

LCC-2 Special Topic Report

CRUD in *PWR/VVER* and BWR Primary Circuits

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ACRONYMS AND EXPLANATIONS

ABWR	Advanced boiling water reactor with internal recirculation pumps
AES	Auger Electron Spectroscopy
AOA	Axial Offset Anomaly
ASI	Axial Shape Index
ATEM	Analytical Transmission Electron Microscopy
BOC	Beginning Of Cycle
BOP	balance-of-plant
BRAC	BWR Radiation Assessment and Control
BWR	Boiling Water Reactor
CANDU	Pressurized Heavy Water Reactor developed by AECL of Canada ("CANada Deuterium Uranium")
CCM	The Constant Capacitance Model
CILC	Crud Induced Localised Corrosion
CIPS	Crud Induced Power Shift
CORD	Decontamination process developed by Siemens ("Complexing Organic Reduction Decontamination")
CRUD	Chalk River Unidentified Deposits
CVCS	Chemistry and Volume Control System
DCP	Distinctive Crud Pattern
DF	Decontamination Factors
DLM	Diffuse Layer Model
DZO	Depleted Zinc Oxide
EBA	Enriched Boric Acid
ECP	Electrochemical Corrosion Potential
EFPD	Effective Full Power Days
EFPH	Effective Full Power Hours
FAC	Flow-Accelerated Corrosion
FPHD	Forward Pumped Heater Drains
FRP	Fuel Reliability Program
FSD	Full System Decontamination
HFM	High-Field Model
HFT	Hot Functional Test
HWC	Hydrogen Water Chemistry
IAEA	International Atomic Energy Agency
IASCC	Irradiation Assisted Stress Corrosion Cracking
KWU	KraftWerkUnion
LHGR	Linear Heat Generation Rate
LOCA	Loss Of Coolant Accident
LWR	Light Water Reactor
MSLR	Main Steam Line Radiation
MCM	The Mixed Conduction Model
NM	Noble Metal
NMCA	Noble Metal Chemical Addition

NMT	Noble Metal Technology
NPP	Nuclear Power Plant
NWC	Normal Water Chemistry
O&M	Operation and Maintenance
PDM	The Point Defect Model
PIE	Post Irradiation Examination
PLR	Primary Loop Recirculation
PWR	Pressurised Water Reactor
PWSCC	Primary Water Stress Corrosion Cracking
RCP	Reactor Coolant Pumps
RCS	Reactor Coolant System
RHR	Reactor Heat Removal system
RPV	Reactor Pressure Vessel
RW	Reactor Water
RWCU	Reactor Water Clean-Up
SCC	Stress Corrosion Cracking
SEM	Scanning Electron Microscopy
SGHWR	Steam Generating Heavy Water Reactor
SGR	Steam Generator Replacement
SHE	Standard Hydrogen Electrode
SIMS	Secondary Ion Mass Spectroscopy
SNB	Subcooled Nucleate Boiling
SPP	Second Phase Particle
SR	Steaming rate
TR	Technical Requirements
TMI	Three Mile Island
VCT	Volume Control Tank
VGB	See www.vgb.org
VHR	Vessel Head Replacement
VVER	Russian version of the PWR (“Voda Voda Energo Reactor”)
GDOES	Glow Discharge Optical Emission Spectroscopic
XAS	X-ray absorption spectroscopy
XPS	X-ray Photoelectron Spectroscopic
ZIRLO	Zirconium Low Oxidation

UNIT CONVERSION

TEMPERATURE		
°C + 273,15 = K		
°C*1,8 +32 = °F		
T(K)	T (°C)	T(°F)
273		0
289		16
298		25
373		100
473		200
573		300
633		360
673		400
773		500
783		510
793		520
823		550
833		560
873		600
878		605
893		620
923		650
973		700
1023		750
1053		780
1073		800
1136		863
1143		870
1173		900
1273		1000
1343		1070
1478		1204

DISTANCE	
x (µm)	x (mils)
0,6	0,02
1	0,04
5	0,20
10	0,39
20	0,79
25	0,98
25,4	1,00
100	3,94

PRESSURE		
bar	MPa	psi
1	0,1	14
10	1	142
70	7	995
70,4	7,04	1000
100	10	1421
130	13	1847
155	15,5	2203
704	70,4	10000
1000	100	14211

MASS	
kg	lbs
0,454	1
1	2,20

STRESS INTENSITY FACTOR	
MPa√m	ksi√inch
0,91	1
1	1,10

CONVERSION OF DIMENSIONS	
1 Sv	= 100 Rem
1 Ci	= 3.7 x 10 ¹⁰ Bq = 37 GBq
1 Bq	= 1 s ⁻¹

EXECUTIVE SUMMARY

All system materials used in Light Water Reactors rely on a passivating oxide film. It means that the oxide film formed by the corrosion attack of water on the material will protect the underlying material from further attack. Such oxide formation can be characterized by the thickness, the composition, the electrical and electrochemical properties of the film. During the growth of such films an interaction of the coolant and the films takes place whereby an inner barrier layer oxide is formed which can be characterized by its uniform composition and nanocrystalline structure. It can also be concluded, that the overall alloy corrosion rate is limited by the net processes in this barrier layer.

The importance of the oxide film on stainless steel and nickel base material in *LWRs* is not only limited by the formation, growth, and stability of the barrier layer (e.g. influencing the corrosion behaviour of Ni-based material), but also by an outer oxide deposit. This outer oxide deposit is a result of an interaction of the environment with the oxide film. Such interaction which includes metal oxide dissolution, transport, activation, re-dissolution and re-deposition is responsible for a variety of operational problems, like activity build-up, fuel integrity and Axial Offset Anomalies. The surface concentration of the various elements and the corresponding radio nuclides will be a function of their concentration in the water, the extent of surface complexation, and the transport rate into different oxide layers.

The above described, "basic", scenario is benchmarked by an evaluation of the operational experiences with crud in light water reactors, which are using stainless steel and nickel base alloys as system materials. In addition, the results of research and development work are included in this description. Finally, the currently available countermeasures against the negative effects of crud are identified and evaluated. They include preventive mitigation methods like a suitable selection of the Steam Generator tubing material and they consist out of considerations to improve the properties of the barrier oxide layer, a minimization of the crud inventory available for transport inside the *RCS*, and a chemistry which minimizes such crud transport and activation. The addition of Zinc to *LWR* coolants is an example of a countermeasure suitable to achieve a minimization of crud impact on plant operation.

In summary, the intent of this report is to describe the formation of crud and to identify the crud specific situation in the operating plants. However, the main objective is to identify all possible countermeasures that help to minimize the impact of crud on plant operation.

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1 INTRODUCTION (ROLF RIESS)

The three main issues in having a safe and economic operation of a nuclear power plant is to minimize:

- the risk and occurrence of stress corrosion cracking
- the exposure of the staff and other people to ionizing radiation
- the risk of fuel deposits and the consequences thereof e.g. *AOA*

Key factors allowing to achieve this goal are associated with the corrosion product in the primary coolant of both *PWRs* and *BWRs*.

On one hand side the corrosion products are forming tenacious oxide films on the structural materials and thereby assure the integrity of the systems. On the other hand corrosion products are released to the coolant, then they are transported to the core, activated, re-dissolved and re-deposited on out-of-core surfaces. Thus, they are contributing to an enhanced risk for the occurrence of the three main issues mentioned above.

1.1 IMPORTANCE OF THE PROBLEM

All materials used in a nuclear power plant rely on a passivating oxide film. This means that the oxide film formed by the corrosion attack of water on the materials will protect the underlying material against further attack. Otherwise the material would decompose into a mixture of metal oxides without a protective layer. The protective effect of the oxide layer originates from a low solubility and a slow reaction rate for any chemical interaction between the oxide film and the surrounding environment. However, the protective effect may never be perfect. This means, that corrosion of the base material is always occurring to some extent, which is eventually caused by changes in the chemical composition (like hydrogen) or pH of the surrounding water, or an increase in temperature which would increase the reaction rate and hence minimize the protective ability of the oxide film.

Almost all use of materials is based on experience gained from similar systems in another application. The use of materials in new environment requires substantial investigation of the materials behaviour in the expected range of environmental conditions. Fundamental work made in this regard on stainless steels and nickel based materials for application in *LWRs* has been reviewed. The data are also analyzed and evaluated in order to establish a fundament for further development in this field.

During the almost 50 years of commercial use of *LWRs*, a huge experience has been gained about the materials behaviour, yet, the increasingly faster change of the environmental conditions has made it difficult to test all possible combinations of materials and environments in order to assess the long term behaviour of materials, or rather, the behaviour of the protective oxides on the materials. Some examples of such changes during the last 20 years are for the *BWRs*:

- Reduction of the iron input
- The introduction of hydrogen water chemistry, *HWC*
- The application of noble metals
- The change from stellite to other non-cobalt hard-facing materials
- Zinc injection
- The up-rating of power plants leading to changes in the local chemistry and the flow assisted erosion.

Similar developments were occurring in the *PWRs* like:

- Increased maximum allowed pH
- Wider pH range from extended cycles
- Elevated outlet temperature
- Increased power density leading to significant sub-cooled nucleate boiling
- Change of steam generator materials
- Zinc injection

The corrosion behaviour of certain materials is always depending on the environment, which influences the corrosion release, and for example, the release of corrosion products from the already existing oxide surfaces in other parts of the reactor. The behaviour of oxide films in the primary system as well as the release and transport of corrosion products is a complex function of their behaviour in a couple of localized areas depending on each other and all local environmental factors. The inference of this situation is that a full assessment of the materials behaviour in *LWRs* can only be gained by collecting operational experience as well as materials testing in the laboratory. In addition, there is a need for a theory or modelling tools that can take the interaction between the various local oxides with their local chemistry in order to have an integral description and understanding of the stress corrosion cracking, the activity build-up, and the fuel cladding behaviour in any *LWR*.

1.2 *SURFACE FILMS AND STRESS CORROSION CRACKING*

The protective ability of an oxide film is hindering significant corrosion of the base alloy and thereby assures that no significant material thinning is occurring. Even very small localized attacks on the oxide film could be detrimental. The passive behaviour of the oxide film could then be important in two ways:

The first is the localized corrosion attack itself. In order to have stress corrosion cracking, the material must have some tensile stress and it must be susceptible to localized attack, e.g. by sensitisation. Furthermore, there must be an aggressive chemistry, causing the attack. Although the actual chemistry in *BWRs* is rather different compared to *PWRs* and *VVERs*, still the same factors are needed. If the stressed oxide film is prone to localized attacks via chemical interaction with the coolant, so-called pitting could develop on the materials surface. The pits are forming where the oxide film is locally the least protective and will establish an aggressive chemistry in the bottom of the pit. If a certain depth of about 20 µm or slightly deeper is reached, the pit or incipient attack can develop into a propagating crack, when sufficient stress is applied. The weakest spot in the oxide film is thus transformed into the weakest spot for cracking of materials. Chlorides and other halides are known to cause localized attacks but many more chemical impurities and combinations thereof could be the possible cause of such attack.

The second aspect is the re-passivation kinetics. That means the ability to quickly reform the protective passive layer, which is also important for the development of stress corrosion cracking. If the material does not re-passivate, the localized attack would be more extended and actually open up the attack area to allow a wash-out of the local chemistry. The re-passivation hence allows the slightly less stressed areas of exposed metal to rebuild an oxide, which will protect them against further attack, confining the attack to a small area.

The re-passivation kinetics is always important when it comes to *SCC* in *LWR* environments.

1.3 *SURFACE FILMS AND ACTIVITY BUILD-UP*

The activity build-up in nuclear power plants is influenced by the oxide films in several ways. To have activity build-up, a certain corrosion release from the material is needed to allow the corrosion products to deposit in the core region and become activated. Without corrosion products from the non-core structural material, basically only the cladding and its oxide would be the source for any activity distribution. This means, that without deposited corrosion products in the core the activity release would be almost exclusively due to flaking of oxides of the cladding material. However, the activation products of zirconium have short half lives and the activation build-up problem would be non-existent in *LWRs*.

In reality, the materials of the *LWR* primary systems do release a significant amount of products to the coolant by corrosion. The reactor core is than a very efficient filter when it comes to collecting the corrosion products transported in the coolant. The main parameter removing corrosion products from the coolant is the sub-cooled nucleate and nucleate boiling, Asakura et al., 1979, Kawaguchi et al., 1983, and Pan et al., 1985.

In case of soluble corrosion products, Nichino et al (a), it seems that the heat flux and boiling are also important parameters. At least in the *BWR*, a certain amount of hematite is needed to form a significant crud build-up, Hosokawa et al. 1998. Currently it is unknown if a similar base deposit is needed also for core crud formation in pressurized water reactors. The main reason that much less knowledge is available about *PWR* than of *BWR* crud formation, is the general absence of cold leg sampling line, which makes proper mass balance assessment impossible, and the fuel crud stripping normally performed by environmental changes during *PWR* shutdown as well as during regular sampling.

The neutron activation of the core crud will depend on the amount of crud and the residence time for the deposit on the core. These aspects are indirectly related to the integral corrosion release from all the materials in contact with the coolant before the core passage. The activity released from the core is then partly in form of transmuted corrosion products, but still to a large extent the transmuted nuclides are of the same or similar element, for example: Cobalt (Co-58 and Co-60), Iron (Fe-59), Manganese (Mn-54), Zinc (Zinc-65), and Chromium (Cr-51). Still, most of the released core crud will be non-transmuted and hence the core will be a sink and source for the corrosion product being distributed by the coolant.

1.4 *SURFACE FILMS AND FUEL INTEGRITY*

The fuel integrity in nuclear power plants is also influenced by the oxide films in several ways. In order to enhance the risk for fuel integrity, a certain corrosion release from the system materials is needed to allow the corrosion products to deposit in the core region and cause various problems. Such issues are for example: Corrosion enhancement by increasing the surface temperature of the fuel cladding. A second problem is the ability of the deposited corrosion products to concentrate impurities of the coolant. Especially the Axial Offset Anomaly in *PWRs* is such a phenomenon.

1.5 *STRUCTURE OF THIS STR*

The objective of the present Special Topical Report is to summarize the knowledge of the operational experience with oxide film behaviour and properties in *LWR* environment. This includes the formation of crud as well as the consequences on the operational performance (caused by the mobile Crud) of the various primary side components. With the “basics” as background information, the oxide film behaviour mainly in relation to activity build-up and fuel and material integrity behaviour including the impact on the axial offset phenomenon is evaluated in detail.

The present Report discusses in Chapter 2 the “basics” by using information contained in extensive reviews of the crud problem by Wikmark & Cox, 2001 and Bojinov et al. 2004.

This Chapter 2 contains a review of the oxide thicknesses and composition of oxide films on stainless steel as well as on nickel base materials. This is followed by the description of the fundamental processes involved in the solid state growth and restructuring of oxide films. Connected to this fact, important interface processes are described. Furtheron the localized interface chemistry, known as surface complexation, is analyzed. Finally, Chapter 2 describes the basic limitation for the oxide film growth rate, which is a solid state transport within the inner barrier oxide film layer.

The basics are followed in Chapter 3 by the *PWR* field experience of crud related disturbances. This chapter contains information about fuel cladding failures due to accelerated corrosion and a description of the current status of the Axial Offset Anomaly. Connected to this phenomenon, the potential pressure drop problems are discussed and the interference with inspection necessities is analyzed. Another set of operational disturbances in *PWRs* is the build-up of out-of-core radiation fields, which also influences the shutdown duration due to possible high activity releases. An enhanced transport of corrosion products in the *RCS* leads also to an increased generation of radioactive waste.

Chapter 4 of this Report handles the *BWR* field experience of crud related operational disturbances. Like for the *PWR* plant, the crud induced fuel cladding corrosion experience is described. In analogy the shutdown radiation fields and exposures and the crud release at shutdown is summarized. Connected to this, disturbances in the waste production are analyzed. Other problems resulting from enhanced crud concentrations in *BWRs* are the reduced fuel burn-up, fuel inspection obstructions and clogging problems.

In Chapters 5 and 6 the mitigation methods against the negative consequences of crud are described for *PWR* and *BWR* plants. These mechanisms can be handled in two categories, which are either related to an improvement of the oxide barrier layer or the handling of the crud, which can be mobilized during operation.

In Chapter 7, the open issues related to the above described problems are summarized and this is followed by the recommendations related to the improvements against crud.

2 BASICS REGARDING *CRUD* (ROLF RIESS)

2.1 THICKNESS AND COMPOSITION OF OXIDE FILMS

The rates of general corrosion and the susceptibility of structural materials to different forms of localized and stress-enhanced corrosion in the aqueous environments encountered in nuclear power plant circuits are assumed to be strongly influenced by the mechanical, electrical and electrochemical properties of the oxide films formed on these materials. It is well known that these properties of oxide films are determined by their thickness, chemical composition, structure and morphology. In addition, the composition and structure of the oxide films affects the system materials cracking, the kinetics of radioactivity build-up in the plant circuits and the consequences of the fuel performance.

Accordingly, it is of primary importance to establish a correlation between the structural characteristics of the oxide films formed on construction materials and their mechanical, and physico-chemical properties. A quantitative model for such a correlation should be based on a large data base of experimental results on structure and properties of oxide films. The present chapter summarizes the existing data on thickness, composition and structure of oxide films formed in both laboratory and plant conditions reported in the recent scientific literature. In the compilation, an effort is made to emphasize the analogies between structural data for the films on typical construction materials in model electrolytes, simulated and real nuclear power plant coolants. This chapter represents an important step towards drawing a consistent, albeit sparse, picture of the influence of different factors, such as temperature, water chemistry, redox conditions and composition of the base material - on the thickness and in-depth chemical composition of the oxide films.

With such a consistent picture in mind, the present chapter describes the thickness, in-depth composition, morphology and structure of the oxides formed on stainless steels and nickel-based stainless alloys in the following conditions:

- Simulated and real (in-plant) boiling water reactor (*BWR*) coolant
- Simulated and real (in-plant) primary pressurized water reactor (*PWR*) coolant (including *VVER*)
- Model electrolytes simulating the aggressive water chemistry in pits, crevices and stress corrosion cracks.

Each sub-section presents first the data on thickness of the oxide films and then describes the typical in-depth composition of these films in the specific environment under discussion. Some attempts at commenting the effect of different factors on the in-depth composition are made, whenever the data needed are available. On the basis of the reviewed literature, a range of conclusions regarding the establishment of correlations between structural/compositional data and the kinetics of film growth and restructuring are drawn and some limitations of the surface analytical approach are discussed.

2.1.1 Stainless Steel

The stainless steels used in Light Water Reactors are summarized in Table 2-1.

Table 2-1: Composition of Stainless Steels used for LWRs.

Material	C	Cr	Cu	Fe	Mn	Ni	S	Si	Mo	Others
AISI 304	0.08	19		Bal.	2	9.3	0.03	1		N: 0.1
AISI 316 L (Ng)	0.015	16.5	0.26	Bal.	1.73	10.5	0.002	0.54	2.55	N: 0.056
AISI 316 L	0.03	17		Bal.	2	12	0.03	1	2.5	N: 0.1
08X18H10T (AISI 321)	0.05	18	0.15	Bal.	2	10.4				Ti: 0.47
1. 4541	Max. 0.10	17.0-19.0		Bal.	Max. 2.0	9.0-11.5	Max. 0.03	Max. 1.0		Nb/C min. 8
1.4550	Max. 0.03	18-19		Bal.	Max. 2.0	9-12	Max. 0.01	Max. 0.5		Nb/C min. 13

2.1.1.1 BWR Environments

The available data on the thickness of oxide films formed on 304 and 316 stainless steels in typical BWR coolant conditions (both in-reactor and out-of-pile) are collected in Table 2-2. A look at the data gives the impression that the oxidation time has no clear effect on film thickness after a couple of weeks, Lister & Davidson, 1989; Degueldre et al., 1998). It has to be emphasized, however, that no quantitative comparison between in-reactor and out-of-reactor data is possible, because part of the film growing in-reactor is a secondary layer, deposited from the cationic impurities present in the coolant. The effect of the degree of saturation of the coolant with impurities on film thickness was demonstrated e.g. by Lister et al, 1989. It has usually been reported that the film growth kinetics is close to parabolic or cubic for both AISI 304 and AISI 316 steels, Lister & Davidson, 1989; Degueldre, al. 1996, Wambach et al., 2002 although also logarithmic laws have been used to fit the film thickness vs. time dependences, Inagaki et al., 2003.

Table 2-2: Summary of Oxide Thickness Data for Stainless Steel in BWR Coolant Conditions.

Material	Temp. °C	Ex-posure time, h	Water chemistry	Oxygen/peroxide Content	Hydrogen content	Thickness nm	Ref.
304	288	24	"pure water", <1 μScm^{-1}	10 ppb 8 ppm	-	7200 3200	Lumsden & Stocker, 1983
304	288	8	<0.1 μScm^{-1}	<1 ppb 50-200 ppb	n.q.	20 30	Tani et al., 1998
304	288	2000	<i>NWC</i> <i>HWC</i>	200 ppb 15 ppb	15 ppb 100 ppb	400 50	Lin et al., 1996
304	288	330	<i>NWC</i> <i>NWC in core</i> <i>HWC</i>	200 ppb 200 ppb H₂O₂	150 ppb	1200 1400 900	Kim, 1999
304	280	450	0.4 μScm^{-1} (NaCL)	6 ppm, 300 ppb H²O² 250 ppb	-	500 160	Saito et al., 1998
304	280	117 703 1456	0.5 μScm^{-1}	200 ppb	25 ppb	120 430 500	Lister & Davidson, 1989
304	270	7920	<0.12 μScm^{-1}	200 ppb	-	600	Bojinov et al., 2002
316	288	330	<i>NWC</i> <i>HWC</i>	200 ppb 15 ppb	20 ppb 200 ppb	850 650	Kim, 1995
316	290	250	<0.1 μScm^{-1}	200 ppb	<1ppb	160	Degueldre et al., 1996
316	290	720 6000	<0.1 μScm^{-1}	400 ppb	<1 ppb	270-310 350-480	Degueldre et al., 1998
316	270	2000 400	<i>NWC</i> <i>NWC in core</i> <i>HWC</i>	200 ppb 200 ppb H₂O₂ 15 ppb	25 ppb 100 ppb 100 ppb	300 400 200	Hemmi et al., 1994
316	285	500	<i>NWC</i> "in core"	400 ppb 650 ppb H₂O₂	60 ppb	300 490 (prefilmed at 700°C, 20h)	Uruma et al., 2002
316	290	6	<0.05 μScm^{-1}	250-400 $\mu\text{g L}^{-1}$	-	80 250	Wambach et al., 2002
316	270	7920	<0.12 μScm^{-1}	200 ppb	-	400	Bojinov et al., 2002
1.4550 + 1.4551	~280	Several cycles	<i>NWC</i> <0.1 μScm^{-1}	~ 250 ppb ~250 ppb H₂O₂	-	~ 5000	Stiepani, 2006

An overall conclusion from the collected data is that the films formed on AISI 304 stainless steel are somewhat thicker than the corresponding films on AISI 316 stainless steel Table 2-2. This fact can be tentatively related to the higher Ni content of AISI 316 in comparison to AISI 304, as discussed below. In addition, the films formed under Hydrogen Water Chemistry (*HWC*) are considerably thinner than those formed under Normal Water Chemistry (*NWC*), Kim, 1999; Kim, 1995 and Hemmi et al., 1994. It is worth mentioning that the films formed in simulated (with hydrogen peroxide addition) or real in-core *NWC* are thicker than those formed out-of-core (without H₂O₂). An interesting observation stemming from the comparison of the data presented by Lumsden & Stocker, 1983 and Lister & Davidson, 1989 (for AISI 304), Degueldre et al., 1996, Degueldre et al., 1998; and Wambach et al., 2002 (for AISI 316) is, that the films formed in water with lower room temperature conductivity, tend to be thinner. No firm conclusion on that issue can be reached; however, without a systematic investigation of the effect of water conductivity on the thickness of films formed on otherwise similar conditions. Similarly, there are not enough data to assess the effect of the additives or impurities on the film thickness, although some indications, that the films grown on AISI 304 in the presence of chloride are thinner than in the absence of chloride, can be found, Saito et al., 1998 and Lister & Davidson, 1989

As reported by Stiepani, 2006, several decontamination activities in *BWR* components/systems revealed that on stainless steel surfaces in *BWRs* a more or less constant thickness of ~5 µm can be found. Changes in this thickness are insignificant so that the crud layer seems to be in an equilibrium with its environment. Because there is a minimum of uptake of feed-water iron, the majority of this material will go to the fuel surface area. Fuel is an excellent filter for the iron oxide which enters the reactor vessel.

In-Depth Composition of the Oxide Films

Figure 2-1 shows a typical X-ray Photoelectron Spectroscopic (*XPS*) depth profile of the atomic concentration of the main constituents of the oxide on 316 stainless steel in high purity water (RT conductivity <0.05 µS cm⁻¹, oxygen content 250-400 ppb), Wambach et al., 2002.

A duplex layer is formed, the outer iron- and nickel-rich layer being significantly thinner than the inner oxide which seems to contain more Cr. More detailed *XPS* examinations and chemical speciation showed that Fe in the outer layer is a mixture of FeOOH and Fe₂O₃ whereas in the inner layer it is a mixture of Fe₂O₃ and FeO (probably Fe₃O₄). Cr was found to be present in the outermost layer as CrOOH+Cr₂O₃ together with some higher-valency Cr oxide, whereas Cr₂O₃ was suggested to be the dominating Cr species in the inner layer, Wambach et al., 2002.

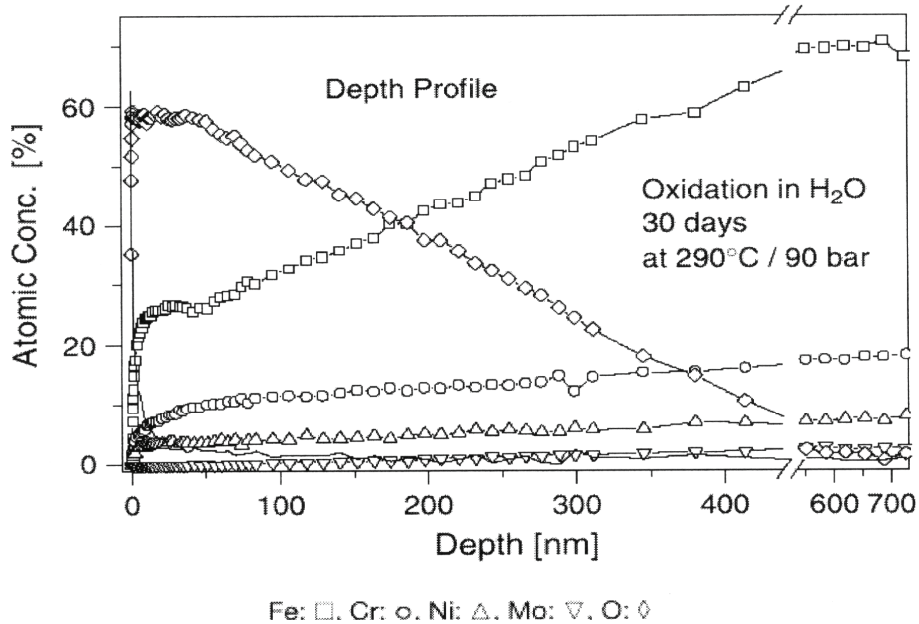


Figure 2-1: XPS depth profile of the oxide grown on 316 stainless steel simulated BWR water at 290°C for 30 days, Wambach et al., 2002.

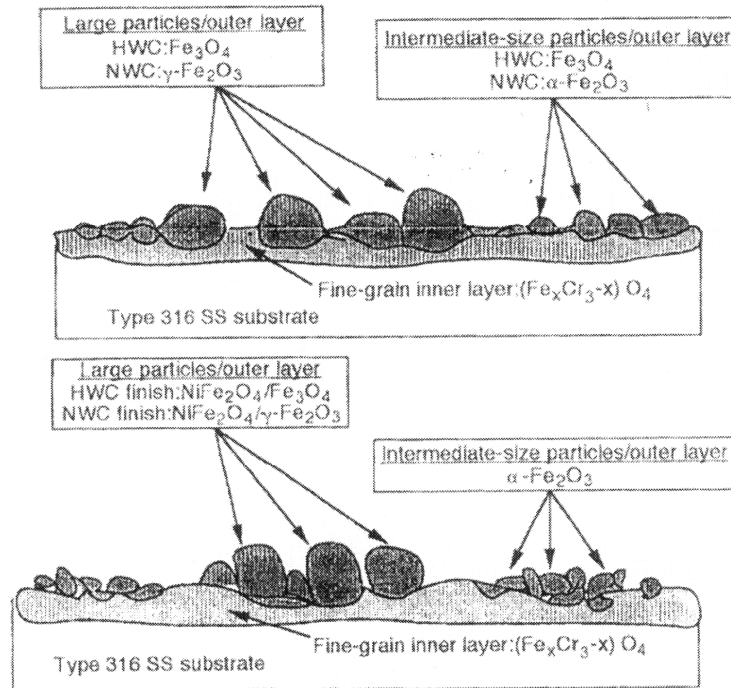


Figure 2-2: A sketch of the structure of the oxide film on AISI 316 stainless steel after exposure to NWC or HWC after exposure to NWC or HWC alone (above) or after several NWC/HWC cycles (below), according to Kim, 1995.

A more detailed picture of the composition and structure of the oxide film formed on austenitic stainless steels in simulated *BWR* coolant conditions has been obtained by Kim using Analytical Transmission Electron Microscopy (*ATEM*) and Auger Electron Spectroscopy (*AES*), Kim, 1999; Kim, 1995 and Uruma et al., 2002. These data are supported by recent in-situ Raman spectroscopic results of Kumai & Devine, 2001 as well as by the results of Saito et al., 1998 and Wada et al., 2001. A sketch of the structure of the film according to these authors is shown in Figure 2-2. The particulate outer layer has been reported to have a distinct composition as depending on the grain size. The large particles were reported to consist of γ -Fe₂O₃ under *NWC* and Fe₃O₄ under *HWC*, whereas the intermediate size particles consist of α -Fe₂O₃ and Fe₃O₄, respectively (Figure 2-2, above). The fine-grained inner layer is characterized as Fe_xCr_{3-x}O₄, although especially under *NWC* its structure is proposed to be closer to γ -Fe_xCr_{2-x}O₃, Kumai & Devine, 2001. In this connection, it is worth mentioning that the phases identified in the oxide layer on 304 stainless steel in air-saturated pure water at 326 °C by Raman spectroscopy were CrOOH and NiFe₂O₄, Maslar et al., 2002.

Cr enrichment in the inner layer of the film on 304 stainless steel has been reported for oxides grown in demineralized water with oxygen contents lower than 5 ppb, Ono et al., 1995. Sequential cycling of the oxide between *NWC* and *HWC* results in an incorporation of Ni in the large particles of the outer layer (Figure 2-2, below). In addition, it has been recently reported that under excess *HWC* condition, the presence of noble metals such as Pt and Rh on/in the oxide surface promoted the transformation of α -Fe₂O₃ to a spinel Fe₃O₄ structure, Kim et al., 2003. On the other hand, films formed in simulated in-reactor conditions (with hydrogen peroxide) are significantly enriched in Ni and impoverished in Cr, as demonstrated by *AES* depth profiling, Kim, 1999; Saito et al., 1998; Wada et al., 2001 and Murajama et al., 2002.

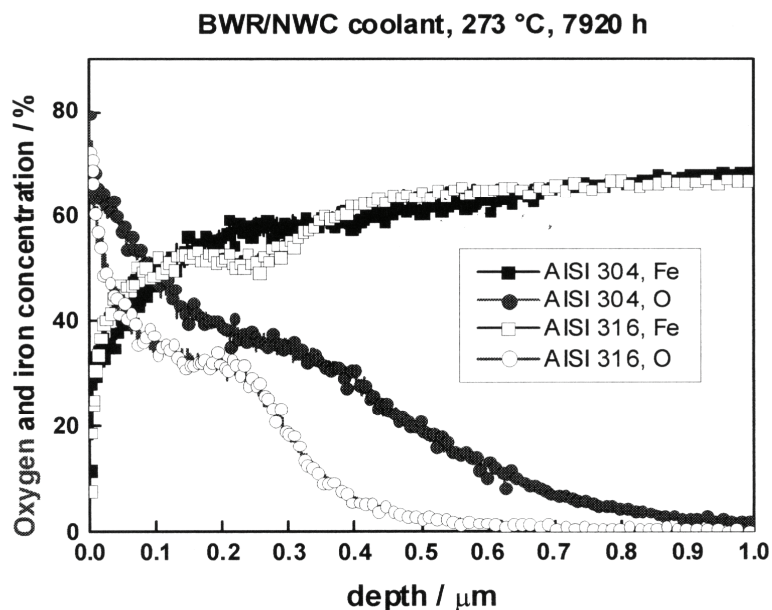


Figure 2-3: GDOES profiles of oxygen and iron in AISI 304 and AISI 316 stainless steels exposed for 7920 h in BWR coolant at Olkiluoto 1, Bojinov et al., 2002 used to determine the oxide film thickness.

Figure 2-3 shows Glow Discharge Optical Emission Spectroscopic (GDOES) depth profiles of oxygen and iron in the oxide films on 304 and 316 stainless steels exposed for 11.5 months (7920 h) in a BWR coolant at Olkiluoto-1 plant, Bojinov et al., 2002, whereas Figure 2-4 shows the depth profiles of the chromium, iron and nickel concentrations normalized to the total metallic element concentration for the same films. The film thicknesses as estimated from the oxygen profiles (Figure 2-3) fall well into the limits set by the data shown in Table 2-2. Also in accordance with the results shown in Table 2-2, the film on AISI 304 steel appears to be significantly thicker than that on AISI 316 stainless steel. The duplex structure of the films is evident from Figure 2-4. The films comprise an outer iron-rich layer and an inner layer containing more Cr (Cr is impoverished in the films with respect to its content in the alloy substrate). A shallow maximum in Ni concentration is detected close to the metal / film interface in the oxide formed on AISI 304, whereas a well-pronounced maximum of Ni concentration exists at the boundary between the inner and outer layers formed on AISI 316 (Figure 2-4). This maximum correlates with a local minimum in the Cr content. In general, it can be stated that the difference in thickness between the films formed on 304 and 316 stainless steels is largely due to the inner layer being thicker on 304 steel (Figure 2-4). A somewhat conjectural explanation of this fact is that Ni-enrichment at the inner / outer layer boundary acts as a diffusion barrier preventing further growth of the inner oxide on 316 stainless steel by hindering the transport of oxygen-containing species.

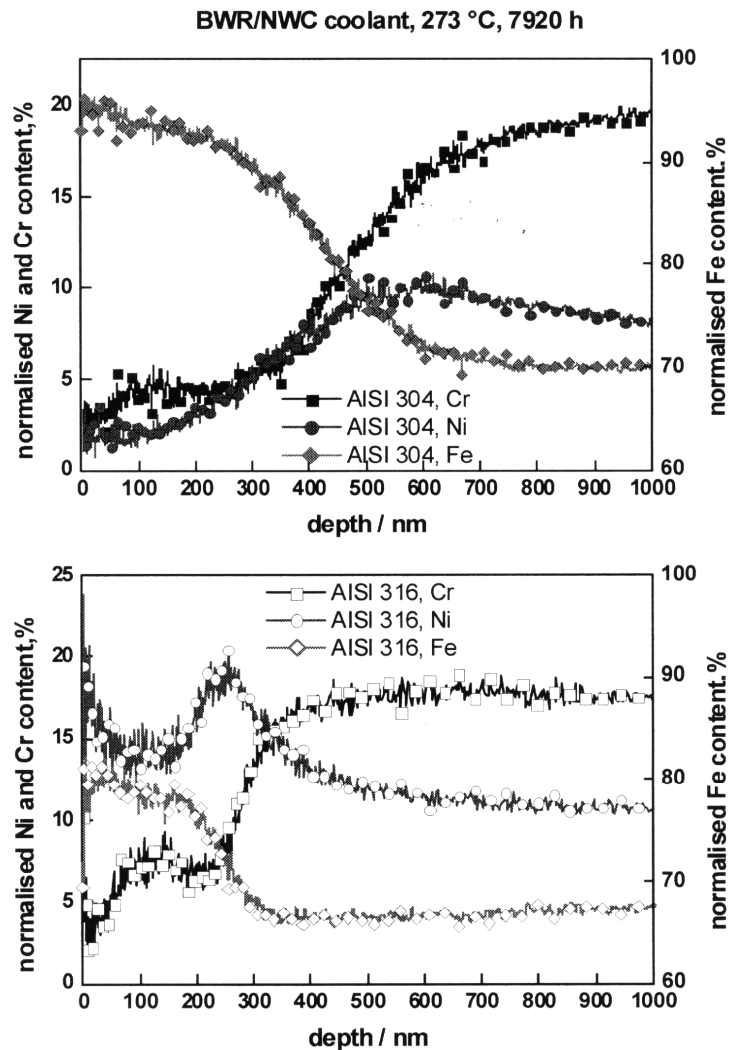


Figure 2-4: Normalised *GDOES* profiles of Cr, Ni (left axis) and Fe (right axis) in the films on AISI 304 and 316 formed after 7920 h exposure to a *BWR* coolant at Olkiluoto-1, Bojinov et al., 2002.

Distribution of Minor Elements in the Oxide Films

An important question for activity build-up is the effect of ionic additions to the *BWR* coolant on the distribution of radioactive cobalt (and other elements) in the oxide films formed on primary loop recirculation piping, Ono et al., 1995; Honda et al., 1987; Hosokawa et al., 2002; Inagaki et al., 2003. Typical *GDOES* profiles for Fe, Cr, Ni, Zn and Co in the oxide formed on AISI 304L after 1000 h of exposure to simulated *BWR* water containing 1 ppb of Co and different amounts of Zn, Ni and Zn+Ni are collected by Inagaki et al., 2003. In case of either Zn or Ni addition, the oxide film presents the typical bi-layer structure. Co seems to be incorporated to a larger extent in the inner layer and its incorporation is decreased by either Ni or Zn addition. Specifically, Zn reduces the amount of Co in the inner layer probably by substituting it in the Cr-rich spinel, whereas Ni reduces the content of Co in the outer layer by promoting the formation of nickel ferrite. A synergistic effect of Zn and Ni on Co deposition has been reported by Inagaki et al., 2003. It can be concluded that the mechanisms of incorporation of minor species such as Co in the inner and outer layer differ from each other which reflects the contrasting mechanisms of growth of the two layers (solid state mechanism for the inner layer and dissolution-precipitation mechanism of the outer layer).

2.1.1.2 PWR Environment

Thickness Data for Oxide Films on AISI 304 and AISI 316

Table 2-3 summarizes the data on the thickness of oxides formed on AISI 304 and 316 in primary *PWR* coolant conditions, Tapping et al., 1986; Lister et al., 1987; Szklarska-Smialowska et al., 1992 and Byers & Jacko, 1993. On the overall, the reported film thicknesses are lower than those reported for *BWR* conditions (Table 2-3). The thickness of the film has been reported to increase up to 168 h according to a quasi-parabolic growth law, Tapping et al., 1986. The thickness has been shown to increase with increasing temperature in the range 100-350 °C according to an Arrhenius' law with an apparent activation energy of ca. 40 kJ mol⁻¹, Szklarska-Smialowska et al., 1992. Unfortunately, there are not enough data in the literature for films formed after exposure time sufficiently long to be compared with oxides formed in real in-plant conditions. Some data from real plant operation and German materials are added to Table 3. Similarly the scarce data do not allow any conclusion on the effect of water chemistry and Redox condition on the thickness of the oxide films.

Table 2-3: Oxide Thickness Data for Stainless Steels under PWR Conditions.

Material	Temp. °C	Time h	H ³ BO ³	LiOH (or KOH)	H ₂	pH	Thick-ness nm	Ref.
304	300	5 48 168	1200 ppm B	1.5 ppm Li	18 cm ³ /kg	10.3 (RT)	27 122 166	Tapping et al., 1986; Lister et al., 1987
304	300-350	72	0.01 M	0.001 M	1.58 ppm	7.9-8.1	8-40	Szklarska-Smialowska et al., 1992
304	330	2500	1200 ppm B	2.2 ppm Li	25 cm ³ /kg	n.q.	550	Byers & Jacko, 1993
321	250	8600	0...7 g/l	K: 10...20 mg/l NH ₃ 13 mg/l		6.7 (250 °)	330	Bojinov et al., 2002
316	350	960	1000 ppm B	2 ppm Li	27 ppm	n.q.	200	Da Cunha Belo, 1998
316	250	8600	0 ... 7 g/l	K: 10 ... 20 mg/l NH ₃ 13 mg/l		6.7 (250 °)	180	Bojinov et al., 2002
1.4550 and 1.4551	Avg. 300	Several cycles	< 1000 ppm B	Max. 2 ppm Li	2-4 ppm H ₂	6.9-7.4	4000-5000	Stiepani, 2006

Composition of the Oxide Films under PWR-Conditions

The effect of temperature on the film composition on AISI 304 exposed to lithiated water was studied by Szklarska-Smialowska 1992. One important finding of this work is that the Cr concentration in the surface oxide passes through a minimum at 200 °C and is higher at 250 °C than it is at 300 °C. The minimum at 200 °C is preserved also in the inner oxide layer.

Figure 2-5 shows a GDOES depth profile of an oxide film formed on AISI 316 after 960 h exposure to a typical primary PWR coolant, Byers & Jacko, 1993. The depth profile evidences the presence of a duplex oxide film, the outer part being an iron-nickel oxide and the inner part a chromium/iron oxide, respectively. Raman micro-spectroscopic analysis shows that the outer well crystallized layer is composed of a mixture of $Ni_{0.75}Fe_{2.25}O_4$ and a low symmetry form of Fe_3O_4 , whereas the inner layer is a mixture of Cr_2O_3 and spinels such as $FeCr_2O_4$ and is considered to be nano-crystalline, Byers & Jacko, 1993.

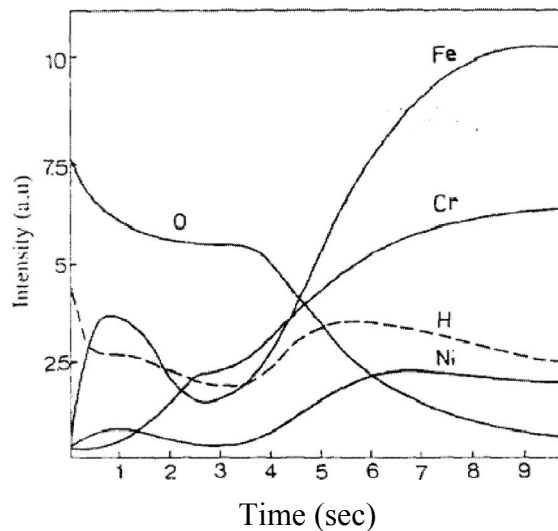


Figure 2-5: GDOES depth profile of the oxide film formed on 316 stainless steel by a 960 h exposure to PWR primary coolant at 360°C.

Recently considerable attention has been paid to the composition and structure of the films formed on stainless steels in VVER conditions, Bojinov et al., 2002; Zmitko et al., 2002a and Grygar et al., 2002. Figure 2-6 shows GDOES depth profiles of oxygen and iron concentrations in the oxide films formed on AISI 321 (OX18H10T) and AISI 316 after ca. 1 year of exposure to a primary VVER coolant at Loviisa 1, Bojinov et al., 2002, whereas Figure 2-7 presents the corresponding profiles of Cr, Fe and Ni concentrations normalized to the total metallic element concentration in the same films. The films formed in PWR coolant are significantly thinner than those formed in a BWR coolant (Figure 2-3 and Figure 2-6) in accordance with the results collected in Table 2-2 and Table 2-3. Moreover, the thickness of the film on AISI 316 after 1 year of exposure (ca. 150-200 nm, Figure 2-6, see also Bojinov et al., 2002) is practically the same as that on a similar steel after 960 h of exposure to a primary PWR coolant, Byers & Jacko, 1993. Thus longer exposure times do not necessarily lead to higher film thicknesses, as was also outlined when discussing the data obtained in BWR conditions (Table 2-2 and Figure 2-3).

In a certain analogy to the results in a BWR coolant (Figure 2-3 and Figure 2-6) the film on AISI 316 is clearly thinner than that formed on AISI 321 (OX18H10T; the composition of the latter steel is closer to that of AISI 304, see Table 2-1). The duplex nature of the oxide is quite evident in Figure 2-7, comprising an outer Fe- and Ni-rich layer of comparable thickness for both steels and an inner layer strongly enriched in Cr which is ca. 2 times thicker on AISI 321 when compared to AISI 316. In this inner layer, Ni concentration is somewhat higher on AISI 316 than on AISI 321, maybe reflecting the somewhat higher Ni content of the former steel substrate. This higher concentration of Ni at the interface acting as an additional diffusion barrier could be again offered as a conjectural explanation of the fact that a thinner film is formed on AISI 316 when compared to AISI 321 (OX18H10T).

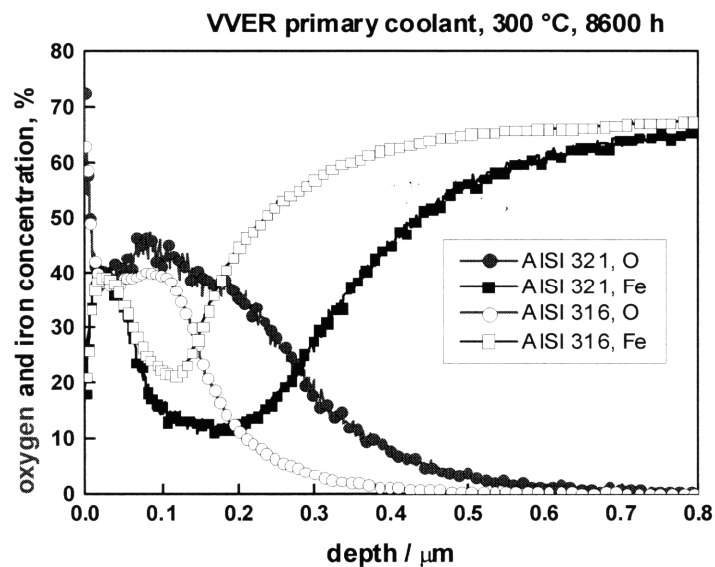


Figure 2-6: GDOES Profiles of Oxygen and Iron in AISI 321 and AISI 316 Stainless Steels exposed for 8600 h at Loviisa I, Bojinov et al., 2002.

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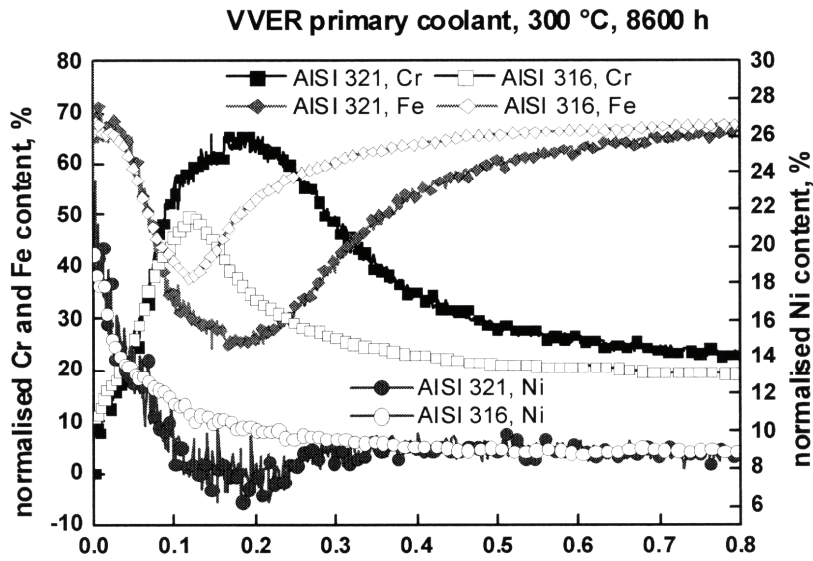


Figure 2-7: GDOES Normalised Profiles of Cr, Fe (left axis) and Ni (right axis) in the films of AISI 321 and 316 formed during exposure at Loviisa for 8600 h , Bojinov et al., 2002.

2.1.2 Nickel Base Alloys

The Nickel base alloys used in Light Water Reactors are summarized in Table 2-4.

Table 2-4: Composition of nickel-based alloys and Alloy 800 (weight-%).

Material	C	Cr	Cu	Fe	Mn	Ni	S	Si	Others
Alloy 600	< 0.15	16	≤ 0.5	8	≤ 1.0	Bal.	0.015	≤ 0.5	
Alloy 690	< 0.05	30	≤ 0.5	9	0.31	Bal.	0.006	≤ 0.5	
Alloy 82	0.036	20.23	0.03	0.71	2.92	73.05	0.001	0.05	Nb 2.48
Alloy 182	0.03	15.24	0.01	8.07	7.57	66.36	0.001		
Alloy X-750	0.041	15.48	0.006	6.39	0.75	72.52	0.001	0.3	Ti 2.50, Nb+Ta 0.97, Al 0.82
Alloy X-718	0.05	18.48	-	22.5	0.05	52.26	0.0021	0.1	Ti 0.89, Nb+Ta 5.12, Al 0.52
Alloy 625		22.5	0.01	2.5		64.8			Mo 8.7, Nb 3.5
Alloy 800	0.022	20.5	0.07	Bal.	0.75	32.5			Ti 0.44
Alloy 800 NG	0.03	20-23	0.75	Bal.	0.4-1.0	32-35	0.015	0.3-0.7	Ti/C ≤ 12, Ti/(C+N) C ≤ 8, N ≤ 0.03

2.1.2.1 *BWR* Conditions

Film Thickness

Recent results on thickness and composition of the oxide films formed on Ni-based alloys in a simulated in- and out-of-core *BWR* environment are reported by Saito et al., 1998, and Uruma et al., 2002. The thickness results are summarized in Table 2-5. The difference between the film thickness of Alloy 600 in simulated in-reactor and ex-reactor *BWR* conditions is more than an order of magnitude, albeit the exposure time in simulated ex-reactor condition is more than two times longer. This clearly indicates the accelerating effect of the higher oxygen concentration and the addition of hydrogen peroxide on the film growth rate on Alloy 600. Moreover, the film thickness on a model alloy (Ni-5%Cr-10%Fe) simulating a sensitized grain boundary composition in

Alloy 600 (Table 2-5) is practically the same as that on Alloy 600, indicating that the film growth rate in the simulated in-reactor condition is most probably not controlled by the Cr content in the alloy. This seems the more reasonable when considering the fact that the corrosion potential of Alloy 600 in the simulated in-reactor condition was found to be in the transpassive region, Saito et al., 1998. It has also been shown that the thickness of the oxide after 500 h exposure of Alloy X-718 (18.5% Cr, 72.5% Ni, 6.4% Fe) to a simulated in-reactor condition is ca. two times higher than that on Alloy X-750 (15.5% Cr, 52.3% Ni, 22.5% Fe), Uruma et al., 2002. In addition, higher exposure times (11-12 months) result in a substantially higher film thickness on nickel-based alloys in *BWR* conditions, Bojinov et al., 2002, (upper graph in Fig. 2.8) which confirms that film growth on such alloys in the transpassive condition is faster than on stainless steels (cf. Table 2-2 and Table 2-5).

Table 2-5: Summary of Oxide Thickness Data for Nickel-based Alloys in BWR Coolant Conditions (in-reactor-conditions are marked with bold).

Material	Temp. °C	Exposure time, h	Water chemistry	Oxygen/ peroxide content	Hydrogen content	Thickness nm	Ref.
600	280	450	0.4 μScm^{-1} (NaCl)	6 ppm, 300 ppb H_2O_2 200 ppb	-	900	Saito et al., 1998
		1000				60	
X-750	285	500	< 0.1 μScm^{-1}	400 ppb 650 ppb H_2O_2	60 ppb	890	Uruma et al., 2002
X-718	285	500	< 0.1 μScm^{-1}	400 ppb 650 ppb H_2O_2	60 ppb	1610	Uruma et al., 2002
Ni-5% Cr-10% Fe	280	450	0.4 μScm^{-1} (NaCl)	6 ppb 300 ppb H_2O_2	-	1010	Saito et al., 1998
182	270	7920	< 0.12 μScm^{-1}	200 ppb	-	2700	Bojinov et al., 2002
82	270	7920	< 0.12 μScm^{-1}	200 ppb	-	1100	Bojinov et al., 2002

The fact, that a certain Cr enrichment is observed in the inner layer on Alloy 82 probably means, that the dissolution rate of Cr from Nickel based Alloys is not a straightforward function of the Cr content in the Alloy cf. Table 2-5.

In-Depth Composition of the Oxide Films

The duplex nature of the films formed on nickel-based alloys in simulated in-reactor *BWR* conditions has been demonstrated, Saito et al., 1998; Uruma et al., 2002; Bojinov et al., 2002. According to the *AES* results of Saito et al. the films on Alloy 600 after 450 h exposure comprise an external layer (200-300 nm) containing a substantial amount of Fe (up to 40%) and practically no Cr, whereas the inner layer contains mainly Ni with ca. 10% of Fe and Cr. Conversely, the layer formed in simulated ex-reactor conditions is thin, homogeneous and Cr-enriched. The lower graph in Figure 2-8 shows the depth profiles of metallic elements in the films on Alloys 182 and 82 after 11.5 months of exposure to a primary *BWR* coolant, Bojinov et al., 2002. The composition of the layer on Alloy 182 is largely analogous to that described by Saito et al., 1998, both the inner and outer layer being considerably thicker on Alloy 182 probably because of the much longer exposure time in comparison to Alloy 600, Bojinov et al., 2002. On the other hand, the film on Alloy 82 is more than two times thinner than that on Alloy 182 and some enrichment in Cr is observed in the inner layer formed on that alloy (Figure 2-8). Furthermore, the Ni content in the outer layer formed on Alloy 82 is much higher than in the outer layer on Alloy 182, and iron content is correspondingly much lower. It can be argued that the film growth rate on nickel-based alloys in the transpassive condition (i.e. in *BWR* / *NWC* coolant) is controlled by the nickel and iron contents in the layer, which are a function of the respective contents in the alloy substrate (Alloy 82 contains significantly more Ni and less Fe than does Alloy 182, Table 2-4). The fact that a certain Cr enrichment is observed in the inner layer on Alloy 82 probably means that the dissolution rate of Cr from nickel-based alloys is not a straightforward function of the Cr content in the alloy (cf. Table 2-4).

3 PWR FIELD EXPERIENCE OF CRUD RELATED OPERATIONAL DISTURBANCES (ROLF RIESS)

Just as for the *BWRs*, most of the corrosion products determined in the primary water are in the form of particles, whereof the main bulk (approx. 60%) is in the range of 4-3 μm and a substantial amount (approximately 25%) larger than 2 μm , Vanbrandt et al., 1980; Comley et al., 1989 and Bolz et al., 1996. It should here be borne in mind that particle counting and size determination are very delicate tasks. Unless well-specified and reliable methods of sampling and determination are known to have been employed, results should be treated with caution. An interesting observation is that the amount of larger particles increases significantly with the age of the plant, at least during the first 3 cycles, Comley et al., 1989. The increase is mainly due to formation of larger particles, reportedly $>8 \mu\text{m}$. Of course, during transients, especially start-up and shutdown, the number on density of particles can increase by 3 orders of magnitudes, Comley et al., 1989.

The fuel crud deposits in the *PWRs* are normally consisting of a single, more adherent layer with a thickness of 10 – 350 $\text{mg}\cdot\text{dm}^{-2}$ (0.8 – 29 μm , generally in the lower range), and an estimated density of 1200 $\text{kg}\cdot\text{m}^{-3}$ and hence rather porous, despite being adherent, Hazelton, 1987. The crud thickness in the mid-core positions is typically less (4 – 6 $\text{mg}\cdot\text{dm}^{-2}$ or 0.3 – 0.5 μm) than at the top (50 – 65 $\text{mg}\cdot\text{dm}^{-2}$ or 4 – 5 μm), Hazelton 1987. It has been reported from earlier operation that 30 – 78 % of the fuel crud metal content consisted of iron and 8 – 57% of nickel in an extensive review of *PWR* and *BWR* crud deposits, Hazelton 1987. A more modern average composition of the fuel crud has been reported by Polley & Pick, 1986 as shown in Table 3-1.

Table 3-1: Fuel crud elemental compositions in Westinghouse plants per 1986 (10 plants during 1 – 3 cycles), Polley & Pick, 1986.

Element	Composition	Range
Fe	68 \pm 7 %	57 – 80%
Ni	29 \pm 6 %	19 – 38%
Cr	3 \pm 2 %	1 – 6%
Co	0.2 \pm 0.2 %	0.03 – 0.5%

An example of axial crud distribution has been reported also for the *PWR* KWO (Obrigheim), which is an older German plant that had considerably corrosion and crud deposits in the 1970's, Riess 1976. The reason was that the hydrogen pressure was insufficient and that no lithium was used during that period. The total amount of crud was considerably higher in the hotter top part of the core than in the lower part, as seen in Figure 3-1. It is also interesting to note that the nickel concentration is much higher in the top with a nickel-to-iron ratio above 0.5, being then at risk to produce *AOA* (axial offset anomaly), which actually also was observed (see Section 3.2). The excessive crud input is not typical for modern *PWRs*, but the case would be of interest in the analysis of the *AOA* phenomenon today.

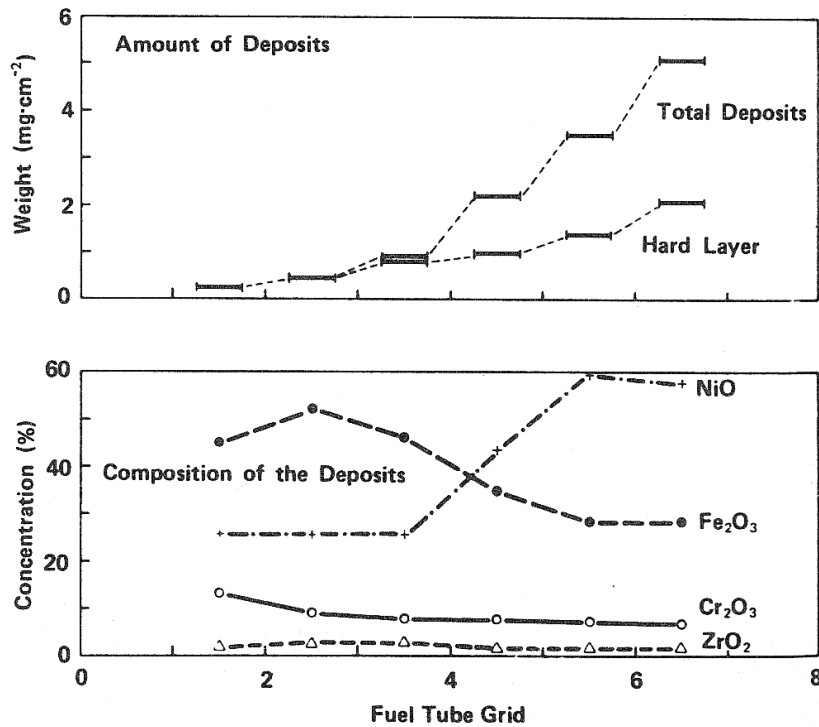


Figure 3-1: The fuel crud deposits in the PWR KWO. The maximum deposits was $\sim 8\text{mg cm}^{-2}$, which is extremely high for a PWR. From Riess 1976, Fig. 5.

The nickel ferrite deposited on the fuel crud is normally a mixed spinel of the form $\text{Ni}_x\text{Fe}_{(3-x)}\text{O}_4$, with $x = 0.5 - 0.9$, Sandler & Kunig, 1977 and Sandler 1979. It has been estimated, based on thermodynamics, that any excess nickel will deposit as metallic nickel in the lower half of the rod, but as nickel oxide in the upper, Nishimura & Kasahara, 1998. This would mean that the crud conditions could be very axially inhomogeneous in a plant with high nickel input.

Possible Impacts from Crud on Fuel

The possible impacts of crud are the formation of:

- a local environment (e.g. enhanced risk of hide-out)
- an increased thermal resistance due to insulation of the crud
- the crud as a parasitic absorber of neutrons and
- the crud deposits as a flow restriction in the assembly.

Local Chemistry

The high voidage of the crud will permit the crud to form a local environment since enrichment in the constricted water may occur. Depending on the heat flux, degree of boiling the enrichment of various species could be significant. This behaviour is normally described as a “hide-out” mechanism, i.e. that significant amounts of soluble species actually will be enriched in the crud voidage and will be released as transients when the heat flux is lowered. The only well described case where this has had any impact on the fuel behaviour is the *AOA* phenomenon (see Chapter 3.2). The hide-out, or rather the enrichment possible is a potential problem, especially in the *PWRs* going to higher temperatures and heat-fluxes and consequently more boiling.

Thermal Resistance

If a heat transfer surface, as the fuel cladding, is covered with an insulating layer, the thermal resistance will increase the temperature of the surface. Such a temperature rise will increase the corrosion rate of the cladding. Normally, the corrosion rate of zirconium alloys will increase approximately two times by a temperature increase of 15°C, *IAEA TECDOC 996, 1998*. As discussed in the following, thick oxide layers or deposits could produce temperature increases in the order of 100°C or more, hence accelerating the corrosion of the cladding by almost 2 orders of magnitude. Thick zirconium oxide layers are causing an auto-acceleration of the cladding corrosion, since a thick oxide layer will cause increase in temperature, which will lead to further enhanced corrosion rate, and so on. There are several reasons for the start of such an acceleration, *IAEA TECDOC 996, 1998*, often seen in *PWRs* today, but all those reasons, except the influence of the water chemistry and crud, are left out in this context.

The water chemistry and crud could produce such thermal acceleration in two ways. In the first case, the water chemistry or crud accelerate the corrosion, producing the auto-acceleration mentioned in the previous paragraph. In the second case, the crud deposit in its own could provide an insulating layer. This effect could also be split into two cases. The first case is when the thermal conductivity of the deposit is much lower than that of the water and the second when the physical and geometrical appearance of the deposit will increase the amount of steam. Steam is a very good insulator. A crud layer so hot that the water would be evaporated immediately, forming steam, could hence be a very damaging insulating layer. The real situation is, however, a little bit more complicated. Many investigations have been made to determine the thermal conductivity of various deposits.

4 BWR FIELD EXPERIENCE OF CRUD (KLAS LUNDGREN)

4.1 REACTOR WATER CHEMISTRY AND ACTIVATED CORROSION PRODUCTS

The characteristic feature of the *BWR* design, in contrast to the closed, one-phase *PWR* design, is the heat removal from the reactor core by boiling water, i.e. by a mixture of steam and water. The significant in-core boiling plus the turbine plant included in the primary loop put several restrictions on the water chemistry in the coolant that differs from the *PWR* conditions. The most significant differences are:

- The reactivity of the core during normal operation can not be controlled by boron or other additives in the coolant. On the other hand, the possibility to control the void content in the core with the recirculation pumps provides an efficient way to adjust the power level.
- Reducing conditions with a sufficient low corrosion potential in the primary loop can not be achieved just by applying a hydrogen pressure in a volume control tank. The traditional water chemistry in *BWRs*, called Normal Water Chemistry (*NWC*), means no hydrogen injection and therefore oxidizing conditions in the coolant. Continuous injection of hydrogen to the feedwater has been introduced in many plants during the last 20 years, so called Hydrogen Water Chemistry (*HWC*), in order to achieve protection corrosion potential in parts of the primary loop. Significant amounts of hydrogen are needed, and more sophisticated techniques, e.g. use of Noble Metal Technology (*NMT*), are being introduced to improve the efficiency of the hydrogen injection.
- The possible risk to have turbine condenser leakage calls for measures to avoid an intrusion of harmful species, e.g. chlorides, directly into the primary loop. The condensate cleanup plant plays an important role in that context. This system in combination with material selection in the turbine plant is also of very large importance to maintain low levels of corrosion products in the final feedwater.

There are in principle three types of *BWR* designs. The first generation of *BWRs* introduced by GE had external recirculation loops. A similar type of *BWR* design was later used by ASEA-ATOM for Swedish plants. The number of recirculation loops varies between four and six. The main drawback with this type of design from a safety perspective is the large number of big recirculation lines in the containment that may be subject to a pipe breaks causing a *LOCA* situation. The jet-pump design was later introduced by GE in order to reduced the number of recirculation loops inside the containment. Typically 1/3 of the core flow is passing the recirculation loops in the containment, and the rest of core flow is driven by the jet-pumps located in the downcomer inside the reactor vessel, see Figure 4-1. The reduced flow rate means that the number of recirculation loops normally are reduced to only two. The dominant fraction of *BWRs* in US and Japan is of the jet-pump design. The third generation of *BWRs* with internal recirculation pumps was introduced by ASEA-ATOM and Siemens at the end of the 70:ies. Big recirculation loops in the containment are avoided by installing recirculation pump impellers in the bottom downcomer region, see Figure 4-2. The most recent design of GE, the *ABWR*, has a similar design as the ASEA-ATOM and Siemens internal pump plants. Some *ABWRs* have been build and put in operation in recent years in Japan. The number of internal pumps varies normally between six and eight depending on size of the reactor.

A special type of boiling water reactor is the RBMK design, which has been exclusively erected within the borders of the former Soviet Union. The characteristic difference of this design compared to the *BWR* designs described above is that it uses graphite as moderator. This reactor type is not further treated.

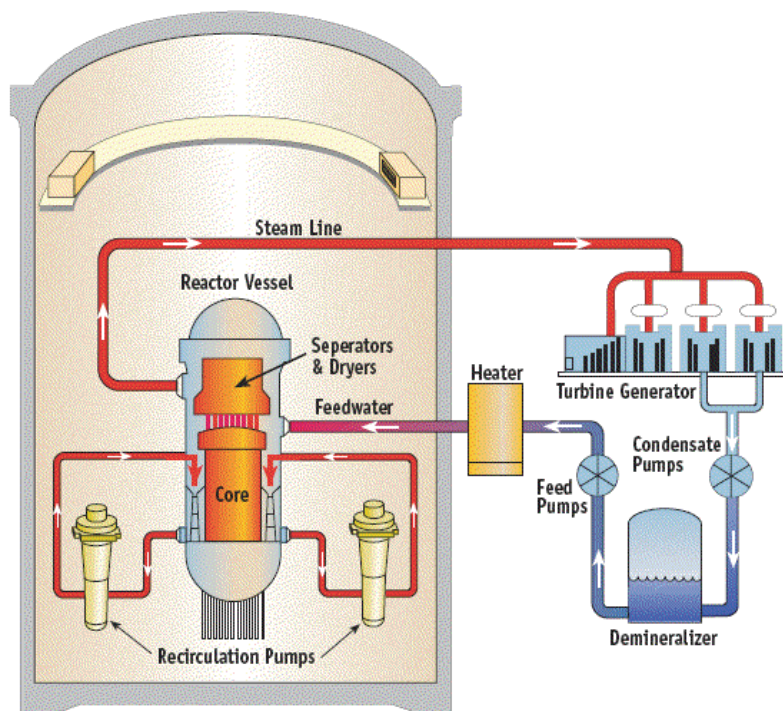


Figure 4-1: Principal scheme of *BWR* with jet-pumps.

5 PWR MECHANISMS AND MITIGATION METHODS (ROLF RIESS)

In recent years *PWR* primary chemistry has become complicated by demands of longer fuel cycles, causing e.g. higher initial Boron concentration. In addition, increased sub-cooled boiling and material- as well as fuel- concerns required further optimization of the coolant chemistry.

The key problem, caused by the above mentioned demands, is the existence of a crud inventory, which creates problems due to (1) its volume/mass of material and (2) the complex chemical composition of the participating elements. From the fuel element perspective the resulting main area of concern is Axial Offset Anomaly (*AOA*) or Crud Induced Power Shift (*CIPS*), whereas from a plant operational view the material integrity and the radiation exposure situation may obtain highest attention. In all cases discussed e.g. in Chapter 3 of this report, corrosion products were involved in the basic mechanism. Since the objective of this report is to describe how to mitigate the crud-related problems, the attempt is made to identify the countermeasures which are appropriate to improve the operational situation.

In order to achieve these goals, the mitigation methods are classified in three categories:

- Mitigation methods which have a preventive character like a “Hot functional test” at the first start-up, surface pre-treatment, selection of the SG tubing material, development and use of stellite replacement materials.
- Measures to be taken at normal operation like pH-control, zinc-addition, use of *EBA*, oxygen control, lowering hydrogen concentration, start-up and shutdown procedures.
- Adhoc mitigation strategies like: ultrasonic fuel cleaning, chemical and mechanical decontamination.

These mitigation methods shall be benchmarked in the light of the previous chapters and the current understanding of the transport mechanism which consists out of the following steps:

- Metal release (amount and chemical composition)
- Crud transport (Lithium strategy, H₂-strategy, role of oxygen, role of other impurities)
- Deposition on fuel surface
- Activation
- Re-dissolution
- Deposition on out-of-core surfaces
- Start-up and shut-down

- With respect to the PWR plant operational situation the existing experience shall also be included in the discussion wherever possible. To start this subject, Figure 3-27 shall be discussed in more detail. It is duplicated as Figure 5-1

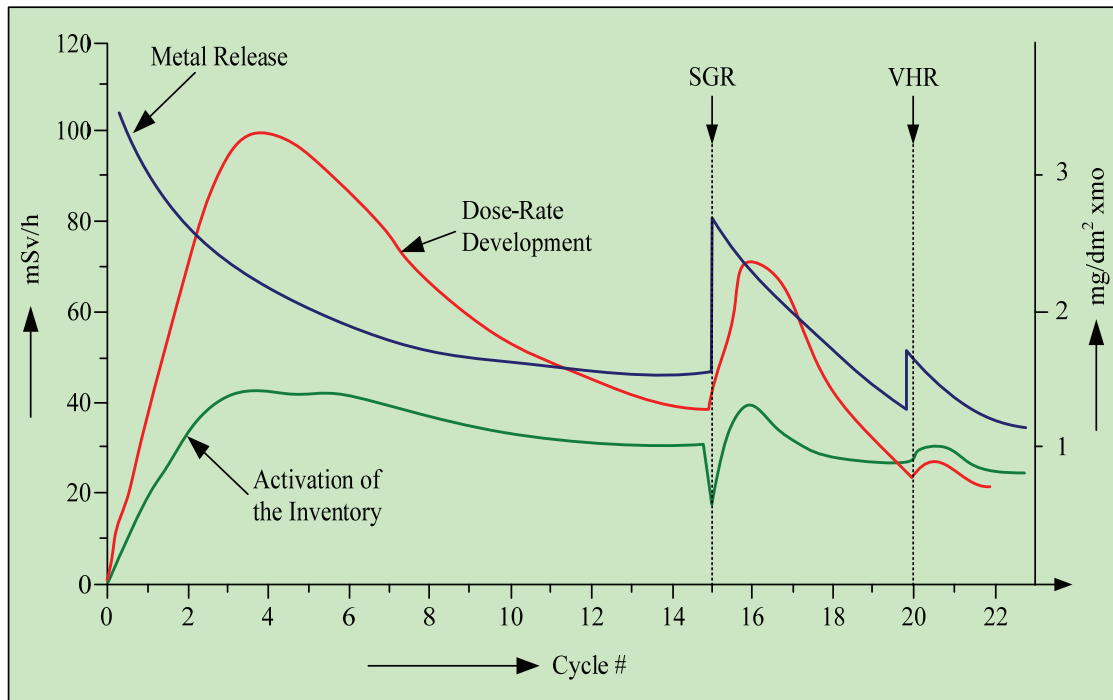


Figure 5-1: Scenario for Metal Release, Activation of the Inventory, and Dose-Rate Development.

Despite the fact, that Figure 5-1 is of general nature, it can be used to explain the situation regarding the necessity of crud control from the very beginning of plant operation. Crud formation occurs by general corrosion of the structural material and the crud inventory depends strongly on the properties of the barrier oxide layer formed during the first hot functional test. The whole metal release rate will be lowered in case optimum conditions were selected during this start-up phase. If in a plant a steam generator replacement is performed, the fresh surface will not have the option to see the same conditions like the plant at the very first start-up. So the metal release will see a steep increase at this time but will not reach a release rate like at hot functional test.

The second event shown in Figure 5-1 is the vessel head replacement (*VHR*) which has an impact to the crud inventory by offering some fresh surfaces. The question is, which mitigation measures can be taken in order to positively influence the metal release rate. Many decisions in this regard can be made already several years before the first start-up. One typical example is the selection of the steam generator tubing material and others as described above.

5.1 PREVENTIVE METHODS SUITABLE TO MINIMIZE *CRUD* INVENTORY

5.1.1 Selection of steam generator tubing material

Ziemniak & Hanson, 2005, presented an interesting paper regarding the corrosion behaviour of NiCrFe Alloy 600 in high temperature, hydrogenated water. In their introduction to this paper, they say: "Recent advances in the ability to characterize indigenous oxide layers that form on corroding NiCrFe Alloy substrates have revealed a synergism between alloy corrosion and chemical aspects of the metal oxide corrosion layer". In these cases, spinel oxides (AB_2O_4) are formed and an understanding of the manner in which their metal cations distribute among two lattice sites in the oxide – octahedral and tetrahedral – is important. For example, the B cations are Fe(III) and Cr(III) and the AFe_2O_4 oxides (ferrites) are inverse spinels while the ACr_2O_4 oxides (chromites) are normal spinels. One consequence of this distribution is that a single phase, solid solution is not stable over an unlimited range of composition and solid phase immiscibility occurs: One phase is chromite rich (inner layer) and one phase is ferrite rich (outer layer). Investigations of an austenitic iron-base CrNi Alloy (304 stainless steel) demonstrated the coincidence between compositions of the inner and outer corrosion oxide layers (see Ziemniak & Hanson, 2002) and solvovous phases in the Fe_3O_4 - $FeCr_2O_4$ binary (see Ziemniak & Castelli, 2003).

Follow-on work with the Ni-base Cr-Alloy (Alloy 625) found that non selected oxidation created inner- and outer layer spinel oxide corrosion films representative of solvus phases in the $NiFe_2O_4$ - $NiCr_2O_4$ binary. The higher Ni levels, however, led to two additional chemical phenomena:

- 1) Recrystallisation of excess Ni(II) ions in the inner layer as metallic Nickel and
- 2) pick-up of non indigenous iron ions from the aqueous phase to create additional amounts of hydrothermally CrNi Ferrite from outwardly diffusing Ni(II) ions in the inner layer.

Both reactions are a consequence of the inability to form a separate phase of Ni(II) oxide in the presence of dissolved hydrogen.

In order to complement an ongoing immiscibility study of the $NiFe_2O_4$ - $NiCr_2O_4$ binary a second Ni-base CrFe alloy corrosion test was undertaken and the results are reported by Ziemniak et al., 2005. In a separate paper Ziemniak et al. are also reporting about the immiscibility in the $NiFe_2O_4$ – $NiCr_2O_4$ spinel binary.

As described several times in this Review, the barrier oxide layer is most important for the passivation of the inner surface of the reactor system. Furthermore it became clear that chromium spinels enhance the protective properties of the barrier oxide. So the expectation towards the formation of the barrier oxide layer by the steam generator tubing material may be considered.

Unfortunately, the discussion about the most suitable SG tubing material was determined by the SG Secondary Side problems. Therefore, this aspect is decisive in this discussion.

6 BWR MECHANISMS AND MITIGATION METHODS (KLAS LUNDGREN)

6.1 WATER CHEMISTRY CONTROL

The water chemistry control in *BWRs* with respect to radiation buildup is very much a matter of optimization of the corrosion product balance in the primary circuit. Six different general types of corrosion product balance is schematically illustrated in Figure 4-1. Based on the discussion performed in chapter 4 it is concluded that the fuel crud composition shall be well balanced, i.e. the relation between iron (Fe) and nickel (Ni) plus zinc (Zn) shall be maintained close to the spinel relation, but with only a small excess of Fe. A significant inflow of Fe may result in fuel corrosion problems, especially if the Fe inflow is occurring together with a considerable inflow of Zn (and copper¹ (Cu)). High inflow of Fe normally also results in a fuel crud that is prone to release particles resulting in hot spot radiation sources in the plant. A too low inflow of Fe, on the other hand, may lead to formation of less stable monoxides, resulting in increased reactor water activity concentrations, and, especially in connection to somewhat increased steam moisture content, increased turbine plant radiation levels. Fuel crud with a too high Ni/Fe ratio seems also to be involved in increased local fuel cladding corrosion, especially for fuel with spacers of Inconel.

The above general recommendation means different actions whether the plant is operating with *NWC*, *HWC* or has applied *NMCA*.

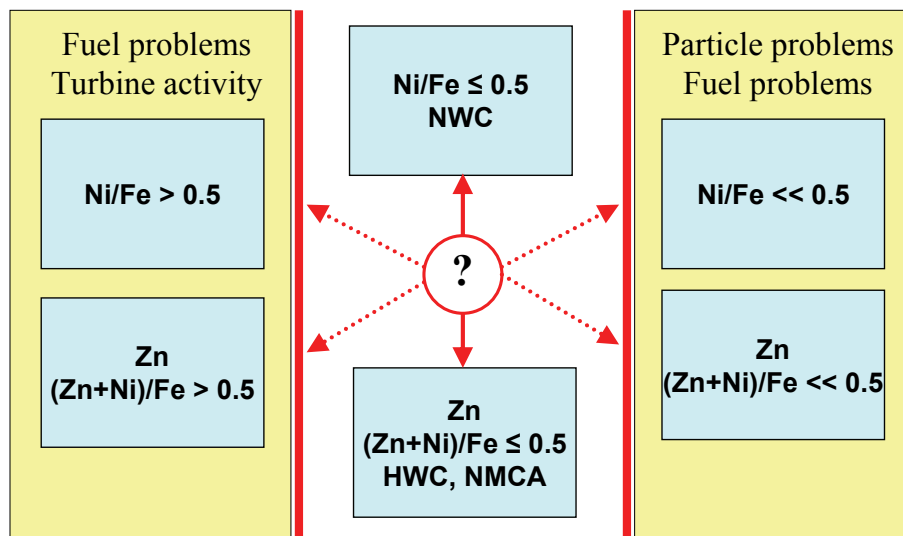


Figure 6-1: *BWR* Corrosion product balance Fe/Ni/Zn - Six different cases: Where to go?

¹ Cu shall be avoided for several reasons. Cu is known in several cases to cause fuel cladding corrosion (*CILC*, see section 4.2.2). Cu also makes *HWC* operation less effective, see section 4.1.2. There are, however, some indications that a moderate amount of Cu in the fuel crud may form oxide forms that have a high affinity for cobalt (Co), resulting in reduced Co-60 reactor water activity (see section 4.2.1).

6.1.1 NWC plants

The Fe inflow in plants operating with *NWC* is very much dominated by the inflow by the feedwater (see e.g. Figure 4-10). That means that the key to control the fuel crud composition is to control the feedwater chemistry, and especially the feedwater Fe. The most recent EPRI water chemistry guideline proposes that the feedwater Fe concentration during *NWC* conditions shall be maintained in the interval 0.5 – 1.5 ppb (see Table 4-8). The proposed amount of Fe is probably rather conservative, especially in the case with low feedwater Zn. Experience from Scandinavian *BWRs* has shown, that a well balanced fuel crud with respect to Fe and Ni can be maintained with a feedwater Fe concentration as low as about 0.2 ppb, if the Zn level is low. This level is supported by the fuel crud Ni amounts presented in Figure 4-15. Zn in the feedwater, natural or injected, increases the amount of feedwater Fe needed to maintain a fuel crud of the spinel type:

Eq. 6.1
$${}^{FW}C_{Fe} \geq 0.2 + 2.3 \cdot {}^{FW}C_{Zn}$$

where:

${}^{FW}C_{Fe}$ – Feedwater Fe concentration [ppb]
 ${}^{FW}C_{Zn}$ – Feedwater Zn concentration [ppb]

A control of the feedwater Fe according to **Eq. 6.1** will result in a fuel crud close to the ideal spinel type, i.e. further injection of Zn is not needed and will only result in an increased demand of feedwater Fe. On the other hand, if the minimum feedwater Fe is not easily obtained, Zn injection can help to improve the characteristic of the fuel crud. The 1.5 ppb EPRI 2004 upper bound of feedwater Fe (see Table 4-8) corresponds to a feedwater Zn level of maximum 0.6 ppb, which corresponds to the recommended maximum EPRI level (see Table 4-8). Higher Zn (and Fe) levels may result in increased fuel cladding corrosion.

6.1.2 HWC and NMCA plants

The prerequisites for Fe control change considerable when *HWC* operation is applied, and even more when *NMCA* application is performed. The feedwater is no longer the only source of Fe, considerable contribution is also expected from sources in the reactor circuit obtaining low corrosion potential (see Figure 4-10). These internal sources is not easily monitored, and significant variation may exist between different plants. Factors affecting besides reactor design features are the degree of H₂ injection in the case of *HWC*, the degree of *NM* coverage in the case of *NMCA*, and the pre-history with respect to feedwater Fe and Zn inflow. The recent EPRI recommendations consider this effect, and low feedwater Fe is accepted, see Table 4-1 and Table 4-8. Recommended interval for feedwater Fe is 0.1 – 1 ppb. The lower limit represents the limit of today's US *BWR* experience, and a practical interpretation is that actually no lower limit exists in the case of *HWC* and *NMCA* plants. In practice, large efforts are made in US plants to lower the feedwater Fe input, see section 4.3.1.2.

Zn injection seems to be especially effective in the case of *HWC* and *NMCA* plants to form a more stable fuel crud composition. The amount Zn injection needed is, however, not so easily determined due to the above mentioned non-monitored internal sources of Fe. The recent EPRI guidelines propose that a reactor water Zn level of >5 ppb shall be maintained in *HWC* plants (Table 4-2). In the case of *NMCA* plants a relation between soluble ^{60}Co and Zn is instead proposed (Table 4-2: $<2.0 \cdot 10^{-5} \mu\text{Ci/g}$ per ppb, or $<720 \text{ Bq/kg}$ per ppb), which in reality normally means a somewhat lower reactor water Zn level than 5 ppb. The reactor water specifications have, however, to consider the proposed feedwater Zn limits, <0.6 ppb in *HWC* plants and <0.4 ppb in *NMCA* plants (Table 4-1), which may override the reactor water limits. The feedwater Zn limits are due to fuel concerns.

As mentioned above, the Zn injection may be complicated to control due to the non-monitored sources of Fe in *HWC* and *NMCA* plants. One Scandinavian *HWC* plant with low feedwater Fe has therefore used an alternate way of controlling the feedwater Zn injection based on relation between reactor and feedwater Zn:

$$\text{Eq. 6.2} \quad {}^{FW}C_{Zn} \geq 2 \cdot \frac{f_{RWCU}}{f_{FW}} \cdot {}^{RW}C_{Zn}$$

$$\text{Eq. 6.3} \quad {}^{RW}C_{Zn} \leq {}^{Max}C_{Zn}$$

where:

${}^{FW}C_{Zn}$ – Feedwater Zn concentration [ppb]

${}^{RW}C_{Zn}$ – Reactor water Zn concentration [ppb]

${}^{Max}C_{Zn}$ – Maximum allowed reactor water Zn concentration [ppb]

f_{RWCU} – Reactor water cleanup flow [kg/s]

f_{FW} – Feedwater flow [kg/s]

The above relation **Eq. 6.2** means that at least about half of feedwater Zn shall be consumed in restructuring of fuel crud and system surface oxides, and maximum about 50% of the feedwater Zn is allowed to be cleaned-up by the *RWCU*. The feedwater Zn is primarily adjusted to reach the reactor water Zn target level, ${}^{Max}C_{Zn}$. If the Zn target level can not be reached together with the relation **Eq. 6.2**, the Zn injection is decreased to a point where **Eq. 6.2** is fulfilled and a somewhat lower reactor water Zn level than the target is accepted. This operation strategy is to assure that a certain iron surplus in the fuel crud is maintained.

7 OPEN ISSUES AND RECOMMENDATIONS (ROLF RIESS)

The open issues and recommendations can be evaluated in accordance with Chapter 5 (for PWRs) and Chapter 6 (for BWRs). This evaluation will be accomplished by summarizing the relevant issues in a tabular form. A general recommendation for both PWRs and BWRs is to keep a list of all mitigation methods in order to be prepared for an application of one of the methods. Such occasions will occur in shutdown periods and as well during unscheduled interruptions. The mitigation methods discussed in detail in Section 5 and 6 of this report will be evaluated by repeating them as a recommendation and/or by identification of the open issues. The mitigation methods for PWRs are handled in Table 7-1, Table 7-2 and Table 7-3, and the corresponding methods for BWRs in Table 7-4, Table 7-5 and Table 7-6.

7.1 PWR PLANTS

Table 7-1: Is an evaluation of the crud formation preventive methods suitable to minimize the crud inventory.

Method	Recommendation	Open Issues
Steam Generator tubing material selection	For primary side application the first choice is Alloy 800 NG followed by Alloy 690 TT	What is the best barrier oxide layer composition? What kind of improvements have to be identified? Zinc injection during HFT? Cr coating? Zr or Ti coating?
Stellite replacement material	Siemens development of replacement materials. EPRI development of NOREM family materials.	Where to focus the replacement activities? Core or out-of-core area? Sizewell-B phenomenon to be explained!
Co specifications for RCS materials	The ALARA principles should also be applied for the Co specifications in the RCS material	Same open issues like for Stellite replacement material.
Surface pretreatment technologies	Electropolishing?	Long term effect of electropolishing. Chromium coating. Alternative coatings or preoxidation methods to be qualified.
Hot Functional Testing	Based on plant experience HFT is recommended during first start-up.	Investigation of the importance of the two HFT steps: HFT without B HFT with B Zinc addition during HFT?

Table 7-2: evaluates the mitigation methods in the operating phase.

Method	Recommendation	Open Issues
High pH primary water chemistry	Higher Li concentrations during steady state operation are recommended	Better information about crud composition is required. Compatibility of higher pH and fuel cladding must be varified. High pH values and high radiation fields?
Zinc injection	Dose reduction has varified the positive effect of Zinc injection. Application also recommended because SCC crack initiation prevented. Use of depleted Zinc (< 1% Zn-64)	Effective for mitigation of SCC crack growth.
Use of enriched boric acid	No recommendation for crud minimization (~30% enrichment)	> 95 % enrichment allows higher pH; indirect effect
Oxygen control	Active control of O ₂ prevents: Changes in the compound composition Increased metal release rates. Recommended actions, e.g. Sampling line downstream HP injection pump Keep CVCS free of oxygen	Hardware/sytems to control oxygen
Hydrogen control	Avoid hydrogen concentrations close to the Ni/NiO transition	What is the better option? Decrease or increase the H ₂ compared to the standard specs
Start-up and shutdown	Use all options to minimize the inventory. Establish for a reasonable time acid/reducing conditions (Ni-ferrite removal) Outer layer crud removal (Ni-removal)	Waste production enhanced?
Hydrazine treatment	Not yet a recommendation	R & D-work to be done. Role of ammonia
Redox-cycling	In case of severe delta p–problems: Hydrogen peroxide flushing Allow for a short period the radiolytic formation of oxygen	

Table 7-3: Summarizes the adhoc mitigation methods for crud control.

Method	Recommendation	Open Issues
Ultrasonic fuel cleaning	Recommended as a viable tool for crud removal	Impact on fuel behaviour
Chemical decontamination of subsystems and full systems	Full system decontamination is recommended as the most effective way to minimize crud inventory	Re-contamination behaviour Passivation possibility
Mechanical decontamination methods	As part of steam generator replacement activity recommended and for SGs with heavy ID deposits.	Availability of remote control equipment

When being faced with all these Recommendations and Open Issues regarding the methods for crud minimization there is one main open question:

What is the best strategy to keep crud and its consequences under control?

A possible answer to this question is to establish conditions where the solubility of corrosion products on the hot leg side, e.g. at the inlet of the steam generator channel heads, is greater than on the cold leg side. In other words, the solubility behaviour should be a regular one under the thermodynamic conditions in the RCS. This means for example to increase the Lithium concentration in order to operate a plant at least at a pH_{300 °C} of 7.4. However, the solubility behaviour of the corrosion products should be confirmed by measurements.

Simultaneously the hydrogen concentration in the RCS should be kept at the lower end of the specification. The risk associated with these Recommendations is a slight increase in occupational radiation exposure.

All other methods for crud control have a kind of supporting function in controlling crud and the consequences thereof.

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