

# ZIRAT-6 SPECIAL TOPICS REPORT



AQUARIUS SERVICES CORP.  
17 POKAHOE DRIVE  
SLEEPY HOLLOW, NY 10591  
USA

ADVANCED NUCLEAR TECHNOLOGY  
UPPSALA SCIENCE PARK  
SE-751 83, UPPSALA  
SWEDEN



## Water Chemistry and Crud Influence on Cladding Corrosion

*Prepared by*

Gunnar Wikmark

Advanced Nuclear Technology Sweden AB, Sweden

*and*

Brian Cox

University of Toronto, Ontario, Canada

**15 November 2001**

*Project ANT-P-11-0055*

*Approved by*

Peter Rudling

Advanced Nuclear Technology Sweden AB

[ant@ant.se](mailto:ant@ant.se)

*Copyright © Advanced Nuclear Technology Sweden AB, ANT, and Aquarius Services Corporation, Aquarius, 2001. This information was compiled and produced by ANT and Aquarius for the ZIRAT-6 membership. This report, its contents and conclusions are proprietary and confidential to ANT and Aquarius and to the members of ZIRAT-6 and are not to be provided to or reproduced for any third party, in whole or in part, without the prior written permission by ANT in each instance.*

## SUMMARY

In the early days of nuclear reactor operation, there were a number of incidents where not suitable water chemistry was causing considerable problems with the operation of the plant and occasional fuel failures. Efforts in improving feed water piping and condenser tubing material ameliorated the situation notable. Yet, presence of copper has been plaguing a few plants with Crud Induced Localised Corrosion, CILC, failures for approximately twenty years. CILC has actually by far been the primary failure cause for BWRs in the US even during the 1990's. Considerable efforts has been spent for the last twenty years to improve the water chemistry with the purpose to reduce activity build-up and stress corrosion cracking of primary piping, both in BWRs and PWRs. Little concern has generally been given to attain a fundamental understanding for crud induced fuel problems and solving the CILC problem. This has been so much more obvious since the increased power rating, longer cycles, higher burn-ups and other means to improve the plant output has correlated with the occurrence of a number of crud related fuel problems, in most cases leading to considerable fuel damage and a notable number of fuel failures in each case. Such incidents have been experienced in both BWRs, PWRs, and WWERs, in Japan, Switzerland, Russia, Finland, and a number of cases in the US during the last 10 years. Considering the requirement to further improve the economical situation for the nuclear power, we must anticipate even higher duty for the reactor system and the fuel and smaller margins to anomalous operation. This can only be performed successfully if the margins, and the consequences of operating beyond the margins, are well known. The objective of this review report is to provide a basis for such evaluation. All important fundamental aspects on the fuel crud formation has been reviewed and critically evaluated. This includes fundamental physical and chemical phenomena controlling particle adhesion, water phase reactions, solubility, etc. With this basis, the sources for corrosion products in the BWR and PWR are reviewed, and the chemical forms of the impurities are examined. The form and amount of crud in various applied water chemistries is presented and discussed. The possible impact from crud and the fundamentals for this impact are evaluated. A large part of the report is spent on reviewing and discussing all published crud induced incidents in PWRs and BWRs, from the 1960's to 2000. Current BWR and PWR water chemistry regimes are reviewed and the respective possible influence to produce crud-induced failures is evaluated. The general conclusion of the report is that too little analysis has generally been done in order to fully understand the mechanism producing the incidents. This is especially true for the more recent cases. On several occasions, several hundred kilograms of iron and copper have been deposited on the fuel, without any notice of the existence of the crud source, or any appropriate water chemistry monitoring system signalling the presence of detrimental water chemistry. Better monitoring and better understanding is hence needed and several possible ways to attain or develop improved monitoring and understanding are presented in the report.

## CONTENTS

<b>1. INTRODUCTION .....</b>	<b>7</b>
<b>2. FUNDAMENTALS .....</b>	<b>8</b>
2.1. <i>PROPERTIES OF WATER</i> .....	8
2.2. <i>SOLUBILITY AND COMPLEXATION</i> .....	10
2.3. <i>BASIC BWR, PWR, AND WWER CHEMICAL CONDITIONS</i> .....	11
2.4. <i>ION DEPOSIT MECHANISMS</i> .....	13
2.4.1. <i>Formation of Solid Phases</i> .....	13
2.4.2. <i>Ion Exchange</i> .....	14
2.5. <i>COLLOIDS</i> .....	14
2.6. <i>PARTICLES AND PARTICLE DEPOSITS</i> .....	14
2.6.1. <i>Gravity</i> .....	15
2.6.2. <i>Electric and Molecular Attraction</i> .....	15
2.6.2.1. <i>Coulombic Attraction</i> .....	15
2.6.2.2. <i>van der Waals Attraction</i> .....	16
2.6.2.3. <i>The Double Layer Impact</i> .....	16
2.6.2.3.1. <i>Zeta Potential Influence</i> .....	18
2.6.2.3.2. <i>Other Electro-kinetic Phenomena</i> .....	21
2.6.3. <i>Influence of Magnetic Properties</i> .....	21
2.6.4. <i>Geometry Influence - Surface Roughness</i> .....	22
2.6.5. <i>Assessing the Relative Influence of Depositing Phenomena</i> ..22	
2.7. <i>PARTICLE TRANSPORT</i> .....	25
2.7.1. <i>Hydrodynamic Re-suspension Force</i> .....	25
<b>3. OBSERVATIONS AND THEORY .....</b>	<b>26</b>
3.1. <i>CRUD SOURCES</i> .....	27
3.1.1. <i>Corrosion and Corrosion Release</i> .....	27
3.1.2. <i>Materials Corroding in the LWRs</i> .....	29

# ZIRAT-6 Special Topics Report on Water Chemistry and Crud Influence

3.2.	CHEMICAL COMPOSITION OF CORROSION PRODUCTS AND FUEL CRUD	32
3.2.1.	Spinel Structure Oxides .....	33
3.2.2.	Solubility of Iron, Nickel, and Chromium in LWRs .....	34
3.3.	WATER CHEMISTRY IN BWRs .....	36
3.3.1.	Non-monitored Crud Sources .....	39
3.4.	WATER CHEMISTRY IN PWRs .....	39
3.5.	CRUD TRANSPORT .....	40
3.5.1.	The RW Concentration and Removal of Crud in the BWR .....	40
3.6.	FUEL CRUD DEPOSITION .....	43
3.6.1.	Boiling Impact - Experiments and Theory .....	47
3.6.2.	A Tentative Model of the Boiling and Crud Deposits .....	50
3.6.3.	An Important Observation of Impact of Boiling .....	52
3.7.	CRUD DEPOSITS IN LWRs .....	53
3.7.1.	Crud Deposits in BWRs .....	53
3.7.1.1.	BWR Crud Profiles .....	54
3.7.2.	Crud Deposits in PWRs .....	56
3.7.3.	Crud Deposits in Other Components, Threatening Fuel Performance .....	58
3.7.4.	Solubility of Crud .....	59
<b>4.</b>	<b>POSSIBLE IMPACT FROM CRUD .....</b>	<b>59</b>
4.1.	LOCAL CHEMISTRY .....	60
4.2.	THERMAL RESISTANCE .....	60
4.3.	NEUTRON POISON .....	63
4.3.1.	Activity Dispersion in the Reactor System .....	63
4.3.2.	Impact of Fuel Failures .....	63
4.4.	FLOW RESTRICTION .....	63
<b>5.</b>	<b>KNOWN CASES OF CRUD-INFLUENCED FUEL FAILURES .....</b>	<b>64</b>

## ZIRAT-6 Special Topics Report on Water Chemistry and Crud Influence

5.1.	EARLY EXCESSIVE IRON DEPOSITS IN BWRs .....	66
5.2.	EARLY EXCESSIVE CRUD DEPOSITS IN PWRs.....	67
5.3.	EXCESSIVE DEPOSITS WITH COPPER IN THE SGHWR AND OTHER PLANTS 69	
5.3.1.	Other Plants with Copper-rich Crud Deposits.....	71
5.4.	CRUD INDUCED LOCALISED CORROSION (CILC) .....	71
5.5.	CRUD INDUCED FAILURES IN WWERS.....	76
5.5.1.	Carbon Deposits .....	76
5.5.2.	Excessive Iron Deposits in Loviisa-2 .....	76
5.6.	EXCESSIVE CRUD DEPOSITS IN PWRs .....	80
5.6.1.	Axial Offset Anomaly (AOA) Incidents.....	80
5.6.2.	PWR Local Crud Deposits Producing Fuel Failures ....	83
5.7.	THE HAMAOKA-1 INCIDENT.....	84
5.8.	ENHANCED SPACER SHADOW CORROSION (THE KKL INCIDENT) .....	87
5.9.	EXCESSIVE IRON DEPOSITS IN BWR (RIVER BEND-1) .....	89
<b>6.</b>	<b>DISCUSSION.....</b>	<b>91</b>
6.1.	EXPLANATIONS FOR WATER CHEMISTRY CAUSES FOR FUEL FAILURES ..	91
6.2.	CURRENT BWR WATER CHEMISTRY TRENDS AND THEIR IMPLICATIONS	92
6.2.1.	Hydrogen Water Chemistry (HWC) .....	92
6.2.2.	Noble Metal Chemical Addition .....	93
6.2.2.1.	The Nature of the Noble Metal Deposits.....	95
6.2.2.2.	Impact of Noble Metal Addition on Fuel Cladding ....	98
6.2.2.3.	Impact of Noble Metal Addition on Water Chemistry	101
6.2.3.	Iron Addition.....	103
6.2.4.	Zinc Addition .....	103
6.2.5.	Ultra Low Crud Control Operation.....	106
6.3.	CURRENT PWR WATER CHEMISTRY TRENDS AND THEIR IMPLICATIONS	107
6.3.1.	Effects of LiOH on Zirconium Alloys (Brian Cox) .....	107

# ZIRAT-6 Special Topics Report on Water Chemistry and Crud Influence

6.3.1.1. Introduction .....	107
6.3.1.2. Effects on Zirconium Alloy Corrosion .....	107
6.3.1.3. Mechanisms.....	129
6.3.1.3.1. Corrosion Enhancement by LiOH .....	129
6.3.1.4. Consequences for PWR fuel cladding performance..	138
6.3.2. Low Hydrogen Chemistry .....	140
6.3.3. Zinc Addition .....	141
6.4. ADDITIONAL RESEARCH AND DEVELOPMENT NEEDED .....	143
<b>7. CONCLUSIONS .....</b>	<b>145</b>
<b>8. ACKNOWLEDGEMENTS .....</b>	<b>146</b>
<b>9. REFERENCES .....</b>	<b>147</b>
<b>10. DEFINITIONS AND NOMENCLATURE .....</b>	<b>175</b>
10.1. FUNDAMENTAL CONSTANTS.....	175
10.2. TEMPORARY CONSTANTS .....	175
10.3. VARIABLES .....	176
10.4. NOMENCLATURE.....	178
10.5. ABBREVIATIONS .....	179
<b>11. APPENDIX I: THERMODYNAMIC CALCULATIONS .....</b>	<b>180</b>
11.1. LITERATURE USED FOR THERMODYNAMIC CALCULATIONS .....	180
11.2. THE FE-NI-CR SYSTEM AT 573 K USED IN THE THERMODYNAMIC CALCULATIONS .....	181

## 1. INTRODUCTION

The formation, transport, and deposition of crud<sup>1</sup> in Light Water Reactors (LWRs) have been reviewed a number of times since 1963 [ref. 1, ref. 2, ref. 3, ref. 4, ref. 5]. Considerable experience and knowledge has been collected in this matter during the 40 years, and thousands of operational years, for the commercial PWRs and BWRs. Yet, in relation to other fields of reactor operation, the water chemistry aspect on crud formation has been mainly based on removing the symptoms of the incidents, instead of developing a fundamental understanding. This lack of fundamental understanding is very pronounced when it comes to the influence on fuel cladding and occasionally occurring fuel failures, correlated with crud deposits on the fuel. Only in the trivial cases, when the crud is so thick as to be mechanically impeding the coolant flow in the fuel assembly, or depositing in so thick and dense layer that the thermal insulation inhibits the cooling of the rods, do we have a good and unambiguous explanation for the resulting fuel failures. In all other cases, comprising thousands of fuel failures that have been caused by cladding fuel deposits, we do lack an understanding regarding the mechanism. Even worse, in most cases, not even the correlation between the crud and water chemistry is very well established or understandable, at least when it comes to the reports found in the literature. Hence, the appropriate information is not available to learn from for the nuclear community.

The purpose of the present review is to describe the fundamentals in crud formation, transport, and deposition, in order to provide a solid basis for evaluating and analysing any fuel operational problem due to crud deposits. The ultimate purpose is to provide knowledge and insight for staff involved in the operation and materials selection in nuclear power plants, in order to prevent the occurrence of any crud-related fuel problems. Such insight is increasingly more important, considering the escalating use of water chemistry control and introduction of new materials in the LWRs, in order to enhance fuel burn-up, elevating the power density, suppressing the activity build-up, and alleviate stress corrosion cracking of austenitic structural materials.

Many aspects, such as basic crud sources, the mechanisms of crud release, crud transport, and crud deposits are common for all water cooled plants and are consequently discussed for several reactor designs in this review. The related experience, whether from BWRs, PWRs, or WWERS, is generally of interest for all plant designs.

---

<sup>1</sup> 'crud' is the term used generally, and also in this report, to describe any solid matter that is or has been deposited on system surfaces or fuel cladding surfaces in water cooled nuclear power plants. CRUD is often interpreted as "Chalk River Unidentified Deposit", but according to Dr. Bill Lindsay (at the EPRI Crud Related R&D meeting in Palo Alto, CA, USA, 17 - 18 Nov. 1993), the acronym CRUD appeared years after the crud was found and investigated in the Chalk River NRX reactor in the mid-fifties.

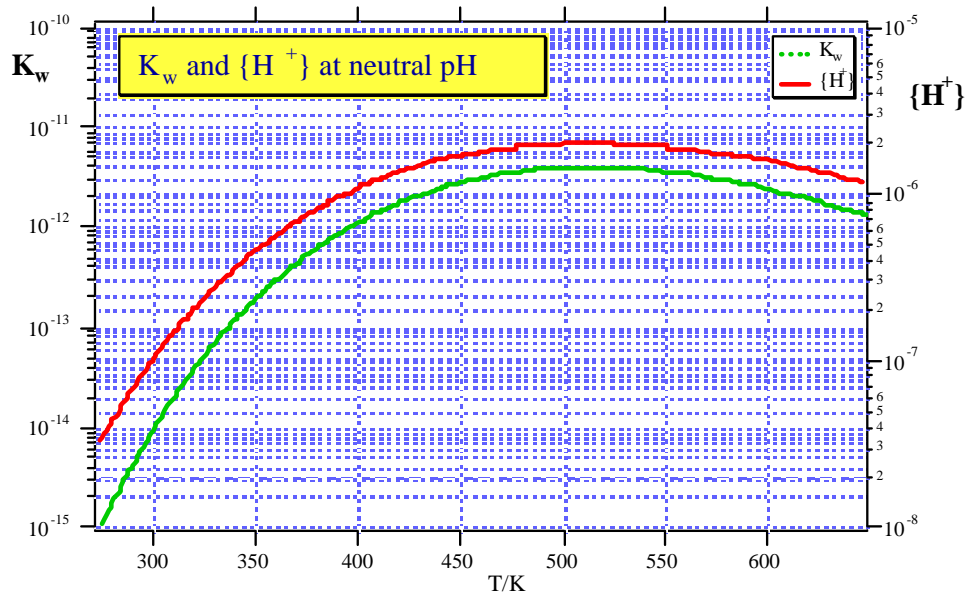
The first part of the report covers the fundamentals of the phenomena discussed in the latter parts. This part can be left for later reference while reading the parts describing the actual crud behaviour and the last part discussing known cases of crud-related fuel operational problems. A list of acronyms, used symbols, and an index are found at the very end of the report.

## 2. FUNDAMENTALS

In the following, the most important aspects involved in crud formation, deposition, and re-distribution are discussed in order to form a basis for the evaluation of the different phenomena known or suspected to be involved in the interaction between crud and fuel cladding.

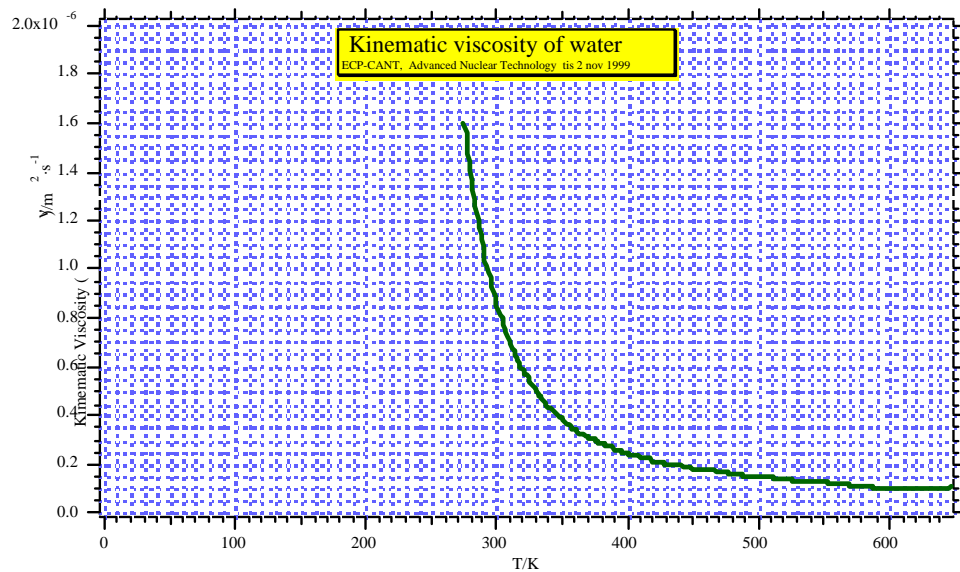
### 2.1. PROPERTIES OF WATER

Water is a dipolar solvent that will have a steam and water phase up to the critical point at 374°C. The properties of water, however, are varying considerably with temperature, as shown in Figure 1 to Figure 3 [ref. 6] below.

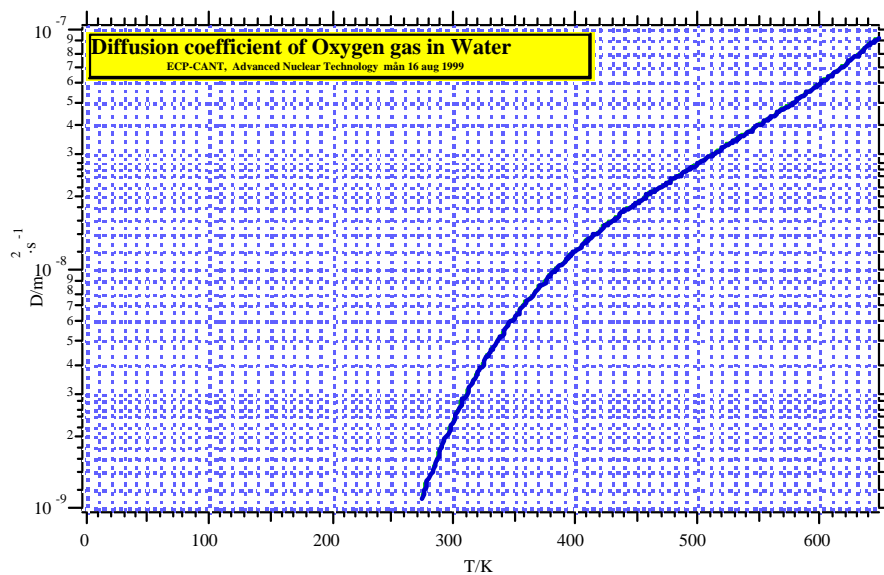


**Figure 1. The variation of the water autoprotolysis constant and neutral pH with temperature**





**Figure 2. The variation of the water viscosity with temperature**

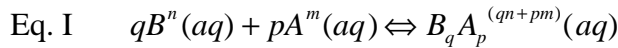


**Figure 3. The variation of the water diffusion coefficient with temperature**

The properties of water and water solutions are hence not similar at LWR operating temperature (270 - 340°C) and room temperature. Many observations of phenomena at room temperature are therefore not accurate or at least quantitatively different close to 300°C.

## 2.2. SOLUBILITY AND COMPLEXATION

Two species,  $A$  and  $B$ , may attract each other in a water solution, forming a complex,  $B_qA_p(s)$ , as given by Eq. I.

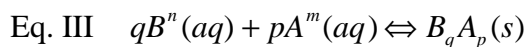


The equilibrium for the reaction in Eq. I is given by a stability constant,  $K_{stab}$ , as shown in Eq. II (charges are omitted for brevity in the expression).

$$\text{Eq. II} \quad K_{stab} = \frac{[B_qA_p(aq)]}{[B]^q[A]^p}$$

Such complexation is very common in water solutions when the concentration of species  $A$  and  $B$  is relatively high. At such low concentrations of anions and cations that we find in BWR water (see Section 3.3), there are virtually no complexes formed in reality in the water bulk phase, except for the trivial cases when  $A$  is a proton and  $B$  is a base, i.e. acid-base equilibria. In enriched confined locations, such as crud pores and crevices, and in PWRs with high lithium and boron concentrations, complexes may, however, form.

The special case when the complex has a low solubility is of more general interest for the LWR application. The solubility can be described as follows. Consider two chemical species,  $A$  and  $B$ . If  $A$  and  $B$  can form a non-charged solid complex, as shown in Eq. III,



the equilibrium of Eq. III is governed by a stability constant normally called the “solubility product”,  $K_{sol}$ , see Eq. IV.

$$\text{Eq. IV} \quad K_{sol} = \frac{[B]^q[A]^p}{\{B_qA_p(s)\}}$$

Note that the solid phase  $B_qA_p(s)$  will have a chemical activity equal to one ( $\{B_qA_p(s)\}=1$ ) if it is a pure phase.

Correspondingly, for a three species complex, we obtain the following expression.

$$\text{Eq. V} \quad K_{sol} = \frac{[C]^r[B]^q[A]^p}{\{C_rB_qA_p(s)\}}$$

Note that, since  $K_{sol}$  is a constant at a given temperature and ionic strength<sup>2</sup>, a change of the concentration of any of the species will affect the concentration of the others.

---

<sup>2</sup> The concept of ionic strength is describing the influence of other charged species on the stability of the complex. The very low ionic contaminants in BWR water will have little influence, due to the pronounced dissociation of water at 288°C (see Section 2.1). In

The expressions for complexation and solubility are only valid at equilibrium. In very few cases, equilibrium will be attained in LWR systems, despite the elevated water temperature. The thermodynamic (equilibrium) properties are however of interest to determine the ultimate goal for any kinetic process. They will also provide the “ceiling” and “floor” for some of the concentrations of species in the reactor water, as discussed later.

### 2.3. BASIC BWR, PWR, AND WWER CHEMICAL CONDITIONS

The BWR water chemistry is in principle “as clean as possible”. Normally, no additions to the reactor water is done, except in very limited amounts. The amount of additions and impurities is low, normally in the order of 0.01 – 20 ppb<sup>3</sup>. The species in highest concentrations are normally hydrogen peroxide, silica (see Section 3.3), hydronium ( $\text{H}_3\text{O}^+$ ) and hydroxide ions (from the water auto-protolysis, see Figure 1), which can all be above 1  $\mu\text{mole per litre}$  (1 – 100 ppb depending on molecule weight)<sup>4</sup> or even above 10  $\mu\text{mole per litre}$  in some cases. The BWR water chemistry is oxidising, except some parts under hydrogen water chemistry, HWC<sup>5</sup>, when hydrogen gas is injected in order to suppress the radiolytic decomposition of water from the gamma and neutron irradiation. The effect of the water chemistry on the corrosion potential of stainless steel is shown in Figure 4.

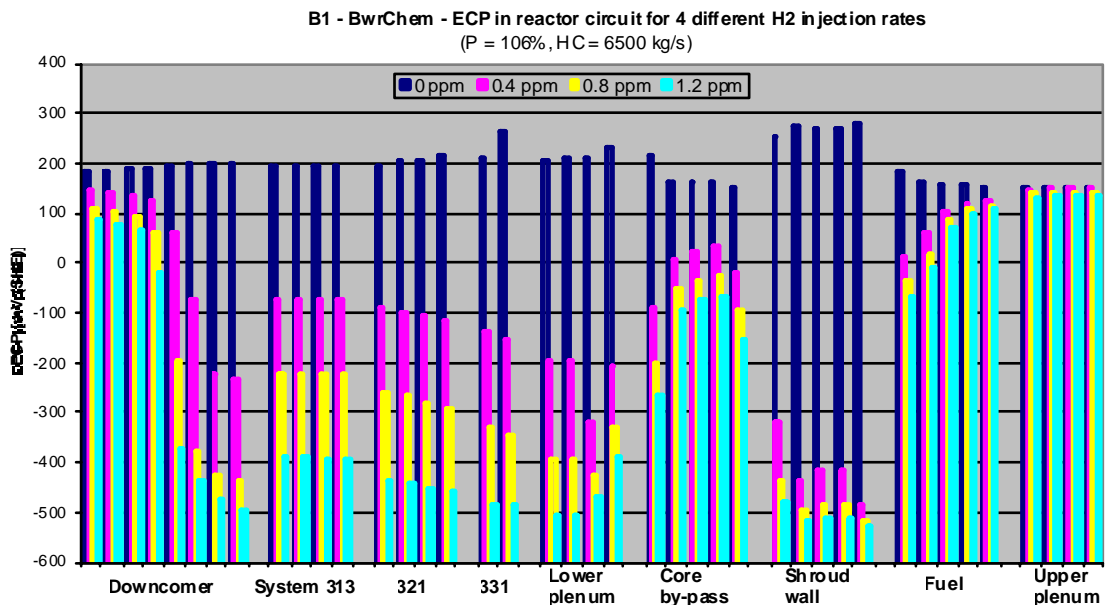
---

*PWRs, the presence of boron and lithium will provide a buffering impact, but the change during the cycle will definitely affect the ionic strength and hence also the value for the stability (and solubility) constants.*

<sup>3</sup> *ppb, parts per billion, 1:10<sup>9</sup>.*

<sup>4</sup> *The neutral pH of 5.65 at 288°C corresponds to 2.2  $\mu\text{M}$  (M equals moles per litre) or 2.3 ppb  $\text{H}^+$  and 2.2  $\mu\text{M}$  or 38 ppb  $\text{OH}^-$ .*

<sup>5</sup> *For an explanation of all abbreviations, see Section 10.5.*



**Figure 4. Calculated ECPs for stainless steel in various locations in a BWR during NWC and HWC operation. System 313 means the MRL, 321 the RHR, and 331 the RWCU systems. The inlet of flow to each system is to the left and the outlet to the right. From ref. 6.**

Since the boiling is absent in the PWR (at least as a design basis), the problem of enrichment and deposition due to the evaporation is not an obstacle to change the water chemistry. Boron in the form of boric acid is dissolved in the coolant (primary reactor water) in order to adjust the reactivity of the core. In the beginning of the cycle, typically 800 – 1200 ppm is present for a one-year cycle and up to 1900 ppm for a 24-month cycle. Reducing conditions are also established by addition of gaseous hydrogen to a level of 2.2 – 4.4 ppm ( $25 - 50 \text{ N}\cdot\text{cm}^{-3}\cdot\text{kg}^{-1}$ ), normally. The hydrogen concentration in this concentration interval, today normally in the order of 2.2 to 3.1 ppm, is kept constant during the cycle until the shutdown.

The acid conditions that result from the addition of boric acid have to be adjusted to minimise the corrosion release and corrosion product deposition. Lithium hydroxide<sup>6</sup> is therefore added to neutralise the boric acid. This means that initially 2.2 to 4 ppm of lithium is added, giving a BOC pH of 6.7 to 7.0. Experience has shown that the pH should be in the range 6.9 to 7.4 to have the best conditions to suppress corrosion release. During the cycle, the boron concentration is decreasing in order to match the lowered reactivity of the core. In most PWRs

<sup>6</sup> The lithium hydroxide is enriched in <sup>7</sup>Li in order to suppress the tritium formation of other lithium isotopes. due to transmutation by neutron capture.

today, the lithium concentration is kept constant until a pH of 7.2, or sometimes 7.4, is reached and then the lithium concentration is matching the decreasing boron concentration in order to keep a constant pH around 7.2 (or 7.4). This PWR primary water operation scheme is called a modified chemistry operation. This means that the highest pH around 7.2, which is normally considered the optimal pH to suppress corrosion release from the primary system and also to minimise the fuel crud deposits, is attained at the end of the cycle, when coolant activity will have its largest impact on system activity build-up. It also means that there are not constant crud deposit conditions in the PWR and that much of the crud present in the early period of the cycle has been released due to the changed chemistry at the later period of the cycle. This effect is further stressed by the common change to oxidising condition by addition of hydrogen peroxide during the shutdown, with the purpose of releasing fuel crud to the clean-up system.

To summarise, the PWR is hence operating under reducing conditions (with a stainless steel ECP of below -600 mV vs. SHE (the standard hydrogen electrode)), to be compared with the much more oxidising conditions of the BWR (see Figure 4). The PWR operation has also a steadily increasing coolant pH during the cycle from 6.9 to 7.2 or higher. The ionic strength (i.e. a measure of the sum of the charged species dissolved) will change drastically during the operating cycle.

The WWER operates with a similar chemistry as the PWR in regard of boron concentrations and pH. Potassium hydroxide is, however, used instead of lithium hydroxide to increase pH, and ammonia is added instead of hydrogen to obtain reducing conditions.

## 2.4. ION DEPOSIT MECHANISMS

### 2.4.1. Formation of Solid Phases

Solid phases, incorporating ions in solution, will form if the solubility product is exceeded (see Section 2.2) and the kinetics for the deposition processes are reasonably fast. The largest kinetic hinder is normally the activation energy for nucleation, i.e. the activation energy to form the first seed of the crystal structure. This means that deposit growth from ionic species often is initially slow, requiring significant super-saturation to start. The deposition rate will, however, accelerate once the first crystal seeds are formed. This also means that larger crystals, having lower surface energy per unit area, will grow preferentially to new or smaller crystals if the super-saturation is significant, but not extremely high. In the case of extreme super-saturation, less well-ordered structures are formed. Such less well-ordered structures are normally meta-stable, and will undergo restructuring in order to lower the surface energy. The restructuring can go through re-dissolution and re-precipitation, involving the local solvent conditions or through solid phase reactions, especially solid phase diffusion, which is often relatively slow.

#### 2.4.2. Ion Exchange

Oxides in particles or on surfaces may act as ion exchangers, if the difference in binding energy is small between the original ion and the ions in solution. As rule of thumb, a 15% or less difference in ionic radius will make it possible for a substitution of a foreign ion for the original ion in an oxide, if the charges are reasonably compatible.

### 2.5. COLLOIDS

Very small particles, less than 200 nm in diameter, are called colloids. Such very small particles will normally not settle due to gravitation but instead remain in the liquid medium due to Brownian movement [ref. 7]. The colloidal particles will have a very high surface to mass ratio and hence the surface effects, especially surface charge, will be controlling the behaviour of the colloids rather than mass effects, such as gravity, in the interaction with surfaces and other particles or colloids.

### 2.6. PARTICLES AND PARTICLE DEPOSITS

Particles may be formed by mechanical interaction between solid components, by erosion corrosion of structural materials, by agglomeration of colloids, or by precipitation from (super)saturated solutions. Particles are, by definition, larger than approximately 200 nm in diameter, otherwise they are classified as colloids (see Section 2.5). Particles will be affected by gravity, i.e. have the ability to settle in low flow parts of the reactor system.

Although the colloids can be abundant, it has to be noted that a particle, which has a diameter 10 times larger than a colloidal particle (see Section 2.5), will have a 1000 times larger mass. Larger particles hence have the ability to transport and keep relatively considerable amounts of mass and radioactivity even if they are few and not so abundant.

The particles, and colloids, may attract other (smaller) particles to the surface. If the original particle and the attracted particles have opposite charges, the net charge of the original particle will be changed, even to the extent that the net charge can be opposite to the original charge before the colloid or particle adhesion. A similar surface charge effect could be the result from adsorption of ionic forms. Since the ionic forms will normally not be attracted if the charge changes, ionic attraction will lead to net charge reduction, but not to charge reversal, unless there is some specific adsorption between the ion and the original particle. It should be noted that charge reversal due to such absorption will, of course, drastically change the deposition behaviour of particles. Hematite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ) colloids or particles could hence have a very different behaviour if cobalt and nickel oxides deposit and form ferrites (see Section 3.2.1) on the surface.

If the surface charge difference is opposite and large, the deposit formed on a surface will be adherent and relatively dense. On the contrary, if the difference is small or negligible, the adherence will not be controlled by electrostatic forces

(see Section 2.6.2.1), but rather by van der Waals forces (Section 2.6.2.2). The attraction force will then be weaker, forming a less dense and less adherent crud layer.

This influence of the surface charge effects in relation to the mass forces were first pointed out to the industry by Gasparini et al. [ref. 8], and were assessed quantitatively for the nuclear applications by Rodcliffe and Means [ref. 9], as discussed below.

### 2.6.1. Gravity

The effect of the gravitational force on particles in a medium is described by Stokes' law [ref. 10]. For a spherical particle of radius  $r$ , the following expression is hence valid for the frictional force of the medium<sup>7</sup>.

$$\text{Eq. VI} \quad F_{\text{fluid-friction}} = -6\pi r\eta v$$

The drag force is given by the gravitation ( $F_{\text{drag}} = m \cdot g$ ). Since the actual gravitational force is affected by the buoyancy of the medium, the proper expression for the gravitational force of a spherical particle with radius  $r$  will be as given in Eq. VII.

$$\text{Eq. VII} \quad F_{\text{grav}} = \frac{4\pi}{3} r_{\text{particle}}^3 (\rho_{\text{particle}} - \rho_{\text{aq}}) g$$

A constant falling velocity will be attained for the particle when the drag and gravitational forces are equal<sup>8</sup>. This limiting velocity,  $v_{\text{grav}}$ , for a particle in water is described by Eq. VIII.

$$\text{Eq. VIII} \quad v_{\text{grav}} = \frac{2 \cdot (\rho_{\text{particle}} - \rho_{\text{aq}}) \cdot r_{\text{particle}}^2 \cdot g}{9\eta_{\text{aq}}}$$

### 2.6.2. Electric and Molecular Attraction

#### 2.6.2.1. Coulombic Attraction

Coulomb's law (Eq. IX) describes the interaction between two charged bodies A and B (point charges) in vacuum at a distance  $l$  from each other, as follows.

$$\text{Eq. IX} \quad F = \frac{q_A \cdot q_B}{4\pi \cdot \epsilon_0 \cdot l^2}$$

---

<sup>7</sup> Definitions for parameters and variables in the expressions are given in Section 10.

<sup>8</sup> Note that this is only really true for stagnant water. For water in laminar flow, the constant falling velocity will be valid in relation to the moving co-ordinate system given by the water flow rate. For turbulent flow, convection will influence or override the gravitational force.

An attractive force (negative expression in Eq. IX) is obtained if the bodies have opposite charges, otherwise we obtain a repulsive force. The expression is, of course, more complicated for a particle of some extension or a small particle moving close to a planar surface or interaction takes place in a dielectric medium, such as water.

#### 2.6.2.2. *van der Waals Attraction*

The van der Waals force,  $F_{vdW}$ , is an attractive force interacting between all uncharged atoms and molecules. The origin of this attractive force is the mutual polarisation due to electron cloud distortion. The force is given by the following expression [ref. 9], for a sphere at a distance  $l$  from a planar surface.

**Eq. X** 
$$F_{vdW} = \frac{A_H \cdot r_{part}}{6 \cdot l^2}$$

The Hamaker constant,  $A_H$ , is reportedly in the order of  $2 \cdot 10^{-20} - 8 \cdot 10^{-20}$  J at 20°C for water-oxide systems [ref. 9]. The van der Waals force is hence very small except at distances in the order of a few nm or less. The expression in Eq. X is actually only valid for  $l < 100$  nm. The actual Hamaker constant value in high temperature water has not been reported to our knowledge and can be different due to the changed water structure at elevated temperatures in comparison to at room temperature.

Since the force grows only linearly with the diameter, the importance of the van der Waals force is much more pronounced for small particles than for larger.

#### 2.6.2.3. *The Double Layer Impact*

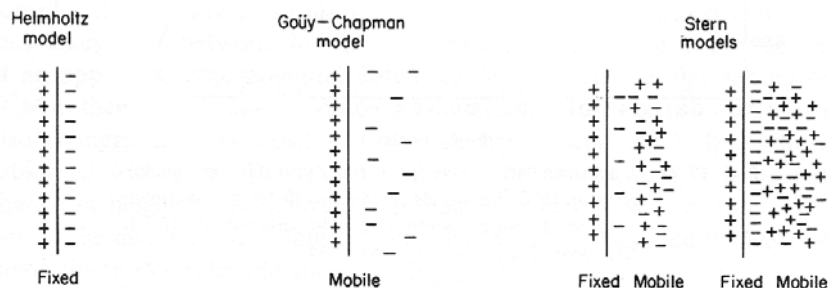
A surface that is exposed to a medium will immediately interact with that medium. In a gas, the gas molecules will collide with the surface, either without chemical interaction (elastic collision) or with interaction, when some attractive or repulsive forces will affect the collision. The extent of interaction will depend on the electric charge and surface properties of the surface and the chemical form and electric charge of the gas.

Interaction between a surface and the medium will also occur when the medium is a liquid. Important parameters are, of course, the electric charge and surface properties of the surface, and the dipolar properties of the liquid, and properties and amount of any dissolved matter in the liquid. Water, which has a very dipolar molecule and a high dielectric constant, will exhibit very strong interactions between many surfaces and the water.

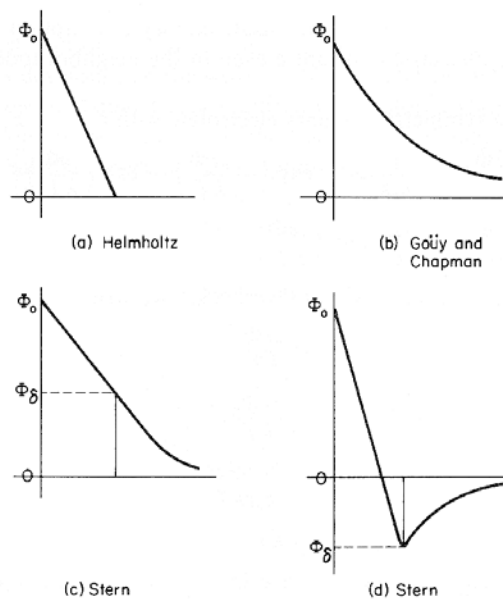
If the surface has a positive or negative charge, the water molecules will preferentially orient the adsorbed water molecules with the oxygen atoms or the hydrogen atoms, respectively, towards the surface. The water molecules will have a rather strong binding force to the surface since we have a very short distance and an electric interaction between the water molecules and the surface (see Eq. IX).



Since we have a preferential orientation of the water molecules, there will be a strong electric field variation close to the surface. First, we have the intrinsic surface charge. On the surface, we have the water molecules oriented by the attraction, hence having the opposite charge closest to the surface, but then having the same sign of the charge (although not exactly the same charge due to geometry, losses etc.) just one water molecule depth onto the liquid. Any chemical or electrochemical reactions or other interactions taking place at the surface will depend very much of the orientation, since the local electric field is very strong due to the water molecule preferential orientation. This first layer of oriented molecules of the solvent is called the Helmholtz layer, after the model developed for this interaction by Helmholtz. The principle of the “Helmholtz layer” is shown in Figure 5. Due to the mobility of the solvent molecules, the preferential orientation will not (only) be a fixed layer but rather will the preferential orientation be dispersed into the solvent forming a decaying solvent molecule orientation going from the surface out into the solvent. A model for this behaviour was developed by Gouy and Chapman, and such a model with a diffusive layer is called a “Gouy-Chapman” model. A mixed model, being most accurate, was eventually developed by Stern. The complexity of the model is, of course, increasing, going from the static, via the dynamic to the mixed. The simpler models are consequently sometimes used to illustrate the behaviour. Typical calculated electric fields close to the surface are shown for various models in Figure 6.



**Figure 5. The different models for the interaction of surface and solvent. To the left the static Helmholtz model, with the “Helmholtz layer”, in the middle the dynamic (mobile solvent) Gouy-Chapman model with the “diffusive layer”, and to the right the mixed Stern model. From ref. 7.**



**Figure 6. Schematic presentation of typical examples of the electric fields close to a surface in a solvent according to the Helmholtz, Goüy-Chapman, and Stern models. Example (d) is showing a case of specific adsorption. This means that some species in the solvent is chemically bound to the surface (e.g. iodine to a steel surface) and hence the surface Helmholtz plane (the outmost part of the Helmholtz layer) will have the opposite sign of the charge compared to the case without specific absorption. From ref. 7.**

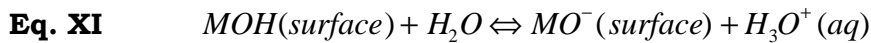
In some cases, as when the surface is an oxide, we have a preferential surface charge due to the chemical form of the surface. Such cases are, actually, the most common in the LWRs and will be treated in more detail in Section 2.6.2.3.1.

#### 2.6.2.3.1. Zeta Potential Influence

Particles (see Section 2.6) and colloids (see Section 2.5) can have a certain surface charge, i.e. a charge separation between the surrounding liquid (“electrolyte”) and the particle surface may occur. The mechanisms producing such a charge separation are the following.

1. Specific adsorption of ions from the electrolyte onto the surface (see Figure 6)
2. Preferential dissolution of an ion from a crystal lattice
3. Ionisation of surface groups

Of special attention is the influence of the hydrogen ion activity on the surface charge. Very common in all water-oxide systems is the following normally reversible reaction.



The charge of the surface is hence changed due to the equilibrium with the proton activity, normally referred to as the pH. In one particle of a given composition, it is possible that several equilibria such as shown in Eq. XI can be effective simultaneously, depending on the actual chemical composition of the particle. Of special interest is the situation when the net surface charge of the particle will be zero, i.e. when the number of positive and negative charges are equal<sup>9</sup>. This point, which occurs at a certain pH value for a given oxide at a given temperature, is called the “Point of zero charge”, PZC. Since the deviation from the PZC will result in a net charge, and since the charge will produce a potential, the surface potential,  $\psi(0)$ , will be given by Eq. XII [ref. 9].

**Eq. XII** 
$$\psi(0) = \frac{R \cdot T}{F} (PZC - pH)$$

Because of the influence of the double layer effect, the practically used measure is not the surface potential, but instead the “zeta potential”. This is the electrical potential in the shear plane (the net charge effect with the adhered diffusive layer (see Section 2.6.2.3), which is retained during movement of the particle in the electrolyte). The definition of the zeta potential,  $\xi$ , is as follows.

**Eq. XIII** 
$$\xi = k_\xi (IEP - pH)$$

Note that we now use the IEP (iso-electric point), which is the pH when we have zero net charge in the shear plane. This pH is not equal to the pH for the PZC of the surface, due to the double layer effects, i.e. the presence of the Stern, as well as the inner and outer Helmholtz layers, see Section 2.6.2.3. The difference between IEP and PZC can be significant if we have specific absorption, i.e. when the surface has a specific affinity for a certain ion in the medium<sup>10</sup>. Generally, it can be assumed that the concentration of the ions is too low in BWR water to produce such specific absorption.

One problem with the zeta potential approach is that there are very few measurements reported from elevated temperatures, due to experimental difficulties. Of considerable value is therefore the following (Eq. XIV) thermodynamic relation derived by Bérubé and de Bruyn, found consistent with observations by Tewari and Campbell [ref. 11].

**Eq. XIV** 
$$4.6 \cdot R \cdot (0.5pK_w - IEP) = \frac{\Delta H_{H^+,OH^-,surf}}{T} - \Delta S_{H^+,OH^-,surf}$$

---

<sup>9</sup> A special case occurs of course when the surface has no negative or positive charges at all. This situation is, however, for oxides in water, probably never the case, due to internal effects in the particles giving the surface non-uniform chemical potential.

<sup>10</sup> Examples of ions often producing specific absorption are iodine and other complex forming ions.

The thermodynamic values refer to the transfer of the  $H^+$  and  $OH^-$  from the bulk to the interfacial region. Since few measurements have been performed at elevated temperatures, this expression allows the extrapolation to the temperatures of interest.

Eq. XIV implies that there is an inverse linear relationship between the absolute temperature and the zeta potential. This suggests that the zeta potential influence should be weaker at LWR operating temperature than at room temperature.

**Table 1**

**IEPs in water for some important oxides at ambient temperature**

Material	IEP	Reference
$Fe_3O_4$	6.5	ref. 12
$\alpha-Fe_2O_3$	5.5	ref. 12
$\alpha-Fe_2O_3$ (hydrous)	8.6	ref. 12
$ZrO_2$	4.0	ref. 12
$ZrO_2$ (hydrous)	6.8	ref. 12
NiO (hydrous)	11.0	ref. 12
CoO (hydrous)	11.2	ref. 12
CuO (hydrous)	9.5	ref. 12
ZnO (hydrous)	9.0	ref. 12
$Cr_2O_3$ (hydrous)	7.0	ref. 12
$NiFe_2O_4$	~7.0	ref. 13

*“hydrous” means that the oxide contains bound water at least to some extent*

The IEP of many oxides and hydroxides has been reviewed by Parks [ref. 12]. He states that (at least at room temperature) the surfaces of hematite ( $\alpha-Fe_2O_3$ ) and zirconium oxide ( $ZrO_2$ ) normally are hydrated on the surface, and hence the IEP for hematite is rather given as for  $\alpha-FeOOH$  than for the oxide<sup>11</sup>. Whether this is the case at full reactor temperature is not known. Parks reports evaluated values of the IEP as given in Table 1.

It can be immediately noted that the IEP is very dependent on whether the particles are hydrous, i.e. have significant amounts of water in the structure or not. The higher temperature in an operating LWR will possibly speed up the process to have a more anhydrous structure [ref. 14], especially for the zirconium oxide. The hematite will assumedly have a value in the range between the anhydrous and

<sup>11</sup> Of course, in doing measurements in water, this distinction is normally not noted, since the chemical form of the surface in the water is normally not determined. It is, however, important to note the difference when comparing values measured in water with any theoretical evaluations or comparisons with values from measurements by other methods under quite different conditions.

hydrous structures, since there is a constant input of iron mainly in the hydrous iron hydroxide form from the corrosion at lower temperatures in the turbine and feed water systems in the BWR. In the PWRs, there is normally no hematite but nickel ferrite particle input, with an IEP that could at least tentatively be approximated by that of the magnetite. This indicates that there is an IEP difference between zirconium oxide and the iron oxides, according to Table 1. The difference is probably similar at full reactor temperatures, according to Eq. XIV. This implies that attractive electro-kinetic forces between hematite and a fresh fuel surface is existing in a BWR, but probably not between magnetite or nickel ferrite in the PWR (due to the higher pH).

In a more recent work, the IEP was found to be 4.0 for  $\alpha\text{-Fe}_2\text{O}_3$  and 6.6 for  $\text{ZrO}_2$  at 25°C [ref. 15], to be compared with the (critically evaluated) data in Table 1. It was, however, obvious that the scatter in IEP between samples of solid oxides was significant (but not reported) in the experiments. This indicates the difficulty in assessing the aspect of the IEP difference properly without additional accurate measurements.

#### 2.6.2.3.2. Other Electro-kinetic Phenomena

There are a number of other electro-kinetic phenomena that occur in a system with charged particles in a fluid, as listed below [ref. 7]:

- Electro-osmosis, the flow of matter due to an electric current, by uniform pressure
- Electro-osmotic pressure, the pressure difference due to a potential difference when the flow of matter is zero
- Streaming potential, the potential difference due to a pressure difference at zero electric current, given by Eq. XV [ref. 16].

**Eq. XV** 
$$i_{stream} = \frac{\Delta P \cdot D \cdot r^2 \cdot \xi}{4\pi \cdot \eta \cdot l}$$

Although the quantification of these electro-kinetic effects is often hard to derive in the real systems, since the electro-kinetic phenomena are governed by the zeta potential, it should be noted that some potential difference will occur due to the flow of electrolyte, that is the LWR coolant in core and piping.

#### 2.6.3. Influence of Magnetic Properties

The magnetic interaction force,  $F_{magn}$ , between a uniformly magnetised sphere in contact with a flat surface of a semi-infinite magnetizable medium has been derived by Rodcliffe and Means [ref. 9] as follows.

**Eq. XVI** 
$$F_{magn} \approx 0.8\mu_0 \frac{(\mu_r - 1)}{(\mu_r + 1)} M^2 \cdot r_{part}^2$$

The magnitude of the attraction force  $F_{mag}$  is approximately independent of the distance, as long as the distance to the flat surface is much smaller than the radius of the sphere.

The relative permeability is related to the magnetic susceptibility,  $\chi_m$ , which is normally found listed, as  $\mu_r = 1 + \chi_m$ . The magnetic properties for two important particle materials are given in Table 2.

**Table 2**  
**Magnetic properties**

Material	Composition	Saturation magnetisation	Curie temperature	Reference
Magnetite	$\text{Fe}_3\text{O}_4$	$4.85 \cdot 10^5 \text{ A} \cdot \text{m}^{-1}$	848 K	ref. 9
Theorize	$\text{NiFe}_2\text{O}_4$	$2.40 \cdot 10^5 \text{ A} \cdot \text{m}^{-1}$	863 K	ref. 9

It should be noted that the magnetic susceptibility is affected by the temperature, and is actually 35% lower at 288°C than at 25°C for  $\text{NiFe}_2\text{O}_4$  [ref. 17].

#### 2.6.4. Geometry Influence - Surface Roughness

At least qualitatively, it would be expected that a smooth surface would have less ability to collect and retain particles than a rough surface. It is also true that the drag force due to the flow (see Section 2.7.1) has less friction counteracting the removal of a particle on a smooth surface. In reality, however, the surface roughness or geometry effect seems to be negligible. Hence, it was found that the deposition rate under boiling conditions was linear going from smooth metal surfaces (stainless steel, platinum, copper), via spotted hematite layers to rather thick hematite layers with obvious pits [ref. 18]. This implies that the surface roughness is not important during boiling conditions. During non-boiling conditions (i.e. PWR lower half of core), it is less certain that there is negligible influence. In reality, however, considering the influence of crud in cladding corrosion, experience has shown us that it is possibly only boiling conditions that will give us adverse conditions, we may conclude that any surface roughness effect in particle depositing on LWR fuel cladding is of third order.

#### 2.6.5. Assessing the Relative Influence of Depositing Phenomena

The electric forces between particles of similar composition are repulsive due to the similar electric surface charges. The same situation is also true for a particle close to a surface of similar composition, for instance a hematite particle close to a fuel crud layer. Nevertheless, if the distance between the particles is sufficiently small (<approximately 5 nm in water), the attractive forces of the van der Waals attraction will be effective, attracting and possibly adhering the particle to the

other particle or surface. This “collide-and stick” mechanism is certainly of importance when it comes to particle agglomerating, when colloidal particles agglomerate to form larger particles, but could also be of importance in coolant borne particles. Since this is a surface attraction, it means that the larger the particle, the less important are the adherent and retaining forces in relation to the mass and volume of the particle. This effect will certainly mitigate any van der Waals attraction mechanism for deposit and agglomeration of larger particles.

One very important aspect regarding the influence of the double layer and the zeta potential is that in the steady-state situation there will probably only be repulsive forces between the fuel surface and the particles in the coolant, as noted already by Rodcliffe and Means [ref. 9]. The idealised situation with a  $ZrO_2$  surface interacting with coolant-borne magnetite or hematite particles often contemplated, e.g. by Lister [ref. 19], will only be a very short-term situation while the fresh fuel, probably within days, will be covered with the first thin layer of deposited crud. From then on, the interaction will be within a fuel surface covered with a surface layer of deposited crud of the same composition as the coolant-borne particles. Even if we have a constant transformation of the inner parts of the crud layer, producing nickel spinels etc. (see Section 3.2), the outer parts, controlling the zeta potential interaction with the particles in the coolant, will consist of a layer of deposited crud. Only in transient situations can we expect a possible difference in the chemical composition and hence a possible change in the zeta potential between the surface and the particles. A zeta potential difference producing a possible attractive force between the surface and the particles in the coolant is hence probably of very little importance for deposits in LWRs. Much more important is the repulsion produced by equal zeta potentials. This repulsion has to be small in order to allow attractive forces to adhere the particles to the surface to build up the crud layer.

There is one report very often referred to being an classic example of the zeta potential effect causing crud deposits. It is the report by Gasparini and Ioanelli [ref. 13] from the Garigliano BWR. There were massive nickel ( $10 \text{ g}\cdot\text{h}^{-1}$ ), iron ( $7 \text{ g}\cdot\text{h}^{-1}$ ), and copper inputs during a certain period. The heavy fuel deposits resulting from the corrosion products inputs caused the core pressure drop to increase by up to 0.3 bars. The main reason to the pressure drop was formation of copper rich (>60% copper) deposits in the bottom tie plate. Based on a theory Gasparini et al. had developed a few years earlier [ref. 8], they concluded that the reason was the adherence of hematite on the zirconium oxide of the cladding (see Table 1 for zeta potential differences). They further concluded that the positive effect<sup>12</sup> they saw from injection of nickel hydroxide was that trevorite (nickel ferrite) was formed in the flow and on the crudded surfaces. The trevorite, having an IEP of neutral pH, would according to Gasparini et al. not stick but would have been released due to the flow erosion since there was no zeta potential attraction. It seems today in the light of the new knowledge that the conclusions were not correct and that the real

---

<sup>12</sup> *actually, their experiments showing the nickel effect were performed when component materials changes had been undertaken, eliminating the basic problem, so a real positive effect relating to the nickel addition could not have been discerned*

improvement was that the nickel and copper inputs to the plant were reduced, as discussed later in this report. Gasparini et al. should, however have credit for pointing out the importance of the electro-kinetic effects in deposits in flowing systems. There is obviously an important electro-kinetic effect just in the case of magnetite deposits in small orifices (see Section 3.7.3), but not for the more macroscopic effect of fuel deposits in a boiling system (see Section 3.6.1).

It was observed by Iwahori et al [ref. 18] in experiments with hematite particles depositing on heat-transfer surfaces at atmospheric pressure, that once boiling was occurring there was no influence of applied potential of the heat-transfer surface. This implies that once boiling occurs the mechanism described in 3.6.1 is much more controlling than any surface charge effects. In the BWR (and probably also in the PWR), we should hence concentrate on the boiling effect rather than the electro-kinetic effect when it comes to deposits on the fuel cladding.

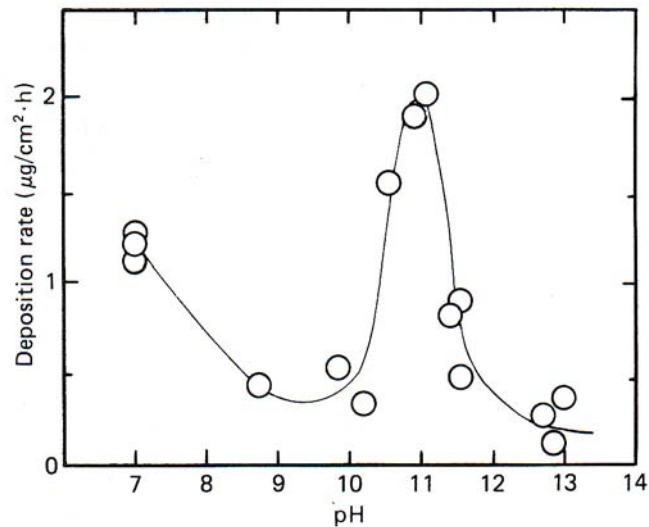
In the short-term experiments of hematite deposition by boiling performed at atmospheric pressure by Iwahori et al. [ref. 18], it is obvious that there is nevertheless a pH effect on the deposit rate. This is showing up as a minimum in deposits in experiments performed with a pH ~8.5 (which perfectly corresponds to the IEP of hydrous hematite, see Table 1) for the deposit on metallic surfaces (platinum, silver, stainless steel SS 304, and copper)<sup>13</sup>. Interestingly, the deposits on a Zircaloy-2 surface, which always has a thin ZrO<sub>2</sub> layer after contact with air or water, had a strong dependence on the rate and saturation level of hematite with pH. Hence, at pH 2, the saturation level was only 1% of the level at pH 6 (which had the maximum level), obtained in the same time. In experiments in simulated BWR conditions (without radiation), Kawaguchi et al. [ref. 20] found exactly the same minimum in the deposition rate for a pH<sub>25°C</sub> of 8.5 – 9 on a ZrO<sub>2</sub> surface (with a 5.8 W·cm<sup>-2</sup> heat flux, 1 ppm of iron). A considerable maximum was found around pH<sub>25°C</sub> 11, see Figure 7.

On the contrary, Hermansson and Arveson [ref. 21] found for a low-flow non-boiling system (in practice almost stagnant) that the deposition of “~FeOOH” had a very pronounced maximum when the zeta potential was zero, which occurred at pH 7 at 25°C.

---

<sup>13</sup> *in oxygenated water, the metals normally have a positive zeta potential, in hydrogenated water a negative potential*





**Figure 7. Deposition rate of hematite particles in simulated BWR conditions (without radiation). Heat flux  $5.8 \text{ W}\cdot\text{cm}^{-2}$ . From Fig 11, ref. 20.**

Not only boiling will have an important effect, but also the high in-core flow rate in itself is important in understanding the deposit process. The turbulence will give a possibility for a particle to overcome any electro-kinetic repulsion forces. The turbulence will produce a velocity vector for the particle in the normal direction towards the cladding surface. Larger particles with a higher momentum can overcome considerably larger repulsive barriers and have a possibility to reach the surface despite the repulsion. This aspect has been analysed by Urrutia et al. [ref. 15]. The need for a distribution of the transversal velocity vectors for the particles makes the quantification difficult, however. It should, however, be remembered that this effect could produce deposition in turbulent high flow systems although the repulsive forces are larger than the attractive forces. Urrutia et al. do point out that the Brownian motion will not be sufficient to give any significant momentum to overcome reasonable expected repulsive forces in the LWR fuel - coolant colloid situation.

## 2.7. PARTICLE TRANSPORT

### 2.7.1. Hydrodynamic Re-suspension Force

The drag force,  $F_{drag}$ , in tangential direction due to a medium flow acting on a spherical particle resting on a surface has been derived and discussed in detail by Rodcliffe and Means [ref. 9]. The calculated drag force is proportional to the square of the flow velocity (averaged over the projected area of the particle in the flow) and, as expected, the square of the particle radius, as shown below.

**Eq. XVII**       $F_{drag} = const \cdot u_{flow}^2 \cdot r_{part}^2$

This means that the relative drag force actually decreases with increasing particle diameter (since the mass increases with the cube of the radius). In reality, the adhesion forces are, however, relatively weaker with increasing radius for spherical particles on a flat surface (see Section 2.6). This means that there is a certain particle size where the drag force is too large (at a certain flow velocity) to retain the particle. The very largest particles will hence not stick to the cladding surfaces but instead go with the flow, possibly until either

- the particle is mechanically stuck in a narrow component (e.g. a spacer grid)
- the particle is reaching a low-flow area where gravity (see Section 2.6.1) will allow deposition (typically in the low flow of the control rod guide tubes in the BWR).

Calculations for a sphere on a flat surface [ref. 9] have shown that the van der Waals force (always present) will be larger than the drag force for all particles smaller than approximately 1 µm at a flow of 0.3 m·s<sup>-1</sup>. In reality, the additional adhesion forces normally present, the in reality rougher surfaces, the more irregular particle form, etc. will further increase the limiting size to significantly above 1 µm diameter. Very large particles (above some 5 µm?) will, however, not stick to the cladding or crud surfaces but will be re-suspended, even if the larger momentum in the turbulent flow (see Section 2.6.5) will give such particles a relatively high probability to reach the cladding surface again.

### 3. OBSERVATIONS AND THEORY

The fuel crud deposition phenomenon does include seven different steps, as follows [ref. 2].

1. Generation (of corrosion products)
2. Release (of corrosion products, due to dissolution, erosion or scaling)
3. Transport (by the coolant)
4. Deposition on the fuel elements
5. Release from the fuel element
6. Transport by the coolant
7. Deposition on, or incorporation in, system surfaces

In the following, we will discuss the various phenomena in this listing for both PWRs and BWRs.

### 3.1. CRUD SOURCES

#### 3.1.1. Corrosion and Corrosion Release

Corrosion is the process by which the environment will degrade a material. More specifically for metallic materials, this involves the process by which the metal is oxidised by the environment. During the metal oxidising process, oxides or salts are formed. If the formed oxides or salts have a high solubility in the corroding environment, or inferior physical forces between the corroding surface and the solid corrosion product exist, there will be a considerable corrosion release, i.e. dissipation of the formed corrosion products to the surrounding. If the solubility is low or the physical interaction force is high (see Section 2.6.2), all or a large part of the formed corrosion products are left (or re-deposited) on the corroding metal. A special case occurs when the formed corrosion product is forming a dense and protecting layer impeding further corrosion attack. The formed corrosion film is then called a passivating film, since it hinders and in some cases almost inhibits further corrosion attack.

It should be clear when we discuss corrosion that corrosion is never controlled by thermodynamics, but always by the kinetic rate of the corrosion process. This rate is normally controlled by one or several chemical reaction rates. Any thermodynamic treatment of the corrosion behaviour will hence only give an understanding what chemical transformation are possible, and what the final, asymptotic goal will be for a certain material in a certain environment. The corrosion process will, however, in most cases never reach that goal in the lifetime of the plant. This is also what we rely on: that only a few tens of micrometers of the stainless steels or Zircaloy structural material will be consumed within 5 to 40 years in operation.

The use of virtually every material in the LWRs is based on the principle of a passive corrosion film. Hence, even such metals as zirconium alloys, which are thermodynamically very unstable, and react almost explosively with water even at room temperature, are protected from aggressive corrosion attacks by a very dense and relatively impervious film of corrosion products [ref. 22]. This means, of course, that any chemical or physical effect on the protective film will pose a considerable potential risk for very quick corrosion attack of the material. This could threaten the structural integrity, of, for instance, Zircaloy cladding or carbon steel piping, but this is not the scope of this review, and is not further discussed, except of some special cases regarding effects on zirconium alloys.

Accelerated corrosion is, however, important in the present context since this could lead to excessive corrosion release, resulting in elevated corrosion product input to the RPV and thus threatening to deposit on the fuel in excessive amounts. It must be pointed out that increased corrosion does not necessarily lead to increased corrosion release, but is a matter of the actual materials and the environment. By this, we should also be aware that changes, even small changes, in the environment, could affect the corrosion rate and the corrosion release considerably. Temperature, pH, oxidising potential (i.e. whether excess of oxidising or reducing species are available in the environment, i.e. coolant in our

case), and specific impurities are important factors in determining the corrosion rate and corrosion release.

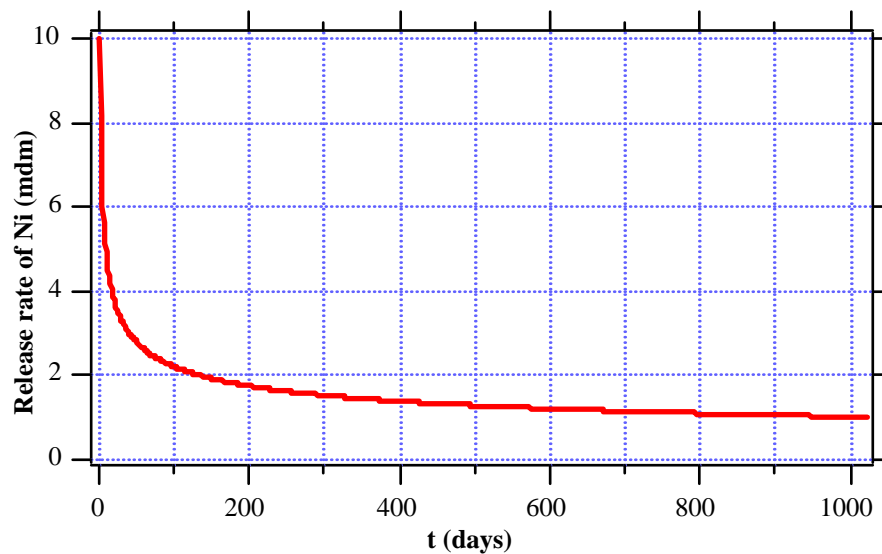
The corrosion release could be in the form of ions dissolved, that is, the corrosion product release given by a expressions like Eq. III – Eq. V, which is the actual case for iron release from magnetite films in reducing environments. In other cases, the release could be in the form of colloids or small particles, as is often the case with rust, i.e. release of oxidised iron compounds from carbon steels in more oxidising conditions. The corrosion release could also be in the form of scales, that is flakes of oxide released to the environments, as is normally the case for corrosion release from Zircalloys. In the latter case, the oxide flakes could remain as flakes, then being able to produce extreme radioactive hot-spots if released from radioactive materials. They could also in such a case form a physical hinder to flow, if the flakes stick in narrow locations. Flakes could also, at least in principle, be transported as flakes, in a new local environment become soluble, and hence release the corrosion products in a different form in the new location.

Most materials in the LWR, carbon steels (in feed water piping etc.), low-alloy steels (in turbine system piping), stainless steels (in RHR piping), nickel-base materials (Inconel, Alloy 600, etc. in in-core components and PWR steam generators), Stellite (in valves), and zirconium alloys (in fuel cladding and BWR flow channels) rely on the principle of a passivating oxide film. This is also why the water chemistry of the PWR is adjusted with lithium and hydrogen, i.e. to have the best possible passive film and lowest possible corrosion release (of the nickel base material in the steam generators). The passive films are sometimes of constant chemical composition, as for the corrosion film on zirconium alloys [ref. 22] or a double layer, with the inner layer being a diffusion barrier, and the outer a protection against attack of the environment on the diffusion barrier, as for stainless steels [ref. 23].

The passive film is in reality always a barrier against mass transport, i.e. hinders the release of oxidised ions (for all steels and nickel base alloys) or intrusion of oxidants (for zirconium alloys). The corrosion attack and corrosion release,  $r_{corr}$ , is therefore depending on the oxide film thickness under otherwise constant conditions. This dependence is often given by the inverse square or inverse cube of time, as shown in Eq. XVIII.

**Eq. XVIII**      $r_{corr} = k_{corr} \cdot t^{-n}$       $n = 0.33 - 0.5$

A typical example is shown for Inconel in simulated BWR environment in Figure 8.



**Figure 8. Corrosion release from Inconel X-750 in BWR environment**  
*Data from ref. 24.*

The corrosion release from stainless steel, carbon steel, and nickel-base materials will follow a curve such as the one in Figure 8. This means that a much higher corrosion release is found for new surfaces, which have a very thin corrosion film. This explains why many LWR plants have had crud problems during the first cycle of operation (see Sections 4.4 and 5.1), and after extensive decontamination (see Sections 5.5.2 and 5.9).

After a year or so in the plant, the corrosion and corrosion release curves, as shown in Figure 8, seem less and less time dependent, and the corrosion behaviour is then approximately constant. Very often, a constant value for the corrosion product formation is therefore reported in the form of “mg of corrosion product formed per month and per dm<sup>-2</sup>”, normally abbreviated as “mdm”.

The corrosion and corrosion release are normally similar for stainless steels and nickel base materials both in PWR and BWR environments, with values typically as given in Figure 8 for BWRs. For carbon steels, the corrosion rate and corrosion release is about 10 times higher [ref. 25, ref. 26].

In some cases mass balance calculations have been performed to assess the corrosion release rate for various materials [ref. 27]. Such evaluations should be treated with care, since they assume a corrosion release proportional to the composition of the corroding material, which is often not true. Instead, preferential dissolution of iron is often recorded from stainless steels and nickel base materials.

### 3.1.2. Materials Corroding in the LWRs

Zirconium alloys are sometimes releasing particulate matter, i.e. oxide scales. It is also often reported that zirconium oxide has a notable solubility, and that

zirconium in soluble form should be circulating in the LWR coolant. However, not even radioactive zirconium (Zr-95 and Zr-97 or Nb-95 and Nb-97) are found in measurable amounts in soluble form (but always in particulate form) in a BWR. There could be two reasons for this discrepancy, either is the zirconium deposited during cooling in sampling lines, or the claims of a relatively high solubility wrong. Considering the extremely large areas of Zircaloy and the normally very low concentrations even of particles of activated zirconia, it is most probable that the real solubility of zirconia is very low. The elevated pH by at least 1 – 1.5 orders of magnitude will possibly increase the zirconia solubility in the PWR coolant, but the soluble zirconium (as a hydroxide complex, see section 2.2) is still very low, probably only a small fraction of a ppb.

**Table 3**  
**Estimated relative surface areas of reactor materials [ref. 2]**

Reactor Type	Material	Relative Area	Remark
US PWRs	Zircaloy-4	20%	Fuel cladding
	Inconel 600	75%	Mainly steam generators
	Stainless steel	5%	
US BWR (GE)	Zircaloy-2 and -4	48%	Fuel cladding and channels
	Stainless steel	44%	System piping and RPV buttering
	Carbon steel	8%	
AECL PHW (PWR)	Zircaloy <sup>14</sup>	13%	Fuel cladding
	Monel 400, Inconel 600, or Incoloy 800	77%	Mainly steam generators
	Carbon steel	10%	
AECL BLW (BWR)	Zirconium Alloys (Zry-2 and Zr2.5Nb)	18%	Fuel cladding and pressure tubes
	Carbon steel	84%	

<sup>14</sup> Actually, both Zircaloy-4 as fuel cladding and Zr-2.5Nb as pressure tubes are in contact with the coolant in the AECL PHW.

HWC plant had, however, problems with control rod drift due to magnetite clogging of the control rod drive crud clean-up flow, fed with water from the RWCU [ref. 73]. Obviously, the extremely reducing conditions in the RWCU system, further depleted in oxygen and hydrogen peroxide during transport to the control rod drives had dissolved extreme amounts of iron, also visible in the high reactor water concentrations of iron recorded simultaneously. This recent incident is hence a combination of the design (the control rod drive crud clean-up flow taken from the RWCU instead of auxiliary feed water, not having a high hydrogen concentration) and HWC operation. The risk for the fuel is of course a control rod drop following the control rod drift, which could be quickly reversed due to a pressure or chemistry transient. Again, this phenomenon has to be considered in all systems where a locally reducing condition is occurring and where extensive magnetite crystal formation could be a problem.

#### 3.7.4. Solubility of Crud

An impressive amount of work has been done in order to investigate the solubility of the various phases in the crud as described in Section 3.2. Such measurements have also been extensively reviewed [ref. 2]. As pointed out by Turner [ref. 75], most of such measurements have been performed without having control of the most fundamental rule in order to establish thermodynamic solubility equilibria, the Gibbs' phase rule [ref. 7]. This states that the degrees of freedom ( $F$ ) has a relation to the number of component ( $C$ ) (basic species) and the number of present phases ( $P$ ) such that

**Eq. XXV**       $F = C + 2 - P$

This means that if we have too few phases present, e.g. only nickel ferrite, in a system with the required components to form the nickel ferrite ( $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{H}_2\text{O}$ ) the number of degrees of freedom is too high, even if we fix the temperature and pH [ref. 75]. The result will hence depend on how much of, for instance, a deposition of  $\text{NiO}$  and/or  $\text{Fe}_2\text{O}_3$  has occurred in the system. If we do not have control of these extra phases, the measurements will only provide results valid for this specific experimental set-up and not fundamental any thermodynamic data.

Consequently, great care should be taken using "solubility" data for mixed phases (i.e. simultaneous presence of at least two different metallic elements) unless the experimenter has considered Gibbs' phase rule in the experiment design and execution.

## 4. POSSIBLE IMPACT FROM CRUD

The possible impacts of crud are the formation of a local environment, 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.

#### 4.1. 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 Section 5.6.1). 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

#### 4.2. 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 increase 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 [ref. 22]. 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 is 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 [ref. 22], often seen in PWRs today, but all such 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 mention in the previous paragraph. In the second case, the crud deposit in its own could provide a 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, as shown in Table 12.



**Table 12**  
**Thermal conductivity of different layers and deposits on fuel cladding at 288°C, 7 MPa**

Layer	Thermal conductivity $W \cdot m^{-1} \cdot K^{-1}$	Ref.	Remark
Water	0.57		
Steam	0.063		
Zircaloy-2	15	ref. 76	At 300°C
Zirconia, sintered	2	ref. 77	At 300°C
Zirconia, corrosion film	4	ref. 77	At 300°C
“Porous magnetite crud”	1	ref. 78	Approx. 90% density
Porous hematite crud	> 6	ref. 48	Approx. 10% density
PWR zinc crud	1.1	ref. 63	At 350°C
CuO	3.3	ref. 76	At 15°C
Compressed hematite	0.5	ref. 76	At 100°C
Dense copper-iron crud	2	ref. 76	At 220°C

In reality, however, much more important than the thermal conductivity is actually the mode of the boiling. It has hence been found that the boiling in porous crud is by so called “wick boiling”, which drastically reduces the thermal resistance of the crud layer. Wick boiling is a process where small pores exist in the crud layer. Water is sipping in to the heat transfer surface by capillary action in the thin pores, 0.1 – 0.5  $\mu\text{m}$  in diameter [ref. 78]. The water then reaches the heat-transfer surface and evaporates. The steam is transported through considerably wider (~5  $\mu\text{m}$ ) pores, which act as chimneys, letting the steam reaching the medium outside the deposited layer. The number of such chimneys is typically 5000 per  $\text{mm}^2$  ( $5 \cdot 10^9 \text{ m}^{-2}$ ) [ref. 78]<sup>35</sup>. The principles and main features of wick boiling are shown in Figure 19.

---

<sup>35</sup> The average distance between the steam chimneys is 14  $\mu\text{m}$  in such a case. The total voidage due to the chimneys is hence approximately 10%.

occur if the hydrodynamic diameter for the flow passage is significantly reduced. The increased pressure drop will reduce the coolant flow and hence will lower the elevation where nucleate boiling starts in the BWR and will risk the start of boiling in a PWR. If the flow is impeded, we will run into risk of having insufficient core cooling, leading to fuel overheating due to dry-out (BWR) or departure from nucleate boiling (PWR). As is discussed in Section 5 below, there seems to be only one case (Tsuruga in 1972 – 1975 [ref. 4]) where such a situation causing failures has been identified, although this situation could have been partly or fully effective in a few more cases, as discussed in Section 5.

There are, however, several cases from the early era of BWR operation when considerable flow restriction and pressure drop was experienced. Hence, in the small Garigliano BWR, a pressure drop of 0.3 bars was experienced, mainly due to deposits in the core tie plate [ref. 13] in the late 1960's. In Isar-1 [ref. 4, ref. 48, ref. 81], up to 8 – 30 mg·cm<sup>-2</sup> of mainly iron crud (hematite) deposits were found. There was in some cases only a very small gap between the crudded rods, yet no fuel failure was experienced in Isar-1. The crud had a very low density, and the average thickness was up to 0.2 mm (8 mg·cm<sup>-2</sup>), with peaks up to 0.8 mm (30 mg·cm<sup>-2</sup>).

In addition, some early PWRs had significant iron deposits, then normally of magnetite. Siemens PWRs with Inconel 600 steam generators had up to 1.7 to 8 (maximum) mg·cm<sup>-2</sup> of crud during the first cycle [ref. 48], and also other PWRs, for instance in Trojan, showed similar crud levels [ref. 4]. One important aspect noted early [ref. 48] was that the excessive crud deposits in the PWR could be very uneven in the rod circumference, as discussed also for later observations in Section 5.6.

## 5. KNOWN CASES OF CRUD-INFLUENCED FUEL FAILURES

It is somewhat distressing to note that it was reported in 1979 [ref. 2], that there was “only a few cases of ...(increased thermal resistance and increased hydraulic resistance due to crud deposits on the fuel)... and these have occurred under unusual operating conditions”. As will be shown in the following, the number of cases today is increasing, and the reason for the deviation from the normal operation is often hard to find.

Reviewing the relative amount of crud or water chemistry induced fuel failures, we can see that the number of crud induced fuel failures is by no means down to zero, but constitute actually the major cause for failures in the BWRs even during the 1990's, as shown in Table 14.

**Table 13**  
**PWR Fuel Cladding Failures 1990 – 1999 [ref. 82]**

Failure Cause	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	Total	
Handling failure		6	2			1	1		2			12	1%
Debris fretting	146	11	67	20	13	6	10	1	10	3		287	29%
Grid fretting	14	18	9	33	36	9	33	52	21	57	5	287	29%
Primary hydriding		1		4								5	1%
Crudding/Corrosion							4		4			8	1%
Cladding creep collapse							1					1	0%
Other fabrication failures	1	15	1	5	3	1	15	5			1	47	5%
Other hydraulic failures					1							1	0%
Unknown					36	36	13	9	10	2	1	107	11%
Uninspected	43	58	35	61	14	3	12	3	8		3	240	24%
<b>Annual total</b>	<b>204</b>	<b>109</b>	<b>114</b>	<b>123</b>	<b>103</b>	<b>56</b>	<b>89</b>	<b>70</b>	<b>55</b>	<b>62</b>	<b>10</b>		100%

**Table 14**  
**BWR Fuel Cladding Failures 1990 – 1999 [ref. 82]**

Failure Cause	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	Total	
Debris fretting	2	2	17	2	6	4		2	3	5	3	46	20%
Grid fretting												0	0%
Fabrication failures	3	3	1	1	1	2						11	5%
PCI		1			2		2	2	1	1		9	4%
Crudding/Corrosion											7	7	3%
CILC	52	5	3						3	46		109	48%
Unknown/Uninspected		4	3	9	7	9	2	10	1	1	1	47	21%
<b>Annual total</b>	<b>57</b>	<b>15</b>	<b>24</b>	<b>12</b>	<b>16</b>	<b>15</b>	<b>4</b>	<b>14</b>	<b>8</b>	<b>53</b>	<b>11</b>		100%

Despite the long time since the first CILC (Crud Induced Localised Corrosion) failures in 1979, there is not enough knowledge to avoid the problems with CILC today, 20 years later (see Section 5.4). The industry is hence in no position to consider crud and water chemistry related fuel cladding failures as a passed problem that current, applied knowledge has eliminated. Yet, as we shall describe in the following, applying the knowledge developed during the last 30 years would have eliminated, or at least let the industry anticipate, some of the failures recorded today, in both PWRs and BWRs.

The first incidences, where water chemistry was reported to cause factual or threatening fuel failures, were caused by the fact that the feed water system in the early BWRs was designed according to fossil plant experience, i.e. with carbon steel feed water piping and copper and nickel alloy heater tubing [ref. 26]. The

difference to the fossil plants was, however, that no corrosion inhibitor could be used in the BWR. This resulted in considerable copper and carbon steel corrosion release, as exemplified below. BWR designs from 1964 and on has consequently been equipped with stainless steel feed water heater piping. The condenser tubing was, however, generally in admiralty brass until the early 1980's. Such condenser tubing was then replaced generally, but not always, to avoid the CILC (Crud Induced Localised Corrosion) failures, see Section 5.4.

### 5.1. EARLY EXCESSIVE IRON DEPOSITS IN BWRS

As mentioned in Section 4.4, a number of plants in the early days of BWR operation did suffer from excessive corrosion, leading to very high iron releases and consequently fuel crud deposits. Eighteen such "high crud events" were listed by Strasser et al. [ref. 4] in a review of crud deposits on BWR and PWR fuel cladding in 1985. They were then divided in three categories, as shown in the following.

- Excessive mainly colloidal and particulate iron oxide crud in full flow demineraliser plants (5 plants)
- Excessive particulate iron oxide crud in forward-pumped heater-drain plants (3 plants)
- Excessive iron and copper crud deposits (10 plants, including the prototype SGHWR, discussed in Section 5.3).

Strasser et al. defined excessive crud as a crud layer above  $5 \text{ mg}\cdot\text{cm}^{-2}$ , which seems to be a very adequate measure, since it was stated in Section 3.6.1 that  $4 \text{ mg}\cdot\text{cm}^{-2}$  hematite deposit normally is the maximum steady-state crud thickness, where fuel crud depositing and release normally balance each other.

Most of these excessive crud cases did not lead to fuel failures. Such non-failure cases were Nine Mile Point-1 in 1972, with a maximum deposit slightly above  $10 \text{ mg}\cdot\text{cm}^{-2}$ , Tarapur and Nuclenor with up to around  $20 \text{ mg}\cdot\text{cm}^{-2}$ , TVO-1 by EOC 1, which had maximum deposit of  $3 \text{ mg}\cdot\text{cm}^{-2}$ . The latter record was actually not very high, but the significant deviation in the crud deposit from the rod average ( $0.74 \text{ mg}\cdot\text{cm}^{-2}$ ) and the high concentration of nickel in the crud, due to the stainless steel feed water piping, were remarkable.

In Tsuruga [ref. 4], there was a most significant crud-induced fuel failure incident during its cycles 3, 4, and 5 (1972 – 1975). In this case, all fuel affected was of the 7x7 type. Densely packed crud was found mainly between the 2 and 3 spacer grid positions from bottom, with typical bottom-peaked axial crud deposition over the rods. Very thick deposits were found in the spacer areas, which were suspected to cause enhanced fuel temperature in these locations. The failures were relatively small. Strasser et al. suspected that some failures were due to PCI, and not due to crud, considering operation with limited operating restrictions and 7x7 fuel. The iron levels in the feed water was up to 55 ppb in average, due to extremely low oxygen level in the feed water, promoting the iron corrosion release (see Section

*cuts have been presented from the River Bend incident in order to determine any lateral cracking or other possibilities for steam blanketing to occur. If the crud layers are really 1 mm thick of adherent crud as reported by Potts, then we have a situation more severe than in the prototype SGHWR incident (see Section 5.3) only that we in the present case do not know the sources of iron and copper.*

One aspect that differs from the CILC and Hamaoka-1 cases (Sections 5.4 and 5.7) is that the cladding does not show any nodular corrosion in the examples above. This indicates that exactly the same phenomenon cannot be controlling in the River Bend-1 as in either of the other cases. It is also notable, that there were no crud deposits on or adjacent to the craters with penetrations. One reason could be the crud cleaning effect often seen by uranium deposited on the fuel (see Section 4.3.2), another that there was no direct correlation between thick crud and the corrosion attacks. The appearance of the River Bend failures is actually rather similar to the failures in KKL, except that the attacks in KKL were only in the spacer shadows and took at least 6 years to develop into penetration. *Another interpretation could be that the River Bend-1 failures actually are dry-out failures, caused by too low assembly coolant flow.* Unfortunately, the available information is yet too scarce to allow a full analysis.

Just as the case in Loviisa-2 (see Section 5.5.2), the source for the iron in the River Bend incidence remains unknown, and even more so for the copper. Mass balance calculations including the feed-water input are implying a much lower expected iron and copper input, since the water chemistry guidelines reportedly were followed. It has been suggested that the elevated iron abundance should be due to excess iron release after decontamination of some larger components. A possible source of copper has not been openly discussed, which is very unfortunate for the industry. The River Bend-1 plant was operating with zinc injection during the last cycle. Detailed and accurate information about the injection rate etc. has not yet been made official.

*It is, again, very unsatisfying that all details about the failure has not been determined or reported, since the nuclear community then still lacks knowledge how to avoid such problems in future.*

## 6. DISCUSSION

### 6.1. EXPLANATIONS FOR WATER CHEMISTRY CAUSES FOR FUEL FAILURES

In 1971, Williamson and Ditmore wrote [ref. 112]: “Cladding failures caused by excessive amounts of system corrosion products depositing on the fuel should not occur in modern BWR plants because of improved feed water treatment and the selection of stainless steel...”. It is thus disturbing that we now experience an increasing number of crud related fuel failures that we do not fully understand. The reason is that the fundamental mechanisms of the fuel failures are so little investigated and hence so little knowledge is gathered from each new case. Not even a reliable mechanism for the CILC problem, having caused so many fuel

failures in a number of plants, has been previously reported, although we provide a brief but consistent model in this report. A correlation between the copper and the CILC is well established, but since copper and zinc are found together in the admiralty brass condenser plants, not even the correlation with copper being instrumental in the corrosion acceleration is well founded. The correlation could in reality be with excessive zinc, or with a combination of copper and zinc instead. It is also possible that many other, yet untested, elements could give similar acceleration.

The situation is even more unsatisfying when it comes to most of the other, more modern, fuel failures caused by an unsuitable water chemistry. The excessive iron inputs in the Loviisa-2 and River Bend (see Sections 5.5 and 5.9, respectively) plants correlate principally with the occurrence of the failures, but not clearly when we compare where in the core the iron deposits and the fuel failures occur. The mechanism for the failures is not at all known.

## 6.2. CURRENT BWR WATER CHEMISTRY TRENDS AND THEIR IMPLICATIONS

Despite the fact that the BWR water chemistry has been developed to be as clean as possible (see Section 2.3), there has been a trend during the 1990's to tailor the water chemistry to decrease either the activity build-up or to mitigate stress corrosion cracking of the stainless steel and nickel base austenitic materials. The BWR reactor water chemistry changes to obtain more reducing condition to mitigate the stress corrosion cracking has been the introduction of hydrogen water chemistry in 1979, and the introduction of noble metal chemical addition in 1996. To improve the radiological situation zinc injection, iron addition, and ultra-low crud operation has been introduced on a wider scale.

There is still a trend to investigate and develop new chemistry regimes, especially to improve the radiological situation such as pH adjustment and mixed metal additions (see for instance [ref. 113]).

It is notable that the effect on the fuel cladding has not been the focus. In several cases of development and test of a new water chemistry regime, the impact on fuel crud and cladding corrosion has not even been investigated within the development programme.

### 6.2.1. Hydrogen Water Chemistry (HWC)

Hydrogen injection (HWC) has been applied on a large scale in the US [ref. 114] and in Sweden. No direct negative impact on the fuel cladding corrosion has been reported [ref. 65]. In some cases, notably in high crud plants, has there been a negative effect on the activity build-up [ref. 162]. This effect is probably caused by the dissolution of deposited crud in the reactor system due to the more reducing atmosphere. Although such an effect could indicate a more pronounced crud transport and increased risk for core deposits in current or former high crud plants, there has been no record of such impact yet.

Extensive experience and no noted correlation between any crud problems and HWC puts this water chemistry regime on the list of possibly innocuous water chemistry regimes in this aspect, at least by application of hydrogen injection rates below 2 ppm in the BWR feed water.

### 6.2.2. Noble Metal Chemical Addition

Noble Metal Techniques are applied in BWRs to enhance the efficiency of hydrogen injection, the so-called HWC (see Section 6.2.1). The purpose of HWC is to minimise the crack growth of stress corrosion cracks in austenitic materials. There are, however, some negative impact from the application of HWC [ref. 115, ref. 6], since it is often necessary to have a rather high injection rate in order to attain a low potential of  $-230$  mV vs. SHE of the austenitic materials, intended to be protected. Noble metal technology was developed to transform the austenitic stainless steel or nickel base material to have an electrochemical behaviour similar to platinum. It would then be possible to use only a slight hydrogen addition level, and hence, in theory at least, to avoid the negative impact from the HWC application.

The principles for use of noble metal in the BWR for this purpose was first suggested by Niedrach and his co-workers [ref. 117, ref. 118]. Since then, several techniques to make the austenitic material in BWR systems to behave similar to a noble metal have been developed [ref. 116].

- Coating of the austenitic material with a noble metal, noble metal coating (NMC), by plasma spraying or other coating technique [ref. 117, ref. 118, ref. 119]
- Alloying of platinum and/or rhodium in the austenitic material (stainless steel or nickel base alloy), so called noble metal alloying (NMA) [ref. 118, ref. 120, ref. 121]
- Depositing the noble metal from a solution containing noble metal(s), noble metal chemical addition (NMCA) [ref. 122]. The noble metal solution is allowed to decompose and deposit noble metal onto all the system surfaces.

Experiments performed to prove the positive effect of noble metal technology (NMT) in order to suppress stress corrosion cracking in stainless steel 304 SS, Alloy 182, and Alloy 600, has been reported from laboratory testing in several publications [ref. 120, ref. 116], also for the NMCA technology [ref. 122, ref. 124]. Only if the level of impurities (sulphate) is very high ( $>1000$  ppb), was the NMT application not sufficient to stop cracking [ref. 120] in the laboratory tests in simulated BWR conditions with reducing conditions (HWC). The NMCA technology application has even been reported to lower the erosion-corrosion, i.e. flow-assisted corrosion, on carbon steels [ref. 126] in laboratory tests. It is,

- High temperature water chemistry is still a rather unknown field. *Except for the development of ECP monitoring even for in core monitoring in commercial plants and some preliminary work on other electrochemical methods to understand the high temperature corrosion of stainless steel and Zircaloy, little has been learnt since the late 1970's.*
- Hydrogen peroxide treatment of PWR primary water during shut-down has been developed since 1979 and is now practically a standard method in order to release crud from the PWR core and collect it on filters. *Although this practice is good in order to minimise the system activity build-up, it means that eventual PIE of the fuel rods will give inadequate results regarding the amount and properties of the crud.*

## 7. CONCLUSIONS

It is obvious that crud related fuel failures are not something that belongs to the past. Elevated fuel duty and enhanced chemical activities in the plant, i.e. chemical additions (see Section 5.8) and chemical decontaminations (see Sections 5.5.2 and 5.9), are obviously increasing the risk for crud related fuel failures, if not investigated and supervised properly.

It is striking that the crud inducing failures in almost all cases develop quickly, in some instances within 40 – 150 days. In this short time, the local corrosion has penetrated the cladding. The corrosion rate is hence several hundred times faster than the normal corrosion, in both the BWRs and the BWRs. This implies that the plant operator cannot rely on annual fuel inspections to have a premonition of fuel degradation.

Another striking fact is that the number of fuel failures generated by the crud induced fuel failures normally is high, typically 10 – 100 pins. This means that the fission gas release quickly can reach the limit for the allowable plant radioactivity release.

The most disturbing fact is, however, that the number of affected assemblies can be high in most cases, typically the main part of one reload or more. This means that the economical consequence is significant if a full reload has to be exchanged or repaired. An even larger financial problem may be the unavailability of a full reload of new fuel with a very short notice, causing forced shut-down of the plant.

The chance for a crud induced fuel failure to occur is, still, lower than for instance debris fretting in a BWR. The risk, i.e. the product of the chance for the occurrence and the potential consequences is much higher. Development of fundamental understanding; deeper analysis of older crud-fuel incidents; improvements of water chemistry and crud build-up monitoring; extended theoretical and practical tests of new water chemistry additions, introduction of new structural material, and decontamination methods; and development of methods and routines for proper investigation of any occurring crud-fuel incidents are all ways to lowering the risk for large scale financial and social consequences from any future crud-fuel incidents.



## **8. ACKNOWLEDGEMENTS**

Prof. Elisabet Ahlberg, Göteborg University, Sweden, is gratefully acknowledged for providing the thermodynamic calculations.

## 9. REFERENCES

- ref. 1        Breden, C. R.  
“Boiling Water Reactor technology status of the art report, vol. 2,  
Water Chemistry and Corrosion”  
Argonne National Laboratory, ANL-6562, 2, Feb, 1963
- ref. 2        Berry, W. E. and Diegle, R. B.  
“Survey of Corrosion Product Generation, Transport and  
Deposition in Light Water Nuclear Reactors”  
EPRI Final Report, NP-522, March 1979
- ref. 3        Urbanic, V. F.; Gray, R.; and Lister D. H.  
“Review of In-Reactor Zircaloy and Crud Deposition Experience at  
AECL”  
EPRI Final Report NP-1254, Dec. 1979
- ref. 4        Strasser, A.; Shepard, K.; and Santucci, J.  
“Corrosion-Product Buildup on LWR Fuel Rods”  
EPRI Final Report, NP-3789, April 1985
- ref. 5        Hazelton, R. F.  
“Characteristics of Fuel Crud and Its Impact on Storage,  
Handling, and Shipment of Spent Fuel”  
Pacific Northwest Laboratory, PNL-6273, Sept. 1987
- ref. 6        Lundgren, K. and Wikmark, G.  
“Möjligheter med OHWC. Utveckling och tillämpning av ECP-  
simulering i svenska BWR. (Possibilities with Optimised HWC.  
Development and Application of ECP Simulations in Swedish  
BWRs)”  
SKI Rapport 00:2, Feb. 2000
- ref. 7        Moore, W. J.  
“Physical Chemistry”  
5th Ed., Longman Group Limited, 1972  
*or other textbook in physical chemistry*
- ref. 8        Gasparini, R.; della Rocca, C.; and Ioanilli, E.  
“A New Approach to the Study and Prevention of Deposits in  
Modern Power Stations”  
Combustion, Nov., 12 – 18, 1969
- ref. 9        Rodcliffe, R. S. and Means, F. A.  
“Factors Governing Particulate Corrosion Product Adhesion to  
Surfaces in Water Reactor Coolant Circuits”  
Central Electric Generation Board, CEGB-RD/B/N4525, 1979

## ZIRAT-6 Special Topics Report on Water Chemistry and Crud Influence

- ref. 10      Alonso, M. and Finn, E. J., "Fundamental University Physics, Vol.1, Mechanics", Addison-Wesley Publ. Comp. Reading, MA, USA, 1971  
*or other textbook in fluid mechanics*
- ref. 11      Tewari, P. H. and Campbell, A. B.  
"Temperature Dependence of Point of Zero Charge of Cobalt and Nickel Oxides and Hydroxides"  
J. Colloid and Interface Sci., 55, 3, 531-539, 1976
- ref. 12      Parks, G. C.  
"The Isoelectric Points of Solid Oxides Solid Hydroxides, and Aqueous Hydroxo Complexes"  
Chem. Rev., 65, 177-198, 1965
- ref. 13      Gasparini, R. and Ioanelli, E.  
"Prevention and Control of Corrosion Product Deposition in a BWR (Garigliano Power Station)"  
Proc. Amer. Power Conf., 33, 776-789, 1971
- ref. 14      Kato, S. and Iwahori, T.  
"Release and Deposition of Corrosion Products in a Simulated BWR Coolant System"  
Proc. JAIF Int. Conf. Water. Chem. Nucl. Power Plants, April 19-22, 1988, Tokyo, Vol. 2, 367- 372, 1988
- ref. 15      Urrutia, G. A.; Passaggio, S. I.; Maroto, A. J. G.; and Blesa, M. A.  
"Model of the Deposition of Colloidal Crud Particles on the Fuel Elements of Nuclear Power Plants"  
Nucl. Sci. Eng, 84, 120-130, 1983
- ref. 16      Tewari, P. H. and Campbell, A. B.  
"The Surface Charge of Oxides and Its Role in Deposition and Transport of Radioactivity in Water-cooled Nuclear Reactors"  
Proc. Symp. Oxide-Electrolyte Interfaces, Ed. Robert S. Alwitt, Electrochem. Soc., 102-111, 1973
- ref. 17      Nishino, Y.; Sawa, T.; Ebara, K.; and Itoh, H.  
"Magnetic Measurements of NiFe<sub>2</sub>O<sub>4</sub> Formation from Iron Hydroxides and Oxide in High Temperature Water"  
J. Nucl. Sci. Techn., 26, 2, 249-255, 1989
- ref. 18      Iwahori, T.; Mizuno, T.; and Koyama, H.  
"Role of Surface Chemistry in Crud Deposition on Heat Transfer Surface"  
Corrosion (NACE), 35, 8, 345-350, 1979

## ZIRAT-6 Special Topics Report on Water Chemistry and Crud Influence

- ref. 19      Lister, D. H.  
"The Mechanism of Corrosion Product Transport and Their Investigation in High Temperature Water Loops"  
Corrosion (NACE), 35, 3, 89-96, 1979
- ref. 20      Kawaguchi, M.; Ishigure, K.; Fujita, N.; and Oshima, K.  
"Deposition of Model Crud on Boiling Zircaloy Surfaces at High Temperature"  
Nucl. Techn., 62, 253-262, 1983
- ref. 21      Hermansson, H-P and Arvesen, J.  
"Parametric Studies of Corrosion Product Deposition in reactor Systems"  
Proc. BNES Conf. Water Chem. Nucl. Reactor Syst. 2,  
Bournemouth 14-17 Oct. 1980, Paper 37, 251-256, 1980
- ref. 22      Waterside Corrosion of Zirconium Alloys in Nuclear Power Plants"  
IAEA TECDOC-996, Jan. 1998
- ref. 23      Robertson, J.,  
"The mechanism of High Temperature Aqueous Corrosion of Stainless Steels"  
Corr. Sci. 32, 4, 443-465, 1991
- ref. 24      Hemmi Y.; Ichikawa N.; and Saito N.  
"Protective Oxide Film on Alloy X750 Formed in Air at 973 K",  
J. Nucl. Sci. Techn. 31(6), 552-561, 1994
- ref. 25      Vreeland, D. C.; Gaul, G. G.; and Pearl, W. L.  
"Corrosion of Carbon Steel and Other Steels in Simulated Boiling-Water Reactor Environment: Phase II"  
Corrosion (NACE), 18, 368t-377t, 1962
- ref. 26      Brush, E. G. and Pearl, W. L.  
"Corrosion and Corrosion Product Release in Neutral Feedwater"  
Corrosion (NACE), 28, 4, 1972
- ref. 27      Polley, M. V. and Pick, M. E.  
"Iron, nickel and chromium mass balances in Westinghouse PWR Primary Circuits"  
Proc. BNES Intl. Conf. Water Chem. Nucl. Reactor Systems 4,  
Bournemouth Oct. 13-17, 1986, 63-70, 1986
- ref. 28      Sandler, Y. L. and Kunig, R. H.  
"The Solubility of Non-Stoichiometric Nickel Ferrite in High Temperature Aqueous Solution"  
Nucl. Sci. Eng., 64, 866-874, 1977

## 10. DEFINITIONS AND NOMENCLATURE

### 10.1. FUNDAMENTAL CONSTANTS

$\epsilon_0$	Dielectric constant in vacuum [ $A \cdot s \cdot V^{-1} \cdot m^{-1}$ ], $8.85418 \cdot 10^{-12}$
$\mu_0$	Permeability of the free space [ $H \cdot m^{-1}$ ] ( $=[V \cdot s \cdot A^{-1} \cdot m^{-1}]$ ), $4\pi \cdot 10^{-7}$
F	Faraday's constant for the charge of one mole of charge [ $C \cdot mole^{-1}$ ], 96 485
R	General gas constant [ $J \cdot mol^{-1} \cdot K^{-1}$ ], 8.3143

### 10.2. TEMPORARY CONSTANTS

g	The gravitation acceleration [ $m \cdot s^{-2}$ ] (the value 9.80665 is normally used, but depends on the location on the earth)
$K_w$	Autoprotolysis constant of water []
D	Diffusion coefficient [ $m^2 \cdot s^{-1}$ ]
$\eta$	Viscosity [ $Pa \cdot s$ ]= $[N \cdot m^{-2} \cdot s]$
$\eta_{aq}$	Viscosity of water [ $Pa \cdot s$ ]= $[N \cdot m^{-2} \cdot s]$
$\rho$	Density [ $kg \cdot m^{-3}$ ]
$\rho_{aq}$	Density of water [ $kg \cdot m^{-3}$ ]
$\rho_{st}$	Density of steam [ $kg \cdot m^{-3}$ ]
$\epsilon$	Dielectric constant [ $A \cdot s \cdot V^{-1} \cdot m^{-1}$ ]
$\mu$	Magnetic permeability []
$\mu_r$	Relative (magnetic) permeability []
$\chi_m$	Magnetic susceptibility []
$A_H$	The Hamaker constant (see Section 2.6.2.2), [J]

### 10.3. VARIABLES

$t$	Time [s]
$T$	Temperature [T]
$l$	Distance or length [m]
$\mathbf{x}$	Distance or length [m]
$A$	Area [m <sup>2</sup> ]
$A_k$	Area of system/component $k$ [m <sup>2</sup> ]
$V$	Volume [m <sup>3</sup> ]
$V_k$	Volume of system/component $k$ [m <sup>3</sup> ]
$d$	Diameter [m]
$\mathbf{v}$	Flow velocity [m·s <sup>-1</sup> ]
$\mathbf{u}_j$	Front growth velocity of $j$ [m·s <sup>-1</sup> ]
$\mathbf{F}$	Force [N](=[kg·m·s <sup>-3</sup> ])
$\mathbf{F}_g$	The gravitational force [N](=[kg·m·s <sup>-3</sup> ])
$f_k$	Flow rate [kg·s <sup>-1</sup> ] for system $k$
$\alpha_{j,i}$	Clean-up fraction [], i.e. relative amount of $i$ leaving system $k$ compared to the amount entering $k$ (has a value between 0 – 1)
$\alpha_{\text{dep}}$	Deposition rate coefficient [] (has a value between 0 – 1)
$C_i$	Bulk concentration of species $i$ [mol·dm <sup>-3</sup> ] (molar (M))
$C_{i,(x=0,t)}$	Surface ( $x=0$ ) concentration at time $t$ of species $i$ [mol·dm <sup>-3</sup> ]
$C_{i,k}$	Concentration of species $i$ in system/component $k$ [mol·dm <sup>-3</sup> ] (molar)
$K$	Equilibrium constant [M <sup>n</sup> ], $n$ depends on the chemical reaction involved
$K_{\text{stab}}$	Stability constant [M <sup>n</sup> ], $n$ depends on the chemical reaction involved
$K_{\text{sol}}$	Solubility constant [M <sup>n</sup> ], $n$ depends on the chemical reaction involved
$k$	Rate coefficient [m·s <sup>-1</sup> ]
$k_{\text{dep},i}$	Deposition rate constant for species $i$ [kg·s <sup>-1</sup> ·m <sup>-2</sup> ]
$k_{\text{rel},i}$	Release rate constant for species $i$ [kg·s <sup>-1</sup> ·m <sup>-2</sup> ]
$h$	Heat [J]
$h_{\text{vap}}$	Heat of vaporisation [J]
$\Delta H$	Differential heat [J·mole <sup>-1</sup> ]
$\Delta S$	Differential entropy [J·mole <sup>-1</sup> ·K <sup>-1</sup> ]

$\Delta H_{H^+,OH^-,surf}$  Differential heat for transfer of  $H^+$  and  $OH^-$  from the bulk to the interfacial region [ $J \cdot mole^{-1}$ ]

$\Delta S_{H^+,OH^-,surf}$  Differential entropy for transfer of  $H^+$  and  $OH^-$  from the bulk to the interfacial region [ $J \cdot mole^{-1} \cdot K^{-1}$ ]

$\left(\frac{dq}{dt}\right)_A$  Specific heat flux [ $W \cdot m^{-2}$ ]

$\mathbf{v}$  Velocity [ $m \cdot s^{-1}$ ]

$r$  Radius [ $m$ ]

$r_{bm}$  Maximum bubble radius [ $m$ ]

$r_{part}$  Particle radius [ $m$ ]

$m$  Mass [ $kg$ ]

$w_{A,i}$  Specific amount of deposit of species  $i$  [ $kg \cdot m^{-2}$ ]

$E$  Potential [ $V$ ]

$U$  Voltage [ $V$ ] (voltage is a potential difference)

$\psi(x)$  Potential at distance  $x$  [ $V$ ]

$\xi$  Zeta potential [ $V$ ] (see Section 2.6.2.3.1)

$q$  Charge [ $C$ ]

$\mathbf{M}$  Magnetisation [ $A \cdot m^{-1}$ ]

## 11. APPENDIX I: THERMODYNAMIC CALCULATIONS

The calculation were performed as formation of each species from the components  $e^-$ ,  $H^+$ ,  $Fe^{2+}$ ,  $Ni^{2+}$ , and  $Cr^{3+}$ , respectively.

Different sources have been used for the evaluation and calculation of constants (see Section 11.1). Whenever extrapolation of the thermodynamic data has been necessary, the following expression has been employed.  $\Delta G_T^0$  is the Gibbs' free energy at temperature T (K),  $\Delta G_{298}^0$  is the free energy in the standard condition,  $S^0$  is the entropy, and  $C_p^0$  is the heat capacity .

$$\text{Eq. XXVI} \quad \Delta G_T^0 = \Delta G_{298}^0 - S^0 \cdot (T-298) + \int_T^{298} C_p^0 dT - T \int_T^{298} \frac{C_p^0}{T} dT$$

### 11.1. LITERATURE USED FOR THERMODYNAMIC CALCULATIONS

- Standard equilibrium potentials in aqueous solution", Bard A. J., Parsons R., Jordan J., Eds., Marcel Dekker, Inc. 1985
- Baes C. F. and Mesmer R. E., "Hydrolysis of Cations", Wiley 1976
- Macdonald D. D., Rummery T. E., Tomlinson M., "Stability and Solubility of Metal Oxides in High-Temperature Water", Proc. Thermodyn. Nuclear Mater. Vienna, 1974
- Zarembo V. I., Slobodov A. A., Kritskii V. G., Puchkov L. V., Sedov V. M., "Thermodynamic Analysis of Coolant Behaviour in a Boiling-Water Reactor on the Basis of the Solubility of the System  $Fe_3O_4-H_2O-O_2$ ", Zhurnal Prikladnoi Khimii, 59, 1030-, 1986
- Paquette J., "The Corrosion of Alloy 600 and Alloy 800 in High Temperature Aqueous Media: Thermodynamic Considerations", Atomic Energy of Canada Limited, Draft Copy, 1990



## 11.2. THE FE-NI-CR SYSTEM AT 573 K USED IN THE THERMODYNAMIC CALCULATIONS

<b>Dissolved species</b>		<b>Solid phases</b>	
<u>SPECIE</u>	<u>log(K)</u>	<u>SPECIE</u>	<u>log(K)</u>
e <sup>-</sup>	0	Fe	-4.69
H <sup>+</sup>	0	Fe <sub>3</sub> O <sub>4</sub>	-15.32
Fe <sup>2+</sup>	0	Fe <sub>2</sub> O <sub>3</sub>	-12.5
Ni <sup>2+</sup>	0	Ni	-1.75
Cr <sup>3+</sup>	0	NiO	-6.1
FeOH <sup>+</sup>	-4.93	Ni <sub>3</sub> O <sub>4</sub>	-34.6
Fe(OH) <sub>2</sub> (aq)	-10.89	Ni <sub>2</sub> O <sub>3</sub>	-31.6
Fe(OH) <sub>3</sub> <sup>-</sup>	-18.23	NiO <sub>2</sub>	-29.39
Fe <sup>3+</sup>	-10.64	Cr	-14.0
FeOH <sup>2+</sup>	-9.35	CrO	-5.42
Fe(OH) <sub>2</sub> <sup>+</sup>	-12.79	Cr <sub>2</sub> O <sub>3</sub>	-2.298
Fe(OH) <sub>3</sub> (aq)	-19.15	Cr(OH) <sub>3</sub> (s)	-1.828
Fe(OH) <sub>4</sub> <sup>-</sup>	-28.75	NiFe <sub>2</sub> O <sub>4</sub>	-16.98
NiOH <sup>+</sup>	-5.94	NiCr <sub>2</sub> O <sub>4</sub>	-9.21
Ni(OH) <sub>2</sub> (aq)	-14.6	FeCr <sub>2</sub> O <sub>4</sub>	-2.55
Cr <sup>2+</sup>	1.1		
CrO <sub>4</sub> <sup>2-</sup>	-46.5		
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	-71.2		
CrO <sub>2</sub> <sup>-</sup>	-14.7		
CrO <sub>3</sub> <sup>-</sup>	-46.5		
CrOH <sup>2+</sup>	0.466		
Cr(OH) <sub>2</sub> <sup>+</sup>	-4.08		
HCrO <sub>4</sub> <sup>-</sup>	-33.8		