, apart from their relatively smooth surface.

Processes such as electropolishing of stainless steel may be expected to produce smoother surfaces with low corrosion rates, and are therefore worth considering as a means of reducing cobalt input from the main primary circuit stainless surfaces and steam generator channel head. This would give a benefit additional to that obtained by minimising the absolute cobalt concentration in the material. Spalaris [41] has recently described the improvements in surface finish obtained by electropolishing steam generator channel heads.

Materials choice may influence out-of-core radiation fields by changing the ability of the material to take up active corrosion products. The capacity of corrosion films to take up activity is dependent on the corrosion film thickness. Thus reducing the material corrosion rate by improving the surface finish could have benefits in reducing out-of-core radiation fields as a result of reduced uptake of activity. This is likely to be particularly beneficial in the case of the primary circuit stainless steel surfaces, and provides a further incentive for applying polishing/electropolishing procedures to them.

It was mentioned above that Soviet designed VVERs do not contain high cobalt materials and this is believed to be responsible for their very low  $^{60}\text{Co}$  radiation fields. The cobalt content in all structural materials at VVERs is also limited to <0.05% but practice is usually lower than this specification.

### 3.2.5. Effect of surface finish

The surface finish of primary circuit components can affect the deposition and uptake of radionuclides and the release of activatable corrosion products to the coolant. If the effective surface area is reduced then the surface area of oxide into which soluble activity can be taken up is reduced. Smooth surfaces are also less liable to trap particulate material than rough ones. Mechanical polishing results in abrasive scratches and the deeper the scratches the more likely it is that particulate material will accumulate [42]. In addition the force applied in abrasion causes surface damage. The most extensively damaged portion extends approximately to the depth of the cuts caused by abrasion [43] and this is effectively the layer that will be

subject to corrosion over the reactor lifetime. The damaged layer, consisting of fractured grains and which can contain some phase transformed material, is more prone to corrosion than the underlying metal. There is thus an incentive to avoid coarse abrasives and to electropolish or chemically remove damaged material by pickling.

Honda et al [44] claim that electropolishing and a fine abrasive finish to the same roughness resulted in similar corrosion rate and  $^{60}\text{Co}$  uptake (BWR conditions) and so fine abrasive may be a sufficient treatment to minimise metals release and activity uptake. This tends to be confirmed from experiments on Zircaloy fuel pins. These are already treated by belt grinding to a very fine finish. Electropolishing is possible although the roughness average (Ra) values achieved approximate to those achieved by belt grinding [45]. Tests of the two finishes in BWRs showed no discernible difference in crud pickup [45] so there is little incentive, in BWRs at least, to electropolish fuel pins. The nucleation of precipitates and the trapping of particulates on fuel surfaces may be governed by similar principles in both BWR and PWR and hence the conclusions could be tentatively transferred to the PWR case. KWU electropolish completed fuel rods as standard practice at little additional cost. This acts as a final proof cleaning process as well as providing excellent surface finish to the Zircaloy cladding [46].

During tests with SG channel heads Spalaris [46] found the effective surface area could be reduced by a factor of 20 by an initial mechanical polish of the rough strip cladding followed by electropolishing. The effective surface area of the initially smoother Inconel 600 divider plate could also be reduced by a factor of 4 by the same treatment. Electropolishing can be readily carried out prior to erection and Spalaris advocates a hand held electropolishing device with 15 minutes or less exposure. Presumably the area of this device can be made larger but he experimented satisfactorily with a 48 in<sup>2</sup> device. About 140 hours per steam generator would be needed for its dimensions but there is obvious scope for improvement. Several U.S. utilities are considering in-situ channel head electropolishing before start up of new PWRs [47].

Manway covers of various surface finish (as received, mechanically polished, electropolished and mechanically polished plus electropolished) have been exposed for up to 3 cycles in the French Chinon B1 plant [48]. Activity deposition improvement factors for  $^{58}\text{Co}$  and  $^{60}\text{Co}$  of 2 for mechanically polished and 3-5 for electropolished plus mechanically polished were observed and maintained for 3 cycles. The combination of electropolishing and mechanically polishing was found to be more efficient than electropolishing alone. The reduction factors of deposited activity were higher on the cold leg than on the hot one. The latter effect was also observed in a surface finish study, also on manway covers, in Tihange 1 ([49]). This study also examined surface finish and pretreatment effects of insert specimens placed in Doel 2 for 6 months. Electropolishing and passivation of stainless steel 304L improved dose rates by a factor about 2. Inconel 600 showed no increased benefit with passivation over electropolishing.

In addition to affecting activity uptake the surface finish also has an effect on metal release rates. It is usually taken that the metal release rate follows a relationship of the following type:-

$$R = At^{-n} + B \quad \text{A and B are constants, } 0 < n < 1, t = \text{time}$$



Curves of total corrosion against time for Inconel 600 under laboratory PWR conditions tend to show the non-linear form indicated by the above equation. Non-linearity is especially pronounced for rough surfaces but where smoother surfaces are involved the curves tend to linearity. Metal release rates have been measured for both Inconel 600 and Inconel 690 under laboratory PWR conditions [50]. Up to 5000 hours the metal release rate was observed to be linear for both alloys although the release rate was greater for Inconel 600. Data from operating plant and from short term laboratory experiments on smooth or pickled surfaces show the marked non-linearity for the corrosion of rough surfaces in the first thousand hours or so tending to disappear.

From the evidence reviewed it therefore appears unlikely that a two month preconditioning of Inconel 600 or 690 would significantly reduce the total release of metals to the RCS in the first operating cycle.

Parallel evidence for stainless steel is much more limited. That from plant shows oxides growing on steel at an appreciably faster rate than on Inconel and this may be a function of the relative surface finish or perhaps of some other phenomenon. As surface finishes on some reactor stainless steel can be rough, non-linear corrosion on some components may be more marked than on Inconel. Although non-linear behaviour appears in laboratory experiments it is not yet possible to confirm this from sparse reactor data. The possibility remains that, like Inconel 600 and 690, growth may be linear with time, albeit at a faster rate. If non-linear metal release was apparent there would be a benefit from preconditioning especially as metal release rates from stainless steel in PWRs are believed to be much greater than those from Inconel 600 [19]. That there is uncertainty in the conclusions reached on metal release by direct observation of corrosion rates is evidenced by the fuel crud loading in cycle 1 which appears to be greater than that in subsequent cycles [19]. As plants will have undergone an appreciable period of preconditioning before fuel loading, the extra crud burden could come about as a result of further non-linear corrosion of alloys in the period after hot functional testing until the end of the first cycle. Alternatively, or in addition, the extra crud could result from adventitious material not removed in the flushing procedures prior to core loading, in particular from systems outside the RCS which cannot be "hot" preconditioned.

### 3.2.6. Effect of preconditioning

Preconditioning can affect the release of activatable corrosion products to the coolant and the uptake of radionuclides from the coolant. Preconditioning techniques can be categorised into one of two areas:

1. preconditioning undertaken during the hot functional testing period using the normal PWR chemistry variables i.e. temperature, lithium, boron and hydrogen.
2. preoxidation or passivation techniques.

Evidence for the benefit of preconditioning on dose rates is mainly restricted to laboratory and loop studies although there are limited data from studies where coupons have been exposed in reactor circuits. Any benefit achieved by preconditioning must still be evident at the end of the reactors operational life.

Preconditioning procedures vary from utility to utility but the procedures followed by KWU are fairly typical: preconditioning is performed during the first hot functional test period under the following water chemistry conditions:

Lithium	1-2 ppm (max 5ppm)
Oxygen	<10 ppb
Chloride	<0.2 ppm
Temperature	>260°C

Oxygen reduction is performed by degassification and by hydrazine addition if necessary. The preconditioning should last at least 50 hours and cannot be finished until the iron content of the primary coolant water is  $\leq 0.1$ ppm.

A study covering 12 US PWRs [51] could find no correlation between dose rates and preconditioning procedures or times but it has to be said that there was probably not much difference between the preoperational procedures of the plants examined. Other operational factors are more likely to have caused the differences noticed between subsequent operational dose rates.

The recontamination rate of replacement steam generators or freshly decontaminated surfaces have been found to be the same as that after initial plant start up. Since such replacement or decontaminated surfaces have effectively no pretreatment before being placed into service compared with the usual several hundred hours before initial start up, it can be concluded that the pretreatment did not affect eventual dose rates.

The Loviisa and Ringhals 2 PWRs have exceptionally low dose rates. At Loviisa, preconditioning included 2 months hot functional testing in alkali and 2 months after fuel load but before full power operation in the presence boric acid. Ringhals 4 had a longer preconditioning than normal (the political situation in Sweden resulted in 2 hot functional testing periods).

However, in the case of Loviisa low dose rates are considered to be due to the absence of Stellite and consequently negligible  $^{60}\text{Co}$  levels in the coolant while the low dose rates at Ringhals 4 are believed to be due to operation with particularly favourable and strictly controlled primary circuit chemistry (high pH) very soon after start up. The Ringhals 3 reactor also underwent extended preconditioning but its dose rates are at least double those at Ringhals 4 at the end of cycle 1 [52]. Thus, while it is not possible to be unequivocal, factors other than the length of the hot functional test are believed to be more likely to account for the low dose rates in Ringhals 4 and Loviisa.

Decomposition of metal chelates in solution at high temperature to form protective oxide films has been routinely applied as a precondition technique in CANDUs [53] and has replaced the previous hot condition in alkali. However, this technique is geared to the particular needs perceived for CANDU, namely to rapidly protect coolant system carbon steel surfaces and to complex and remove impurity zinc whose activation to  $^{65}\text{Zn}$  has proved to be one of the major activation nuclides in the Bruce CANDUs. In PWRs  $^{65}\text{Zn}$  is not a significant contributor to dose (approximately 10% of  $^{60}\text{Co}$ ). The time for preconditioning CANDUs was reduced from 8 days to 3 days by the use of metal chelates. Both these times are very much shorter than have been applied to

PWRs and it was apparently felt that the preconditioning of CANDU steam generator tubes (Inconel 1 600 or Monel 400) for prolonged periods was not necessary as a means of minimising dose rates. There was however no discernible difference in operational dose rates between CANDU plants preconditioned in alkali or those preconditioned with chelating agents present.

Loop experiments in the US [54] have examined the uptake of  $^{60}\text{Co}$  into oxide films, produced by preconditioning and passivation techniques, over a 200 hour period under PWR conditions. The various techniques included electroless palladium, boric acid, EDTA and chromate treatments. The electroless palladium passivation treatment resulted in the least  $^{60}\text{Co}$  activity pick-up.

Electropolished and electropolished plus passivated (by means of hot moist air at 250-315°C) stainless steel 304L and Inconel 600 coupons were exposed in the Doel 2 PWR for a total of 3800 hours [49]. The stainless steel 304L coupons which were electropolished and passivated showed a dose rate reduction of a factor of 2 compared with the electropolished only coupons. No increased benefit was observed for the Inconel 600 coupons passivated in addition to being electropolished.

Attempts to decompose chelates to form protective films on austenitic stainless steel by Carter et al [55] did not lead to a durable protective film. Winkler et al [56] have shown how compounds like  $\text{TiFeO}_4$  may be produced on PWR surfaces from chelates. The key questions to be addressed in any proposal for chelate decomposition relate to:

1. the durability of the oxide films under variable reactor conditions of temperature and chemistry,
2. the long-term absorption of nuclides, and
3. the applicability to PWR materials.

The principle of seeking to produce a layer resistant to the flow of ions either from underlying metal or from the coolant is attractive provided the questions above can be answered satisfactorily. The uncertainties in metal release rates of both stainless steel and Inconel alloys, whether the release rates are linear or non-linear, coupled with the limited number of reactor studies makes it impossible to come to any firm conclusion on the benefit of increasing the preconditioning period during the hot functional test beyond the period necessary for engineering proving tests. On the balance of available evidence dose rates in early reactor life are not sensitive to the length of the preconditioning period. In current western PWRs  $^{60}\text{Co}$  gives an approximate 60 to 80% contribution to station lifetime collective occupational dose. Since Stellite is now believed to be the major source of the cobalt precursor to  $^{60}\text{Co}$  reconditioning the main circuit alloys will have little effect on the  $^{59}\text{Co}$  input rate. However, as most of the occupational dose is incurred from stainless steel components preconditioning should be largely directed to reducing  $^{60}\text{Co}$  deposition on stainless steel. This emphasises the importance of the surface finish of stainless steel components considered in 3.2.5.

### 3.2.7. Summary

We may summarize the order of priorities for action relating to materials choice for minimising cobalt input to the primary circuit and therefore minimisation of radiation fields as follows:

1. Ensure absolute minimum cobalt content for all in-core materials.  
  
Replacement of Inconel 718 by Zircaloy would be an effective way of doing so in the case of fuel grids, and this should be seriously considered. In addition to the obvious benefit of reducing direct release of  $^{60}\text{Co}$ , replacing Inconel 718 grids with Zircaloy ones might reduce activation of cobalt from out-of-core sources by reducing the amount retained in in-core corrosion films. If this replacement is not possible, however, then all materials associated with the grids, and in particular the nickel plating and brazes should have the minimum cobalt level achievable.
2. Reduce to a minimum the use of high cobalt alloys (Stellites) in all areas of the primary circuit and the auxiliary systems.  
  
These two measures are considered to be by far the most important materials choice options for minimising  $^{60}\text{Co}$  activity, given relatively low (<0.1%) cobalt concentrations in other primary circuit materials. However, the options indicated below are considered to offer significant further benefit if the measures above are effectively implemented.
3. Ensure the smoothest possible surface finish for stainless steel components in the primary circuit to minimise the corrosion rates of these surfaces. This is also likely to offer further benefit in reducing out-of-core fields as a result of the reduced capacity of the corrosion film for active species.
4. Reduce the residual cobalt content of stainless steel and Inconel surfaces in the primary circuit to a minimum. A specification of <0.05% is readily achieved and <0.02% can be achieved for steam generator tubing.
5. Specify low cobalt material for the CVCS regenerative heat exchanger, and CVCS pipework and vessels handling concentrated boric acid solutions.
6. Consider the further treatment of CVCS make-up water to the primary circuit to remove influent corrosion products, particularly from the boric acid storage tank system. Simple low temperature cation exchange may be sufficient in the latter case.

Finally, it is most important that cobalt input to the primary circuit during commissioning and initial start-up is minimised, since its removal once it has entered the system is extremely difficult. All the measures indicated above could be negated if poor pre-operational practices lead to substantial input of cobalt (as little as about 20 grams in total). The clean-up of circuits and pre-operational fluids before normal operation is therefore essential.

### 3.3. Primary Circuit Coolant Chemistry Control During Normal Operation

#### 3.3.1. Objectives of coolant chemistry control

The overriding requirement for the primary circuit coolant is that it should perform the function of heat transfer and contribute to core reactivity control without prejudice to the integrity of structural materials, components and fuel cladding.

For structural materials (stainless steel, Inconel) general corrosion is unlikely to be a significant issue, but environmentally assisted cracking of Inconel 600 steam generator tubes has been observed and would place some constraints on levels of deliberately added dosing agents and permissible impurity levels in the coolant for reactors employing this alloy.

For fuel cladding material, a chemistry regime which restricts general corrosion is required in order to prevent the formation of thick films of  $ZrO_2$ , which would impair heat transfer to the coolant and lead eventually to fuel failure. In addition, the coolant chemistry conditions should ensure that deposition on fuel of corrosion product material released from structural materials is not excessive. Excessive deposition could again lead to impaired heat transfer which in turn would lead to accelerated clad corrosion and eventually to fuel failure. Thick deposits in-core have also in the past led to unacceptable pressure drop and reduced core reactivity. These more severe problems associated with excessive deposition on fuel would only be anticipated in the event of very poor chemistry control and are now rare. Under these circumstances the main issue relating to deposition in core is the generation of activated corrosion product species. The purpose of this section to identify an optimum coolant chemistry strategy during normal operation which will restrict the consequential out-of-core radiation fields and the levels of corrosion product radionuclides in the coolant.

#### 3.3.2. Constraints on coolant composition

The various corrosion related issues tend to define a limited range of coolant redox potential, pH and impurity concentrations under which materials performance is acceptable.

Oxygen level (which determines redox potential) is controlled to very low levels (typically specified as <5 ppb; in practice, likely to be very much lower) for two reasons: its effect (in combination with  $Cl^-$ ) in promoting stress corrosion cracking in stainless steel (see Figure 11) and its effect on Zircaloy corrosion. Low levels of oxygen are ensured by dosing the primary system with hydrogen. The hydrogen may be dosed into the system directly or via the radiolytic decomposition of ammonia. The level of hydrogen is dictated by the need to suppress the formation in-core of the  $HO_2$  radical in order to minimise Zircaloy corrosion. This leads to a reasonable working minimum for the hydrogen concentration of  $25 \text{ cm}^3(\text{NTP})\text{kg}^{-1}$ . The upper limit is restricted by operational requirements.

The control of coolant pH in PWR primary circuits is complicated by the presence of boric acid, which is present for core reactivity control. The concentration of boric acid varies during the normal reactor cycle from a

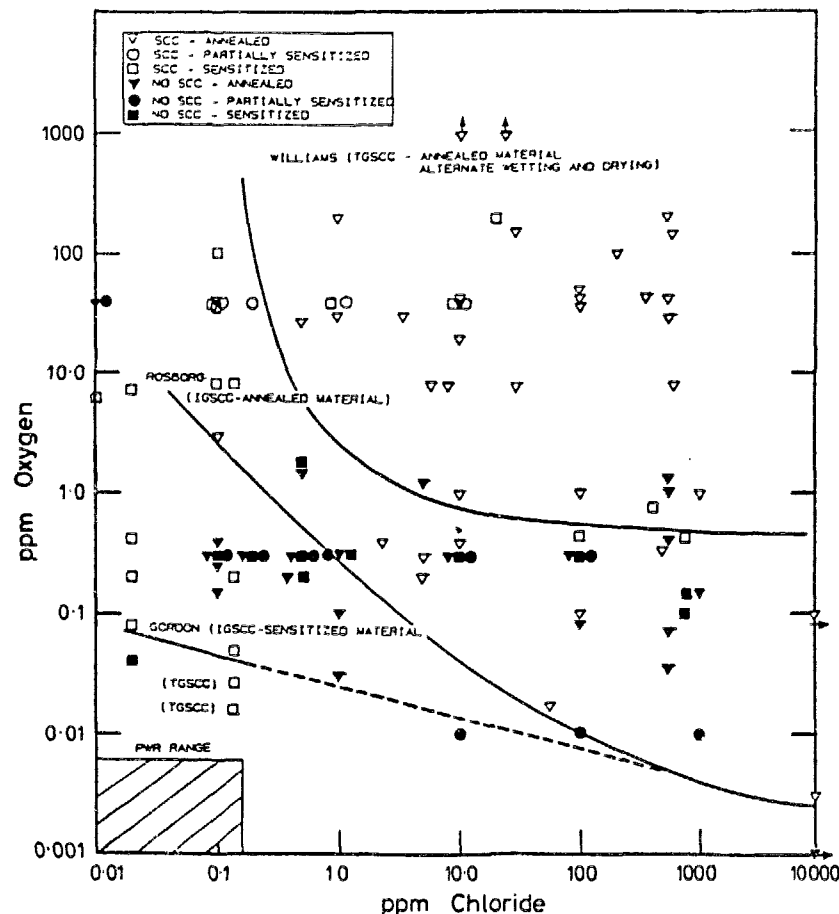


FIG. 11. Effects of oxygen and chloride on the SCC of austenitic stainless steels in high temperature water [103].

value of around 1200 ppm (as B) at the beginning, reducing with burn-up down to zero at the end of the cycle. For extended fuel cycles, using more highly enriched fuel, the initial value could be as high as 1800 ppm (although on physics grounds the preferred option for reactivity control would be the use of burnable poisons).

To restrict general corrosion of stainless steel and Inconel and to control the build-up of activated corrosion products, the pH of the coolant must be raised to some degree. At present  $^7\text{LiOH}$  is used to do this in western PWRs and KOH is used in Soviet designed VVERs. The chemical behaviour of corrosion

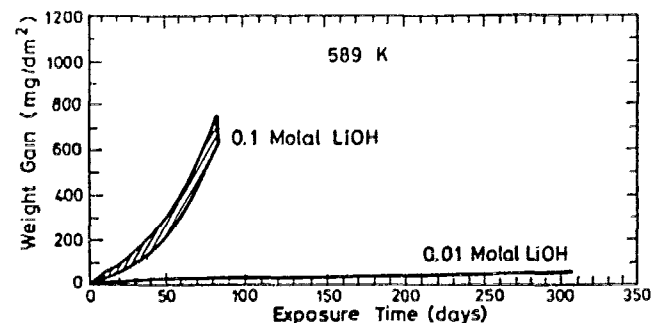
products which must be examined to determine the optimum lithium or potassium control strategy is discussed in detail below.

There are two major issues which restrict the level of lithium which might otherwise be thought desirable. The first relates to primary side cracking of steam generator tubes. There is some indication that high lithium concentrations may promote this, although the experimental evidence is ambiguous and further evidence is being actively sought in this area [57] second, and potentially very serious issue, is the possibility of enhanced Zircaloy corrosion. High concentrations of lithium hydroxide have been observed to increase the corrosion rate of Zircaloy dramatically and a detailed study has been undertaken by McDonald et al. [58] some results from this work are shown in Fig. 12. The lithium concentrations involved are very much higher than would be contemplated for use in PWR coolant, but the possibility of local concentration, particularly on cladding where some degree of boiling heat transfer is operative, must be considered. Lithium 'hide out' would also be favoured on fuel surfaces with significant levels of extraneous deposits. Work by Coriou et al. [59] shows that LiOH is considerably more aggressive than KOH, but the data refer only to the early stages of corrosion; extrapolation to the effect at longer exposure time is not straight-forward. Recent French work has indicated that the major area of concern is likely to be when conditions lead to a degree of local boiling in the coolant together with a significant degree of voidage [60]. The study employed an out-of-pile loop (CIRENE) and a significant enhancement of the Zircaloy corrosion rate (up to a factor of about 5) due to increase of void fraction under sub-cooled nucleate boiling was observed, even under 'normal' pWR chemistry (2.2 ppm Li, 650-1000 ppm B, 25-55  $\text{cm}^3(\text{NTP})\text{kg}^{-1} \text{H}_2$ ). An experiment with 10 ppm lithium and 1000 ppm boron, with average void fraction at outlet of 15%, led to a 35  $\mu\text{m}$  thick film after 51 days operation, when in the absence of any enhancement, only a 2  $\mu\text{m}$  oxide thickness would have been expected. The results from the French study are disturbing; it is clear that enhanced Zircaloy corrosion is a major issue requiring further investigation.

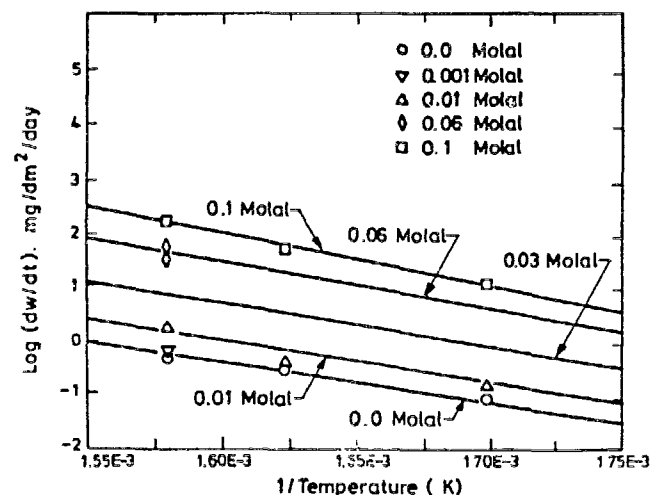
Under conditions currently employed in operating PWRs corrosion experience has, in general, been good although variations between different fuel vendors and different batches of material have been noted. The almost universally adopted present maximum specification of 2.2 ppm Li may be unnecessarily restrictive (a level of 3.5 ppm has been employed at Ringhals without any apparent problem), and for the purpose of limiting activity transport there is good reason to raise it (see below). Nevertheless, any increase in the lithium concentration will require careful justification.

To help to ensure fuel cladding integrity, there are a number of impurities whose concentrations should be restricted to an achievable minimum. Fluoride, which enhances Zircaloy corrosion, is one. A second group, Ca, Mg, Al and  $\text{SiO}_2$  (often referred to as Zeolite forming minerals), can lead to the formation of dense, tenacious, low thermal conductivity deposits on fuel surfaces. The consequent impairment of heat transfer and increase in clad surface temperature would lead to enhanced corrosion. The presence of these species in the coolant is therefore undesirable, and their levels should be restricted

The coolant particulate burden needs to be controlled in order to restrict fouling of fuel and build-up of radiation fields. Initial particulate burden can be significantly influenced by pre-operational practices, the



(a) LiOH Corrosion Data Obtained at 589 K.



(b) Arrhenius Curve for Zircaloy Corrosion in LiOH Solutions

FIG. 12. Effect of lithium concentration on Zircaloy corrosion (redrawn from Ref. [58])

commissioning procedure should be designed to restrict the amount of residual material deposited around the circuit. During normal operation, care must be taken to restrict the particulate levels in make-up water and dosing agents; the prevailing primary circuit coolant particulate levels will then be determined largely by the operating pH.

### 3.3.3. Coolant corrosion product sampling

Sampling of the primary coolant of PWRs is necessary for reactivity control and chemical monitoring. Information will also be required on release of fission products into the primary coolant as a measure of fuel status, and on circulating levels of activation products.

Existing sampling facilities installed in PWRs are adequate for the normal operational control and specification measurements such as lithium, boron, hydrogen, chloride and fluoride concentrations. They are also probably adequate for elements such as calcium, magnesium and silica, which are important to limit the formation of zeolites on fuel cladding. However, the veracity of the data for corrosion, activation and fission product species in the primary coolant of PWRs is dependent upon any effects which are introduced by the sampling system itself.

The potential problem in measuring corrosion, activation and fission product concentrations is that it is necessary to cool the sample from the normal operating temperature of 300°C to ambient temperature. Such a process, particularly in a stainless steel line, can introduce effects due either to deposition in the line or to dissolution of previous deposits and/or line components themselves.

The sampling system needs to provide representative samples of both dissolved and particulate species in the coolant. Consideration should be given during the design of sampling facilities to minimise particulate deposition in valves and fittings. Sampling systems are normally constructed of stainless steel which is generally satisfactory provided that it is noted that there may be a conditioning period of up to 3 months and even then there could be some deposition of radionuclides (e.g.  $^{60}\text{Co}$  and  $^{58}\text{Co}$ ).

An adequate flow velocity in the sample lines is vital to minimise crud deposition. It is also necessary to minimise the release of chemical species from the walls of the sample lines and the deposition of dissolved and particulate species into the oxide layer. In addition, continuous flow is preferable for sample lines in that this avoids the inevitable disturbance when any line is brought into service. The coolant flow through conventional 10mm bore sample lines is too high for continuous operation. A capillary sample line can provide both isokinetic samples and a continuous flow without involving large quantities of sample flowing to waste. Capillary sampling also has the advantage that the narrow bore reduces pressure and sample flow without the need for pressure and flow control valves which are well known crud traps and sources of impurity ingress. The Winfrith SGHWR depends on continuous capillary sampling for all measurements of dissolved and particulate corrosion species [61] and capillary sampling systems have been developed, installed and operated on the PWRs at Doel with equal success [89].

### 3.3.4. The spinel solubility model as a basis for radiation field control

As indicated in the previous sections, the only significant parameter influencing corrosion product transport behaviour which can, to some degree, be varied by the plant chemist is the coolant pH (via the choice of lithium or potassium dosing level). Understanding of the detailed effects which pH has on the behaviour of corrosion products under PWR conditions has increased significantly since the early days of reactor operation. This has led to modification of the strategies adopted to combat build-up of radiation fields and plant corrosion product radionuclide inventories. This section describes the way in which current understanding has evolved and how it may be used to formulate a coolant pH control strategy. It expands on some aspects of the theoretical framework outlined above. Subsequent sections describe how

coolant pH control has actually been implemented by different organisations on operating plant and correlations of radiation field behaviour with chemistry regime are discussed.

The detailed discussion in this section will avoid reference to the quantity 'coolant pH' and concentrate on the behaviour of iron solubility with respect to boron and lithium concentrations. The motivation for this is clear from the discussion in section 1, pH is itself a function of temperature; the absolute value calculated for a given temperature and composition depends on the choice of correlation for  $K_w$  which has been used in the calculation. Furthermore, the value of the temperature coefficient of solubility of iron at a given temperature and pH is, to some extent, dependent on how the pH has been achieved (the magnitude of the boron and lithium concentrations, not just their relative values). These points are illustrated in Figures 14 and 15. Figure 14 shows the calculated pH versus temperature for different Li, B combinations using two different correlations for  $K_w$  while Figure 3.15 shows the temperature coefficient of solubility of iron at 300°C versus pH for different boron concentrations.

Despite these potential ambiguities, pH is a useful and universally adopted shorthand for characterising coolant conditions. In subsequent discussion we follow current practice (see for example, [62]) and quote pHs at a reference temperature of 300°C, but we prefer values based on the Marshall and Franck [63]  $K_w$  correlation rather than the more often used Mesmer, Baes and Sweeton [63] correlation. At 300°C this leads to a difference in quoted pHs of about 0.15 units, with values based on Marshall and Franck being higher. See the paper entitled "Corrosion products, activity transport and deposition in boiling water reactor recirculation systems" by H.P. Alder, D. Buckley, G. Grauer, K.H. Wiedemann.

The development of coolant chemistry control as a means to restrict build-up of out-of-core radiation fields has been reviewed by Solomon [64]. This work has formed the basis of the Westinghouse recommendations for 'coordinated chemistry' control of coolant pH. The strategy focuses on build-up of corrosion products in-core using a relatively simple formulation of the form:

$$dW_a$$

$$dt = k_D[\text{Particles}] + k_{S-P}[Fe_S(T_1) - Fe_S(T_2)] - k_E[W_a]$$

$$W_a = \text{Surface concentration of crud (gm}^{-2}\text{)}$$

$$k_D = \text{Deposition coefficient (ms}^{-1}\text{)}$$

$$k_{S-P} = \text{Dissolution or precipitation coefficient (ms}^{-1}\text{)}$$

$$Fe_S(T): \text{Fe solubility at temperature T (gm}^{-3}\text{)}$$

$$(T_1 = \text{Bulk coolant temperature;}$$

$$T_2 = \text{Fuel clad surface temperature})$$

$$k_E = \text{Erosion coefficient (s}^{-1}\text{)}$$

The level of in-core deposits is assumed to govern the extent of corrosion product activity generation. The model clearly represents a major simplification of the overall activity transport process.

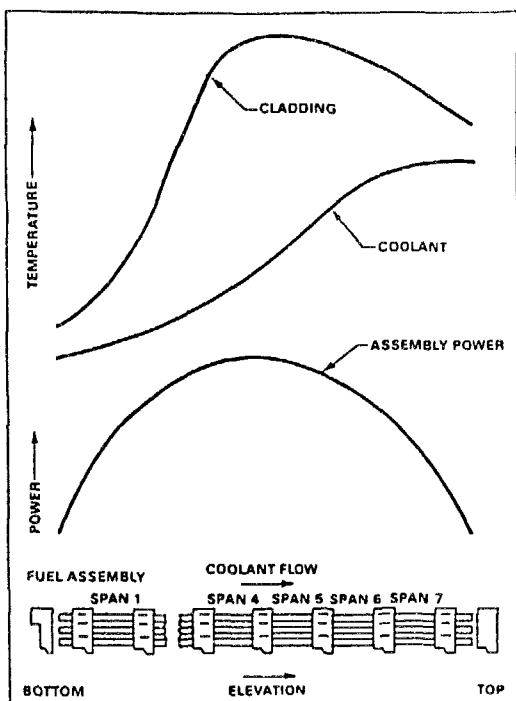


FIG. 13. Typical axial power and temperature distribution in a PWR core [8].

Although it is recognised that the terms describing particulate behaviour ( $k_D$  and  $k_e$ ) may be functions of chemistry, the basis of the control strategy focuses on the differential solubility term [ $Fe_S(T_1) - Fe_S(T_2)$ ]. Attention is concentrated on iron behaviour as this is the major crud forming element for core deposits. As noted, the temperature coefficient of solubility,  $dFe/dT$  may be positive, negative or zero depending on the coolant composition (boron and lithium levels) and temperature. Thus for a given coolant composition, iron will exhibit a minimum in its solubility at a particular temperature and it is this which has formed the basis of the Westinghouse control philosophy. This condition may be expressed formally as:

$$\left(\frac{\partial Fe}{\partial T}\right)_{B, Li, H_2} = 0$$

If the coolant composition (i.e. lithium level) is chosen to achieve this zero temperature coefficient of solubility at core inlet temperature then, if coolant iron concentrations are at equilibrium values, there will always be a driving force for dissolution at the fuel clad surface. Figure 13 shows a typical range of bulk coolant and fuel clad surface temperatures between core

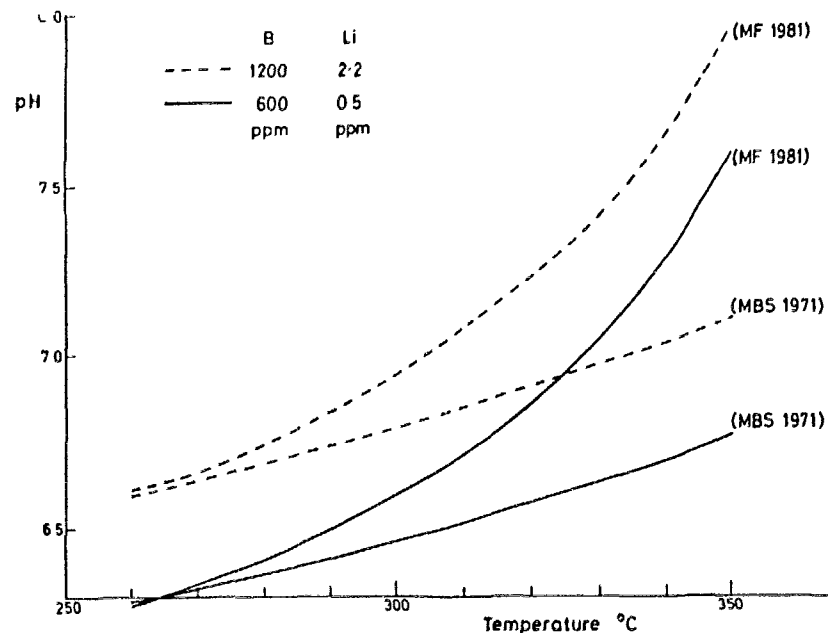


FIG. 14. Temperature dependence of pH based on two different correlations for the ionic product of water ( $K_w$ ).

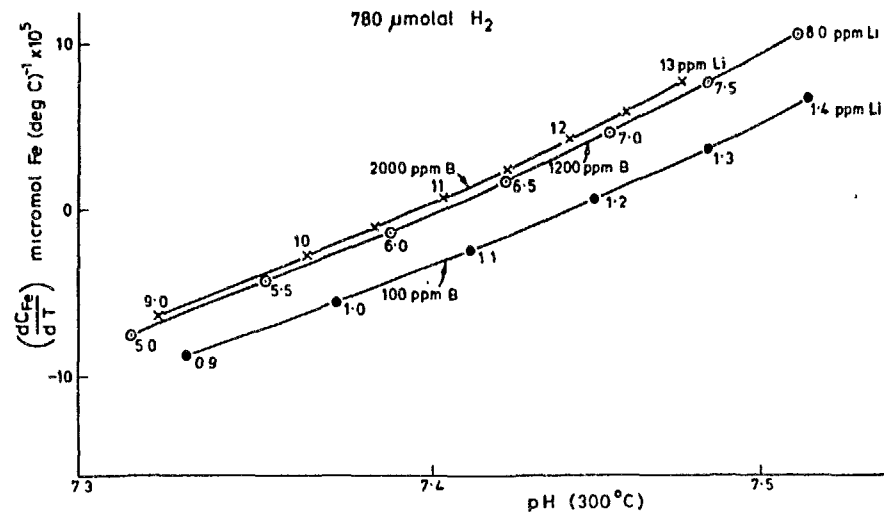


FIG. 15. Temperature coefficient of iron solubility at 300°C for  $Ni_{0.5}Fe_{2.5}O_4$  [66].

inlet and outlet to illustrate this point. In the past, bulk coolant core inlet temperature has been taken to be 285°C, but a value of 290°C to 295°C would be more appropriate at some plant.

To determine the coolant composition required to achieve a zero temperature coefficient of solubility at a given temperature, good data on corrosion product oxide solubility behaviour are required, as discussed in detail above. Early recommendations were based on the magnetite data of Sweeton and Baes [65]. On the basis of these data, the lithium concentration required to give a zero temperature coefficient of iron solubility at 285°C may be determined. This leads to a maximum lithium level of 1.9 ppm required at start of cycle (1200 ppm B), and is consistent with the current maximum specification of 2.2 ppm.

It is now felt that the magnetite solubility data lead to underestimation of the lithium level required to achieve a zero or positive temperature coefficient of corrosion product solubility in the PWR core. Circulating and deposited crud is not magnetite, it is a substituted ferrite containing nickel,  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ . Using the Kunig and Sandler [7] data for nickel ferrites Lindsay [66], determined the boundary for positive temperature coefficient for iron solubility. This boundary is shown in Fig. 3 and compared with the Westinghouse coordinated chemistry band (based on magnetite solubility). The levels of lithium implied are well above the limits set by most fuel vendors. These data are the reasons for the current trend in a number of organisations to consider operation with lithium levels somewhat higher than the usual 2.2 ppm maximum.

There are a number of shortcomings in the formulation of the strategy as described: the effect of any changes in hydrogen concentration has been neglected (although its effect over the restricted range encountered in PWR primary coolant is likely to be insignificant); only the behaviour of iron has been specifically addressed (the behaviour of nickel and cobalt is clearly important); and instantaneous achievement of equilibrium solubility conditions has been assumed (in practice this will not be the case and the direction of the driving force for dissolution/precipitation may not be the same as that indicated by predictions based on equilibrium conditions). The restriction of attention to iron behaviour is important; many authors have assumed that cobalt and nickel behaviour will follow that of iron. In general, this need not be the case and it is quite possible for the nickel (or cobalt) zero temperature coefficient of solubility to occur at distinctly different coolant composition from that for iron. However, it is well recognised that iron is the major constituent of in-core crud and the best solubility data are available for iron species so concentrating on iron behaviour is probably justified. In particular, adsorption of cobalt on crud could be important for activation and subsequent out-of-core deposition. In this case the solubility behaviour of iron dominates since it controls the mass of corrosion product deposit. The potential differences in behaviour for other in-core crud constituents should be borne in mind in any attempt to model more quantitatively corrosion product transport.

Despite some limitations, qualitative aspects of the iron solubility model have been useful in rationalising some aspects of the behaviour observed in operating plant, as discussed below.

### 3.3.5. Laboratory and loop studies

Data from operating plant are obviously essential in developing procedures for coolant chemistry control, but of necessity the range of conditions for which information is available is very narrow. There is thus an important role for laboratory studies and loop experiments to put theoretical understanding on a firmer footing and provide information which may help to establish more effective plant coolant chemistry control strategies.

Many laboratory studies have been devoted to solubility measurements on corrosion product oxide phases and much of this work has been critically reviewed by Thornton and Polley [67]. The most comprehensive study of phases directly relevant to PWR fuel crud has been attempted by Kunig and Sandler; this work is fully documented in an EPRI report [7]. The importance of solubility data has been referred to in previous sections: it forms the detailed basis for the formulation of the coolant pH control strategy.

Measurements on operating plant are broadly in line with predictions based on the solubility model but the range of measurements and conditions examined has been limited. Valuable additional information has come from carefully conducted, detailed experiments on in-reactor loops. Early Canadian work confirmed that low coolant pH operation was associated with heavy deposition on fuel [68]. This work has been significantly extended to cover a wide range of conditions relevant to PWR primary circuits in a recent programme using the DIDO Water Loop (DWL) [15][67].

The DWL studies have confirmed heavier fuel deposition and enhanced corrosion product mobility under low pH conditions. There was also some indication that higher boric acid concentrations might lead to increased deposits in-core for a given pH. In addition, a mechanism involving direct incorporation of corrosion product species into the zirconium oxide film formed on fuel clad was identified and inferred to be potentially significant for PWR operation under conditions where the well recognised spinel deposition process has been minimised. This proposal had been made previously by Lister, based on a series of loop experiments [14]. This mechanism has recently been considered by Van den Hoven [70], who concludes that it may be of major importance. These observations indicate that there may be some compromise necessary when optimising coolant chemistry to restrict activity transport. In order to restrict the  $\text{ZrO}_2$  incorporation of corrosion product species it may be wise not to raise the pH significantly beyond the value required for zero temperature coefficient of spinel solubility.

A wide range of loop studies relating to corrosion and corrosion release behaviour have also been conducted; the most fully documented are those of Lister et al. [71][72][13]; in general terms, it lends support to operation at relatively high coolant pH and is not in conflict with pH values required on the basis of the spinel solubility model.

The potential role of colloidal particulate material in corrosion product activity transport mentioned above was first recognised by Maroto et al [73]. They showed that interactions between colloidal corrosion products and fuel element surfaces can be adequately described by classical DLVO theory, and pointed out that the extent of such interactions is governed by coolant pH. The possible impact of colloid chemistry in this area has been discussed by Smith-Magowan [10][74], who concluded that interfacial electrochemical forces

are significant in determining deposition behaviour and that these forces are very sensitive to minor changes in coolant chemistry. The most detailed work on materials of relevance to PWR activity transport has been performed by Matijevic and co-workers [75], although only at temperatures well below primary circuit operating conditions. Relevant work has also been carried out by Maroto and co-workers (Blesa et al, [76][77][78]), however, extrapolation to temperatures of interest is once again difficult. Some work at higher temperatures has been undertaken by Tewari and Lee [79].

At the present time our knowledge of colloidal behaviour under PWR primary circuit conditions is inadequate as the extrapolation of low temperature data cannot be regarded as reliable. It is possible that colloidal chemistry is important in determining the build-up of out-of-core radiation fields and that some impact can be made on colloid behaviour through coolant chemistry control. Indeed it is considerations of this sort which, in part, lead EPRI to prefer operation at constant pH rather than merely operation above a certain minimum pH with detailed control being regarded as unimportant [80]. However, at present there is no firm evidence, either from operating plant or from laboratory studies, to support this recommendation. Further work will be required before any change in coolant chemistry control strategy based on the behaviour of colloidal species can be considered. The issues involved in coolant chemistry control to minimise transport via colloidal material have been discussed in some detail by Ponting and Rodcliffe [9]; the need for more reliable data under relevant conditions is clearly highlighted.

### 3.3.6. World experience and data from operating plant

In this section the build-up of out-of-core radiation fields and fuel crud deposition will be considered with respect to the influence of the operating coolant chemistry employed. The data reviewed will largely be categorised by country. The coverage is not comprehensive, but is intended to highlight cases in which relatively firm conclusions can be drawn. Attention is concentrated on more recent information.

#### 3.3.6.1. American experience

The most extensive experience in operating PWRs is to be found in the USA and careful examination of available data is useful in shedding some light on the role played by coolant chemistry in determining radiation field build-up. The most comprehensive studies are, in general, documented in reports produced by the Electric Power Research Institute (EPRI) and these will frequently be referred to in this section.

In considering US plants it should be borne in mind that early plant chemistry data were usually reported only as monthly averages of boron and lithium concentrations (although measurements would have been made more frequently), so that fluctuations in pH may have been much wider than is apparent from the reported data. More recent data, especially from France and Sweden, are usually recorded at least three times weekly (and at least at Ringhals daily) so that any fluctuations are obvious. This makes it difficult to provide reliable comparisons.

reflects the large number of factors which are involved in determining out-of-core radiation fields. In an attempt to home in on the specific influence of coolant pH, EPRI sponsored a detailed comparison between two Westinghouse designed reactors (Trojan and Beaver Valley). The results from this work have been reported in detail by Bergmann and Roesmer [40], and summaries of the work are also available [8][81]. The experiment covered 3 cycles of reactor operation for Trojan, but detailed measurements were only made for the first cycle at Beaver Valley. Trojan was deliberately operated throughout its first cycle at low pH, before switching at cycle 2 to Westinghouse coordinated chemistry. Beaver Valley was nominally operated with coordinated coolant chemistry throughout. The coolant histories for the two reactors are shown in Figs 16 and 17.

During reactor operation, radiation field measurements were made on cross-over pipework and around steam generators at comparable locations on each plant. During cycle 1 coolant samples were taken at regular intervals from both plants for chemical and radiochemical analysis. At the first refuelling shutdowns core crud samples were collected, radiation fields in the channel heads were measured and gamma spectrometry measurements of the activity deposited on the inside of the coolant piping in each plant were made.

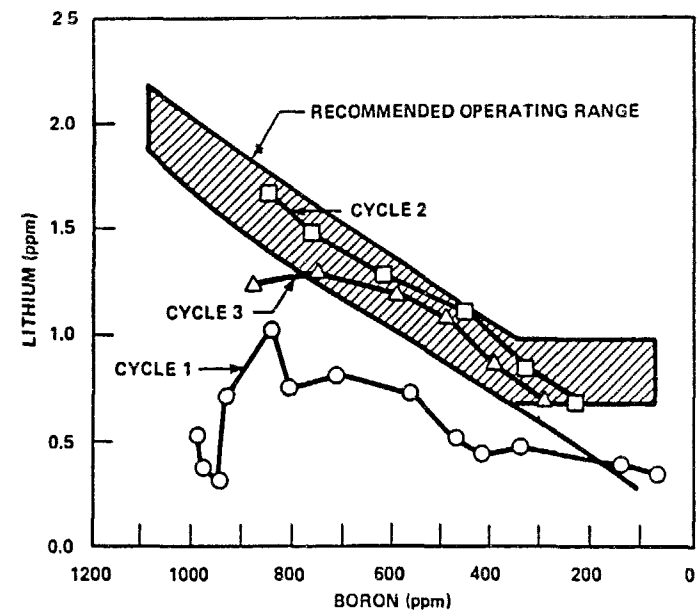


FIG 16 Boron versus lithium concentrations in the Trojan reactor coolant during cycles 1, 2 and 3 [8]

The wide variation in behaviour which is observed between different reactors has already been highlighted (Figs 3 and 4) and it has become clear that this



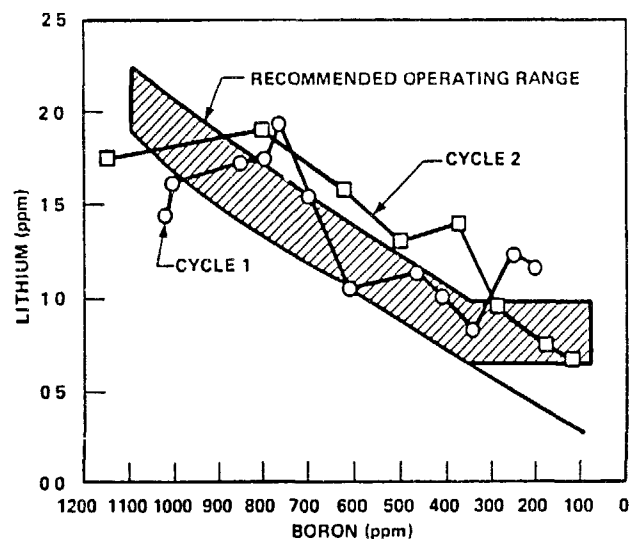


FIG 17 Boron versus lithium concentrations in the Beaver Valley unit 1 reactor coolant during cycles 1 and 2 [8]

Information on in-core deposits for the two reactors is summarised in Tables 6 and 7 and Fig. 18, core regions are identified in Table 8. Fig. 18 illustrates the crud build-up on Trojan fuel assemblies over 3 cycles. The conclusions regarding core crud build-up are clear: operating at a consistently low coolant pH leads to very much heavier deposition than operating with reasonably high pH (ca. 6.9) coordinated coolant chemistry. Switching to coordinated chemistry very much reduces deposition on fresh fuel but does not effect the removal of previously laid down deposits (if anything, deposition appears to beget deposition: crud levels may be higher on crudded fuel after cycle 2 compared with cycle 1).

The position with regard to build-up of out-of-core radiation fields is far less clear cut. These are shown for cross-over pipework in Fig. 19 and for steam generators (external and internal) in Fig. 20. There is some indication of significantly lower fields on cross-over piping at Beaver Valley, particularly for survey points expected to be influenced by crud-traps. Furthermore, switchover to coordinated chemistry at Trojan appears to be correlated with some decrease in cross-over piping dose rates. However, for steam generator dose rates there is little to choose between the two plants. Again Bergmann et al [8] suggest that some benefit from the switchover to coordinated chemistry can be discerned at Trojan, but the effect is not dramatic.

An example of the benefits to be gained by improving coolant chemistry control and implementing a coordinated chemistry regime is provided by Indian Point 2 (a Westinghouse 4 loop PWR), as discussed by Gaynor et al. [82]. Although

TABLE 6 AVERAGE SURFACE CONCENTRATIONS OF DEPOSITS ON THE BEAVER VALLEY CYCLE 1 CORE

Region	Surface Concentrations (mg/dm <sup>2</sup> ) <sup>a</sup>		
	Span 7	Span 6	Span 4
A	32 ± 17	39 ± 10	15 ± 8
B	35 ± 30	28 ± 9	10 ± 6
C	36 ± 21	24 ± 12	9 ± 3

TABLE 7 AVERAGE SURFACE CONCENTRATIONS OF DEPOSITS ON THE TROJAN CYCLE 1, 2 AND 3 CORES

Cycle	Region	Surface concentrations (mg/dm <sup>2</sup> ) <sup>a, b</sup>		
		Span 7	Span 6	Span 4
1	A	156 ± 88	361 ± 275	48 ± 48
1	B	195 ± 87	83 ± 78	69 ± 64
1	C	106 ± 58	not det'd	73 ± 60
2	B	350 ± 244	152 ± 169	9 ± 8
2	C	147 ± 94	86 ± 52	24 ± 18
2	D	3 ± 3	5 ± 3	4 ± 3
3	B	341	65	3
3	C	106 ± 36	82 ± 499	60 ± 53
3	D	43 ± 02	6	4
3	E	2	2	2

<sup>a</sup> Error indicators are standard deviations

<sup>b</sup> Entries without error indicators are single measurements

TABLE 8 ALLOCATION OF FUEL ELEMENT GROUPS TO CORE REGIONS

Cycle	Core Region		
	Centre	Intermediate	Periphery
1	A	B	C
2	B	C	D
3	C	D	E
4	D	E	F
5	E	F	G

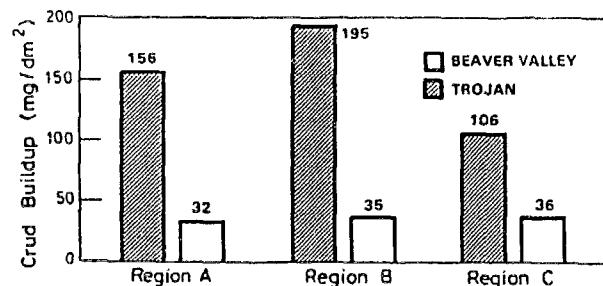


FIG. 18a. Crud buildup on span 7 of cycle 1, Trojan and Beaver Valley fuel assemblies.

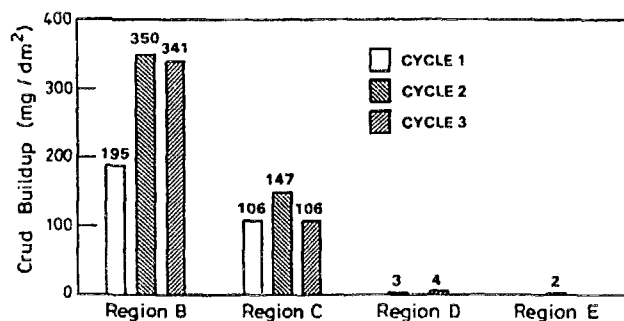


FIG. 18b. Crud buildup on span 7 of Trojan cycle 1, 2 and 3 fuel assemblies.

not described in detail, the coolant chemistry control during the first five cycles of operation did not adhere to the coordinated chemistry philosophy and included significant periods of operation at low pH. During cycle 6 attempts were made to implement coordinated chemistry control, but some problems were encountered. Reasonable coordinated control at pH ca. 6.9 was achieved after about two months of cycle 7. The steam generator channel head dose rate history is shown in Figure 21 and the fall at the end of cycle 7 is considered to be a consequence of the move to higher pH, coordinated chemistry. In addition to lower primary system radiation fields, the filterable crud levels in reactor coolant were also very much lower leading to less contamination of primary system filters. The authors concluded that the changes during a single cycle cannot be regarded as conclusive but that the results are highly encouraging.

Other attempts to demonstrate the connection between coolant chemistry and dose rate build-up have concentrated on evaluation of operating coolant chemistry and dose rate data from a wide range of plants. Early attempts were pioneered by Solomon and Roesmer [83].

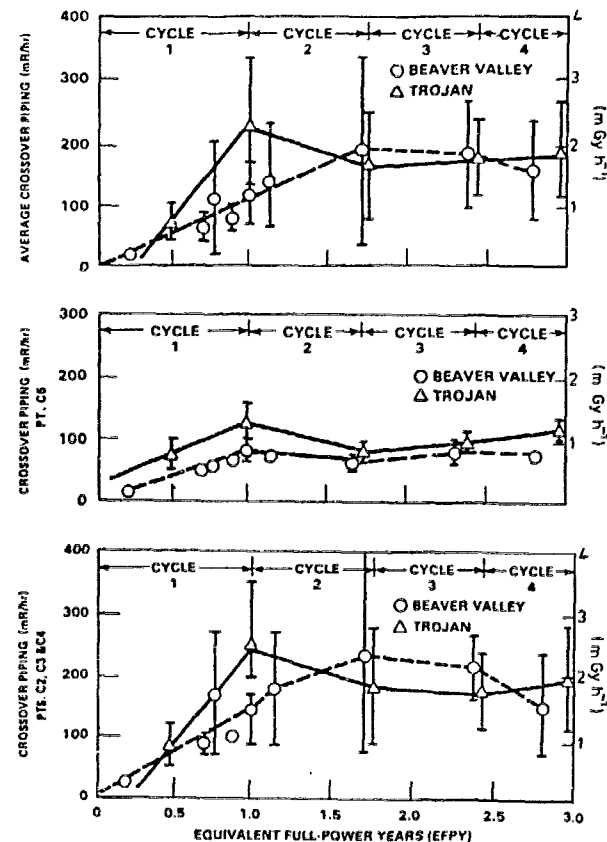


FIG. 19. Exposure rate buildup on the crossover piping in the Beaver Valley unit 1 and Trojan plants [8].

More recently, a number of attempts have been made to put this connection on a more quantitative footing. The various approaches adopted by Westinghouse workers are described in detail by Bergmann et al. [8].

The simplest approach adopted was to use a parameter, the coolant chemistry quality factor (QF), against which to correlate SG channel head dose rate. QF was originally defined as the ratio of the number of lithium-boron measurements below the boundary for zero temperature coefficient of magnetite solubility at 285°C to the total number of lithium-boron measurements for a given cycle. Although a number of refinements to this parameter were attempted correlations obtained were relatively weak; an example is shown in Fig. 22 for dose rates at the end of the first cycle for 12 reactors.

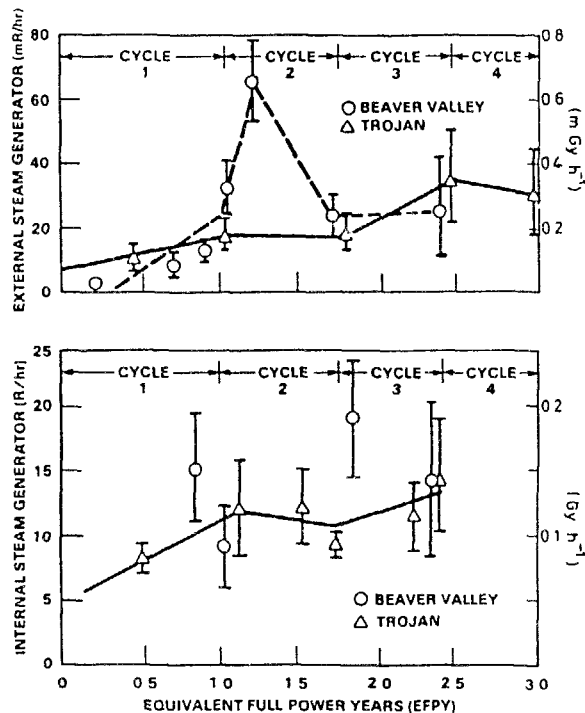


FIG 20 Exposure rate buildup on the inside and outside of steam generators in the Beaver Valley unit 1 and Trojan plants [8]

Another correlation evaluated was the effect of a change in quality of coolant chemistry on channel head dose rates. The change in quality factor,  $\Delta QF (= (QF_2) - (QF_1))$ , between cycles 1 and 2 and the corresponding change in dose rate  $\Delta D$  were calculated and the correlation shown in Fig. 23 was obtained. The correlation is weak but may be taken to indicate that 'improving' the operating chemistry of plant is likely to lead to benefits in restricting out-of-core radiation fields.

A somewhat more elaborate approach to data correlation for Westinghouse plant has been developed. It is based on the use of the CRUDSIM [66] solubility model for activity transport. CRUDSIM represents a reactor as two tanks - hot and cold. Activation of corrosion products takes place in the hot tank and transport between the two tanks is governed by the behaviour of soluble species, in a manner determined by the Kunig and Sandler solubility data and the operating history of the plant (coolant chemistry and power levels). The programme calculates a relative out-of-core activity inventory. Table 9 lists the results of calculations for eleven first cycle plants and includes not only the relative activity value for the actual operating chemistry but the

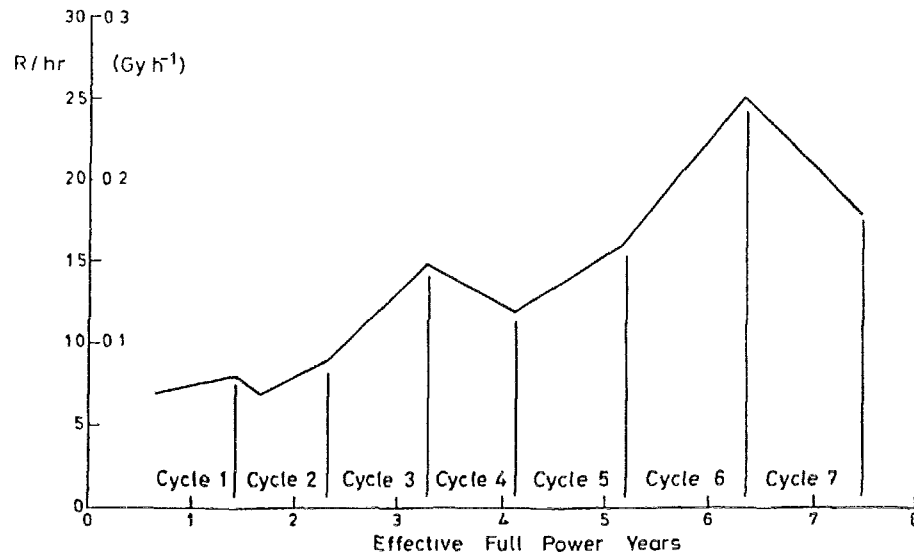


FIG 21 Steam generator channel head dose rates at Indian Point 2 (redrawn from Ref [82])

relative activity if the plant had been operated with coordinated chemistry (the ratio of the two is the CRUDSIM chemistry factor). Fig. 24 shows the correlation of observed SG channel head dose rates with CRUDSIM predicted relative activity and with CRUDSIM chemistry factor. The good correlation obtained in the latter case highlights the importance of coolant chemistry during the first cycle operation.

Polley [17] has considered data from nine Westinghouse plants in some detail to establish possible correlations between SG channel head dose rates and operating coolant chemistry. The fundamental coolant chemistry parameter was judged to be the pH at 300°C, based on arguments relating to the temperature coefficient of solubility of fuel crud. Three approaches to deriving correlations based on coolant chemistry history for individual plants were attempted. The three parameters, all based on expressions involving coolant pH, were

$$B = \frac{100 \sum \Delta t_1}{t} \quad (\text{percentage bad chemistry})$$

$\Delta t_1$  : the time spent at a coolant  $pH_T$  below a nominal value  $pH_T^0$  at which the temperature coefficient of (iron) solubility is zero.

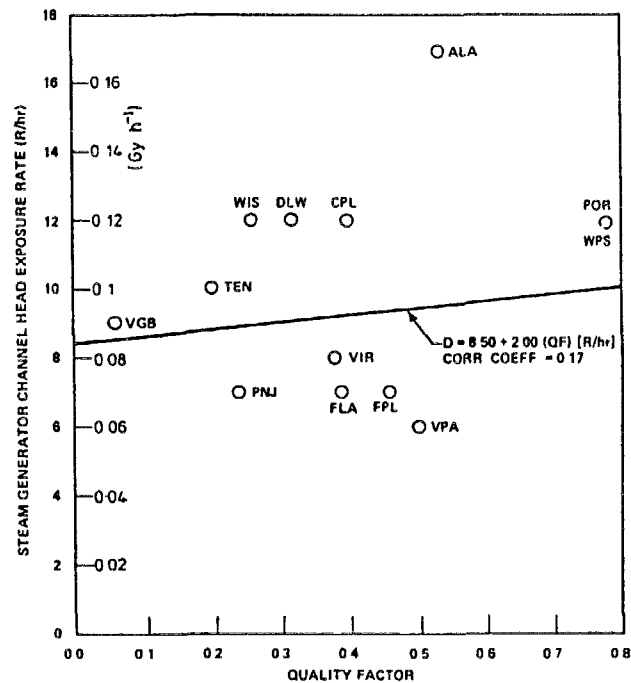


FIG 22 Channel head exposure rate versus quality factor for 13 Westinghouse reactors after one cycle of operation [8]

TABLE 9 CRUDSIM CHEMISTRY FACTOR VALUES AND STEAM GENERATOR EXPOSURE RATES AT THE END OF THE FIRST CYCLE

Plant	Relative Activity		Chemistry Factor (ratio actual to coordinated)	S/G Exposure Rate (R/hr)
	Actual Chemistry	Coordinated Chemistry		
R	418	269	1.55	16
G	446	295	1.51	12.4*
S	329	315	1.03	7
T	309	281	1.10	10
U	159	163	0.98	6.9*
P	315	290	1.09	7
V	356	365	0.98	6
W	188	219	0.86	3.9
C	444	376	1.18	5
X	228	255	0.89	9
Y	275	278	0.99	5.5

\* Exposure rate adjusted for decay based on actual gamma spectroscopy measurements

$$P = \frac{100 \sum_{i=1}^n \Delta t_i (pH_T^0 - pH_{Ti})}{t} \quad (\text{Crud precipitation index})$$

$pH_{Ti}^0 < pH_T$ , only.

$$pH_{300} = \frac{\sum_{i=1}^n \Delta t_i pH_{Ti}}{t} \quad (\text{the time averaged } pH_{300})$$

It should be noted that the pH (300°C) values used in Polley's work are based on the Mesmer, Baes and Sweeton [63]  $K_w$  correlation; we will use the Marshall and Franck correlation here. Two values for  $pH_T$  were tried; 6.7 and 6.9., 6.7 had the merit that there was a reasonable certainty, from available solubility data, that precipitation would be favoured for  $pH_T$  values below it; 6.9 was of interest since it is approximately the value recommended for plant operation by Westinghouse.

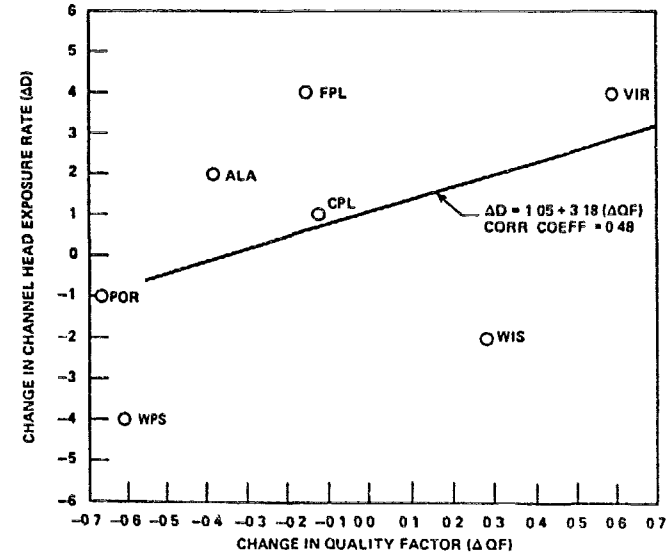


FIG 23 Change of channel head exposure rate (cycle 2-cycle 1) versus change in quality factor for 7 Westinghouse reactors [8]

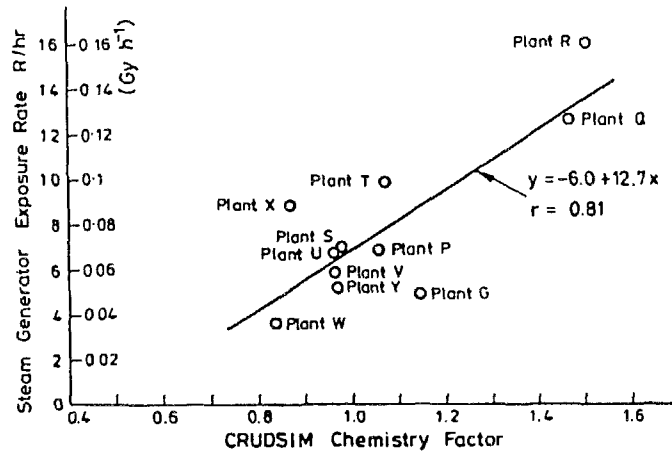


FIG. 24. Relationship between CRUDSIM chemistry factor and steam generator exposure rates at end of first cycle (redrawn from Ref. [21]).

It is clear that P is a more sophisticated parameter than B, since it takes into account the extent as well as the duration of any negative excursions in pH, while both parameters rely on the assumption that positive deviations are not effective in modifying dose rates.  $\text{pH}_{300}$  on the other hand weighs positive and negative deviations equally. All three parameters showed correlations with SG channel head dose rates (Table 10). A typical example is given in Figure 25. For the cycle 1 data and cycle 2 minus cycle 1 data. All the correlations were found to lie between the classifications 'significant' and 'probably significant' (Table 10). Correlations for longer term data were found to be weaker, possibly because of the effects of refuelling and long  $^{60}\text{Co}$  half life. Although Polley suggests the results be treated with some caution because of the relatively small data base, his work clearly indicates that operation at low  $\text{pH}_T$  is to be avoided.

On the basis of data from operating American PWRs, other worldwide reactor experience, and laboratory and loop studies EPRI have formulated guidelines for coolant chemistry conditions during normal operation [80]. Their present recommendation is based on Figure 26, in which three regions on the plot of lithium concentration against boron concentration are defined. Region A, corresponding to low pH, is to be strenuously avoided. Region B, 'coordinated' lithium-boron, constant pH (ca. 6.9) is the preferred approach but plant experience suggests that operation in Region C ('elevated lithium') is an acceptable way to manage lithium and boron.

An example of good experience from operation in region 'C' is provided by the Combustion Engineering Calvert Cliffs plant, described by Barshey et al [84]. The Combustion Engineering lithium specification is 1.0–2.0 ppm and thus differs from the Westinghouse coordinated chemistry specification. Some C-E plants have adhered rigidly to the 1.0–2.0 ppm specifications, others have

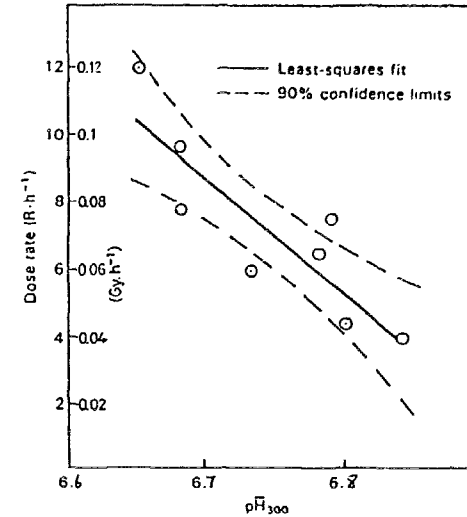


FIG. 25. Dose rate versus average pH value,  $\text{pH}(300^\circ\text{C})$ , cycle 1 (Note:  $\text{pH}(300^\circ\text{C})$  based on MF  $K_w$  [17]).

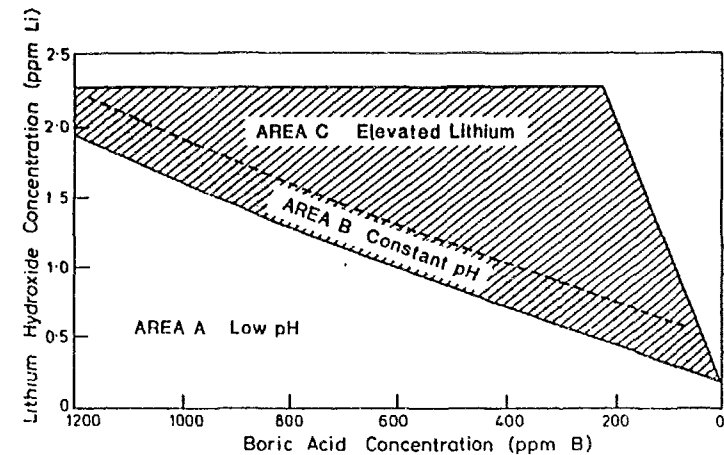


FIG. 26. Various lithium-boron modes of operation identified in EPRI primary water chemistry guidelines [80].

TABLE 10 RESULTS OF CORRELATIONS BETWEEN COOLANT CHEMISTRY (pH<sub>T</sub>) AND SGU DOSE RATES

Cycle No		Type of Chemistry Parameter	pH <sub>T</sub> Value	Number of Stations Co-related	Intercept <sup>a</sup> (R h <sup>-1</sup> )	Slope <sup>a</sup> (R h <sup>-1</sup> per Unit Chemistry Parameter)	Correlation Coefficient	Probability of Positive Correlation (%)
For Chemistry Data	For Dose Rate Data							
1	1	P	6.6	8	3.8 ± 2.6	0.54 ± 0.35	0.77	99
		P	6.8	8	0.7 ± 4.4	0.36 ± 0.23	0.77	99
		ΣP	6.6	8	1.2 ± 4.7	0.15 ± 0.11	0.73	98
		ΣP	6.8	8	7 ± 11	0.19 ± 0.15	0.72	98
		pH <sub>300</sub>	-	8	230 ± 50	-33 ± 16	0.86	99.7
2 minus 1	2 minus 1	P	6.6	8	1.4 ± 1.6	0.26 ± 0.16	0.78	99
		P	6.8	8	1.9 ± 1.8	0.13 ± 0.09	0.75	98
		ΣP	6.6	8	2.1 ± 1.9	0.058 ± 0.045	0.72	97
		ΣP	6.8	8	2.7 ± 2.5	0.050 ± 0.049	0.63	95
		pH <sub>300</sub>	-	8	2.4 ± 2.1	-8.8 ± 7.2	-0.70	98
Mean over 1,2,3	Mean over 1,2,3	P	6.6	6	6.8 ± 3.6	0.39 ± 0.66	0.53	86
		P	6.8	6	6.4 ± 3.9	0.19 ± 0.29	0.56	87
		ΣP	6.6	6	6.8 ± 4.0	0.08 ± 0.16	0.49	84
		ΣP	6.8	6	5.3 ± 5.2	0.07 ± 0.10	0.59	89
		pH <sub>300</sub>	-	6	80 ± 110	-11 ± 16	0.57	89
Mean over 1,2,3,4,5	Mean over 4,5,6 <sup>b</sup>	P	6.6	6	4.6 ± 6.7	1.5 ± 1.7	0.69	93
		P	6.8	6	4.9 ± 9.3	0.55 ± 0.91	0.54	86
		ΣP	6.6	6	5.3 ± 9.1	0.26 ± 0.55	0.52	86
		ΣP	6.8	6	7 ± 16	0.08 ± 0.36	0.22	66
		pH <sub>300</sub>	-	6	150 ± 370	-20 ± 54	0.36	76

<sup>a</sup> ± values are 90% confidence values<sup>b</sup> Some plants did not measure dose rates after all three cyclespH<sub>T</sub> based on MBS K<sub>w</sub> correlation

followed a coordinated chemistry regime and some have followed a hybrid of the two schemes (staying above the coordinated chemistry lower limit curve and below an upper limit of 2.2 ppm) corresponding to operation in Region 'C' of the EPRI Guidelines diagram (Figure 26). The Calvert Cliffs reactors have followed this last approach and have channel head dose rates in the range 4-6 Rh<sup>-1</sup> after 6 and 7 cycles of operation.

### 3.3.6.2. European experience

In general, ORE figures on EdF plant have been good, as shown by Figure 6. It should be noted that the anticipated accumulated annual average for total dose received by operating personnel is 2.85 man Sv [2].

Menet et al [88] have summarised EdF data on operational chemistry. The EdF specification for lithium-boron coordination is shown in Figure 27. It can

been seen that it involves coordination at a pH of 6.9-7.0 until close to the end of the cycle when a sharp rise to a pH of 7.4 occurs (pH values based on MF K<sub>w</sub>).

EdF use an 'activity index' to quantify the extent of build-up of out-of-core radiation fields. The value of this index is the arithmetic mean of the radiation fields measured at a number of specified locations. Attempts have been made to correlate the values observed for this index on a number of plants with the coolant chemistry history of those plants. The correlations are made against a parameter representing the deviations in actual pH from the specified optimum pH; the approach bears some resemblance to that adopted by Polley described above. The strongest correlations are obtained for first cycle data against acidic pH deviations.

Menet concludes that acidic deviations are clearly unfavourable, but that no conclusion about the optimum operation pH can be drawn and that there is no

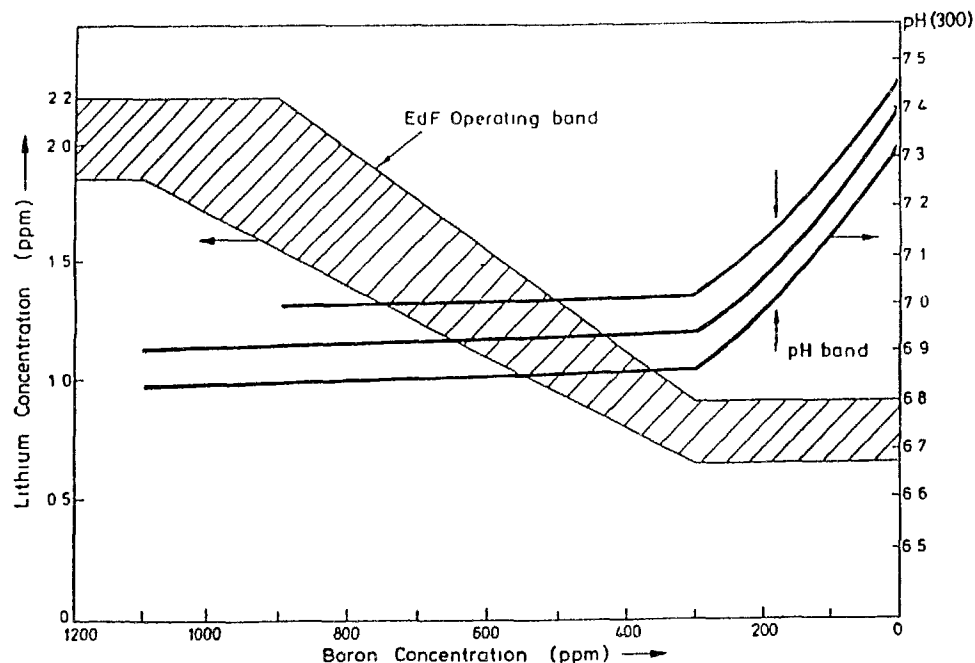


FIG 27 EdF lithium-boron co ordinated chemistry and calculated pH (300°C)  
(Note pH (300°C) values calculated using MF  $K_w$ ) (redrawn from Ref [2])

evidence of a specific influence of the chemistry quality at the end of the cycle (boron concentrations less than 270 ppm). He also finds no significant correlation between coolant chemistry and activity index for fuel cycles beyond the first. He cites two points to be considered:

1. After the first fuel cycle all EdF units have a good and similar chemistry quality.
2. 'Memory Effects' of chemistry and activities from one cycle to the next have not been computed.

Menet stresses that good chemistry control is important; a control band of 0.08 pH units is adopted by EdF.

Further information is given in the paper entitled "Observations on recent application of high coolant pH in French PWRs and optimization of chemistry during shutdown" by P. Beslu to show that operation, of 6 EdF plants at a pH of 7.2 has led to a stabilisation or even a reduction in out-of-core dose rates.

Radiation field build-up and its relationship to primary coolant chemistry control has been followed in some detail on the three Ringhals PWR stations

(reactors 2 - 4) with particular emphasis on Ringhals 4. This work has been reviewed by Gott et al [52]. The variation of SG channel head dose rate with time at which high 'constant pH' chemistry was introduced is shown in Figure 28. The coolant chemistry regimes for the three reactors between 1983 and 1986 are shown in Figure 29. The specified coolant chemistry for the Ringhals reactors was increased to 3.5 ppm Li at start of cycle, maintained at this value until the gradual decrease in boron concentration lead to a pH (300°C) of 7.4. thereafter Li and B were coordinated to give a constant pH of 7.4 until the end of the cycle. The restriction of the Li level to 3.5 ppm reflects concern about enhanced Zircaloy corrosion. So far no detrimental effects have been observed; the maximum oxide thickness measured on clad has been 40  $\mu\text{m}$  for fuel with a burn-up of 32 MWD/kgU, but it was not known to what extent, if any, this fuel operated with boiling heat transfer [86].

Ringhals 2 has operated for much longer than the other two reactors. Early operation at low pH led to heavy crud deposition during cycle 1; out-of-core radiation fields at this stage were ca  $8 \text{ Rh}^{-1}$ . The sudden increase in build-up of SG dose rates (at a rate apparently greater than the  $^{60}\text{Co}$  decay rate). The reduction in dose rate appears to reflect both the move to high pH coolant chemistry and the removal of in-core cobalt sources.

Ringhals 3 and 4 have both been operated with relatively 'good' coolant chemistry from cycle 1, with the change to high pH chemistry taking place after 1.25 EFPY and 0.5 EFPY respectively. The behaviour of the two reactors is significantly different, with Ringhals 4 showing a particularly low build-up of out-of-core radiation fields. Detailed dose rate and gamma - spectrometry measurements have been made on Ringhals 4 and to a lesser extent

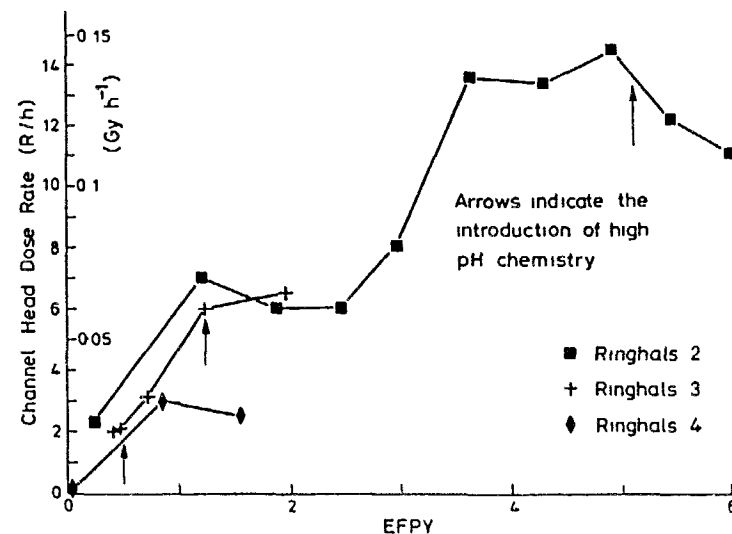


FIG 28 Evolution of steam generator channel head dose rates in the Ringhals reactors (redrawn from Ref [52])

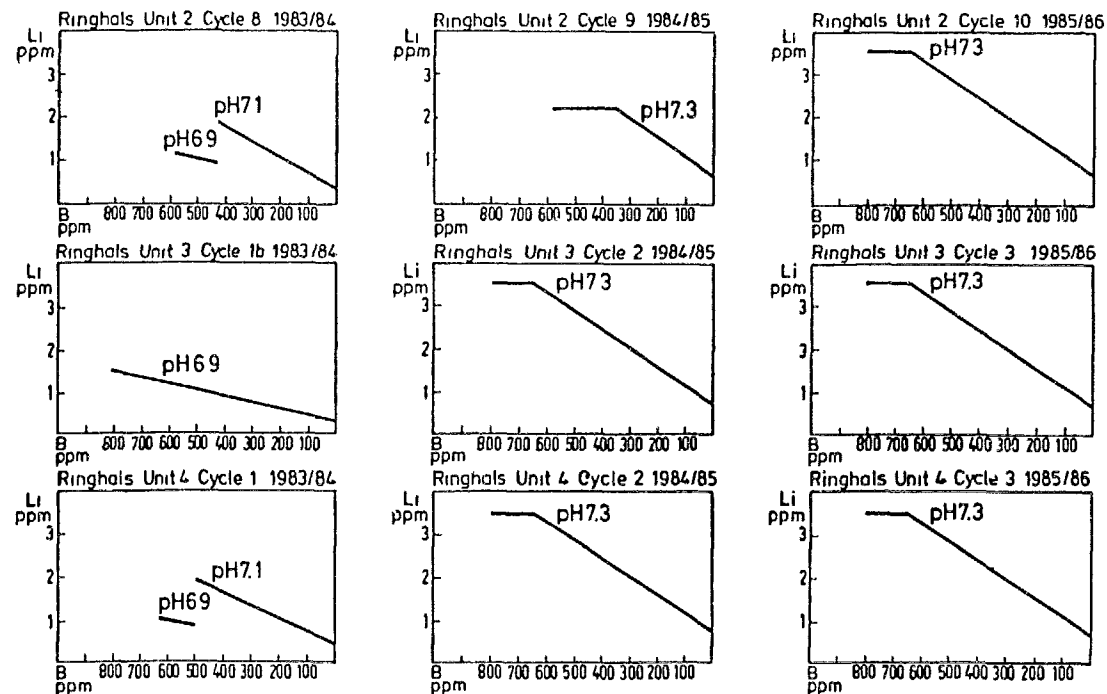


FIG 29 Recent coolant chemistry regimes for the Ringhals reactors (schematic) (redrawn from Ref [52]).

on the other reactors. Although a clear cut rationalisation of all these data is difficult, the differences in radiation field development between Ringhals 3 and 4 appear to be associated more with  $^{60}\text{Co}$  than with  $^{58}\text{Co}$ . Gott et al [52] suggest that this is likely to be due to high cobalt concentrations in constructional materials in Ringhals 3 and seem to suggest that the different levels in SG tubes (0.06% and 0.05% respectively) may be responsible.

The detailed control of coolant chemistry at Ringhals may also be significant in achieving the very good dose rate experience. Lithium concentrations are measured daily (compared with 3 times per week on many PWRs) and a very tight control band is achieved.

On balance, the Ringhals experience demonstrates the benefits of high pH coolant chemistry and tight chemistry control in restricting out-of-core radiation field levels; the Ringhals 4 experience is particularly encouraging. There is, however, a need to obtain information on oxide thickness measurement, particularly for the most highly rated fuel.

KWU, in collaboration with reactor operators, have considered in detail the comparative build-up of SG channel head dose rates in two reactors

(Goesgen-Daeniken in Switzerland and Neckarwestheim in Germany). This work has been described by Weitz et al [29] and Greger et al [87] and has been discussed with reference to in-core cobalt sources in Section 2.2. Both reactors are 3 loop plants with similar power outputs but Neckarwestheim showed dose rates about half those experienced at Goesgen. The SG channel head dose rates (hot leg side) are shown in Figure 30. The Goesgen dose rates are quite high compared with recent world experience (about  $22 \text{ Rh}^{-1}$  after 4 years of operation and extrapolated to rise to  $50 \text{ Rh}^{-1}$  within 15 years if no ameliorating action is taken).

In order to rationalise the observed dose rates,  $^{60}\text{Co}$  to  $^{58}\text{Co}$  ratios were measured as a function of the fuel charge by a wet sipping technique applied to the fuel elements after discharge. The important conclusion from this work was that some fuel could be associated with high levels of cobalt contamination in the fuel element grid material (Inconel 718). The data were used to define a 'Fuel Element Influence Factor' (FEI) for each cycle of operation at each plant. FEIs were, in general, much larger for Goesgen than for Neckarwestheim. Although a correlation of observed dose rates with FEI could be discerned, the correlations showed some anomalies. Very much better correlations were achieved when coolant chemistry histories for the two plants



were taken into account. The coolant chemistries were examined to derive a 'potential crud mobility' term for each cycle, based on the Kunig and Sandler nickel ferrite solubility data [88] and the temperatures around the primary circuit. These results were corroborated by examining other PWRs also. Approximately 45 cycles of 10 PWRs have been examined for correlation between potential crud mobility and radiation field build-up. The results confirm that the higher the chemistry influence factor to crud mobility the faster the build-up of dose rate.

As far as coolant chemistry control is concerned, the authors draw the conclusion that this is a very important parameter in determining radiation field build-up; Riess [62] on the basis of this work and other worldwide experience has advocated a coolant chemistry control strategy similar to that currently adopted by Ringhals: operate at the highest constant lithium level compatible with avoiding enhanced Zircaloy corrosion until reaching a pH (300°C) of ca. 7.4 then follow lithium-boron coordination at that pH. The conclusion with regard to contaminated grid material is also clear and has been made in 3.2.2: there are severe penalties on out-of-core dose rates from operating with cobalt-contaminated grids.

For several years a collaborative programme of measurement of coolant corrosion product burdens and activities has been undertaken by the United

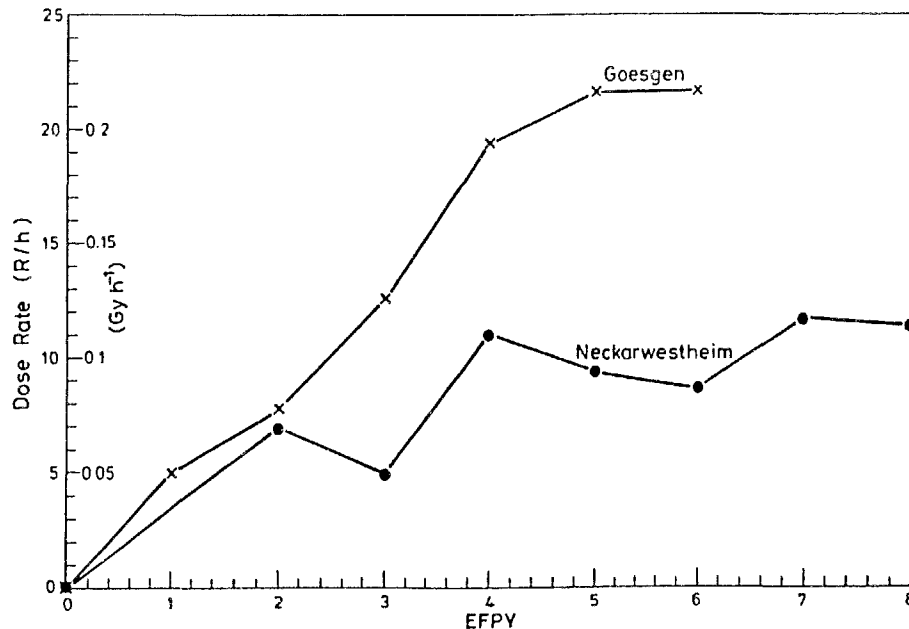


FIG. 30. Dose rate buildup in the SG primary channel head at the divider plate, hot leg side for the Geosgen and Neckarwestheim plants (redrawn from Ref. [87]).

TABLE 11. CHANNEL HEAD DOSE RATES FOR DOEL 3 AND 4

Year	Dose Rate (R.h <sup>-1</sup> )*			
	Doel 3		Doel 4	
	Cold leg	Hot leg	Cold leg	Hot leg
1983	6.7	7.5	-	-
1984	8.0	10.0	-	-
1985	7.6	7.6	-	-
1986	6.8	8.8	3.2	4.2
1987	7.0	9.0	3.7	4.5

\*Corresponding levels for Doel 1 and 2 are 8-15 R.h<sup>-1</sup> but the data are not reliable.

Kingdom Atomic Energy Authority and Laborelec on the Doel and Tihange reactors. These measurements have employed isokinetic sampling lines (introduced into the existing sample lines and not into the primary circuit), and a large body of data accumulated.

Doel 1 and 2 adopted the Westinghouse coordinated chemistry regime in the late 1970s and SG channel head dose-rates have been reported between 10 and 15 R.h<sup>-1</sup>. Doel 3 adopted the coordinated chemistry regime in its first cycle but was late in establishing the initial lithium concentration, the highest lithium level recorded being 1.7 ppm. At Doel 4 during the first cycle the lithium levels were above the Westinghouse coordination envelope throughout the cycle, being established very early at 2.5 ppm and in general maintaining values between 1.5 and 2.0 ppm until late in the cycle (<200 ppm boron) [89]. The dose rates at Doel 3 and 4 (Table 11) are lower than those for Doel 1 and 2, and it is noticeable that the dose rates for Doel 4 are very low and did not increase significantly from cycle 1 to cycle 2.

### 3.3.6.3. Japanese and Korean experience

The dose rate build-up and ORE experienced on Japanese plant has been quite good compared with general world experience (Figure 6). As with other operators, the Japanese consider pH control to be the overriding issue for operational coolant chemistry. Again the control philosophy is based on the spinel solubility model and, recognising the fact that the relevant solid phase is a nickel ferrite, measurements of corrosion product solubility have been made using the hot and cold leg sample lines of the primary circuit of the Tsuruga-2 plant [90]. Minimum iron and nickel solubility were found between pH 7.0 and 7.5 at 285°C. Plans for laboratory experiments to measure the temperature coefficient of corrosion product solubility have been reported by Kasahara et al [91].

Yamada and Ojima [92] have reported the results of a back to back plant comparison exercise covering the first four cycles of operation of two similar

PWR plants. One plant operated with steadily improving pH control over the four cycles starting off with <50% time averaged operation in the range 6.8<pH<7.1 and ending up with >90% operation in that range while the second plant had relatively poor chemistry control throughout. Introducing this improved chemistry control resulted in a decrease in the surface concentration of fuel deposits. Plant (steam generator channel head) radiation fields in the two plants were virtually identical at the end of the first cycle (around 5 Rh<sup>-1</sup>) but at the end of the fourth cycle the radiation field of the well controlled plant was 85% of that of the plant which had not introduced good control.

Lee [93] has described the chemistry surveillance program operating during commissioning of Korean PWRs. He advocates a minimum passivation time of 300 hours at 160°C in deoxygenated (by degassing and hydrazine addition) water containing 0.7 to 2.2 ppm Li. Korean PWRs operate with a conventional Westinghouse coordinated chemistry.

### 3.3.6.4. Experience with Soviet-designed VVER stations

The coolant chemistry regime adopted on VVER stations is significantly different from that adopted for Western designed PWRs: although boric acid is employed as a chemical shim for core reactivity control, potassium rather than lithium is used as the pH raising agent and ammonia (which generates hydrogen through radiolysis in the core) rather than direct hydrogen injection is used to suppress the radiolytic formation of oxidising species. However, when evaluating dose-rate build-up experience it must be borne in mind that there are a number of very significant design and operation differences which may be more crucial than the coolant chemistry in determining behaviour: VVERs have horizontally configured, stainless steel tubed steam generators, are operated at lower temperature and at lower rating than Western PWRs and, probably most significant, avoid the use of cobalt-based hard facing alloys.

VVERs for which information is most readily available are the Loviisa reactors in Finland, the Paks Nuclear Power Plant in Hungary and Czechoslovakian PWRs. In general, ORE has been relatively low in these plants, with the dose rate experienced being less influenced by <sup>60</sup>Co than by other nuclides, using <sup>110m</sup>Ag [94] and <sup>124</sup>Sb, than in Western PWRs. The strategy for coolant chemistry control at the Loviisa VVER-440 has been outlined by Järnström [35]. The control of potassium dosing is complicated by the production of lithium associated with the burn-out of <sup>10</sup>B and by the presence of ammonia (which affects the potassium level through its influence on the cation exchange bed); nevertheless, tight control of coolant chemistry can be fairly readily achieved. The specification for total equivalent potassium concentration in the VVER-440 (based on potassium, lithium and sodium concentrations) is related to the boric acid concentration and is given by the expression:

$$[K_{\text{tot}}]^+(\text{ppm}) = 4 + \frac{4}{3} [H_3BO_3](\text{gkg}^{-1}) \pm 2$$

In terms of primary coolant pH this is quite similar to a lithium-boron coordinated chemistry with lithium in the range 0.7–2.3 ppm.

A detailed evaluation of the resulting pH is given in the paper entitled "Method for pH calculation" by E.W. Thornton. Also included in a pH evaluation for the VVER 1000 reactor type which has a different specification for K<sup>+</sup>.

In general, deposited activities and the resulting dose rates are lower in VVER reactors than in most other PWRs (Fig. 31). Since cobalt hard facings are absent, the residual impurities in the alloys of construction determines the <sup>60</sup>Co generation. The effect can be clearly seen in Fig. 32 which compares dose rates in steam generators of Russian and Czechoslovakian manufacture respectively. The differences are attributed to the different impurity levels, those of Czechoslovakian manufacture having very low levels indeed (about 0.02%) compared to the specification of 0.05%). Very high <sup>58</sup>Co/<sup>60</sup>Co ratios in Czechoslovakian stations with Czechoslovakian steam generators testify to the importance of <sup>58</sup>Co as the main cause of dose rate in these plants (Fig. 33). The relatively short half life (71d) of <sup>58</sup>Co means that generation and transport in the latter part of the fuel cycle largely determines the dose rates at the main outage. The control strategy for pH is therefore based on the requirement to minimise <sup>58</sup>Co production.

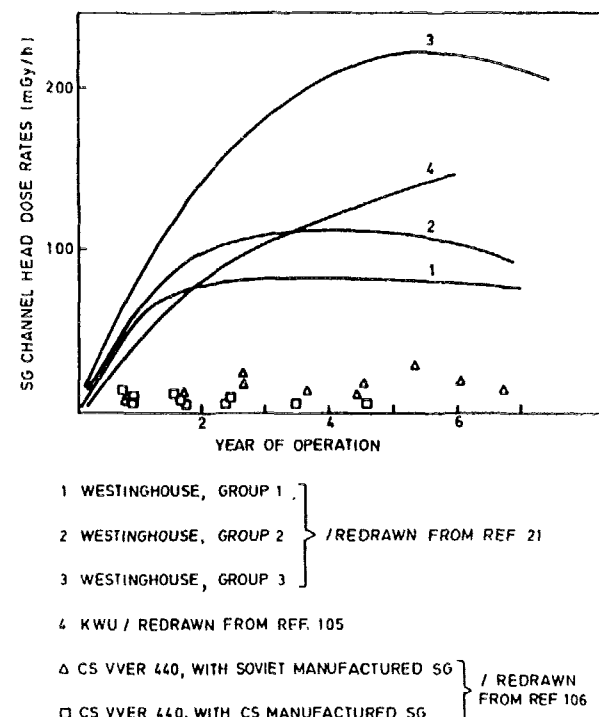


FIG. 31. Buildup of steam generator channel head dose rates.

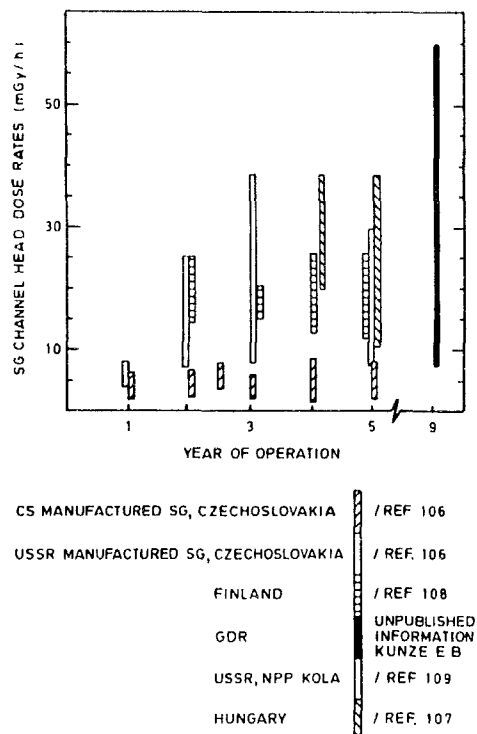


FIG. 32. Steam generator channel head dose rates — buildup in VVER 440 with steam generators manufactured in the USSR and Czechoslovakia.

Plant measurements (Fig. 34) show that an average  $\text{pH}_{300}$  of about 7.2 minimises dose rates. Since this value is required in approximately the last one third of the fuel cycle, a period corresponding to low concentrations of boric acid, alkali metal concentrations are at levels low enough not to cause concern about the integrity of fuel cladding or steam generation tubing.

$^{110m}\text{Ag}$  is often a characteristic of the nuclides generated in VVER reactors. Its contribution (in Czechoslovakian PWRs) is less than 10% of the total dose rate but it is colloidal in nature, not readily ion exchangeable or filterable and the principal hazard is from airborne contamination although in practice, dose from internal contamination are less than 1% of total doses. Stainless steel is a source of the parent silver but also boric acid and ammonia.

Further recent evidence from the USSR (paper entitled "USSR experience in decontamination and water chemistry of VVER type nuclear reactors" by V.I. Pashevich) provides confirmation of the continuing advantages of the

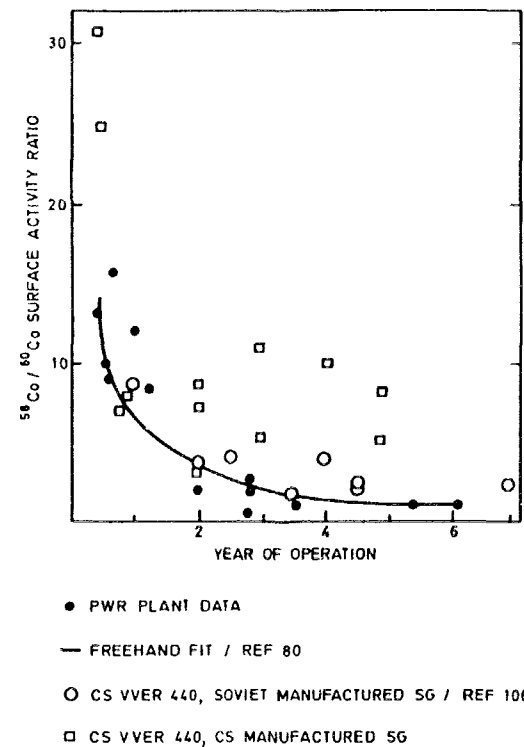


FIG. 33.  $^{58}\text{Co}$ - $^{60}\text{Co}$  surface activity ratio.

hydrazine regime. Fig. 35 shows the dose rate situation in the Kolskaya unit 3 steam generators. Dose rate measurements are shown for 4 successive years of this unit which started its commercial operation with the hydrazine regime. Maximum dose rate does not exceed  $1 \text{ r h}^{-1}$ . The relation of dose rates in this plant with those of two others is shown in Fig. 36. The Novovoronejskaya plants have never operated the hydrazine regime while the Rovenskaya plant changed to hydrazine after an initial period of ammonia operation. Dose rates from the Novovoronejskaya plants continue to increase while those from the Rovenskaya plant dropped dramatically after hydrazine introduction showing not only a reduction in activity generation but a positive decontamination of long lived nuclides from out of core surfaces. Fig. 37 shows the distribution of dose rate in the Revenskaya steam generator clearly showing the reduction of activity over much of the steam generator collector chamber. In general, the ammonia regime has given rise to dose rates in the collectors of  $4\text{--}8 \text{ r h}^{-1}$  for VVER 440 reactors and  $3\text{--}10 \text{ r h}^{-1}$  for the VVER 1000 type. The hydrazine regime results in a range from  $0.2\text{--}1.25 \text{ rh}^{-1}$ .

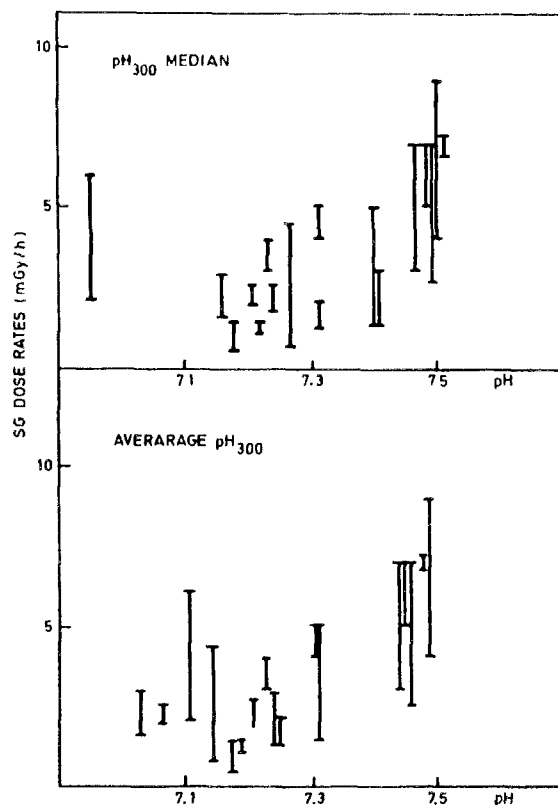


FIG. 34. Influence of pH (300°C) during last three months of a fuel cycle (cycles 1-5) on SG dose rates for VVER 440 plants (6 units) with steam generators manufactured in Czechoslovakia (redrawn from Ref. [106]).

The explanation offered in the paper entitled "USSR experience in decontamination and water chemistry of VVER type nuclear reactors" by V.I. Pashevich is as follows:

The principal oxide on alloy surfaces is  $\text{Fe}_2\text{O}_3$ , nickel exists mainly in the metallic state since the redox potential of  $\text{Ni}/\text{Ni}^{2+}$  is low enough in 'standard' chemistry. Under these conditions nickel ions are not produced in quantity and play little part in corrosion product transport or activation. When redox potential is lowered further by addition of hydrazine, cobalt is also predominantly in metallic form and virtually immobilised. Transport to core regions is much reduced and subsequent activation much lower.

This simple explanation may not be sufficient in itself since one of the observations on addition of hydrazine was a decontamination of surfaces, that

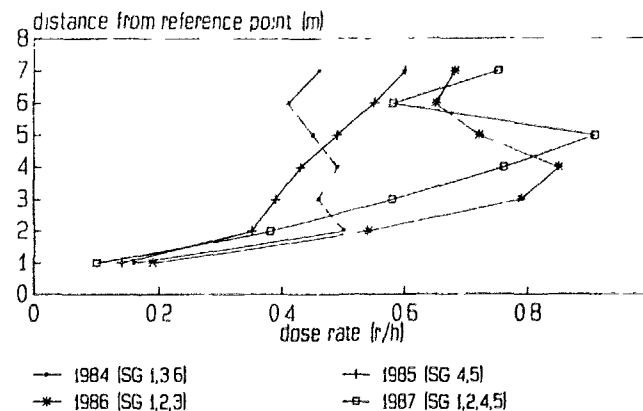


FIG. 35. Dose rates in Kolskaya unit 3 steam generator, 1984-1987 (source: V.I. Pashevich, "USSR experience in decontamination and water chemistry of VVER type nuclear reactors" (these proceedings)).

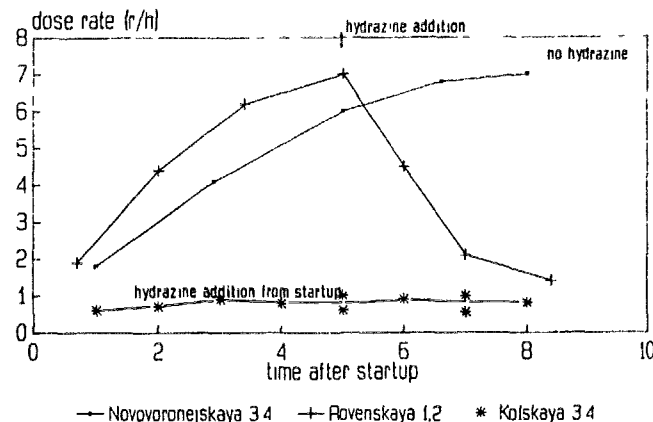


FIG. 36. Effect of hydrazine on dose rates in the steam generators of VVER type reactors (source: V.I. Pashevich, "USSR experience in decontamination and water chemistry of VVER type nuclear reactors" (these proceedings)).

is, a mobilisation of cobalt ions which are subsequently removed in the cleanup circuit. Furthermore, nickel is still mobile, presumably as ion, since  $^{58}\text{Co}$  is still produced in large quantities in 'standard' chemistry. Nevertheless, while the detailed chemistry is not yet clear, the results are very encouraging and extension to other types of PWR could be profitably investigated.

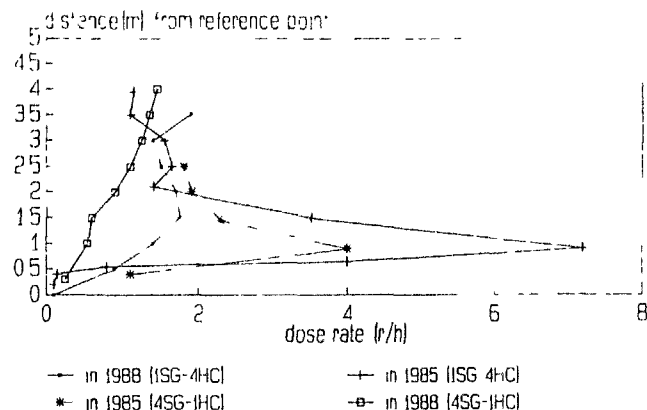


FIG 37. Dose rates as a function of time in the Rovenskaya nuclear power station (source V I Pashevich, "USSR experience in decontamination and water chemistry of VVER type nuclear reactors" (these proceedings))

Some preliminary work on hydrazine chemistry was commenced outside the USSR in Germany [104] at the Rheinsberg VVER. An initial trial over a period one month before shutdown established the feasibility of hydrazine dosing. As subsequent trial over a complete cycle showed the following: (Table 13)

1. Circulating activity was reduced in the hydrazine regime.
2. dose rates were marginally reduced.
3. loose contamination was reduced
4. corrosion and corrosion release had reduced.

While the experiments are incomplete due to the closure of the Rheinsberg reactor the observations in the USSR are qualitatively supported.

The deposition of activity and the corrosion of metals in the primary circuit of some Soviet VVERs are claimed to have been substantially reduced by the continuous dosing of hydrazine instead of ammonia into the circuit [39][95]. A permanent reduction in dose rates and in the quantity of activity produced in normal transients has resulted.

### 3.3.6.5. Experience with CANDU reactors

Although different in many respects from conventional PWRs, some observations from operating CANDU plant are relevant to the present discussion. Radiation fields around CANDUs are, in general, low and strongly dominated by  $^{60}\text{Co}$  (with little contribution from  $^{58}\text{Co}$ ) [96]. Although direct comparison with conventional PWRs is difficult because of the different plant configurations,

TABLE 12 LITHIUM LEVELS REQUIRED TO ACHIEVE CERTAIN pH VALUES FOR DIFFERENT BORIC ACID CONCENTRATIONS

pH	Lithium Concentration (ppm) for a Boron Concentration (ppm) of	
	1200	1800
6.9	2.0	3.2
7.0	2.5	4.0
7.4	6.0	10

TABLE 13. CHANGE IN CORROSION PRODUCT BEHAVIOUR AFTER THE APPLICATION OF HYDRAZINE FOR ONE CYCLE IN THE RHEINSBERG VVER [104]

	Standard ammonia chemistry	Hydrazine chemistry
Circulating $^{58}\text{Co}$ , $^{60}\text{Co}$ , $^{54}\text{Mn}$ , $^{59}\text{Fe}$	1	0.75-0.9
Corrosion release	1	0.9
Total surface oxide	1	0.9
Corrosion rate	1	0.9
$^{60}\text{Co}/\text{Fe}$	1	0.6-0.8
Optical impression	dull black	bright black
Loose contamination	high	low

CANDUs do not use boric acid dosing of the coolant, thus simplifying chemistry control. With modest dosing levels of lithium (up to 2 ppm), pH 300°C is maintained in the range 7.4-7.8.

The deposition of crud on CANDU fuel is extremely low [97], reflecting the high pH (positive temperature coefficient of solubility) coolant regime; this is probably a major factor contributing to the low radiation fields experienced around CANDU plant.

### 3.3.7. Possible approaches to elevated pH operation

The solubility data on nickel ferrite, loop studies and the worldwide operating experience reviewed in the previous sections indicate that operation at a coolant pH (300°C) of 7.4 is desirable. As more plants move towards higher lithium operation, it may be anticipated that the benefits on out-of-core radiation fields will become clearly established.

To achieve a high pH at the beginning of a cycle requires a lithium level well in excess of the current maximum allowed by most fuel vendors. The problem would become more severe for an extended fuel cycle if the approach to reactivity control were to increase start of cycle boron level to 1800 ppm. The lithium levels required to achieve a given pH (300°C) for different boron levels are summarised in Table 12.

The major concern over high lithium levels is that Zircaloy corrosion may be enhanced to an unacceptable degree. This problem has been considered in 2.3.2., where it was noted that French data indicated particular problems when high lithium conditions and significant voidage in the coolant occurred simultaneously.

The lithium levels required for high pH operation are a direct consequence of the high boric acid levels which need to be used for core reactivity control. Reactivity control exploits the  $^{10}\text{B}(n, \alpha)$  reaction. Since  $^{10}\text{B}$  is only about 20% abundant in natural boron, the use of boron enriched in  $^{10}\text{B}$  is an approach to reducing the required boric acid concentration in the primary coolant. In principle, a factor of 5 reduction is possible: this would eliminate the need for lithium levels above about 3 ppm, even for extended cycle operation. Purely from the point of view of corrosion product activity transport control, this is a highly desirable approach. However, there is obviously a significant cost penalty (efficient boron recovery would be essential) and logistical problems - to eliminate any possibility of using boric acid of the wrong isotopic composition it is likely that all systems on the plant containing boric acid would need to use enriched material. An initial appraisal of the use of  $^{10}\text{B}$  has been reported by Roesmer [98].

A second approach to reducing the boric acid required in the coolant would be to use burnable poisons either in the fuel itself or in separate inserts (as in the first cycle). It is recognised that this involves issues of reactivity control, particularly in terms of hot to cold reactivity changes, but again this approach is worth evaluating.

A third approach to achieving high coolant pH is to use KOH as the pH raising agent. Potassium is known to be less aggressive in enhancing the early stages of Zircaloy corrosion [59] and thus, in principle, operation at the required pH through potassium dosing should not pose too many difficulties. However, the longer term enhancement of Zircaloy corrosion by potassium hydroxide requires examination. Solomon (1984) has suggested that under these circumstances the lithium generated through the  $^{10}\text{B}(n, \alpha)$  reaction would need to be continuously removed in order to insure against lithium induced enhanced corrosion. It is not clear whether this is true: there has been no work on Zircaloy corrosion enhancement in mixed alkalis. Solomon [99] has also suggested that potassium would be more aggressive than lithium in inducing crevice corrosion in core structural materials. These points need

careful consideration before operation with potassium dosing to achieve high coolant pH could be recommended. In addition any radiological hazard deriving from the generation of  $^{40}\text{K}$  would need to be assessed.

### 3.3.8. Coolant chemistry and load following operation.

It is important to recognise that there are coolant chemistry control implications should it be decided that load following operation is required.

Until quite recently it has been general policy worldwide to use nuclear power plant for base load operation whenever possible, for obvious economic reasons. Experience with PWR load following operation is thus limited. However, since 1984 French PWRs have been used increasingly for load-follow operation. This experience has been reviewed by Bertron [100].

Various different requirements are covered by the general term 'load-follow', including, for example, diurnal load following (response to the daily cyclical variations in demand placed on the grid) and participation in the 'spinning reserve'. The different requirements lead to different demands on the reactor power control system (eg, depth of power modulation, rate of change of power). These demands may be met by a combination of control rod movements and variation in reactor coolant boron concentration; the details are complicated by the need to take account of the effect of xenon variation on core reactivity. EdF have modified their reactors for 'gray mode' operation using special, less absorbent (gray) control rod assemblies to expedite control.

The main issue for coolant chemistry control relates to the variations in boric acid concentration which may be required. It should be pointed out that the absence of a Boron Thermal Regeneration System makes the problem of boron variation more difficult and generally reduces the operational flexibility of the plant. Variation in the RCS boric acid concentration is effected using the Boron Control System. The RCS boron concentration is changed by modulating relevant valves in the BRS-CVCS to inject either boric acid solution (7000 ppm B) or water (B <10 ppm) depending on whether a boration or dilution effect is required. In the absence of an accompanying injection of lithium hydroxide, both these operations will inevitably lead to a decrease in reactor coolant pH which is undesirable from the activity transport point of view.

The extent of such negative pH deviations will be determined by the extent of boration or dilution required. This change implies a need for regular (at least daily) corrections to be made to the RCS lithium concentration. Ideally the boration and dilution operations would be performed with solutions containing the appropriate level of lithium hydroxide; this approach has been adopted on some French reactors (Menet et al,) [85].

Control of reactivity by 'gray' control rod operation offers the advantage that boration and dilution can be avoided or minimised, and the consequent difficulty in maintaining constant pH does not arise. However, control rod movements are likely to lead to the release of particulate corrosion products to the coolant, particularly from wear of latch tips; this release is undesirable. Nevertheless, since the method involves control rod movements as

well as boron variation this penalty probably cannot be avoided, and the use of 'gray' control rods appears to be an attractive approach.

In summary, there is little evidence from operating plant on the impact load following has on the build-up of out-of-core radiation fields. World experience in this area should be carefully monitored, with particular attention being paid to French plant. In order to keep negative pH deviations to a minimum any load following operations will require a detailed lithium surveillance and correction programme.

### 3.3.9. Summary

The present philosophy of coolant chemistry control, which underlies the various coordinated chemistry regimes, is based on a model of in-core corrosion product deposition in which deposition is favoured when the solubility of iron in the boundary layer near the surface is lower than that in the bulk coolant. For the fuel pin surfaces this will be the case when the temperature coefficient of solubility is negative. The original Westinghouse coordinated chemistry regime was based on solubility data for magnetite; data for nickel-iron spinel suggest that the appropriate pH (and lithium concentration) to ensure that the temperature coefficient is not negative may be underestimated, and coordination at a higher pH would be desirable.

There are abundant reactor and experimental data which demonstrate that operation at pH values below that of the Westinghouse coordinated regime leads to increased in-core deposition and increased out-of-core radiation fields during shut-down periods. The Westinghouse coordination regime defines the minimum acceptable operational band. Experimental data and limited plant data suggest that an optimum pH would be 7.4 (MF  $K_w$ ); further plant data are accumulating and require continuous monitoring to confirm this view.

There is evidence of enhanced Zircaloy corrosion at higher lithium concentrations under nucleate boiling conditions with some degree of voidage, and there is uncertainty on the susceptibility of Inconel to stress corrosion cracking in high lithium concentrations. Reactor trials and loop experiments with increased lithium levels are in progress. These may well serve to validate an increase in the permitted lithium level; indeed Ringhals has operated with up to 3.5 ppm Li without any apparent adverse effect.

Under these circumstances the best operating regime would appear to be that which adopts the highest substantiated lithium level until the reduction in boron concentration leads to a pH of 7.4, followed by coordination at this pH. pH values below 6.9 are to be strenuously avoided. It is also desirable that fluctuations in pH should be minimised.

The limitations posed by restriction of lithium concentration could be avoided by the use of boron enriched in  $^{10}\text{B}$  or by the use of burnable poisons. One or other of these approaches would appear to be necessary if extended fuel cycle operation with more highly enriched fuel is to be undertaken. Load following requires movements of control rods or changes in boric acid concentration or both. In particular diurnal load following would involve cyclic variation of the boric acid concentration unless 'gray' control rods were to be employed. While any control rod movements can lead to the input of particulate material, cyclic variations of boric acid level impose severe

problems of lithium control, and introduction of lithium hydroxide into the make-up water and the boric acid solution would be necessary.

The other important coolant chemistry parameter which can be varied is the hydrogen concentration. The present specification is widely agreed, but in view of some concerns with regard to the effect of hydrogen on cracking of steam generator tubes, operation at the lower end of the permitted band seems advisable.

It is important that the levels of dissolved and particulate corrosion product species in the coolant should be monitored, and in particular there is a need for information on the contribution made by the CVCS and auxiliary systems.

## 4. OVERALL SUMMARY - PWR

### 4.1. Materials Choice

The order of priorities for action relating to materials choice for minimising cobalt input to the primary circuit and therefore minimisation of radiation fields are as follows:

1. Ensure absolute minimum cobalt content for all in-core materials.

Replacement of Nickel plated inconel support grids by Zircaloy would be an effective way of doing so in the case of fuel grids. In addition to the obvious benefit of reducing direct release of  $^{60}\text{Co}$ , replacing Inconel 718 grids with Zircaloy ones might reduce activation of cobalt from out-of-core sources by reducing the amount retained in in-core corrosion films. If this replacement is not possible, then all materials associated with the grids, and in particular the nickel plating and brazes should have the minimum cobalt level achievable.

2. Reduce to a minimum the use of high cobalt alloys (Stellites) in all areas of the primary circuit and the auxiliary systems.

These two measures are by far the most important materials choice options for minimising  $^{60}\text{Co}$  activity, given relatively low (<0.1%) cobalt concentrations in other primary circuit materials. However, the options indicated below may offer significant further benefit if the measures above are effectively implemented.

3. Ensure the smoothest possible surface finish for stainless steel components in the primary circuit to minimise the corrosion rates of these surfaces. This is also likely to offer further benefit in reducing out-of-core fields as a result of the reduced capacity of the corrosion film for active species.
4. Reduce the residual cobalt content of stainless steel and Inconel surfaces in the primary circuit to a minimum. A specification of <0.05% is readily achieved and <0.02% can be achieved for steam generator tubing.

5. Specify low cobalt material for the CVCS regenerative heat exchanger, and CVCS pipework and vessels handling concentrated boric acid solutions.
6. Consider the further treatment of CVCS make-up water to the primary circuit to remove influent corrosion products, particularly from the boric acid storage tank system. Simple low temperature cation exchange may be sufficient in the latter case.

Finally, it is most important that cobalt input to the primary circuit during commissioning and initial start-up is minimised, since its removal once it has entered the system is extremely difficult. All the measures indicated above could be negated if poor pre-operational practices lead to substantial input of cobalt (as little as about 20 grams in total). The clean-up of circuits and pre-operational fluids before normal operation is therefore essential.

#### 4.2. Coolant Chemistry

The philosophy of coolant chemistry control, which underlies the various coordinated chemistry regimes, is based on a model of in-core corrosion product deposition in which deposition is favoured when the solubility of iron in the boundary layer near the surface is lower than that in the bulk coolant. For fuel pin surfaces this will be the case when the temperature coefficient of solubility is negative.

1. The Westinghouse coordinated chemistry regime was based on solubility data for magnetite. Data for nickel-iron spinel suggest that the pH required to ensure that the temperature coefficient of solubility is not negative based on magnetite data may be underestimated, and coordination at a higher pH would be desirable.
2. There are abundant reactor and experimental data which demonstrate that operation at pH values below that of the Westinghouse coordinated regime leads to increased in-core deposition and increased out-of-core radiation fields during shut-down periods. The Westinghouse coordination regime defines the minimum acceptable operational band.
3. Experimental data and limited plant data suggest that an optimum pH would be 7.4 (MF  $K_w$ ); further plant data are accumulating and require continuous monitoring to confirm this view.
4. There is evidence of enhanced Zircaloy corrosion at higher lithium concentrations under nucleate boiling conditions with some degree of voidage, and there is uncertainty on the susceptibility of Inconel to stress corrosion cracking in high lithium concentrations. Reactor trials and loop experiments with increased lithium levels are in progress. These may well serve to validate an increase in the permitted lithium level; indeed Ringhals is operating with up to 3.5 ppm Li without any apparent adverse effect.

Under these circumstances the best operating regime would appear to be that which adopts the highest substantiated lithium level until the reduction in boron concentration leads to a pH of 7.4, followed by

coordination at this pH. pH values below 6.9 are to be strenuously avoided. It is also desirable that fluctuations in pH should be minimised.

5. The limitations posed by restriction of lithium concentration could be avoided by the use of boron enriched in  $^{10}\text{B}$  or by the use of burnable poisons. One or other of these approaches would appear to be necessary if extended fuel cycle operation with more highly enriched fuel is to be undertaken.
6. Load following requires movements of control rods or changes in boric acid concentration or both. In particular diurnal load following would involve cyclic variation of the boric acid concentration unless 'gray' control rods were to be employed. While any control rod movements can be lead to the input of particulate material, cyclic variations of boric acid level impose severe problems of lithium control, and introduction of lithium hydroxide into the make-up water and the boric acid solution would be necessary.
7. The only other important coolant chemistry parameter which can be varied is the hydrogen on cracking of steam generator tubes, operation at the lower end of the permitted band seems advisable.
8. It is important that the levels of dissolved and particulate corrosion product species in the coolant should be monitored, and in particular there is a need for information on the contribution made by the CVCS and auxiliary systems.

#### 5. OVERALL SUMMARY OF POSITION FOR BWRs

This section is almost entirely a summary of the information presented in the papers entitled "Corrosion products, activity transport and deposition in boiling water reactor recirculation systems" by H.P. Alder, D. Buckley, G. Grauer, K.H. Wiedemann and "Review of the state of the art", May 1990 by H.P. Alder.  $^{58}\text{Co}$  and  $^{60}\text{Co}$  constitute 80- 90% of dose rate and dose rate reduction measures will be primarily directed at these nuclides.  $^{60}\text{Co}$  is the more important.

##### 5.1. Activity build up processes

Deposition onto fuel may be via colloidal sized and crud particles. The deposition is promoted by the heat flux and by bubble evaporation. Large particles in the range of 1 to 10  $\mu\text{m}$  adhere less well. Their residence time ranges from some days to weeks. Activity transport from the fuel element to the recirculation loops is carried out by large particles or in ionic form. It is not clear which process dominates. The oxide film on austenites have a limited capacity for cobalt adsorption at some concentration and incorporation of cobalt becomes proportional to the rate of oxide growth.

Cobalt is incorporated into the oxide lattice as it is produced and subsequent ion exchange processes play only a small part in activity uptake. Since



corrosion rate is dependent upon water chemistry it follows that activity uptake can be limited by proper control of water chemistry.

While  $\alpha\text{-Fe}_2\text{O}_3$  is the major constituent of loose fuel crud, circulating particulate and loosely adherent deposited material in out-of-core regions, the cobalt content of fuel crud is significantly higher for reasons which are not understood.

### 5.2. Water chemistry

Correct control of water chemistry will limit damage to structural alloys but will also control the transport, activation and redeposition of activated corrosion products.

Considerable reductions in the amounts of corrosion products transferred to the recirculation system from the feedwater system can be achieved by addition of 20-60 ppb of oxygen to the feedwater before the condensate polishing plant. It is also essential to achieve very low conductivity in feed water. Conductivities close to that for pure water can be achieved - perhaps the most efficient method being deep bed demineralisation for good ion removal preceded by a powdered resin filter as a particulate filter. Ultimate conductivity will also depend on whether drains are pumped forward to a feedwater tank, so that more than one third of the recirculating medium is not purified by the condensate polishing system or CASCADED with full flow condensate polishing. By recycling feedwater drains, very low crud levels can be achieved (~ 1 ppb). The water quality in the recirculation system itself depends on the fraction treated in the clean-up loop. Plant designs can differ by an order of magnitude in this respect.

Experience in Japan and Sweden [110] has shown the Ni/Fe ratios in feedwater are important as well as absolute levels. Too low a ratio causes increases of activity generation, especially  $^{58}\text{Co}$ . The production of less stable oxides on fuel is proposed as a reason. While absolute quantities of iron remain low, it has been deliberately added at some plants to optimise the Ni/Fe ratio. The Ni/Fe ratio should be below 0.5, a recommended value is 0.2.

In contrast to the need to add oxygen to feedwater to suppress corrosion in the feedtrain, experience has shown that in order to stop intergranular stress corrosion cracking in sensitised, stressed recirculation piping (austenitic), radiolytic oxygen must be suppressed by additions of hydrogen (so called hydrogen water chemistry, HWC). Ideally redox potential should be below -230mV(SHE), corresponding to 2 ppb residual oxygen. In practice, reduction of oxygen to 20 ppb achieves significant improvement. Conductivity should be <0.2 $\mu\text{S}/\text{cm}$ . Crack growth is observed to cease on commencement of HWC. The wide variations in the amount of hydrogen to suppress oxygen in different plants is not understood. An adverse observation associated with HWC is an increase in N-16 volatility by conversion of dissolved nitrate to gaseous Ammonia and an increase in the turbine radiation field.

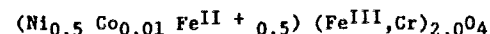
Besides the transition metals there are other impurities in water whose role in activity production is not understood. Two examples are silicate and organic carbon and these may be involved in complex formation. Older data from US reactors indicate 700 to 900 ppb dissolved organic carbon (DOC).

Recent measurements in Swedish and Swiss reactors showed only a few ppb during steady state operation.\*

### 5.3. Crud characteristics

Both particulate and soluble concentrations increase considerably in transients, especially in cold shutdown. The proportions of corrosion products either in steady operation or in transients, that exist between particles, colloids and ions is unknown. It is common practice to simply refer to everything passing a 0.45  $\mu\text{m}$  filter as 'soluble' but this is an arbitrary definition.

Out-of-core oxides exist in two layers, one adherent to base metal and a loose overlay of particles. The latter is predominantly  $\alpha\text{-Fe}_2\text{O}_3$  while the former is a mixed spinel whose limiting formula may be



If the final spinel saturates with cobalt to the level shown then activity uptake will only increase on a surface if total oxide increases.

Circulating crud is predominantly  $\alpha\text{-Fe}_2\text{O}_3$  although it is noted that, in Swedish reactors, iron is only a relatively small fraction (~20%) of total circulating transition metals. In feedwater in contrast, iron is predominant (50%) and  $\alpha\text{-Fe}_2\text{O}_3$  generated here may persist in the recirculation system. Some 10 kg per year may be transferred to the recirculation system.

Fuel crud may also be described in terms of loose and adherent. The mass and composition varies considerably from plant to plant. The thickest oxides occur where there is nucleate boiling.

Fuel crud residence times vary from relatively short periods to several hundred days. The reasons are not well understood. In general one may expect the release rates of active atoms to be relatively insensitive to residence time since low residence times infer high release rates of low specific activity material while long residence times conversely imply low release rates of high specific activity material. Since fuel is withdrawn after some 3 years very long residence times could be advantageous.

Fuel crud is predominantly  $\alpha\text{-Fe}_2\text{O}_3$  although it is important to note that in reality fuel crud is very inhomogeneous. The  $^{60}\text{Co}$  activity is almost entirely associated with a very small number of particles rich in transition metals other than iron, possibly the particles tending to the spinel form. [110].

### 5.4. Cobalt sources

Cobalt levels in adherent oxides on out-of-core piping are higher than base metal and suggest an external source of cobalt. Stellite hard facing erosion

\* H. Loner, H.P. Alder, E. Schenker, B. Covelli "The Behaviour of Dissolved Organic Carbon in BWR's 59", JAIF International Conference on Water Chemistry in Nuclear Power Plants, Fukui City, Japan, April 22 - 25, 1991

or corrosion is an obvious candidate. The effect of water chemistry on Stellite losses is not clear. Feedwater appears to be a minor contribution of cobalt most originally within the recirculation system.

#### 5.5. Modelling of transport processes

Many attempts have been made to construct models with a predictive ability. They all remain semi-empirical due to a lack of fundamental understanding of the processes involved. It follows from this that their predictive abilities are at present questionable. Fundamental understanding is missing in the following areas:

1. deposition mechanisms on fuel
2. characteristics of ions, colloids and particles under operating conditions
3. amounts and form of cobalt releases from cobalt alloys and other surfaces
4. effect of radiation
5. influence of coolant chemistry including the influence of impurities.

#### 5.6. Scope for control

Accumulation of data by EPRI from many different plants led to little increase in understanding of the underlying mechanisms of activity production and deposition but there is nevertheless much that can be done to reduce activity by exploitation of semi-empirical observations. No single method of dose rate reduction has proved to be sufficient on its own and several approaches are best tried simultaneously. However, areas for consideration can perhaps be divided for convenience into two:

- a) reduction of circulating activity
- b) control of deposition.

Reduction measures applied in practice, not necessarily all on the same plant, are as follows:

1. reduction of circulating activity
  - a) O<sub>2</sub> injection into feedwater before condensate polishing plant
  - b) Use of optimum layup procedures and chemistries in plant commissioning and in cold shutdowns.
  - c) Select cobalt free hard facings, eg 440C wrought steel for flow control valves. Many other alternatives to Stellite are being proposed.

- d) Increase crud removal efficiency in recirculation system clean-up. High temperature filters are proposed to reduce power losses.
- e) Reduce impurity levels in feedwater by a powdered resin filter and a deep bed demineralizer with full flow condensate polishing.
- f) Select low corrosion materials in feedwater system; low cobalt austenites and in-core materials.
- g) Control Ni/Fe ratio such that spinel formation is encouraged rather than oxides of cobalt or nickel. The former are much less mobile than the latter.

#### 2. Control of deposition

Activity deposition has been controlled by:

- a) Electropolishing and Prefilming (by steam/air, oxygen saturated water or alkaline treatment, incorporation of Al<sup>3+</sup> ions), reduces the cobalt deposition. This technique has been widely applied to replacement recirculation system piping.
- b) Inhibition of deposition by Zn<sup>2+</sup> addition to recirculation system water.

#### 6. CONCLUSIONS

1. The interactions between coolant circuit materials and coolant chemistry which govern the production and movement of radioactivity are very complex and are not well understood. There is, however, a large body of experimental and theoretical work which suggests the ways in which activity production and deposition can be minimised.
2. Co<sup>60</sup> is identified as the principal contributor to high dose rates in PWR and BWR and its reduction depends on selecting materials of low cobalt impurity and avoiding cobalt hard facings. Experience suggests an order of priority for selection of materials of low cobalt content.
3. In PWR, chemistry control is aimed at establishing the pH at which the temperature coefficient of solubility of the iron spinel crud is a minimum at core inlet temperature and positive across the core so as to promote conditions for crud to dissolve in the core region. For most of the fuel cycle this pH is above the realisable with the maximum permitted concentration of alkali presently allowed by fuel vendors and results in various compromise pH regimes being employed by different Utilities. There is as yet no clear relationship between coolant chemistry and the resulting radiation dose rates but it is apparent that low pH operation should be avoided.

In BWR, chemistry control for restriction of radiation dose rates is aimed largely at reduction of oxygen in feed water to reduce corrosion and crud transport in the feed train and at establishing an optimum ratio of iron to nickel injected into the core region to minimise production of Co<sup>60</sup>.

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## NATIONAL CONTRIBUTIONS

## COMPARISON OF STANDARD AND HYDRAZINE WATER CHEMISTRY OF VVER 440 UNITS

J. BURCLOVA

Nuclear Power Plants Research Institute,  
Trnava, Czechoslovakia

### Abstract

The comparison of primary coolant circuit surface activities, dose rates and occupational radiation exposures is done for PWR and VVER 440 units. The detailed description of VVER 440 units using standard and hydrazine water chemistry including corrosion products coolant activities and occupational radiation exposures for works at various parts of primary circuit is presented.

### Introduction

The radiation field in the primary system of VVERs during shut-down periods is essentially generated by activated corrosion products. The origin of radiation fields is linked firmly to the chemical composition of water circuit construction materials and to the control of primary circuit water chemistry. For a given reactor design, only the water chemistry may be changed to influence the level of dose rate build-up. Although the design of all VVER-440 units is principally the same, the dose rate build-up and occupational radiation exposure (ORE) vary considerably from plant to plant. The different levels of:

- robotics
  - job management
  - cobalt impurities in in-core and out-of-core materials
  - chemistry control
- may explain these facts.

The first two items influence the ORE itself, but have no effect on dose rate build-up, whereas optimization of primary coolant chemistry and decreasing of cobalt impurities affect directly the out-of-core surface activities.

### Standard and hydrazine water chemistry of VVER 440

32 units of VVER 440 were in operation, now Armenia and Greifswald units are out of operation. At most of them, standard primary circuit water chemistry is used, whereas Kola 3,4 and Rovno 1,2 (1-4) are operated in hydrazine water chemistry (Tab.1).

Tab.1 VVER 440 Units Data

Country	Unit	Start	SG Material Origin	Water Chemistry
			Country/ Co Content	%
BG	Kozloduy 1,2	74/75	USSR	standard
	Kozloduy 3,4	80/82	USSR	standard
CZ	Bohunice 1,2	78/80	USSR/0.03-0.04	standard
	Bohunice 3,4	84/85	CZ/0.015-0.02	standard
	Dukovany 1,2	85/86	CZ/0.015-0.02	standard
	Dukovany 3,4	86/87	CZ/0.015-0.02	standard
			USSR (3 SGs)	
GDR	Greifswald 1,2	73/74	USSR	standard
	Greifswald 3,4	77/79	USSR	standard
HU	Paks 1,2	82/84	USSR/0.04-0.06(11)	standard
	Paks 3,4	86/87	USSR/0.04-0.06(11)	standard
SF	Loviisa 1,2	77/80	USSR	standard
USSR	Novovoronezh 3,4	71/72	USSR	standard
	Kola 1,2	73/74	USSR	partially hydrazine
	Armenia 1,2	76/80	USSR	partially hydrazine
	Rovno 1,2	80/81	USSR	hydrazine from 1985
	Kola 3,4	81/84	USSR	hydrazine

Co content in Soviet stainless steel OCH18N10T (18%Cr, 10%Ni) is given by Ampelgova (5) as 0.02-0.35% with the average value of 0.075%. The standard water chemistry is similar to the water chemistry used for western PWRs (Tab.2), potassium-boron mode is the same for all VVER 440 units (Fig.1).

Tab.2 Primary Coolant Chemistry Guidelines

		EPRI(6)	VVER440(6) Standard	VVER440(1) Hydrazine
Hydrogen	cc(STP)/kg	25-50	30-60	73*
Chlorides	mg/kg	<0.15	<0.1	<0.1
Fluorides	mg/kg	<0.15	<0.1	<0.1
Oxygen	mg/kg	<0.01	<0.005	<0.005
Ammonia	mg/kg	-	>5	64*
Hydrazine	mg/kg	-	-	0.089*

\* data from Armenia plant experiment (1)

### Data Basis for VVER 440 Units

The data for water chemistry, surface activities, coolant activities, dose rates and occupational radiation exposures were collected and evaluated under an agreement among Czechoslovakia (8), GDR (9), USSR (10) and Hungary (11).



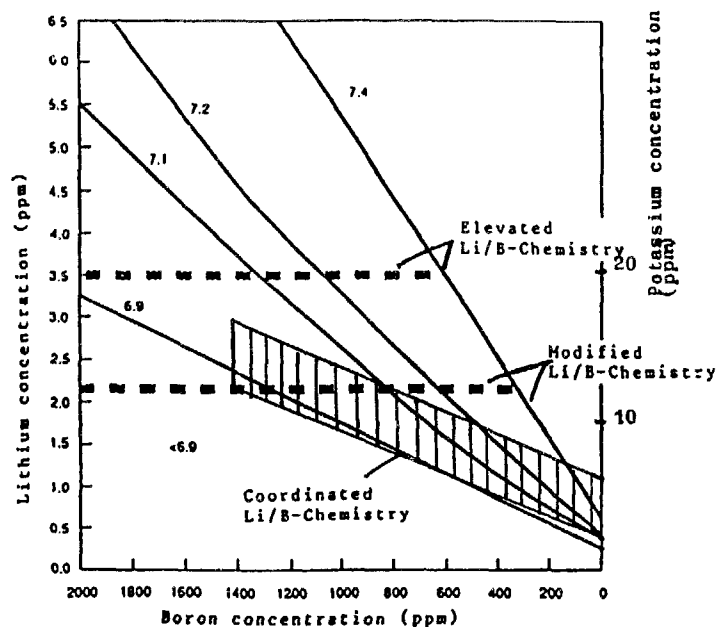


Fig.1 Various Lithium-Boron Modes for done  
pH /300°C/ /6/

Potassium-Boron Mode of Operation for  
VVER 440

#### Surface Activity Build-up

The main radioactive corrosion products (the source of dose rates) are cobalt isotopes created by the reaction (7)

$^{58}\text{Ni} (n,p) ^{58}\text{Co}$   $\sigma = 0.1$  barn

$^{59}\text{Co} (n,\gamma) ^{60}\text{Co}$   $\sigma = 18$  barn

$^{60}\text{Ni} (n,p) ^{60}\text{Co}$   $\sigma = 0.005$  barn

The theoretical ratios of surface activities (SA) for Inconel 600 (nickel content 75%) and stainless steel (nickel content 10%) used for steam generator (SG) tubes are:

for  $^{58}\text{Co}$  SA (PWR)/ SA (VVER) = 7.5

for  $^{60}\text{Co}$ , cobalt content 0.05%

SA (PWR)/ SA (VVER) = 1.4

cobalt content 0.02%

SA (PWR)/ SA (VVER) = 1.9

These values were obtained by calculations under the conditions of equal transport of cobalt and nickel in primary circuits, of the average ratios of epithermal and

thermal neutrons of 7 for VVER 440 and 5 for PWR, and of approximately the same neutron densities, corrosion rates and total areas of SGs tubes. The measured values of surface activities are given in Tab.3.

Tab.3 SG and MCP Surface Activities (kBq/cm<sup>2</sup>)

H-Hot Surface		C-Cold Surface		MCP-Main Circ.Pump	
Unit	Cycle	<sup>60</sup> Co	<sup>58</sup> Co	<sup>54</sup> Mn Place	Ref.
EdF	3	370	700	60 SGH	12
	3	630	1200	52 SGC	12
Fessenheim 1	4	550	890	75 SGH	12
	4	700	1260	100 SGC	12
Ringshals 2		152	68	7 SG	5
		74-145		4-11 SG	5
Novovoronezh	4	10-100		SG	13
	6	80		SG	13
Kola 1,2	5	13	42	35 SGH	5
	5	7	11	15 SGC	5
	6	11	34	10 SGH	5
	6	5	10	10 SGC	5
Bohunice 1	8	50	60	12 SGH	
	8	18	26	11 SGC	
Bohunice 3	5	5	20	17 SGH	
	5	5	15	7 SGC	
Dukovany 1	5	2	16	2 SGH	
	5	3	15	5 SGC	
Kola 3	5	12	6	7 SGH	10
	5	9	7	5 SGC	10
Kola 1,2	5	23	70	47 MCP	5
Bohunice 1	5	26	52	28 MCP	
Paks 2	2	15	55	10 MCP	11
Bohunice 3	5	9	48	32 MCP	
Bohunice 4	4	4	30-70	2-10 MCP	
Kola 3	6	20-60	20-80	30 MCP	10
	7	10-70	20-100	8-60 MCP	10

From the point of view of both cobalt isotopes, surface activity values at VVER 440 units are considerably lower than at western PWRs using stellite and high nickel content alloys. The difference among various VVER 440 units is only in  $^{60}\text{Co}$  activity (higher level for older units with higher content of cobalt impurities). The units using hydrazine water chemistry reach lower level of  $^{58}\text{Co}$  on SG surfaces, the other values are comparable for both types of

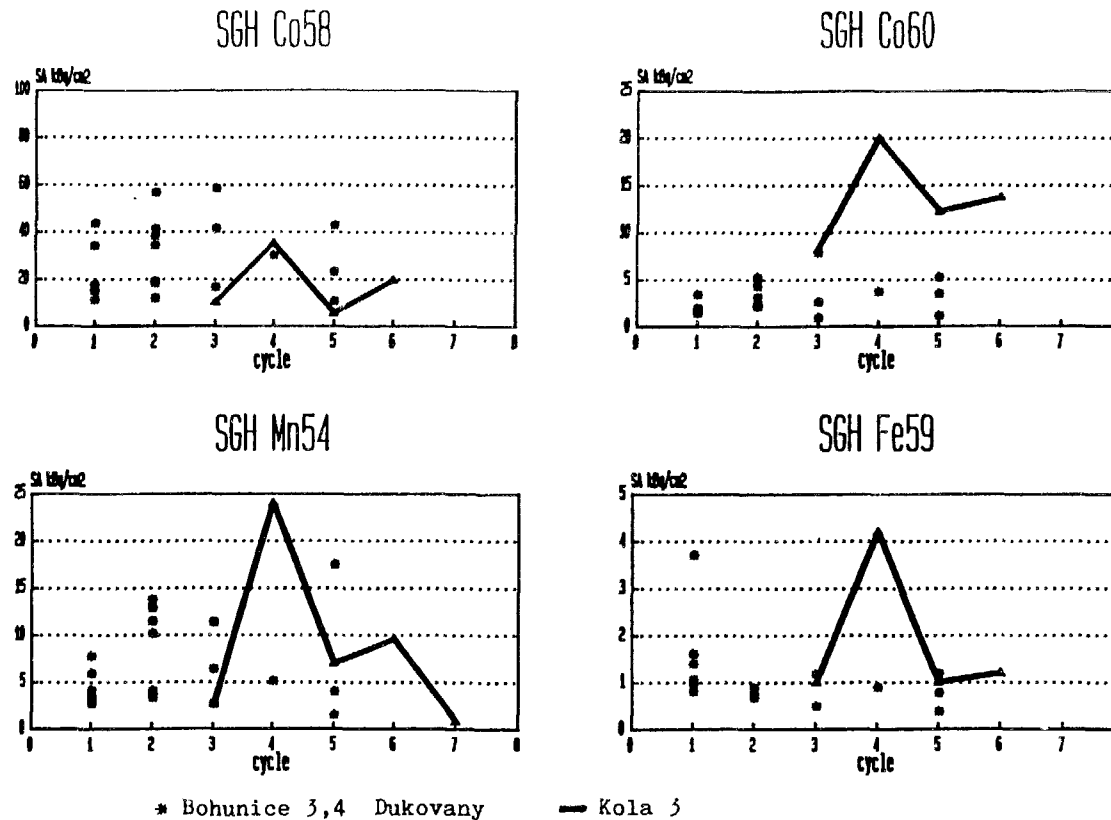


Fig.2 Steam Generator Hot Surface Activities for the newest VVER 440 with Standard and Hydrazine Water Chemistry

units with standard and hydrazine water chemistry (see Tab.3, Fig.2-3).

#### Corrosion Products (CP) Coolant Activity

The solubility of corrosion products in the coolant and the amount of insoluble corrosion products released from the outer layer determine the level of CP activity in the coolant. Pashevitch (3) describes a considerable decrease of CP deposition constant for units using hydrazine water chemistry. The deposition constant for USSR units under standard water chemistry is  $(1-5) \cdot 10^{-4} \text{ sec}^{-1}$  (3), for Czechoslovak units were measured the values  $(1-10) \cdot 10^{-4} \text{ sec}^{-1}$  (14).

Using hydrazine, the deposition constant decreases to  $(1-5) \cdot 10^{-5} \text{ sec}^{-1}$  (3). The consequences of this fact are higher activity of CP in coolant and higher removal of CP from coolant by CVCS. The changes of coolant activity of Kola 3 and Bohunice 3 (during standard water chemistry and during a short hydrazine experiment 4 months in the middle of a fuel cycle 2) are given in Fig.4. Under standard water chemistry, CP coolant steady-state activity is lower than under hydrazine water chemistry with the exception of 54Mn. Other CP coolant activity of the units using hydrazine water chemistry rises immediately after start-up for several weeks and then decreases to the level of the units using standard water chemistry.

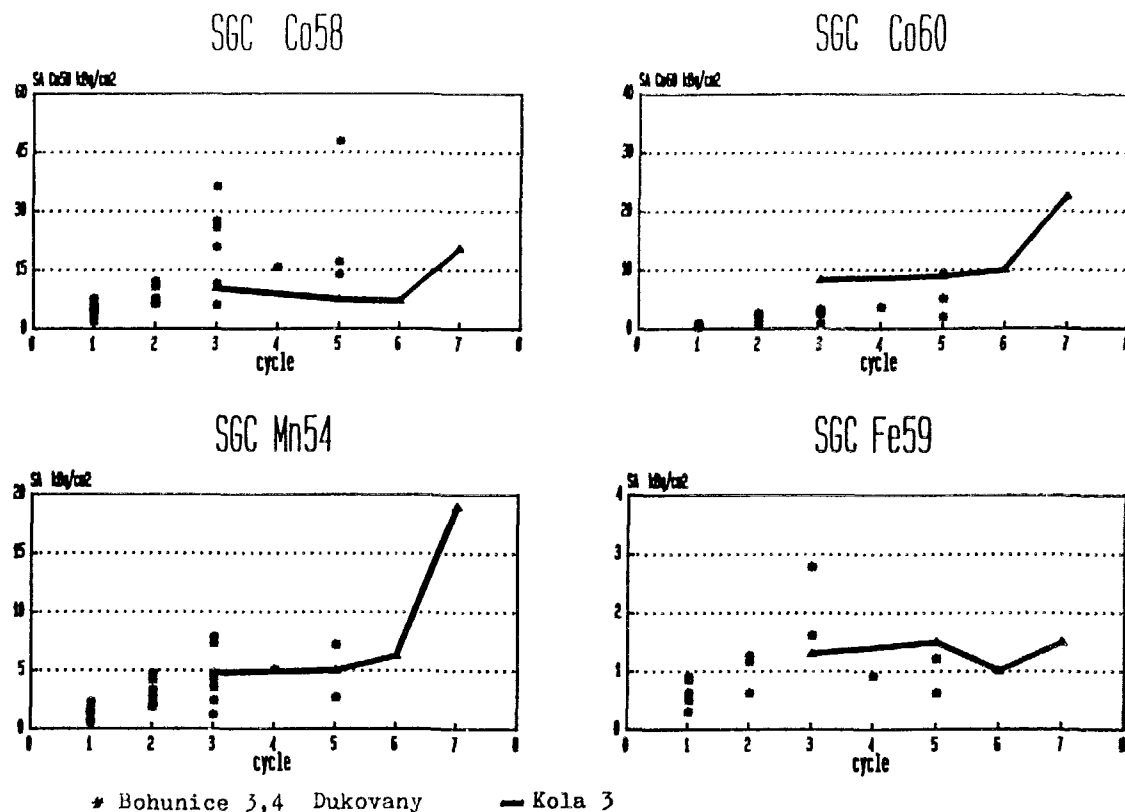


Fig.5 Steam Generator Cold Surface Activities for the newest VVER 440 with Standard and Hydrazine Water Chemistry

#### Dose Rates Build-up

SG channel head dose rates (for PWRs with vertical SG) and dose rates in the primary tubesheet manifold of horizontal SGs (VVER) in the depth of 2-2.5 m (the place of maximum dose rate value for central point of tube bundle) are compared in Fig.5, as well as the values for older and newer VVER 440 units ( Fig.6 ) with standard and hydrazine water chemistry (Fig.7). The SG dose rates for VVER 440 are in general lower than or comparable with the dose rates for western PWRs. The SG dose rates for VVER 440 vary from higher values for older units to lower values for newer ones with lower cobalt content, and for units using hydrazine

water chemistry. There is no significant difference in SG dose rates for Bohunice 3,4 , Dukovany 1-4 and Kola 3,4 (Fig.7) as well as there was no considerable change in SG dose rates after the hydrazine experiment in Bohunice 3. The explanation of the very significant change in SG dose rates for the units Rovno 1,2 (see Fig.6) as the result of the application of hydrazine water chemistry (2,3) is in contradiction to (4), where SG dose rates at central point of tube bundle for the last year before the dosing of hydrazine are much lower and there are comparable with the value at the same place after 3 years of hydrazine water chemistry. Extremely high value of SG dose rate was measured at the upper part of the tubesheet primary manifold

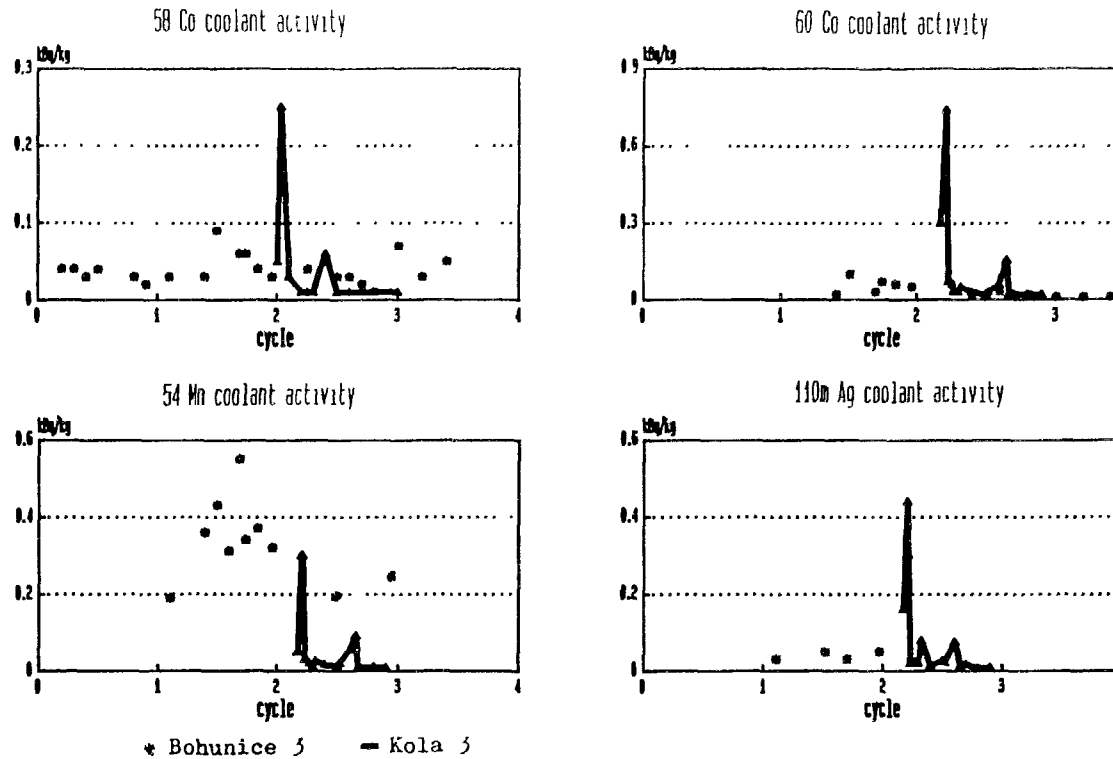


Fig.4 Corrosion Product Coolant Activities for the newest VVER 440 with Standard and Hydrazine Water Chemistry

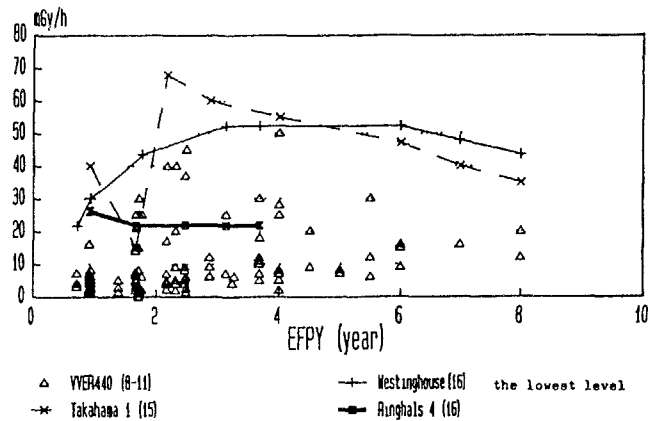


Fig.5 PWRs Steam Generator Dose Rates

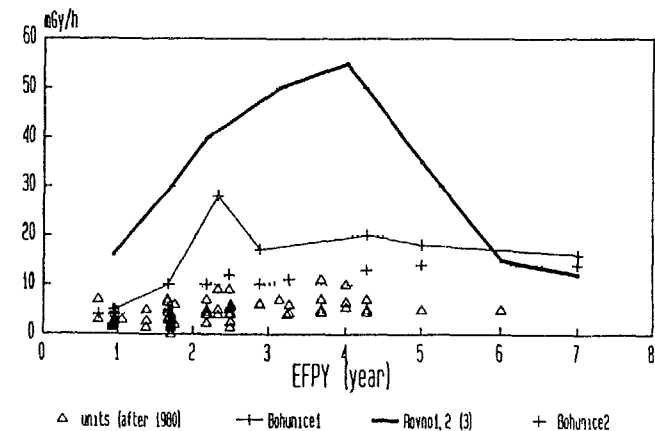


Fig.6 VVER 440 Steam Generator Dose Rates

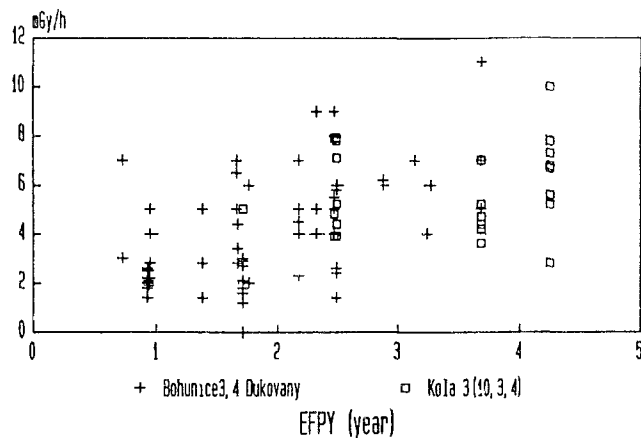


Fig.7 Steam Generator Dose Rates for the newest VVER 440 with Standard and Hydrazine Water Chemistry

The reason of such high dose rate probably was not mainly the activity of corrosion products.

#### Occupational Radiation Exposure

The ORE during shut down periods depends very considerably on the range of works done, robotics and job management, so it is very problematic to evaluate the influence of different type of water chemistry to the ORE. The ORE for the latest western PWRs is comparable with the ORE for older VVER 440 units and the latest Soviet VVER 440 units (17). The lowest levels of the ORE were reached in Bohunice 3,4, Paks 2 and Dukovany 1-4.

The total ORE and the ORE for works at steam generator, main circulation pump and CVCS are given in Fig.8 for Kola 3 (9,10), Bohunice 3,4 and Dukovany 1-4 (8). Only the values for the ORE at steam generator are comparable for both water chemistries, other OREs are considerably higher for the Kola 3 unit.

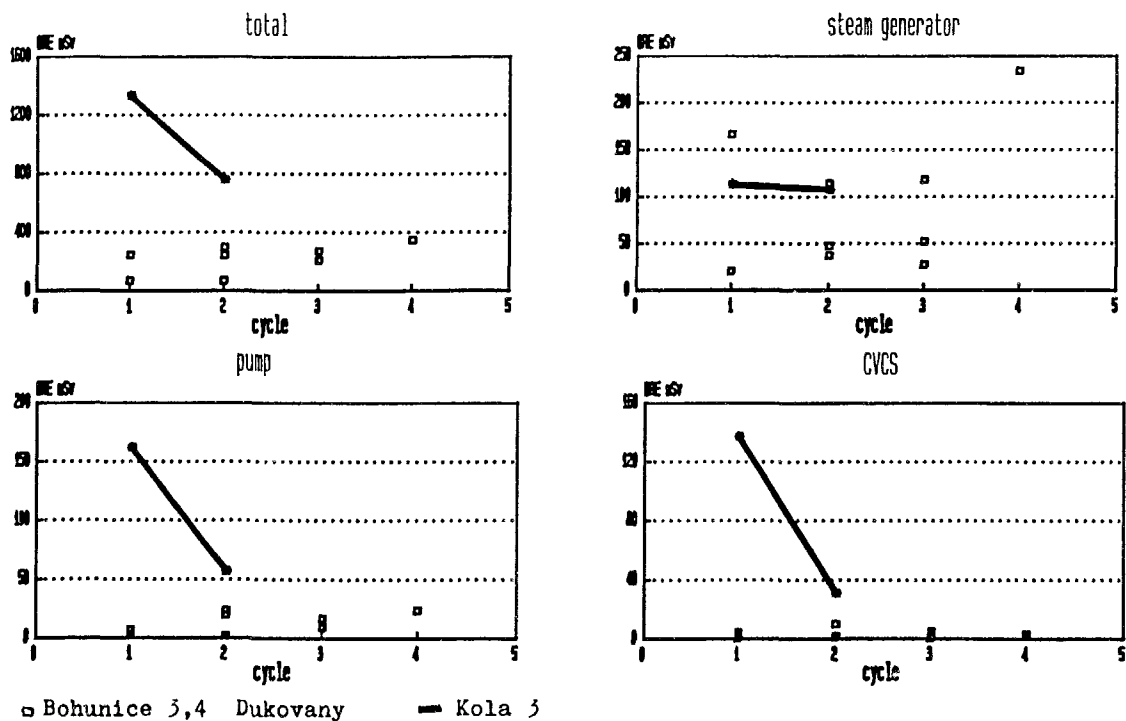


Fig.8 The ORE for the newest VVER 440 with Standard and Hydrazine Water Chemistry

## Conclusions

Hydrazine water chemistry slightly influences the level of  $^{58}\text{Co}$  activity on steam generator tube surfaces, so the short hydrazine Bohunice 3 experiment (finished in second third of the cycle 2) could not lead to successful results.

The level of  $^{60}\text{Co}$  activity depends on the level of cobalt impurities in in-core and steam generator materials.

There is no significant difference between new VVER units using hydrazine water chemistry and new VVER units working under standard water chemistry conditions.

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## OBSERVATIONS ON RECENT APPLICATION OF HIGH COOLANT pH IN FRENCH PWRs AND OPTIMIZATION OF CHEMISTRY DURING SHUTDOWN

P. BESLU

Centre d'études nucléaires de Cadarache,  
Commissariat à l'énergie atomique,  
Saint-Paul-lez-Durance, France

## Abstract

In this paper several results of PWR chemistry in French reactors are presented. It shows that excessive crud build-up in the core can usually be avoided with a well adapted, carefully operated coolant chemistry. Optimization of the lithium/pH/hydrogen treatment combines the objectives of reducing the sources of radiation fields and crud build-up. Optimization of chemistry in order to avoid excessive contamination during steady state and shutdown is described.

## Chemistry during the power operation

These requirements can be served together (since crud deposition in the core and its activation is the cause of out of core dose rate) by maintaining the pH in a desired range to maintain a positive temperature coefficient of solubility for nickel ferrite in the core and at the same time by maintaining a zeta potential which prevents attractive effects of colloid species on the cladding surface. It was demonstrated and confirmed by the observations on French reactors that a  $\text{pH}_{300}$  above 6.8 is sufficient to avoid the presence of a thick deposit in the hot part of the fuel.

A low pH in circumstances where lithium concentrations are low (below 0.2 ppm when boron is below 10 ppm) is responsible of the formation of thick in-core deposits. The same effect may be observed with hydrogen concentration below the limit required to suppress radiolysis, or more generally, with the presence of oxygen in the primary coolant. One of these conditions is sufficient to produce undesirable effects due to the presence of the heavy deposits on the fuel rods which can be summarized as follows:

- An increase in pressure drop leading to reduced flow of the primary coolant.
- A thermal barrier between the water and the cladding increasing the temperature of the cladding and subsequently the temperature of the uranium dioxide with a change of the power coefficient (Doppler effect).
- Variations of coolant local density leading to reactivity effects.

The EdF/FRA chemical specification was established on the basis of PACTOLE code calculations and has been applied to EdF/SPT units since 1981.

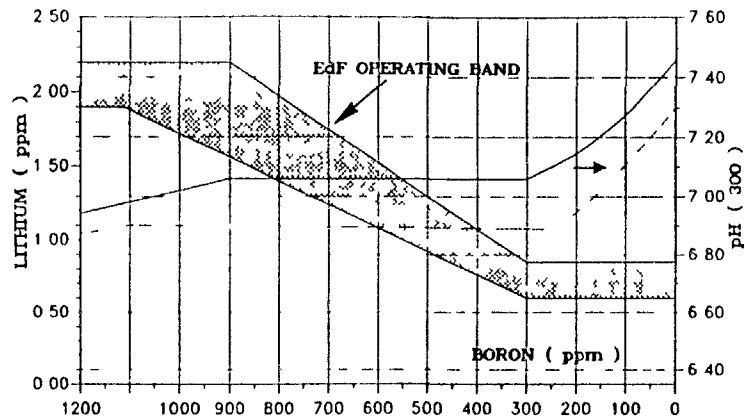


FIG 1 EDF lithium-boron co-ordinated chemistry and calculated pH (300°C)

It consists of maintaining a pH higher than 6.9 throughout the duration of a cycle (see figure 1).

Radiation fields around the circuits (table 1) and resulting collective doses are moderate where this specification is applied. The thickness of deposits observed on fuel element is generally negligible ( $< 1 \mu\text{m}$ ). This situation would indicate that our conservative approach is correct. However, minimum solubility measurements as a function of the temperature observed under normal operating conditions by Westinghouse has persuaded the international community to recommend high  $\text{pH}_T$  operation (7.4 at  $300^\circ\text{C}$ ). For its part, the CEA has carried out a critical study of all the data in this field and undertaken similar measurements to those of Westinghouse, though coming to different conclusions. Nevertheless, the synthesis carried out on laws of solubility forecasts a slight reduction in contamination by maintaining a pH of 7.2 at  $300^\circ\text{C}$  throughout the cycle and limiting the lithium content at the start of the cycle to 2.2 ppm. (All pH values quoted in the present paper are calculated using the ionisation constant of water proposed by Marshall and Franck).

In addition, several other observations indicate that  $\text{pH}_{300}$  higher than 7.2 are not necessary to reduce the activity contamination. As an example, the corrosion release measurements from the CEA CORELE loop show clearly that there is a very weak dependence of corrosion release rate or pH between 7.2 and 7.5 whatever the material. That point can be seen from figure 2 for Inconel 600 thermal treated material. The trend is similar for the mill-annealed Alloy 600 or TT Alloy 690. The presence of a minimum around 7.2 is not certain due to the range of the measurement. Nevertheless, it is interesting to note that CORELE loop is designed (once through coolant) to produce a release rate proportional to the solubility.

TABLE 1 AVERAGE DOSE RATES IN THREE GENERATIONS OF FRENCH PWRs

<b>AVERAGE DOSE RATE</b> around the primary pipes in french P.W.R ( dose rate index )		
		$\text{mSv h}^{-1}$
900 MWe reactors 3 loops	first generation in operation before 1980	<b>1</b>
	2 <sup>nd</sup> generation in operation beyond 1980	<b>0.6</b>
1300 MWe reactors 4 loops	beyond 1985	<b>0.5</b>

On these predictions, the EdF/SPT decided to apply this pH to six of its units and to compare the results obtained with other reactors and with observations made during previous cycles. One or two years later, the first results are encouraging. Stabilization in dose rate and decrease in corrosion product contamination has been observed on units in which the new conditioning was introduced during the 4th cycle is a good example: the dose rate index and the mean dose rate in the channel head both decreased by 30% between the end of the 3rd and the 4th cycle. The development of deposited activity confirms this tendency, as can be seen in Figures 3, 4 and 5.

We may conclude:

- that any  $\text{pH}_{300} > 6.9$  is sufficient for avoiding the problem of deposit on the fuel.
- from the contamination point of view, a consensus seems to exist in France and elsewhere (e.g. Ringhals, Millstone 3) concerning higher values of the (coolant) pH e.g.  $\text{pH}_{300}$ : 7.2. However, some plant operators are reluctant to proceed with high pH due to the potential effect of high lithium concentration on Zircaloy oxidation and Inconel Stress Corrosion Cracking. So the decision of the extension of this pH regime to all French plants has been postponed and the experience of the 6 units will be continued for one year more.

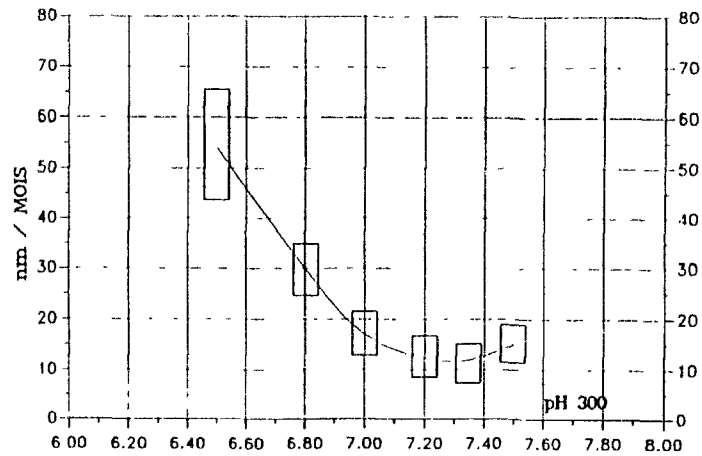


FIG. 2 Alloy 600 (thermally treated)  
cobalt release rate vs pH (300°C) from CEA CORELE loop.

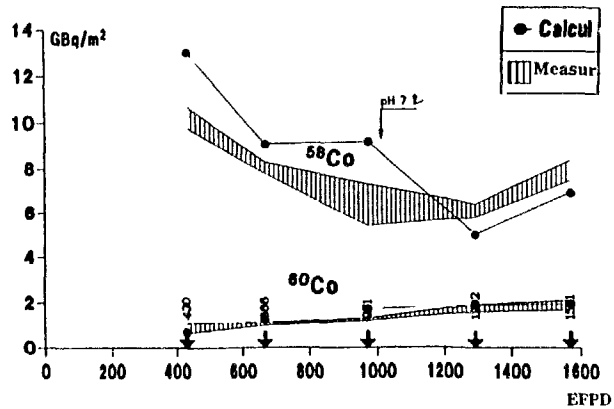


FIG. 3. CRUAS 1 — activity across the loop.

#### Behaviour of corrosion product during shutdown procedure

Changes in the physical characteristics of the primary coolant during cold shutdown for refuelling cause a considerable increase (between 2 and 3 orders of magnitude) in the water activity of corrosion products. The liberated activity reaches or even exceeds the total activity deposited on the out-of-core walls of the primary circuit. One kg (or more) of nickel are often dissolved.

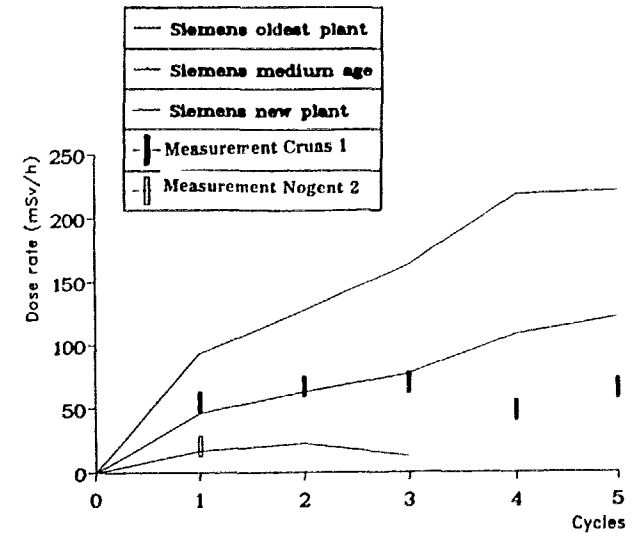
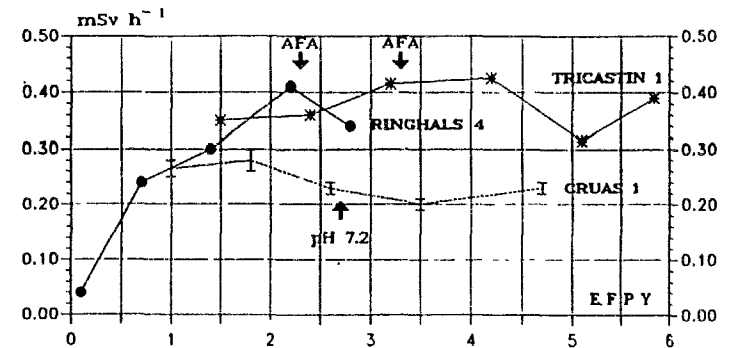


FIG. 4. Dose rate in the SG channel head centre.



RINGHALS 4 pH = 7.4  
 TRICASTIN 1 pH > 6.9  
 CRUAS 1 pH > 6.9 and 7.2 beyond the 3<sup>rd</sup> cycle

FIG. 5. Dose rate across the loop.



2 This activity is eventually trapped in the purification system, but it may also be deposited inside the circuits. The shutdown procedure must meet the following objectives:

- Facilitate fuel handling operations while maintaining water transparency and reducing the surface dose rate of the refuelling pool;
- Reduce primary water activity as quickly as possible ( $^{58}\text{Co} < 2 \text{ GBq/t}$ ) and generally facilitate operations designed to reduce the time between reactor shutdown and opening of the vessel head;
- Minimise release or dissolution of corrosion products when they do not constitute a real or efficient reduction of out-of-vessel contamination;
- Dissolve the (nickel) deposits on the cladding which may increase the temperature of the fuel;
- Avoid the contamination of the primary circuit surfaces.

Measurement carried out by CEA on the EdF reactors allowed us to understand the behaviour of the corrosion product during the shutdown and to propose a procedure able to fulfill the previous goals.

This important phases can be distinguished:

- A cooling phase including boration of the primary water when the temperature is below  $150^{\circ}\text{C}$  and in reducing conditions;
- The oxygenation phase which occurs either after the deliberate injection of hydrogen peroxide or after part of the circuit has been opened to the air.

For the first phase ( $T < 150^{\circ}\text{C}$  and reducing condition) the activity and element released come from the corrosion release of the structural (austenitic) material (grids, baffle, etc.) under neutron flux. The elements are soluble. That means that the large activity trapped on the mixed-bed resins during this phase does not correspond to a dissolution of oxides and is undesirable.

The procedure should aim to reduce the duration of this period and avoid any precipitation which could lead to a contamination of the circuit. Therefore we must avoid circumstances leading to increases in temperature, in hydrogen content, or in lithium content.

For the second phase, aeration or oxygenation, there is a sudden increase of stable cobalt activity and Ni content in the water. It corresponds to a dissolution of a pure nickel deposit on the fuel cladding.

Elimination of this nickel has no effect on the contamination of the out-of-vessel circuit but nevertheless reduces the activity for the subsequent period or fuel cycle.

To avoid any contamination of the circuit during this phase, it is absolutely vital to oxygenate at a temperature below  $100^{\circ}\text{C}$ , whatever the mode of oxygenation ( $\text{H}_2\text{O}_2$  or air).

As for the previous phase, changes in temperature, redox potential or pH are also undesirable.

We may note that the presence of oxygen in the primary circuit:

- Dissolves only a limited amount of nickel deposited on the fuel cladding (1 kg)
- Suppresses the release rate of the base metal which existed in the initial reducing and low pH and temperature conditions. It is therefore possible to reduce the activity of the water by ion exchange and filtration.

To sum up, the best procedure for the shutdown seems to be

- cool down the circuit quickly when the temperature is below  $150^{\circ}\text{C}$  and;
- introduce oxygen in the primary coolant when the temperature is below ( $\sim 100^{\circ}\text{C}$ ).

### Conclusion

The efforts made in France during the 70's in the field of circuit contamination have now borne fruit. Radiation fields around EdF PWR primary circuits are always moderate and often compare favourably with the best non-French results, as Figures 4 and 5 show.

This is the case even though the planned improvements have not yet all been introduced throughout France. It is hoped that improvements resulting in a few tens of percent reduction in the radiation field can still be achieved by:

- Gradually replacing all standard fuel grids with Zircaloy grids like Fragma AFA fuel
- Replacing alloy 600 with alloy 690 in new steam generators and reducing their cobalt content
- Polishing channel head surfaces
- Introducing chemical control at pH 7.2 in all reactors
- Refining cold shutdown procedures

As well as the foregoing, particular attention will also be paid to factors likely to mar these expected improvements, both as concerns

contamination (ageing of equipment etc.) and exposure of personnel during regular or exceptional maintenance operations such as steam generator replacement like at Dampierre in 1990<sup>(1)</sup>. The know-how and computer tools developed when the EdF PWRs were first put into service are proving extremely valuable in good maintenance management for the future. Computer tools like PACTOLE and PROFIP for forecasting, EMECC for measuring and the TIGRE data base can be used to predict radiation fields in various situations encountered during maintenance operations.

The considerable effort expended by EdF and CEA in utilizing Research and Development to produce prediction computer tools is a mark of the importance attached in France to Radiation Protection.

## LOWERING THE CORROSION RATE TO LIMIT RADIOACTIVE DEPOSITS

R. WINKLER

Institut für Energietechnik,  
Technische Universität Dresden,  
Dresden, Germany

### Abstract

Conditioning methods for corrosion protective layers on steel surfaces in LWR reactor plants can contribute in suppressing activity build-up. The main theoretical foundation of such procedures is to influence the porosity of the covering. Porosity comes from a dissolution/precipitation process in the course of corrosion and film generation and can be considered to be connected with the appearance of corrosion product colloids in the cooling water. Some problems in investigating oxide-covered metal specimens are discussed and new methods are suggested.

### 1 INTRODUCTION

Inspection and maintenance work in the region of the primary system cause financial expenditures for radiation protection. According to American authors 1...2 million dollars per unit and year have to be spent for shielding, decontamination, personal training, accommodation for additional manpower etc.

Over a period of 30 years some hundred papers were published on activity build-up in nuclear reactor units. But the process has not been understood sufficiently and only partial success was achieved in suppressing it. It turned out that numerous processes are interlinked in an intricate mode.

In the past the main effort in limiting radioactive deposits was directed to

- Selection of corrosion resistant materials with low cobalt content
- Improvement of primary water cleaning
- Optimizing the pH regime
- Decontamination
- Improvement of the maintainability of components
- Maintenance planning

In doing so the increasing trends of collective dose rates in NPPs could be stopped in the early 80's

During the last years more attention has been drawn to the properties of corroding steel surfaces.

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(1) 2.2 Sv in 70 days was needed for this operation.

Proceeding from updated models of activity build-up, the direct connection between corrosion rate, corrosion product release and contamination level seems to be clear. Without penetration of the corrosion protection layer by metal compounds no corrosive action can occur.

Aimed at lowering the corrosion rate electropolishing of the steam generator tubes has been introduced. Another way is the preforming of high quality corrosion protection layers. There are proposals for treating the virgin metal surface with steam, steam-air-mixtures or oxygen containing water. Referring to all of these procedures it is presupposed that the corrosion protection layer becomes more compact and less porous. Some explanations on structure and behaviour of corrosion protection layers seem to be necessary here.

## 2 INVESTIGATIONS ON CORROSION PROTECTIVE LAYERS

### Passivity break-down

Metallic materials in reactor coolant circuits passivate themselves under atmospheric conditions. Therefore, the surfaces are passive previous to the first start-up of the plant. Here is meant passivity in the classic sense of electrochemistry. The thickness of the oxide layers is in the range of only a few nanometers, the amorphous and non-porous structure of these layers cause excellent protection against uniform corrosion attack. Unfortunately, the passivating layer cannot be preserved under operational conditions. They will get destroyed or altered in hot water within a few hours when a temperature of about  $180^{\circ}\text{C}$  is exceeded. In a phase of initially accelerated corrosion a crystalline oxide layer begins to grow. Only after the new layer has reached a thickness within the micrometer range after a time of about thousand hours corrosion rate<sub>2</sub> has decreased to an almost constant value of 0.5 to 1 mg/(m<sup>2</sup> h). Then, the surface looks pale-black due to octahedral oxide crystals with diameters in the range of mainly 0.1 to 1  $\mu\text{m}$ .

### Structure and composition of the oxide layer

In the depth profile of the surface layer alloy elements deviate from the alloy composition. Chromium enrichment is marked in the metal vicinity, whereas chromium depletion is observed in the vicinity of water. A number of authors postulates the existence of chromium-iron-spinel  $\text{FeCr}_2\text{O}_4$  in the internal layer and that of nickel-iron-spinel  $\text{NiFe}_2\text{O}_4$  in the external layer. Structure and composition of such oxide layers are in no case of scientific importance, exclusively. They can give indications to the growing of the layer and its susceptibility

towards an increased corrosion protective value. But there are serious problems to get relevant information on this.

In some cases a look into the layer is possible after preparing transverse sections or brittle ruptures. But nowadays sputtering by ion beam in combination with physical surface analysis is especially promising. Recently published depth profiles /1/ were obtained by using those methods. However, they do not correspond with earlier results. Most confusing is the appearance of uncharged atoms of nickel, iron and chromium within the oxide layer. We found out that sputtering vertical to the surface leads to some serious disadvantages:

- Chemical modifications occur by energy exchange of the target with the high energy ions. Under the conditions of high vacuum metal oxides can be reduced. That means uncharged metal atoms result from ion beam sputtering. Element-dependent differences of sputter rates as well as pores in the oxide layer promote the occurrence of a cleft surface during bombardment by ions.
- The roughness of the metal surface influences the depth profile of alloying elements in the oxide layer. On approaching the phase boundary metal/oxide it is marked in particular. Here we observe a superposition of signals from metal and its oxides.

The disadvantages of even general sputtering will be farly eliminated by an ion beam slope cutting method. This method was developed at the Dresden University of Technology /2/ and we are going to adapt it to oxide layers. Thereby the sample is bombarded with rare gas ions at certain angles to the surface over the edge of a shield difficult to atomize. Fig.1 illustrates the principle, figures 2 and 3 show SEM photographs of slopes in oxide layers of different structure. To ascertain depth profiles of element distribution following the slope AUGER-microprobe or electron-microprobe can be suitable.

### Electrochemical measurement techniques

Electrochemical measurements can be used to investigate the corrosion behaviour of metals exposed to electrolyte solutions. Here these methods are intended to estimate corrosion protective values of oxide films on steel surfaces. One of the most serious problems thereby is that the corrosion of somehow covered metal surfaces is not activation controlled. In so far the well known Tafel-equation and Stern-Geary-equation are not qualified for calculating corrosion rates. But as described earlier /3/ the comparison of samples with reference specimen using polarization resistance seems to be possible. Another problem is to conclude from cold measurements to the probable corrosion behaviour of the oxide covered metals in hot

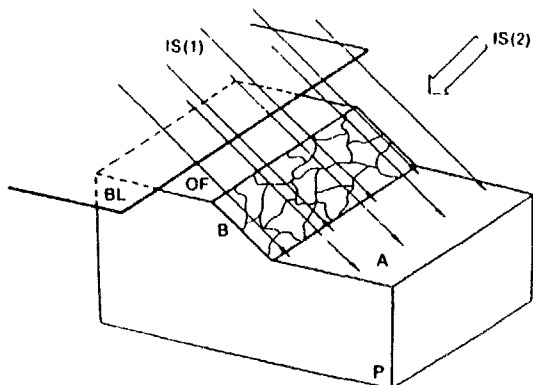


Fig.1. Principle of ion beam slope cutting (IBSC)

IB	Ion beam	B	Slope
BL	Shield	P	Specimen
OF	Surface	A	Surface after sputtering



Fig.2. SEM photograph of an IBSC-produced cut into an oxide layer on 12CrMoV4.3 after exposure to superheated steam

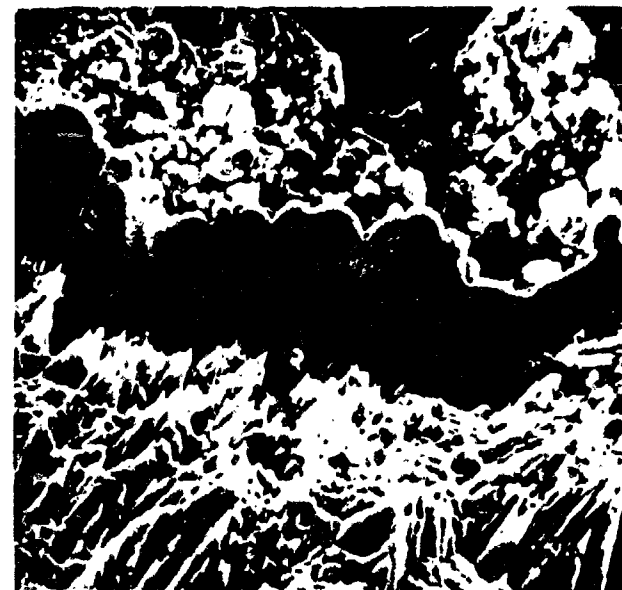


Fig.3. SEM photograph of an IBSC-produced cut into the oxide layer on 12CrMoV4.3 after exposure to hot water

water. For self-passivating metals as e.g. high-alloy steels this task cannot be solved. That is why there is no marked difference in the electrochemical behaviour between samples passivated in the classical sense and samples covered with a crystalline oxide layer after exposing to hot water. Investigating the latter samples by cold electrochemical measurements you will find the metal at the bottom of the pores within the oxide layer passive. In contrast to this, in hot water with a temperature beyond 200 °C active metal dissolution at the pore bottom occurs.

Lately, we have been carrying out measurements even at temperatures up to 250 °C. Aspecially made autoclave of 1 liter capacity serves as an electrochemical measurement cell (fig.4). Its closure head contains three electrical penetrations sealed and electrically insulated by PTFE. The autoclave is not completely filled. Beyond the water line the electrodes are clamped and contacted. In oxygen-free electrolytes a platinum wire can serve as reference electrode. But an external silverchloride electrode will be put in operation soon.

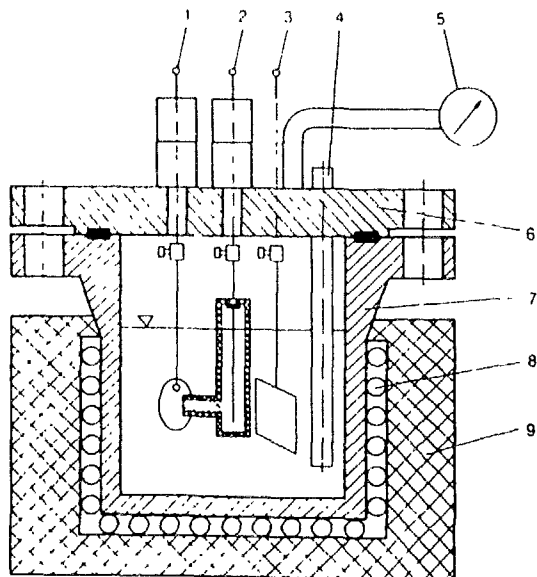


Fig. 4. Measurement cell for electrochemical testing at temperatures up to 250°C

- |                       |                      |
|-----------------------|----------------------|
| 1 Working electrode   | 6 Autoclave cap      |
| 2 Reference electrode | 7 Pressure vessel    |
| 3 Counter electrode   | 8 Electrical heating |
| 4 Instrument well     | 9 Thermal insulation |
| 5 Manometer           |                      |

Fig. 5 shows current/voltage curves of chromium-nickel steels with different surface films. Active-passive transitions prove the existence of pores reaching the metal. The above mentioned problems of computing corrosion rates have been existing further. Our ideas how to resolve this task in future are based upon measurements of polarization resistance  $R_p$  at different temperatures. Here shall be given a brief explanation only.

The ARRHENIUS-equation for the temperature dependence of the reaction rate can be adapted to corrosive action as follows:

$$\ln i_{\text{kor}} = \ln C - \frac{E}{R \cdot T}$$

The constant C characterizes the reacting system. Among other things it should depend on the degree of coverage

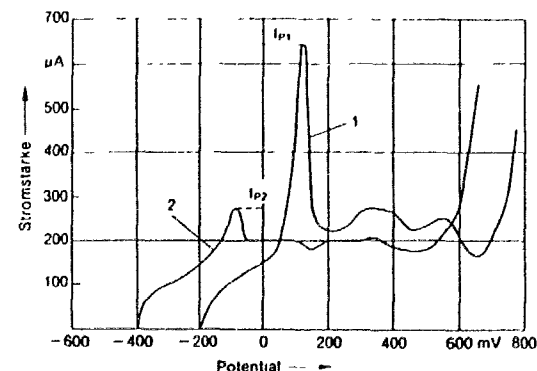


Fig. 5. Current/voltage curves at 230 °C of CrNi-steel specimens with different protective layer quality

- 1 Oxidized in hot water with Fe/EDTA addition
- 2 Oxidized in hot water with Zn/EDTA addition

of the surface. The activation energy  $E$  is determined by the passage of metal ions at the pore bottom and the diffusion of reactants through pores. The equation can be applied if the logarithm of the corrosion current  $i_{\text{kor}}$  depends linearly on  $T^{-1}$ . We proved this experimentally and determined activation energies for the corrosion of steels as well.

Further investigation showed that the linear relationship will preserved if by means of the STERN-GEARY-equation

$$i_{\text{kor}} = \frac{B}{R_p}$$

the corrosion current is substituted by polarization resistance  $R_p$ . Consequently, factor B must be independent of the temperature. If it were also independent of thickness and other characteristic attributes of the surface layer the corrosion rate could be calculated from measured  $R_p$  values. A precise numerical value for B has still to be detected on the basis of gravimetrically determined losses of metal.

### 3. GROWTH MECHANISM OF CORROSION PROTECTIVE LAYERS

The duplex layer on steel after exposure to hot water suggested the idea of two different growth mechanisms.

The inner layer is supposed to grow into the metal in a solid state reaction. This is indicated by the classical term "topotaxial layer". Simultaneously dissolved metal compounds are assumed to be responsible for epitaxial growth of the outer layer. Porosity on the base of interstices between the oxide crystals could be detected both in the outer and the inner oxide layer. Referring to the inner layer the crystal size amounts to 0.1  $\mu\text{m}$  and is thus significantly below that of the underlaying metal. For these facts the above mentioned model of layer growth does not offer any plausible explanation. Furthermore, the conclusion drawn from the model that metal oxidation bases on two energetically different reactions can hardly be accepted. One of them would be the direct oxide formation and the other one the passage of metal ions into the water.

The questions discussed suggested to study temperature and time dependence of corrosion once more profoundly. In detail these problems are referred to in /4/. The corrosion rates obtained were too high by some orders of magnitude as to be related to lattice diffusion. From activation energies estimated as some 10 kJ/mol a domination of diffusion of reactants not through oxide lattice but through water-filled pores should be deduced.

For the corrosion of steels in hot water we would like the following model to be discussed:

At corrosion-prone sites of the metal surface dissolution takes place. The deposition of oxides out of the solution follows. Thereby preferred are oxides with high enthalpy of formation and low solubility. This is chromium-iron-spinel on steels rich in chromium. Growth of the layer restricts metal dissolution to the pore bottom. Corrosion becomes increasingly a function of diffusion currents through pores. But now it must be explained why regardless of the pore diffusion the growth of the layers continues. Obviously we have to assume the continuance of a dissolution/precipitation process at the phase boundary metal/oxide. About this important detail further investigation is needed. Generally spoken we are sure that the overall layer grows following a mechanism of dissolution and precipitation. Thus, crystal size and porosity of the oxide layer close to the metal can easily be explained.

#### 4. METHODS FOR IMPROVING CORROSION PROTECTIVE LAYERS

When we started our work in the early 80's the first idea was to modify the oxide composition. The oxide lattice should be a stronger hindrance to electron and ion transfer. For this purpose complex compounds of titanium and zirconium were decomposed in the corrosive medium to deposit hydroxides of these metals on the corroding surface. Growing mixed spinels were thought



Fig.6. Single crystals of Magnetite generated by chemical transport

to fulfill the above mentioned tasks. But the theoretical foundation which we worked out later did not fit this undertaking. Investigations on single crystals of magnetite (fig.6) and mixed spinels proved to be helpful when we rejected the mechanism of lattice diffusion. Incidentally, we could demonstrate that zirconium cannot get together with iron oxides in mixed spinels. But nevertheless both titanium and zirconium improved the quality of corrosion protective layers on unalloyed steel. The reason for this should be diminished porosity of the covering. Therefore it does not matter that zirconium does not build mixed spinels.

In the time being we try to prove the usefulness of our preforming methods by using the above mentioned new methods of investigation. As for the application of zirconium we think a lowering of the corrosion rate by more than 50% is possible. A task in the future is to optimize the process and to carry out experiments in a technological scale.

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## BEHAVIOUR OF COLLOIDAL CORROSION PRODUCTS

F. HÜTTNER, R. WINKLER  
Institut für Energietechnik,  
Technische Universität Dresden,  
Dresden, Germany

### Abstract

The limited effect of elevated pH values in the cooling water of PWRs on activity build-up suggests to consider not only the genuine dissolved fraction of corrosion products but the colloidal fraction, too. Referring to relevant publications sources of colloids in the coolant and their contribution to corrosion product transport are discussed.

Reactor circuit material corrosion products can be found as ions or molecules and particles in the coolant. Thermodynamic conditions for existence of the latter mentioned will be given when the concentration of corrosion products exceeds solubility. Solubility depends on the nature of the material dissolved, on temperature and chemical composition of the solvent. The fraction of solids is subdivided qualitatively into colloids and coarse disperse material.

Both surface forces and mass forces may play a role for the behaviour of solid particles in the coolant. It will be decisive which forces prevail under the given hydrodynamic and chemical conditions. Among the forces proportional to the surface size of a particle are forces of viscosity and such forces resulting from interactions with electric surface charge. However, forces of gravity and inertia are proportional to the mass of a particle and thus (at constant density) proportional to their volume.

The behaviour of a solid particle will essentially depend on its size. If the existence of spherical particles is assumed for reasons of simplification, the particle surface increases with the square of radius, whereas the particle volume increases with its third power. Consequently, with increasing particle size the influence of the mass forces will grow more rapidly than that of the surface forces /9/. Thus, there is a certain particle size from which forces of the mass will prevail. Corrosion product particles in the coolant, where surface forces are prevailing compared to mass forces, are referred to as colloids. Starting from this definition the upper limit of colloidal range of size will not be

regarded as a constant value but as dependent on the nature of corrosion products and hydrodynamic conditions. The transition is rather to be considered fluid.

The subdivision of corrosion products into genuinely dissolved, colloidal and coarse disperse material as often done for practical purposes is of actually arbitrary character taking into account qualitative differences only relatively. Thus, it is suitable for the investigation of mechanisms of activity build-up to a limited extent only. Here even substantially improved coolant sampling and sample treatment will be required.

In general corrosion products not retained by a filter of  $0.45\ \mu\text{m}$  are regarded as genuinely dissolved. Investigations by LISTER /1/ demonstrate how arbitrary such an approach is. There reactor coolant samples were filtered through filters with pore widths of  $0.45$  and  $0.2\ \mu\text{m}$  and the activity of the filtrate was determined. There was no significant variation stated between untreated samples and the filtrate of the  $0.45\ \mu\text{m}$  test. However, the activity at the  $0.2\ \mu\text{m}$  filter test was only half as high. This result emphasizes the importance of colloidal particles of small particle sizes for processes of activity build-up. This share will not be regarded as a colloidal fraction by conventional experiments.

If a solid sample is dipped into an aqueous solution an electric charge will be generated on its surface due to interactions with this medium. This process is described in detail in /2/. The quantitative expression of this surface charge is the zeta potential, which depends above all on the nature of the surface and the pH value of the solution. The surface charge of a particle yields an interaction with other electrically charged surfaces, this concerns both further particles and larger surfaces (tube walls etc.). The interactions are of electrostatic or electrodynamic nature. Phenomena such as electrostatic force of attraction (or repulsion) between surfaces play a role as well as electrophoresis or electromigration. The peculiarity of colloids to other dispersed particles consists in the fact that such interactions caused by the surface are absolutely prevailing in comparison to other interactions. Hence, a colloidal solution is stable up to a certain critical particle size due to repulsion between surfaces of the same charge.

According to /3/ the colloidal fraction amounts roughly to 90% of the total mass of corrosion products in the primary coolant of PWRs. Thus, these corrosion products provide a relatively large total surface in the circuit, which greatly favours adsorption processes. With a negative zeta potential of colloidal particles the adsorption of positively charged cobalt ions will be promoted. Therefore, colloids are perfectly suitable to exert a carrier function for ions relevant for activity build-up.

Sources for colloids in the primary coolant circuit of PWRs are basically the direct liberation of corrosion products of material surfaces as well as the dissolution of oxide layers. There are indications that the colloidal fraction mainly consists of "fresh" corrosion products /4/.

During growth and ageing of particles the scope of colloidal size is exceeded /5/. With the interaction of colloids large-sized agglomerates emerge. This process is subdivided into two phases: The transport of particles to collision and their subsequent interaction resulting in the formation of bigger particles /6/. Flow effects oppose particle growth such that a maximum stable agglomerate size is obtained.

Sinks for colloidal fractions can be primary water purification, deposition on surfaces, ageing (exceeding of the scope of colloidal size by particle growth) and dissolution due to changes in existence conditions of colloids.

For mathematical modelling of colloidal corrosion product behaviour, especially relevant for predictions of deposition on fuel elements and other surfaces within the circuit there are various theoretical approaches known. RODLIFFE et al. /6/ base on the fact that colloidal particle transport through the hydrodynamic boundary layer towards the wall is mainly effected by BROWNIAN diffusion. If a temperature gradient is present thermophoresis influences bigger colloidal particles. Both transport mechanisms are combined as a simple superposition. Thermophoresis is opposed to the temperature gradient, thus deposition will be reduced on heating surfaces and promoted on cooling surfaces by this effect.

BRUSAKOV et al. /7/ however assume thermodynamics of irreversible processes in order to describe material transport through the hydrodynamic boundary layer. Thereby, a gradient of the electric potential is generated through the boundary layer by the temperature gradient when a heat flow is present /8/. The electric field generated in this way is considered the main cause of material transport in the vicinity of the wall and moreover to exert an essential influence on electrochemical processes. Other influences on material transport, such as zeta potentials, electrostatic interactions, thermodiffusion and BROWNIAN diffusion of particles are not considered in this model. The Peltier-effect as a probable initiator of material transport in the boundary layer is seen as an absolute cause. According to the model by BRUSAKOV it depends on the type of potential forming ions whether particle deposition on heating surfaces is promoted or inhibited.

Doubtlessly it is of high importance to apply the thermodynamics of irreversible processes to physico-chemical relations in the phase boundary layer. However,



it should also be noted that for many processes the distance from thermodynamic equilibrium can be sufficiently wide to act clearly in the nonlinear scope of irreversible thermodynamics. This also includes the variant of the formation of dissipative structures due to the impact of irreversible processes proceeding in the boundary layer.

Considerations on the effect of electric conductivity of the coolant, temperature and flow rate to the expansion of the electric field generated by the surface charge and thus on material transport of colloidal particles are described by GASPARINI et al. /9/.

A fundamental paper on the formation of electro-chemical surface forces and on the possible effect on material transport processes was published by SMITH-MAGOWAN /2/. There the zeta potential of the surface plays an essential role. The direct relationship between this parameter and the streaming potential experimentally accessible relatively simply is indicated. Probably, the lack of experimental data on colloidal behaviour under high temperature conditions may be overcome by utilizing this relationship.

For experimental investigations the generation of artificial colloidal corrosion products is important. A paper by MATIJEVIC /10/ deals with this problem as well as with the possible influence of colloids in nuclear power stations.

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# CORRELATION OF OUT-CORE SURFACE ACTIVITIES AND PRIMARY WATER CHEMISTRY IN VVER-440 REACTORS

G.L. HORVÁTH

Institute for Electrical Power Research (VEIKI),  
Budapest, Hungary

## Abstract

A systematic data collection programme launched at PAKS Nuclear Power Plant (NPP), gave a unique possibility to prove the correlation between the out-core surface radioactivities and primary water chemistry conditions. Analysis showed that out-core corrosion product surface activities (Co-60) are decreasing with increasing cycle average  $\text{pH}(T=270^\circ\text{C})$  values in the range of  $\text{pH}(T=270^\circ\text{C}) = 6,7 - 7,0$ .

## 1. INTRODUCTION

Theoretical studies [1-5] and plant experience [6] of the past years indicated that increasing alkalinity (pH) in the primary circuit may reduce out-core surface corrosion product radioactivities. Results of these corrosion product transport studies have been applied to the case of VVER-440 type of reactors [1,2,5], and a computer code RADTRAN has been elaborated [1]. Calculations by the code mentioned gave similar results. Figure 1 gives an example of effect of increasing alkalinity. Curves given are relative to the "zero gradient case", when there is no concentration gradient of corrosion product Iron between the fuel cladding surface and the bulk of the coolant. This case has been taken as 100%. Increasing alkalinity increases the gradient mentioned, in this way enhancing the removal of deposited to the fuel cladding particulate corrosion products by dissolution and reducing their activation. It can be seen on Fig.1 that if alkalinity increases to the conditions where  $\text{pH}(T=25^\circ\text{C without H}_3\text{BO}_3) = 10,2$ , than a 6 - 7 fold decrease of out-core surface activities can be expected.

A systematic data collection programme launched at PAKS Nuclear Power Plant (NPP), gave a unique possibility to prove the above mentioned trend. Surface activity sampling programme is described in [10]. Surface activities (Co-60) has been correlated with operational water chemistry data  $\text{pH}(T=270^\circ\text{C})$  of the plant.

## 2. EVALUATION OF HIGH TEMPERATURE pH CALCULATIONS

In most of the cases primary water chemistry conditions are characterised by the high temperature pH. Calculational methods

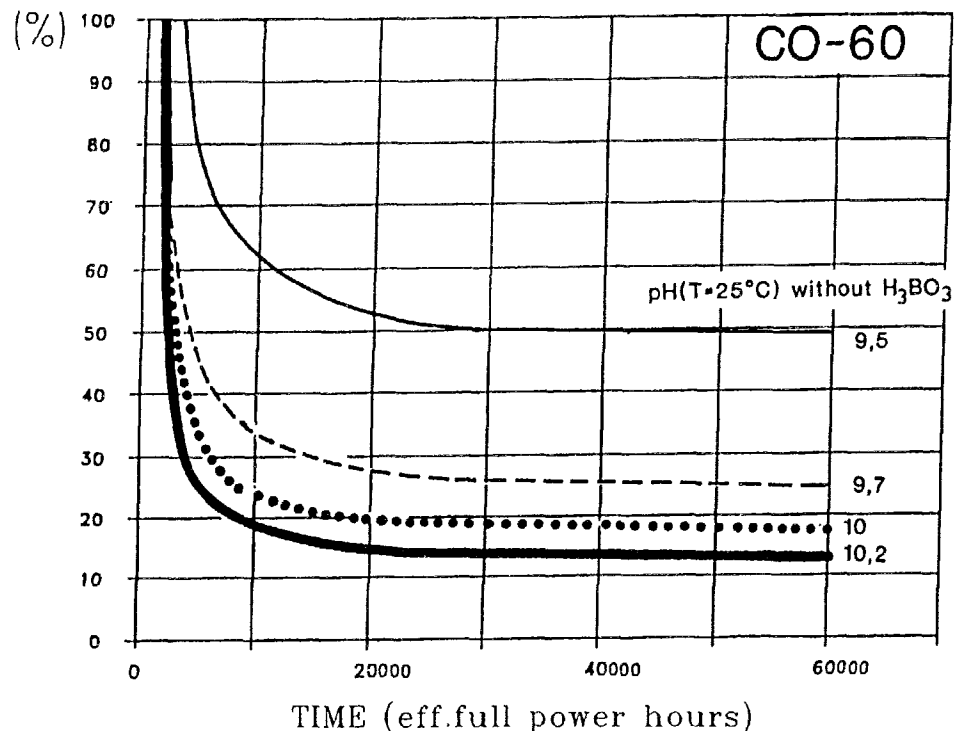


FIG. 1. Relative surface activity.

give diversing results first all due to differences in ion product ( $K_w$ ) of water [7]. pH calculational method [10] used in this study (based on [8,9]) has been compared to other methods available (Fig.2). Our method is using  $K_w$  according to Marchall-Franck [11], and it is close to the majority of curves, especially to those using activity coefficients. Differences in the range of high boric acid concentrations may be due to different boric acid dissociation correlations.

## 3. MEASUREMENTS AT PAKS NUCLEAR POWER PLANT

Primary water chemistry measurement data ( $K, Na, Li, H_3BO_3$ ) has been used to calculate the time average value of  $\text{pH}(T=270^\circ\text{C})$  for the first cycles of four units of PAKS NPP. Value of  $270^\circ\text{C}$  is the core inlet temperature. Samples of radioactivity has been collected by electrochemical dissolution of oxide layer, with a subsequent measurement of the sample by High Purity Germanium

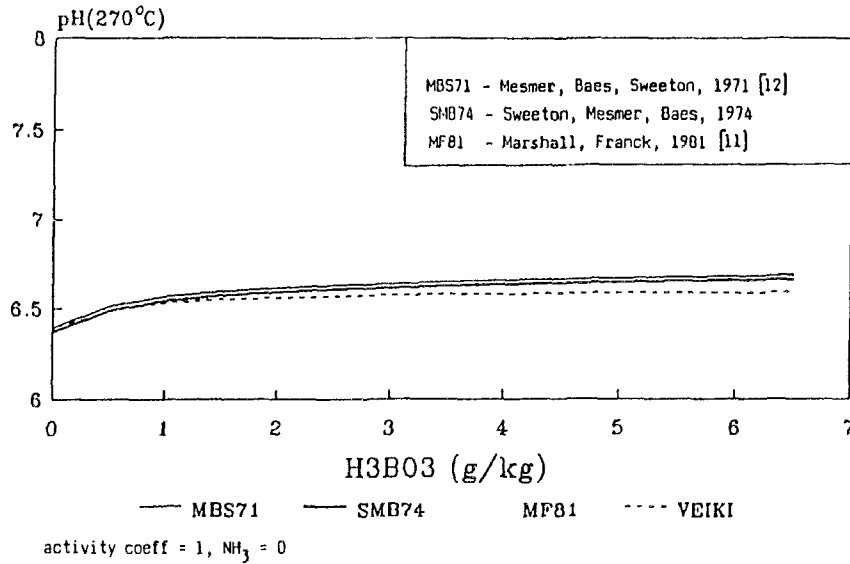


FIG. 2. Comparison of pH calculations (Westinghouse vs VEIKI).

(HpGe) detectors and multichannel analyzer. Activity data on figures are from electrochemical sampling if not indicated otherwise. In case of main circulation pipeline contact measurements by HpGe detector were also done, with a subsequent calibration procedure moving a known source on the perimeter of a piece of reserve primary pipeline. Some of the decontamination data of main coolant pumps were also used to derive specific surface activities.

Cycle averages of pH(T=270 °C) have been correlated to the activities measured on the same surfaces of different units (fig.3 - 9). A linear regression line was fitted to each set of data.

Most of the surfaces (except pump housings) showed a decreasing trend of Co-60 activity versus increasing pH(T=270 °C). In case of pump housings only a considerable scatter of data can be noticed. This is in agreement with the theoretical conclusions and other measurements.

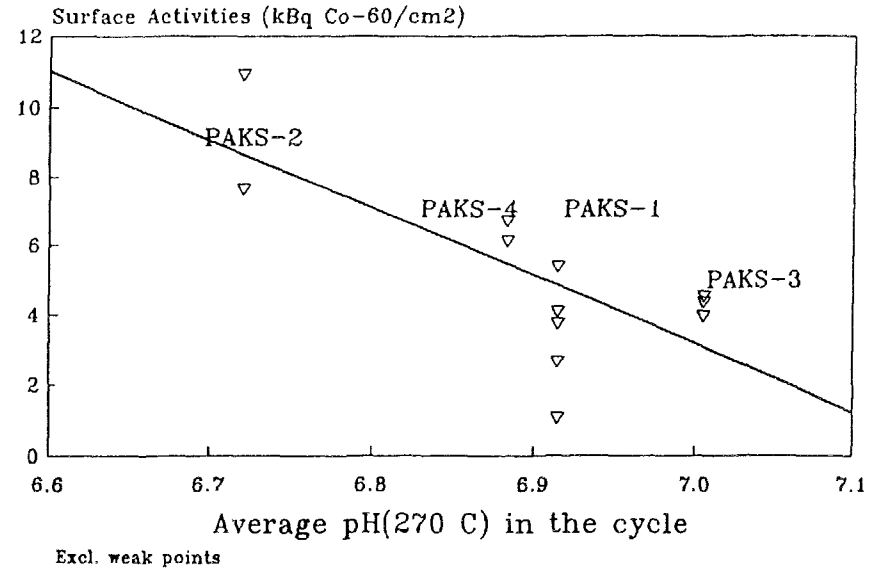


FIG. 3. Reactor cover (first cycles).

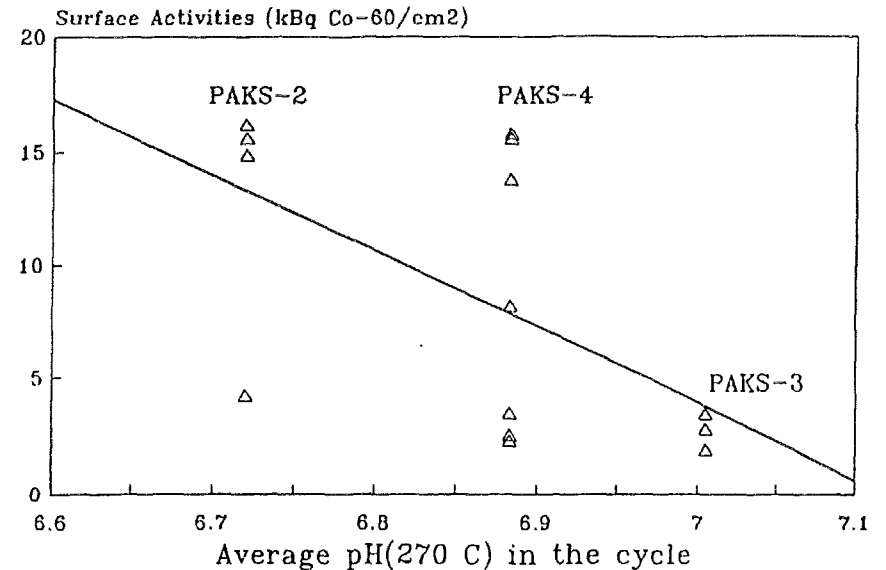


FIG. 4. SG manhole cover (primary), hotleg (first cycles).

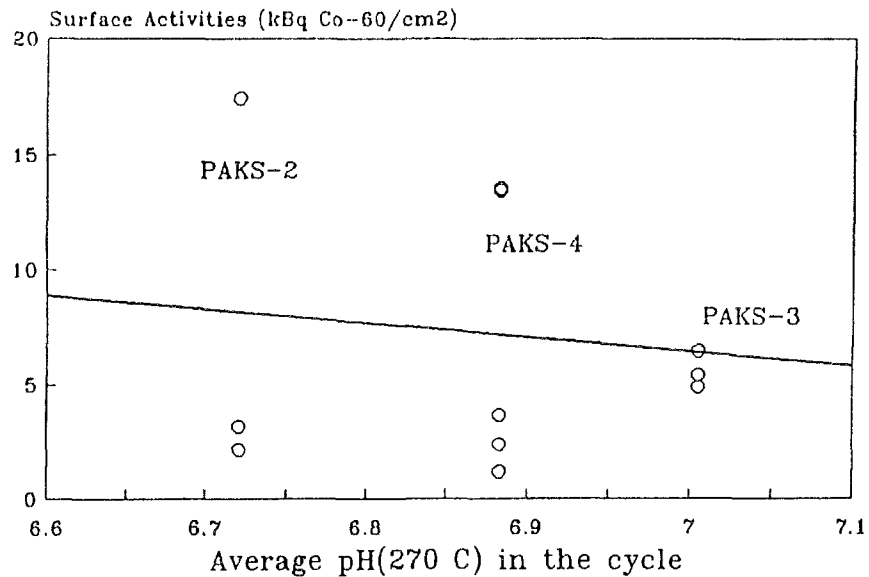


FIG. 5. SG manhole cover (primary), coldleg (first cycles).

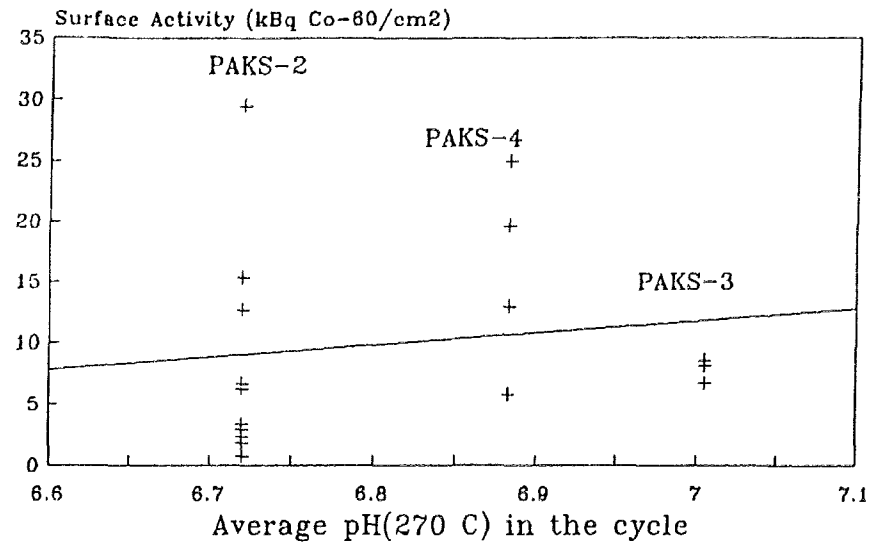


FIG. 7. Main pump housing (first cycles).

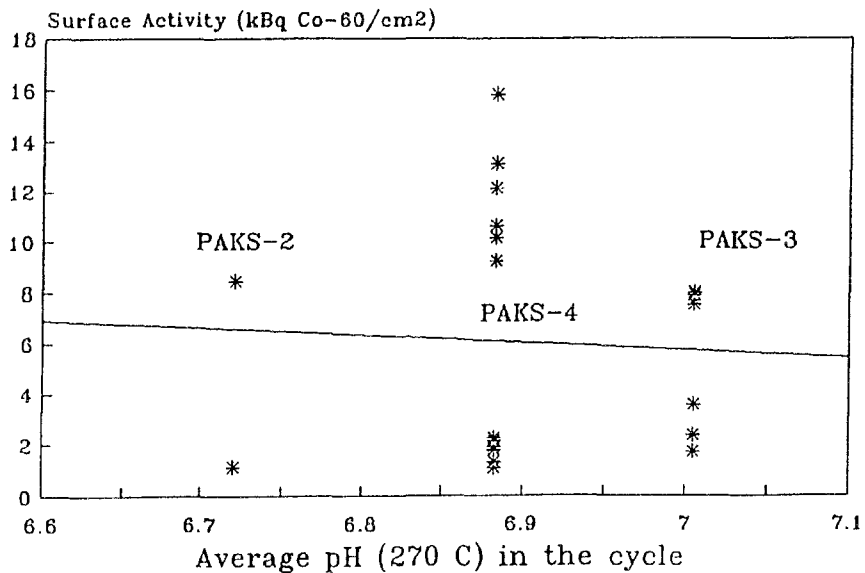


FIG. 6. SG headers (hotleg and coldleg) (first cycles).

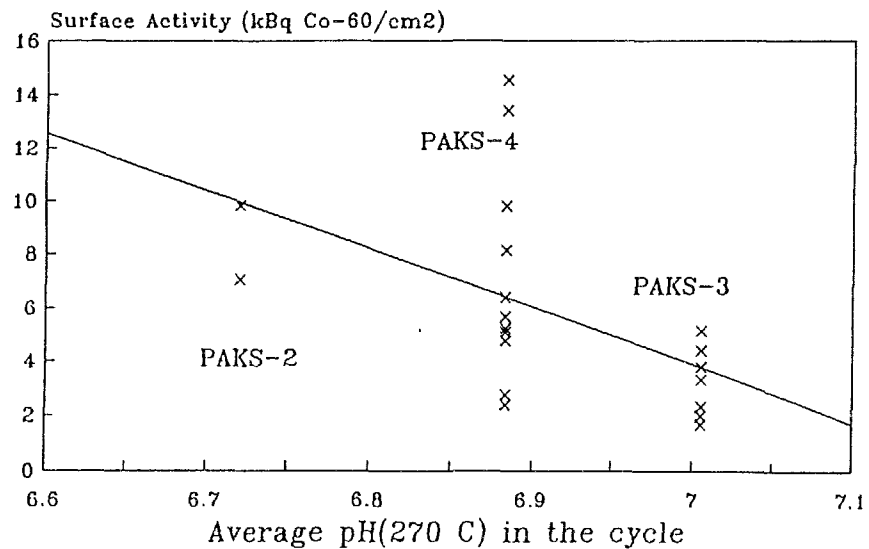
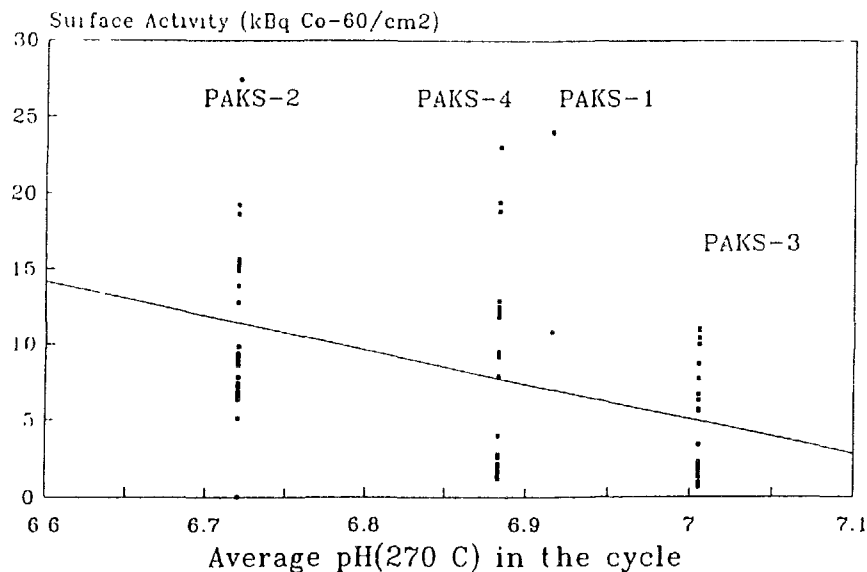


FIG. 8. Main pump rotor (first cycles).



Coldleg & Hotleg

FIG. 9. Main primary pipeline (HpGe measur.) (first cycles).

#### 4. CONCLUSIONS

- (a) Analysis of surface activity and primary water chemistry data showed that out-core corrosion product surface radioactivities (Co-60) are decreasing with increasing cycle average pH( $T=270$  °C) values in the range of  $\text{pH}(T=270$  °C) = 6,7 - 7,0.
- (b) A relatively small data base and a considerable scatter of activity measurements make it necessary to involve data of other VVER-440 units operating.

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# INFLUENCE OF THE PRIMARY CIRCUIT WATER CHEMISTRY ON OUT-CORE SURFACE ACTIVITIES

G L. HORVÁTH, V CIVIN  
Institute for Electrical Power Research,  
Budapest

P. ORMAI, T PINTÉR  
Nuclear Power Plant Paks,  
Paks  
Hungary

## Abstract

In this paper is recalled the importance of water chemistry on solubility of corrosion products in the primary circuit of water cooled reactors

Methods of pH calculation at high temperature are given and discussed  
Radioactivity measurements on Hungarian reactors PAKS are then given showing that application of high pH coordinated chemistry is favorable

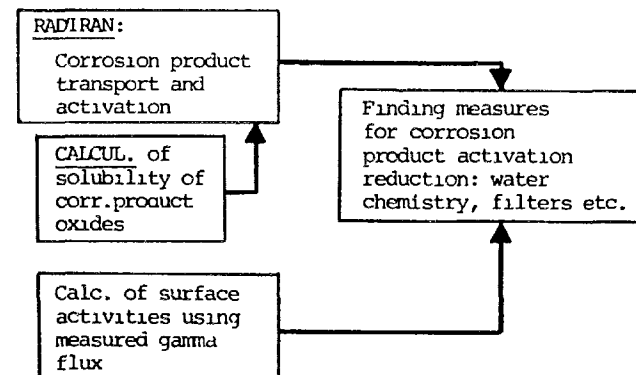
## 1. INTRODUCTION

In the present generation of nuclear power plants the majority of the operational personal doses are created by maintenance work as a result of activated corrosion products mostly during shut-downs.

Limited access to major primary circuit components reduces plant availability, involves economic aspects and may influence plant safety. In this way it is obvious that a reduction of corrosion product activities on out-core surfaces is desirable.

Activated corrosion product transport research in Hungary started several years before the first operation of Paks units and a considerable theoretical and calculational work was done, including transport codes /RADTRAN, fig./ Theoretical studies gave the scientific basis for the understanding of the most important physico-chemical processes in the corrosion product activation, but needed experimental and operational support. One of the major findings of the theoretical works were the type of influence of primary water chemistry to activity build-up [16] .

As an obvious continuation, an attempt to verify these findings followed, in operational conditions. Therefore the *main research objective* of the coming years is to correlate out-core corrosion product



Code system for corrosion product transport modelling and the decision making process [16] .

surface activities with water chemistry of the primary circuit of real power plant units.  
In the framework of this objective the following tasks were formed:

- developing a method for the evaluation of the primary water chemistry,
- evaluating the operational data of VVERs using the above method,
- systematic collection of surface activity data from VVER-440s,
- correlating surface activity data with the primary circuit water chemistry to find optimal conditions for the minimal out-core corrosion product activities.

In the present report the progress in the first three tasks is reported, in the framework IAEA coordinated Research Programme "Influence of Primary Water Chemistry on Fuel Cladding Reliability" /WACOLIN/, to fulfil the IAEA Research Agreement N°4742/CF for 198 .

## 2 IMPORTANCE OF PRIMARY COOLANT CHEMISTRY

It is widely covered in the literature, that corrosion product /Fe,...etc./ concentrations on primary circuit surfaces /at the boundary layer bottom/ are in equilibrium with oxide layer, i.e. in saturation state. If the corrosion product concentrations in the bulk of coolant are higher than, that on the surfaces, than soluble corrosion products transported to the surface by brownian or turbulent diffusion are crystallised on the surface.

If this happens on fuel cladding surface, than corrosion products are activated and due to subsequent release contaminate the out-core surfaces.

The above mentioned situation may be encountered if corrosion product solubility decreases with increasing temperature i.e. in case of negative solubility vs. temperature gradient. Therefore in most of the reactors, in the whole primary circuit temperature range, a positive solubility gradient is kept during operation.

The sign of temperature gradient of solubility /at given temperature/ depends first of all on high temperature  $pH_{T,O}$  / $pH_T$ / of coolant. There is a certain value of  $pH_T = pH_{T,O}$  at which the gradient is zero. In the region above this point, the gradient is positive and under it, it is negative.

The mentioned  $pH_{T,O}$  is mostly defined as the  $pH_T$  value where:

$$k = \frac{dC_s}{dT} \cdot \frac{1}{C_s} = 0$$

where:

$C_s$  - corrosion product /Fe/ solubility at T temperature, in equilibrium with corrosion product oxides /magnetite/.

There are very limited data for  $pH_{T,O}$ . Some calculations were published in [1] using classical Sweeton & Baes data as source /fig.1/. This figure shows that  $pH_{T,O}$  increases with decreasing temperature. Additional available data on  $pH_{T,O}$  were summarised in table 1. Early calculations by McDonald et al. [2] are obviously overestimating the  $pH_{T,O}$  because these are not considering the temperature dependence of dissociation constants of LiOH. The other sources show that a range of

$$pH_{270^\circ C, O} = 6,8 - 7,14$$

may be expected. Temperatures in table 1 have been chosen to be typical for VVER-440s

270 °C - bulk coolant temperature at core inlet,

300 °C - bulk coolant temperature at core outlet

There is considerable evidence about the crystallization due to negative value of k. Some cases were reported in [5-8], when the application of  $NH_3$  alone as an alkalisng agent caused severe depositions on fuel, while using strong bases /LiOH or KOH/ eliminated these problems. Similar observations were reported in [3] and [9].

The value of  $pH_{T,O}$  determines the place of crystallization in the primary circuit. In case of

$$pH_T = pH_{T,O},$$

this means, that crystallisation will take place at places with temperature lower than T. /This happens because  $pH_T$  decreases and  $pH_{T,O}$  increases with decreasing temperature in the operating temperature range of the primary circuit/. If there is no such temperature in the core, than crystallization will take place outside the core.

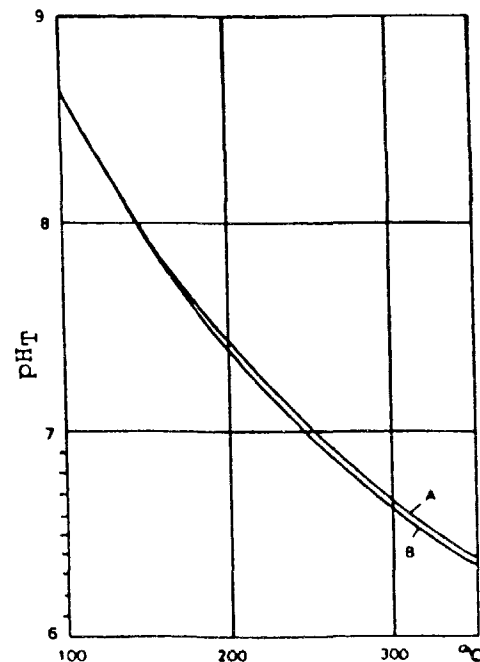


Figure 1. Temperature dependence of  $pH_{T,O}$  /Fe in equilibrium with magnetite/ [1]

A -  $pH_T$  values corresponding to minimum of Fe solubility vs.  $pH_T$ ,

B -  $pH_T$  values corresponding to  $k=0$  value:

$$\text{where: } k = \frac{dC_s}{dT} \cdot \frac{1}{C_s} =$$

temperature coefficient of Fe solubility  
 $C_s$ -Fe solubility

Table 1 Comparison of different sources for  $pH_{T,0}$   
 $pH_{T,0}$  is the value of  $pH_T$  where  $k = \frac{dCs}{dT} \frac{1}{Cs} = 0$  is  
 valued/

SOURCE	$pH_{T,0}$	
	$T=270^{\circ}C$	$T=300^{\circ}C$
D.D. McDonalds et al. [2]	7,38*	7,12*
Bosselman et al. [1]	6,81	6,61
Sweeton Baes [3]	7,14	6,8
Lambert Sandler	n.a.	7,1
Barge et al. [4]	n.a.	6,6*

\*/  $pH_T$  value at which  $Cs=f/pH_T/= \min$ , which is very close to conditions for  $k=0$  according to [1] /see Fig.1/.

In operating reactors fuel cladding surface temperatures are always higher than core inlet bulk temperatures. For the case of VVER-440 type reactors this is  $270^{\circ}C$  and if:

$$pH_{270} \geq pH_{270,0}$$

than corrosion product solubilities on fuel cladding surfaces are higher, than that in the bulk of coolant. This means the cladding has self-cleaning properties.

The slightly positive value of "k" is ensured by the primary coolant quality specifications.

### 3. PRIMARY COOLANT QUALITY SPECIFICATIONS

There are certain differences in the design of different reactors in

- temperature \*
- pressure of boric acid,
- alkalisng agent /LiOH or KOH+NH<sub>3</sub>/,

	Temperature / $^{\circ}C$ /	
	core inlet	core outlet
VVER-440	270	300
CANDU	266	310
PWR 900 MW /France/	284	321
PWR 1300 MW / " /	292	329
Atucha-1	262	?

### PRIMARY COOLANT SPECIFICATIONS Ranges Independent of Boron

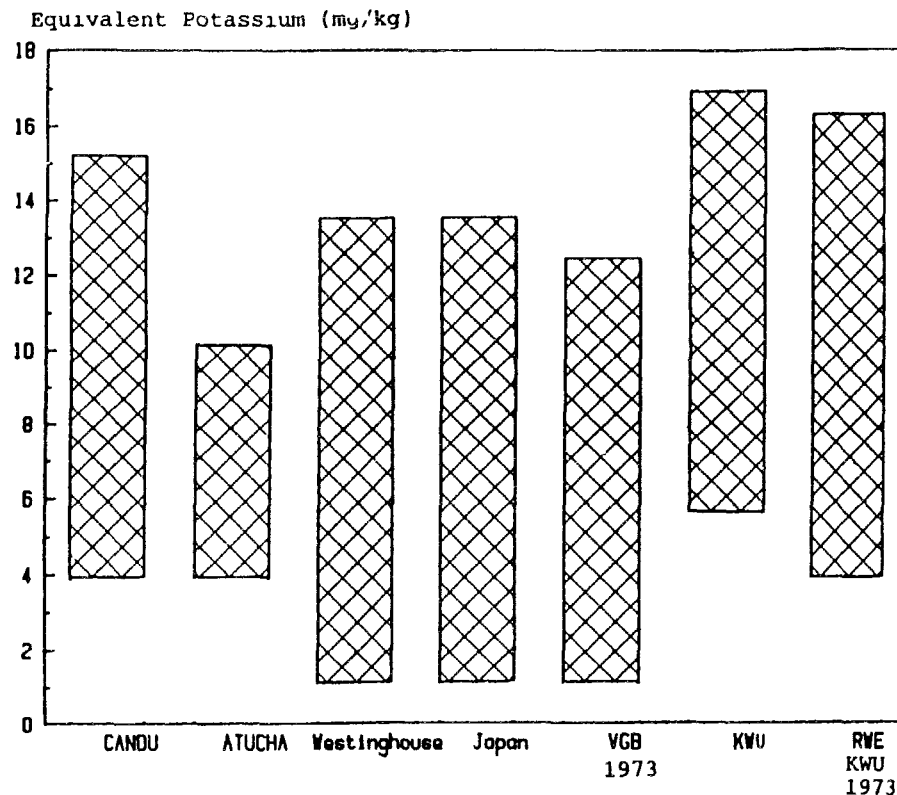


Figure 2. Comparison of different primary coolant specifications independent of boron concentrations. (Li and boron concentrations have been converted to equivalent potassium and boric acid.)

therefore these specifications may be different. Fig 2 summarizes the specifications for the case when alkalisng agent concentration is independent of boric acid content. Fig. 3 gives the cases where the coordinated water regime is applied. Coordinated coolant specifications are mostly a narrow range of the boron-independent specifications, and are similar against the differences in the reactor design. They are expected to ensure a slightly positive value of "k" at the coldest place in the primary circuit.



PRIMARY COOLANT SPECIFICATIONS  
Ranges Dependent on Boron

VVER-440 (5mg NH<sub>3</sub>/kg)  
E d F. 1982  
RWE (Biblis)  
CANDU 1972

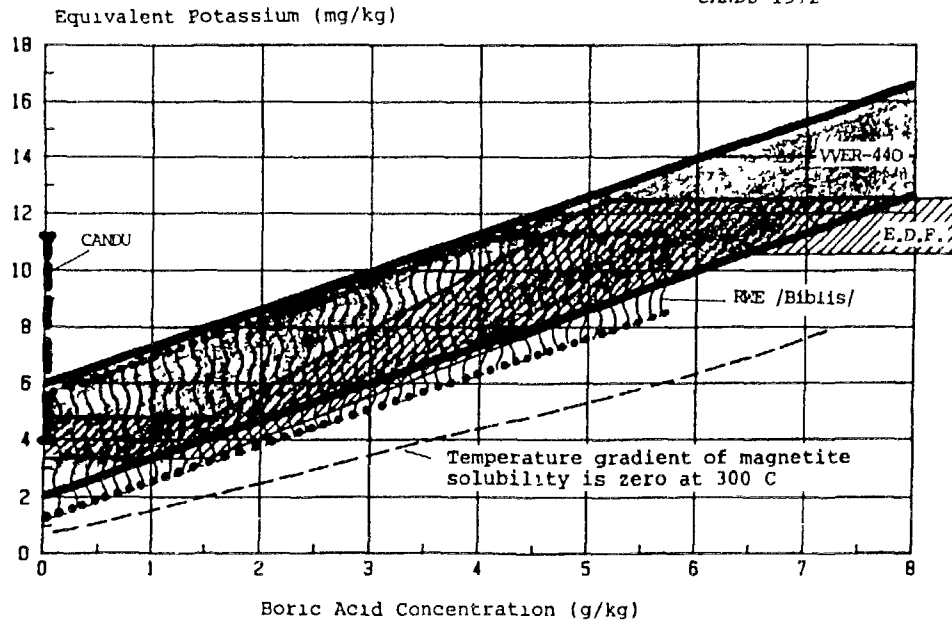


Figure 3. Comparison of boron correlated primary coolant specifications. (Li and boron concentrations have been converted to equivalent potassium and boric acid.)

#### 4. EVALUATION METHODS OF THE PRIMARY COOLANT CHEMISTRY

Primary water chemistry is mostly evaluated in

$$\text{Base } [Li, K] = f \text{ /Boric acid/}$$

or

$$pH_T = f \text{ /Boric acid/}$$

terms and compared to minimal base concentration or minimal  $pH_T$  needed for positive magnetite solubility coefficient [3], [8]. A detailed analyses based mostly on the last method has been reported in [10] accounting also the time spent while values of  $pH_T$  higher than certain critical levels, were valued. For the evaluation of primary coolant chemistry the  $pH_T$  method was selected, because  $pH_{T,0}$  is independent of the boric acid con-

centration and different base  $[Li, K, Na, NH_4OH]$  concentrations can easily be taken into account.

In VVER-440 type reactors in normal power operation the boric acid concentration is below 6,5-7 g/kg, therefore cases higher than that should not be considered.

As a respective temperature for  $pH_T$  calculation the liquid bulk temperature at core inlet  $[ \approx 270^\circ C ]$  has been selected. Only those chemical data were analysed where all base  $[K, Li, Na]$  data were available.

To calculate the high temperature pH a method described in [11] and [12] has been used /App.A/. Method described in [11] is based mostly on early data [13], which considerably overestimates the  $pH_T$  in comparison with Mesmer data [12,14]. Overestimation reaches 0,6 pH units in the range of higher  $[6 \text{ g/kg}]$  boric acid concentrations and 0,15 pH units without boric acid. In case of [11] only two dissociation species of  $H_3BO_3$  in treated, but in [12] number of these species reaches three. Comparison to other calculations [1,15] gave similar results, although the differences were smaller. Figure 4 shows the differences in  $pH_{270^\circ C}$  calculated by the two methods mentioned.

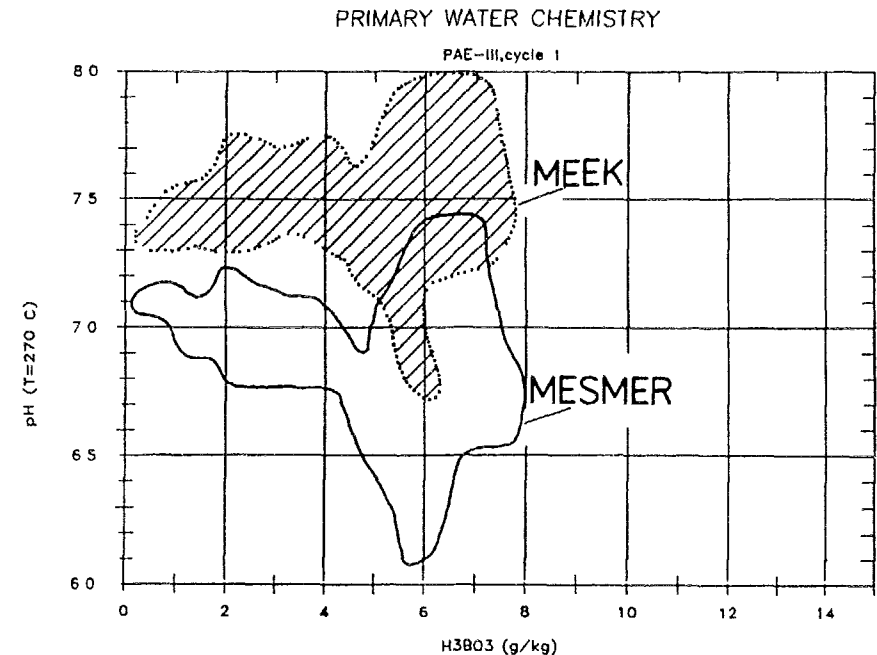


Figure 4. High temperature pH calculated for PAKS Nuclear Power Plant Unit III cycle 1 using early [11] and developed ([12], Mesmer) data.

Some of the preliminary evaluation have been done using the early data /Fig. 5. and 6 /, but for further work the pH calculation method based on Mesmer data has been selected.

##### 5. SURFACE ACTIVITY DATA COLLECTION AT PAKS NUCLEAR POWER PLANT UNITS

An intensive survey and sampling programme has been initiated at Paks Nuclear Power Plant since the start of the first unit. The surface activities of the primary circuit components were determined by:

- electrochemical dissolution of the oxide layer fig.7. and measuring the active and inactive constituents by HpGe detector and CANBERRA-80 analyzer and atomic adsorption device resp.,
- measuring the gamma flux outside the main primary circuit pipeline by a collimated HpGe detector and calculating the surface activities by computer codes and by using calibration data\*/ /in-line measurements/.

After the first few trials mostly electro-chemical dissolution of the oxide layer was used /duration of sampling is 1 minute/, because the black oxide layer grown on high temperature surface turned to be very dense and adhesive, not suitable for mechanical sample taking. Typ cal sampling places are the followings:

- reactor cap /Fig.8/,
- steam generator primary header walls and cover /fig.9/,
- main primary circulating pump's wheel and housing /fig.10/,
- control rod drives,
- steam generator tubing... etc.

"In-line measurement" places on the main circulating pipeline /4 places on each loop/ core given on fig.11.

First experience shows that in the primary circuit the Co-58, Co-60 isotopes dominate /fig.12/. Abbreviations used for different primary circuit parts in fig.12:

- R.Cap - reactor cap /cover/
- CRD - control rod drives
- H.Head - hot header of steam generator /cover/,
- H.leg - hot leg piping
- SG tubes - steam generator heat exchange tubes,
- C.Head - cold header of steam generator /cover/,

\*/ Measurements were calibrated on a reserve 2m long piece of primary pipeline by moving a source of known activity along the internal perimeter of the tube [17].

PRIMARY COOLANT CHEMISTRY HISTORY  
PAKS-I and II units , cycle-1, 1983-84

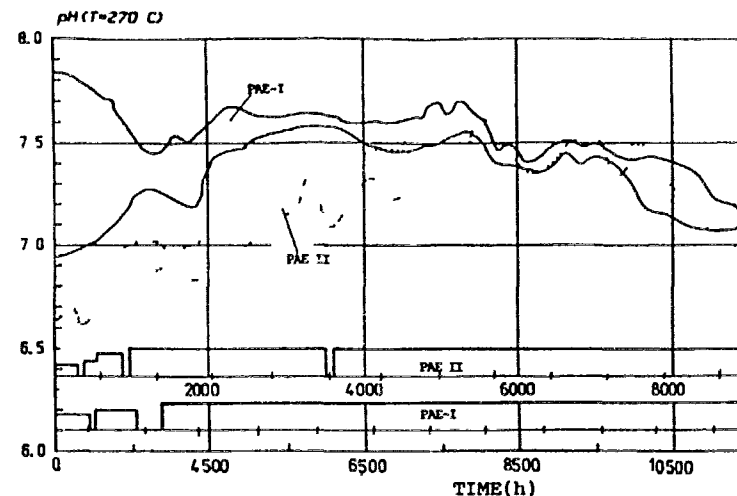


Figure 5. Comparison of pH(T=270 C) calculated using Meek [11] data for the first cycles of PAKS-I and II units versus time.

PRIMARY COOLANT CHEMISTRY HISTORY  
PAKS-I and II units , cycle-1, 1983-84

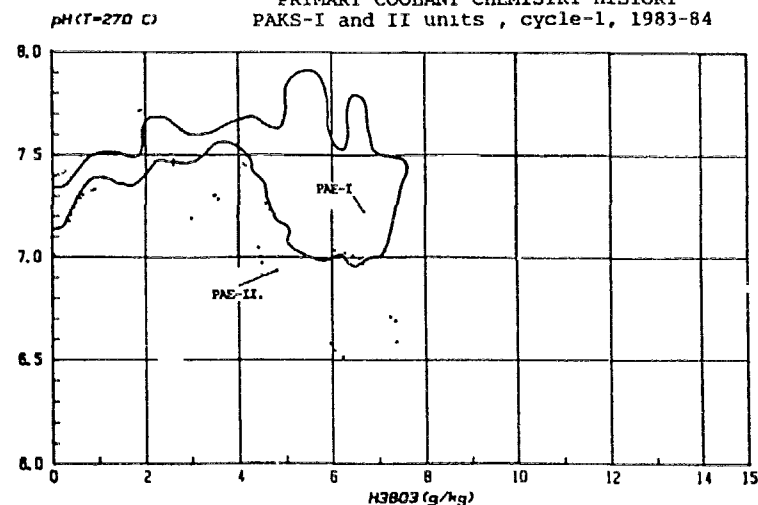


Figure 6. Comparison of pH(T=270 C) calculated using Meek [11] data for the first cycles of PAKS-I and II units versus boric acid

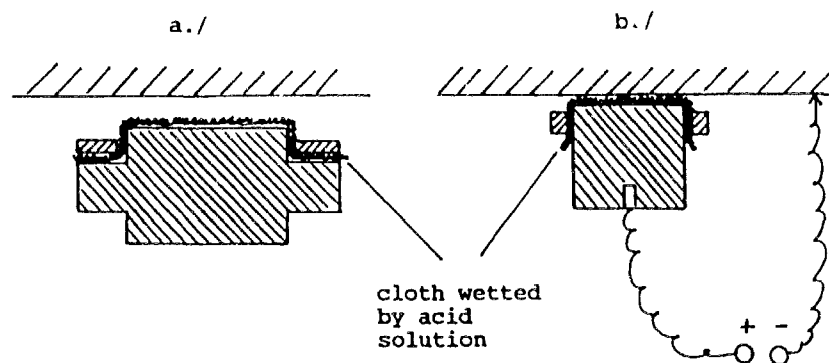


Figure 7. Devices used for sample-taking of oxide layer from internal surfaces of the primary circuit equipment.  
a./ mechanical sampling device  
b./ electrochemical sampling device

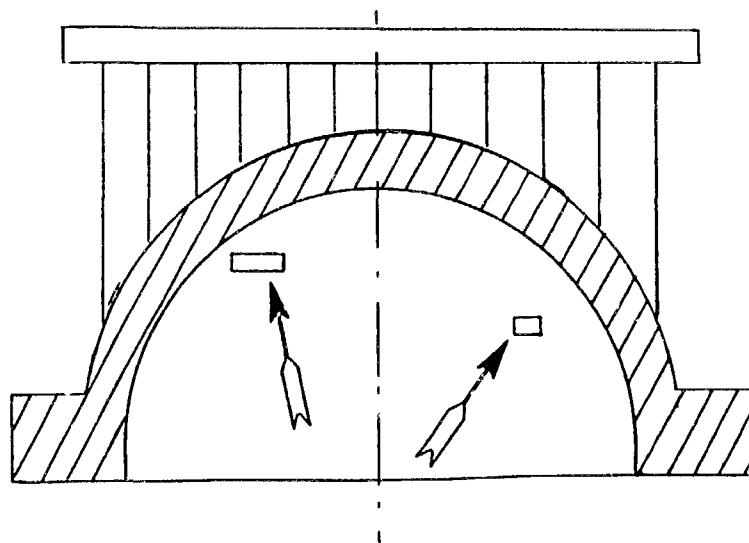


Figure 8. Typical sample-taking places at the reactor cap of VVER-440 reactors.

P Pump housing } - main primary pump housing,  
C.leg } - cold leg piping,  
P.Pump } - cold leg piping at the main primary  
C.leg } pumps,  
P.Pump } - bladed wheel of the main primary  
wheel } pumps.

Share of fission products and non-stainless steel activated products in doses are not very significant except Ag-110 m /see fig.13/.

Results of surface activity data collection of unit-1 of Paks plant are given in fig. 14-18. Abbreviations and legend on these figures is given as:

#### PAKS-1 measurements:

- - cold leg main primary pipeline,
- ⊙ - hot leg main primary pipeline,
- ⊕ - SG tubes,
- ① - reactor cover,
- ② - neutron detector casing
- I - cold leg range including main primary pumps cold leg piping, SG header covers,

#### OTHER DATA:

- + - data of other PWR nuclear power plants including different surfaces:
  - Rheinsberg /GDR/,
  - Armjanskoe-1 /SU/,
  - Kola-1 /SU/,
  - Novovoronezh /SU/,
  - R-900 /France/,
  - Plant A,B /USA/,
- ....- average data of other VVER-440 reactors,
- - early model's calculated equilibrium.

Figures 14-18 high-light that the Co-58 and Co-60 activities of PAKS-1 unit are considerable lower than those of other /first of all western/ nuclear power plants, which could be attributed to absence of cobalt containing alloys in the primary circuit of VVERs.

The greatest activities in the primary circuit in PAKS-1 were near the main primary pumps. Even though a great scatter of data is observed, it is remarkable that the surface activity of steam generator heat exchange tubes is lower than that of the rest of surfaces.

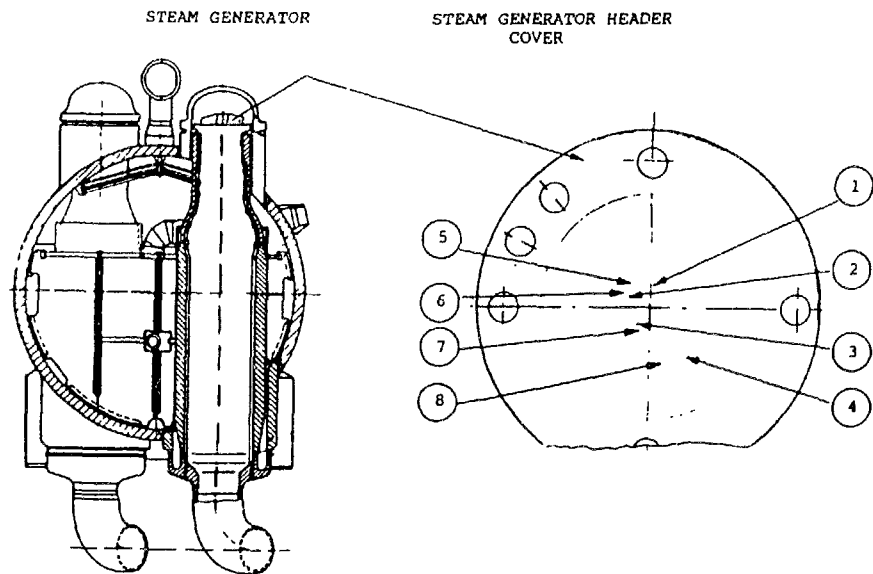


Figure 9. Typical sample-taking places at the steam generator primary header and its cover.

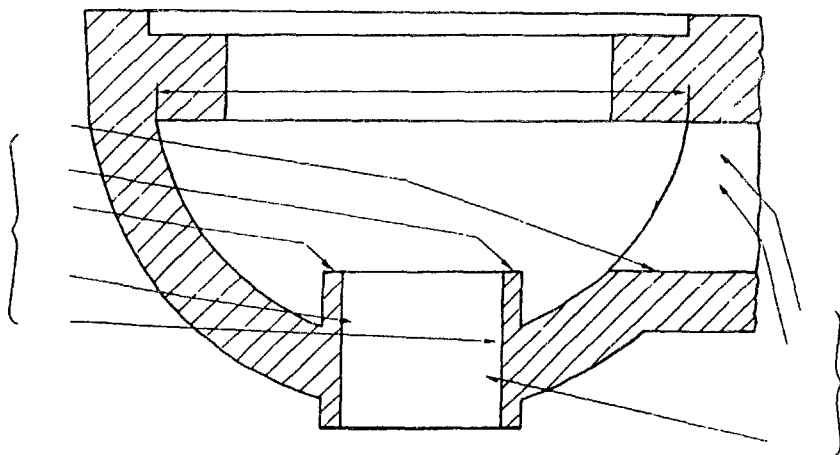


Figure 10. Typical sample-taking places at the housing of main primary circulating pumps.

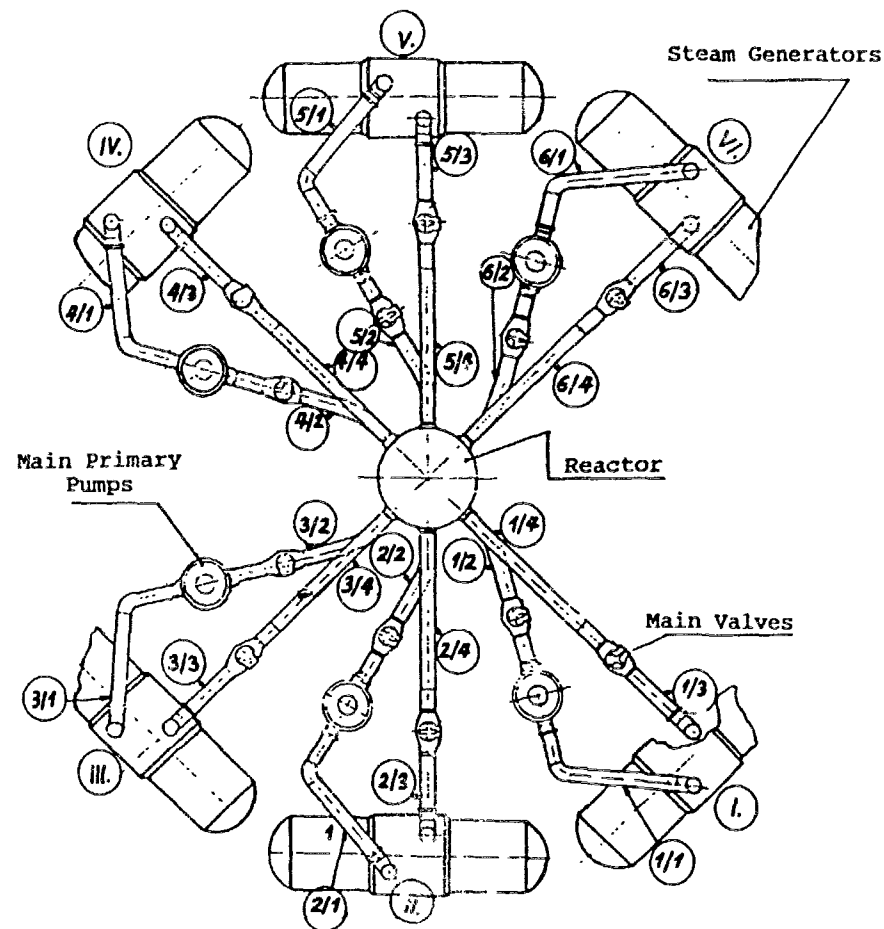


Figure 11. Places for "in-line" measurements on the main circulating pipelines of VVER-440 reactors. (Measuring the gamma radiation flux by collimated HpGe detector outside the tube to determine surface activities on inside walls.

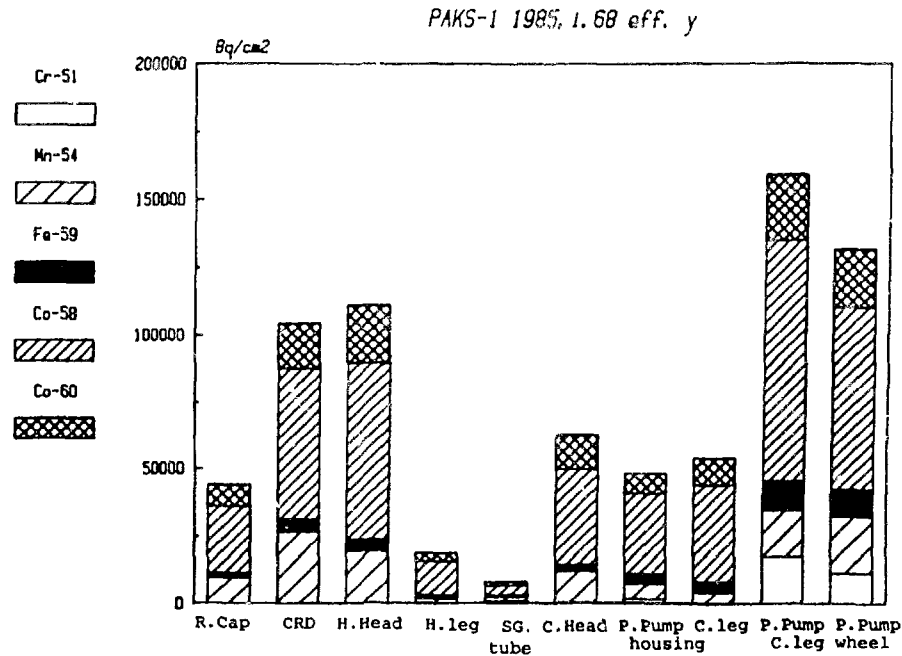


Figure 12. Activated stainless steel corrosion products on different primary circuit surfaces in case of unit-1 of PAKS Nuclear Power Plant after the 2nd cycle (1.68 eff. full power years)

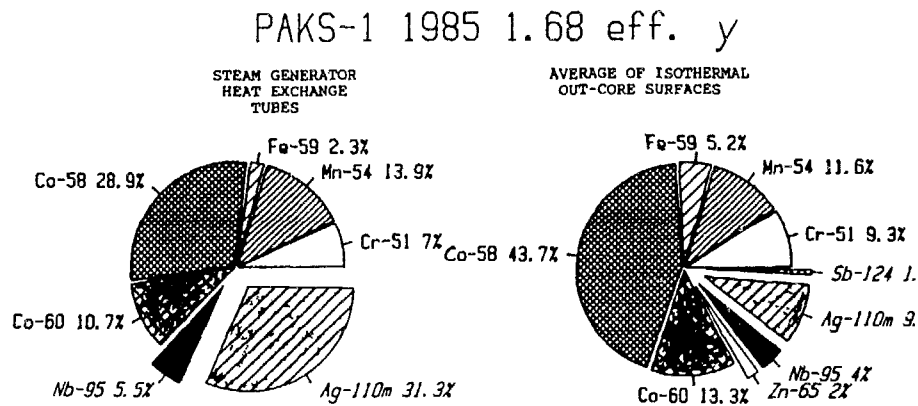


Figure 13. Proportions of stainless steel and non-stainless steel originated activated corrosion products in the primary circuit of unit-1 of PAKS Nuclear Power Plant after the 2nd cycle (1.68 eff.f.p.years).

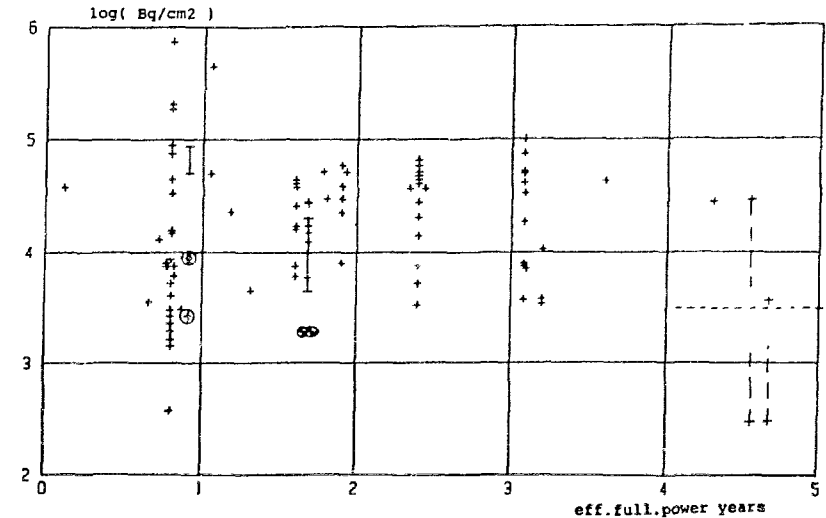


Figure 14. Mn-54 surface activities of different parts of the primary circuit at Unit-1 of PAKS Nuclear Power Plant after the first and second cycles compared to surface activities of other PWR and VVER type reactors.  
Legend See p 82

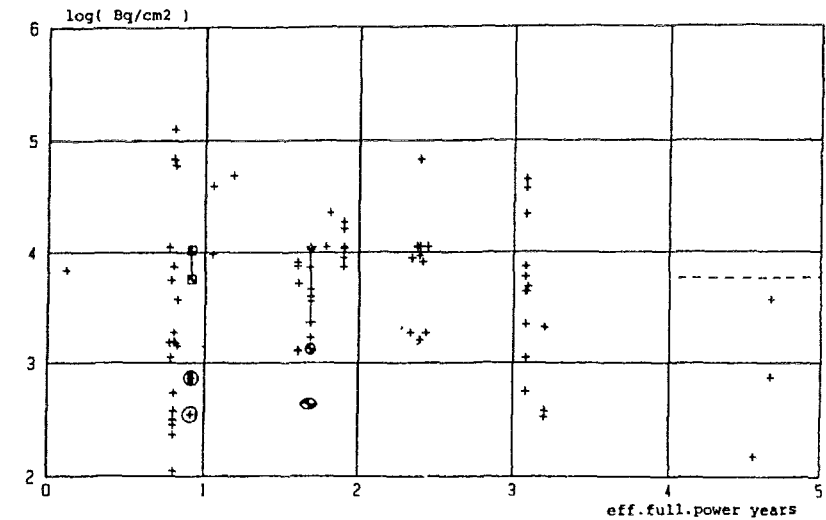


Figure 15. Fe-59 surface activities of different parts of the primary circuit at Unit-1 of PAKS Nuclear Power Plant after the first and second cycles compared to surface activities of other PWR and VVER type reactors.  
Legend See p 82

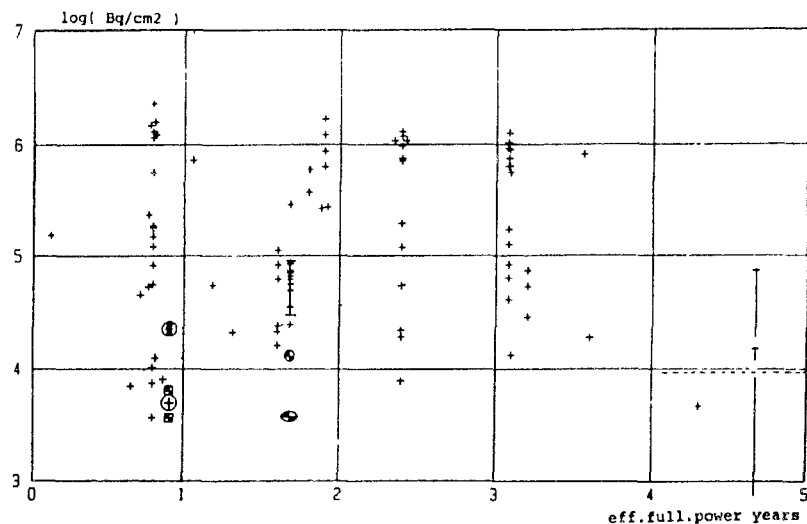


Figure 16. Co-58 surface activities of different parts of the primary circuit at Unit-1 of PAKS Nuclear Power Plant after the first and second cycles compared to surface activities of other PWR and VVER type reactors.  
Legend: See p.82.

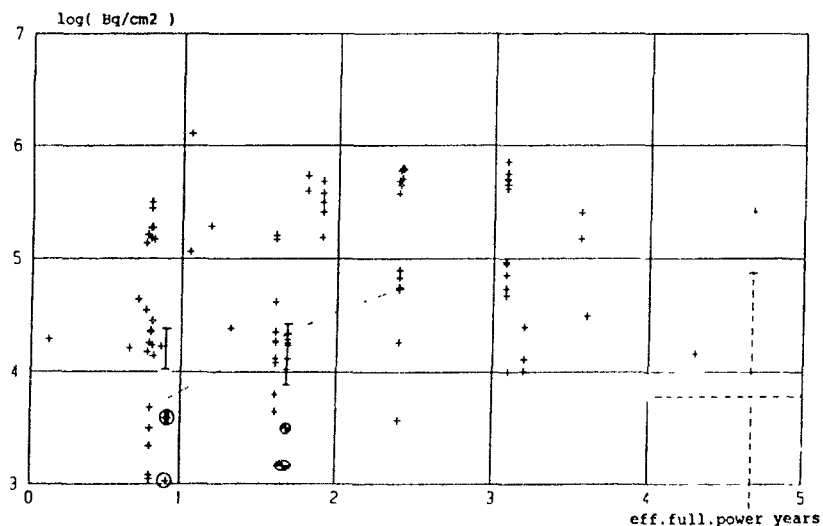


Figure 17. Co-60 surface activities of different parts of the primary circuit at Unit-1 of PAKS Nuclear Power Plant after the first and second cycles compared to surface activities of other PWR and VVER type reactors.  
Legend: See p.82

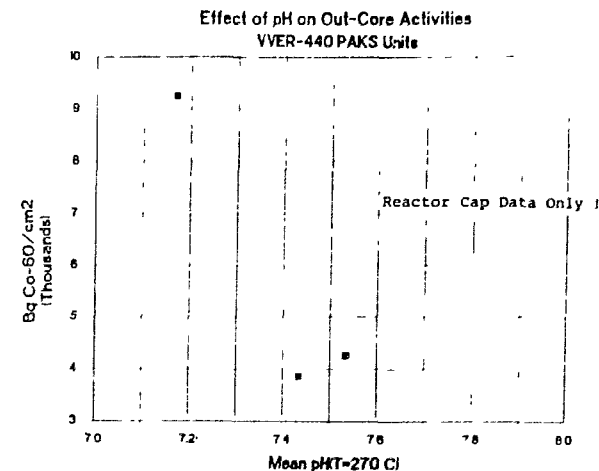


Figure 18. Correlation between the out-core surface activities and mean pH(T=270 C) during the first cycles of PAKS-1,2 and 3 units. pH(T=270 C) values are based on early Meek data and are therefore overestimated.

#### 6. CORRELATION OF SURFACE ACTIVITIES WITH PRIMARY COOLANT CHEMISTRY

As it was mentioned in ch. 2-4, dependence of surface activities on primary coolant chemistry parameters is expected. The first preliminary analysis was done using the old /Meek, [11] / data for pH<sub>T</sub> calculations therefore pH<sub>T</sub> values on fig. 18 are overestimated by 0,3-0,5 pH units. Apart from the overestimation fig.18 reflects the main trend showing a serious decrease of surface activities with increasing pH<sub>T</sub>. It should be noted, that the data base for final conclusions is at present limited /only reactor cover data of first cycles of PAKS-1, 2 and 3 units were analysed/, therefore these data should be treated with some care. The evaluation of activities of other surfaces and 2nd cycles of Paks units is at present under preparation. The water-chemistry will be evaluated by the Mesmer based pH<sub>T</sub> calculations.

#### 7. CONCLUSIONS

1. Primary coolant chemistry has a decisive role on corrosion product activity build-up on out-core primary circuit surfaces.
2. Most of the present primary coolant quality specifications apply the Base ≅ f /Boric acid/ type "cor-related" water chemistry.
3. Systematic data collection of Paks Nuclear Power Plant units proved that a correlation between high temperature pH and out-core corrosion product activities may exist.

The calculational algorithm in this appendix is given for the Mesmer method [12].  
The early calculational method /Meek [11] / is obtained if  $K_2 = 0$  is choosen.

## CONTENT OF CELLS:

lines	columns	A	B	C	D	E
1	Titles					
2						
3						
4						
5						
6				C6 = A		E6 = $K_W$
7						E7 = $K_K$
8						E8 = $K_N$
9				C9 = D		E9 = $K_1$
10				C10 = E		E10 = $K_2$
11				C11 = a		E11 = $K_3$
Where:						
		$K_W$ = ion product of water			$A = 61,81.6.K_3$	
		$K_K$ = dissotiation constant of KOH				
		$K_N$ = " " of $NH_3$				
		$K_1$ = first dissotiation constant of $H_3BO_3$			$D = 0,001.K_N/17$	
		$K_2$ = second " " "			$E = 0,001.K_K/39,1$	
		$K_3$ = third " " "			$a = 2.K_2/(3.K_3)$	

A/2

Content of columns for calculation of primary coolant data  $pH_T$ . Each line  
represents one set of primary coolant data. /X- means the index of lines/

Column	Mathematical form	VisiCalc form
A	Year, Month	$A_x$ /plant data/
B	Day, hour	$B_x$ /plant data/
C	Calendar time since the beginning of each month /h/ 24	$\times (INT(B_x) - 1) + (B_x - INT(B_x)) \times 100$
D	Calendar time since the previous data line /h/	$C_x - C_{x-1}$
E	Calendar time since the start of cycle /h/	$E_{x-1} + D_x$
F	Boricacid concentration / $Q_B$ , g/kg/	$F_x$ /plant data/
G	Sodium concentration /mg/kg/	$G_x$ / " /
H	Potassium " /mg/kg/	$H_x$ / " /
I	Lithium " /mg/kg/	$I_x$ / " /
J	Equivalent potassium concentration / $Q_K$ , mg/kg/	$39,1 \times (G_x/23 + H_x/39,1 + I_x/6,94)$
K	$NH_3$ concentration / $Q_N$ , mg/kg/	$K_x$ /plant data/

Content of columns for calculation of primary coolant data /pH<sub>T</sub>/

Column	Mathematical form	VisiCalc form
N	$[H^+]$ -hydrogen ion concentration before the next iteration	Before the first calculation: $10^{-7}$ at further calculations: $10^{-R_x}$
O	$[HB1] = \frac{a^3}{27} - a \cdot \left( \frac{[H^+] + K_1}{18 \cdot K_3} \right) - \frac{Q_B [H^+]}{61,81.6 \cdot K_3}$	$\$C\$11^{3/27} - \$C\$11 * (N_x - \$E\$9) / (18 * \$E\$11) - F_x * N_x / \$C\$6$
P	$[HB2] = \left[ \left( \frac{[H^+] + K_1}{9 \cdot K_3} - \frac{a^2}{9} \right)^3 + [HB1]^2 \right]^{1/2}$	$@SORT(((N_x + \$E\$9) / \$E\$11 - \$C\$11^2)^{3/729} + O_x^2)$
Q	$[HB] = \left( -[HB1] + [HB2] \right)^{1/3} + \left( -[HB1] - [HB2] \right)^{1/3} - a/3$	$-O_x + P_x / ^{1/3} / + ( -O_x - P_x )^{1/3} - \$C\$11/3$

Content of columns for calculation of primary coolant data /pH<sub>T</sub>/

Column	Mathematical form	VisiCalc form
R	$pH_T^{next} = -\frac{1}{2} \log_{10} \frac{K_V + K_1 [HB] + K_2 [HB]^2 + K_3 [HB]^3}{1 + \frac{K_N \frac{0.001}{17} Q_N}{(K_N [H^+] + K_V)} + \frac{K_K \frac{0.001}{39.1} Q_K}{(K_K [H^+] + K_V)}}$	$-(0.5 * LGT((\$E\$6 + \$E\$9 * Q_x + \$E\$10 * Q_x^2 + \$E\$11 * Q_x^3) / (1 + \$C\$9 * K_x / (\$E\$8 * N_x + \$E\$6) + \$C\$10 * J_x / (\$E\$7 * N_x + \$E\$6))))$
S	$pH_t^{next} - pH_t^{previous}$	$R_x + LGT(N_x)$
T	$pH_t^{next} \cdot \Delta t$	$R_x * (D_x / 2 + D_x + 1/2)$



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## GOOD PRACTICES OF MAN-REM REDUCTION IN PHWRs

K S VENKATESWARLU, P K MATHUR,  
S.V. NARASIMHAN, G VENKATESWARAN  
Water Chemistry Division,  
Bhabha Atomic Research Centre,  
Trombay, Bombay,  
India

### Abstract

Good practices for man-rem reduction in PHWRs are described based on the effective control of both source and recipient terms. Various important steps viz., proper structural materials selection, preconditioning, maintenance of low dissolved  $O_2$  and high narrow range pH control for the primary coolant, increased rate of coolant purification and frequent chemical decontamination for control of radiation field build-up on out-of-core surfaces have been discussed. Quick detection of failed fuel and its removal are described for minimising the levels of fission products.

### 1 Introduction

The contribution to plant radiation levels depends on the deposition of radioactivity onto the surfaces of components in the heat transport circuits and depends on two major terms. They are

- 1 Source term - the concentration of  $^{60}Co$  (in the coolant) flowing over the surface
- 2 Recipient term - the ability of the surface to take up radioactivity

Good practices for man-rem reduction in PHWRs are based on the control of the above mentioned terms with the help of the following parameters

- 1 Chemistry
- 2 Material of Construction
- 3 Location of failed fuel and removal
- 4 Decontamination

### 2 Source of radiation fields

The major cause of radiation fields in PHWRs is the radionuclide  $^{60}Co$ , though fission product nuclides and  $^{65}Zn$  have been dominating in some specific reactors due to variety of other reasons like the presence of failed fuel and loose Zinc. The primary system structural alloys (steels and high Ni

alloys) corrode rather slowly in the primary coolant and are transported as both soluble and insoluble matter (crud). The corrosion products that are deposited on fuel surfaces, during their residence time, become radioactive due to n irradiation.

e.g.

$^{59}Co (n, \gamma) ^{60}Co$

Source of  $^{59}Co$

- 1 trace Co impurity in structural alloys
- 11 high cobalt hard facing alloys used in valves

The radioactive corrosion products are released from the fuel surface and get deposited on out-of-core surfaces after transportation by the coolant.

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 radioactivity in the outer layers.

### Material of construction currently used in PHT system of PHWRs

1 Piping (Feeders, headers etc.)	Carbon steel
2 Core components (fuel clad, coolant tube etc.)	Zircaloy - 2
	Zircaloy - 4
	Zr-2.5 Nb alloy
3 SG tube material	Monel - 400
	Inconel - 600
	Incoloy - 800

### Presently practised coolant chemistry with reducing environment

pH	10.3 - 10.7 (with $Li_2O$ 0.35 - 1.4 mg/kg of $D_2O$ )
Diss $H_2$	3 - 10 cc/kg ( $D_2O$ removal)

### 3 Material selection

The source term can be effectively controlled by a suitable material selection and by lowering the content of cobalt ( $^{59}Co$ )

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

## 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.

## Dependence on Chemistry

In the temperature range 250 - 315° C and pHs 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/m<sup>2</sup>. 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 radiolysis due to oxidising radicals. Hence pH > 10.7 should be avoided.

## Diss O<sub>2</sub> effects

The oxygen excursion has a direct influence on

- a) CS pitting, corrosion
- b) Attack of Monel tubes of boilers
- c) SCC of austenitic alloys
- d) Zirconium alloy corrosion

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 O<sub>2</sub>/kg D<sub>2</sub>O by H<sub>2</sub> injection.

The recipient term and source term are interlinked and is dictated by the water chemistry. The interdependency is system specific and may also be a function of features like preconditioning, decontamination and chemistry excursion in a single system.

## 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. This reduces the radiation build up during actual operation. An improvement in the quality of magnetite layer by carrying out hot conditioning under controlled chemistry conditions. Introduction of EDTA hotconditioning and/or Zinc injection passivation (ZIP) could provide 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.

## 5 Decontamination

Annual decontamination removes the deposited radioactive corrosion products from out of core surfaces enabling

- 1 Low radiation penalty to personnel to carry out maintenance activities
- 11 Reduced radiation exposure to O/M personnel during subsequent regular plant operations
- 111 As a result of increase in the efficiency of preventive maintenance of critical components, plant life extension is achieved
- 1V In systems where fuel failures have been dominating the radiation levels, decontamination is the only solution

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 result in a system in which the corrosion of materials and the activated corrosion product are both minimised.

## 6 Failed fuel detection and removal

PHWR design feature allows on-line refueling. It has facility for failed fuel detection and removal of fuel bundles as soon as the clad leak occurs. Since there are technical specification limits on radiation levels on systems with failed fuel (< 100 µCi <sup>131</sup>I/kg D<sub>2</sub>O), the contribution to man-rem problem due to failed fuel is not anticipated as against in BWR. In fact with a sheath failure rate per fuel bundle of about 0.1%, the contribution to man-rem problem from fission products radiation will only be marginal.

However, if some minor leaky pins have been left in core due to some other limitations, it could lead to high levels of fission products (<sup>95</sup>Zr-<sup>95</sup>Nb etc.) overshadowing the contribution from <sup>60</sup>Co. Implementation of effective fuel failure detection methods and removal of failed fuel are the only answers. Should such a contamination occur in a system, increased purification and decontamination are suggested for system cleaning and reduction of radiation levels.

## 7 Conclusion

Thus, sequentially the following steps should ensure good practices for man-rem reduction in PHWRs

- 1 Select materials with low Co content
- 2 Allow proper preconditioning of metal surfaces prior to nuclear run
- 3 Ensure reliable operating chemistry
- 4 Employ good filter purification circuit
- 5 Execute planned biennial or triennial decontamination followed by conditioning, if any

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## ASSESSMENT OF FAILED FUEL AND TRAMP URANIUM BASED ON THE ACTIVITY OF FISSION PRODUCTS IN THE PRIMARY CIRCUIT

Jae-Choon YANG

Department of Physics,  
Chungnam National University,  
Taejon, Republic of Korea

### Abstract

We have proposed a model for the nuclear fuel state of the operating power reactor from the physical characteristics of nuclear fission products which have been produced by nuclear reaction between neutron and uranium-235

The model equation for nuclear fission products release has been split into six independent steps 1) calculation of the fission products generation inside the solid nuclear fuel, 2) release from the fuel to the fuel surface in three different ways, 3) release between the fuel surface and gap 4) release from the defective nuclear fuel to the reactor coolant, 5) mass balance in the coolant taking into account the purification rate 6) separation of fission products sources with two parts i.e. fuel and tramp uranium

We have solved the equation of the model calculated the activity of fission products released from the defected fuel to coolant and put the experimental activity data of the nuclear fission products in the primary coolant to determine the number of defective fuel and amount of tramp uranium by using the computer

The measurement and analysis of nuclear fission products in the primary coolant of nuclear power reactors have been carried out at the pressurized water reactor, Korea Nuclear Unit 2, 7 and 8 We have used the iodine isotopes among the nuclides of fission products

The analysis results have been well agreed with the results of diffusion model and of kinetics model

### 1 Introduction

Considerable effort has been directed toward understanding fission products release from defected fuel element Physical release processes for defective fuel have generally been deduced from analysis of coolant activity measurements in nuclear power plants and of model equation calculation

The fission products release model have been proposed by many researchers

The release of fission products within the fuel pellet and at the its surface may occur in the three different ways recoil, knockout and diffusion. In the interspace fuel pellet and cladding, the kinetic model[1] had been proposed by Beraha et al. The diffusion model[2] had also been proposed by Morrison et al.

The comparison of diffusion model with kinetic model[3] had been performed by Lewis et al. T. Aoki had proposed the graphical method[4] which had analyzed the number of defected fuel and the amount of tramp uranium.

We have set up new model which has calculated the generation of fission products in the solid fuel, the release from the fuel to the gap, and the release of fission products into the reactor coolant.

The measurement and analysis of fission products in the primary coolant of nuclear power reactor have been carried out at the full power operating condition. We have analyzed the defected fuel and tramp uranium by comparison of the measured activity with calculated activity.

Among the fission products we have mainly focused to the iodine isotopes. We have analyzed the radioactivity of fission products with continuous time intervals to obtain the optimum cooling time of the samples.

The study has been carried out at the pressurized water reactor, Korea Nuclear Unit 2, 7 and 8.

## 2 Model Equation

The model equation for fission products release have been split into six independent steps:

- 1) calculation of the fission products source term on the fuel
- 2) release from the fuel to the gap in three different ways, such as migration, recoil and knockout
- 3) release between the fuel surface and gap
- 4) release from the defective nuclear fuel to the reactor coolant
- 5) mass balance in the coolant taking into account the purification rate
- 6) separate the fission products with two parts, the one is the release from the fuel and the other is from the tramp uranium

### 2.1 Source Term Calculation

The rate at which the amount of nuclide  $i$  changes as a function of time ( $= dB_i/dt$ ) is described by a non homogeneous first-order ordinary differential equation as follows[5]:

$$\frac{dB_i}{dt} = \sum_{j=1}^N l_{ij} \lambda_j B_j + \phi \sum_{k=1}^N f_{ik} \sigma_k B_k - (\lambda_i + \phi \sigma_i + r_i) B_i + F_i \quad (1)$$

$i = 1, 2, 3, \dots, N$

where

- $B_i$  atom density of nuclide  $i$
- $N$  number of nuclides
- $l_{ij}$  fraction of radioactive disintegration by other nuclides, which leads to formation of species  $i$
- $\lambda_j$  radioactive decay constant
- $\phi$  position- and energy- averaged neutron flux
- $f_{ik}$  fraction of neutron absorption by other nuclides which lead to formation of species  $i$
- $\sigma_k$  spectrum-averaged neutron absorption cross section of nuclide  $k$
- $r_i$  continuous removal rate of nuclide  $i$  from the system
- $F_i$  continuous feed rate of nuclide  $i$

Since  $N$  nuclides are being considered, there are  $N$  equations of the same general form one for each nuclide. This equation is solved by employing the matrix exponential method. In the homogeneous case the system of equations that is being solved can be denoted by

$$\underline{B} = \underline{A} \underline{B} \quad (2)$$

where

- $\underline{B}$  time derivative of nuclide concentrations( a column vector )
- $\underline{A}$  transition matrix containing the transformation rates
- $\underline{B}$  nuclide concentrations( a column vector )

This equation has the solution

$$B(t) = \exp(\lambda t) B(0) \quad (3)$$

where

$B(t)$  : concentration of each nuclide at time  $t$

$B(0)$  : vector of initial nuclide concentrations

$t$  : time at end of time step

## 2.2. Release in the Fuel

### 2.2.1. Kinetics Model

The release of fission products from fuel may occur in three different ways.

#### 2.2.1.1. Recoil

For fission occurring at a distance from the fuel surface of less than the average length of the fission fragment in  $UO_2$ , fission products may be released directly from the fuel.

The number of nuclide  $i$  per second by recoil is<sup>(4)</sup>

$$N_{Ri} = B_i \cdot \frac{R}{d} \cdot \frac{h}{R_s} \left( 2 - \frac{h}{R_s} \right) \quad (4)$$

where

$d$  : diameter of pellet

$h$  : gap between the pellet and clad

$R$  : recoil length in the  $UO_2$  fuel

$R_s$  : recoil length in the gap

If cladding material is defective and fuel material is exposed to the water, this equation is

$$N_{Ri} = B_i \cdot \frac{R}{d} \quad (5)$$

### 2.2.1.2. Knockout

A fission fragment that passes through the fuel surface ejects an elementary volume and fission products are included in this volume. The number of nuclide  $i$  by knockout is given by

$$N_{ki} = \frac{4}{\pi} \cdot \frac{R}{d^3 l_0} V_m \cdot B_i \frac{\lambda_i F_0 P}{(\lambda_i + \nu_{1i})} \quad (6)$$

$l_0$  : length of fuel rod

$V_m$  : ejection volume

$F_0$  : fission/MWt.s

$P$  : power(MWt)

$\nu_{1i}$  : release constant in the fuel

### 2.2.1.3. Migration

In accordance with the work of Bayer and Hahn<sup>[6]</sup> of stable gases, we assume only the fraction  $f_m$  of the nuclide quantity in the fuel participates in migration;  $f_m$  depends only on the species in the fuel is given by

$$\frac{dN_m}{dt} = f_m B_i - (\lambda_i + \nu_{1i}) N_{mi} \quad (7)$$

The rate of release for this migrating fraction is assumed to be proportional to the concentration in the fuel, such that

$$N_{Di} = \nu_{1i} N_{mi} \quad (8)$$

### 2.2.2. Diffusion Model

The number of nuclides which have been released from nuclear fuel by diffusion are

$$N_{fi} = 3 \left( \frac{D'}{\lambda_i} \right)^{1/2} H_i B_i \quad (9)$$

where  $D'$  is an empirical diffusion coefficient and  $H_i$  is the correction factor.

## 2.3 Release in the Gap and in the Coolant

### 2.3.1 Kinetics Model

The mass balance in the gap is given by<sup>[1]</sup>

$$\frac{dN_{g1}}{dt} = (N_{R1} + N_{K1} + N_{D1}) - (\nu_{21} + \lambda_1 + \sigma_1 \phi) N_{g1} \quad (10)$$

where  $\nu_{21}$  is release constant in the gap<sup>[4]</sup>

For a failed element the release rate of the nuclide through the failure is proportional to the concentration in the gap

$$N_{C1} = \nu_{21} N_{g1} \quad (11)$$

The concentration of fission products in the reactor coolant is given by

$$\frac{dN_{C1}}{dt} = N_{C1} - (\lambda_1 + \beta_1 + \sigma_1 \phi) N_{C1} \quad (12)$$

where  $\beta_1$  is the total purification rate

### 2.3.2 Diffusion Model

The diffusion equation of the fission products in the fuel-to sheath gap is

$$\frac{\partial N_{g1}}{\partial t} - D \nabla^2 N_{g1} - \lambda_1 N_{g1} + N_{f1} \quad (13)$$

where  $D$  is the diffusion coefficient in the fuel to sheath gap

The rate of release  $N_{C1}$  of fission products into coolant is given by the surface integral of the flux, which has reached the defect according to Fick's law of diffusion

$$N_{C1} = D \int_S \vec{\nabla} N_{g1} \cdot d\vec{A} \quad (14)$$

$d\vec{A} = \hat{n} dS$ , and  $\hat{n}$  is the unit normal into the defect face from surface element  $dS$

## 2.4 Tramp Uranium

There are two kinds of fission products source in the primary coolant of the nuclear power reactor. The one is the fission products from defected fuel element, the other is the fission products from tramp uranium in the reactor core.

So we can consider separately the fission products from defected fuel and from tramp uranium,

$$q_1 = \frac{N_{C1} \lambda_1}{W_p} \quad (15)$$

$$P_1 = \left( \frac{\lambda_1}{\lambda_1 + \beta} \right) \frac{N_{R1}}{W_p} \quad (16)$$

$$m_1 = q_1 D + P_1 \theta \quad (17)$$

where

$W_p$  mass of primary coolant

$m_1$  measured activity of nuclide 1

$D$  number of defected fuel

$\theta$  mass of tramp uranium

## 3 Result

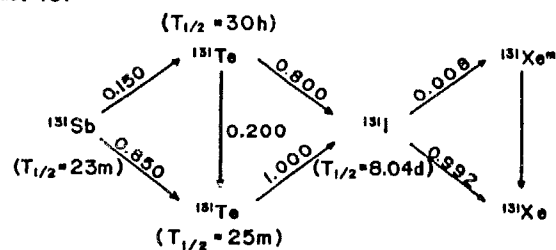
### 3.1 Calculation of Fission Products

The generation of fission products in the solid nuclear fuel have been calculated by equation (1). The solution method of this equation is the matrix exponential technique. The half-life, the cross section and the decay chain data of the fission products to be used in the calculation have been extracted from the ENDF/B-V, Fission Product Library. The decay chain data of the fission products are shown in the Table I and Fig. 1. The calculated results have been shown in the Tables II and III.

Table I. Nuclear Data Used in the Calculation

Isotope	Half-life (s)	Independent fractional yield(%)	Daughter	Branching ratio
$^{131}\text{Sb}$	$1.380 \times 10^3$	$1.59 \times 10^0$	$^{131}\text{Te}^m$	0.150
			$^{131}\text{Te}$	0.850
$^{131}\text{Te}^m$	$1.080 \times 10^5$	$1.90 \times 10^{-1}$	$^{131}\text{I}$	0.800
			$^{131}\text{Te}$	0.200
$^{131}\text{Te}$	$1.500 \times 10^3$	$1.19 \times 10^{-1}$	$^{131}\text{I}$	1.000
$^{131}\text{I}$	$6.947 \times 10^5$	$4.15 \times 10^{-3}$	$^{131}\text{Xe}^m$	0.008
			$^{131}\text{Xe}$	0.992
$^{133}\text{Sb}$	$1.440 \times 10^2$	$2.08 \times 10^0$	$^{133}\text{Te}^m$	0.720
			$^{133}\text{Te}$	0.280
$^{133}\text{Te}^m$	$3.324 \times 10^2$	$2.88 \times 10^0$	$^{133}\text{I}$	0.870
			$^{133}\text{Te}$	0.130
$^{133}\text{Te}$	$7.470 \times 10^3$	$1.32 \times 10^0$	$^{133}\text{I}$	1.000
$^{133}\text{I}$	$7.488 \times 10^4$	$1.65 \times 10^{-1}$	$^{133}\text{Xe}^m$	0.024
			$^{133}\text{Xe}$	0.976

## \* Mass 131



## \* Mass 133

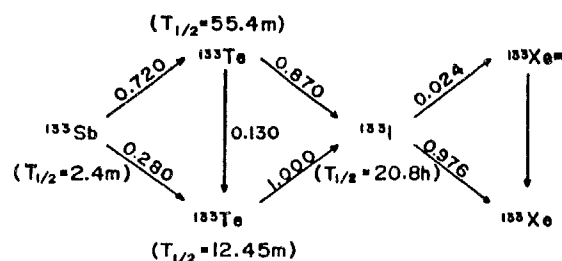


Fig. 1. Nuclear Fission Products and Its Decay Chains.

Table II. The Calculated Radioactivity of Iodine Isotopes in the Reactor Fuel of KNU2. ( $\mu\text{Ci/g}$ )

Irradiation time Isotopes	32.3d	77.6d	150.0d	300.0d	397.0d
$^{131}\text{I}$	$8.558 \times 10^5$	$9.401 \times 10^5$	$9.571 \times 10^5$	$9.709 \times 10^5$	$9.793 \times 10^5$
$^{132}\text{I}$	$1.377 \times 10^6$	$1.401 \times 10^6$	$1.411 \times 10^6$	$1.415 \times 10^6$	$1.423 \times 10^6$
$^{133}\text{I}$	$2.118 \times 10^6$	$2.122 \times 10^6$	$2.109 \times 10^6$	$2.027 \times 10^6$	$2.057 \times 10^6$
$^{134}\text{I}$	$2.382 \times 10^6$	$2.376 \times 10^6$	$2.349 \times 10^6$	$2.291 \times 10^6$	$2.267 \times 10^6$
$^{135}\text{I}$	$1.972 \times 10^6$	$1.974 \times 10^6$	$1.960 \times 10^6$	$1.926 \times 10^6$	$1.914 \times 10^6$

Table III. The Calculated Radioactivity of Iodine Isotopes in the Reactor Fuel of KNU7. 8. ( $\mu\text{Ci/g}$ )

Irradiation time Isotopes	27.5d	63.2d	128.0d	255.9d	359.5d
$^{131}\text{I}$	$9.231 \times 10^5$	$1.037 \times 10^6$	$1.059 \times 10^6$	$1.075 \times 10^6$	$1.085 \times 10^6$
$^{132}\text{I}$	$1.518 \times 10^6$	$1.550 \times 10^6$	$1.562 \times 10^6$	$1.567 \times 10^6$	$1.575 \times 10^6$
$^{133}\text{I}$	$2.337 \times 10^6$	$2.334 \times 10^6$	$2.329 \times 10^6$	$2.289 \times 10^6$	$2.272 \times 10^6$
$^{134}\text{I}$	$2.628 \times 10^6$	$2.624 \times 10^6$	$2.593 \times 10^6$	$2.529 \times 10^6$	$2.502 \times 10^6$
$^{135}\text{I}$	$2.176 \times 10^6$	$2.180 \times 10^6$	$2.165 \times 10^6$	$2.127 \times 10^6$	$2.114 \times 10^6$

From these calculated values, the release of fission products to the fuel surface have been calculated.

## 3.2. Release in the Fuel

The fission products which are released from the fuel to the fuel surface have been calculated by recoil, knockout, migration and diffusion. The results are shown in Table IV.

## 3.3. Release in the Gap and in the Coolant

The fission products which transport in the fuel-to-sheath gap have been calculated, and the fission products which release from the defective nuclear fuel to the coolant have been calculated by our model and by the diffusion model. The results are shown in Table V. The concentrations of fission products in the reactor coolant have been calculated by taking into account the purification rate. This results are shown in Table VI.



Table IV Calculated Activity by Recoil Knockout and Migration ( $\mu\text{Ci}/\text{rod}$ )

Site	Isotope	Recoil	Knockout	Migration
KNU2	$^{131}\text{I}$	$1.849 \times 10^6$	$2.449 \times 10^5$	$4.456 \times 10^6$
	$^{133}\text{I}$	$4.075 \times 10^6$	$5.463 \times 10^5$	$1.071 \times 10^6$
	$^{135}\text{I}$	$3.787 \times 10^6$	$5.083 \times 10^5$	$3.210 \times 10^5$
KNU7-8	$^{131}\text{I}$	$1.959 \times 10^6$	$4.204 \times 10^5$	$4.520 \times 10^6$
	$^{133}\text{I}$	$4.308 \times 10^6$	$9.352 \times 10^5$	$1.084 \times 10^6$
	$^{135}\text{I}$	$4.005 \times 10^6$	$8.707 \times 10^5$	$3.250 \times 10^5$

Table V Calculated Activity in the Fuel to cladding Gap ( $\mu\text{Ci}/\text{rod}$ )

Site	$^{131}\text{I}$		$^{133}\text{I}$	
	Our model	Diffusion model	Our model	Diffusion model
KNU2	$6.263 \times 10^6$	$6.747 \times 10^6$	$3.292 \times 10^6$	$1.761 \times 10^6$
KNU7-8	$6.718 \times 10^6$	$7.160 \times 10^6$	$4.106 \times 10^6$	$1.867 \times 10^6$

Table VI Calculated Activity in the Primary Coolant ( $\mu\text{Ci}/\text{rod cc}$ )

Isotopes Site	$^{131}\text{I}$	$^{133}\text{I}$	$^{135}\text{I}$
KNU2	$2.671 \times 10^{-3}$	$1.121 \times 10^{-2}$	$8.750 \times 10^{-3}$
KNU7-8	$1.490 \times 10^{-3}$	$5.775 \times 10^{-3}$	$4.537 \times 10^{-3}$

### 3.4 Measurement and Analysis of Fission Products

The measurement and analysis of fission products in the primary coolant of nuclear power reactor have been carried out at the KNU 2, 7 and 8. The selected results of the measured activity have been shown in Table VII. The detector has been used the Ge(Li) semiconductor detector and gamma spectrum has been analyzed with computerized multichannel analyzer.

We have analyzed the radioactivities of iodine isotopes depend on cooling time to obtain the optimum cooling time of the primary coolant samples of operating reactor core. This results have been shown in Table VII.

Table VII Analysis Results of Defected Fuel and Tramp Uranium of KNU2, 7 and 8

Site	Measured Activity ( $\mu\text{Ci}/\text{cc}$ )		Number of Failed Fuel	Weight of Tramp Uranium (Kg)
	$^{131}\text{I}$	$^{133}\text{I}$		
KNU2	$1.75 \times 10^{-4}$	$1.22 \times 10^{-3}$	0.0	0.0
	$7.39 \times 10^{-4}$	$1.08 \times 10^{-3}$	0.0	0.0
	$2.87 \times 10^{-3}$	$2.39 \times 10^{-3}$	1.0	0.0
	$1.39 \times 10^{-2}$	$2.09 \times 10^{-2}$	3.0	3.95
	$6.86 \times 10^{-3}$	$6.79 \times 10^{-3}$	1.5	1.98
KNU7	$2.78 \times 10^{-2}$	$3.63 \times 10^{-2}$	5.8	8.30
	$2.45 \times 10^{-4}$	$4.15 \times 10^{-3}$	0.0	0.0
	$3.19 \times 10^{-4}$	$4.56 \times 10^{-3}$	0.0	0.0
	$3.55 \times 10^{-4}$	$5.11 \times 10^{-3}$	0.0	0.0
	$3.57 \times 10^{-4}$	$6.40 \times 10^{-3}$	0.0	0.0
KNU8	$3.53 \times 10^{-4}$	$6.66 \times 10^{-3}$	0.0	0.0
	$5.60 \times 10^{-4}$	$3.90 \times 10^{-3}$	0.0	0.0
	$5.70 \times 10^{-4}$	$3.10 \times 10^{-3}$	0.0	0.0
	$9.37 \times 10^{-3}$	$7.55 \times 10^{-3}$	3.8	4.5
	$1.32 \times 10^{-3}$	$4.66 \times 10^{-3}$	1.0	0.0
	$8.63 \times 10^{-4}$	$4.34 \times 10^{-3}$	0.0	0.0
	$8.57 \times 10^{-4}$	$5.40 \times 10^{-3}$	0.0	0.0
	$8.18 \times 10^{-4}$	$5.32 \times 10^{-3}$	0.0	0.0
	$7.70 \times 10^{-4}$	$5.50 \times 10^{-3}$	0.0	0.0
	$7.70 \times 10^{-4}$	$5.20 \times 10^{-3}$	0.0	0.0

Table VII Dependence of the Measured Radioactivity of Iodine Isotopes on Cooling Time ( $\mu\text{Ci}/\text{cc}$ )

Cooling time Isotopes	2 Hrs	6 Hrs	22 Hrs	46 Hrs
$^{131}\text{I}$	$(2.27 \pm 0.156) \times 10^{-2}$	$(2.67 \pm 0.116) \times 10^{-2}$	$(2.78 \pm 0.088) \times 10^{-2}$	$(2.90 \pm 0.082) \times 10^{-2}$
$^{132}\text{I}$	$(6.33 \pm 0.073) \times 10^{-1}$	$(6.33 \pm 0.125) \times 10^{-1}$	-	-
$^{133}\text{I}$	$(3.52 \pm 0.046) \times 10^{-1}$	$(3.56 \pm 0.043) \times 10^{-1}$	$(3.63 \pm 0.047) \times 10^{-1}$	$(3.53 \pm 0.062) \times 10^{-1}$
$^{134}\text{I}$	$(1.10 \pm 0.017) \times 10^0$	-	-	-
$^{135}\text{I}$	$(7.26 \pm 0.015) \times 10^{-1}$	$(7.47 \pm 0.071) \times 10^{-1}$	$(6.59 \pm 0.367) \times 10^{-1}$	-

### 3.5 Analysis of Defected Fuel and Tramp Uranium

The analysis results of the defected fuel and the tramp uranium deduced from comparison of the calculated activity with measured activity have been shown in Table VII.

### 3.6 The activity change during the fuel failure are shown in Fig 2

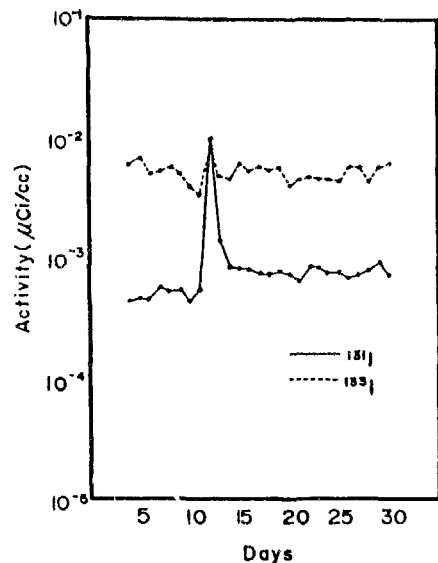


Fig. 2. Activity Change During Fuel Failure.

#### 4. Conclusion

A model describing the fission products release from fuel pellet to reactor coolant has been presented.

We have analyzed the defected fuel and the tramp uranium from comparison of calculated activity by above model equation with the measured activity. The analysis results have been well agreed with the results of the kinetics model and of the diffusion model.

We conclude that the I-131 activity is order of  $10^{-3} \mu\text{Ci/cc}$  for one rod failure. It is well agreement with the results of P. Beslu et al<sup>[7]</sup>. The I-131/I-133 ratio has its value between 0.6 and 1.0 in case of fuel failure.

The physical model used for the calculation show that long-lived nuclides with half lives of several days are released by temperature-dependent phenomena: i.e. migration and that short-lived fission products are released mainly by recoil and knockout.

We have analyzed the radioactivity of the primary coolant by various cooling time to evaluate the experimental error and the optimum cooling time. We can conclude that optimum cooling time for fission products and Co-58 are from 2 hours to 6 hours as shown in the Table VII.

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# CORROSION PRODUCTS, ACTIVITY TRANSPORT AND DEPOSITION IN BOILING WATER REACTOR RECIRCULATION SYSTEMS

H.P. ALDER, D. BUCKLEY,  
R. GRAUER, K.H. WIEDEMANN  
Paul Scherrer Institute,  
Würenlingen, Switzerland

## Abstract

The deposition of activated corrosion products in the recirculation loops of Boiling Water Reactors produces increased radiation levels which lead to a corresponding increase in personnel radiation dose during shut down and maintenance. The major part of this dose rate is due to cobalt-60.

Based on a comprehensive literature study concerning this theme, it has been attempted to identify the individual stages of the activity build-up and to classify their importance. The following areas are discussed in detail:

- the origins of the corrosion products and of cobalt-59 in the reactor feedwaters
- the consolidation of the cobalt in the fuel pins deposits (activation)
- the release and transport of cobalt-60
- the build-up of cobalt-60 in the corrosion products in the recirculation loops.

Existing models of the build-up of circuit radioactivity are discussed and the operating experiences from selected reactors are summarised.

The state of the art of knowledge concerning the different stages in the development of the activity build-up is depicted here. This highlights the existing gaps in knowledge and thus identifies areas for possible research and development activities. Corrosion chemistry aspects of the cobalt build-up in the primary circuit have already been studied on a broad basis and are continuing to be researched in a number of centers. The crystal chemistry of chromium-nickel steel corrosion products poses a number of yet unanswered questions.

There are major loopholes associated with the understanding of activation processes of cobalt deposited on the fuel pins and in the mass transfer of cobalt-60. For these processes, the most important influence stems from factors associated with colloid chemistry.

Accumulation of data from different BWRs contributes little to the understanding of the activity build-up. However, there are examples that the problem of activity build-up can be kept under control. Although many details for a quantitative understanding are still missing, the most important correlations are visible. The activity build-up in the BWR recirculation systems cannot be kept low by a single measure. Rather a whole series of measures is necessary, which influences not only cobalt-60 deposition but also plant and operation costs.

## 1. INTRODUCTION

In most boiling water reactors (BWR), the water is recirculated in an external loop system. During operation, activated corrosion products are deposited in the recirculation loops. This may lead to

the build-up of a considerable radiation field and associated dose rate to which the service personnel may be exposed. During normal operation the deposited activity mainly consists of those indicated in Table 1.1. Depending upon the plant, the nuclides cobalt-60 and cobalt-58 contribute between 80 and 90 % of the total dose rate. Therefore, the activity build-up problem is primarily one of cobalt, whereby the influence of cobalt-60 is predominant (see Table 1.2).

Table 1.1: The Most Important  $\gamma$ -Emitters in Reactor Water, Generated by Activation of Corrosion Products /1/.

Radio-Nuclide	Parent Nuclide	Isotopes Abundance %	Half-Life	Formation Process	$\gamma$ -Radiation Energy MeV
Cr-51	Cr-50	4,3	28 d	n, $\gamma$	0,3
Fe-59	Fe-58	0,33	45 d	n, $\gamma$	1,1; 1,3
Co-58	Ni-58	68	71 d	n,p	0,8
Zn-65	Zn-64	49	244 d	n, $\gamma$	1,1
Mn-54	Fe-54	5,8	313 d	n,p	0,8
Co-60	Co-59	100	5,28 a	n, $\gamma$	1,2; 1,3

Table 1.2: Nuclides Deposited in the Recirculation Loops of Different Nuclear Power Plants /5, App.C/.

Power Plant (Operation Time, h)	Contribution to $\gamma$ -Radiation, %						
	Co-60	Co-58	Mn-54	Fe-59	Zn-65	Zr-95	Ru-103
Tsuruga (50057)	82.0	5.8	7.7	2.3	—	0.1	2.1
Nine Mile Point-1 (50096)	93.7	2.8	2.2	1.3	—	—	—
Monticello (38598)	85.4	2.5	1.8	1.5	2.7	2.2	4.0
Millstone-1 (30144)	77.3	5.4	7.1	2.5	—	2.2	5.5
Quad Cities-1 (35571)	91.0	1.7	2.0	0.4	—	2.7	2.3
Shimane (8000)	68.0	13.3	12.8	5.8	—	—	—
Oskarshamn-1 (27600)	75.9	11.0	—	—	13.1	—	—

An introductory overview of the distribution of corrosion products and of the cobalt in a reactor is given in Figure 1 1

SPECIES	CRYSTAL STRUCTURE	ELEMENTAL COMPOSITION (%)				PARTICLE SIZE (µm)	FILM THICKNESS (mg/dm <sup>2</sup> )	Co-60 CONCENTRATION (%) IN LAYER	1975 ISOTOPIC RATIOS	
		Fe	Cr	N	Co				Co-60/Co-58	Co-60/Mn-54
FUEL CLADDING	-	-	-	-	-	-	-	-	-	-
FUEL DEPOSITS	α-Fe <sub>2</sub> O <sub>3</sub>	95	0.8	2	0.2	~0.1	725	-	8.6	3.8
REACTOR WATER	-	-	-	-	-	-	-	-	-	-
INSOLUBLE	α-Fe <sub>2</sub> O <sub>3</sub>	95	2	2	0.1	-	-	-	5.6 <sup>a</sup>	2.0
SOLUBLE	-	-	-	-	-	-	-	-	2.5	50
OUT-OF-CORE DEPOSITS	-	-	-	-	-	-	-	-	-	-
LOOSELY ADHERENT	α-Fe <sub>2</sub> O <sub>3</sub>	95	2	3	0.1	0.1-0.2	50	12	13	3.3
TIGHTLY ADHERENT	-	-	-	-	-	-	-	-	-	-
SPECIES 1	γ-Fe <sub>2</sub> O <sub>3</sub>	82	1	15	0.5	0.1-0.2	36	72	7.7	35
SPECIES 2	γ-Fe <sub>2</sub> O <sub>3</sub>	70	8	20	0.6	0.1-0.2	12	16	18	90
PROTECTIVE FILM	AMORPHOUS	-	-	-	-	-	(20A)	-	-	-
STAINLESS STEEL	-	74	18	8	0.1	-	-	-	-	-

a) Reactor water data taken in 1974

Fig 1 1 Distribution and Composition of the Corrosion Products in the Nine Mile Point Reactor /6/

The components made of austenitic chromium nickel steel become covered with a fine grained, tightly adhering mixed oxide layer spinel, generated by corrosion In general there are two different spinel phases, differing from each other by their chromium content Typically the spinel layer has a higher cobalt content than the bulk material, indicating that the layer has taken up cobalt from the reactor water This is plausible from chemical structure like nickel which is chemically very similar, cobalt (II) can replace iron (II) in the spinel structure

On the spinel layer there is another layer of loosely packed haematite (α-Fe<sub>2</sub>O<sub>3</sub>), consisting of corrosion products (crud), and partly of transformation products of the spinel layer Since divalent metal ions can hardly be built in the haematite structure, the cobalt content in these deposits is relatively small Part of the cobalt is probably adsorbed The composition of the suspended particles in the water is similar to that of the haematite layer, with a typical concentration in the order of a few µg/kg (ppb) The deposits upon the oxide layer of zirconium, the fuel pin cladding material, is also mainly haematite with a small proportion of spinel Compared with steel surfaces, the haematite on fuel pins typically has a higher cobalt content which is of importance to the build up of activity

The input of corrosion products into the reactor water is in the order of 10 kg • yr<sup>-1</sup> Most of this is deposited upon the fuel element's cladding and upon other reactor components The corrosion product removal through the reactor water clean up system is small

The literature dealing with the build up of activity in BWRs is very extensive The importance of the corrosion products upon activity distribution in water cooled reactors is described in two reviews containing comprehensive bibliographies /1, 2/ Two extensive publications deal with the water chemistry of nuclear power plants /3, 4/, therefore this subject will neither be treated in full nor detail here However fundamental mechanisms concerning activity build up will be indicated in order to identify any gaps in knowledge, possible themes for research and development and possible measures for reactor operation

## 2. SUMMARY MODEL OF ACTIVITY BUILD-UP

To understand activity build up, the different steps will be discussed firstly in a summary with the aid of Figure 2 1 The dissolved, as well as the suspended corrosion products are brought into the reactor water with the feedwater, and to a much lesser extent by corrosion of reactor components The extent of corrosion product input by the feedwater is primarily influenced by the efficiency of the condensate clean-up system and the oxygen content, which controls the corrosion rate There are considerable differences between power plants with and without recirculation of the high pressure condensates into the condenser

In practice the corrosion behaviour of the reactor components can be controlled only by the conductivity of the water and redox conditions In addition to operating at steady state conditions, the outage periods have an important influence upon the total input of corrosion products

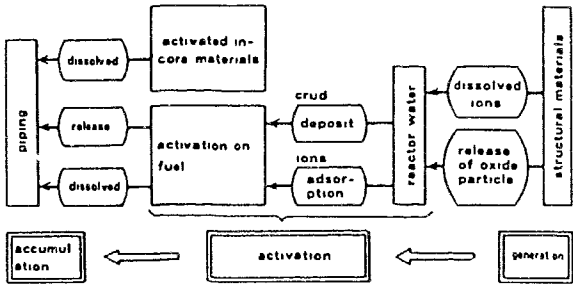


Fig 2 1 Schematic Transport Model of the Activity Build-Up /7/

The source of the activation products cobalt 58 and 60 is the release of material from alloys containing both nickel and cobalt which become exposed to the reactor's neutron flux. However, this material has to remain 'in core' for a period of time, in the order of days to weeks, where it becomes activated on the fuel pins. This occurs by the mechanism of adsorption of the suspended solids (crud) onto the fuel pin's surface. The deposition and release of crud within the core is controlled by colloid chemical reactions, of which very little is as yet understood.

The residence time of cobalt 59 on the fuel pins is a critical factor for the build up of activity. The activity is at a minimum when the residence time is either very short, or very long such that the activated cobalt is removed together with the fuel elements when refueling.

The activation products released from the fuel pins as dissolved ions are built into the corrosion products on the austenitic recirculation loops directly from the reactor water. This occurs for the most part during the build up of the corrosion product layer, and only for a small part by ion exchange in the existing spinel layer. Thus the corrosion rate of the recirculation system is another important factor. At a given temperature the corrosion rate depends mainly on the ionic conductivity of the water and upon the thickness of the existing spinel layer.

Also the activated crud, loosened from the fuel elements, is in part deposited on the recirculating loops contributing to the dose rate. Here too colloid chemical processes participate in the mechanism. The activated crud has a higher cobalt content than the corrosion products brought in with the feedwater. During the residence time of the crud in the recirculation loop this excess cobalt content is reduced. Thus the activated crud is also a source of ionic cobalt.

### 3. WATER CHEMISTRY

#### 3.1 GENERAL

The importance of cleanliness of the feed water and reactor water, both for materials damages and for activity build up has been recognised. The chemical environment determines the corrosion behaviour of the structural materials. Release of corrosion products in the feed system is greatly reduced by the presence of dissolved oxygen in the low conductivity feed water. Oxygen addition has proven to be a powerful method for maintaining sub ppm concentrations of corrosion products in the feed.

Boiling water reactors are fed with neutral feedwater. Theoretically, the ionic conductivity of pure water at 25 °C is  $0.055 \mu\text{S} \cdot \text{cm}^{-1}$ . In the reactor water of some power plants this value is roughly achieved (Olkiluoto  $0.06 \mu\text{S} \cdot \text{cm}^{-1}$  /10/), and in many reactors the conductivity of the water is

less than  $0.1 \mu\text{S} \cdot \text{cm}^{-1}$  during steady state operating conditions. The water quality depends upon the kind of condensate cleaning system and above all on whether the high pressure condensates are cascaded back, or fed in directly. To clean the condensates two systems are used, deep bed demineralisers and Powdex filters. Deep bed demineralisers eliminate dissolved ions more efficiently than Powdex filters. Suspended corrosion products are however retained with particularly high efficiency by this latter system (Table 3.1).

**Table 3.1** Typical Concentrations of Corrosion Products in the Feedwater of Boiling Water Reactors with Different Cleanup Systems /1/

Condensate Cleanup System	Corrosion Product Content, ppb	
	with High Pressure	without Condensate Recirculation
Deep Bed Demineralizer	10	14 - 17
Deep Bed Demineralizer	6	10 - 13
with Ultrasonic Cleaning		
Powdex Filter	3	7 - 10
Powdex Filter and	0.5	4 - 7
Deep Bed Demineralizer		

In addition, the quality of the reactor water depends upon the throughput of the reactor water clean-up system (RWCU), which varies considerably from plant to plant (e.g. 0.7% Muhleberg, 7% Shimane of the feed water). The total metallic impurities in the feedwater are in the order of magnitude of  $1 \mu\text{g} \cdot \text{kg}^{-1}$  (ppb), (Table 3.2) while the metallic impurities in the reactor water are in the order of 10 ppb (Table 3.3).

The classification of the impurities into soluble and insoluble is arbitrary because of the  $0.45 \mu\text{m}$  filters used, therefore materials passing through are taken as soluble species. Presently it is not possible to estimate the proportions of particles, colloids and ions.

**Table 3.2** Corrosion Products in the Feedwater of Swedish Nuclear Power Plants (Average Values in ppb) /12/

Power Plant	Fe	Cr	Ni	Cu	Zn	total
Oskarshamn 1	0,6	0,08	0,08	0,7	0,27	1,7
Oskarshamn 2	0,8	0,08	0,07	0,09	0,09	1,1
Ringhals 1	0,3	0,02	0,16	0,6	0,12	1,2
Barsebeck 1	0,6	0,06	0,16	0,10	0,04	1,0
Barsebeck 2	0,5	0,07	0,15	0,12	0,04	0,9

Table 3.3: Corrosion Products in the Reactor Water of Swedish Nuclear Power Plants  
(Average Values in ppb) /12/.

Power Plant	Fe	Cr	Ni	Cu	Zn	total
Oskarshamn 1	1,4	2,7	0,3	18,0	6,6	29,0
Oskarshamn 2	1,5	2,3	0,6	0,8	1,3	7,0
Ringhals 1	2,9	0,9	0,3	3,7	1,3	9,0
Barsebeck 1	1,4	2,3	0,4	0,6	0,3	5,0
Barsebeck 2	1,3	4,7	0,5	0,8	0,3	8,0

Table 3.4: Typical Activation Product Contents in the Reactor Water of Boiling Water Reactors /3/.

Radio-Isotope	Parent Nuclide	Half-Life	Content, $\mu\text{Ci/kg}$		
			soluble	insoluble	total
Mn-56	Mn-55	2,6 h	11,0	11,0	22,0
Cu-64	Cu-63	12,7 h	30,0	2,7	33,0
Na-24	Na-23	15,0 h	2,7	0	2,7
Cr-51	Cr-50	27,7 d	1,6	0,23	1,8
Fe-59	Fe-58	44,6 d	0,006	0,17	0,18
Sb-124	Sb-123	60,2 d	0	0,02	0,02
Co-58	Ni-58	71,3 d	0,10	0,044	0,14
Zn-65	Zn-64	244,0 d	0,085	0,052	0,14
Mn-54	Fe-54	313,0 d	0,031	0,18	0,21
Co-60	Co-59	5,27 a	0,17	0,24	0,41

A considerable proportion of the particles are smaller than  $0.45 \mu\text{m}$ . The different elements are disproportionately distributed over the particle size fractions, this may be different in each reactor /5, App.B; 13/. The typical contents of reactor water activation products for BWRs is given in Table 3.4.

The values of the metal contents as well as the conductivity of the water are much higher at the start up, shut down and during power transients than during steady state operation (Fig. 3.1). Though the periods of contamination are relatively short they have a large effect upon the activity mobilisation, transport and deposition. During these times the corrosion rate of the structural materials is increased, and a redistribution of the crud takes place.

The redox conditions of BWRs reactor water is given by the radiolysis of the water. The oxygen content is recorded to be within the range 165 to 400 ppb /10;14/. According to systematic investigations at 8 reactors the oxygen/hydrogen ( $\text{O}_2/\text{H}_2$ ) ratios in the recirculation loops are in the range between 14.3 and 55 /14/. For unknown reasons the  $\text{O}_2/\text{H}_2$  ratios are significantly higher than the stoichiometric ratio of 8.

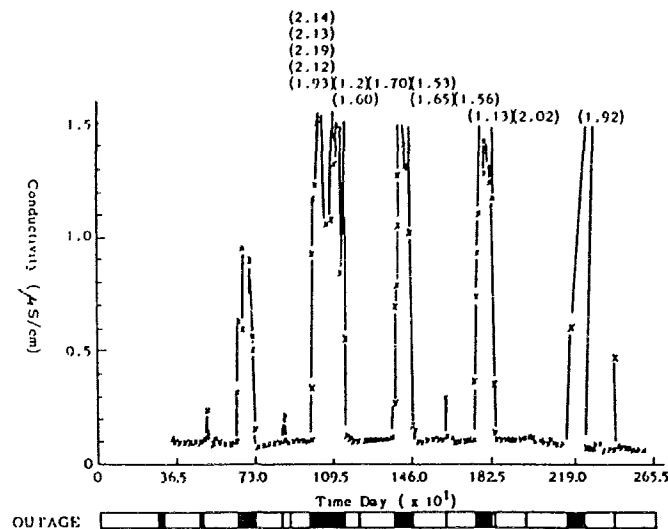


Fig. 3.1: Conductivity of the Reactor Water versus Time in the Shimane Nuclear Power Plant /5, App.E/.

### 3.2 HYDROGEN WATER CHEMISTRY (HWC)

In the recirculation loops of BWRs the oxygen content of the reactor water is in the order of 200 to 400 ppb at full power operation, and this oxygen concentration is sufficient to cause intergranular stress corrosion cracking (IGSCC) in sensitised stainless steel subject to tensile stress. It has been demonstrated in reactor tests that the injection of hydrogen into the feed water will reduce the concentration of dissolved oxygen, and as a consequence of this the IGSCC susceptibility of sensitized stainless steels was suppressed /15; 16; 17; 18; 19/. The IGSCC is suppressed if the electrochemical potential (ECP) is reduced to below  $-230 \text{ mV}$  (the suppression potential) compared to the standard hydrogen electrode (SHE), by approximately 50-100 mV, and the conductivity is maintained at a level below  $0.3 \mu\text{S} \cdot \text{cm}^{-1}$ . The  $-230 \text{ mV}$  suppression potential has been found to be associated with an oxygen concentration of approximately 2 ppb /19; 21/. Although laboratory tests indicate that oxygen is the key parameter for IGSCC, plant tests show that other species also play a rôle in establishing the ECP under hydrogen addition conditions /19/.

Crack propagation ceases almost immediately after the start of oxygen reduction by hydrogen injection. No crack growth was measured as long as hydrogen water chemistry was maintained, but restarted when this treatment was ceased (Fig. 3.2) /18/.

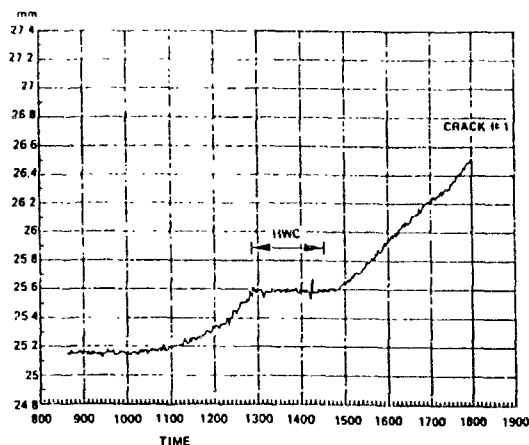


Fig. 3.2: Crack growth versus Time during Hydrogen Water Chemistry Treatment (HWC) /18/.

Very slow to no crack growth was observed at oxygen levels as low as 20 ppb in the reactor water, much before the ECP monitoring indicated immunity to IGSCC /18/. This experience shows, at the suppression potential, a wide plant to plant variation in required hydrogen, main steam line radiation increase and dissolved oxygen in recirculation system. The cause of large variations among BWRs in the hydrogen addition, to establish a HWC, is poorly understood. One explanation which has been suggested is that impurities in the reactor water may interfere with the recombination process (Fig. 3.3) /19; 20/.

In Fugen Nuclear Power Plant, Japan, the oxygen concentration in the condensate has been reduced by hydrogen addition from between 10-20 ppb to less than 1 ppb. No symptoms of IGSCC crack growth on type 304 stainless steel has been observed, but the low oxygen concentration has caused an increase in the soluble iron concentration in the condensate from between 2 - 5 ppb to 6 - 10 ppb, and in addition there is an increase in the cobalt-60 concentration in the reactor coolant, and as a consequence accelerated cobalt build-up on the pipe surface /22/.

### 3.3 SILICATE AND ORGANIC CARBON

Besides the discussed corrosion products there are other impurities in the water, such as silicate ( $\text{SiO}_2$ ) and organic compounds. Their possible rôle in the activity build-up has scarcely been investigated. These substances are able to form complexes with dissolved metals or to modify the chemical properties of the colloidal material by adsorption /23/.

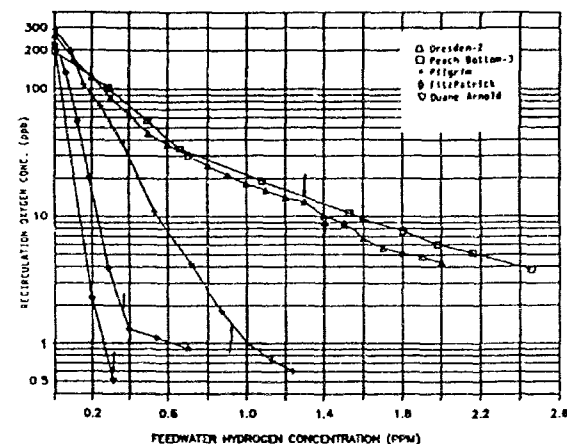


Fig. 3.3: Relationship between Recirculation Oxygen Concentration and Feedwater  $\text{H}_2$  Addition Rate /19/.

There are two possible sources for the silicate in the reactor water, namely the silicon content in the metallic components, and the feedwater. The silicate content of the reactor water is specified by the plant manufacturers to between 1 and 4 ppm  $\text{SiO}_2$ ; during operation, these concentrations are significantly lower /4/. The silicate content of the water is mostly between 100 and 300 ppb, this is significantly higher than the metal content /2; 4; 5; 24; 25/. The concentration of silicate depends upon the age of the filters in the reactor water clean-up system /24; 25/.

There is little information concerning the content of organic carbon impurities in reactor water. In one cited instance the organic carbon content was between 700 and 900 ppb /26,9-5/. These concentrations are also higher than those of the corrosion products. It is not clear whether the organic substances are thermal or radiolytic degradation products from the ion exchange resins /27/, or whether they are brought in with the addition of feedwater /28; 29/.

## 4. THE INPUT OF CORROSION PRODUCTS INTO REACTOR WATER

In most reactors the largest part of corrosion products brought into the water originate in the feedwater. For example at Mühleberg approximately 10 kg of crud are deposited per year. In the same plant, however about  $130 \text{ g} \cdot \text{yr}^{-1}$  of cobalt is found in the reactor water, of which 60 % originated from reactor components (Table 4.2), the remaining coming from feedwater. The amount of dissolved and suspended metals is in the order of  $1 \text{ g} \cdot \text{yr}^{-1}$ , added to which there is approximately  $25 \text{ g} \cdot \text{yr}^{-1}$  of silicate.

**Table 4.1** Yearly Feedwater Input of Corrosion Products in the Nuclear Power Plants Muehleberg /5, App B/ and Shimane /5, App E/

	Muehleberg		Shimane	
	Input g/yr	Removed g/yr (%)	Input g/yr	Removed g/yr (%)
Iron < 0,45 µm	1500	25 (1,7)	2050	246 (12)
Iron > 0,45 µm	1500	15 (1,0)		
Copper	2100	100 (4,8)		
Chromium	2600	350 (13,5)		
Nickel	1000	10 (1,0)		
Cobalt	50	5 (10)	48 (?)	11 (23)
total	8750	505 (5,8)		

**Table 4.2** Yearly Cobalt Input from the Feedwater and Reactor Components in Muehleberg Nuclear Power Plant /5, App B/

	Cobalt Input	
	g/yr	%
Feedwater	49,4	38
Reactor Components		
Cr-Ni Steel	9,1	7
Inconel	16,9	13
Stellite	54,6	42
total	130,0	100

Only a small proportion of the crud brought in is removed by the reactor water clean up system, the larger portion is deposited within the reactor. The variation in crud deposition from reactor to reactor can be remarkably different, and depends upon the different throughput in the ion exchange systems /2, 7/, for example Muehleberg and Shimane, Table 4.1

In addition to the total input of corrosion products the origin of the different elements is also a matter of concern. In a detailed analysis of the Brunswick 2 power plant it was found that 99 % of the total iron in the reactor water originated in the feedwater system, whereas 35 % of the cobalt is released from reactor components /30, 32, chapter 16/. A second source of cobalt, other than that of cobalt alloys is from nickel alloys, the cobalt content of which may be 1 to 2 % of the nickel content. In Muehleberg about 40 % of the cobalt originate from reactor components made from stellite, which represents only a small part of the surface but with a high corrosion rate

In spite of the above mentioned example, Stellite is not necessarily the direct influence upon the cobalt 60 deposition in recirculation loops, in Shimane, containing Stellite, a low dose rate has been measured on the recirculation loops /5/

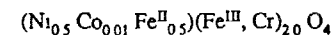
## 5. CRUD INVESTIGATIONS

### 5.1 CRUD IN RECIRCULATION LOOPS

The deposition and corrosion products on chromium nickel steel components of the recirculation system have been investigated in different reactors /6,33,34,35/. Figure 1.1 gives a view of the distribution and composition of the deposits and corrosion products

The layers consist of loose deposits having a haematite structure, and a tight, partially porous spinel layer (Table 5.1). There are no clear indications from X ray analysis that the spinel can be subdivided. As to its composition, the chromium depleted first component, corresponds approximately to the corrosion products of austenitic steel in oxygen containing water. Whereas the chromium rich second component corresponds to corrosion products in oxygen free high temperature water

The spinel layer in contact with the water consists of particles of about 0.1 - 0.3 µm in diameter. Thin layers have trench like depressions along the grain boundary /6, 33/, in which fine grained haematite may settle. In general the cobalt content of the spinel layer is significantly higher than that of the metal, which is about 0.1 - 0.2 %, unfortunately this is rarely given for the steels that have been investigated. Secondary ion mass spectrometric analysis (SIMS) of removed oxide layers shows that the nickel to cobalt ratio remains constant, irrespective of the profile over the entire layer. From this it is concluded that only a limited number of nickel ions can be replaced by cobalt in the spinel /33, 36/. From References 33 and 37 can be derived the following possible limiting formula



It follows that the incorporation of cobalt, into the spinel layer, is controlled by the corrosion rate of the steel and not by the cobalt concentration in the water. The condition being that the cobalt concentration is sufficient to saturate the spinel /33, 36/

There is one element of caution to be taken from Table 5.1 the nickel to cobalt ratio in haematite is not significantly different from those in the spinel layer. This can only be understood if the haematite is the  $\alpha$  metathesis product of the spinel. However this is not absolutely sure, at least part of the haematite comes from the feedwater /23/



Table 5.1: Corrosion Products on Austenitic Components of Boiling Water Reactors /39/.

	Structure	Composition, %				Mass Ratio		Deposition mg/dm <sup>2</sup>	Co-60 Percentage %	$\frac{\mu\text{Ci}(\text{Co-60})}{\mu\text{g Co}}$	$\frac{\mu\text{Ci}(\text{Co-60})}{\text{mg Fe}}$	Co-60 Co-58
		Fe	Cr	Ni	Co	Ni/Co	Fe/Ni					
<b><u>NMP Clean-Up Duct</u></b>												
Loose Layer	$\alpha\text{-Fe}_2\text{O}_3$	95	2	3	0,1	30	32	50	12	2,6	3	13
Adherent Layer												
Component 1	$\text{NiFe}_2\text{O}_4$	83	1	15	0,5	30	5,5	36	72	4,9	27	8
Component 2	$\text{NiFe}_2\text{O}_4$	70	9	20	0,6	33	3,5	13	16	2,3	20	16
<b><u>Quad Cities Bypass Duct</u></b>												
Loose Layer	$\alpha\text{-Fe}_2\text{O}_3$	90	5	5	0,2	25	18	12	9	1,3	3,6	—
Adherent Layer												
Component 1	$\text{NiFe}_2\text{O}_4$	88	1	10	0,4	25	8,8	56	79	1,4	6,7	—
Component 2		68	18	14	0,5	28	4,9	17	12	0,6	4,2	—
<b><u>Millstone Bypass Duct</u></b>												
Loose Layer	$\alpha\text{-Fe}_2\text{O}_3$	86	7	5	0,1	50	17	14	7	2,7	2,6	9
Adherent Layer												
Component 1	$\text{NiFe}_2\text{O}_4$	87	2	9	0,2	45	9,7	53	92	5,9	12,4	6
Component 2	$\text{NiFe}_2\text{O}_4$	78	15	6	0,1	60	13	2	1	2,3	3,8	19
<b><u>Millstone Recirculation Flange</u></b>												
Loose Layer	$\alpha\text{-Fe}_2\text{O}_3$	82	10	8	0,1	80	10	13	2	0,7	1,2	18
Adherent Layer												
Component 1	$\text{NiFe}_2\text{O}_4$	82	3	15	0,3	50	5,5	38	90	4,3	18,3	6
Component 2	$\alpha\text{-Fe}_2\text{O}_3$	89	5	6	0,1	60	15	21	8	1,4	2,6	15

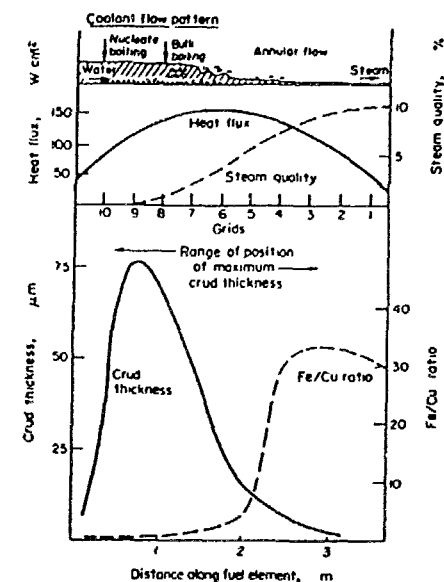


Fig. 5.2: Crud Distribution on a Fuel Rod in Winfrith Nuclear Power Plant /3/.

## 5.2 DEPOSITS ON FUEL PINS

The investigation of fuel element crud is problematic in so far as alterations during shut down of the reactor and during the decay phase, cannot be excluded. Often the deposits are distinguished by their solubility, or their adhesion: loose portion being removed by brushing; tight adherent portion by scraping.

As well as the deposited quantities, the crud composition shows considerable differences between different power plants. In general the crud deposits preferentially in the zone where nucleate boiling begins (Fig. 5.2) (Table 5.2.).

The fuel element crud has predominantly a haematite structure /5, App. D; 38; 39/ though in individual plants, it may contain considerable portions of different metals besides iron. In comparison with the suspended crud, increased cobalt content is typical for fuel element crud and is of importance to the build up of activity /39/.

Fuel elements from plants with slightly contaminated recirculation loops have little crud deposit with a small proportion of loosely bound material. The residence time of cobalt on the fuel elements can be estimated from the specific activity. In several plants the residence time is as long

Table 5.2: Composition of Crud on Fuel Rods (Expressed as Percentage)

Element	OSK-1+2 /12/	Brunswick-2 /39/	Monticello /39/	Nine Mile Point (Atom-%) /3/	Effect of Condensate Cleanup /38/ Deep Bed    Powder	
Fe	50-80	93,2	62    80	85-95	94	65
Cu	1-20	0,7	20    7	2-4	1	4
Ni	7-20	2,5	5    4	3-8	3	6
Zn	5-15	1,1	5    3	1	0,3	14
Cr	1-8	1,2	1    0,7	1		
Mn	2-4	2,1	6    4	3		
Co	0,1-0,4	0,1-0,6	0,6    0,4	0,3	0,1	0,4
Other					2	10

as 5 - 6 years, and hence the cobalt-60 is mainly removed together with the replaced fuel elements /5, App. A; 40; 41; 42/. The residence time of loose crud is significantly shorter and comparable with that of deposited crud on the recirculation loops, for example 50 and 230 days respectively are quoted in Reference 43.

## 6. THE PROCESSES OF ACTIVITY BUILD-UP.

According to Fig. 2.1 the essential steps of the activity build-up are:

- cobalt input into the reactor water
- activation of cobalt-59 in the neutron flux
- build up of cobalt-60 onto the recirculation loops.

In the following section this sequence will be changed in favour of a chemical schematic representation. Both cobalt input and build-up have aspects of corrosion chemistry in common, whereas the activation of cobalt depends upon the deposition of the crud on the fuel elements as well as upon its release, which are controlled by colloid chemistry processes (see Section 6.3).

### 6.1 CRUD INPUT AND COBALT RELEASE BY CORROSION.

The largest part of the corrosion products are brought into the reactor with the feed water. Thus besides the corrosion behaviour of the recirculation loop material, the efficiency of the condensate clean-up system and the refeeding of the high pressure condensates determine the crud input (Table 3.1)

The corrosion behaviour of low alloy steels in neutral water is determined by temperature, oxygen content, ionic conductivity and flow rate (Fig. 6.1.1; 6.1.2) /45/. In various power plants the iron input was successfully reduced by an oxygen addition of 20 - 60 ppb in the feed water. A threshold value of 15 ppb, recorded in reference 46 would seem to be too low according to reference 34 (Fig. 6.1.3; 6.1.4).

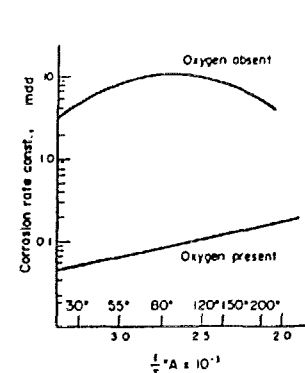


Fig. 6.1.1: Corrosion Rate of Carbon Steel as a Function of Temperature, with and without Oxygen /3/.

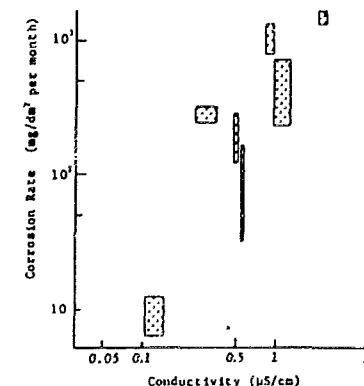


Fig. 6.1.2: Influence of the Conductivity of Flowing Water Containing 5 ppm Oxygen on the Corrosion Rate of Carbon Steel /34/.

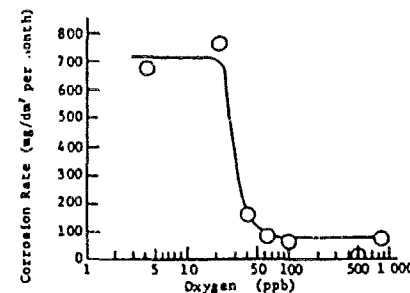


Fig. 6.1.3: Influence of Oxygen Content in 100 °C Water on the Corrosion Rate of Carbon Steel /34/.

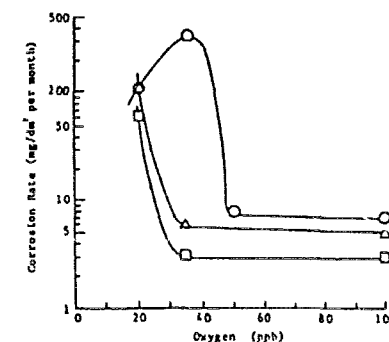


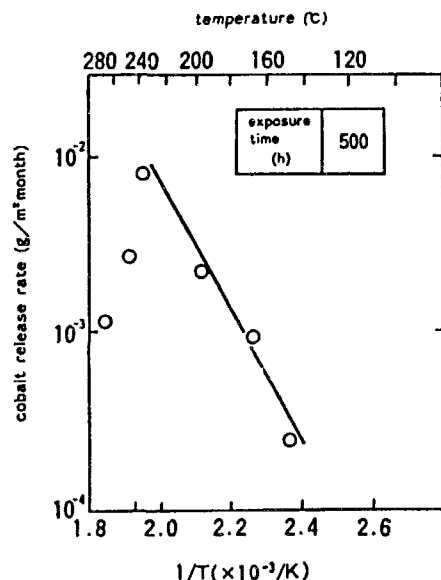
Fig. 6.1.4: Influence of Oxygen Content on the Corrosion Rate of Low Alloy Steels in Flowing Water (1 m/s) at 35 °C and with a Conductivity of 0.15 μS/cm /34/.

To keep corrosion of low alloy steels low during outage periods, recirculation of oxygen containing water is recommended. The beneficial influence of a flow rate in conjunction with low conductivity is shown in Table 6.1.

The corrosion rate of austenitic chromium-nickel steels at feed water heater temperature (190 °C) is approximately 12 mg · m<sup>-2</sup> · yr<sup>-1</sup> /5, App. A; 47/. From experience gained under operating conditions, oxygen and flow rate have little influence upon the corrosion rate which becomes gradually smaller, and is roughly 0.15 μm · yr<sup>-1</sup> after 8'000 h of operation /36/.

**Table 6.1:** Release of Corrosion Products from Unalloyed Steel at Different Flow Rates and Conductivities of the Water (52 °C, 5ppm Oxygen) /46/.

Flow Rate (m/s)	Release Rate (mg/dm <sup>2</sup> · mo)	
	$\sigma = 0,1 \mu\text{S/cm}$	$\sigma = 3,6 \mu\text{S/cm}$
0	278	515
0,3	12	46
0,9	3	52
1,8	2	12



**Fig. 6.1.5:** Cobalt Release during Corrosion of CrNi 18 8 - Steel in Pure Water as a Function of Temperature /48/.

Among numerous publications a Japanese study is of interest /47; 48; 49/ concerning the temperature dependence of cobalt release, found it to be at a maximum at 240 °C, and decreasing again at higher temperatures (Fig. 6.1.5), for type 304 steel containing 0.22 % cobalt. This behaviour is said to be connected with the formation of a denser oxide layer above 250 °C.

The change in the layer formation raises the question of corrosion behaviour of steel under temperature transients. Probably the denser layer is formed after every temperature cycle, which

would result in a temporary increase in cobalt release. However because the corrosion products on the recirculation loop often have a higher cobalt content than the base metal (Fig. 1.1; Table 5.1) the austenitic reactor components would seem to be a cobalt sink than a cobalt source.

Under the influence of radiation (500 Gy · h<sup>-1</sup>, Co-60, 250 °C, 20 ppb O<sub>2</sub>) the release of particles is increased, whereas the release of ions is little affected /50/.

Cobalt release from austenitic feed water heater pipes would seem to be unimportant in the build-up of activity on the recirculation loops. The cobalt content of the heater pipes is 0.02 % in Oskarshamn-1 and 0.2 per cent in Oskarshamn-2, but both plants have low dose rates on the recirculation loops.

The cobalt release from Stellite is heavily dependent upon the oxygen content of the water /5, App. A/. For reactor conditions corrosion rates of 0.7 - 10 μm · yr<sup>-1</sup> are recorded in reference 38 (pp.5-24). However the considerable scattering of the values under similar reactor conditions /5/ ensures a difficult prognosis. Stellites are used as abrasion resistant alloys, in areas of possible high wear, and the cobalt may be from wear rather than corrosion. As with austenitic steels, gamma radiation causes an increase in crud release, and again the effect upon the ionic cobalt is negligible /50/. In reference 50, it is noticeable that different oxygen contents do not significantly influence the corrosion behaviour, compared to Reference 5 (App. A).

## 6.2 COBALT BUILD-UP ON AUSTENITIC STEELS

The main portion of cobalt on recirculation loops is incorporated in the tightly adherent spinel layer. This occurs during corrosion of the material, and depends upon the concentration in the reactor water, and proceeds in parallel to the corrosion rate (Fig. 6.2.1.; 6.2.2) /51; 52; 53; 54; 55; 56/. At a certain temperature the influence of conductivity becomes important. The cobalt uptake is greatly increased when the conductivity of the water is increased from 0.1 - 0.5 μS · cm<sup>-1</sup> /51/. An inexplicable difference is seen between types 304 and 316 steels contrary to References 53 and 57.

A simplified model conception of the build-up of cobalt is shown in Figure 6.2.3. According to Lister /55/, cobalt is built up in a thin, growing, passive layer, and is transported in both, the presently formed fine grained spinel, and haematite layers by diffusion through pores. It follows from this model that the cobalt-60 release from the spinel layer occurs by solid state diffusion, a slow process compared to the build-up. A fast cobalt release from a spinel can only be achieved by an oxidizing reaction. The cobalt build-up in an already existing spinel layer by ion exchange is of secondary importance.

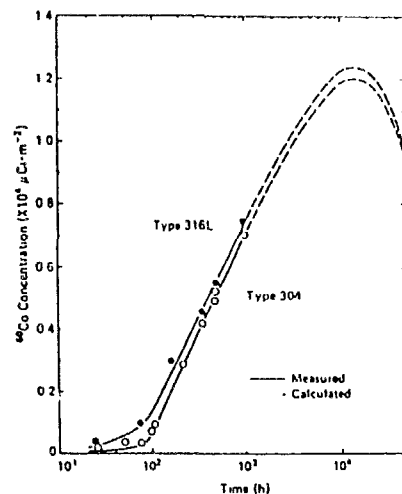


Fig. 6.2.1: Kinetics of Cobalt Uptake by Austenitic Steels at 230 °C /53/.

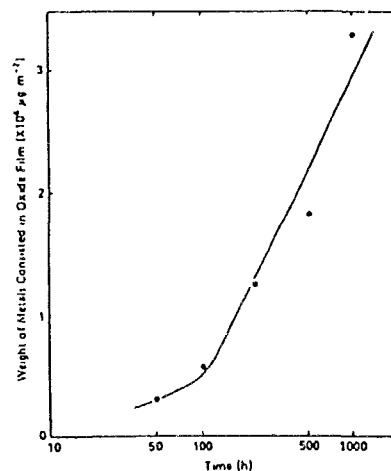


Fig. 6.2.2: Kinetics of Oxide Layer Growth on Austenitic Steel 304 at 230 °C /53/.

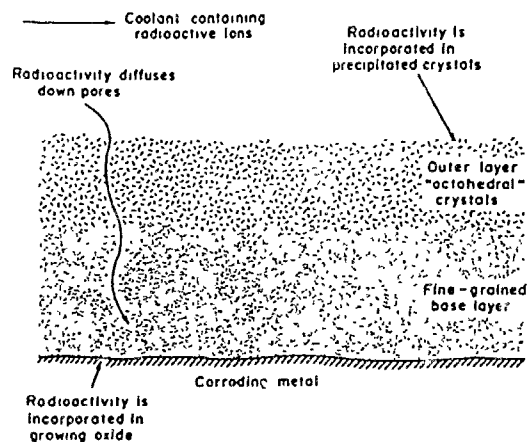


Fig. 6.2.3: Simplified Schema for Reactions of Cobalt-60-Build-Up into the Oxide Layer of Austenitic Steels /1/.

From the repeatedly observed connection between cobalt build-up and corrosion rate it may be concluded that the rate can be reduced by pre-oxidation (prefilming) of the steel surface. As a precondition for this, the oxide layer must be stable under reactor operating conditions. After the pre-oxidation under similar conditions, oxygen content between 200 and 400 ppb, temperature

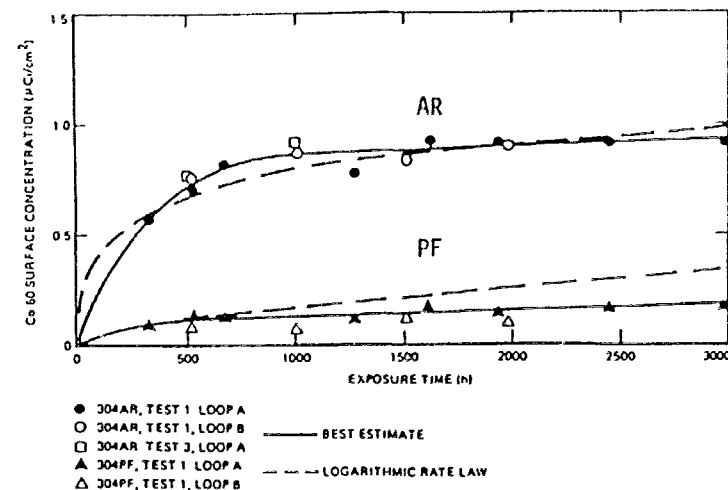


Fig. 6.2.4: Influence of Preoxidation (Prefilming) on Cobalt Uptake by Steel 304 at 280 °C.

AR: As Received Condition Samples

PF: Preoxidised Samples (280 °C, 200 ppb O<sub>2</sub>, 500 h) /51/.

approximately 280 °C, the build-up of activity is greatly retarded (Fig. 6.2.4 /51; 58; 59/). Pre-oxidation with a low oxygen content and chemical passivation, for example with nitric acid, have shown no effect, or are even disadvantageous /52/. Alkalation of the reactor water by sodium ions gave a thirty per cent reduction in cobalt-60 deposition on type 316L in a Japanese reactor, even at a relatively low oxygen content of between 80 and 90 ppb at 285 °C (during 500 hours of the warm up-phase /60/). Figure 6.2.4 also shows indirectly that cobalt-60 build up is determined by the corrosion rate, not by ion exchange with the already existing spinel /23/. However a contrary opinion is held in Reference 61.

The presence of trace quantities of dissolved zinc, between 5 and 15 ppm in the reactor water greatly inhibits corrosion of chromium-nickel steels at reactor temperature. This reduction of the corrosion rate influences the cobalt uptake of the steel surfaces (Figs. 6.2.5; 6.2.6). Zinc and cobalt compete for the same lattice sites in the spinel, in the sense of ion exchange equilibrium. Thus the zinc suppresses the concentration of cobalt in the oxide. It is not yet clear though why zinc is distinguished from other divalent heavy metal ions. The benefits to be gained from zinc requires the constant maintenance of ionic zinc in the reactor water, it then limits the cobalt-60 build-up by a measured factor between 3 and 20. A pretreatment of the steel surfaces with zinc containing water is insufficient /62; 63/.

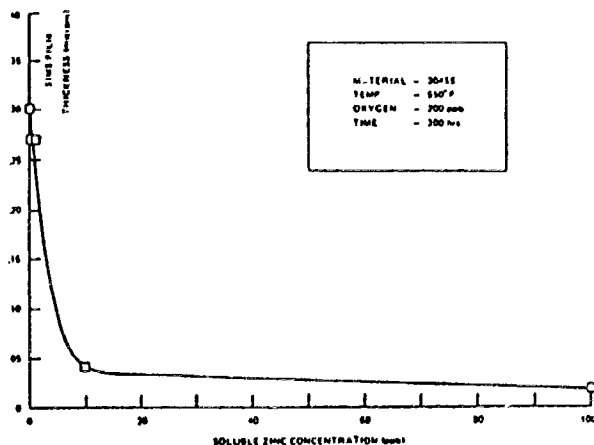


Fig. 6.2.5: Zinc Inhibition Effect on 304 Stainless Steel /62/.

### 6.3 ACTIVATION OF COBALT AND COBALT-60 TRANSPORT.

The critical parameter of influence for activity build-up is the residence time of cobalt-59 in the neutron flux. Theoretically the problem could be mastered if the residence time is kept short (towards zero), or as long as possible, that is some years so that cobalt-60 would be removed with the fuel elements.

Adsorption of ionic cobalt on zirconium oxide is only important with new fuel elements for a short time. The exchange process is irreversible and proceeds relatively fast /41; 64/.

In the reactor the cobalt activation occurs when cobalt in the crud (built into the structure or adsorbed) deposits on the fuel element. Crud deposition has to be looked at as well as the crud adhesion on the fuel elements, which are influenced by colloid chemistry /65; 66/, as is the mobile haematite in the recirculation loops. In neutral reactor water the spinel layer is negatively loaded, and the haematite particles are slightly positively loaded, these are ideal conditions for the adhesion of crud onto austenitic steel /14; 67; 68/.

After an initial phase, haematite deposition on the fuel rods can be regarded as homo-coagulation, this deposition is promoted by heat flux and predominantly by bubble evaporation. Under these conditions the crud deposition is given by:

$$R = k \cdot Q/L \cdot c$$

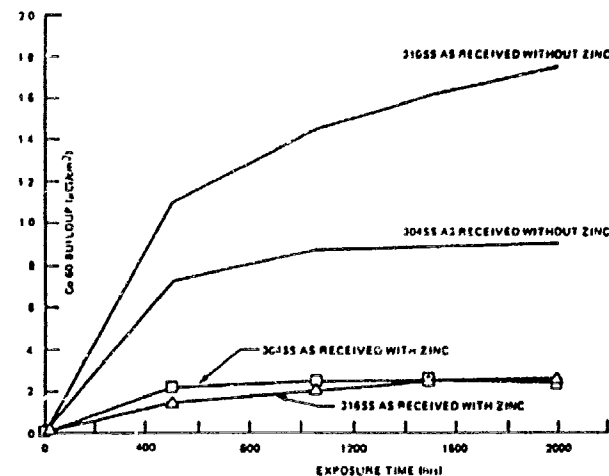


Fig. 6.2.6: Zinc Benefit Test with Continuous Zinc Presence /62/.

Where:  $k$  constant;  
 $Q$  heat flux;  
 $L$  heat of vapourization;  
 $c$  crud concentration in water.

The quotient  $Q/L$  is the flow of the water to the wall, caused by the boiling process /69;70;71;72/.

Crud particles with diameters smaller than the bubble diameter (about 0.2  $\mu\text{m}$  in the reactor) are transported by the growing bubbles to the surface, where they frit together to form a tightly adherent layer. Larger particles, about 0.1 - 1  $\mu\text{m}$ , are deposited by whirl processes. They sinter together with the fine grained, tightly adhered material, having good adhesive properties /71/. Particles with larger diameters, in the range 1 - 10  $\mu\text{m}$ , adhere less well. Their residence time ranges from some days to weeks; they carry out the largest part of activity transport from the fuel elements to the recirculation loops. It is still an open question why the cobalt content in the fuel element crud is higher than in the circulating material. Possible causes are: neutron induced lattice defects; partial formation of spinels containing nickel and cobalt; increase in adsorption at elevated temperatures; and may also be the oxidation to trivalent cobalt /71/.

Until now the chemistry of colloid particles at reactor operating conditions has scarcely been investigated. Careful extrapolations are possible in the temperature range 25 - 80  $^{\circ}\text{C}$ . The adsorption of cobalt on haematite and magnetite up to 80  $^{\circ}\text{C}$  is well known, and some work has been done up to 200  $^{\circ}\text{C}$  /73; 74; 75/. The influences of silicate and organic material upon the properties of colloids is still unknown /23/, they are rarely determined analytically.

The activation products can be released from the fuel elements either together with the crud or in ionic form, it is unsure which is the predominant process for contamination transport. The cobalt content of the crud may be in equilibrium with that in the reactor water. The cobalt release with the crud is again a question of crud adhesion, which depends upon the particle size distribution, the age of the crud (because of sinter processes), and the thickness of the crud layer [23].

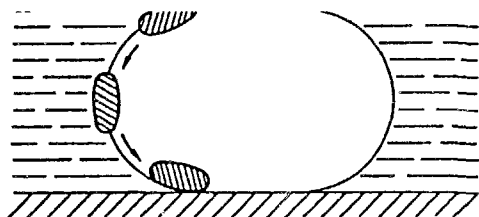
## 7. ACTIVITY BUILD-UP MODELS

When drawing up a model describing the activity build-up, the state of knowledge of the different processes are to be taken into consideration. Initially the problem seems to be easily solvable, however upon further more detailed consideration there are inconsistencies and contradictions.

### 7.1 DETERMINING PROCESSES

In the relevant literature, there is no agreement on the parameters determining the activity build-up. It is worthy to note that the extreme points of view, activity build-up being a corrosion problem of the recirculation loops, or being a matter of crud behaviour, are both represented by a competent source, namely by co-workers of General Electric Company.

In a model Dehollander [71] connects the activity build-up in a boiling water reactor primarily with the crud inventory (see also [76]). According to this, the residence time of cobalt in the neutron flux and the cobalt-60 transport are determined by the crud quality. For an understanding of this model one has to recall that, as observed in some power plants, the cobalt content in the fuel rod crud is higher than in the material circulating or deposited in the recirculation loops.

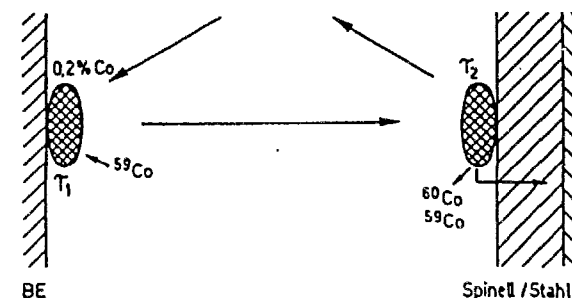


**Fig. 7.1.1:** Concerning the Deposition Mechanism of Fine Grained Crud on a Vapor Bubble. Under Reactor Conditions, the Bubble Diameter is about  $0.2 \mu\text{m}$ . According to [71].

The fine grained crud ( $< 0.1 \mu\text{m}$ ) is deposited on the fuel rods mainly by bubble vaporization (Fig. 7.1.1) and forms a tightly adherent sintered layer. The cobalt fixed in this fraction reaches, together with the crud, the long residence times desired, that is several years.

The crud fraction with  $0.1 - 1 \mu\text{m}$  diameter will not be deposited by vapour bubbles. According to Dehollander these particles still have a good adhesion because they sinter together with the fine grained crud forming a "cement" on the fuel element surface. Particles in the fraction 1 to about  $10 \mu\text{m}$  do not sinter together, their adhesion on fuel element surface is only due to the attachment of a colloid following its collision with a surface by electrostatic and van der Waals forces between particle and surface. These physical effects govern the colloid chemistry. After a certain time they will be transported away by the flow. Nevertheless, their residence time in the neutron flux is long enough to take up additional cobalt from of the reactor water; this cobalt will also be activated during its stay on the fuel pin.

This particle fraction actually acts as a "conveyor belt" for cobalt-60 (Fig. 7.1.2): The activated particles will be transported to the spinel layer on the recirculation loops, where they will be deposited again due to the conditions of the electrical charges of the surfaces. When residing on the spinel layer the excess cobalt will be withdrawn again. The released cobalt-60 will be directly built into the growing spinel layer. These layers are fissured and have trench-like depressions along the grain boundaries of the bulk material [6; 33], in which particles with diameters of a few  $\mu\text{m}$  can settle. After a certain residence time these particles can be transported again back to the fuel rods. According to Dehollander, particles with diameters more than  $10 \mu\text{m}$  are less important because of their short residence time on the fuel elements due to their size, and because their specific cobalt activity corresponds to that of the reactor water. Taking into consideration,



**Fig. 7.1.2:** In the Reactor, the Crud Fraction 1 to  $10 \mu\text{m}$  Acts as a "Conveyor Belt" for Cobalt-60.  $\tau$ : Residence Time.  $\tau_3 \ll \tau_1 \cong \tau_2$ . According to [71].

however, that coarse grained particles may spall from solid crud and may get into the water /70/, their influence can be neglected. These split off particles have a high specific activity and, due to their size, can deposit in zones of poor flow, thus contributing to the generation of hot spots.

A summary of the rôle of the different particle fraction in the activity build-up is given in Table 7.1.

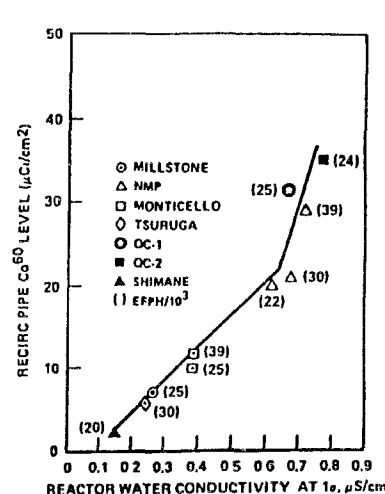
**Table 7.1:** The Roles of the Different Crud Fractions in the Buildup of Activity in Recirculation Loops. According to /71/.

D $\mu\text{m}$	Adhesion	Residence Time	Role
< 0,1	sintered	Years	Co-Fixing
0.1...1	Stuck Together	Years	Co-Fixing
1...10	Loose	Days...Weeks	"Conveyor Belt"
> 10	Spalling	Weeks...Years	Hot Spots

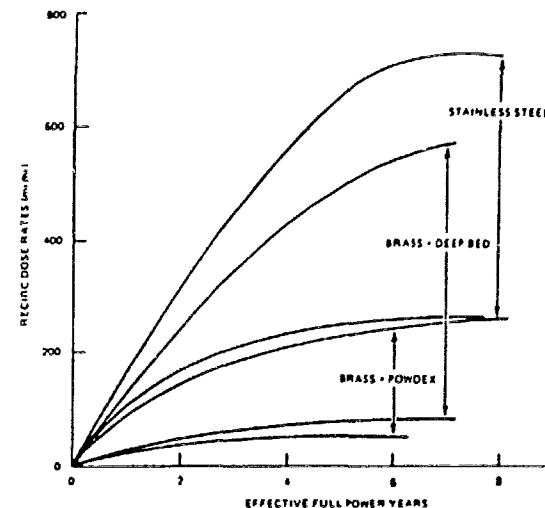
Large importance is attributed to the conductivity of the reactor water (Fig. 7.1.3), which should be as low as possible. Naturally, measures leading to a reduced crud input have also positive effects on the conductivity of the reactor water. These additional aspects have been, for example, taken into consideration in the General Electric model of activity build-up /76; 77/.

According to Marble et al. the cobalt build-up in the spinel layer is of greatest importance. As already mentioned in section 6.2, the cobalt build-up can be reduced by adding zinc to the reactor water /62; 63/. The motive for this is the correlation between the contamination of the recirculation loops and the zinc content of the reactor water, which was discovered in 1983. The zinc source was the brass tubes of the condensers. The lowest dose rates in the recirculation loops have been measured in plants with brass tubes and with a feedwater clean-up system containing Powdex-filters (Fig. 7.1.4). Because deep bed demineralizers are able to keep back dissolved ionic metals more efficiently than Powdex-filters, it is, according to reference /62/, plausible that the combination of brass tubes and deep bed demineralizer results in heavier contamination of recirculation loops.

It must be considered, that zinc-65 as an activation product, with a half-life of 244 days will also be deposited on the recirculation loops (Table 1.2). Together with zinc, copper will be released from brass. Under certain circumstances copper can precipitate on austenitic surfaces, so the corrosion rate will be increased by the formation of local galvanic elements. This is a footnote in reference 62.



**Fig. 7.1.3:** Correlation between Deposited Co-60-Activity in Recirculation Loops and Reactor Water Conductivity at 1  $\sigma$  (Average Square Error) /71/.



**Fig. 7.1.4:** BWR Radiation Behaviour for Generic Plants Differentiated by Condenser Materials and Condensate System Type /62/.

## 7.2 MATHEMATICAL MODELS

There are several attempts to describe the activity build-up in BWRs by mathematical models. In doing so, the influence of the variables of the system on activity build-up is hoped to be elucidated, and by comparing the predictions with the reactor data the critical quantities of influence will be recognized. Essentially the models are based on a materials balance for the iron transport and on a materials and activity balance for the cobalt transport. Such models are partly very complex. Even a high stage of development cannot obscure the fact that they are semiempirical. The reaction rates as well as the reaction orders needed for the calculation are mostly empirical or even just assumptions.

### 7.2.1 The General Electric Model

The model by General Electric /76; 77/ is one of the most comprehensive for the analytical description of the activity transport as well as of the activity build-up in the reactor water of BWRs (Fig. 7.2.1). It includes the following processes:

- 1) Fouling of metallic surfaces by ions, colloids and particles
- 2) Impurities from the feedwater, from the condensate, and from the corrosion of the metallic surfaces of the reactor and recirculation loops

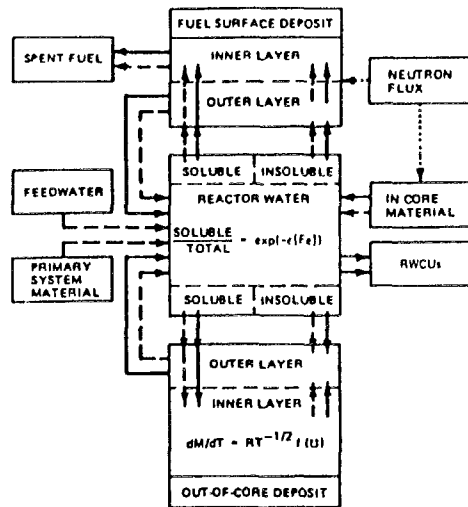


Fig. 7.2.1: Block Diagram of the General Electric Model for Cobalt Transport. Continuous Line: Co-60 Transport. Broken Line: Co-59 Transport /77/.

- 3) Interaction between solid particles and dissolved material
- 4) Different deposition mechanisms for dissolved impurities and for solid particles
- 5) Activation of the deposited layers on the fuel rod surfaces
- 6) Release of radioactive impurities from the core as dissolved and undissolved substances, in consideration of the hydraulic forces
- 7) Two-layer model of the corrosion product layers outside the core.

In this model iron and cobalt fouling is taken into account in separate equations of balance. The model requires many empirical transport coefficients, which can only be gained by aid of a large number of data sets from comparable reactor types. Therefore the model is scarcely applicable to BWRs other than built by General Electric. The model does not include the analytical mechanisms of the deposition and build-up of impurities into the corrosion product layer. The comprehensive transport coefficients contain all chemical-physical information /78/.

### 7.2.2 The Tsuruga Model

The Tsuruga Model /43/ is based upon data measured on the Tsuruga reactor (1070 MW, operation started in 1970) and takes into account the following transport processes in a mass and activity balance (Figure 7.2.2):

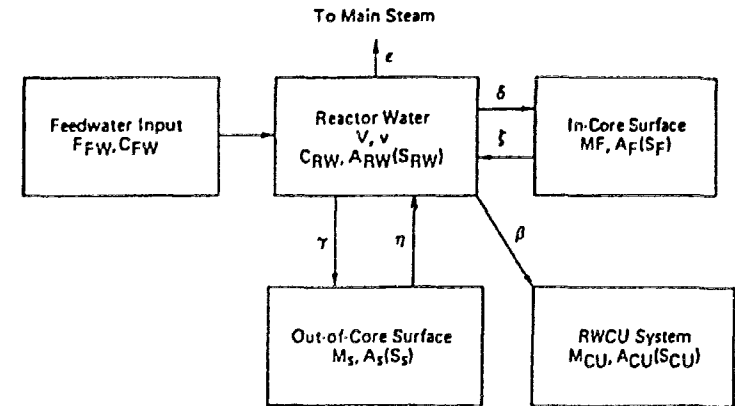


Fig. 7.2.2: Corrosion Product Transport According to the Tsuruga Model /43/.

- 1) Corrosion products from the feedwater are deposited on the surfaces inside and outside the core, and are partly reduced by the clean-up systems
- 2) Corrosion products are activated during their time in the core
- 3) After a residence period, deposits are released again into the reactor water systems
- 4) The activated and inactive corrosion products are mixed homogeneously in the reactor water and will be carried into the other plant components.

The Tsuruga model has the following aims in view:

- Understanding the deposition mechanisms
- Prediction of the dose rate
- Testing of measures to reduce the amount of corrosion products.

This model is suitable to describe the activity build-up of a specific BWR, providing there are enough reliable measured data. The deposition and release mechanisms are not modeled but expressed by regressed transport data valid for the Tsuruga plant only. The determining transport rates in this model cannot be established by measurements in test loops or in laboratory experiments; such conversions would lead to wrong results. If the Tsuruga model could be supplemented with fouling models, a generally applicable model could be worked out, in which measured data from experiments could be used /78/.



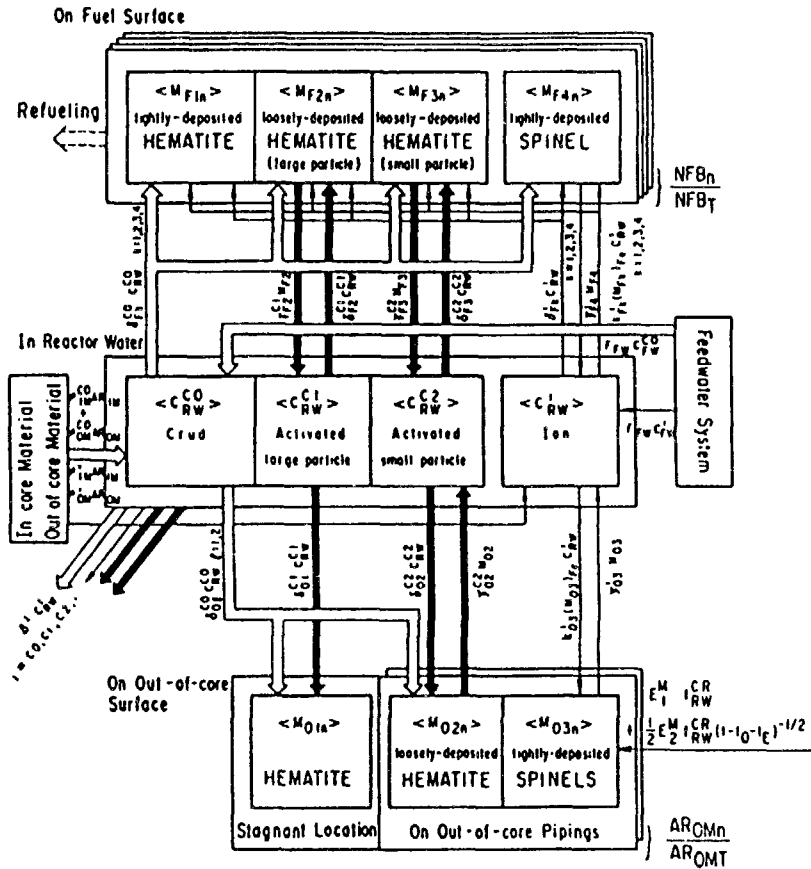


Fig. 7.2.4.1: Block Diagram of the Toshiba Model for Mass Transport /5, App.D/.

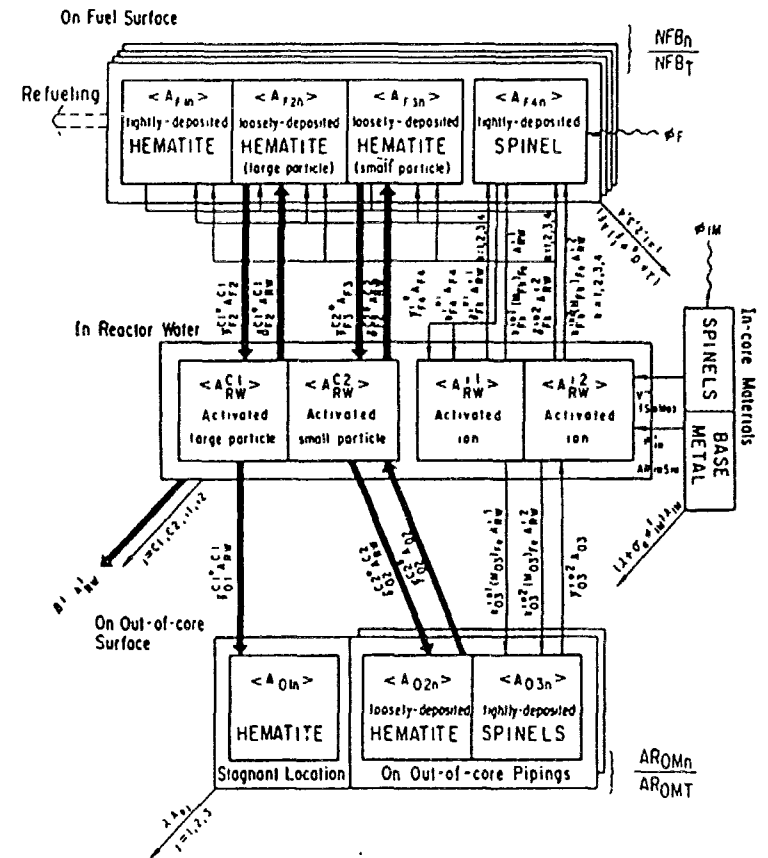


Fig. 7.2.4.2: Block Diagram of the Toshiba Model for Activity Transport /5, App.D/.

### 7.2.3 The ASEA Model

The ASEA model /79/ is based on the following processes:

- Materials transport from the turbulent flow through the boundary layer to the upper deposition layer
- Adsorption to and removal from the upper deposition layer
- Build-up or reduction of activity in the growing lower oxide layer

In this model, all the activated, depositable corrosion products are regarded as dissolved, and a two layer model of the corrosion film is taken into consideration, an upper loose accumulated layer, and a tightly adherent, solid lower layer. The ASEA model is restricted to the deposition of radioactive corrosion products from turbulent flowing reactor water on metallic surfaces. By assuming a material transport coefficient based on diffusion, the depositing activity is postulated to be dissolved.

The two layer model with time depended build-up coefficients is of special interest. In this model the behaviour over the time can be executed elegantly, however, it requires reliable data measured over some time to calibrate the coefficients properly. The ASEA model also includes the behaviour of corrosion product layers on metallic surfaces with integral coefficients, which are calculated by regression analysis of measured data. However, like with other models, the mechanism of the layer build-up is neither explained nor understood /78/.

### 7.2.4 The Toshiba model

Out of a number of Japanese papers /43; 80; 81; 82/ only the Toshiba model /5, App. D/ will be mentioned; it postulates rather complex relationships of mass and activity transport (Fig. 7.2.4.1 and Fig. 7.2.4.2).

## 7.3 JUDGEMENT OF THE MATHEMATICAL MODELS

The existence of several mathematical models of activity build-up could lead to the opinion that the elementary steps are well known. However, such models are at least semiempirical. Moreover, very complex models may be misleading in that by conscious and unconscious calibration of coefficients, all results can be produced. The models mentioned, laboratory experiments and experimental loops can contribute very little to the calibration of a comprehensive transport process as too many conditions have to be varied compared to a power plant. To develop a causative model based on physico-chemical principles, some work is necessary to elucidate the mechanisms and the kinetics of the steps involved in activity build-up. Presently the state of knowledge is still incomplete /23; 78/. The situation as described by Shaw and Naughton 1980 /83/ has scarcely changed:

"Modelling at its best for LWR plants remains semiempirical. There are too many aspects of corrosion product transport for which little is known. A few which could be cited are (1) the mechanism whereby corrosion products are deposited on fuel, (2) the nature at operating conditions of circulating corrosion product ions, colloids and particles, (3) the amounts and forms of cobalt released from various surfaces, both high cobalt alloys and those containing cobalt as a trace contaminant, (4) the effects of radiation on corrosion product forms and transport and (5) the influence of coolant chemistry on corrosion product deposition and incorporation in corrosion films. The challenge is before us to develop models that (1) adequately describe radiation built-up in present LWR plants and (2) reasonably predict the effect of design and operational changes on these build-ups. We are not yet there."

## 8. SCOPE OF CONTROL AND INTERVENTION

### 8.1 INTRODUCTION

Together with General Electric, the Electric Power Research Institute (EPRI) has tried (within a grand scale program) to discover the influences of operation conditions and plant characteristics on the activity build-up. The results of this BRAC Program (BWR Radiation Assessment and Control) are put in an extensive report /5/. The report includes data from 28 BWRs with varying degrees of loop contamination (Fig. 8.1). From the analysis of the data from these BWRs critical parameters of influence upon the activity build-up were sought.

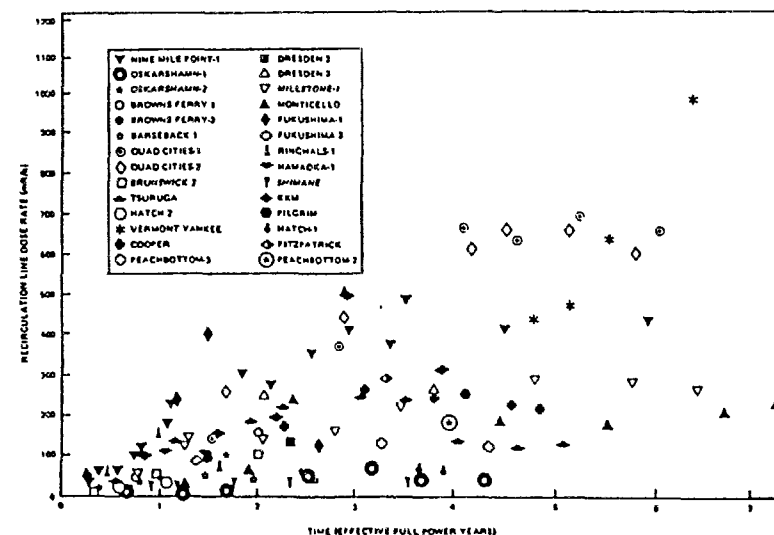


Fig. 8.1: Recirculation Line Dose Rates of Different Reactors /5/.

As the most essential result the EPRI report /5/ lead to the conclusion that, accumulation of data from different plants contributes little to the understanding of the activity build-up. However, operation experiences on individual plants with slightly contaminated recirculation loops demonstrates that the problem of activity build-up can principally be kept under control. As to the individual reactions participating, the phenomenon can be understood by physico-chemical fundamentals. Although many details for a quantitative understanding are still missing, the most important correlations are visible.

However, it cannot be expected that the activity build-up in the recirculation loops can be kept low by a single measure which is cost free. Rather a whole series of measures is necessary, which influences not only cobalt-60 deposition but also plant and operation costs.

In the single steps

- cobalt input into the reactor water,
- cobalt activation, and
- cobalt-60 build-up in the recirculation loops,

the cobalt behaviour in a reactor is closely connected to the crud inventory. So, the crud inventory should be primarily influenced. Therefore, the measures of radiation level reduction aim to:

- reduce of reactor water radionuclide concentration, and
- control of radionuclide deposition.

In the planning stage of new plants, the crud and cobalt input can be controlled by materials choice and also by the design of the water cleanup systems. Also special measures are important when a new plant starts up.

## 8.2 REDUCTION OF REACTOR WATER RADIONUCLIDE CONCENTRATION

In principle the contamination of reactor circuits, particularly by cobalt-60, can be reduced and kept under control by selection of appropriate materials for construction and for retrofitting, in association with good management of water chemistry both at power and during annual outages. The following aspects will be described in more detail:

- reduction of corrosion product (crud) input from the feedwater system
- reduction of cobalt containing materials
- corrosion product (crud) removal
- control of water quality.

### 8.2.1 Crud Generation Control

Corrosion product generation can be reduced by using corrosion resistant materials and by exposing them to the appropriate conditions.

#### a) Corrosion resistant materials for upstream condensate systems:

The main crud source in a reactor system is from the turbine side, which is almost completely made of carbon steel. To reduce the crud generation low carbon, low alloy steels should be used in the system lines. For example main steam pipes, extraction steam pipes, main condenser and feedwater pipes, feedwater heater shells, and drain pipes should be made of materials that are atmospheric corrosion resistant, that is, when left in a damp atmosphere or with wetted surfaces they should give little corrosion product input /85; 86/. Also titanium is used for condenser tubing /84/.

However at present there are no clear or definitive recommendations cited in published literature for specific replacement materials. Some comparative data are given in /86/ although not in full detail.

#### b) Feedwater oxygen control:

Oxygen injection into the feedwater line is applied at most BWR plants to reduce the iron release rate (corrosion rate) from carbon steel piping. Control of the oxygen content in the feedwater in the range 20 - 60 ppb has proved to be successful /3; 5, App. E; 7; 34; 84 - 88/.

#### c) Practises during start-up and outage:

The reduction of crud into the reactor can be achieved by reducing corrosion product generation during the plant outage. If, for example, carbon steel pipes on the turbine side are left in wet condition during this period there will be severe corrosion. To prevent corrosion certain 'lay-up' practises have been found to be an effective measure /85; 86/ and in one cited case a decrease to one tenth of previous iron crud input has been observed. These 'lay-up' practises should be applied during the construction phase as well as at annual inspections and start-up. The following measures are applied in Japan /85; 86/:

- For condensate and feedwater systems: During the construction period the system should be filled with oxygen containing water controlled by hydrazine addition. For short 'lay-up' periods it should be drained completely. During annual inspection, an initial period of recirculation should be followed by complete drainage.
- For main steam, extraction steam and heater drain system: During the construction phase a dry 'lay-up' procedure by the application of a continuous supply of dry air should be followed. This method is also applied during annual inspections.

## 8.2.2 Low Cobalt Containing Materials

Cobalt is present in nuclear reactors as a low-level impurity in stainless steels ( $\leq 0.2\%$ ). In some countries the authorities propose for new plants and for retrofitting a low cobalt content, e. g. for materials in the neutron radiation field of the core  $\leq 500$  ppm, for other materials less than 2000 ppm. The effect of such a reduction of the cobalt content for materials outside the neutron field of the core remains questionable.

Hardfacing alloys, e. g. Stellite, used in applications requiring resistance to mechanical wear, have cobalt contents of about 50 - 60 %. Apart from corrosion, wear of the cobalt-base alloys, used to hardface valves (particularly feedwater regulator valves) and as pins and rollers for control blades, were found to be the primary cobalt sources in many BWRs /84; 86; 89; 90/.

Presently some alternative low cobalt alloys are being tested in two commercially operating BWRs. For example, Nitronic-60/CFA and PH 13-8 Mo/Inconel X-750 are currently being used as alloys in pin/roller combinations, and measurements show that type 440 °C stainless steel has better wear characteristics than the cobalt-base alloys in BWR feedwater regulator valves (Table 8.2.2) /89/.

**Table 8.2.2:** Composition of some Low-Cobalt and Cobalt-free Hardfacing Alloys for Prototype Tests /89/.

	Ni	Co	Cr	C	Si	Fe	Mo	B	Mn
Low-cobalt alloy									
CFA	Balance	< 0.5	33.0 . 39.0	< 0.10	< 0.10	1.5		1.7	
Cobalt-free alloys									
Nitronic-60	8.0 .. 9.0		16.0 . 18.0	< 0.1	3.5 . 4.5	Balance			7.0 . 9.0
PH13 - 8MO	7.5 .. 8.5		12.25 . 13.25	< 0.05	< 0.1	Balance	2.0 ... 2.5		< 0.1
Inconel X-750	Balance		14.0 .. 17.0	< 0.08	< 0.5	5.0 . 9.0			< 0.1
Type 440 C stainless steel			16.0 . 18.0	0.95 . 1.20	< 1.0	Balance	< 0.75		< 1.0

The examples given in the preceding paragraph show that for certain specific applications commercially available alloys can be substituted for cobalt containing alloys without compromising components performance.

A considerable number of cobalt free hardfacing alloys have been developed; the responses to laboratory wear and corrosion tests of many of them suggest that they could replace the cobalt-base Stellite hardfacings. Their long-term behaviour under BWR operational conditions however is not yet proven. Therefore, definite recommendations for the replacement of cobalt-base hardfacings by particular cobalt free alloys cannot be given.

## 8.2.3 Improvement of Crud Removal Efficiency

### a) Condensate treatment system:

To reduce crud input into the reactor from leakage of the condensate treatment system, a condensate filter demineralizer can be adapted up-stream of a deep bed type condensate demineralizer, called dual condensates treatment system /5, App. E; 7; 84; 85; 86; 88/. For economic reasons, the demineralizer plants have a small throughput, therefore high temperature filters with a high throughput would keep the heavy metal content of the water low. For this, reactive filters seem to be particularly qualified because they fix dissolved ionic metals irreversibly /5, App. A; 64/.

### b) Optimization of reactor water clean-up system:

In order to eliminate an as large as possible part of the crud by the reactor water clean-up system, its throughput should be as large as possible, e.g. at least 2 - 4 %, or better about 7 %, of the water flow /7; 84/.

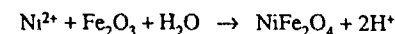
## 8.2.4 Water Quality Control

### a) Reactor water quality control:

Results from section 6 show that the activity build-up in the recirculation loops can be kept under control if the corrosion rate of the austenitic steels is low. As a precondition for a low corrosion rate, the conductivity of the reactor water must be low. In practice the corrosion behaviour of the reactor components can only be influenced by the conductivity of the reactor water, as other parameters such as temperature and redox conditions cannot be chosen freely. Efficient feedwater cleaning leads to a lower conductivity of the reactor water, and consequently to a reduced corrosion rate of recirculation loop materials. For example, in the Tsuruga power plant a crud elimination of more than 90 % in the condensate clean-up system was coupled with a reduction of the feedwater conductivity to about  $0.07 \mu\text{S cm}^{-1}$  /43/.

### b) Control of nickel to iron ratio in feedwater:

Although control of crud input from feedwater into reactor water is effective in the reduction of insoluble cobalt-60, there is an optimum feedwater iron concentration to maintain a low concentration of soluble cobalt. A clear correlation has been found between the ionic nickel to iron ratio in feedwater and reactor water concentration of cobalt-58 and cobalt-60. The optimum nickel to iron ratio was found to be  $\leq 0.2$  (Fig. 8.2.4). As a corrective action for mitigating the activity build-up in a reactor, a sufficient amount of iron should be fed into the reactor water, to suppress ionic cobalt-58 and cobalt-60 concentrations. A key process may be the reaction between nickel and iron, forming a nickel ferrite:



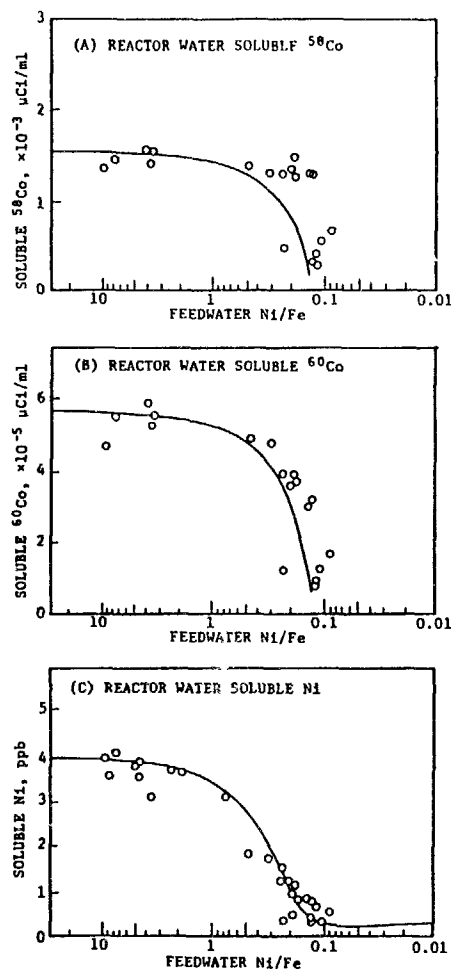


Fig. 8.2.4: Optimum Ni/Fe Ratio for Reduction of (A) Co-58, (B) Co-60 and (C) Nickel in Reactor Water /84/.

Ionic cobalt also reacts with iron, forming cobalt ferrite. Thus ionic nickel and ionic cobalt are stabilized by iron. At present an increase in iron concentration is an acceptable method to control the Ni/Fe ratio, but in the long term a more satisfactory solution is to reduce nickel generation in future plants, as lower corrosion product input is desirable for total plant operation /16; 84; 86; 88/.

### 8.3 Control of Radionuclide Deposition

#### 8.3.1 Water Quality Control

Radionuclide deposition is also controlled by the water quality. This was already dealt with in section 8.2.4.

#### 8.3.2 Preconditioning of Material Surface

The fresh steel surfaces of new plants have a relatively high corrosion rate. That means on the one side an increased crud and cobalt input, on the other side, however, also an increased cobalt build-up rate in the recirculation loops. Therefore, the suppression of corrosion in reactor water containing cobalt ions should prevent its incorporation. Prefilming and polishing have been proved to be suitable methods for suppressing corrosion and deposition of radioactive ions.

##### a) Prefilming

Prefilming of austenitic steels in high temperature water (about 280 °C) containing dissolved oxygen (200 - 400 ppb) or of slightly alkaline pH at relatively low oxygen concentrations (80 - 90 ppb) for 500 hours can effectively suppress the corrosion and deposition of cobalt. Oxide films containing aluminium ions provide greater protection. (See section 6.2) /51; 58; 59; 60; 84; 88/.

##### b) Polishing

Cobalt deposition rates can be reduced by polishing the surfaces before start-up. This reduces the surface area available for cobalt pick-up. The deposition of cobalt and corrosion are suppressed to about one third by mechanical or electro-polishing compared with a pickled material /58/. Other authors find mechanical polishing alone not very effective because it leaves a surface of microscratches, which are good sites for deposition. Electropolishing, on the other hand, is highly effective because it leaves a smooth microstructure, and can reduce cobalt pick-up by a factor of 2 (whereas sandblasting increases pick-up). Moreover, electropolishing will probably increase longterm resistance to intergranular stress corrosion cracking (IGSSC). Almost all BWR plants that are replacing recirculation piping are now specifying electropolishing for new piping. Loop tests have shown that the benefits of electropolishing and air oxidation are additive /59/.

#### 8.3.3 Inhibition of Reactor Water

Also a zinc concentration of between 5 and 15 ppm in the reactor water can inhibit the corrosion of austenitic chrom-nickel steel, and also the cobalt uptake is reduced by a factor of between 3

and 20 The constant maintenance of an ionic zinc concentration in the reactor water is necessary, a surface preconditioning with zinc containing water is not sufficient /62, 63/ It is still an open question whether zinc, according to /62/, decreases the activity build-up or whether, in the end, in plants with small cobalt input the activity build-up in the recirculation loops is determined by deposited Zinc-65

## 8.4 GENERAL REMARKS

It has been demonstrated at existing power plants, that the contamination of the recirculation loops could be kept low for years by controlling the crud input and the quality of the reactor water as well as by particular measures during the outage. Moreover, one example (Tsuruga plant) shows that a contaminated plant can also be restored by a combination of measures, i.e. decrease of the iron input by oxygen injection into the feed water, forming filterable crud from iron (II) compounds, and by minimizing the corrosion in the feedwater system during outage by means of water circulation and drying respectively /43/.

## 9. REVIEW OF THE STATE OF THE ART

Using the text at hand, an extended summary was made to review the state of the art.

### 9.1 DEFINITION OF THE PROBLEM

In boiling water reactors (BWR) with external recirculation loops the dose rate to the service personnel is mainly due to the deposition of activated cobalt, - Co-58 and Co-60. Co-60 alone contributes 68 - 94 % to the total dose rate

The essential steps leading to the activity build-up are:

- Cobalt input into the reactor water
- Activation of Co-59 in the neutron flux
- Deposition of Co-60 in the recirculation loops.

The material input into the reactor water can be divided into two groups by filtration: dissolved and particulate. The standard classification by filters of 0.45 µm pore size only permits the distinction between particles larger than 0.45 µm ("particles") and material (particles, colloids, ions) below 0.45 µm ("dissolved"). The particulate cobalt is mainly due to the feedwater, the soluble cobalt to cobalt-containing materials. Data from Mühleberg e.g. show a cobalt input of

approximately  $0.1 \text{ kg} \cdot \text{yr}^{-1}$ , 40 % with the feedwater, 50 % from incore Inconel and Stellite components and only a small portion from austenitic steel.

Corrosion product particles (mainly haematite) play an important role in the cobalt transport. These crud particles can act as a "conveyor belt" for the activated cobalt between the fuel pin cladding and the surface layer of the recirculation loop. Data from Mühleberg show a crud deposition of approximately  $10 \text{ kg} \cdot \text{yr}^{-1}$ , the largest part originating from the feed water system

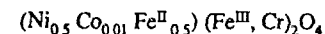
## 9.2 THE CORROSION OF AUSTENITIC STEEL AND THE COBALT BUILD-UP

### 9.2.1 Characterization of the Stable Corrosion Layer

The oxide layer after several thousand hours of operation on austenitic chromium-nickel steel (there seems to be little difference between 304 and 316 steel) can be characterized as follows:

- a) A tightly adhering film of nm-thickness of spinel grown on the base material
- b) A tightly adhering film of nickel-iron spinel  $\text{NiFe}_2\text{O}_4$  of µm-thickness containing most of the cobalt activity. This layer consists at least of two species:
  - a chromium depleted (1 - 3 % Cr), nickel rich Ni-Fe spinel with little Co-activity (corresponding to the corrosion product of austenites in oxygenated water).
  - a chromium rich (9 - 18 % Cr), nickel depleted Ni-Fe spinel with most of the Co-activity (corresponding to the corrosion product of austenites in oxygen depleted water).

The cobalt content in both species (0.1 - 0.6 %) is significantly higher than in the stainless steel (0.1 - 0.2 %). The ratio of nickel to cobalt is constant for the oxide layer which leads to the conclusion that only a limited number of nickel atoms can be replaced by cobalt. The following possible limiting formula can be derived for the spinel:



- c) A loosely adhering film of haematite particles  $\alpha\text{-Fe}_2\text{O}_3$  (82 - 95 %) of µm-thickness with a low cobalt content (0.1 %). This film is formed from mobile corrosion product particles present in a concentration of a few ppb in the reactor water ("conveyor belt")

### 9.2.2 The Cobalt Build-up in the Corrosion Layer

The cobalt build-up in the corrosion layer proceeds in parallel to the corrosion rate. Typically, following a logarithmic rate law, a maximum build-up is reached after 10'000 hours at 230 °C.

The cobalt build-up is proportionate to the reactor water conductivity in the recirculation loop. Typically, a strong increase occurs if the conductivity increases from 0.1 to 0.5  $\mu\text{S} \cdot \text{cm}^{-1}$ . Since the input of corrosion products directly affects the conductivity a reduced input of crud also reduces the cobalt build-up.

The cobalt release from the corrosion layer appears to be a slow process of solid state diffusion, therefore the austenitic corrosion layers can be considered as an efficient cobalt sink.

### 9.2.3 Electropolishing and Preoxydation of the Austenitic Steel Surface

Electropolishing leads to a reduction of the cobalt build-up by a factor of 2 over "as received" steel surfaces. Preoxydation at 280 °C and 200 - 400 ppb  $\text{O}_2$  retards the cobalt build-up by a factor of 10 over "as received" steel surfaces.

### 9.2.4 Inhibition of the Corrosion Layer Formation and Cobalt Build-up by the Addition of Zinc.

Addition of 10 - 20 ppm ionic zinc to the reactor water retards the formation of the corrosion layer by a factor of 10. Typically after 300 hrs at 280 °C and 200 ppb  $\text{O}_2$  the thickness of the corrosion layer is 0.03  $\mu\text{m}$  instead of 0.3  $\mu\text{m}$ . The cobalt build-up is reduced by a factor of 3 to 20 since cobalt and zinc compete for the same lattice sites in the spinel layer. Pretreatment with zinc alone is insufficient, a steady concentration should be maintained.

Low dose rates have been measured in plants with brass condensers (Cu-Zn) and Powdex filters. The disadvantages are that Zn-65 is an activation product ( $\tau_{1/2} = 244 \text{ d}$ ) and also deposited in the recirculation loop, further that copper may precipitate on austenitic surfaces and increase the corrosion rate by the formation of local galvanic elements.

### 9.2.5 Control of the Nickel to Iron Ratio

Soluble cobalt and nickel react with iron to form cobalt- and nickel-ferrites. Since there is little control over the nickel input, it is recommended to feed sufficient iron into the reactor water to maintain the optimum Ni/Fe ratio  $\leq 0.2$ . Compared to higher Ni/Fe ratios a reduction of soluble cobalt by a factor of 5 is achieved.

## 9.3 THE DEPOSITION OF CORROSION PRODUCTS ON THE FUEL PIN CLADDING MATERIAL AND THE ACTIVATION OF COBALT

The corrosion products in the reactor water, mainly haematite particles (95 % Fe) with a higher cobalt content (0.2 %) are deposited on the fuel pin cladding material. The deposition occurs preferentially in the zone where nucleate boiling begins, - about 1 m from the bottom end of the pin -, and depends on the following factors:

$$R = k \cdot \underbrace{Q / L}_{\text{water flow to the wall}} \cdot c$$

rate of deposition      constant      heat flux      heat of vaporization      crud concentration

Water vapour bubbles of typically 1  $\mu\text{m}$  size transport small crud particles ( $< 0.2 \mu\text{m}$ ) to the pin surface where they form a tightly adhering film. Medium sized particles (0.1 - 1  $\mu\text{m}$ ) sinter with the tightly adhering film. Large particles (1 - 10  $\mu\text{m}$ ) adhere less well and return after a residence time of days to weeks into the reactorwater ("conveyor belt").

The adsorption of ionic cobalt on the zirconium oxide is only important for new fuel elements for a short initial period. Little is known about the influence of silicic acid and organic materials on the adsorption of colloids on the fuel pin surface.

The residence time of Co-59 on the fuel pins is a critical factor. A long residence time of several years leads to the removal of the activated crud with the fuel elements, e.g. Oskarshamn-2, Tsuruga. Medium residence times, e.g. of 250 days as in Mühleberg, of the loosely adhering crud, leads to full activation, return into the reactor water and deposition in the recirculation loops.

## 9.4 THE QUALITY OF THE FEED WATER

### 9.4.1 Introduction

At steady state conditions the largest part of the corrosion products are brought into the reactor water with the feed water. At a feedwater temperature of 190 °C the corrosion rate of austenitic chromium-nickel steels is constant and low ( $12 \text{ mg} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ ). The corrosion rate of carbon steels depends on the corrosion resistance of the material, the oxygen content and the conductivity of the feedwater. The total input of corrosion products into the reactor water depends on the efficiency of the condensate clean-up system.

#### 9.4.2 Reduction of the Corrosion Rate of Carbon Steels by Oxygen Addition

The maintenance of 20 - 60 ppb oxygen concentration in the feedwater reduces the corrosion rate of carbon steels by a factor of 100 and leads to a content of corrosion products in the sub ppm range.

#### 9.4.3 Hydrogen Injection to Avoid Corrosion of Austenitic Steel in Recirculation Loops

The injection of 0.2 - 2 ppm hydrogen to the feedwater is recommended, - see 9.5.3.

#### 9.4.4 The Efficiency of the Condensate Clean-up System for the Removal of Corrosion Products and Metal Ions

The efficiency of the condensate clean-up system determines the concentration of corrosion products in the feedwater and its conductivity. Maximum efficiency is achieved by a dual condensate treatment: deep bed demineralizers (to preferentially eliminate metal ions) and Powdex filters (to preferentially eliminate corrosion products), combined with high pressure condensate recirculation. The conductivity of less than  $0.1 \mu\text{S} \cdot \text{cm}^{-1}$  is near the theoretical value (at  $25^\circ\text{C}$   $0.055 \mu\text{S} \cdot \text{cm}^{-1}$ ) and the corrosion product concentration less than 1 ppb.

Without high pressure condensate recirculation the corrosion products concentration increases by a factor of 10.

#### 9.4.5 Practises during Outage Periods

During outage periods corrosion of the carbon steel in a damp atmosphere or by wetted surfaces should be avoided. This is either done by the recirculation (flowrate  $\sim 1 \text{ m} \cdot \text{s}^{-1}$ ) of oxygenated water (e.g. 5 ppm) with low conductivity (e.g.  $0.1 \mu\text{S} \cdot \text{cm}^{-1}$ ) or by draining the system completely and maintaining a constant purge of dry air. At least in one case the input of iron crud was reduced by a factor of 10 through these "lay-up" practises.

- 9.4.6 a) Addition of zinc, - see 9.2.4)
- b) Nickel to iron ratio, - see 9.2.5)
- c) Organic carbon, - see 9.5.6)
- d) Silicate, - see 9.5.7)

### 9.5 THE QUALITY OF THE REACTOR WATER

#### 9.5.1 Introduction

At steady state conditions the quality of the reactor water depends mainly on the quality of the feedwater and on the throughput through the reactor water clean-up system (RWCU). The corrosion products are mainly haematite particles (95 %), the concentration is in the order of 10 ppb.

#### 9.5.2 The Influence of the Oxygen Concentration on Austenitic Steels

The oxygen content of the reactor water at power is determined by the water radiolysis; typical values are 200 - 400 ppb. The corresponding hydrogen value is far below the stoichiometric ratio of 8; typical values for  $\text{O}_2/\text{H}_2$  are 14 to 55.

The high oxygen concentration may cause intergranular stress corrosion cracking (IGSCC) in sensitized austenitic steels under tensile stress. On the other hand, if the oxygen content is below 1 ppb then the soluble iron concentration in the reactor water increases from 2 - 5 ppb to 6 - 10 ppb with a corresponding increase in the Co-60 concentration.

Ideally then, the electrochemical potential should be at or below - 230 mV (standard hydrogen electrode) corresponding to an oxygen content of about 2 ppb. In practice no crack growth has been observed at oxygen levels of 20 ppb.

#### 9.5.3 Hydrogen Injection to Control the Oxygen Concentration

To maintain the oxygen level at a few ppb, the injection of 0.2 - 2 ppm hydrogen into the feedwater is recommended; hydrogen water chemistry (HWC).

#### 9.5.4 The Efficiency of the Reactor Water Clean-up System for the Removal of Corrosion Products and Metal Ions

The throughput of reactor water through the clean-up system (RWCU) varies considerably from plant to plant; Mühleberg 0.7 %, Shimane 7 % of the feedwater. Evidently a high throughput is recommended.

To avoid power losses high temperature filters with high throughput appear a promising new development. Candidate materials are stainless steel, magnetite and titanium oxide.



### 9.5.5 The Effect of Transients on the Activity Transport

Start-up, shut-down and transients have a large effect on the activity mobilisation, transport and deposition. Typically, the conductivity of the reactor water may increase by a factor of 3 - 20. During these periods the corrosion rate of structural materials is increased and the corrosion products are redistributed.

### 9.5.6 The Rôle of Organic Carbon

Typically the organic carbon content in the reactor water is 700 - 900 ppb. It is not clear whether the organic carbon is brought in with the feed water or is a degradation product of the ion exchange resins. The rôle of organic carbon in the activity build-up is unknown.

### 9.5.7 The Rôle of Silicate

Typically the content of silicate ( $\text{SiO}_2$ ) is between 100 and 300 ppb. The content apparently depends on the age of the filters in the clean-up system, RWCU. The rôle of silicate in the activity build-up is unknown.

- 9.5.8 a) Addition of zinc, - see 9.2.4)  
b) Nickel to iron ratio, - see 9.2.5)

## 9.6 THE QUALITY OF STRUCTURAL MATERIALS

### 9.6.1 Introduction

The corrosion product input can be reduced by using corrosion resistant materials and by exposing them to the appropriate conditions. A low cobalt content in these materials is also desirable to reduce the cobalt inventory.

### 9.6.2 Carbon Steel

The feedwater system is essentially constructed from carbon steel. Severe corrosion occurs during outage periods, when the material is left in a damp atmosphere or in wet condition, - see 9.4.5. To reduce the crud generation low carbon, low alloy steels are recommended, however the published literature is not very explicit.

### 9.6.3 Austenitic Steel

Austenitic steel contains cobalt, typically in the order of 0.2 %. A low cobalt content ( $\leq 500$  ppm) is recommended for materials in the neutron radiation field of the core. Whether or not a reduction of the cobalt content in the austenitic steel in other parts of the primary system is an effective measure, remains questionable.

### 9.6.4 Stellite

Although Stellite represents a negligible fraction of the surface area, it contributes to a large extent to the cobalt input. At reactor operating conditions a loss of 0.7 to 10  $\mu\text{m}$  per year is estimated.

The corrosion rate is high ( $\text{g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ ) and depends on the oxygen content of the water. The cobalt is mainly released in ionic form. At feed water temperature, 190 °C, the Stellite corrosion rate increases by a factor of 2 if the oxygen content goes from 15 to 150 ppb. Since Stellite is used in areas of high wear, the cobalt release from abrasion, in particulate form, may be even more important than water corrosion.

A considerable number of cobalt free hardfacing alloys have been tested as a replacement for Stellite, however no firm recommendations are found in the literature. On the other hand there are reactors with Stellite, e. g. Shimane, with low dose rates in the recirculation loops.

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# CORROSION PRODUCTS, ACTIVITY TRANSPORT AND DEPOSITION IN BOILING WATER REACTOR RECIRCULATION SYSTEMS

*Review of the state of the art, May 1990*

H.P. ALDER

Paul Scherrer Institute,  
Würenlingen, Switzerland

## Abstract

In September 1989 a review of current practices to reduce the radiological exposure of the personnel in BWR's was made. Since then additional information especially from Japan and General Electric was presented and it seemed timely to update the review of the state of the art.

## Introduction

In September 1989 a review of current practices to reduce the radiological exposure of the personnel in BWR's was made [1]. Since then additional information especially from Japan and General Electric was presented and it seemed timely to update the review of the state of the art. Not considering improvements in equipment and working conditions (automation of inspection and operation, improved design, shortened worktime and radiation shielding) the following topics are of particular interest:

### Iron crud reduction in the feedwater

- Prefiltration of the condensate water
- Dual condensate polishing system
- Corrosion resistant materials
- Oxygen injection
- Nickel to iron ratio control
- Practices during outage periods

### Low cobalt alloys

### Cobalt reduction in the reactor water

- The efficiency of the reactor water clean-up system
- Practices during reactor shutdown

### Cobalt deposition in the corrosion layer of austenites

- Alkaline prefilming of the primary piping
- Zinc addition
- Hydrogen water chemistry

Since the Japanese have a large family of new and old BWR's and a wealth of information is available, it seemed appropriate to devote a special chapter to the progress made in Japan.

## 1 Iron crud reduction in the feedwater

### 1.1 Prefiltration of the condensate water

Already in Shimane-1, 1974, a prefilter was installed to clean the condensate water. Typically the condensate water contains 20 to 30 ppb iron, at the prefilter inlet, at the outlet 1 to 3 ppb [12] mostly in the form of crud. Prefilters are used in modern Japanese reactors, e. g., Shimane-2, 2F-1, 2F-2, 2F-3, K-1 [2].

### 1.2 Dual condensate polishing system

Powdered resins (Powdex) are excellent particulate filters, but only 70 to 90 % effective at removing ionic impurities:

< 2 ppb iron in feedwater,  
5 - 15 ppb Zn, 10 - 30 ppb Cu with brass condenser

Deep bed demineralizers eliminate dissolved ions more efficiently

< 5 ppb iron in feedwater [5]

The best efficiency is achieved by a dual condensate treatment: Deep bed demineralizers to preferentially eliminate metal ions, Powdex filters to preferentially eliminate particulates, combined with high pressure condensate recirculation [1]

Conductivity < 0.1  $\mu$ S/cm corrosion products, < 1 ppb

Without high pressure condensate recirculation the corrosion products concentration increases by a factor of 10.

Already in Shimane-1, 1974, a dual condensate purification system was installed resulting in an iron concentration of less than 1 ppb at the outlet. Dual systems are used in modern Japanese reactors, e. g. Shimane-2, 2F-1, 2F-2, 2F-3, K-1 [2].

### 1.3 Corrosion resistant materials

In modern Japanese reactors, e. g. Shimane-2, 2F-1, 2F-2, 2F-3, K-1 corrosion resistant steels are used to reduce the iron crud concentration in the feedwater system [2] [4].

Upstream of the condensate prefilter for condensor internals and heater drain pipes atmospheric corrosion resisting steels to at least 70 % are used.

Iron in the condensate water (ppb)

Old BWR, carbon steel	30
Modern BWR, corrosion resisting steel	10

Downstream of the dual condensate polishing system low alloy steel for the heater body (instead of carbon steel) and low cobalt stainless steel (<0.05 % Co) for heater tubing is used [2] [4].

Iron in the feedwater (ppb)

Old BWR, carbon steel	1
Modern BWR, low cobalt stainless steel	0.5

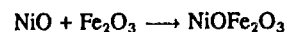
## 1.4 Oxygen injection

“Oxygen injection into the feedwater to prevent corrosion of carbon steel piping has been one of the most successful counter measures for shutdown dose reduction” [4]. 20 to 60 ppb oxygen injection into the feedwater before the condensate polishing system reduces the corrosion rate of carbon steels by a factor of 100 and leads to a content of corrosion products in the sub ppb range [1].

Oxygen injection was introduced already in Shimane-1, 1974 and subsequently in Japanese BWR's [2],[4], 1981 in KKM and today 84 % of the US-plants use it [3].

## 1.5 Nickel to iron ratio control

In the reactorwater at  $p_H$  6 and 300 °C Ni-ion in its stable form NiO is deposited on nucleate boiling sites on the fuel cladding surface. NiO reacts with deposited iron crud,  $\alpha$  -  $Fe_2O_3$  :



The chemical behaviour of cobalt is similar to nickel.

If the iron crud concentration in the feedwater reaches a practical minimum of e. g. 0.1 ppb an increase in the ionic Co-60 concentration in the reactor water is noticed. This is due to the high dissolution rates of the monoxides (NiO, CoO), which is about 3 to 10 times faster than of the iron spinel oxides. Therefore the Ni/Fe ratio should be kept at least at the theoretical value of 0.5, in practice e. g. at 0.2.

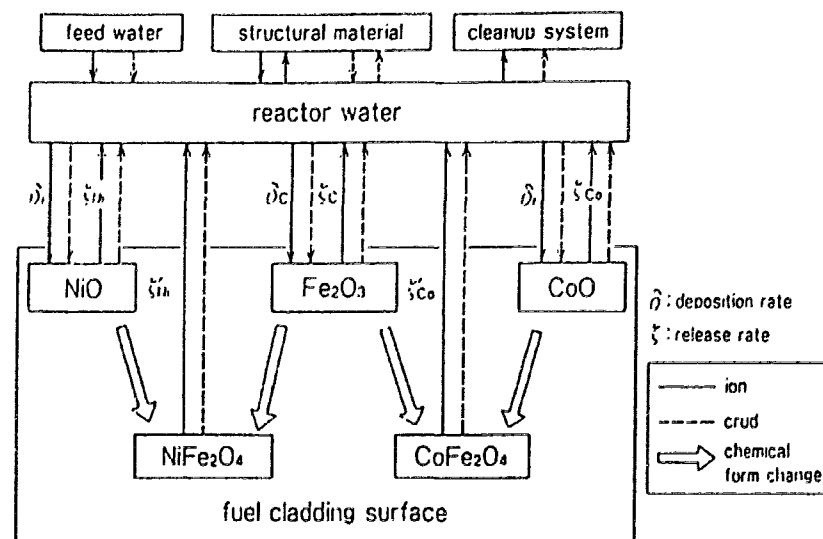


Fig. 1: Deposition of Ni- and Co-ion from the reactor water on the fuel cladding surface as iron oxide spinels [4].

Especially during the early stages of plant operation up to several thousand hours a high concentration of nickel-ion up to 1 ppb is due to the corrosion of austenites, later the level in the reactor water is constant and low, typically 0.1 ppb. To form iron spinel oxides the feedwater iron concentration is adjusted by condensate by-passing some of the condensate filter units e. g. at 2F-2, 2F-3, K-1 or by electrolysis of pure iron steel, at a maximum rate of 15 g/h, e. g. at 2F-4, S-2. Adjusting the Ni/Fe ratio in the feedwater to 0.2 reduces the ionic Co-60 content in the reactor water by a factor of 5 to about 10 pCi/ml [2],[4], [12].

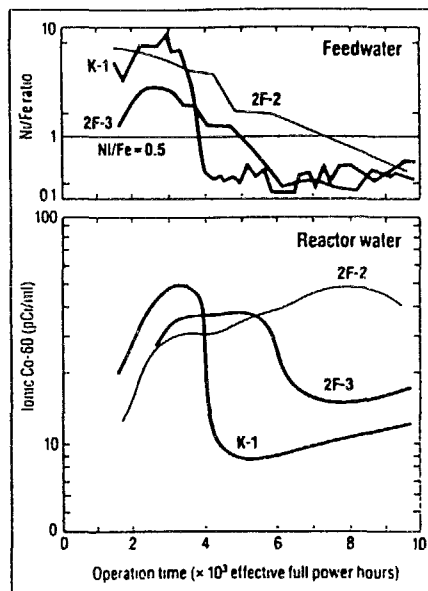


Fig. 2: The effect of nickel to iron ratio control in the feedwater on the ionic Co-60 concentration in reactor water. At 2F-3 and K-1 a sharp drop is noticed as the ratio reaches 0.2 [2].

For GE reactors no application of Ni/Fe ratio control is known, this may be due to the fact that GE reactors operate in general at higher iron crud levels in the feedwater.

## 1.6 Practises during outage periods

During outage periods the corrosion of the carbon steel in a damp atmosphere or by wetting should be avoided by

- recirculation of oxygenated water (e. g. 5 ppm)
- complete drainage and drying
- cleaning before reactor start-up

Through these lay-up practises at least in one case the input of iron crud was reduced by a factor of 10 [1], [2].

These practises are followed in modern Japanese reactors e. g. 2F-1, 2F-2, 2F-3, K-1 but also in old BWR's e. g. 1F-3 [2].

## 2 Low cobalt alloys

To decrease the cobalt inventory in LWR's a large number of Co-free or Co-poor alloys are proposed [11], [1]. Little is known about the in-plant application and long-term behaviour in plant operation.

For modern Japanese BWR's e. g. 2F-1, 2F-2, 2F-3, K-1 the following low cobalt alloys were used [2]:

Feedwater heater tubing

Low cobalt stainless steel (< 0.05 %)

Springs in fuel

Inconel X 750 with a cobalt content of 0.05 % instead of 0.22 %.

Control rods

Nitronic 60 for pins

CFA for rollers (Co < 0.2 %)

Stainless steel for sheaths, cobalt content 0.03 % instead of 0.2 %.

For valve seats Stellite is still in use.

Table 1: Low cobalt alloys in modern Japanese BWR's

	Ni	Co	Cr	C	Si	Fe	Mn	B
Nitronic-60	8.0 - 9.0		16.0 - 18.0	< 0.1	3.5 - 4.5	Bal.	7.0 - 9.0	
CFA	Bal	< 0.5	3.0 - 39.0	< 0.1	< 0.1	1.5		1.7
Inconel X750	Bal	0.05	14.0 - 17.0	< 0.08	< 0.5	5.0 - 9.0	< 0.1	

Experience in modern Japanese BWR's with these low cobalt materials indicates a reduction of the relative contribution of Co-60 to radiation by a factor of 4, compared to old BWR's. In old BWR's the Co-60 radiation is to 70 % attributed to crud and 30 % to ionic Co-60. In modern plants this ratio is reversed [2],[4].

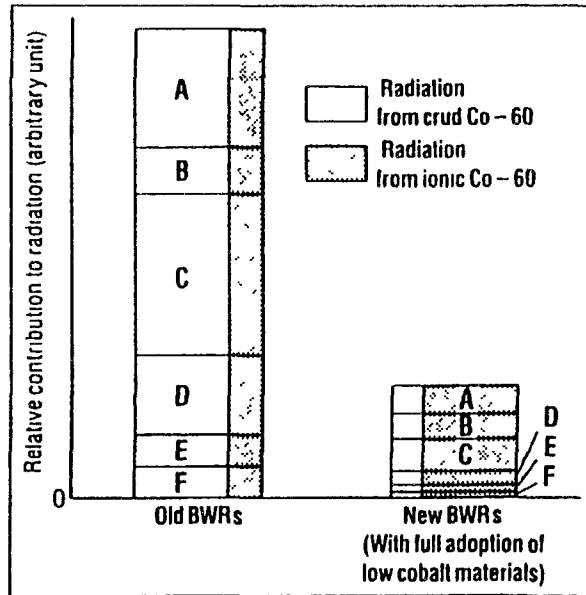


Fig. 3: Effect of low cobalt materials on the contribution of Co-60 to radiation, a comparison of old and modern Japanese reactors [2].

- A Stellite in reactor
- B Stainless steel in reactor internals
- C Inconel in reactor core
- D Stainless steel in feedwater heater
- E Stellite of turbine blades
- F Carbon steel, other

### 3 Cobalt reduction in the reactor water

#### 3.1 The efficiency of the reactor water clean-up system

A special feature already of Shimane-1, 1974, is a high throughput through the reactor water clean-up system (RWCU). The ratio of clean-up to the feedwater flow rate is 7 %. This high capacity as compared to current operating BWR's is also a special feature for Shimane-2, 1988, 5 % [12]. For comparison Mühleberg 0.7 % [1].

### 3.2 Practises during reactor shutdown

#### a) Experience in Japanese reactors

Extensive tests were made in Japan in the old BWR's 1F-3, 1F-5 and in modern BWR's 2F-2, 2F-3, K-1 [7].

During reactor shutdown a peak in the radioactive crud concentration in the reactor water occurs. This crud is partly deposited in low flow areas. The peak height depends on the shutdown procedure. Following, an example of the Japanese 1100 MW Fukushima-Daini No. 2 plant, 2F-2 [7].

Cooling Rate (°C/h) *	Holding Time at 50 bar (h)	Total Crud release (Ci Co-60)	
35/13	—	5.7	Conventional
<15/<15	3	0.4	Modified

\* First half, second half

For a conventional shutdown the crud concentration peak is in the order of  $10^{-2}$   $\mu\text{Ci/ml}$ , compared to an operational level of  $10^{-4}$  to  $10^{-5}$   $\mu\text{Ci/ml}$  at 280 °C [7]. For a modified shutdown this peak is depressed by one to two orders of magnitude.

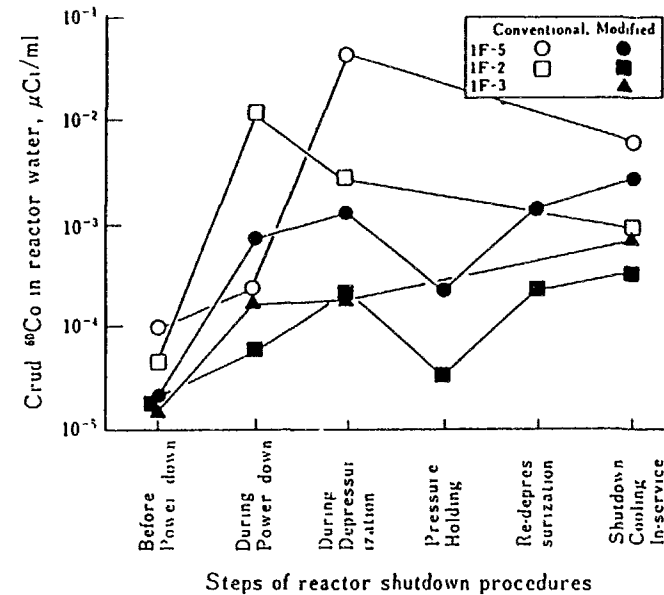


Fig. 4: Maximum Co-60 crud concentration in reactor water at each step of shutdown procedures [7].



During the conventional and the modified shutdown procedure an increase in the ionic radioactivity (Co-58, Co-60) and metal ions ( $\text{Ni}^{+2}$ ,  $\text{Co}^{+2}$ ) occurs. Between 160 °C and 80 °C a maximum value in the order of  $10^{-3}$   $\mu\text{Ci/ml}$  ionic Co-60 is reached, one to two orders of magnitude above normal operation at 280 °C. This is due to the fact that the metal oxides from fuel crud and from structural materials have a maximum solubility at around 100 °C. The increase of ionic radioactivity in the reactor water is a desirable phenomenon since it will not redeposit on low temperature surfaces and is removed by the RWCU system. On the RWCU piping the Co-60 deposit in the order of 3 mCi/cm<sup>2</sup> is reduced after a period of 20 to 30 hours by about 10 % [7].

#### b) Experience in European reactors

At Gundremmingen Plant C [6] the total Co-60 concentration in the reactorwater is at  $10^7$  Bq/m<sup>3</sup> ( $10^{-3}$  to  $10^{-4}$   $\mu\text{Ci/ml}$ ) at 270 °C. During the shutdown, similar to the modified Japanese procedure, the Co-60 concentration increases by one order of magnitude from 70 to 45 bar (280°C to 240 °C) in about 2 hours. During a holding period of a few hours the Co-60 concentration decreases slightly faster than would be expected from the clean-up rate alone, meaning some deposition takes place. After this holding period the cooling rate is about 15 °C/h and the Co-60 concentration does not exceed  $4 \cdot 10^8$  Bq/m<sup>3</sup> ( $10^{-2}$   $\mu\text{Ci/ml}$ ).

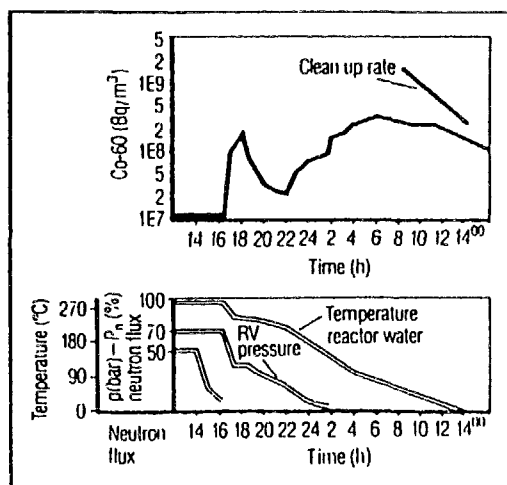


Fig. 5: Total Co-60 release during the modified shutdown at Gundremmingen Plant C [6]

In the Leibstadt Plant the total Co-60 concentration in the reactor water is at  $10^{-3}$  to  $10^{-4}$   $\mu\text{Ci/ml}$  during normal operation. During the shutdown the total Co-60 concen-

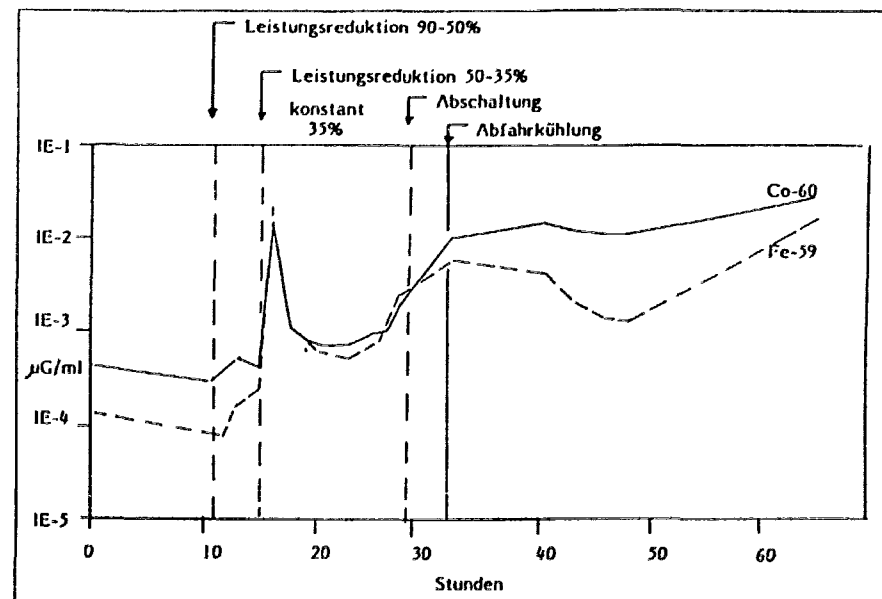


Fig. 6: Co-60 concentration in the reactorwater during the shut-down at Leibstadt [9]

tration increases by one to two orders of magnitude. In contrast to Gundremmingen during the cooling period, 30 to 60 hours, the Co-60 concentration in the reactor water stays high ( $10^{-2}$   $\mu\text{Ci/ml}$ ), even increases [9].

## 4 Cobalt deposit in the corrosion layer of austenites

### 4.1 Alkaline prefilming of the primary loop

To control the activity deposition on the primary piping surface preoxidation treatment at  $p_H$  8.0 to 8.6 at zeropower for 400 hours was carried out at 2F-4 before startup of the new plant. Test specimens were inserted into the primary loop and for 3000 hours exposed to 25 to 100 % power [4].

Cobalt deposition ( $\mu\text{Ci/m}^2$ )

	as is	alkaline prefilming
unpolished	4	3
polished	1.8	1.3

Alkaline prefilming is applied for currently constructed Japanese BWR's to reduce shutdown dose rates, e. g. 2F-2, 2F-3, 2F-4, K-1.

## 4.2 Zinc addition

### a) Basic Data

- A review of GE BWR plant experience shows an apparent correlation between the material of the condenser tubing, the condensate treatment system and activity buildup. A powdered resin condensate treatment system appears to have a lower activity buildup in the recirculation lines than other combinations.
- Reactors with this combination contain 5 to 15 ppb zinc in the reactor water. Corrosion films of austenitic steel samples from a limited number of plants indicate that the Co-concentration in weight percent is the same for all plants but that the thickness of the film is lower at plants with the mentioned combination. 10 to 20 % zinc were incorporated in the corrosion film of austenites.
- A series of autoclave tests on 304 stainless steel samples at 288 °C for 300 hours showed a decrease in the oxide thickness by a factor of 10 at 10 ppb ionic zinc.

Without zinc = 0.3  $\mu\text{m}$ , 10 ppb zinc = 0.03  $\mu\text{m}$

ionic zinc acts as a corrosion inhibitor for stainless steel surfaces.

- Inhibition of the corrosion translates into a reduced Co-60 buildup. In a loop 304 stainless steel samples at 288 °C for 2000 hours showed a decrease in Co-60 buildup by a factor of 3.5

Without zinc = 1.0  $\mu\text{Ci}/\text{cm}^2$ , 10 ppb Zinc = 0.3  $\mu\text{Ci}/\text{m}^2$

- For oxide layers grown under "non-zinc" conditions, a transformation of the existing oxides is postulated. Lab tests indicate that zinc infiltrates these films and causes a restructuring of the crystals followed by sloughage of some fraction. This transition is believed to be slow [5].

### b) Review of plant experience

Not considering Leibstadt Plant, 5 GE plants are injecting zinc:

- Hope Creek, 1170 MW, startup 1986, zinc injection since startup.
- Nine Mile Point 2, 1214 MW, startup 1987, zinc injection since startup.
- Millstone Point 1, 690 MW, startup 1970, zinc injection since 1987 after decontamination

- James A. Fitzpatrick, 821 MW, startup 1975, zinc injection and hydrogen water chemistry after decontamination in 1989
- Perry plant 1, 1252 MW, startup 1986, zinc injection since 1989. Zinc is added as sub-micron zinc oxide powder into the suction side of the feedwater pumps.
- For the Leibstadt plant a passive system is foreseen, as the hot feedwater at 214 °C passes through a bed of compressed zinc oxide pellets.

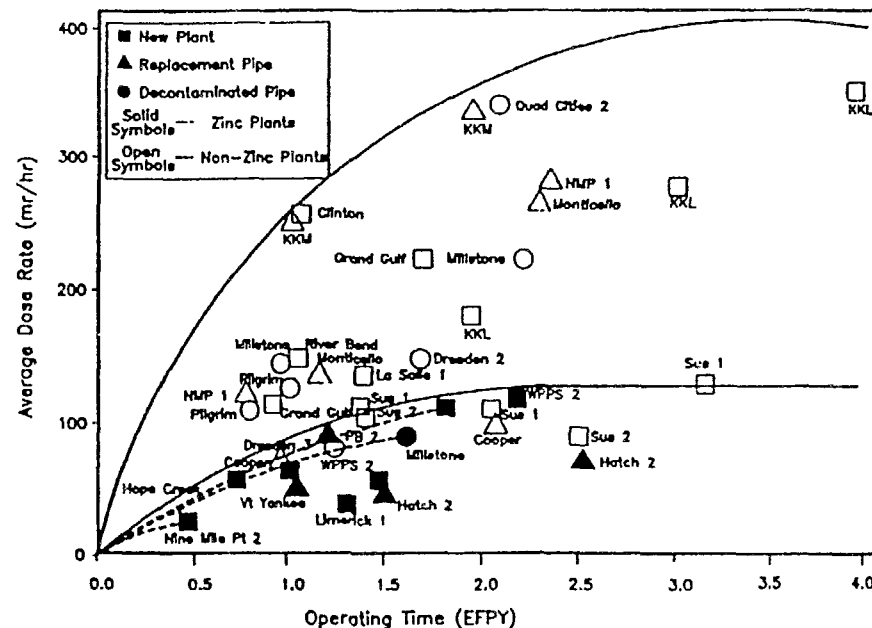


Fig. 7: Radiation buildup for GE BWR recirculation system piping [5]

### c) Experience with new plants

- Hope creek, 1170 MW, startup 1986, with zinc injection shows a dose rate of the recirculation system piping of approximately a factor 2 below other new BWR's started up in the same time frame. During the first shutdown 1988 a significant release of Zn-65 from the fuel deposit to the reactorwater occurred, probably due to the high iron concentration in the feedwater of 11 ppb and enhanced by the non-availability of the RWCU system. The plant decided to reduce the zinc input to 2 ppb which is not adequate for full protection [8].

EFPY	0.75	1.02	1.81
Co-60 ( $\mu\text{Ci}/\text{cm}^2$ )	1.0	1.2	2.3
Zn-65 ( $\mu\text{Ci}/\text{cm}^2$ )	5.6	9.7	13.8

- Nine Mile Point 2, 1214 MW, startup 1987, uneventful zinc injection [8]

#### d) Experience with old plants

Millstone Point 1, 690 MW, startup 1970, decontaminated the recirculation loop in 1984 and measured the subsequent recontamination. After a second decontamination in 1987 zinc was injected. Therefore a direct comparison between the period 1984 to 1987 without zinc and 1987 to 1989 with zinc addition can be made. The contact dose rate with zinc addition is by a factor of two lower and of logarithmic shape instead of parabolic, therefore a stabilization in two years is expected [5].

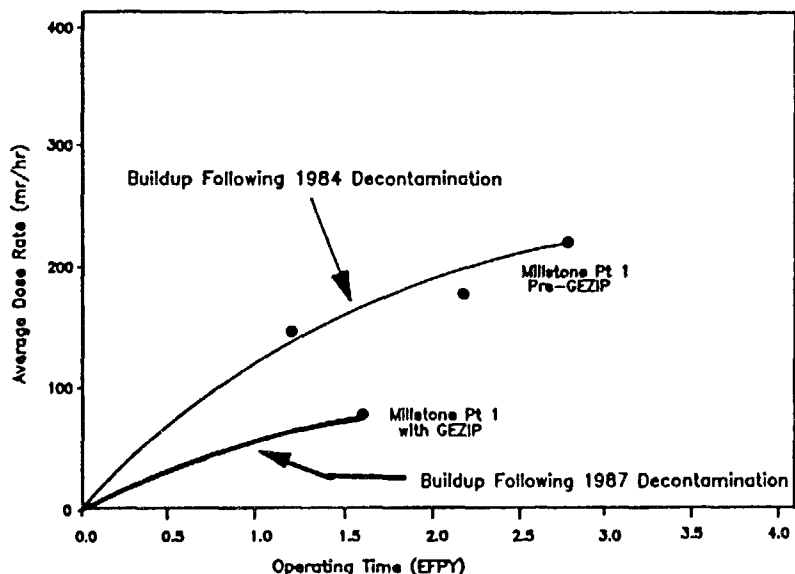


Fig. 8: Primary system radiation buildup, with and without zinc addition, at Millstone Point 1 [5]

An unexplained benefit is that the zinc injection suppresses the soluble Co-60 concentration in the reactor water by a factor of 5 to 10 below the base value of about  $10^{-4} \mu\text{Ci}/\text{cm}^2$ . It is speculated that zinc decreases the release rate of cobalt from the fuel cladding surface.

#### e) Advantages and disadvantages of zinc addition

- The injection of 5 to 15 ppb ionic zinc reduces the contact dose rate by at least a factor of 3, in combination with HWC (see 4.3) by a factor of 10.
- Zn-65 is the activation product of the stable isotope Zn-64, which is 48 % of the naturally occurring zinc. It has a half life of 243 days and contributes a dose of 4.6 lower than Co-60 on a per Curie base. To overcome this disadvantage
  - the Zn-65 inventory should be minimized
  - Zinc source material depleted in Zn-64 should be used.
- Zinc accumulates in the loose crud on fuel rods, is activated and can be set free during transients in particular if the iron oxide concentration in the feedwater is high. Powdered resin condensate systems are recommended to reach the goal of < 2 ppb total iron.

### 4.3 Hydrogen water chemistry

The oxygen concentration in the reactor water is typically 200 to 400 ppb. The high oxygen concentration may cause intergranular stress corrosion cracking (IGSCC) in sensitized austenitic steels under tensile stress. On the other hand, if the oxygen concentration is below 1 ppb then the soluble iron concentration in the reactor water increases from 2 - 5 ppb to 6 - 10 ppb with a corresponding increase in the Co-60 concentration. To maintain the oxygen level at a few ppb the injection of 0.2 - 2 ppm hydrogen into the reactor water is recommended; hydrogen water chemistry (HWC), [1].

In a series of autoclave tests on 304 stainless steel samples at 288 °C for 2000 hours it was shown that there is a synergy between zinc addition and HWC in the reduction of the Co-60 buildup [5]:

		HWC in addition
Without zinc	1.0 $\mu\text{Ci}/\text{cm}^2$	0.7 $\mu\text{Ci}/\text{cm}^2$
10 to 15 ppb zinc	0.3	0.1

Zinc reduces the contact dose by a factor of 3, in combination with HWC by a factor of 10 [5].

An open question is how much more hydrogen would be required to protect in core components vulnerable to irradiation assisted stress corrosion cracking (IASCC) and whether the larger hydrogen concentration required will increase turbine radiation fields by increasing N-16 volatility by converting dissolved nitrate to gaseous ammonia [10].

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## MAIN TRENDS IN INVESTIGATIONS OF CORROSION PRODUCTS TRANSFER PROCESSES IN NPP CIRCUITS

V.V. VERSIN, V.P. BRUSAKOV, I.L. RYBALCHENKO,  
V.G. KRITSKIJ, A.S. KOROLEV  
All-Union Scientific Research and Project  
Institute of Complex Power Technology,  
Leningrad, Union of Soviet Socialist Republics

### Abstr..ct

Numerous attempts have been made to develop models of activated corrosion product mass transfer. The great number of such models demonstrated the lack of the general model, which would properly reflect the operational experience with the transport of corrosion products, especially activated.

This report discusses two theoretical approaches to understanding corrosion products transport processes in NPP circuits.

Safe and reliable operation of a nuclear power unit is closely connected with successful solution of the problems caused by corrosion of constructional materials, mass transfer and deposition of corrosion products in the plant technological circuits.

In the summary report on CRP CCI / 1 / it was mentioned, that maintaining water chemistry within the specified limits eliminated the possibility of straight corrosion attack and provided for faultless performance of fuel cladding during reactor operation.

In connection with the observed trend to increase burnup and fuel heat flux a study is carry out in the USSR of the effects of fuel surface crudding on the reliability of fuel operation. However a steady growth of radiation exposures due to corrosion product deposits on the inner surfaces of the equipment remains quite a serious problem. This becomes most urgent in the periods of reactor shutdown for maintenance and repair.

Numerous attempts have been made to develop models of activated corrosion product mass transfer. The great number of such models demonstrated the lack of the general model, which would properly reflect the operational experience with the transport of corrosion products, especially activated.

TABLE 2.

Steel grade	Deposit value, mg		Corrosion rate, mg/(m <sup>2</sup> ·h)	
	expt.	calcul.	expt.	calcul.
08X14M4D	0,7	1,1	17	15
12X18H10T	0,3	0,4	5	5
Steel 20	0,2	1,4	18	22

TABLE 1. VERIFICATION OF THE MECHANISMS BASED ON THE OPERATING EXPERIENCE OF POWER PLANTS

Designation	Heat-exchange conditions	pH	q W/m <sup>2</sup>	Q MW	Cr mg/L	Deposits				Note
						Local, g/(m <sup>2</sup> ·h)		Summarized, g/h		
						Actual	Calculated	Actual	Calculated	
CANDU	Under pressure	10-7	8·10 <sup>4</sup>	135	1.5 Ci/m <sup>3</sup> (Co 60)	4.2·10 <sup>-4</sup> Ci/m <sup>2</sup>	4.6·10 <sup>-4</sup> Ci/m <sup>2</sup>	-	0.8 Ci/an	C.P. Mobility, U <sub>p</sub> = -3.6·10 <sup>-4</sup> m <sup>2</sup> /(V·h) Deposit on cooling sur- face
Boiler TMM-75	Boiling	-	5·10 <sup>5</sup>	21	2Fe 0.160 Cu	0.13 5·1·10 <sup>-2</sup>	0.2 4.3·10 <sup>-2</sup>	10-15 2	9 1.9	U <sub>Co</sub> = 2.7·10 <sup>-4</sup> m <sup>2</sup> /(V·h) Net copper release
Fuel ele- ment B&K-50	Boiling	7	8.5·10 <sup>5</sup>	-	0.08	1·10 <sup>-2</sup>	1·10 <sup>-2</sup>	-	-	τ = 17000h
SGHWR	Boiling	7	-	150	0.05 (Fe)	-	-	19600 <sup>a</sup> 13000 <sup>b</sup>	19000	<sup>a</sup> Cleaned by de- contamination; <sup>b</sup> en- riched with feed water

This report discusses two theoretical approaches to understanding corrosion products transport processes in NPP circuits.

The first one was reported in detail at IAEA specialist's meeting on "Influence of water chemistry on fuel element cladding behaviour in water cooled power reactors" held in Leningrad in 1983.

To describe the formation of corrosion products in the plant circuits, a theoretical model based on electrochemical nature of the occurring processes is suggested.

It's been experimentally found that in systems with heat transfer the thermoelectromotive force is of the primary importance for the processes of deposit formation and corrosion /2, 3/.

Comparison of calculated values of deposition rates on the heat transfer surfaces with those actually observed in power plants /Table 1/ shows that the deposition process caused by thermoemf is a significant component of the mass transport over a wide range of conditions.

In the circuits without heat transfer the processes of corrosion product formation and deposition proceed under the action of electromotive force of microgalvanic couples /3/. The test and calculated values of corrosion rates and deposit amounts are given in table 2. In most cases these are in good agreement.

TABLE 3. COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF STATIONARY CONCENTRATIONS IN DIFFERENT WATER CHEMISTRY CONDITIONS

Water chemistry Conditions	pH	$C_{\max} - C_{\min}$ mg/kg	$C_{\text{stationary}}$ , mg/kg	
			exp.	calcul.
Neutral	7,0	0,380- 0,070	0,180	0,180
Acid	4,5	5,280- 0,490	1,900	3,200
Alkaline	9,7	0,093-0,007	0,019	0,007

In terms of electrochemically equivalent mass transfer a conclusion about corrosion product equilibrium concentration attainment is made. This concentration depends only on the mobility and concentration of a potential-forming ion as on the electrophoretic properties of corrosion product particles. The experiments in a wide concentration range confirm this conclusion quantitatively /Table 3/.

In table 4 the calculated values of corrosion product stationary concentrations are compared with those measured during long-term operation the systems with different sets of constructional materials.

The values of corrosion rates, deposition and stationary concentration calculated with the proposed model agree well with data measured in various plants.

However this approach is not the only way of understanding the corrosion product transfer processes in NPP circuits. At present attempts are undertaking to work out a semi-quantitative physico-chemical model of corrosion product transfer based on the thermodynamic principles. The results of applying this approach to the corrosion and corrosion product release processes are presented below.

TABLE 4. COMPARISON OF CALCULATED VALUES OF CORROSION PRODUCT CONCENTRATIONS WITH THOSE ACTUALLY OBSERVED IN DIFFERENT CONDITIONS

System and reactor type	Surface material	pH at 25°C	$C_{\text{H}}$ at specified temperature, g - eq/l	Actual stationary concentration of corrosion products, mg/kg	Calculated stationary concentration of corrosion products, mg/kg
Swampport NPS (pressure-water reactor)	Stainless steel	10	$3.6 \cdot 10^{-8}$ (285°C)	0.003 - 0.005	0.004
Dynamic loop	Stainless steel, aluminium	5.5	$3.6 \cdot 10^{-6}$ (260)	0.1 (AL)	0.1 (AL)
Novovoronezh NPS	Stainless steel	8 - 10 $6(\text{HNO}_3)$ 6-6.3	$1.8 \cdot 10^{-6} - 2.1 \cdot 10^{-7}$ $2.6 \cdot 10^{-6}$ (260°C) $2.6 \cdot 10^{-6} - 1.8 \cdot 10^{-6}$ (260°C)	0.09 - 0.11 0.28 0.3 - 0.1	0.2 - 0.02 0.28 0.28 - 0.19
St-1	Stainless steel	6.4 - 8.5	$(2.1-1.6) \cdot 10^{-6}$ (230°C)	0.2	0.23 - 0.17

Direct observation of the morphology and phase composition of steel corrosion products allow to expect the physico-chemical connection between the oxide film characteristics and water chemistry parameters.

Fig.1 shows carbon steel oxidation rates as function of temperature in neutral water with different salt and oxygen contents.

Fig.1b shows calculated values of iron oxides solubilities in the same conditions. The first thing that attracts attention is similarity of the plots on the right and left hand sides of the fig.1.

The upper curves describe steel corrosion in water containing large concentrations salts /a/ and oxygen and total equilibrium  $\text{Fe}(\text{OH})_2$  solubility /b/ respectively. Carbon steel in this medium, carbon steel, is covered with a loose film of ferrous oxide and hydroxide.

The middle curves describe steel corrosion in demineralized water with oxygen content about 3 ppb and solubility of the  $\text{Fe}(\text{OH})_3$  up to 423 K and magnetite  $> 423$  K at the same conditions.

The lower curves describe steel corrosion in demineralized feed water with oxygen concentration about 200 ppb and the hematite solubility at the same conditions.

Despite the difference in water chemistries there is almost full similarity in temperature plots of corrosion kinetics and phase solubilities of some iron-based corrosion products.

Many investigators mention strong effect of dissolved chemically active gases on corrosion processes.

Fig.2 compares plots of experimentally measured steel corrosion rates /4/ and  $\text{Fe}_2\text{O}_3$ -,  $\text{Fe}_3\text{O}_4$  equilibrium solubilities in neutral demineralized water us dissolved  $\text{H}_2$  and  $\text{O}_2$  contents. A symbatic character of the kinetic and thermodynamic plots is clearly seen. Furthermore a sharp drop in the corrosion rate with oxygen injection to the coolant correlates with the change of corrosion product phases, which control

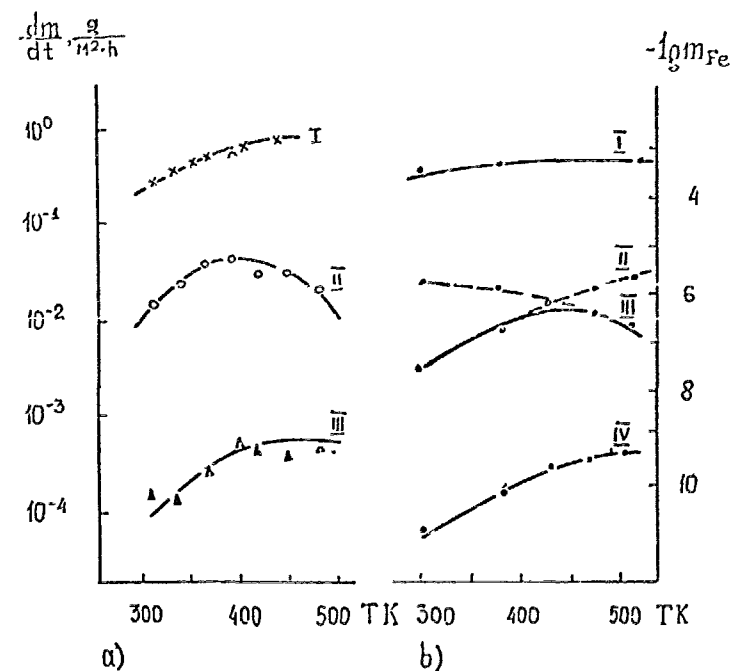


Fig.1 Change of steel corrosion and iron oxide solubility vs temperature

a) Experimental data [4]  $\tau_{\text{test}} = 5000$  h.

I - Tap water 2...11 ppm  $\text{O}_2$

II - desalt water 3 ppb  $\text{O}_2$

III - desalt water 200 ppb  $\text{O}_2$

b) results of our calculations for pH = 7,0 [5]

I -  $\text{Fe}(\text{OH})_2$  3...30 ppm  $\text{O}_2$

II -  $\text{Fe}(\text{OH})_3$  0,1... 3 ppb  $\text{O}_2$

III -  $\text{Fe}_3\text{O}_4$  0,1... 3 ppb  $\text{O}_2$

IV -  $\text{Fe}_2\text{O}_3$  30... 300 ppb  $\text{O}_2$

the corrosion process. Certainly, the value of oxygen passivation threshold remains, though the fact of its existence is quite obvious.

A similar comparison of calculated and experimental data but for acid and base environments has also demonstrated

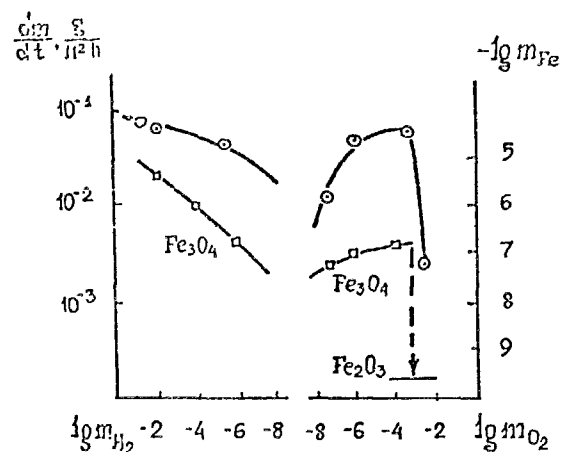


Fig.2 Changes of steel corrosion rate and iron oxide solubility vs hydrogen and oxygen contents in water  
upper curve - experimental data  $\tau_{\text{test}} = 250$  h; pH=7,0;  
T = 562 K  
lower curve - calculated solubilities of  $\text{Fe}_3\text{O}_4$   
and  $\text{Fe}_2\text{O}_3$ ; pH= 7,0; T = 573 K

correlation between the kinetic and thermodynamically equilibrium processes.

In accord with the above view point it's been suggested that the carbon steel corrosion is controlled by the thermodynamic equilibrium of the surface oxide film with the environment. The initial stage of metal oxidation is connected with the topochemical reaction of forming the surface oxides. The latter being completed or definite oxide thickness achieved the oxidation kinetics becomes limited by reagent transport through the oxide layer or corrosion product release into the coolant.

In a common case with two interfaces the integral equation for gaseous oxidation takes the form:

$$\frac{e^2}{K_D'} + \frac{2e}{K_C'} = 2C_0 \tau + B \quad (1)$$

where  $e$  - film thickness;

$C_0$  - reagent concentration on outer oxide surface interface;

$K_C'$  - average rate of film formation on phase boundary;

$K_D'$  - diffusivity;

$\tau$  - time;

$B$  - integration constant.

As the film grows in thickness the diffusion component becomes more significant. The film thickness  $e$ , metal density in the oxide film  $\rho$  and mass of metal ionized per unit area -  $\Delta m$  relate as:

$$\Delta m = e \cdot \rho \quad (2)$$

Then with the diffusion control eq.(1) becomes:

$$\Delta m = \rho \sqrt{2C_0 K_D' V_0 \tau} \quad (3)$$

where  $K_D'$  - rational oxidation constant;

$V_0$  - specific volume of corrosion product layer.

In case of water corrosion a simultaneous corrosion products release take place and the oxide surface is covered by the corrosion products which are thermodynamically stable in the specific water chemistry conditions.

The results obtained have led to a correlation between the corrosion parameters (rational oxidation constant, total corrosion loss, etc) and equilibrium solubility of the corrosion phase that is stable in specific corrosion test conditions (Fig.3). This relationship may be expressed as a function of

$$I_g \Delta m = A + 1/2 I_g m_{\text{Fe}} \quad (4)$$

It generalized practically all the data on corrosion and solubility independent of conditions in which they are obtained and is equivalent to eq.(3)

The suggested thermodynamic approach may be also spread on other mass transfer processes and become the basis for



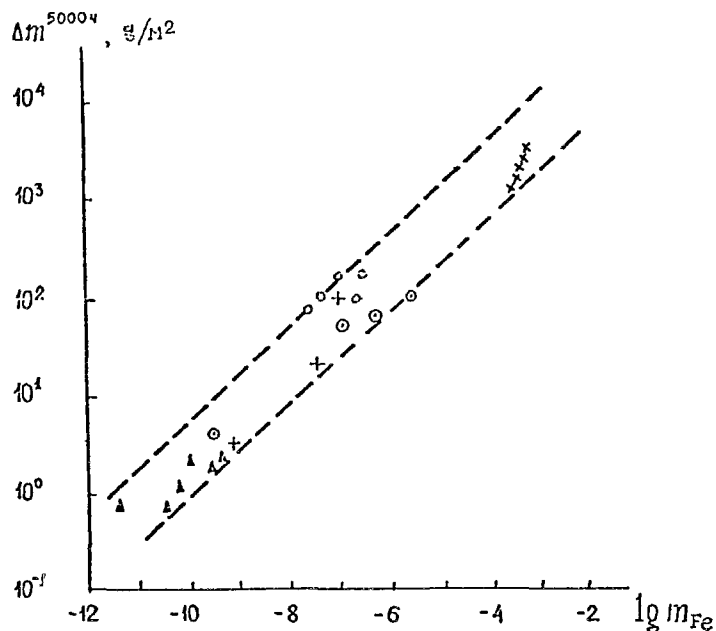


Fig.3 Correlation between solubilities of iron oxides and total steel corrosion at different water chemistry parameters. ( For convinience the experimental data have been recalculated for single test time 5000 h using eq.2.

○ × △ - data from Fig.1  
 ◎ - data from fig.2  
 + - data with pH variation

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formulation a new corrosion product transfer model for NPP's circuits.

At present we can't give preference to any of the considered above theoretical approaches. Each of them has some difficulties which we should get over in the process of modeling the total mass transfer of activated corrosion products.

## TRANSFER OF CORROSION PRODUCT PARTICLES IN REACTOR CIRCUITS

*Quantitative evaluation of corrosion product  
deposition on fuel elements*

V.P. BRUSAKOV, Yu.A. KHITROV,  
V.N. FEOFANOV, V.V. VERSIN

All-Union Scientific Research and Project  
Institute of Complex Power Technology,  
Leningrad, Union of Soviet Socialist Republics

### Abstract

In this paper a mechanism of corrosion product transport is proposed. The model gives a quantitative description of deposition and distribution of radioactive corrosion products on the surface of power reactor circuit. The model is based on the existence of difference of potential in thermal gradients.

Some applications of the model are discussed.

The theoretical basis of the transport processes governed by thermoelectromotive force was described previously. Once the temperature gradient exists, the thermo-emf arises between different temperature areas. The main temperature gradient is observed in the coolant region directly adjoining the heat-transfer surface. The flow of charged particles forced by the thermo-emf is expressed by:

$$\alpha_r = \frac{\varepsilon U_r}{\lambda} C_r q \quad (1)$$

where  $C_r$  is the particle concentration, g-eq/m<sup>3</sup>;  
 $\lambda$  is the heat-conductivity coefficient, W/(m·K);  
 $q$  is the specific heat flow, W/m<sup>2</sup>;  
 $\varepsilon$  is the specific thermo-emf, V/K;  
 $U_r$  is the electrophoretic mobility of particles,  
m<sup>2</sup>/(V·h).

The "r" descriptor indicates that the values it refers to are calculated for colloidal and suspended particles present in the coolant.

The charge value and sign  $\varepsilon$  depend on the nature and concentration of the potential-forming ion (agent).  $\varepsilon$  is negative with hydrogen or cuprum potential-forming ions and it is positive with oxygen potential-forming agent.

In a closed system with heat transfer at negative specific thermo-emf, the heating surface is a cathode on which potential-forming ion reduction is taking place (e.g.  $\text{Me}^+ + \bar{e} \rightarrow \text{Me}^0$ ) and the cooling surface is an anode on which metal dissolution is taking place (e.g.  $\text{Fe}^0 - 2\bar{e} \rightarrow \text{Fe}^{2+}$ ); at positive  $\varepsilon$  the heating surface is an anode and the cooling surface is a cathode.

When the metal ion concentration corresponding to the solubility limit is achieved, the formation of colloidal particles of corrosion products (CP) is taking place. Under the action of thermo-emf solid particles, depending on their charge sign, deposit on heating or cooling surfaces.

The total flow of solid particles on the whole heat-transfer surface is described as follows:

$$A_r = \frac{\varepsilon U_r}{\lambda} C_r Q \quad (2)$$

where  $Q$  is the total thermal capacity, W.

The discharge rate of the potential-forming ion is expressed by the following formulae:

$$\alpha_k = \frac{\varepsilon U_k}{\lambda} C_k q \quad (3)$$

$$A_k = \frac{\varepsilon U_k}{\lambda} C_k Q \quad (4)$$

where "k" index refers to the potential-forming ion.

The calculation of the steady-state value  $\varepsilon$  using the method from nonsteady thermodynamics with the hydrogen potential-forming ion (the most usual case at nuclear power plant), gives the value  $\varepsilon \approx -1 \cdot 10^{-3}$  V/K. For power plant conditions with pH of the medium up to 10, the mobility of colloidal and suspended particles  $U_r$  may be assumed equal to  $\sim 1 \cdot 10^{-4}$  m<sup>2</sup>/(V·h). The mobilities of hydrogen and cuprum ions at high parameters (subcritical temperature) obtained by the table values extrapolation with regard to temperature change of water viscosity and dielectric permeability constant, may be expressed as:

$$U_H = 3,6 \cdot 10^{-4} \text{ m}^2/(\text{V} \cdot \text{h});$$

$$U_{Cu} = 2,7 \cdot 10^{-4} \text{ m}^2/(\text{V} \cdot \text{h}).$$

with the hydrogen ion mobility ( $U_{H^+}$ ) assumed to be equal to its axonic form mobility  $H_3O^+$ .

In a closed circuit with heat transfer there must be reached the steady state at which the velocity of corrosion product entering the water ( $\sum RiFi$ ) is equal to the velocity of a potential-forming ion discharge as well as to the velocity of the corrosion product deposition on the heat-transfer surface:

$$A_k = A_r \quad (5)$$

substituting  $A_k$  and  $A_r$  from (2,4) into (5) we have:

$$\text{from where: } \frac{\varepsilon U_k}{\lambda} C_k Q = \frac{\varepsilon U_r}{\lambda} C_r Q$$

$$U_k C_k = U_r C_r \quad (6)$$

$$C_r = \frac{U_k}{U_r} C_k \quad (7)$$

From the formula (7) it follows that the equilibrium concentration of CP depends on the mobilities of the potential-forming

ion and CP solid particles as well as on the potential-forming ion concentration, but does not depend on the structural material type.

Thermo-emf action is the determining factor for heat-transfer surfaces. In case with non-heat-transfer surfaces or with heat flow action ignored, electromotive force of microgalvanic couples is of major importance. The transfer processes under the action of galvano-emf result from the interaction of a potential-forming ion and charged particles with the electric field in the boundary diffusion layer created by galvano-emf.

The flow of charged particles under the action of galvano-emf is described as:

$$a_r = \frac{\Delta E}{x + \delta} U_r C_r \quad (8)$$

where  $\Delta E$  is the galvano-emf part accounted for the diffusion layer, V;

$y = x + \delta$  is the diffusion layer thickness,

$x$  is the thickness of the resulting deposit layer, m; and

$\delta = \delta_{in,ox} + \delta_{lam}$  is the thickness of the initial deposit layer, m;

$\delta_{in,ox}$  is the thickness of the initial oxide layer, m;

$\delta_{lam}$  is the laminar layer thickness, m.

The value  $\Delta E$  is the metal specific characteristic.

$\Delta E_{s.s.} = 7-10$  mV is the stainless steel and  $\Delta E_{c.s.} = 100-300$  mV is for carbon steel. In the most cases  $\Delta E_{c.s.} = 160$  mV. The physical meaning of  $\Delta E$  is the averaged value of the existing potential difference between microcathodes and microanodes per unit surface:

$$\Delta E = \frac{S_c}{S} \Delta E_{ex} \quad (9)$$

where  $S_c$  is the cathode area per unit surface  $S$ , m<sup>2</sup>;

$\Delta E_{ex}$  is the existing potential difference, V;

The deposit thickness change is equal to:

$$dx = \frac{a_r}{\gamma} d\tau \quad (10)$$

where  $\tau$  is the time, h;  $\gamma$  is the CP content in the unit of volume of the amorphous deposit layer, which includes the structural-bound water, g-eq/m<sup>3</sup> or g/m<sup>3</sup> in terms of iron, and in the majority of cases is equal to 10<sup>4</sup> g/m<sup>3</sup>. This value is characteristic of coagulated deposit of colloidal particles.

In the power plant conditions this layer is compacted in the course of time forming a dense protective film with the iron specific content up to 4 g/cm<sup>3</sup>. According to (8), the layer compaction will lead to the material flow increase; however, when the dense structure is being formed, probably the reduction of the total area of through pores from surface to metal occurs, which results in corresponding compensation, with the total flow per the unit surface remaining invariable in the whole. Therefore may be assumed without taking into consideration the CP layer compaction on the metal surface. In salt containing media porous deposits without protective properties are formed and in this case  $\gamma$  is assumed to be equal to 2·10<sup>6</sup> g/m<sup>3</sup>. After the integration of (10) we have:

$$x + \delta = \sqrt{\frac{2\Delta E u_r C_r \tau}{\gamma}} + \delta^2 \quad (11)$$

For nuclear power plants, where  $\tau$  represents tens thousands of hours, the term  $\delta$  may be ignored; substituting the value from (11) into (8) we obtain:

$$a_r = \sqrt{\frac{\Delta E \gamma u_r C_r}{2\tau}} \quad (12)$$

From this equation it follows that  $a_r \rightarrow 0$  at  $\tau \rightarrow \infty$  i.e. the deposition process on the heat-transfer surface is ceased with time. Integrating the expression

$$dm_r = a_r d\tau \quad (13)$$

the deposit amount may be determined for the time

$$m_r = \sqrt{2\Delta E \gamma u_r C_r \tau} \quad (14)$$

where  $m_r$  is the deposit amount, g-eq/m<sup>2</sup> or g/m<sup>2</sup>.

The discharge rate of a potential-forming ion, in particular, of hydrogen ion is equal to:

$$a_k = \frac{\Delta E}{x + \delta} u_H C_H \quad (15)$$

Substituting  $(x + \delta)$  from (11) into (15), we have:

$$a_k = \sqrt{\frac{\Delta E}{2u_r C_r \tau}} u_H C_H \quad (16)$$

where "H" index refers to a hydrogen ion.

Due to the retaining of neutral electrical conditions, the rate of a hydrogen ion discharge is to be equal to that of the anodic dissolution of metal.

The quantity of the hydrogen released during  $\tau$  time (g-eq) or that of the metal dissolved during the same time is equal to

$$dm_{Fe^{2+}} = dm_H = a_H d\tau \quad (17)$$

or after integration:

$$m_{Fe^{2+}} = m_H = \sqrt{\frac{2\Delta E \gamma \tau}{u_r C_r}} u_H C_H \quad (18)$$

where  $m_{Fe^{2+}}$  is the quantity of the corroded metal in  $\tau$  time, g-eq/m<sup>2</sup>;  $m_H$  is the quantity of the atomic hydrogen released in  $\tau$  time, g-eq/m<sup>2</sup>.

For the closed system with mixing, in which the main motive force of corrosion and CP deposition processes is the galvano-emf of micropairs (isothermal dynamic loops) the equilibrium condition may be written as:

$$a_H = a_r$$

i.e. the rate of the potential-forming ion discharge must be equal to that of CP deposition. Substituting the corresponding expression for  $a_r$  and  $a_H$  from (12) and (16) into this equality we obtain:

$$U_H C_H \sqrt{\frac{\Delta E \gamma}{2 U_r C_r \tau}} = \sqrt{\frac{\Delta E \gamma U_r C_r}{2 \tau}} \quad (19)$$

or

$$U_H C_H = U_r C_r \quad (20)$$

from where

$$C_r = \frac{U_H}{U_r} C_H \quad (21)$$

The obtained expression (21) means that the average concentration of CP particles depends only on the potential-forming ion concentration and on the electrophoretic mobilities of these ions and CP particles.

According to (20) for the closed system  $U_r C_r$  in (16) and (18) is to be replaced with  $U_H C_H$ , then we obtain:

$$a_H = \sqrt{\frac{\Delta E \gamma U_H C_H}{2 \tau}} \quad (22)$$

$$m_{Fe^{2+}} = \sqrt{2 \Delta E \gamma U_H C_H \tau} \quad (23)$$

Thus, it follows from the equations (16) and (22) that in the flow with constant concentration of CP the corrosion rate is directly proportional to the hydrogen ion concentration; in a closed system, where the CP concentration is established spontaneously, the corrosion rate is proportional to the square root of the hydrogen ion concentration.

In the general case the CP transport processes depend on the joint action of thermo- and galvano-emf; however in various periods of the plant operation the action of the forces may be prevailing. In the initial period of a NPS operation the determining are the processes, occurring under the action of galvano-emf. In due course the rates of these processes are decreased and the determining become the processes, occurring under the action of thermo-emf. The time to attain such state depends on the potential-forming ion concentration, the corrosion resistance of structural materials and the rate of CP removal by the use of purification systems. For different NPS types this time may vary from some hundred hours (pressure-water circuits at the neutral water chemistry) to some thousand hours (boiling water reactors).

For the closed circuits with the ideal mixing, i.e. when concentrations of ions in the coolant in any part of the circuit are equal (e.g. circuit I WWER), the corrosion product equilibrium concentration is achieved - equations (7) - (21) under the action of galvano- and thermo-emf.

The above expressions characterize the universal property of a closed system with mixing, which is the result of the conditions considered; the uniform concentration of CP solid particles depends on the potential-forming ion concentration only and does not depend on either the material nature or the surface area of the closed circuit. The necessary condition is the thermodynamic stability of corrosion product solid particles.

The proposed mechanism of CP transport enables a quantitative description of the deposition and radionuclide distribution of radioactive corrosion products on the surfaces of power reactor circuits.

In the following some applications of the model are discussed. As it has already been noted, with  $H^+$ -ions as potential-forming ions (which is the most frequent case), the thermo-emf, caused by the temperature gradient will have a negative sign. The sign of the CP particle charge, however, can be either negative or positive, depending on the solution pH.

The CP particles which are positively charged (at  $pH < 10$ ), deposit on the fuel surfaces under a combined effect of thermo- and galvano-emfs. The profile of the CP deposition is in fact proportional to the heat flux (Fig.1).

The behaviour of the negatively charged particles ( $pH > 10$ ) in the diffusive layer at the heating surface is governed by opposite electrical forces; thus, the galvano-emf causes attraction while the thermo-emf causes repulsion.

This situation is typical for pressurised water reactors and will be discussed in detail.

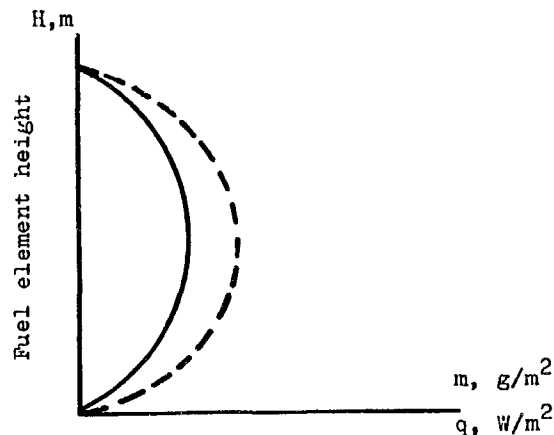


FIG. 1. Distribution of the deposits along the fuel elements in the case of negatively charged particles.

As is seen from (22), initially the rate of deposition which is governed by the galvano-emf, exceeds that of the process, governed by the thermo-emf ( $a_{rg} \rightarrow \infty$ , at  $\tau = 0$ ).

Later on, when the amount of CP, accumulated on the fuel achieves a certain value ( $m_{eq}$ ) the counter-fluxes of charged particles will become equal:

$$A_{rg} = A_{rt} \quad (24)$$

Hence

$$\frac{\Delta E \gamma}{m_{eq}} U_r C_r = \frac{\epsilon U_r}{\lambda} C_r q \quad (25)$$

and

$$m_{eq} = \frac{\Delta E \gamma \lambda}{\epsilon q}, \text{ g/m}^2 \quad (26)$$

Then the deposited layer on the fuel remains constant and has a convex-concave profile (Fig.2).

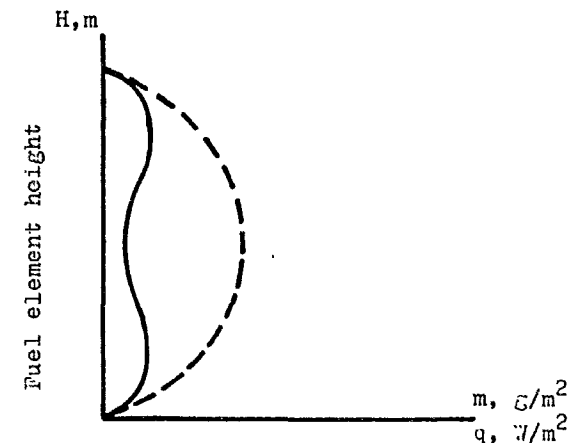


FIG. 2. Distribution of the deposits along the fuel elements in the case of positively charged particles.

The average residence time of the CP on the fuel is defined as

$$\tau = \frac{m_{eq}}{a_{rt}}, h \quad (27)$$

$$\tau = \frac{\Delta E \gamma \lambda^2}{8^2 U_r C_r q^2} \quad (28)$$

Hence it is apparent that once  $m_{eq}$  is achieved the corrosion product residence time on the fuel surface becomes constant.

Therefore, the radionuclide concentrations in the CP layer are also constant.

The nuclide flux towards the coolant is defined by

$$A_f^* = C_{dep}^* A_{rt} \quad , \text{ Ci/(m}^2 \cdot \text{h)} \quad (29)$$

or

$$A_f = C_{dep}^* \cdot \frac{\varepsilon U_r}{\lambda} C_r Q \quad (30)$$

where  $C_{dep}$  is the specific activity of CP deposits on the fuel surface, Ci/g.

The deposition of CP and radionuclides on the cooling surfaces is governed by the thermo- and galvano-emfs, while on the non-heat transferring surfaces the process is governed by the emf of galvanic microcouples alone.

Usually the non-heat-transferring surfaces make a small portion of the total PWR circuit surface. Therefore, in the balance calculations deposits on these surfaces can be neglected.

At high pH-values the equilibrium concentrations of corrosion products in the coolant are small ( $3-15 \text{ mcg} \cdot \text{cg}^{-1}$ ), and the heat flux toward the cooling surface is much lower ( $70-100 \cdot 10^3 \text{ W} \cdot \text{m}^{-2}$ ) compared to that in the reactor core. In this case the deposition of corro-

sion products on the cooling surface, dominated by the galvano-emf of microcouples is similar to that, dominated by the thermo-emf. Besides, in the first 2-5 thousand hours the first process prevails.

In the long-term predictions the effect of the galvano-emf can be neglected. The radionuclide concentration in the coolant is calculated from the balance of activated products release and removal

$$A_f^* = A_{c.s.}^* \quad (31)$$

where  $A_{c.s.}$  is radionuclide flux towards the cooling surface, Ci/m<sup>2</sup>·h.

or

$$C_{dep}^* \frac{\varepsilon U_r}{\lambda} C_r Q = C_r^* \frac{\varepsilon U_r}{\lambda} C_r Q \quad (32)$$

Thus, with long-term reactor operation the specific activity of CP particles in the coolant becomes equal to that of the fuel deposits.

$$C_r^* = C_{dep}$$

The accumulation of a nuclide on the cooling surface is defined as

$$m_r^* = C_{dep}^* \frac{\varepsilon U_r}{\lambda} C_r q \tau \quad (33)$$

The accumulation of a radionuclide on the non-heat transferring surface is described by

$$m_r = C_{dep}^* \sqrt{2 \Delta E \gamma U_r C_r \tau} \quad (34)$$

Then in case of the long-term operation the time dependence of the specific activity of long-lived isotopes ( $^{60}\text{Co}$ ) is defined for cooling surfaces as:

$$m_r = K_1 \tau \quad (35)$$

and for non-heat-transferring surfaces as

$$m_r = K_2 \tau^{0,5} \quad (36)$$

In case of the positively charged CP particles ( $\text{pH} < 9,5$ ) the time dependence of the specific activity of the long-lived isotopes on the out-of-core surfaces is described as

$$m_r = K_3 \tau^{1,5} \quad (37)$$

Then the release of radionuclides from the fuel element deposit layer will be diffusion-controlled.

The results of the calculation of corrosion products and their radionuclides transport and deposition are in good correspondence with the operational data.

## INVESTIGATION ON ELECTROMIGRATION CHARACTERISTICS OF CORROSION PRODUCTS

V.M. SEDOV, V.A. DOJLNITSYN, A.I. OVSYANNIKOV,  
D.S. GASANOV, S.A. MEDVEDED  
Leningrad Institute of Technology,  
Leningrad, Union of Soviet Socialist Republics

### Abstract

The investigation of migration under the electric field influence was carried out for magnetite and oxide mixture - hematite and goethite - in water media of different acidity, as well as the influence of amine polycarbonic complexons (IDA, NTA and DTPA) on oxide migration. The electromigration mass flow values were determined. An additive of complexons results in disappearance of positive charge iron forms over a wide pH range for magnetite and in a more narrow pH range for oxide mixture. Also the extent of EDTA influence on the deposition and electromigration characteristics of iron(+3) hydroxide and magnetite was determined. It was shown that the complexon changes the sign of corrosion product (CP) particles charge from positive to negative. This exchange is accompanied by essential decreasing of deposition resulting rate.

A considerable attention was given to electromigration behaviour of real CP presented in main circuit of reactor RBMK-1000 in different reactor operating regimes. During the reactor shutdown the transition from positive to negative CP was observed. It may be connected with increase of radiolytical hydrogen peroxide concentration in coolant. To verify this assumption, some laboratory and test loop experiments were carried out. The results obtained suggested this proposition.



At present a number of models describing the transference of the corrosion products (CP) and their radionuclides in atomic power plant (APP) circuits was suggested [1-5 e.a.]. According to those models both soluble and insoluble CP can take part in the process of deposit formation, the role of insoluble CP being more essential. The solubility of CP depends on coolant pH value, temperature, presence of oxygen and other impurities and technological additives in coolant and is not more than from units to tens mcg of iron per kg of coolant [6,7]. The size of CP disperse particles ranges from 0,001 to 10 mcm. The colloidal and small disperse particles with the size not more than 1-5 mcm are the main components of CP. The behaviour of these particles is governed by surface properties, specifically by the sign and the quantity of the surface charge. For larger particles these properties are not so important because not volume-mechanical but surface properties are determining factors for them.

The models for calculation of the main contribution of colloidal and small disperse CP in deposit formation [8-10] are based on classic theory of colloid interaction that was given by Deryagin, Landau, Verwey and Overbeek (DLVO). It assumes two types of interaction between the particles: Van-der-Waals attraction and the electrostatic interaction of double layers. To carry out calculations in the range of models in question, it is necessary to know such characteristics as the size of CP particles and the charge of their surface ( $\zeta$ -potential).

Zeta-potential and its equivalent characteristics i.e. CP particles electroforetic mobility are used in calculation of the rate of CP deposits in the theoretical approaches by

V.P. Brusakhov as well [11-13]. The electroforetic CP transport to the metal surface under thermoelectromotive and galvanoelectromotive forces in the system "coolant - circuit surface" is the main thought in the base of this approach.

Many experimental works were carried out to study the CP electrokinetic characteristics [14-17 e.a.]. The properties of real CP have been studied less extensively.

It has been shown that for all investigated systems "metal oxide (hydroxide) - water medium" the strong dependence of the surface charge on pH value is typical: when medium is changed from acidic to alkaline the surface charge is changed from positive to negative. For different iron compounds the pH values corresponding to the isoelectric points (IEP) and points of zero charge (PZC) lie in the range of pH=5,0-8,5 [14,18,19]. The IEP and PZC values depend on the way of oxide and hydroxide formation, on sample pre-treatment and on some other factors. The temperature essentially influences zeta-potential: when temperature rises from 20 C to 235 C its value increases approximately twice [20].

The technological additives and impurities in coolant can strongly influence the CP electromigration behaviour. The amine polycarbonic complexons, for example ethylene diamine tetraacetic acid and its salts, can be used as such additives [21,22].

We carried out the investigation of migration under the electric field influence for magnetite ( $\text{Fe}_3\text{O}_4$ ) and oxide mixture - hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and goethite ( $\alpha\text{-FeOOH}$ ) in water media of different acidity, as well as the influence of amine polycarbonic complexons: iminodiacetic (IDA), nitrilotriacetic (NTA), ethylenedinitrilotetraacetic (EDTA) and diethylenetrinitrilotetraacetic (DTPA) acids on oxide migration. The methods of investigation were discussed in [23].

We used electromigration mass flow (EMMF) as a criterion by which one can judge about CP electromigration. Its G value is defined by the following equation:

$$G = P / S \cdot \tau \cdot H, \text{ Mole/(m.V.s)},$$

where  $P$  is CP quantity in terms of iron transferred by electric field, mole;

$S$  is transverse section area of CP accumulating capillary, sq.m;

$\tau$  is continuance of CP accumulation, s;

$H$  is electric field intensity, V/m.

EMMF is connected with electroforetic (electromigration) mobility as follows:

$$G = \sum_{i=1}^n u_i C_i = C \sum_{i=1}^n u_i \lambda_i$$

where  $u_i$  is mobility of  $i$ -form of iron in investigated system "iron oxide - coolant", sq.m/(V.s);

$C_i, \lambda_i$  is concentration (Mole/cub.m) and mole part of  $i$ -form of iron respectively;

$C$  is total CP concentration in coolant in terms of iron, Mole/cub.m.

So,  $G$  characterizes the electromigration not only oxides dispersed in water medium, but and all the other iron compounds in investigated system. The dissolving iron forms in equilibrium with solid phase are estimated by  $G$ .

The experimental data are shown in Table 1.

The values obtained show that electromigration behaviour of iron oxides in the presence of complexons has complete nature

Table 1

THE INFLUENCE OF COMPLEXONS ON IRON OXIDES ELECTROMIGRATION

Complexon	G.10 <sup>9</sup> , Mole/(m.V.s)				
	pH=3	pH=5	pH=7	pH=9	pH=11
Magnetite					
DTPA	-/34,6	-/40,9	-/37,4	-/32,4	-/17,5
EDTA	-/12,4	-/13,3	-/32,5	-/23,5	-/16,3
NTA	1,7/-	-/3,5	-/4,4	-/7,7	-/9,1
IDA	12,0/1,3	6,0/4,5	-/6,1	-/7,6	-/4,0
Without complexon	31,2/-	20,4/-	-/-	-/7,0	-/8,6
Oxide mixture (hematite + goethite)					
DTPA	-/4,8	-/4,9	-/7,5	4,5/7,5	4,9/7,6
EDTA	-/3,2	-/3,2	-/7,2	5,6/7,0	5,6/4,4
NTA	11,9/4,7	1,9/1,9	The region of coagulation		
IDA	11,4/2,7	3,3/0,2	The region of coagulation		
Without complexon	17,9/-	14,9/1,4	-/8,8	2,0/14,7	6,7/8,4

The numerator is EMMF of CP positive charged forms (+G);

The denominator is EMMF of CP negative charged forms (-G)

and is governed by the same processes including dissociation of OH-surface groups and complexon sorption on oxide surface. An additive of complexons forming a very stable complexes with iron results in disappearance of positive charge iron forms over a wide range of pH for the magnetite and in a more narrow pH range for the oxide mixture. NTA and IDA forming less stable complexes

decrease the quantity of charged forms and displace FZC and ICP of oxides to more acidic region.

It is known that the complexon additives in coolant cause the decreasing of CP deposition on the heating circuit surfaces. This positive effect was used in so-called complexon coolant technology /24/. We made the experiments to find the dependence of the rate of CP deposition on surface-charging characteristics of CP particles (sign of charge, EMMF) and so to determine the extent of EDTA influence on the deposition and electromigration characteristics of model CP - iron (+3) hydroxide and magnetite. The method of investigation suggested by K.N. Brusov /25/ is based on CP deposition on the platinum wire heated by electric current. The heat flow was 1,5-2,0 MW/sq.m.

To study the contribution of small dispersed CP particles in deposit formation the deposition of model CP was developed from suspensions with different concentration of magnetite and hydroxide and also from solutions obtained by filtration of suspensions after nucleonic ultrafilter with porous size 0,15 mcm. The pH value of water media was in the range of 5,5-6,0.

The experimental data given in Table 2 show that the complexon change the sign of CP particles' charge from positive to negative. This exchange is accompanied by essential decreasing of CP deposition resulting rate:

$$V_{dep} = 10^3 m_{Fe} / C_{Fe} \tau, \text{ cm}^3/\text{s}$$

where

$m_{Fe}$  is deposit mass, mg;

$C_{Fe}$  is CP concentration in the count on iron, mg/l;

$\tau$  is CP deposition continuance, s.

Table 2

THE DEPOSITION OF MODEL CP ON THE HEATING SURFACE

Corrosion products	CP concentration, mg/l	10 G.10, Mole/(m.V.s)	Deposit mass, mg	V, dep, cub.sm/s
Magnetite	5,44	17,4/0	9,40	0,72
Magnetite	0,26	3,7/0	0,93	1,49
Magnetite filtrate	0,21	4,3/0	1,09	2,16
Magnetite + EDTA	5,44	0/4,2	3,60	0,28
Magnetite filtrate + EDTA	0,21	0/3,7	0,31	0,48
Iron hydroxide	7,39	11,8/0	7,32	0,41
Iron hydroxide	0,41	5,0/0	0,46	0,47
Filtrate of iron hydroxide	0,41	5,4/0	0,69	0,70
Iron hydroxide + EDTA	7,39	0/6,7	5,00	0,28
Filtrate of iron hydroxide + EDTA	0,41	0/5,8	0,25	0,20
Iron (+3) chloride in HCl solution (pH=1,0)	90,0	-	0,60	0,002

1. The numerator is EMMF of CP positive charged forms (+G); the denominator is EMMF of CP negative charged forms (-G).
2. The ratio of iron and EDTA molar concentrations is 1,0:1,2.
3. The interval of time changing is 2400-3100 s.

Most easily this effect is observed in the case of filtrates consisting of small dispersed CP.

The analysis of table data shows that for investigated systems the following law is held: the greater EMMF, the more is the mass of CP deposits. However, there is no the correlation of this kind between  $G$  and  $V_{\text{dep}}$  values.

One can infer from obtained data that the positive charged CP forms give the main contribution in deposit formation. If one takes into account a small rate of ionic form deposition (the conditions for the last line in Table 2 are agreement with ionic form of iron with a little probability for the polymeric forms /26, 27/) it may be stated that small dispersed, colloidal and maybe composite CP polymeric forms mainly take part in deposit formation. By changing these forms we can control the intensivity of the deposit formation rate.

In our investigations a considerable attention was given to the study the electromigration behaviour of CP presented in the main recirculation water circuit of APP with reactor PBMK-1000. The CP particle charge and CP EMMF were determined with the aid of three-camera flowing accumulating diafragmed cell through which a coolant at 25-30 C was passed. The investigations were carried out at different reactor operating regimes.

The results of investigations are given in Fig.1. From the data presented it follows that during the reactor shutdown succeeded by temperature decrease from 270 C to 60 C, the transition from positive to negative CP was observed. At this moment CP concentration and iron-59 activity of coolant highly increased. It is possible that an increase in radiolytical hydrogen peroxide concentration registred at the reactor shutdown, is responsible for the negative CP concentration increase. The heating of a coolant at the reactor power increase causes the hydrogen peroxide

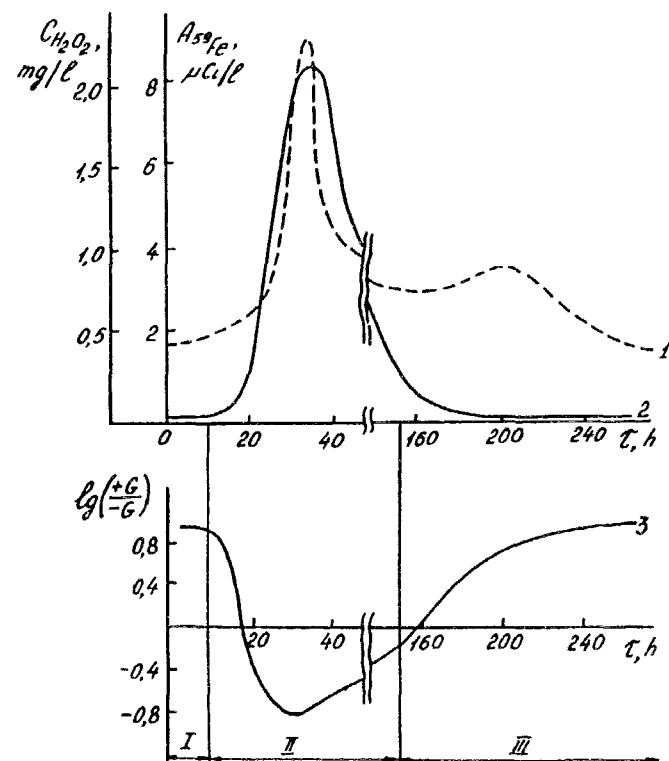


Fig. 1. Fe-59 activity of coolant (1),  $H_2O_2$  concentration in coolant (2) and relation of positive and negative charged forms EMMFs (3) during reactor operation at full power (I), at the time of shutdown and scheduled maintenance (II) and at power rising (III).

oxide thermal decomposition that may give rise to predominance of CP positively charged forms in a coolant.

It can be expected that hydrogen peroxide absorbed on the CP surface balances the CP positive charge and may even so recharge the surface. As a result, the removal of the slightly fixed CP particles from the heating surfaces takes place.

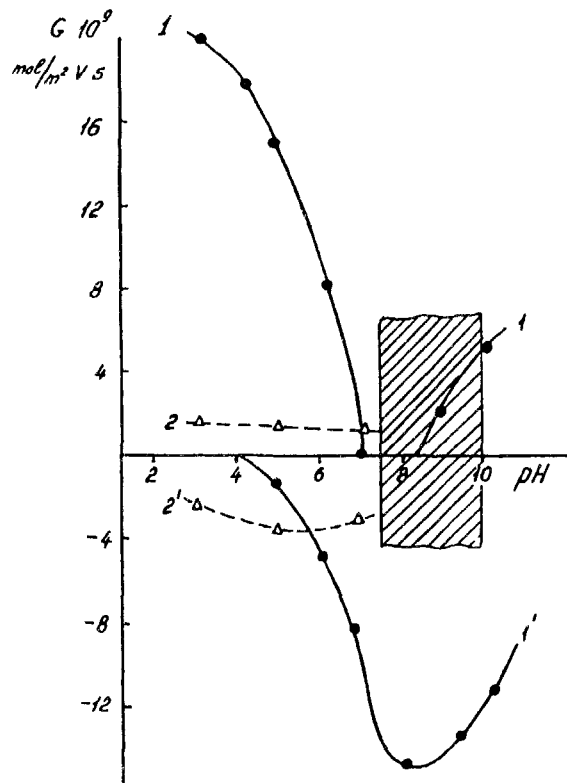


Fig. 2. pH and  $H_2O_2$  influence on the electromigration of iron oxides ( $\alpha-Fe_2O_3 + \alpha-FeOOH$ )

1,1' - iron oxides; 2,2' - iron oxides in the present of  $H_2O_2$

▨ - coagulation region of iron oxides in the present

of  $H_2O_2$  ;

$C_{Fe} = 5 \cdot 10^{-4}$  mol/l;  $C_{H_2O_2} = 10^{-3}$  mol/l;  $t = 20$  C;  $H = 10$  V/cm.

To verify this assumption, the additional laboratory and test loop experiments were carried out. The data of laboratory investigations represented in Fig.2 show that at pH=3-7 the

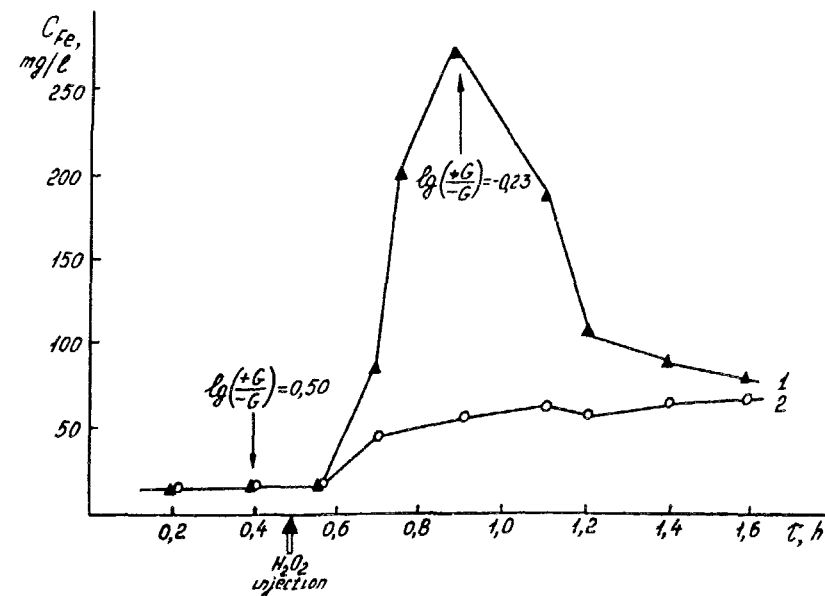


Fig. 3. Removal of the corrosion products from the heating element during  $H_2O_2$  injection.

1 - CP concentration in the coolant after the heating element;

2 - CP concentration in the coolant in front of the heating element.

injection of hydrogen peroxide in a coolant may greatly reduce the electromigration mobility of iron oxides, the mobility of positively charged forms being reduced to a greater extent.

During the loop experiments CP were accumulated for a long time (about 100 hours) on the heating element from the coolant containing 10-50 mg/l of the real CP. After CP accumulating the temperature was dropped from 100 C to 30-50 C and then hydrogen

hydrogen peroxide was injected in the coolant up to concentration of 5,0 mg/l. The heating element was not turned off. The injection of hydrogen peroxide in a coolant produces the recharging of the most corrosion products and causes CP removal from the surface of the heating element (Fig.3).

Results presented show that the control of CP electromigration characteristics provides valuable information not only about CP deposit process but about CP removal from circuit surfaces as well.

In conclusion one should stress the importance of CP electromigration behaviour's study under the circuit conditions as well as the need for carrying out investigations of the influence of different technological additives such as zinc compounds additives in GEZIP - process /28/ on CP electromigration and CP interaction with circuit surfaces.

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## TECHNICAL-ECONOMIC ASSESSMENT OF LOW COBALT CONTENT IN STRUCTURAL MATERIALS

Yu.N. ANISKIN, Yu.A. KHITROV  
All-Union Scientific Research and Project  
Institute of Complex Power Technology,  
Leningrad, Union of Soviet Socialist Republics

### Abstract

The paper shows that the materials used at present and the elements they contain as the basic components and admixtures differ by the level of their potential radiation risk in activation in a neutron flux. The use of materials of a certain composition may strongly reduce ecological risk of a NPP. As for steels which are the main materials used in NPPs, radiation risk reduction of different NPP units may be reached by limiting cobalt content within the range of 2  $\cdot 10^{-2}$  to 2  $\cdot 10^{-1}$  % and the use of nickel-free chromemanganese steels instead of nickel steels. These procedures do not increase significantly the plant cost.

### Introduction

Demands for NPP ecological safety have enhanced in recent years all over the world. One of the ways to increase safety of NPP is to find a special class of materials of lower activation in a neutron flux.

Material activation and radioactive contamination of circuits due to activated corrosion products carry over by coolant is just the specific feature of NPPs. Gamma-radiation induced by these processes is not significant for power operation of the plant. However, this radiation is determining factor for NPP components repair or change time and cost. Another feature of activation of structural materials is significant volume of radioactive wastes. Radioactive contaminations make difficult solid waste processing for material recycling, being the reason of waste accumulation in the process of plant operation and ecological risk after its decommissioning, preventing the plant complete dismantling.

The use of low activation materials is the most reasonable way out of the problem. The paper gives main approach we used for such materials working out and some technical/economical aspects of their utilization in the USSR conditions with due account of the home industry capabilities.

### Materials activation risk

High intensity of activation gamma-radiation and radioactive contamination of materials is attributable to the use of materials in nuclear power engineering which are

specific for the common power engineering of no special requirements to decrease activation levels in a neutron flux.

To create a special class of materials for nuclear power industry, different from those of activation level in a neutron flux, limits are to be imposed on certain element content in them. Different elements may be contained in the materials created as the basic component or admixtures. For this reason, the problem may not be solved without a system permitting to classify elements by their activation risk. As long-lived radionuclides formation, which are basic ecological risk, is due to activation of certain elements only, with only several of these elements forming radionuclides in activation process, which are of radiation risk in maintenance, all these elements may be classified into three groups by their activation risk:

1. Ecologically dangerous elements (long-lived gamma- and beta-radiating elements).
2. Radiation dangerous elements (long-lived gamma-radiating elements).
3. Not dangerous elements.

In selection NPP materials, it is first of all necessary to compare stable nuclides as potential gamma-sources after their activation in a neutron flux. It is usual to assess the potential radiation risk of stable nuclides by the absolute intensity of daughter radionuclide gamma-radiation. This comparison needs matching to particular number values of neutron fluxes. As for spatial -energetic distribution of a neutron flux for NPP, it is rather a complicated problem.

The problem solution may be simplified if to refuse from gamma-radiation absolute intensity calculation with nuclide activation risk being made in respect to a certain parent nuclide. This allows while comparing nuclides which are of greatest radiation risk in the existing NPP to exclude dependence upon the neutron flux level.

As a reference parent nuclide, it is convenient to use  $^{60}\text{Co}$  which under thermal neutron activation gives long-lived  $^{60}\text{Co}$ . For nuclides, elements and materials to be compared the idea of activation risk coefficient is introduced.

The activation risk coefficient,  $K_A$ , for an isotope (nuclide) is referred to the ratio of gamma dose-rates in similar geometry condition by all radionuclides formed in activation of a stable nuclide taken in a quantity corresponding to its content in 1 gram of natural isotope mixture by neutrons of the given energy group and saturated activity of  $^{60}\text{Co}$  formed as a result of 1 g  $^{60}\text{Co}$  activation in thermal neutron flux equal to the neutron flux of the given energy group.

According to this definition  $K_A$ ,  $K_A$  elements activation risk coefficient is  $\sum K_A$  and that of materials activation risk,  $K_M$ , is  $\sum B_i K_A$ , where  $B_i$  is a respective element content (weight) in material.

Table 1 shows activation risk coefficients for elements, calculated for NPP maintenance condition with equal fluxes of thermal, intermediate and fast neutrons. Activation risk coefficient were determined for 25 years activation time.

TABLE 1. ELEMENTS ACTIVATION RISK COEFFICIENTS

N	Element	P of element	Main parent isotope	Active isotope	Half-life
1	Eu	2.3	Eu-151	Eu-152	13 years
2	Ir	1.2	Ir-191	Ir-192	74.4 days
3	Co	1.0	Co-59	Co-60	5.25 years
4	Ag*	0.54	Ag-109	Ag-110M	270 days
5	Sc	0.54	Sc-45	Sc-46	84.1 days
6	Cs	0.39	Cs-133	Cs-134	2.08 years
7	Ta	0.15	Ta-181	Ta-182	115.1 days
8	Tb	$7.2 \cdot 10^{-2}$	Tb-159	Tb-160	73 days
9	Sb*	$5.2 \cdot 10^{-2}$	Sb-123	Sb-124	60.1 days
10	Yb	$1.4 \cdot 10^{-2}$	Yb-168	Yb-169	30.6 days
11	Hf	$5.5 \cdot 10^{-3}$	Hf-180	Hf-181	46 days
12	In*	$1.5 \cdot 10^{-3}$	In-113	In-114	50 days
13	Ni**	$1.4 \cdot 10^{-3}$	Ni-58	Co-58	72 days
14	Zn	$1.2 \cdot 10^{-3}$	Zn-64	Zn-65	245 days
15	Se	$6.6 \cdot 10^{-4}$	Se-74	Se-75	128 days
16	Hg	$6.5 \cdot 10^{-4}$	Hg-202	Hg-203	46.9 days
17	Zr	$2.3 \cdot 10^{-4}$	Zr-94	Zr-95---Nb-95	65 days
18	Cr	$9.8 \cdot 10^{-5}$	Cr-50	Cr-51	27.8 days
19	Ru	$8.6 \cdot 10^{-5}$	Ru-102	Ru-103	39.4 days
20	Fe**	$3.6 \cdot 10^{-5}$	Fe-54	Mn-54	291 days
21	Gd	$8.2 \cdot 10^{-5}$	Gd-152	Gd-153	230 days
22	Os	$7.3 \cdot 10^{-5}$	Os-184	Os-185	94.3 days
23	Ce	$6.3 \cdot 10^{-5}$	Ce-140	Ce-141	32.5 days
24	Sn	$5.8 \cdot 10^{-5}$	Sn-112	Sn-113---Sn-113M	130 days
25	Te	$2.9 \cdot 10^{-5}$	Te-122	Te-123	104 days
26	Cu**	$2.2 \cdot 10^{-5}$	Cu-63	Co-60	5.25 years
27	Sr	$1.2 \cdot 10^{-5}$	Sm-144	Sm-145---Pm-145	240 days
28	Sr	$1.7 \cdot 10^{-5}$	Sr-84	Sr-85	65 days
29	Ti*	$1.4 \cdot 10^{-5}$	Ti-46	Sc-46	84.1 days
30	W	$1.1 \cdot 10^{-5}$	W-184	W-185	74.5 days
31	Ca	$9.9 \cdot 10^{-6}$	Ca-114	Ca-115	43 days
32	Nb	$4.6 \cdot 10^{-6}$	Nb-93	Nb-94	$5 \cdot 10^4$ years
33	Ba	$4.1 \cdot 10^{-6}$	Ba-132	Ba-133	10 years
34	Mn	$9.6 \cdot 10^{-7}$	Mn-55	Mn-54	291 days
35	Na	$7.4 \cdot 10^{-7}$	Na-22	Na-23	2.6 years
36	Mo**	$9.5 \cdot 10^{-6}$	Mo-95	Nb-95	35 days
37	Tl	$7.8 \cdot 10^{-6}$	Tl-203	Hg-203	46.9 days

\* elements with a determining activation commitment from intermediate neutrons.

\*\* elements with a determining activation commitment from fast neutrons.



Table 2 shows activation risk coefficients for elements composing the materials used in nuclear energetics as basic components or admixture.

TABLE 2. ACTIVATION RISK COEFFICIENT FOR ELEMENTS USED IN NPP MATERIALS

Element	K
Co	1.0
Ag	0.54
Ta	0.15
Ni	$1.4 \cdot 10^{-3}$
Zn	$1.2 \cdot 10^{-3}$
Zr	$2.3 \cdot 10^{-4}$
Cr	$9.8 \cdot 10^{-5}$
Fe	$8.6 \cdot 10^{-5}$
Cu	$2.2 \cdot 10^{-5}$
Ti	$1.4 \cdot 10^{-5}$
Nb	$4.2 \cdot 10^{-5}$
Mn	$9.6 \cdot 10^{-7}$
Mo	$9.5 \cdot 10^{-5}$

Table 3 shows comparison of NPP materials by their activation risk.

TABLE 3

Material	Determination elements	Element content in the material, %	$B_1 \cdot K_1$	$K_m$
Ø8X18H10T steel	Co	0.1	$10^{-3}$	$1.4 \cdot 10^{-3}$
	Fe	70	$6 \cdot 10^{-5}$	
	Ni	10	$1.4 \cdot 10^{-4}$	
	Cr	18	$2 \cdot 10^{-5}$	
Steel 221	Co	$3 \cdot 10^{-2}$	$3 \cdot 10^{-4}$	$3.9 \cdot 10^{-4}$
	Fe	98	$8.6 \cdot 10^{-5}$	
	Ni	0.3	$4.2 \cdot 10^{-5}$	
Stellite B3r	Co	60	0.6	0.63
	Ni	2	$2.8 \cdot 10^{-5}$	
Aluminium alloy	Co	$6 \cdot 10^{-5}$	$6 \cdot 10^{-7}$	$1.1 \cdot 10^{-5}$
	Fe	0.2	$1.7 \cdot 10^{-7}$	
	Zn	0.03	$3.6 \cdot 10^{-7}$	
Zirconium alloy	Co	$2 \cdot 10^{-4}$	$2 \cdot 10^{-6}$	$2.3 \cdot 10^{-4}$
	Fe	0.1	$4.2 \cdot 10^{-7}$	
	Zr	98	$2.3 \cdot 10^{-4}$	
Titanium alloy	Co	$9 \cdot 10^{-5}$	$9 \cdot 10^{-7}$	$1 \cdot 10^{-5}$
	Fe	0.3	$2.6 \cdot 10^{-7}$	
	Ti	97	$1 \cdot 10^{-5}$	

Table 1, 2 and 3 shows:

1. Only 36 elements are potentially dangerous sources of activation gamma-radiation. Activation risk coefficients for these elements range within 2.3 for Eu to  $9.5 \cdot 10^{-5}$  for Mo. The most undesirable elements the contents of which is strictly limited in the materials are: Eu, Ir, Co, Ag, Sc, Ta.

2. The largest activation risk of all elements which may be contained in NPP materials are Co, Ag, Ta, Ni, Fe. All these elements compose the materials used as the basic components. The most dangerous of this elements, cobalt, is the most widely used in these materials. And only stellite (cobalt-based alloy) it is the basic component. In all other cases it is an unregulated admixture.

3. Materials used in nuclear power engineering are significantly different by their activation risk. The most dangerous are stellite and X18H10T grade steel. The least dangerous are aluminium and titanium based alloys. In interspaces between these materials carbon steel and zirconium-based alloys are found. Various grade steels are significantly different by the activation risk level. Activation risk of both nickel containing and nickel-free steels depends their cobalt admixture content. The least dangerous are nickel-free steels.

4. Of the elements contained in materials used the most long-lived radionuclide is formed as a result of cobalt activation in neutron flux. Due to this, considering maintenance works, change or removal of equipment after sufficiently long cooling the activation ability of all materials depends upon cobalt concentration in them.

As it follows from all mentioned above, radiation condition improvement in maintenance due to introduction of materials of lower activation in a neutron flux than that of existing ones, may be reached in the following way:

1. The use of the materials of lower activation risk coefficients in NPP. As aluminium based alloys in main reactor water cooling circuits are no corrosion stability required, then titanium-based alloys are to be considered as most promising.

2. Limitation of the materials used by allowable cobalt content.

3. Creation of nickel-free corrosion resistant steels sufficiently close by their main characteristics to X18H10T steels with standardized cobalt content.

4. Stellite change for by another material sufficiently close to it by the characteristics required but not containing cobalt.

Steels with standardized cobalt content.

At present, stellite is not used either in the plants being operated or in those under construction in our country. At the same time, different grade steels will, evidently, remain for a long time the main construction material of NPP. In this connection, the problem to reduce activation risk of steels by cobalt content reduction is one of actual in solving

the problem of NPP ecological safety and radiation condition improvement in maintenance.

The creation of this steels is connected with the determination of physically reasonable, operationally required, technically feasible and economically justified levels of steel cobalt content reduction.

The physically reasonable level of cobalt content reduction depends upon  $^{60}\text{Co}$  formation from  $^{60}\text{Ni}$  in fast neutron reaction and  $^{60}\text{Co}$  formation in nuclear reactions and nuclear conversions from stable nuclides of nickel and iron.

The level of cobalt content in steel reduction required operationally shows possible radiation condition improvement in repair works and NPP assembly change as a result of cobalt elimination in steels. This level is determined by relative  $^{60}\text{Co}$  commitment into the total gamma-dose created from NPP and depends on intensity of gamma-radiation.

The physically possible and operationally necessary level of lowering  $^{60}\text{Co}$  commitment in the activated gamma-radiation intensity is different for NPP components and depends on the NPP design requirements. For NPP's with water coolant the permissible level of cobalt admixtures content is in the range from  $2 \cdot 10^{-3}\%$  up to  $10^{-4}\%$ . To solve the problem of improving the radiation situation under repair conditions, the decrease of cobalt admixture contents in steels below  $5 \cdot 10^{-3}\%$  seems to be not reasonable.

As result of work carried out in our country, steel making process was found practically feasible with cobalt admixture content below  $2 \cdot 10^{-4}\%$  for X18H10T steels. Steels with such cobalt content are made using commercially produced cold-chamber materials. Disadvantage of the current steelmaking practice is a significant increase in steel production cost with higher purity when cobalt content in X18H10T steels is less than  $0,03\%$ . With the above practice, 08X18H10T steel is commercially produced, while those with cobalt content under  $0,005\%$  being on a small scale production.

To cut the production cost of steel with high purity in cobalt and other admixtures, a special technique for commercial steel making has been developed in our country. Relative increase in costs of making 08X18H10T steels of higher purity in cobalt using conventional and special techniques, is seen in table 4.

The above data (table 4) demonstrate that with a conventional steelmaking practice, cobalt content reduction from  $0,03\%$  to  $0,0002\%$  brings about over 6-fold cost increase for 08X18H10T steels, as compared to only 40% increase when using a special technique.

Increase in maintenance costs, due to the influence of radiation conditions, is proportional to increasing gamma-radiation intensity. Thus, the major economic effect in nuclear power engineering is from applying with cobalt content not exceeding  $0,005\%$ . Although, because of a slight cost increase for lower-cobalt steels melted by a special technique

TABLE 4. RELATIVE INCREASE IN COSTS OF 08X18H10T STEELMAKING BY DIFFERENT TECHNIQUES

different technique	Increase in cost with lowering cobalt content, %			
Steelmaking practice	0.1	0.03	0.005	0.0002
Current	1	1.1	2.3	7
Special	1	1.1	1.5	1.5

and taking into consideration that the use of steels with  $0,0002\%$  cobalt contents reduces the cost of NPP safety provision when decommissioned, it is advisable to use steels with this cobalt contents for a number of NPP components (reactor vessel, surfacing, screens etc.), because of short-term cooling the units before their dismantling.

To cut or eliminate the cost rise in NPP construction resulted from decrease of cobalt content in steels, it is advisable:

1. To determine the necessary cobalt admixture for different components considering the plant arrangement and the components mass at the NPP design stage.
2. To replace 08X18H10T steel with cheaper corrosion-resistant nickel-free chrom-manganese steels or chromium steels for units calling for higher cobalt content.

## SUPER-PURE STEELS FOR NUCLEAR POWER

(Summary)

Yu.A. KHITROV

All-Union Scientific Research and Project

Institute of Complex Power Technology,  
Leningrad, Union of Soviet Socialist Republics

In recent years the problem of fabrication and using steels with the low activation levels (in particular, low Co-steels) have received considerable attention, which is due to the worldwide growing stringency of nuclear power safety regulation. We have commercialized a technology of fabricating steels of any type with the extremely low Co- and other impurity levels for use in nuclear installations.

Both the application of these materials and progress in radiation field control during the reactor shut-down periods ensure the nuclear plant operational reliability, environmental safety and energy cost reduction.

Using steels produced by the above technology result in:

- reduction of the plant shut-down periods caused by steam generator failing (due to corrosion cracking) and the need of additional radiation field reduction previous to plant component repair or replacement;
- reduction of the volumes and specific activities of solid and liquid radwastes, which accumulate during plant operation or decommissioning;
- development of installations, which can be disassembled after decommissioning, and the most of the metal mass can be reused.

The mechanical and strength properties, and compositions of super-pure steels are highly persistent, which greatly simplifies the plant component fabrication from these materials, and makes needless to control some properties of metal products during their manufacture. Nickel steels of X18H10T type with  $<0.001$  wt% Co and low-alloy steels with about  $0.0001$  wt% Co can be produced by this technology. Due to new technical solutions the technology of fabrication super-pure steels is ecologically safer than the conventional one. The use of this technology for X18H10T steels production causes, however, the growth of metal product costs: in case of  $<0.005$  wt% Co-steel these were 1.3 times as much, while in case of  $0.0002$  wt% Co-steel - 1.5 - 2 times as much.

To make newly-built and operating plants ecologically safer and more cost-effective by using Co- and other impurity-free steels the following services are offered:

1. Development of the technological standards of the steel purity, which can be applied in manufacturing different reactor components, delivery of the product range (sheets, bars, tubing, a.o.) of the required quality and alloying content.
2. Delivery of metal products at the consumer's request.
3. Sale of know-hows and production of super-pure steels.

## USSR EXPERIENCE IN DECONTAMINATION AND WATER CHEMISTRY OF VVER TYPE NUCLEAR REACTORS

V.I. PASHEVICH

All-Union Scientific Research and Project

Institute of Complex Power Technology,  
Leningrad, Union of Soviet Socialist Republics

### Abstract

A safety operation of nuclear power plants and level of the radioactive contamination of the heat-transfer medium and equipment are determined by interrelated factors the main ones of which are as follows: design, constructional materials, water-chemical regime, processes of decontamination, amount of radioactive waste.

The distinctive feature of operation of the reactor-type equipment of the nuclear power plants is a presence of radioactive contamination on the equipment surface that causes a considerable rise in the cost of repair work in comparison with the common thermal power. The radioactive contamination levels vary over wide limits, both the scope of decontamination and amount of radioactive waste formed in this case vary respectively. An improvement of radiative situation requires an execution of the decontamination operations that results in an increase of the radioactive waste amount. With allowance made for these factors the criteria have been developed that lead the radioactive contamination level, depth of decontamination and waste amount to one denominator. This in turn is determined by labour consumption of the repair or other work and the contamination level is determined by a design, type of the constructional materials and water-chemical regime to be used.

### Cost-benefit of decontamination

At operation of slugs BB3P-440 and BB3P-1000 in the USSR a different radioactive situation arose for the same time. The mentioned condition leads to different scopes of decontamination operations and formation of some liquid radioactive waste (LRW) concerned with. Depending on a value of the taken doses a necessity of performance of decontamination operations is determined having regard to the required coefficient and liquid radioactive waste amount obtained. Thus, using the proposed method of calculation with consideration for the system of indices and norms active for the nuclear power plants in the USSR, calculate the coefficient of ratio of reduction of  $\gamma$ -radiation dose from the equipment during decontamination ( $K_d$ ) with allowance for a tolerable reduction of the personnel during the repair operations and inspection of different types of equipment BB3P-440 and BB3P-1000.

A need for performance of decontamination is determined by correlation of the operation scope planned for the given equipment and labour consumptions concerned with this scope and dose loads of the repair personnel and expenditures concerned with the planned scope of decontamination operations. In this case a saving of decontamination measures should be provided.

A number of workers required for performance of repair and inspection of an unit of a certain type of equipment may be preliminarily planned knowing:

- a scope of repair;
- a standard labour consumptions for repair;

- a radiation situation on the working areas.

A radiation situation forecast is based on the experience of power -generating unit operation and tendency of an increase of radioactive contamination specific for the given power-generating unit which should be taken into account.

Based upon the number of units of the given equipment served by the repair service and annual repair schedule, a total required number of the repair workers may estimated for the given type of equipment.

The normal number (organic table) of repair personnel ( $N_T$ ) does not take into account an influence of the radiation situation on the working stations.

1. The number of workers required for performance of the repair work is:

(a) without performance of decontamination:

$$p = \frac{3.6 \cdot 10^{-3} \cdot T \bar{P}}{D} \quad (1)$$

where  $T$  is labour consumption at performance of the separate repair operations (men/h);

$\bar{P}$  is mean rate of operation dose measured in the working stations,  $\mu\text{r/s}$ .

$$P_1 = \frac{1}{n} \sum_{i=1}^n P_i$$

$3.6 \cdot 10^{-3}$  is factor of conversion of  $\mu\text{r/s}$  into  $\text{r/h}$ ;

$D$  is total permissible annual dose (5 rem).

(b) with performance of decontamination:

$$N'p = \frac{3.6 \cdot 10^{-3} \cdot T \bar{P}}{D} + N_{\text{dec}} \quad (2)$$

where  $P_1$  is mean dose rate in the working stations after decontamination,  $\mu\text{r/s}$ ;

$N_{\text{dec.}}$  is number of workers involved for decontamination.

Labour requirements concerned with the repairs, inspection of equipment are specified in the standard repair documents acting for the nuclear power plants and do not depend on the radiation situation in the repair zone.

2. A rise of the repair work cost due to involvement of the additional number of personnel and additional charges and privileges concerned with.

$$C = N_p T (C_p M_h + K_1 C_{d.w.}) (K_{s.i.} + 1) + C_f M_d \quad (3)$$

where  $C$  are costs concerned with additional charges and privileges of the workers for the work carried out in the strict regime zone (SRZ), (roubles);

$N_p$  is an increase of personnel number for performance of the work in the radiation-hazard conditions, (men);

$C_p$  is base hourly rate of the workers working in the radiation-hazard conditions (roubles/h);

$C_f$  is a cost of special food (roubles/day);

$K_1$  is number of days of additional leave for one month of work in the strict regime zone;

$C_{d.w.}$  is a day wage of worker (roubles/day);

$M_h$  is average monthly number of working hours;

$T$  is time of work in the zone (months);

$M_d$  is average monthly number of working days, (day/month) in the strict regime zone (days);

$K_{s.i.}$  is coefficient of deduction for social insurance.

### 3. Operational expenditures for decontamination

$C_{\text{dec.}}$  is total expenditures for decontamination, (roubles);

$$C_{\text{dec.}} = C_m + C_e + C_w + C_a + C_{r.r.} + C_{c.d.} \quad (4)$$

where  $C_m$  is cost of chemical agents and materials, (roubles);

$C_e$  is energy expenditure, (roubles);

$C_w$  is wage of the workers involved in decontamination, (roubles);

$C_a$  is amortization expenditure, (roubles);

$C_{r.r.}$  is expenditure for running repair, (roubles);

$C_{c.d.}$  are expenditures concerned with conversion and disposal of radioactive waste of decontamination, (roubles).

Savings from performance of decontamination of the equipment may be calculated from the following equation:

$$S = C - (C_{\text{dec.}} + E K) \quad (5)$$

where  $S$  are savings, (roubles);

$C$  are expenditures concerned with involving of additional personnel for repair work, (roubles);

$C_{\text{dec.}}$  are expenditures for decontamination;

$K$  are capital investments for production of the decontamination equipment and units, (roubles);

$E$  is normal coefficient of savings from the capital investments.

For the operations concerned with decontamination and which do not require great expenditures:

$$C_{\text{dec.}} = C_m + C_w + C_{c.d.} \quad (6)$$

Let us consider an example of quantity estimation of requirements of personnel for overhaul of a primary circulating pump (PCP).

For the purpose, use the following data:

- man-hours per job for the overhaul in the zone of higher than usual radiation situation is 450 man/hours;
- including 50 man/hours for unsealing and sealing of the removable part of the primary circulating pump;
- and 400 man/hours for repair of the removable part of the primary circulating pump on the rack.

Radiation situation without conducting of decontamination:

- in the joint of PCP is 20  $\mu$ r/s;
- in the repair zone of PCP is 100  $\mu$ r/s.

The personnel quantity required for repair without performance of decontamination on formula (1) accounts for:

$$p = \frac{3.6 \cdot 10^{-3} \cdot 20 \cdot 50 + 100 \cdot 400}{5} = 30 \text{ (men)}$$

Radiation situation after decontamination:

- 20  $\mu$ r/s in the main joint of PCP;
- 15  $\mu$ r/s in the repair zone of PCP.

The personnel to be required for overhaul of the glandless circulating pump after decontamination calculated on formula (2) amount to:

$$p = \frac{3.6 \cdot 10^{-3} \cdot 20 \cdot 50 + 15 \cdot 40}{5} = 5 + 2 = 7 \text{ (men),}$$

including two decontamination operators.

The savings and necessity of performance of decontamination in this case are obvious.

## Decontamination processes

If the decontamination operations correspond to the specified conditions, a formation of the liquid radioactive waste is minimum and decontamination procedures are effective and ecologically advisable.

The features of a design and the used constructional materials for the acting slugs are unvariable therefore an interrelation: radioactive contamination - constructional materials - design features is the constant value. Consequently, it is necessary to improve a water-chemical conditions which would ensure such levels of equipment contamination which expressed in decontamination coefficients ( $K_{dec.}$ ) amount to a value close to  $K_{dec.} = 1$ . An implementation of these condition makes it possible to solve the problem of the BB3P slugs that meet the requirements of maximum radiation safety without performance of the decontamination operation and considerable reduction of the liquid radioactive waste formation.

The experience of operation of nuclear power plants showed that the following equipment is subjected first to contamination with radioactive products:

- the first loop and pipe-lines;
- the pumps and valves of auxiliary systems;
- the parts of mechanisms of control system and reactor protection;
- the assemblies of transfer equipment;
- the transport containers and fuel assembly covers;
- the vessels, basins and wells;

- the rooms accommodating the auxiliary equipment and service lines and also transport corridors, stores for the used fuel assemblies.

The processes of washing of the specified equipment may be divided in three main groups:

- decontamination of the first loop and its equipment without dismounting;
- decontamination of the removable loop equipment;
- decontamination of the auxiliary rooms and outer surfaces of the equipment.

#### Decontamination of First Loop of Nuclear Power Plant with Reactor of Type BB3P

A process of decontamination of the loop systems consists in the controlled removal of radioactive deposits and oxide layers of metal from the loop internal surfaces.

Three main variants of decontamination of the loop systems of the nuclear power plants may be used: decontamination of whole first loop together with active zone; decontamination of whole loop with the active zone apart; decontamination of the separate loops.

In case of necessity of performance of a large scope of repair work and inspection, the equipment of the first loop may be subjected to decontamination with the first loop assembled. In decontaminating the first loop without active zone, a large scope of work on discharging of the zone should be carried out that considerably increases the time for inspection and repair of the power plant.

In order to save time, whole loop may be decontaminated together with the active zone. This decreases the scope of preliminary and mounting work, makes it possible efficiently to use the organic equipment of the power plant, decreases the plant idle time, saves the equipment reliability due to less number of operations on its opening and sealing. However, this decontamination is possible only at absence of considerable damage to the fuel element sheath.

The decontamination of whole first loop is carried out periodically or continuously. When the periodical method is used, the loop is filled with decontamination solution which is heated and circulated with the use of the primary circulating pump for a certain time, then the used solution is drained. A cease of circulation during decontamination procedure is undesirable due to deposition of slime which is removed with difficulty.

When the loop is decontaminated jointly with the active zone, a discharging of reactor is intolerable because of hazard of fuel overheating. In this case the solution in the reactor is levelled to the branch pipes connecting it to steam generators. Every operation of charging should be simultaneously accompanied with removal of gas from the loop that is required for a normal operation of the pumps.

When the continuous method is used, the solution is discharge by forcing it out with washing water and simultaneously washing the used solution during continuous operation of the pumps. The decontamination solution is circulated during whole process of decontamination. After a drop of the

reagent concentration to the required value, a draining of the loop and supply of water are ceased and the binding decontamination solution is fed without stopping of the pumps. During supply of the solution into the loop, an excess volume is discharged either in the draining system or fed into the volume compensator. In the course of decontamination a maximum level should be maintained in the volume compensator to decrease an amount of decontamination solutions that get into the compensator during variation of pressure in the reactor because these solutions are removed from the compensator with difficulty. The decontamination of the volume compensator is advised to be carried out separately from the loop.

The continuous method is more efficient especially at removal of slime from the loop but in this case it is difficult to maintain a certain pressure in the loop to ensure a trouble-free operation of the pumps at simultaneous delivery and drainage of the solutions and washing water.

The systems which are not used during decontamination procedure should be securely separated from the loop areas to be decontaminated. The packings and bearing assemblies of the pumps should be replaced after decontamination or clean water should be pumped continuously through the specified assemblies at a pressure exceeding the pressure in the loop.

The instrumentation sensing units which are not used during decontamination should be removed from the loop.

At decontamination jointly with the active zone of the reactors operating in a boric control mode, all decontamination solutions and washing water should contain boric acid.

At a complex decontamination of the first loop, the decontamination solution is continuously circulated with the primary circulating pumps. Simultaneously a part of the washing solution is taken from the circulated flow through the organic blowing-off system and delivered into the evaporator where the solution is evaporated to a maximum concentration. The formed steam is condensed in the heat exchanger and the distillate is returned in the loop with the use of make-up pumps. The evaporated concentrated alkali or acid solution is cleared from radioactive corrosion slime in the settlers and collected in the special tanks.

The continuous circuit design of the loop decontamination permits multiple employment of the cleared solution with corresponding saving of chemical reagents. A process of decontamination of the first loop of the reactor with alternate use of several types of washing solutions, for example, alkaline solution of potassium permanganate and solution of oxalic or chromotropic at decontamination by reduction-oxidation method when after gradual discharge of one solution and delivery of the other is repeated many times until a required degree of decontamination is obtained.

The first loop of the nuclear power plant with the type BBGP reactors differs by presence of depositions on the in-



ternal surfaces; these depositions contain primarily magnetite and considerable amount of oxides of chromium and nickel. Such a composition of the depositions limits the use of oxalic acid as a main component of the decontamination solution and causes a necessity of oxidizing treatment for removal of chromium oxides.

The problem of removal of deposition at simultaneous reduction of radioactive waste was solved with the use of complexing agent-complexones. The compound based on trilon B and citric acid and EDTA.

A regulation of pH is most often accomplished by adding ammonia. The two-basin decontamination compoundings are added with such agents as  $\text{KMnO}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{N}_2\text{H}_4$  and the others. To obtain a required pH, use organic acids and as alkali use KOH because even a slight impurity of sodium remained in the water heat-transfer medium increases its activity due to formation of  $24\text{Na}$  at operation of the reactor.

At decontamination of the systems including the assemblies made of carbon steel, the passivation of the surfaces should be carried out as a final operation. For this purpose, use the solution of hydrogen peroxide, hydrazine, ammonium nitrate, corrosion inhibitors, for example, 2 mercaptobenzothiazole.

Heavy demands are imposed upon chemical purity of the reagents used for decontamination of the loop systems in this a special attention is paid to presence of corrosion-active impurities of halogen ions, sulphate ions.

The loop decontamination is usually started from a treatment with an acid solution; in this case the friable depositions are washed and a lot the radioactive slime gets into the circulated solution; the slime is not dissolved completely and it may deposit again in the dead zones of the loop.

A great amount of slime is particularly formed during decontamination of the loop jointly with the active zone. In this case a filtration of the decontamination solution is required.

Rate of dissolution of hematite in the solutions of ethylenediaminetetracetic acid (EDTA) and oxalic acid is described by the following equations:

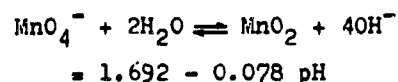
$$v = K_2 [H^+]^{0.1} [H_3Y^-]^{0.5} [H_2Y^{2-}]^{0.15} [HY^{3-}]^{0.5}$$

$$v = K_3 [H^+]^{0.1} [H_2C_2O_4]^{0.1} [HC_2O_4^-]^{0.6}$$

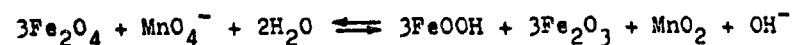
For decontamination, it is worthwhile to use the combined solution containing an organic acid, complexones because in this case the optimum value of pH is easier maintained during dissolution procedure. In the combined solutions of trilon B and organic acids, the maximum rate of dissolution of hematite occurs at pH equal to 2.5, in this case a character of dependence of dissolution rate on pH does not depend on a type of the acid added. A reaction of hematite with trilon B is the determining factor in this case the additions of reducing agents (hydrazine, hydroxylamine and the others) increase the rate of dissolution of hematite in the solutions of trilon B.

The spinel oxides are dissolved in the solutions of mineral and organic acids with great difficulty. For dissolution of such oxides use the two-basin reduction-oxidation treatment with alkaline solution of potassium permanganate and acid (pickling) solution dissolving the formed manganese dioxide.

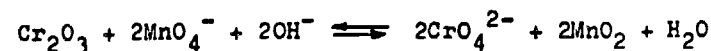
An oxidizing effect of alkaline solution of  $\text{KMnO}_4$  is primarily conditioned by reaction:



Oxidation of Cr(III) and magnetite occurs on reaction:



$$\text{Fe}_2\text{O}_4/\text{Fe}(\text{OH})_3 = 1.20 - 0.059 \text{ pH}$$



$$\text{Cr}^{3+}/\text{O}_4^{2-} = 1.335 - 0.1182 \text{ pH}$$

Alkaline solution of  $\text{KMnO}_4$  oxidizes Cr(III) to the dissolved one in alkaline medium of chromate-ion and Fe(II) to Fe(III). A leaching of chromium from the oxide film surface and oxidation of Fe(II) loosen up the film and increase of free energy of crystal lattice of oxide and impurities contained in it. Besides, at treatment with an oxidizing solution, a layer of  $\text{MnO}_2$  is formed often on the metal surface. In this case a part of the dissolved radioactive contamination may be absorbed with manganese dioxide and remains with it on the steel surface.

In the acid oxidizing solution, the rate of dissolution of chromium dioxide is 1.5 to 2 times less but in this case

iron is simultaneously leached out of the oxide layer surface what does not take place in the alkaline medium. A radioactivity of the acid oxidizing solution is usually higher. After the oxidizing treatment, the decontaminated surface is subjected to effect of alkaline reducing solution that results in a sharp change of the surface electrochemical potential.

Thus, the oxidizing treatment contributes to more effective dissolution of the oxide layer in the acid solution.

The research results showed that at the alkaline-permanganate treatment the chromium is predominantly dissolved while in the acid solutions containing the oxalic acid, nitric acid or trilon B or citric acid the iron and nickel are predominantly dissolved. The combination treatment with both solutions ensures the most effective removal of oxide film. Thus, if the surface layers of radioactive depositions are enriched with iron, first carry out the treatment by means of acid solution and further on perform the reducing treatment. The decontamination efficiency is affected by cyclic alternating of oxidizing and reducing treatments.

The sharp variation of potential, successive oxidation, reduction, leaching increase a defectiveness of oxide layer, increase its reactivity and intensify a dissolution procedure.

A decrease of the liquid radioactive waste volume may be obtained at one-basin decontamination at the expense of transfer of one decontamination solution into the other by putting the required chemical reagents into the first solu-

tion. By this means the alkaline solution of permanganate is converted into the acid reducing solution by adding a mixture of nitric and oxalic acids or citric acid and EDTA in the solution. In this case an effectiveness of decontamination remains similar to that obtained at the usual two-basin method. But the conversion of the acid solutions into the alkaline ones with the use of the same procedure is undesirable due to formation of great amount of radioactive deposits of hydroxides of iron, chromium at increase of pH.

Presently for decontamination of the equipment of the nuclear power plant first loop, mainly the two-basin decontamination is used in the USSR.

The experience of industrial employment of complexones for washing the corrosion depositions in the thermal power engineering at decontamination of nuclear power plant showed that a considerable result was obtained at the use of chelation agents and compounds based on them. It takes place due to a high efficiency of disposition dissolution and tendency to passivating effect on metals.

One of reagents used in the reducing-complexing solution at the two-basin method of decontamination is disodium salt of chromotropic acid (DCHA).

An increase of decontamination effectiveness at the use of DCHA is predetermined by the fact that strontium with DCHA forms quite stable complexes (stability constant of  $(8.91 \pm 0.22)10^6$ ) while oxalic acid with strontium does not form complexones. Besides, an ionizing radiation influence on the water solution of complexone of DCHA and in particu-

TABLE 1. EFFECTIVENESS OF DECONTAMINATION SOLUTIONS

Composition of decomposition solution	Decontamination conditions		Radioactivity, $\mu\text{r/s}$		Decontamination coefficient
	temperature $^{\circ}\text{C}$	duration, h	initial	residual	
Oxalic acid	100	1	2.2	0.3	7.3
Trilon B					
Sulphuric acid					
Sodium nitrate	100	1	2.2	0.3	7.3
Sodium chloride					
Potassium hydroxide					
Potassium permanganate (step I)	100	1	1.5	0.3	5
Oxalic acid (step 2)					
Trilon B					
Citric acid	100	1	0.8	0.35	2.3
2-Mercaptobenzo-thiazole					

lar on complexes of chromotropic acid with  $\text{Sr}^{90}$  increases the complex molecule stability because bond of metal-ligand becomes stronger in these conditions.

The rates of corrosion of structural materials in the decontamination solutions are presented in Table 2

#### Decontamination of Removable Equipment of Nuclear Power Plant with Reactors of Type BB3P

A long-duration operation of the nuclear power plant equipment results in a constant accumulation of radioactive contamination on the internal surface of radioactive loops and also external surfaces of the equipment.

TABLE 2. RATE OF CORROSION OF STRUCTURAL MATERIALS IN DECONTAMINATION SOLUTIONS (g/m<sup>2</sup> h)

Decontamination solution components	Temperature, °C	Material					
		steel 1X18H97	steel 2X13	steel 3	nickel	copper	zirconium
Axalic acid	100	0.007	7.0	10.0	0.12	0.8	0
Trilon B							
Potassium hydroxide	100	0.014	19.0	21.0	0.12	0.5	0
Potassium permanganate							
Oxalic acid							
Trilon B	100	0.016	0.15	102.0	0.23	0.63	0
Citric acid							
2-mercaptobenzothiazole							

A practice of operation of the nuclear power plants shows that the removable equipment to be subjected to decontamination on the specialized areas is as follows:

- removable part and rotor of the circulating pump;
- rods of control linkage and reactor protection;
- stop valves and different parts;
- tools, sending units and the others.

Depending on the equipment dimensions, constructural features the removable equipment may be decontaminated by different methods: by immersing, spraying, ultrasonics, electrochemical and vapor-emulsion and other methods.

The immerse-type basins are equipped with heaters and solution mixing appliances, ventilation suction, instrumentation. The solution is heated with electrical heaters, steam coils, steam jacket or live steam; the solution is

mixed mechanically or by bubbling. The basin body mounts pipe connections for supply and draining of solution and water. The basin is equipped with sealing cover, the decontamination is carried out at slight force (1.3 to 4 kPa) created with the ventilation suction. The basin volumes may be different, they depend on type of the equipment to be decontaminated.

For decontamination of some parts with complex configuration use the spraying-type basins in which the parts are treated by spraying the decontamination solution in the sealed circuit.

As example of decontamination of the removable equipment, the decontamination of the removable part of the primary circulating pump may be taken. The pump removable parts are delivered to the decontamination areas and installed into the special basins: for decontamination of the PCP lower part which directly came in contact with heat-transfer medium and is the most contaminated one and for decontamination of the primary circulating pump rotor which is decontaminated in the vertical and suspended position to avoid a rotor deformation. The decontamination solution is prepared in the special tanks. The solution is fed and circulated in the decontamination basin with the use of a circulating pump. The decontamination basins are provided with the solution steam heater. To increase a speed of a solution flow, a compressed air is supplied in the basins. The design circuit allows for washing whole system with clean condensate and also multiple employment of the solutions. If the chemical agent after a

cycle of decontamination does not reach its saturation (the sample is analysed), it is advise to the agent again (in this case the agent is pumped in the tanks for storage of the decontamination solutions). After the decontamination  $\gamma$ -background of the primary circulating pump is decreased by 30 times. A total amount of the liquid radioactive waste accounts for 5 m<sup>3</sup>. The design of decontamination basins makes it possible to decontaminate not only the PCP removable parts but the other equipment. Usually the obtained coefficient of decontamination vary from 10 to 100.

Taking into consideration the fact that the removable equipment of the first loop is primarily made of stainless steel, the most efficient method of its decontamination is the two-basin reduction-oxidation method with subsequent treatment with alkaline solution of potassium permanganate and then with pickling-oxalic acid with different additions. To increase efficiency of the washing solution, heat it to a temperature of 85 to 95 °C and also mix intensively what favours a faster removal of depositions.

A development of the decontamination systems in the USSR tends to avoiding, where it is possible, decontamination of whole equipment of the radioactive loop and making the independent systems for decontamination of separate elements of the loop. For decontamination of steam generators (SG) an independent system has been produced in the Novovoronezhsky and Kolsky nuclear power plants. For production of this system the following equipment has been mounted: the stoppers in pipe-line  $\Delta V$  500 on the side of primary circulating pump

that exclude getting decontamination solutions into the pipe-lines; flanges on the steam generator collector for entry and circulation of decontamination solutions; tank for preparation of decontamination solutions which is simultaneously used as surge tank; pump with capacity of 45 m<sup>3</sup>/h. The solutions are heated in the steam generator located on the side of the second loop by supplying a steam ( $P = 8$  to  $12 \cdot 10^5$  Pa) in the line of continuous blowing of the steam generator. The decontamination procedure included: treatment with alkaline solution (KOH - 30 g/kg,  $KMnO_4$  - 3 g/kg) at circulation of the solution at 90 °C maximum (alkaline washing is made simultaneously with heating of steam generator), water washing; treatment with the solution of oxalic acid (15 g/kg) and nitric acid (1 g/kg), final washing: first with a slightly alkaline water and then with pure water. Decontamination coefficient is equal to 8 to 10.

For increase of decontamination efficiency the use was made of an installation allowed to get a consumption of the solution of 1600 m<sup>3</sup>/h through the steam generator. The table presents technological processes and conditions of the steam generation decontamination with the use of this installation. A use of two cycles of decontamination at increase of rate of solution flow of up to 0.5 m/s made it possible to decrease a level of power of  $\gamma$ -radiation in the hot collector by 25 times, over the pipe still (through the second loop) by 82 times, in the cold collector by 49 times. Simultaneously, 11.9 kg of iron in terms of  $Fe_2O_3$ , 3.5 kg of NiO and 1 kg of  $Cr_2O_3$  were removed.

TABLE 3. TECHNOLOGY AND CONDITIONS OF SG GENERATOR

Decontamination operation	Solution used	Temperature, °C	Duration, h	Pump operation time, h
First cycle:				
Alkaline washing	KOH+KMnO <sub>4</sub>	43 - 70	3.0	1.0
Washing	condensate	80	2.25	0.25
Acid step*	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> HNO <sub>3</sub>	70 - 83	3.0	1.0
Doubled washing	condensate	70	4.5	0.5
Second cycle:				
Leaching	KOH KMnO <sub>4</sub>	74 - 84	3.0	
Washing	condensate	72 - 75	2.25	0.25
Acid washing	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> HNO <sub>3</sub>			
Washing with weak alkaline solution	KOH	78	2.5	0.5
Washing	condensate	75	2.25	0.25

\*For decontamination efficiency, 3% disodium salt of chromotropic acid is used occasionally.  $K_{dec}$  equal to 25 to 50.

- Note: 1. A complex of operations on alkaline washing and acid treatment includes: filling of the steam generator with the solution, circulation of the solution and its drainage.
2. The solutions based on citric and ethylenediaminetetracetic acid.
3. A washing-off is carried out by filling the steam generator with condensate, short-time circulation and draining the condensate.

At decontamination by the above-mentioned methods, some local difficult soluble contaminations are sometimes not removed. In this case use an electrochemical method of decontamination based on the fact that at anodic polarization the

surface oxide layer is dissolved together with radioactive contaminations contained in it. The electrochemical decontamination is conducted by two methods. At the first method a part to be decontaminated is immersed into electrolyte or electrolyte is poured into the part (for example, sleeves of of main cut-off valves of circulating loops of the first loop). In this case the part is used as anode. The cathode shape should approaches, if possible, the shape of the decontaminated surface. Duration of decontamination is 15 min, DC voltage is 12 to 50 V, current density is 10 to 20 A/dm<sup>2</sup>, a distance between the cathode and anode is 30 mm.

The second-method electrochemical decontamination is carried out with the use of distant cathode; in this case the part is immersed into electrolyte. The decontaminated surface is used as anode. The cathode is made of lead or aluminium. Duration is 1 to 2 min. When the unflat surfaces are decontaminated, the electrodes are bent according to the surface curvature. A felt spacer saturated with electrolyte is fitted to electrodes. An acid solution with current density of 10 to 20 A/dm<sup>2</sup> is used as electrolyte.

At decontamination use the following electrolytes:

- 10% aqueous solution of orthophosphoric acid H<sub>3</sub>PO<sub>4</sub>;
- aqueous solution of oxalic acid, 20 to 30 g/kg;
- aqueous solution containing sulphuric acid or 15% aqueous solution of sodium sulphate.

For decontamination and brightening of stainless steel, use electrolyte prepared from aqueous solution of orthophos-

phoric acid ( $H_3PO_4$ ) and aqueous solution of sulphuric acid ( $H_2SO_4$ ).

The electrochemical method is advisable for use for decontamination of the following equipment:

- parts and units of primary circulating pump;
- units of linkages of fuel assemblies of control system and reactor protection;
- sleeves of main cut-off valves of circulating loops;
- external surfaces of covers for storage of fuel assemblies,
- sections of pipe-lines, packing surfaces, volute chambers of the primary circulating pump and other areas accessible for decontamination with the use of distant cathode;
- steel walls of discharge ponds.

For decontamination of the equipment surfaces and rooms, the vapor-emulsion method and steam-ejection sprayers (SES) are widely used. The principle of the sprayer action is based on the use of kinetic energy of one flow (of steam or compressed gas) for pumping under pressure of the other flow (liquid). A decontamination solution is sucked into the jet of vapor exhausting from the nozzle; the solution is mixed with vapor in a certain ratio. Temperature of the vapor-emulsion jet is  $50^{\circ}C$  at a distance of 0.2 m from the nozzle. The sprayer is removable and connected to the vapor line. The steam-ejection sprayer may be provided with one or several nozzles and may be equipped with a circular brush. Vapor pressure is 0.3 to 0.5 MPa, vapor consumption, 0.5 to 0.7 kg/min, solution consumption, 1 to 1.5 liter./min, optimum distance from the treated surface, 0.2 m.

As decontamination solutions you may use one-basin or two-basin compoundings or aqueous solution of oxalic acid, surface-active substances, complexing agent of type of sodium hexaphosphate. A rate of treatment of the surface is  $1\text{ m}^2/\text{min}$ . This method is highly competitive with the immersing method.

#### Decontamination of External Surfaces and Rooms

The auxiliary equipment and rooms are subjected to contamination due to absorption of radioactive aerosols and gases, precipitation of dust containing radioactive substances, direct contact with liquids containing radioactive nuclei.

As lining materials for the nuclear power plant rooms use is made of easy-decontaminated and chemically resistant plastic materials, enamels, paints and stainless steel.

For washing the paint-and-varnish coatings use the solutions of surface-active substances. Carry out decontamination by spraying a mixture formed during mixing steam and chemical agents in the special steam-ejection sprayer.

At the present time in the USSR the easily removable polymeric coatings show considerable promise as a means for decontamination and also isolation of room surfaces in the nuclear power plants.

These coatings are applied before performance of repair work to the surfaces and serve as protection against possible radiative contamination of the surfaces. After the repair work completion the coatings are removed. Such the coatings may securely isolate the surface for 30 to 60 days.

TABLE 4. EFFECTIVENESS OF DECONTAMINATION OF EQUIPMENT AND ROOMS BY DIFFERENT METHODS

Equipment or surface	Decontamination method	Decontamination coefficient	Remarks
Drive of fuel assembly of control and protection system (CPS):			
drive motor	reduction-oxidation	20	Efficiency is determined by measuring $\gamma$ -activity of equipment
rod and threaded link assembly		5 - 10	
ball-screw pair		15 - 20	
Rotor of primary circulating pump:			
smooth surfaces	reduction-oxidation	10 - 50	Efficiency is determined by measuring $\gamma$ -activity of equipment
bearing mounting seats		1.5 - 2	
fittings:			
parts of main cut-off valves	electrochemical	400	same
CPS fuel assembly drive assembly	same (with distant cathode)	2 - 3	same
reactor stud	electrochemical	10	Efficiency is determined by measuring $\gamma$ -activity of smear
stainless steel transfer basin walls	same (with distant cathode)	50 - 100	same
fuel assembly storage cover	same	100	same
stainless steel transfer basin walls	steam-emulsion	5	same
stainless steel floor	same	30	
carbon steel floor	same	10	
plastic floor	same	60	
walls coated with oil paint	same	10	

Using the coatings you may efficiently decontaminate both metallic and nonmetallic surface. The compound is applied with a brush or by spraying. After a time (4 to 8 h), the dried elastic film is removed (mechanically) and decontaminated as solid waste. The decontamination is obtained due to reaction of chemical components of the polymeric solution with radioactive contaminations with subsequent inclusion of contamination in the solid film which fixes and localizes the contamination, prevents its spreading over the surface and increases the decontamination effect.

In the USSR, many compounds for "dry" decontamination have been produced and used. The compounds are based on polyvinyl alcohol with addition of complexing agents, polyvinyl acetate emulsion, latex, polyurethane dispersions. Application temperatures from +25 °C to -50 °C, decontamination time from 4 to 8 h to 30 min. Recently, the coatings have been developed and used which have simultaneously isolating and properties without addition of nonorganic acids that does not cause corrosion of the metal surface under decontamination.

Application of such the coatings makes possible abandoning a cleaning method that results in formation of great amount of liquid waste.

Water-Chemical Regime of Nuclear Power Plant with Reactor of Type BB3P, USSR

At present an ammonium-potassium water regime at varying concentration of boric acid and normalized content of hydro-



TABLE 5 NORMS OF WATER-CHEMICAL REGIME OF LOOP AT NORMAL OPERATION

Indices	BB3P-440	BB3P-100
pH 25 °C	6.0	5.7 - 10.2
H <sub>3</sub> BO <sub>3</sub> , mg/kg	0 - 8000	0 - 13000
Potassium, mg/kg	2.0 - 16.5	(K <sup>+</sup> + e) 0.05 - 0.35 mmol/kg
Ammonia, mg/kg	5.0	5.0
Hydrogen, mg/kg n.ml/kg	2.2 - 4.5 30 - 60	2.2 - 4.5 30 - 60
Oxygen, mg/kg	0.01	0.01
Chlorides, mg/kg	0.10	0.10
Fluorides, mg/kg	0.05	
Corrosion products in term of Fe, mg/kg		
At normal operation	0.20	0.20
At starting	2.00	

gen is used in the first loop of the nuclear power plant with the BB3P reactor acting.

A salt-free water with boric acid dissolved in it the latter is used as neutron absorber for controlling a fuel reactivity is used as heat-transfer medium in the first loop of the BB3P reactor. To keep pH optimum value varying due presence of the boric acid, the heat-transfer medium is alkelified with potassium hydroxide.

The water regime in the first loop provides for suppression of radiolysis of water by adding the compounds formed under effect of ionizing radiation of hydrogen, for example ammonia into the heat-transfer medium.

The deposits consiting of two layers at the water-chemical regime are formed on the internal surfaces of the first

loop power equipment due to processes of corrosion, washing, migration and deposition of corrosion products of the constructional materials. These deposits are solid, tightly adjoined to metallic surface and chemically bonded to it; porous deposits which are formed during migration of corrosion products activated in the active zone with neutrons. The radioactive isotopes owing to diffusion are introduced into the internal layer available on the equipment surfaces out of the active zone.

At stable operation of the power-generating units, the first layer is tightened in the boundry of the external and internal layers. The process is caused both by chemical structure of the layers and defects available in the their structure: on the one hand, from the viewpoint of solubility of the components of alloys (on metal surface), on the other hand, from the viewpoint of introduction of the components of alloys (delivered by heat-transfer medium) isotope layers.

As a rule, isotopes <sup>60</sup>Co, <sup>58</sup>Co, <sup>51</sup>Cr, <sup>54</sup>Mn, <sup>59</sup>Fe contribute γ-radiation dose rates from the power equipment of the first loop of nuclear power plant with the BB3P reactor; the contribution of isotope <sup>60</sup>Co is dominant. The operation experience shows that 30 to 50% of radioactive contaminations are contained in the external "porous" layer of the deposits. This is caused first by formation of the "porous" layer on the power equipment surfaces out of the active zone at the expense of the activated corrosion products located inside the heat-transfer medium in the dispersed condition. Thus,

a removal of the deposit external layer, that is a washing of corrosion product from the surfaces and their further removal from the heat-transfer medium by means of a special water cleaning units and prevention from its subsequent formation by keeping the certain physico-chemical properties of the heat-transfer medium enables a considerable decrease and stabilization of the power equipment  $\gamma$ -radiation dose rates at low level with advantages resulted from this condition.

As a fission product contamination may be limited by a certain level tolerable with the operation norms, improvement of production technology and strict control of integrity of the fuel element sheathes, the corrosion activity, in contrary, can not be limited by unchangeable level because the accumulation of radioactive products of corrosion in the heat-transfer medium of the first loop is closely related with corrosion processes inevitable at contact of metal with water. Because of this, in the course of the reactor operation, the amount of the activated products of corrosion in the loop increases constantly and at the limited degree of the sheath seal failure the corrosion products are the main sources of radioactive contamination of the loop.

The preposed improvement of radiation situation at the expense of increase of the medium reducing properties served as the basis for creation and assimilation of the water-chemical regime with the use of hydrazine.

The optimization of water-chemical regime of the first loop through the medium reduction-oxidation state was first

used in 1980 in the Kolskaya nuclear power plant (units 3 and 4). In this case the  $\gamma$ -radiation dose rate from the first loop equipment was considerably lower than at the organic boric-ammonium potassium regime. Figs 1 and 2 correlate the dose rate from the collectors of steam generators of three nuclear power plants with reactors BB3P-440. The Novovoronezhskaya nuclear power plant (units 3 and 4) operates in the organic regime, the first unit of the Rovensky nuclear power plant operated in the organic regime till 1985 and then changed over to a modification of the hydrazine regime. Unit 3 of the Kolskaya nuclear power plant operated in the hydrazine regime since the starting (1981) and unit 4 also since the starting made in 1982. An estimation of dose rate levels has been made both on the cold and hot collectors.

At ammonium-potassium water-chemical regime,  $\gamma$ -radiation dose rates for both in the average are within 4 to 8 r/h

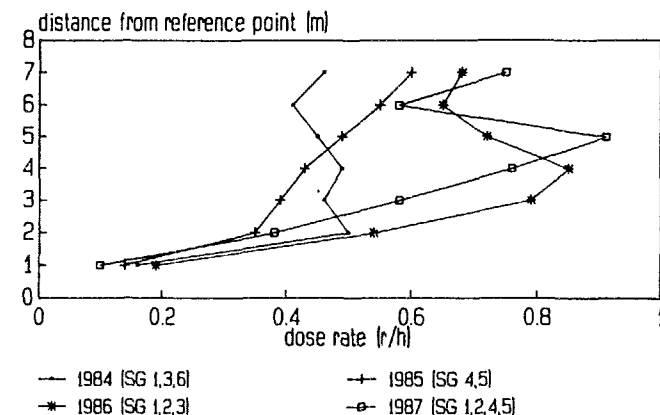


FIG. 1. Dose rates in Kolskaya unit 3 steam generator, 1984–1987.

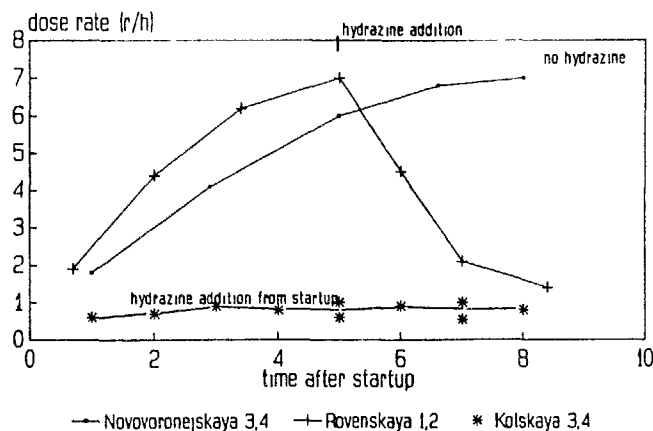


FIG. 2a. Dose rate vs time for VVERs in the USSR (effect of hydrazine addition).

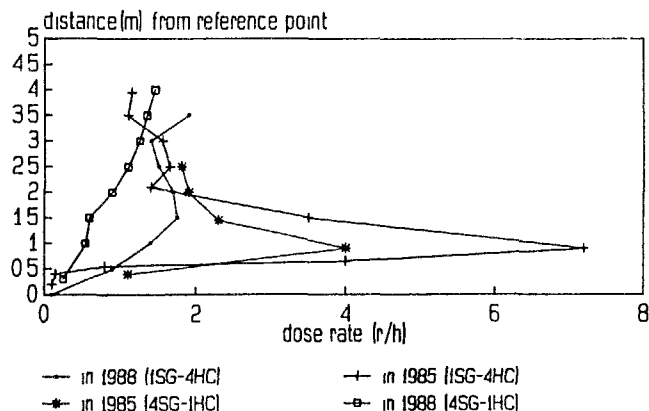


FIG. 2b. Dose rates in the steam generator of Rovenskaya VVER.

(BB3P-440) and 3 to 10 r/h (BB3P-1000). For the units operating according to the technology of the hydrazine water-chemical regime these values are lower and vary from 0.2 to 1.25 r/h at average level of 0.5 to 0.7 r/h.

Such a decrease of radioactive contamination coefficient at use of the hydrazine water-chemical regime may be explained by the results of investigation of composition of oxide films and corrosion products. When the water in the first loop comes in contact with austenitic steel, the oxide films and corrosion products practically consist of mixed spinel  $\text{FeCr}_2\text{O}_4$  in which nickel is, except for the upper layer contacting with water, 50 nm thick, in metallic (elementary) state and isotope  $\text{Co}^{60}$  is gradually distributed over whole thickness in the shape of ions of  $\text{Co}^{2+}$ . In the reducing medium even of ammonium-potassium water regime, nickel is really in the elementary state and standard potential of reduction-oxidation pair  $^{2+} = -0.25$  V. If the reduction-oxidation potential is further decreased by, for example, dosing the hydrazine into water, then cobalt whose reduction-oxidation pair standard potential is more negative ( $\text{Co}/\text{Co}^{2+} = 0.277$  V) than the nickel one and the concentration is lower, also in the metallic (elementary) state and can not be oxidized, form oxides or ions of  $\text{Co}^{2+}$  and doing so it does not take place in the mass transfer of corrosion products, their activation and in the long run, has no influence on the equipment dose rate. This is verified by measured value E in the heat-transfer medium of the Kolskaya and Rovenskaya nuclear power plants. In the Rovenskaya nuclear power plant operated in the boric-ammonium-potassium regime for five years, background is decreased by 4 to 6 times after changeover to the hydrazine water-chemical regime and the equipment decontamination is not required. In the Kolskaya

nuclear power plant, units 3 and 4,  $\gamma$ -radiation dose rate does not exceed 1.0 r/h due to operation of the plant units in the hydrazine regime since the starting. The equipment is also not decontaminated, as a result a great amount of radioactive liquid waste is not formed.

#### Methods of Treatments and Volume of Waste Obtained in Nuclear Power Plants of Type B3BP

A selection of system of processing and removal of radioactive waste directly depends on many factors main of which are: characteristic of waste (specific activity, state of aggregation, chemical and radiochemical composition); amount of waste to be decontaminated; required level of cleaning with allowance for acting sanitary rules; method of final storage of concentrate.

In the two-loop nuclear power plants with boric control, considerable volumes of waste are formed during draining of boron-containing heat-transfer medium from the first loop.

Overall, the following main types of liquid radioactive waste are formed in the nuclear power plants: the water got after draining, leakage of the circulating loop and separate equipment; the water of loosening and washing of absorbers of the heat-transfer medium cleaning system; the water got after arsining of the fuel assembly holding basins; the water got after washing of the rooms; decontamination solutions; the solutions obtained after regeneration of ion exchangers of steam cleaning; shower water; waste of radiochem-

ical laboratory. In chemical and radiochemical composition these waters may differ considerable and the technology of processing of these waters differ respectively.

The solid radioactive waste in the nuclear power plants of all types are formed during repair of fittings, pipe-lines, equipment, primary sending units of instrumentation, replacement of filters for cleaning of water and air and replacement of filtering materials. Among them are the used laboratory utensils, protective cloth, tools, paper, rags and the like.

The liquid radioactive concentrates and slime (cement and bitumen blocks) after conversion into solid state during technological treatment are also the solid waste.

#### Cleaning of Liquid Radioactive Waste by Method of Evaporation

The evaporation method has gained wide acceptance due to possibility of processing of waste practically of any salt content, type and level of radioactivity, independence of the process from variation of composition of impurities in the waste that is significant for processing of the laboratory waters, possibility of production of concentrated precipitation for disposal.

The evaporation process is characterized by the following parameters: coefficient of solution cleaning (ratio of specific activities of solution and condensate of secondary steam), coefficient of evaporator cleaning (ratio of specific activities of bottoms precipitation and condensate of second-

dary steam), evaporation degree (ratio of quantity of coming waste and giving concentrate).

The evaporator system with final evaporator operates in the following way. From a receive vessel the solution is pumped into a heat exchanger where it is heated to a temperature of 90 to 98 °C. The heated solution is fed into a circulating pipe of the evaporator. The secondary steam is supplied from separator into condenser.

The solution under evaporation is delivered from the evaporator into the final evaporator where it is evaporated to the required concentration. The still bottoms are sent for storage. The secondary steam got from the evaporator is cooled and fed to the ion exchangers.

#### Bituminizing the Still Bottoms

The bituminization is a method of inclusion of radioactive substances into a solid inert material based on asphaltites and bitumens that ensure a long-term storage of radioactive waste. The main steps of the process are: (1) evaporation of moisture contained in pulp or concentrate and production of the dried powder; (2) preparation of initial bitumen compound by softening or melting bitumen; (3) mixing the liquid bitumen compound and dried material or concentrated solution to uniform distribution of solid particles in the bitumen; (4) cleaning of gases carried from a bitumen maker and condensation of liquid vapors; (5) pouring of bitumen compound into the blocks and their cooling. When a rotor bitumen makers are used, the water is evaporated from the thin

film of mixture of liquid waste and bitumen which run down over the apparatus cylindrical wall heated with steam (the preliminary drying of the concentrate is not required).

The main advantages of bitumenizing are decrease of volume of the blocks in comparison with the volume of liquid concentrate and possibility of their storage in the simple and cheap storehouses. A rate of leaching of radioactive nuclei is  $10^{-4} - 10^{-6} \text{ g/cm}^2 \cdot \text{day}^{-1}$ . The specific activity of the waste solidified by bitumenizing is limited with reaction stability of hydrocarbons because at the absorbed doses of more than  $10^8 \text{ Gy}$ , the chemical structure of material is disturbed, ratio C/H varies, elasticity increases, ignition temperature decreases and due to formation of gas bubbles, the compound volume increases by 14 to 30%. That is why the concentrates with an activity level not exceeding  $3.7 \cdot 10^{11} \text{ Bq}$ . The industrial employment has been brought to a commercial level in the Leningradskaya nuclear power plant and the adjustment and alignment are being carried out in the Kolskaya nuclear power plant.

The solid waste of lower and medium activity levels are usually buried into the concrete trenches.

At the present time, the solidification of liquid radioactive waste in the nuclear power plant with the B3BP reactor is being brought to a commercial level and waste bulk is stored in the vessels for liquid radioactive waste located in the nuclear power plant territory and placed into the special protective constructions. The solid radioactive waste is stored in the storehouses of dry waste. Briquetting of the

solid waste is used for waste compaction in the shape of approve "Briquet-1" and "Briquet-2". In the USSR, the work on substantiation of possibility of construction, feasibility study and designing of regional storehouses for the solid radioactive waste formed in the nuclear power plants is being carried out.

Summarizing the above material you may estimate the planned total dose expenditures reasoning from the forecasting of radioactive situation on the basis of the scope of the planned repair work.

The experience of operation of the nuclear power plant showed that the prerepair decontamination of separate types of equipment sometimes is not advisable and because of this it is concerned with additional requirements.

Tables 6, 7 present the proposed standard coefficient for steam generators and primary circulating pump.

TABLE 6. STANDARD DECONTAMINATION COEFFICIENTS ( $K_{dec}$ ) FOR STEAM GENERATORS

Radiation situation in area of repair ( $\mu\text{r/s}$ )	Standard $K_{dec}$	
	medium repair	overhaul
1000	10.8	14.4
800	8.64	11.52
600	6.48	8.64
500	5.4	7.2
300	3.24	4.32
200	1.0	2.0

TABLE 7. STANDARD DECONTAMINATION COEFFICIENTS ( $K_{dec}$ ) FOR PRIMARY CIRCULATING PUMPS

Radiation situation in area of repair ( $\mu\text{r/s}$ )	Standard $K_{dec}$
1000	25
800	20
600	15
400	10
200	5
100	2.5

In terms of standard  $K_{dec}$ , the following data have been used:

	Steam generator	Primary circulating pump
labour consumption for medium repair, (man/h)	375	-
labour consumption for overhaul, (man/h)	500	700
repair personnel number, (man)	25	200
limited tolerable (annual) dose, (Bq).	5	5

For this reason, since the moment of introduction of the hydrazine regime in the Kolskaya nuclear power plant at  $\gamma$ -radiation dose rate of up to 1.2 r/h the decontamination operations have been not carried out.

The given experience is also used in the Rovensky nuclear power plant.

# PWR ACTIVITY TRANSPORT WITH REFERENCE TO SOLUBLE AND PARTICULATE CORROSION PRODUCTS

## *Chemical and radiochemical analysis of PWR particulate material*

K.R. BUTTER

UKAEA/Atomic Energy Establishment Winfrith,  
Dorchester, Dorset,  
United Kingdom

### Abstract

This paper presents the results of recent studies that have examined the nature and behaviour of particulates in PWR coolant with emphasis on their chemical and radiochemical analysis. The contribution of particulates to the total coolant burden of cobalt-58 and cobalt-60 is examined in detail both during steady full power operation and during shutdown and start-up associated with refuelling outages.

The samples examined in this report were obtained from the Belgian Doel 4 PWR; the station being a 3 loop Westinghouse design of 1000 MWe capacity.

The proportion of total cobalt activity represented by particulates during steady full power operation averages 50%. During shutdowns and start-ups this proportion changes markedly and is dependent on coolant temperature and pH.

The dominance of the corrosion release rate of Inconel 600 observed during the commissioning period of Doel 4 shows the importance of good chemistry control during this period. Good chemistry control during the commissioning period as well as normal operation is necessary if out-of-core doserates are to be kept to a minimum.

### 1 INTRODUCTION

In order to obtain an insight and understanding of activity transport and build-up in a PWR primary coolant circuit it is necessary to study the behaviour of both soluble and insoluble material.

Previous studies undertaken at AEEW and reported elsewhere (ref 1) have examined soluble elemental and activity levels in PWR coolants. These studies have shown that during steady state operation both nickel and cobalt elemental levels are low (circa  $200 \text{ ng dm}^{-3}$  and  $10 \text{ ng dm}^{-3}$  respectively) and are dependent on the pH of the coolant. The concentration of both increase many orders of magnitude upon temperature reduction and peak at  $\sim 120^\circ\text{C}$ . Soluble cobalt-60 and cobalt-58 activity levels rapidly attain steady levels upon the reactor reaching power and these

levels decrease with reactor cycle. They are also dependent on the pH and temperature of the coolant.

During steady state operation particulate levels are constant and their concentration is low circa  $10 \text{ } \mu\text{g dm}^{-3}$  (ref 1) although the levels vary widely from reactor to reactor with little correlation with age. There is, however, evidence to show that although smaller ( $2 - 5 \text{ } \mu\text{m}$ ) particles are dominant ( $\sim 90\%$ ) early in reactor life, the percentage of the larger particles increases with plant age.

This paper presents the results of recent studies that have examined the nature and behaviour of particulates in PWR coolant with emphasis on their chemical and radiochemical analysis. The contribution of particulates to the total coolant burden of cobalt-58 and cobalt-60 is examined in detail both during steady full power operation and during shutdown and start-up associated with refuelling outages.

The samples examined in this report were obtained from the Belgian Doel 4 PWR; the station being a 3 loop Westinghouse design of 1000 MWe capacity.

### 2 EXPERIMENTAL TECHNIQUES

All samples were taken employing the installed isokinetic modification to the existing W sampling system which has been described elsewhere (ref 1). Insoluble species were collected using  $0.1 \text{ } \mu\text{m}$  Nuclepore polycarbonate membranes while soluble species were collected on Acropor Ion Exchange membranes. The membranes were mounted in a common holder, one Nuclepore membrane being followed by two cation membranes and two anion membranes. Following separation of the membranes, soluble and insoluble cobalt-58 and cobalt-60 were measured by  $\gamma$ -spectrometry. To obtain information on the contribution of the total particulate population to chosen size ranges together with mean composition of the material within that size range samples were analysed using the TRACOR/EDAX particle characterisation and recognition system. In addition some samples were examined using X-Ray Fluorescence (XRF) Spectrometry. Precise elemental analyses of the particulate material collected during steady state operation were obtained by ashing nuclepores at  $700^\circ\text{C}$ , the particulate material fused with lithium borate, solubilised and analysis carried out on the resulting solution using Dionex transition metal ion chromatography.

### 3 RESULTS

#### 3.1 ANALYSIS OF PARTICULATE MATERIAL DURING THE DOEL 4 COMMISSIONING PERIOD

Analyses were carried out for a range of elements and the results are normalised to 100%. These analyses take no account of oxygen and therefore do not represent true percentage composition.

TABLE 1

## DOEL 4: HOT FUNCTIONAL TESTING

COOLANT CONCENTRATION OF INSOLUBLE MATERIAL ( $\mu\text{gdm}^{-3}$ ) FROM XRF  
ANALYSIS OF FILTERS

(\*) = NORMALISED ELEMENTAL COMPOSITION

Steady  
High Temperature  
Operation

Cooldown

Sample No	Iron	Chromium	Nickel	Manganese	Cobalt
1	2.1 (33)	0.11 (1.7)	4.2 (65)	0.02 (0.3)	0.01 (0.2)
2	1.3 (41)	0.05 (2.0)	1.8 (59)	0.05 (2.0)	0.01 (0.5)
3	0.53 (14)	0.11 (2.8)	3.3 (84)	0.05 (2.0)	0.01 (0.3)
4	36 (12)	7.1 (2.4)	256 (85)	0.35 (0.12)	0.12 (0.04)
5	16 (13)	3.1 (2.5)	104 (85)	0.05 (0.04)	0.01 (0.01)

TABLE 2

TRACOR-EDAX ANALYSIS OF MATERIAL COLLECTED PRIOR TO COOLDOWN -  
ANALYSIS WITHIN CHOSEN SIZE RANGES

Particle Size Range	Normalised elemental composition/(wt%)				
	Iron	Chromium	Nickel	Manganese	Silicon
<1 $\mu\text{m}$	4.1	0.8	94	0.1	1.0
1 - 2 $\mu\text{m}$	20	13	62	1.2	0.9
2 - 5 $\mu\text{m}$	44	0.8	50	0.8	1.2
5 - 10 $\mu\text{m}$	54	6.8	13	4.0	0.6
>10 $\mu\text{m}$	21	49	12	6.9	9.9

detailed analysis of two of the samples, one of which was taken pre-initial criticality and one following achievement of steady full power operation. The timing of these samples is indicated in Figure 1.

The most noticeable feature from Figure 1 is the decrease in nickel concentration which fell from over 90% in the initial sample to less than 20% in the sample taken at the first achievement of steady full power operation. This results in a relative increase in the other four elements with iron as the dominant element, followed by zirconium, whilst chromium and silicon are present at relatively low levels.

Examination of data from the two samples taken pre-criticality and following initial full power operation and analysed in greater detail throughout the size ranges show interesting comparisons. In each case the majority of the particles are found in the 0.5 - 1.0  $\mu\text{m}$  diameter size range, but the latter sample shows a greater percentage contribution in this range at the expense of the larger size ranges. In the first sample (Fig 2) it is clear that nickel was the dominant species in the smaller (1  $\mu\text{m}$ ) size range, zirconium being a major constituent of the larger particles. In the second sample (Fig 3) iron dominance was apparent in the smaller size ranges and again zirconium was a major constituent of the larger particles.

## 3.1.1 Hot Functional Testing

Table 1 shows the results of XRF analysis of filters collected at the end of the hot functional testing period. Table 2 shows TRACOR analysis of a sample during this period and indicates the variation in elemental composition between different size ranges.

During this stage of plant operation nickel was the dominant insoluble metallic element and was clearly associated with the smaller particles. Particles greater than 5  $\mu\text{m}$  in diameter were richer in iron, chromium and silicon. The smaller nickel rich particles had a compact crystalline appearance whereas the larger particles were more irregular suggesting they were agglomerates. A number of needlelike particles were observed with a high iron content.

## 3.1.2 Hot Commissioning Post-Fuelling and Approach to Full Power

Analysis of particulate material was carried out for iron, nickel, chromium, zirconium and silicon, both within chosen size ranges and as an overall composition.

The main constituents of all particles throughout the commissioning period are shown in Figure 1 together with reactor power and temperature profiles. Figures 2 and 3 show a more

## 3.2 ANALYSIS OF PARTICULATE MATERIAL DURING STEADY STATE OPERATION

Table 3 shows the analysis of coolant particulates during steady power operation for Doel 4 during cycles 1 and 2. The percentage of nickel present in the particulates increased from cycle 1 to cycle 2 and is accompanied by a corresponding decrease in iron.



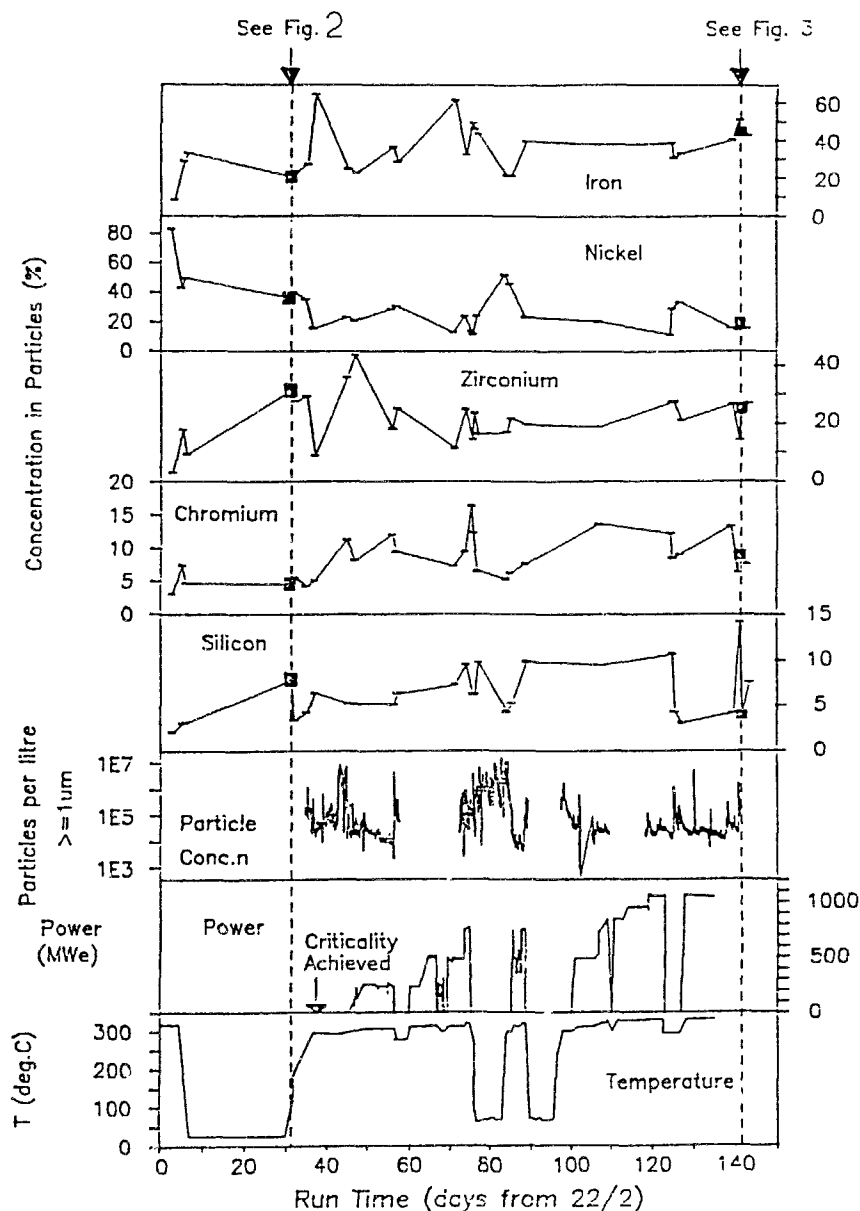


FIG. 1. Elemental analysis of particulate material during initial approach to full power at Doel 4.

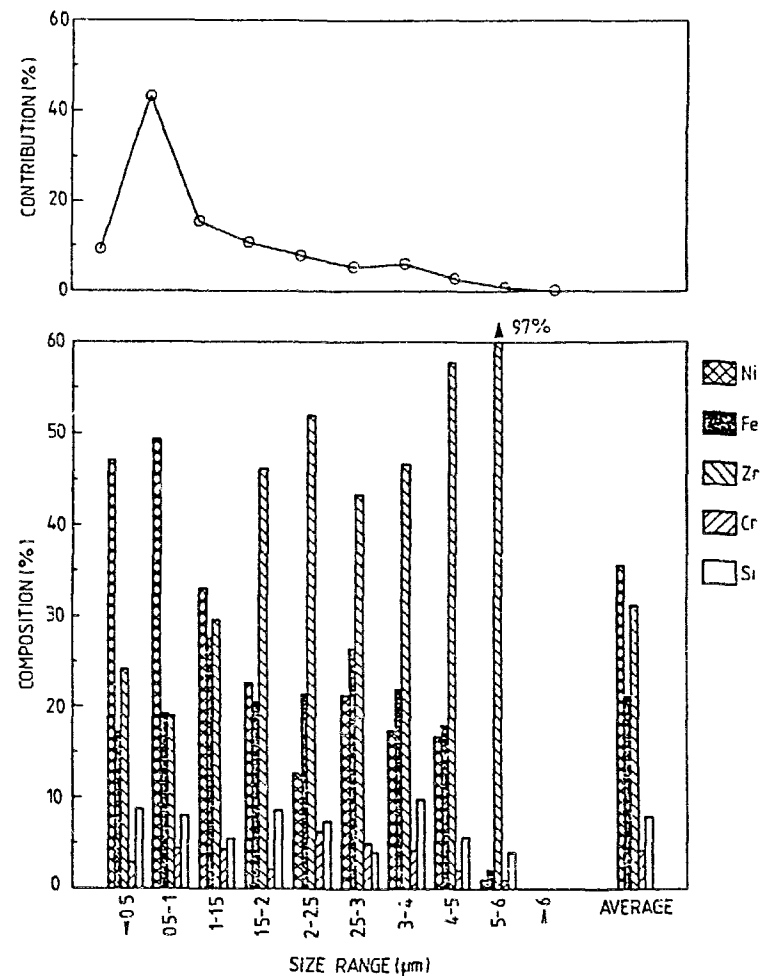


FIG. 2. Percentage of numerical contribution and composition of particles in chosen size range determined using the TRACOR-EDAX system (Doel 4 commissioning pre-criticality).

This trend has also been observed on Doel 3 for cycles 1, 2 and 3 (Table 3). The increase in the percentage of nickel present in particulates implies that the corrosion release rate of the Inconel is increasing with time or that the corrosion release rate of stainless steel 304L is decreasing with time. This observation is the opposite to that made during the commissioning of Doel 4 (Section 3.1.2) where during the approach to full power the nickel concentration of particulates decreased over a 140 day

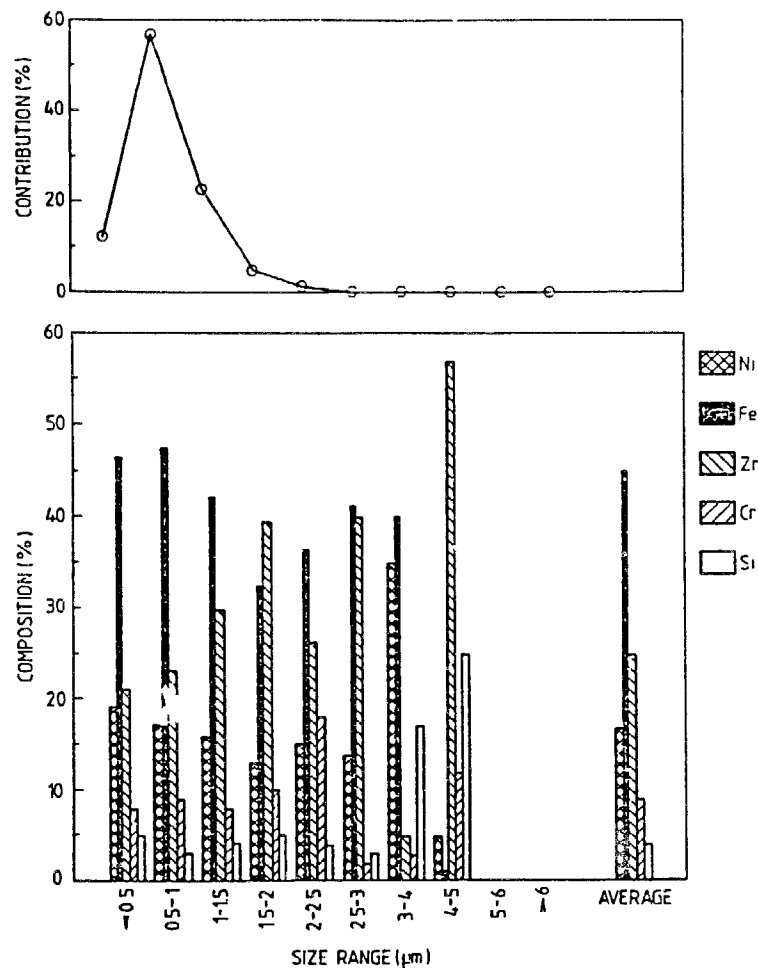


FIG. 3. Percentage of numerical contribution and composition of particles in chosen size range determined using TRACOR-EDAX system (Doel 4 initial full power operation).

period from 80% to 20%. Cobalt averages between 0.1 and 0.2% and the data from Doel 3 showed no increase in the cobalt percentage with reactor cycle.

### 3.3 THE CONTRIBUTION OF PARTICULATES TO THE TOTAL COOLANT BURDEN OF COBALT-58 AND COBALT-60

#### 3.3.1 Doel 4 Commissioning

The approach to full power operation was accompanied by many power fluctuations, trips and two cold shutdowns. These are

TABLE 3  
ANALYSIS OF COOLANT PARTICULATES DURING STEADY POWER OPERATION

PLANT	CYCLE	COOLANT CONCENTRATION/ $\mu\text{g dm}^{-3}$ (% COMPOSITION w.r.t TOTAL OXIDES)				TOTAL AS OXIDES $\mu\text{g dm}^{-3}$ (CALCULATED)
		NICKEL	COBALT	IRON	MANGANESE	
Doel 4	1	0.04 (10.0)	0.001 (0.25)	0.23 (59)	0.01 (2.5)	0.4
Doel 4	2	0.29 (14.5)	0.002 (0.08)	1.10 (55)	0.05 (2.5)	2.0
Doel 3	1	0.10 (4.8)	0.002 (0.12)	1.4 (71)	0.08 (3.4)	2.3
Doel 3	2	0.06 (8.3)	0.001 (0.12)	0.41 (57)	0.03 (4.0)	0.8
Doel 3	3	0.32 (16.0)	0.002 (0.11)	1.02 (52)	0.04 (2.4)	2.0

reflected in the particulate activity and the contribution of particles to the total coolant cobalt-58 and cobalt-60 activity levels (Figures 4 and 5 respectively). Cobalt-58 and cobalt-60 activity associated with particulates showed a steady increase during the initial 25 days when power was increased from zero to 50%. During the following 60 days taken to achieve full power, particulate activity varied by at least two orders of magnitude about a mean value of  $0.1 \text{ kBq dm}^{-3}$  for cobalt-60 and  $10 \text{ kBq dm}^{-3}$  for cobalt-58. Throughout all periods of power operation the proportion of total cobalt activity represented by particulates averaged 50%.

#### 3.3.2 Shutdown and Start-Up Associated with the First Refuelling Outage

The particle contribution to the total cobalt-58 and cobalt-60 activity together with reactor parameters are shown in Figures 6 and 7 respectively for the shutdown and Figures 8 and 9 respectively for the start-up.

During steady full power operation at the end of the first cycle the particulates represented between 40 and 50% of the total coolant cobalt activity. The particulate activity levels were  $0.1 \text{ kBq dm}^{-3}$  cobalt-60 and  $1.0 \text{ kBq dm}^{-3}$  cobalt-58. This represents a change in the cobalt-58/cobalt-60 ratio from 100:1 at the first achievement of full power to 10:1 at the end of the first cycle. The change in ratio was due to a decrease in the cobalt-58 activity level.

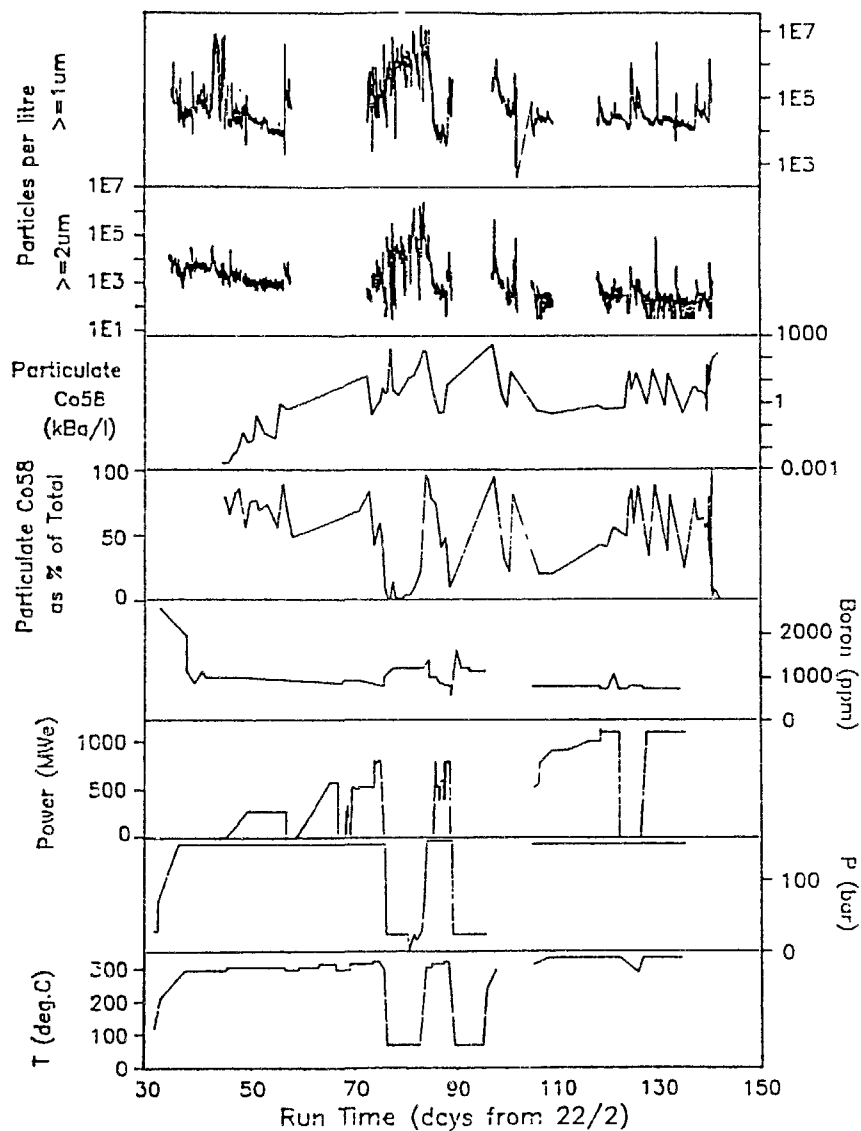


FIG. 4. Doel 4 commissioning (February–July 1985) — particulate contribution to total cobalt-58 activity in coolant.

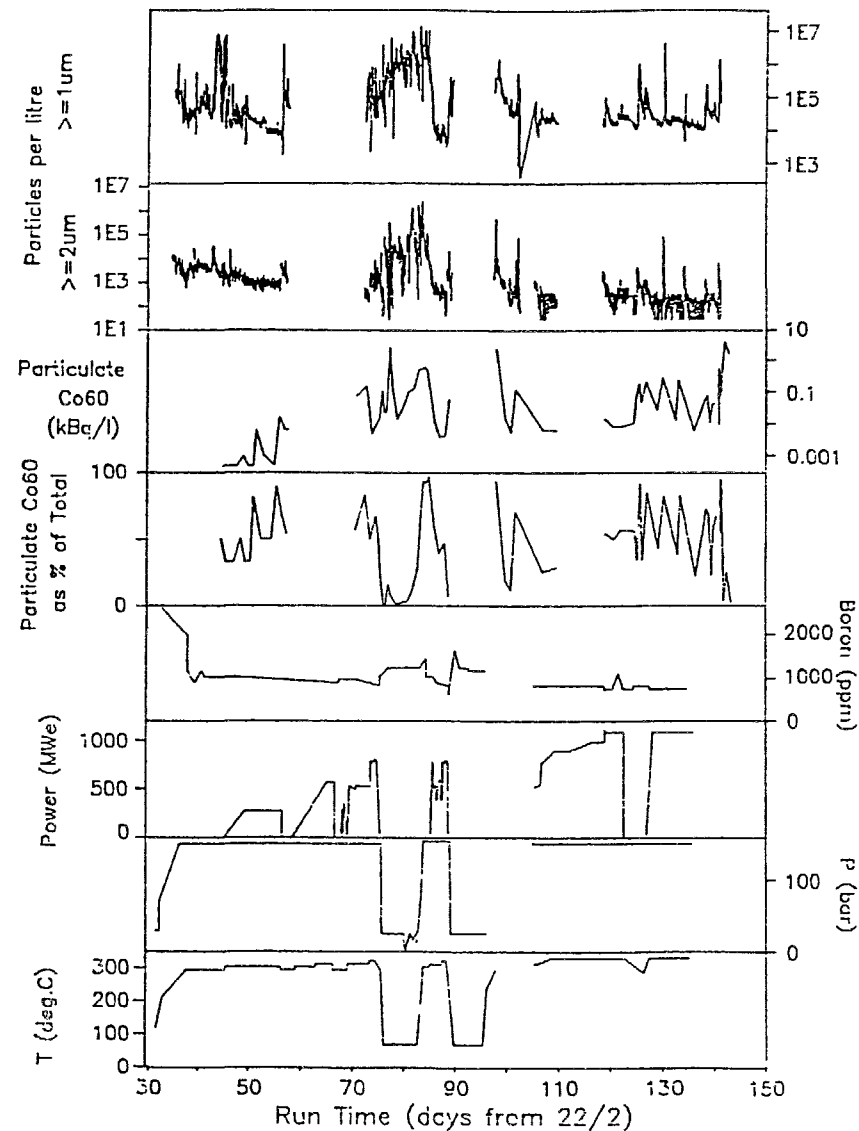


FIG. 5. Doel 4 commissioning (February–July 1985) — particulate contribution to total cobalt-60 activity in coolant.

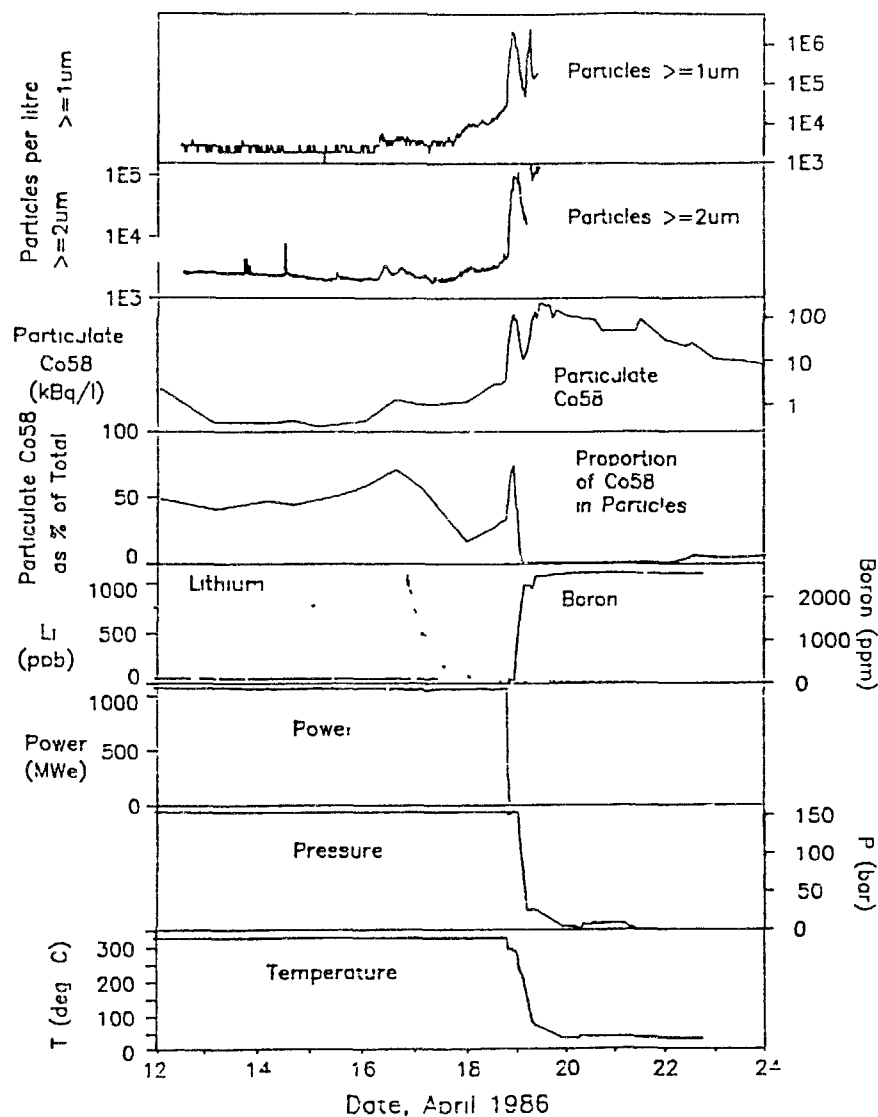


FIG 6 Doel 4 first shutdown (1986) — particulate contribution to total cobalt-58 activity in coolant

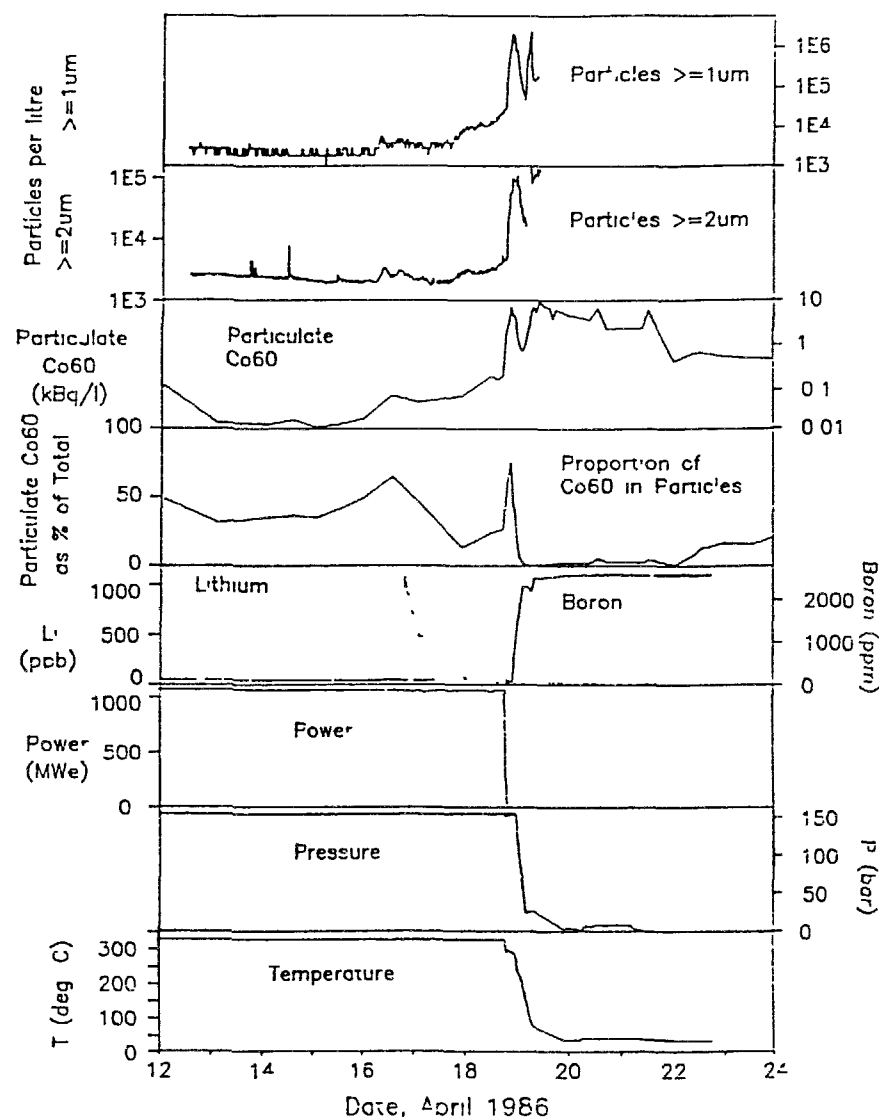


FIG 7 Doel 4 first shutdown (1986) — particulate contribution to total cobalt-60 activity in coolant

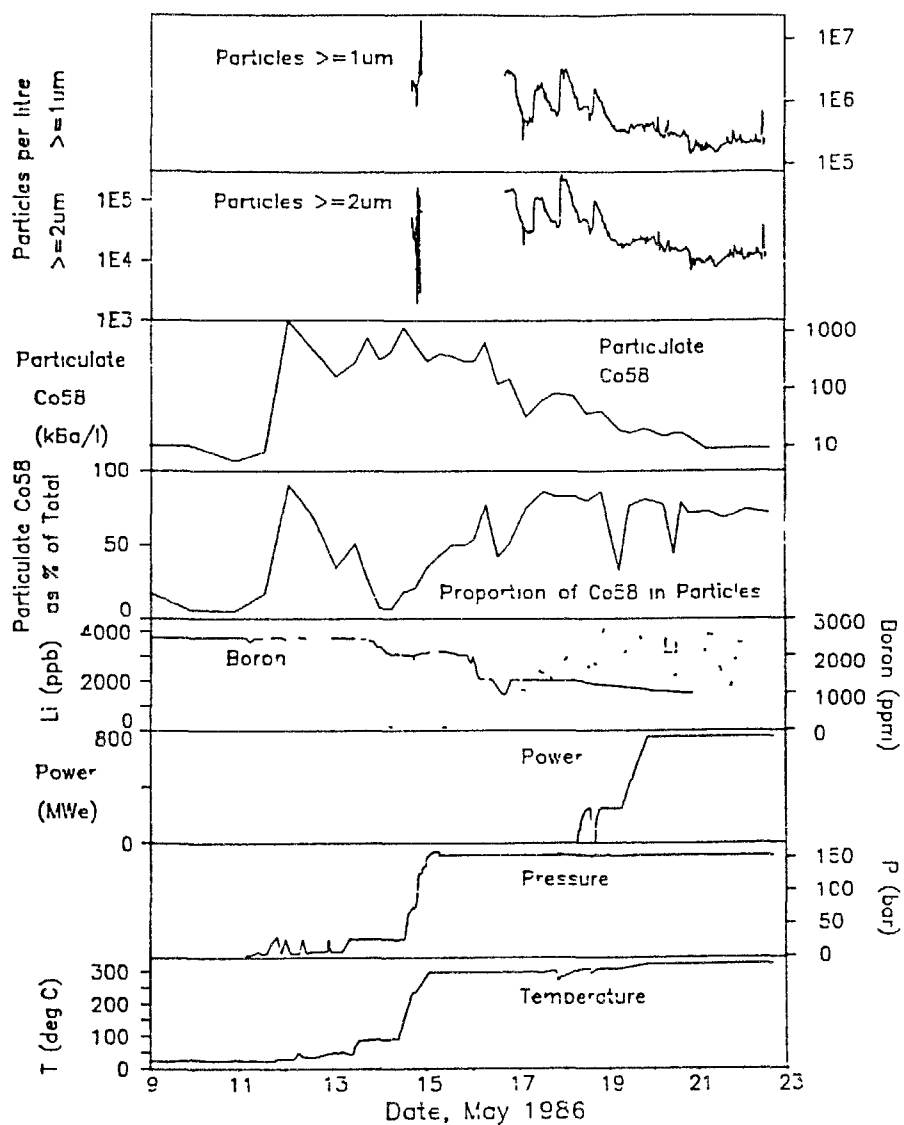


FIG. 8 Doel 4 second startup (1986) — particulate contribution to total cobalt-58 activity in coolant.

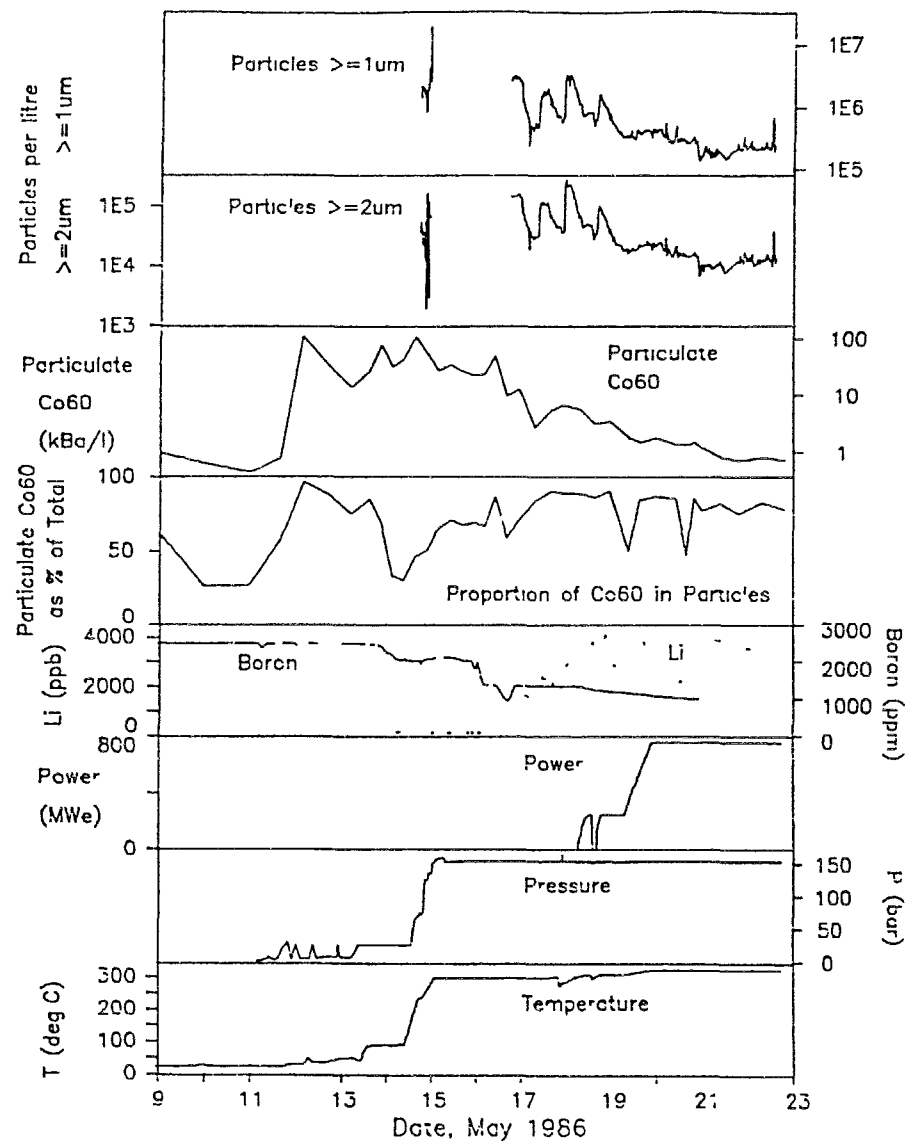


FIG. 9. Doel 4 second startup (1986) — particulate contribution to total cobalt-60 activity in coolant

Lithium removal from the coolant prior to the shutdown had virtually no effect on the particulate activity levels. However, there was a significant change in the percentage of the total activity associated with particles, falling from approximately 60% to < 20%. Soluble elemental and radiochemical species showed a sharp increase concurrent with the lithium reduction. Following shutdown, particle levels increased by two orders of magnitude but at this stage they represented < 5% of the total coolant cobalt activity.

During the start-up period the percentage contribution of particulate activity to the total showed wide variations. During dynamic degassing the particulate cobalt activity was an order of magnitude higher than the maximum observed at shutdown and represented up to 90% of the total activity. Increase in coolant temperature to ~ 120°C produced conditions which promote maximum crud solubility and the contribution from particulate activity fell from ~ 90% to < 20% of the total cobalt activity. Subsequent increase in coolant temperature to ~ 300°C and addition of lithium produced a steady increase in the proportion of total activity attributable to particles despite a decrease in net particulate activity.

#### 4 DISCUSSION

Analysis of particles by XRF and TRACOR/EDAX techniques during the hot functional test period showed the particles to be nickel-rich and that the nickel was clearly associated with the particles in the smaller size ranges. The nickel-rich particles were crystalline and clearly originated from corrosion of the Inconel 600 steam generators. Laboratory studies under PWR conditions (refs 2 and 3) have shown that stainless steel 304L and Inconel 600 have similar corrosion and corrosion release rates, the rates being proportional to (time)<sup>n</sup>. Assuming congruent release, due to the greater surface area of the Inconel steam generators one would expect the particles to be nickel rich. However, as the commissioning period proceeded the nickel concentration decreased and by the approach to full power the nickel concentration had decreased from a high of 80% to less than 20% of the particle composition. Nickel being replaced by iron as the dominant insoluble element. The behaviour of nickel is obviously related to the corrosion rates of Inconel 600 and stainless steel 304L and has been observed and commented on before (ref 4). Measurements made on plant components indicate that the corrosion rate of stainless steel is circa 10x higher than Inconel components. The reason for the discrepancy between the corrosion rates of stainless steel and Inconel as measured in laboratory studies compared to examination of plant specimens is unknown. Surface finish may well provide an explanation, laboratory studies tend to employ polished specimens and rough surfaces are known to corrode faster than smooth ones (ref 5). The heat transfer properties of the Inconel steam generators may also be shown to be a factor in determining corrosion and corrosion release rates. Zirconium was also present in the

particles; being concentrated in the larger size ranges, the zirconium would arise from the new fuel present which would inevitably have surface traces of Zircaloy micro swarf as a result of polishing, individual particles were found to contain up to 80% zirconium.

The percentage of nickel present in the particulates has been shown to increase with reactor cycle (at least up to cycle 3). This implies that the corrosion release rate of the Inconel 600 is increasing with time or that the corrosion release rate of stainless steel 304L is decreasing with time. This observation is the opposite to that made during the commissioning period and is difficult to both understand and interpret solely in terms of corrosion release rates.

Particle measurements at both Doel 3 and 4 have indicated a correlation with lithium levels and hence pH<sub>300</sub> (ref 6). Soluble species and hence the proportion of insoluble activity to the total have been shown to follow closely addition or removal of lithium from the borated coolant. The level of particle activity itself does not show such an instant response but nevertheless changes in the concentration of soluble species must have long-term implications in the formation of active deposits and subsequent particle concentrations.

A steady cobalt-60 activity level is attained within days of the reactor reaching full power operation and the soluble cobalt-60 activity level decreases with reactor cycle whereas the insoluble cobalt-60 level increases with reactor cycle (ref 7). The fact that the distribution of cobalt-60 activity changes with time provides no insight into the activity transport mechanism. Initial specific activity measurements indicate that the cobalt-60 specific activity of the particulates increase with reactor cycle. The increase in specific activity was not mirrored in a similar increase in out-of-core doserates and this may imply that particulate transport is not the major activity transport process but they are simply continually deposited and resuspended in the reactor circuit i.e. reirradiated.

The role of soluble species will be treated in Part 2 of this study.

#### 5 CONCLUSIONS

Analysis of particulate material during the hot functional test period showed the particles to be nickel rich and that the nickel was associated with the smaller (> 2 µm) size ranges.

By the time of approach to full power at the end of the commissioning period the nickel concentration had decreased from a high of 80% to less than 20% of the particle composition. Nickel being replaced by iron as the dominant insoluble element. This implies that the corrosion release rate of Inconel 600 is initially high but rapidly decreases and the corrosion release rate of stainless steel then becomes dominant.

Analysis of particulate material during steady state operation has shown the percentage of nickel present in the particulates increases with reactor cycle (at least up to cycle 3). This implies that either nickel is preferentially released from the stainless steel or that the corrosion release rate of the stainless steel becomes less dominant with time.

The proportion of total cobalt activity represented by particulates during steady full power operation averages 50%. During shutdowns and start-ups this proportion changes markedly and is dependent on coolant temperature and pH.

The dominance of the corrosion release rate of Inconel 600 observed during the commissioning period of Doel 4 shows the importance of good chemistry control during this period. The absence of lithium and hence a low pH at this time will result in higher corrosion release rates. Thus a greater quantity of nickel and more importantly cobalt will be released to the coolant which could have a significant influence on future out-of-core doserates. Good chemistry control during the commissioning period as well as normal operation is necessary if out-of-core doserates are to be kept to a minimum.

#### ACKNOWLEDGEMENT

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## METHOD FOR pH CALCULATION

E.W. THORNTON

Berkeley Nuclear Laboratories,  
Central Electricity Generating Board,  
Berkeley, Gloucestershire,  
United Kingdom

#### Abstract

*In this paper a method for the calculation of pH at high temperature in water reactors is described.*

The PWR primary circuit contains boric acid, base (potassium hydroxide and/or lithium hydroxide) and dissolved corrosion product oxide. The coolant also contains dissolved hydrogen and, in the case of VVERs, ammonia. For the purpose of calculating coolant pH, the presence of the dissolved corrosion products and ammonia can be neglected. Ammonia is a very weak base at primary circuit temperature and boric acid exerts a strong buffering influence.

pH is defined as  $-\log_{10}(\text{proton molality})$  and is calculated by solving the charge balance equation and the boron balance equation simultaneously:

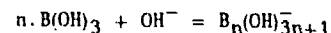
$$H^+ + M^+ = OH^- + B1^- + B2^- + B3^- \quad A.1$$

$$B(\text{Tot}) = BH + B1 + 2.B2 + 3.B3 \quad A.2$$

where:  $H^+$  is the proton molality,  
 $M^+$  is the base cation molality,  
 $OH^-$  is the hydroxyl ion molality,  
 $B1$  is the  $B(OH)_4^-$  molality,  
 $B2$  is the  $B_2(OH)_7^-$  molality,  
 $B3$  is the  $B_3(OH)_{10}^-$  molality,  
 $BH$  is the molality of unionised boric acid,  $B(OH)_3$   
 $B(\text{tot})$  is the total boron molality.

The base cation molality is the sum of the lithium and potassium cation molalities. The dissociation of bases and the formation of base cation/borate complexes or ion pairs are not very well characterised. It is reasonable to assume that LiOH and KOH are fully ionised and that borate complexes are not formed.

The boric acid monomer, dimer and trimer are produced by reactions of the following general type (Mesmer, Baes and Sweeton, 1971):



and their concentrations are given by:

$$B1 = Q_{11}BH.OH^- \quad A.3$$

$$B2 = Q_{21}BH^2OH^- \quad A.4$$

$$B3 = Q_{31}BH^3OH^- \quad A.5$$

The equilibrium quotients are given by:

$$\log_{10}Q_{11} = \frac{1573.21}{T} + 28.6059 + 0.012078T - 13.2258\log_{10}T + f(I)$$

$$\log_{10}Q_{21} = \frac{2756.1}{T} - 18.7322 - 0.00033T + 5.835\log_{10}T - f(I)$$

$$\log_{10}Q_{31} = \frac{3339.5}{T} - 7.850 - 0.00033T + 1.497\log_{10}T - f(I)$$

where T is absolute temperature and

$$f(I) = (0.325 - 0.00033T)I - 0.0912I^{3/2}$$

I is the solution ionic strength.

The proton and hydroxyl ion concentrations are related by the ionisation constant of water:

$$K_w = H^+OH^-\gamma^2 \quad A.6$$

where  $\gamma$  is the mean ionic activity coefficient for univalent ions.  $K_w$  is given by (Marshall and Franck, 1981):

$$\log_{10}K_w = -4.098 - \frac{3245.2}{T} + \frac{2.2362.10^5}{T^2} - \frac{3.984.10^7}{T^3} + \left(13.957 - \frac{1262.3}{T} + \frac{8.5641.10^5}{T^2}\right) \log_{10}\rho_w$$

where  $\rho_w$  is the density of water ( $g\ cm^{-3}$ ). The density of water is given by (Keenan and Keyes, 1936):

$$\rho_w = \frac{1.0 + 0.1341489t_1^{1/3} - 3.946263.10^{-3}t_1}{3.1975 - 0.3151548t_1^{1/3} - 1.203374.10^{-3}t_1 + 7.489081.10^{-13}t_1^4}$$

where  $t_1$  is  $(374.11 - t)$  and  $t$  is the Centigrade temperature. The mean ionic activity coefficient is given by a simple Debye-Hueckel expression:

$$\log_{10}\gamma = \frac{-z^2AI^{1/2}}{1 + 1.5I^{1/2}}$$

where  $z=1$  for univalent ions and the Debye-Hueckel limiting slope is given by (Mesmer, Baes and Sweeton, 1971):

$$A = 3.28377 - 0.031264T - 1.264.10^{-4}T^2 - 2.2151.10^{-7}T^3 + 1.49321.10^{-10}T^4$$

The equations A.1 and A.2 can be solved for the two unknown quantities  $H^+$  and  $BH$  by successive iterative approximations using computer algorithms for solving simultaneous non-linear equations after appropriate substitution from A.3 to A.6.

Figs A.1 to A.3 show the coordinated chemistry bands currently adopted by a number of utilities and countries. In each case the abscissa can be taken as a (non-linear) time axis from around 1200 ppm B at the beginning of the cycle to approach 0 ppm B at the end of the reactor cycle. The upper and lower lines of each pair give the pH values of the upper and lower LiOH or KOH specifications and define the operating band.

The Westinghouse operating band is defined by:

$$\text{Lower Li} = 0.186 + 1.2.10^{-3}B + 2.10^{-7}B^2$$

$$\text{Upper Li} = \text{Lower Li} + 0.3$$

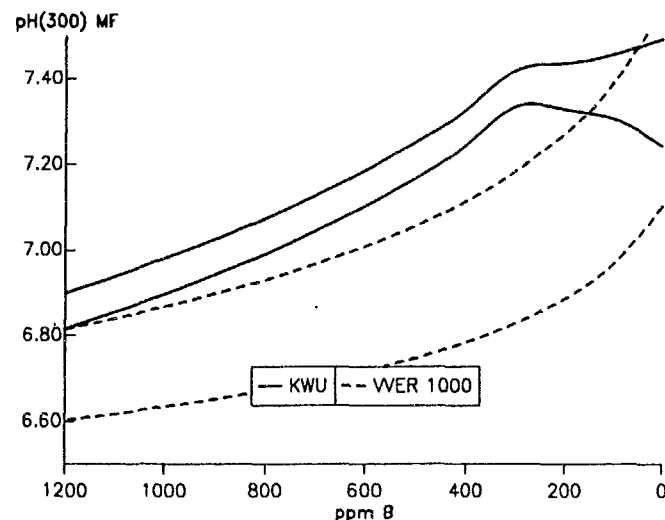


FIG. A1. Co-ordinated chemistry regimes.



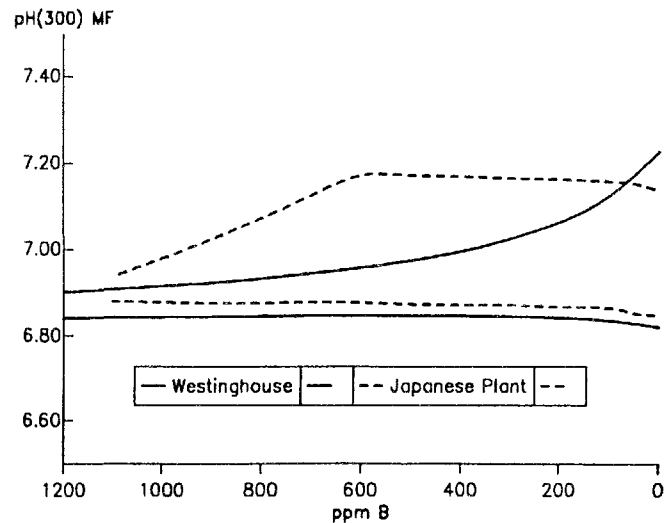


FIG. A2. Co-ordinated chemistry regimes.

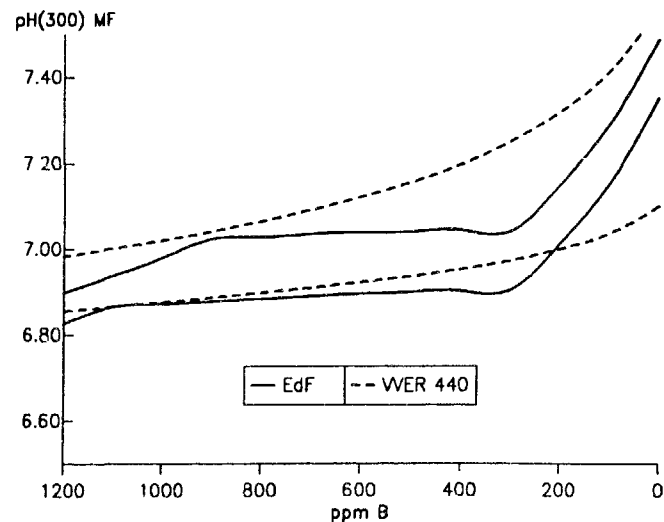


FIG. A3. Co-ordinated chemistry regimes.

The VVER 440 and 1000 operating bands are defined by:

$$\text{Lower K} = 2.00 + 7.6 \cdot 10^{-3} B$$

$$\text{Upper K} = \text{Lower K} + 4.0$$

and

$$\text{Lower K} = 2.00 + 3.37 \cdot 10^{-3} B$$

$$\text{Upper K} = \text{Lower K} + 4.0$$

where B, Li and K are in ppm.

The KWU operating band is defined as operation at 2.0 +/- 0.2 ppm Li until the pH obtained with 2.0 ppm Li reaches 7.4 and then coordinating at pH 7.4 to zero boron but operating in a +/- 0.2 ppm Li band in this range.

The coordination band recommended for Japanese plant was supplied as a table of upper and lower recommended values (M. Yamada, private communication).

The EdF recommended band was recalculated from the graph in Berthet (1985),

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# **PARTICIPANTS IN THE CO-ORDINATED RESEARCH PROGRAMME**

## **ARGENTINA**

Ablesa, M.                      Departamento de Química de Reactores,  
Comisión Nacional de Energía Atómica,  
Avenida del Libertador 8250,  
1429 Buenos Aires

Corti, H.R.                    Departamento de Química de Reactores,  
Comisión Nacional de Energía Atómica,  
Avenida del Libertador 8250,  
1429 Buenos Aires

Maroto, A.J.G.                Departamento de Química de Reactores,  
Comisión Nacional de Energía Atómica,  
Avenida del Libertador 8250,  
1429 Buenos Aires

Piacquadio, N.H.            Departamento de Química de Reactores,  
Comisión Nacional de Energía Atómica,  
Avenida del Libertador 8250,  
1429 Buenos Aires

Regazzoni, A.                Departamento de Química de Reactores,  
Comisión Nacional de Energía Atómica,  
Avenida del Libertador 8250,  
1429 Buenos Aires

## **BELGIUM**

Blanpain, P.                Belgonucléaire SA,  
25, rue du Champ de Mars,  
B-1050 Brussels

## **BULGARIA**

Dobrevsky, I.                University of Chemical Technology,  
8010 Bourgas

Litovska, G.                University of Chemical Technology,  
8010 Bourgas

Vassilev, R.                University of Chemical Technology,  
8010 Bourgas

## **CANADA**

Lister, D.H.                Atomic Energy of Canada Ltd,  
Chalk River Nuclear Laboratories,  
Chalk River, Ontario K0J 1J0

Speranzini, R.A.            Atomic Energy of Canada Ltd,  
Chalk River Nuclear Laboratories,  
Chalk River, Ontario K0J 1J0

## **CHINA**

Fan Junfu                    Reactor Structure Materials and Water  
SWCR Chemistry Experiment Research Division  
Chengdu, Sichuan Province

## **CZECHOSLOVAKIA**

Burclova, J.                Radiation Safety Department,  
Nuclear Power Plants Research Institute,  
Okružná 5,  
CS-918 64 Trnava

Kysela, J.                  Department of Radiation Experiments,  
Nuclear Research Institute,  
CS-250 68 Rez/Prague

## **FINLAND**

Aaltonen, P.                Technical Research Centre of Finland,  
Vuorimiehentie 5,  
SF-02150 Espoo

Aho-Mantila, I.            Metals Laboratory,  
Technical Research Centre of Finland,  
SF-02150 Espoo

## **FRANCE**

Beslu, P.                    Centre d'études nucléaires de Cadarache,  
Commissariat à l'énergie atomique,  
Saint-Paul-lez-Durance

## **GERMANY**

Hickling, J.                Siemens AG, KWU Group U9 23,  
Hammerbachstrasse 12/14,  
D-W 8520 Erlangen

Hüttner, F.                Institut für Energietechnik,  
Technische Universität Dresden,  
Mommensenstrasse 13,  
D-0 8027 Dresden

Riess, R.                    Siemens AG, KWU Group U9 23,  
Hammerbachstrasse 12.14,  
D-W 8520 Erlangen

Winkler, R.                Institut für Energietechnik,  
Technische Universität Dresden,  
Mommensenstrasse 13,  
D-8027 Dresden

**HUNGARY**

Horvath, G.L. Nuclear and Thermal Power Plant Division,  
Institute for Electrical Power Research,  
P.O. Box 233,  
H-1368 Budapest

Matus, L. Department of Chemistry,  
Central Research Institute for Physics,  
P.O. Box 49,  
H-1525 Budapest 114

**INDIA**

Mathur, P.K. Water Chemistry Division,  
Bhabha Atomic Research Centre,  
Trombay, Bombay 400 085

Narasimhan, S.V. Water Chemistry Division,  
Bhabha Atomic Research Centre,  
Trombay, Bombay 400 085

Venkateswaran, G. Water Chemistry Division,  
Bhabha Atomic Research Centre,  
Trombay, Bombay 400 085

Venkateswarlu, K.S. Water Chemistry Division,  
Bhabha Atomic Research Centre,  
Trombay, Bombay 400 085

**JAPAN**

Ishigure, K. Department of Nuclear Engineering,  
University of Tokyo,  
Bunkyo-ku, Tokyo

**KOREA, REPUBLIC OF**

Yang, Jae-Choon Department of Physics,  
Chungnam National University,  
220 Gungdong, Yousung,  
Taejon 300-31

**POLAND**

Ostyk-Narbutt, J. Department of Radiochemistry,  
Institute of Nuclear Chemistry and Technology,  
U. Dorodna 16,  
PL-03195 Warsaw

**RUSSIA**

Antipov, S.A. VNIINM,  
Rogov St. 5,  
123060 Moscow

Khitrov, Yu. VNIPIET,  
Dibunovskaja St. 55,  
197228 Saint Petersburg

Pashevich, V.I. Minatomenergoprom,  
Zotatomenergo,  
Kitajskij PZ7,  
Moscow K-74

Rybalchenko, I.L. VNIPIET,  
Dibunovskaja St. 55,  
197228 Saint Petersburg

Sedov, V.M. Institute of Technology,  
Saint Petersburg

Versin, V.V. VNIPIET,  
Dibunovskaja St. 55,  
197228 Saint Petersburg

**SPAIN**

Martin, L. Nuclear Safety Council,  
Justo Dorado 11,  
Madrid 28040

**SWITZERLAND**

Alder, H.P. Materials Technology,  
Paul Scherrer Institute,  
CH-5303 Würenlingen

**UNITED KINGDOM**

Brookes, I. Plant Chemistry Branch,  
CEGB Berkeley Nuclear Laboratories,  
Berkeley, Gloucestershire GL13 0PB

Butter, K.R. Winfrith Atomic Energy Establishment,  
United Kingdom Atomic Energy Authority,  
Dorchester, Dorset DT2 8DH

Campion, P. Chemistry Division,  
Winfrith Atomic Energy Establishment,  
United Kingdom Atomic Energy Authority,  
Dorchester, Dorset DT2 8DH

## UNITED KINGDOM (cont.)

Comley, G.                    Plant Chemistry Branch,  
CEGB Berkeley Nuclear Laboratories,  
Berkeley, Gloucestershire GL13 0PB

Pick, M.                    Plant Chemistry Branch,  
CEGB Berkeley Nuclear Laboratories,  
Berkeley, Gloucestershire GL13 0PB

Thornton, E.W.            Plant Chemistry Branch,  
CEGB Berkeley Nuclear Laboratories,  
Berkeley, Gloucestershire GL13 0PB

## INTERNATIONAL ATOMIC ENERGY AGENCY

Chantoin, P.                Division of Nuclear Fuel Cycle and Waste  
Management,  
International Atomic Energy Agency,  
Wagramerstrasse 5,  
P.O. Box 100,  
A-1400 Vienna

## Consultants Meetings

Vienna, Austria: 23-25 November 1987, 18-20 October 1988, 6-8 November 1990

## 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