SKI Report 00:5

On the Interaction between Fuel Crud and Water Chemistry in Nuclear Power Plants

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SKI perspective

Crud on fuel has both positive and negative effects on the operation of nuclear power plants. The fuel acts as a trap for corrosion products, limiting deposition on other system surfaces where it would result in dose to personnel. The crud can however be unevenly distributed along the fuel rods and thus lead to differences in heat transfer along the rod, resulting in an uneven effect loading on the rods.

This report presents the results of a project aimed at collecting current information on the subject and also providing a means of introducing a new researcher into the field. The approach has been to perform a literature study and relate this to current research, results and information on fuel crud. The study includes an assessment of how crud properties affect its ability to fasten on the fuel in relation to cobalt release and particle size, distribution, porosity and effect on boiling. The work included a review of current models and indicates areas of interest for future research.

As part of his introduction into the area Jiaxin Chen participated in the 1998 International Water Chemistry conference in Kashiwazaki, Japan, and presented a poster, which was based on the initial study. Part two of this report is a short report from this.

This report provides an all round approach to the area. SKI has a continuing concern for maintaining competence and interest in research areas of importance for the safety of nuclear power plants. This work which not only collates the current state of knowledge has also introduced a young researcher to a new application for his particular interests.

Karen Gott
Department of Structural Integrity
SKI project manager

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On the Interaction between Fuel Crud and Water Chemistry in Nuclear Power Plants

Part 1: A Literature Survey

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Abstract

This report has surveyed the current understanding about the characteristics of fuel crud, its deposition and dissolution behaviour, the influences of water chemistry, and the radioactivity transport in nuclear power plants. The references were mainly sought for from the International Nuclear Information System (INIS) CD-ROM database (1970-1998) and some internal reports of Studsvik Material AB.

The characteristics of fuel crud from discharged fuel rods have been extensively investigated over the last three decades. Fuel crud mainly consists of iron, nickel and chromium oxides. For BWR fuel crud the main phases are hematite and non-stoichiometric nickel ferrite spinels. For PWR fuel crud the main phases are non-stoichiometric nickel ferrite and nickel metal or nickel oxide. Fuel crud is usually thin and relatively porous in the outer layer but dense in the inner layer. Important information is lacking about the adhesion property of crud particles or agglomerates on fuel rods. Little, if any, information is reported about the characteristics of fuel crud before discharging in pool. It is uncertain if the fuel crud can, after pool discharge, largely preserve its characteristics appearing during reactor operation.

Deposition behaviour of corrosion products on fuel rods, in both solid particles and ionic forms in reactor water, has been well studied in the simulated reactor water environments without irradiation. The influences on deposition rate of pH, heat flux, particle size, crud concentration, and flow rate have also been studied in detail. Most of the experimental observations may be qualitatively explained by the theories developed. However, the importance of each influencing parameter remains largely unknown in the complicated reactor water environments, because irradiation, among various influencing factors, may play an important role.

The behaviour of crud dissolution has been extensively studied in various reactor water environments. Generally speaking, the more easily crud dissolves, the less fuel crud deposits. It must be pointed out, however, that many crud solubility investigations may be misleading because they may not comply with the thermodynamic principles. Moreover, little is known about the influence of the hydrodynamics of reactor water, which appears to be very important on crud deposition and radioactivity transport.

There are two major approaches to decrease radioactivity build-up in nuclear power plants. One is to decrease the total amount of corrosion products present in reactor water. The other is to make crud deposition unfavourable through water chemistry control. Most of the countermeasures used today may be qualitatively explained by the theories developed from laboratory simulation studies.

Sammandrag

Denna rapport ger en överblick av vad vi vet idag om bränslecruds karakteristika, dess deponerings- och upplösningsbeteende, inverkan av vattenkemi och aktivitetstransport i kärnkraftverk. Referenserna är huvudsakligen sökta i "International Nuclear Information System" (INIS) CD-ROM databas (1970-1998) och i några av Studsvik Material AB:s interna rapporter.

Egenskaper och karaktärsdrag hos bränslecrud på uttagna bränslestavar har undersökts i stor utsträckning under de tre senaste decennierna. Bränslecrud består till största delen av järn-, nickel- och kromoxider. Vad gäller bränslecrud från en BWR är de huvudsakliga faserna hematit och ickestökiometriska nickelferritspineller. Bränslecrud från en PWR innehåller likaledes mest ickestökiometrisk nickelferrit och nickelmetall eller nickeloxid. Det yttre skiktet av bränslecruden är vanligtvis tunt och relativt poröst medan det inre skiktet är mer tätt och kompakt. Viktig information om crudpartiklars eller anhopningar (agglomerat) av crudpartiklars vidhäftningsförmåga på bränslestavar saknas. Föga, om någon, kunskap finns om bränslecruds egenskaper innan uttaget till bassängen. Det är osäkert om bränslecrudens egenskaper, som uppträder under reaktordrift, kan bevaras efter uttaget från bassängen.

Deponeringsbeteendet hos korrosionsprodukter på bränslestavar, både som fasta partiklar och i jonform i reaktorvatten, har studerats utförligt i simulerad reaktorvattenmiljö utan bestrålning. Inverkan av pH, värmeflöde, partikelstorlek, crudkoncentration och flödeshastighet på deponeringshastighet har också studerats i detalj. Experimentella observationer kan ofta förklaras kvalitativt med hjälp av de teorier som har utvecklats. Emellertid förblir den relativa betydelsen av varje påverkande parameter i stort sett okänd i den komplicerade reaktorvattenmiljön, eftersom bestrålning kan spela en viktig roll tillsammans med flera påverkande faktorer.

Uppträdandet av crudupplösning har studerats i stor utsträckning i olika reaktorvatten-miljöer. Ju lättare crud löser upp sig, desto mindre bränslecrud deponeras. Generellt stämmer detta bra överens med resultat från cruddeponeringsexperiment. Det är dock viktigt att poängtera att många undersökningar vad gäller crudupplösning kan vara vilseledande eftersom de inte stämde med termodynamiska principer. Vidare finns ganska lite kunskap om inverkan av reaktorvattnets hydrodynamik, vilket verkar ha en stor betydelse för cruddeponering och aktivitetstransport.

Det finns två vedertagna tillvägagångssätt att minska aktivitetsuppbyggnad i kärnkraftverk. Ett sätt är att minska den totala mängden korrosionsprodukter som finns närvarande i reaktorvattnet. Det andra sättet är att kontrollera vattenkemin på ett sätt som gör cruddeponering ogynnsamt. De flesta av de motåtgärder som används idag kan kvalitativt förklaras med hjälp av de teorier som har utvecklats genom simuleringsförsök i laboratorier.

Table of Contents

1. Introduction

The current commercial nuclear power programs are comprised mainly of light water reactors. Water chemistry is very important in the plant management and operation. Among others two important problems must be solved. One is the corrosion induced fuel and pipe failure that may jeopardise the safety of power plants. Another problem is the radioactivity build-up on system pipes, which threatens the safety of plant personnel and the general access to the plants.

Fig. 1.1 shows the collective radiation exposure for both BWR and PWR in Sweden. For BWR there is clear tendency that the dose rate has been increasing during recent years. For Swedish reactors the average dose rate is relatively low, but some plants (*e.g.* Oskarshamn 1) showed above-average dose rate.

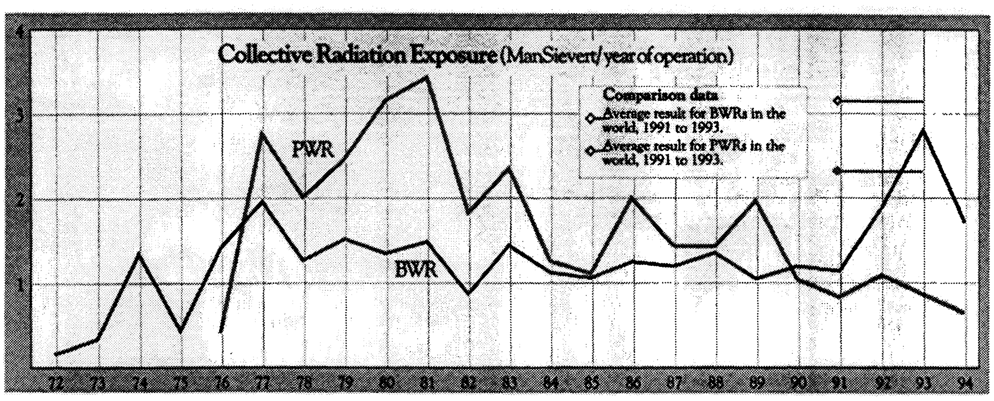


Fig. 1.1 Collective radiation exposure of Swedish nuclear power plants (after ref. [1]).

Extensive research work has been carried out to understand the deposition and release behaviour of corrosion products and their relation to water chemistry and operation practice. This report is an attempt to survey the current understanding in this field.

2. Characterisation of fuel crud

2.1 Origin of fuel crud

Fuel crud is a deposit accumulated on external fuel-rod cladding surfaces. It comes from the corrosion products that are formed on out-of-core system surfaces, in the form of either dissolved ions or solid particles, and are transported to the cladding surfaces by the coolant circulation. The main metal cation species is iron. The constituents of the deposit such as Ni and Co can be activated through nuclear reactions to form radionuclides such as ^{58}Co and ^{60}C. Fuel crud may release from the cladding surfaces into the coolant due to constant interaction between crud and reactor water and to the change in the physical and chemical environments. Fuel crud and activity transport processes occurring in a BWR may be illustrated in Fig. 2.1.

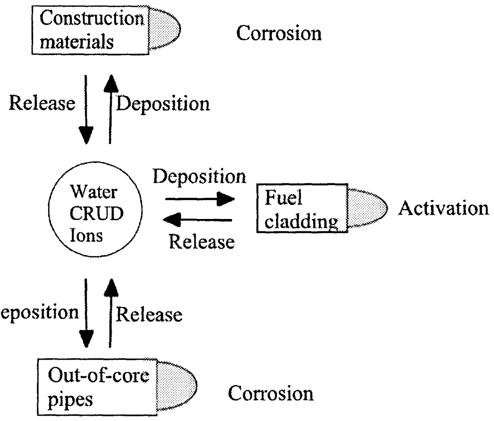


Fig. 2.1 A schematic illustration of build-up of radioactivity in the power plants (after Ishigure [2]).

2.2 Characteristics of fuel crud structure

2.2.1 Fuel crud in BWR

Fuel crud from disposed BWR fuel rods usually has a flaccid reddish or black appearance. The primary source of crud is the corrosion products of stainless steel in the feed water system.

Crud microstructure may be roughly divided into two parts: an outer loose deposit and an inner tightly adherent deposit, as illustrated in Fig. 2.2. The outer deposit consists of clusters of small particles, while in the inner part of some well-crystallised grains and a relatively dense layer. In general, the particle size of crud is in the range of 0.1 to 2 μm [3].

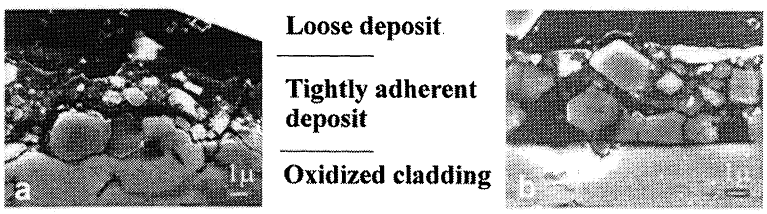


Fig. 2.2 Cross-section SEM images of crud samples from (a) Forsmark 2 reactor and (b) Forsmark 3 reactor. Note that some of the loose deposits on both samples may have been lost during sample preparation (after Hermansson and Lind [3]).

Crud thickness was seen [4-7] to vary axially on the fuel rods. Crud thickness peaked at the lower ends of the fuel rods, while it is negligibly thin near the coolant outlet end. Fig. 2.3 shows the morphology of fuel crud on some Swedish BWRs [3]. The fuel crud on the Ringhals reactor, which was operated in hydrogen water chemistry (HWC) seems to have smaller size and less grown particle than that on Forsmark 2 and 3 operated in neutral water chemistry.

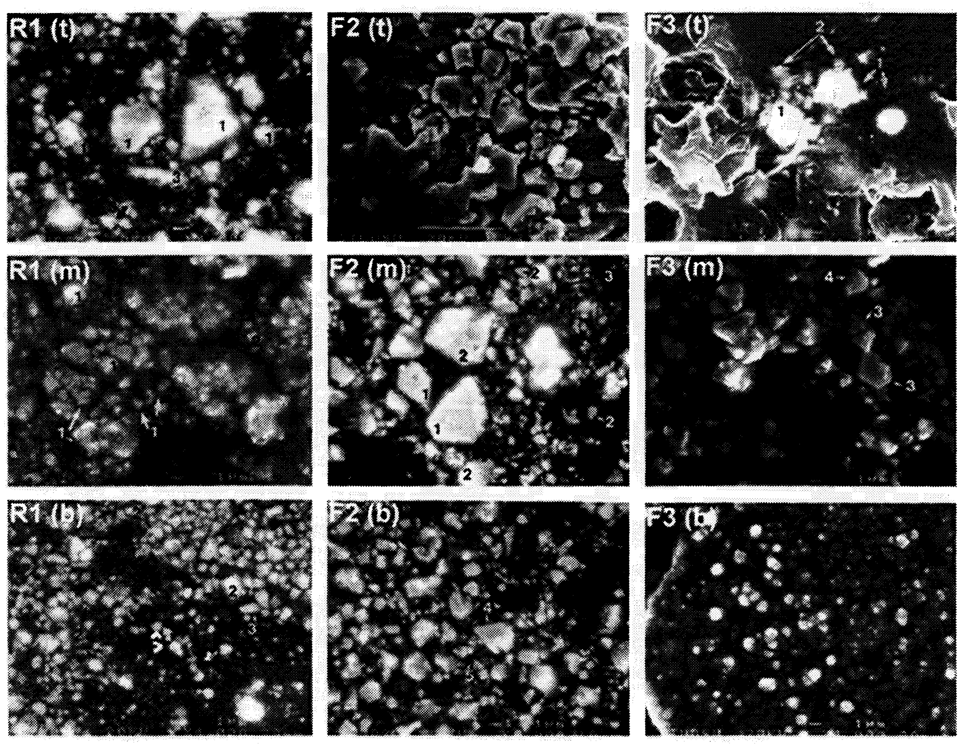


Fig. 2.3 The morphology of fuel crud on Ringhals 1 (R1), Forsmark 2 (F2) and 3 (F3) BWR fuel rods in the top end (t), middle (m) and bottom end (b) [3].

Fuel crud consists mainly of iron oxide and a small fraction of other metal oxides (*e.g.* Me: Ni, Cr, Mn, Co, Cu and Zn), depending on the corrosion rates of different materials and the water chemistry used. Table 2.1 shows the results of elemental analyses of fuel crud from some Swedish BWRs [3].

Table 2.1 Metallic elemental compositions (in atomic fraction) of crud of disposed fuel rods. (Recalculated from ref. [3])

	Cr	Mn	Fe	Co	Ni	Cu	Zn	Σ
Forsmark 3	0.026	0.009	0.760	0.006	0.191	0.002	0.005	1.000
Forsmark 2	0.027	0.034	0.727	0.004	0.178	0.001	0.028	1.000
Ringhals 1	0.009	0.012	0.841	0.007	0.127	0.002	0.003	1.000

Crud compositions and microstructures vary with different construction materials or cleanup systems used [8]. For example, in early BWRs, corrosion of copper alloy preheaters used in the feedwater system led to the introduction of copper and nickel into the primary system at nearly the same rate as that of iron. The resulting crud was hard and tenacious and had poor heat transfer properties.

Iron concentration in crud differs in different types of condensate cleanup systems. For example, the deep bed polishing units result in loose fuel crud. The powder resin units produce much thinner and tenacious fuel crud [8, 9].

The phase compositions of crud, as determined by X-ray powder diffractometry, are mainly red hematite (α-Fe_2O_3) and black spinels of type $M_xFe_{3-x}O_4$ (x=0~1; M=Ni, Zn, Cr, Mn, Co and Cu). The colour appearing on the fuel rod surface may reflect, to some degree, the phase composition of fuel crud. It was found that for the reactor operated in HWC, the phase ratio of nickel ferrite to hematite was much smaller than that in NWC [3].

2.2.2 PWR

Crud from disposed PWR fuel rods has black or shades of grey colour. The crud consists mainly of a nonstoichiometric spinel $Ni_xFe_{3-x}O_4$ with a typical x-value of 0.25 [11]. Table 2.2 gives some characteristics of PWR fuel crud [12].

Most PWR crud, unlike BWR crud, deposits at the top end of the core [13]. In some PWRs, crud thicknesses are inversely proportional to axial fuel assembly power [14, 15].

It must be pointed out that most of the characterisation work on fuel crud was done on fuel rods that had been exposed to wet or dry storage. The crud was susceptible to ongoing oxidation, contamination, dissolution and spallation during that period. The crud characteristics, as described above, may therefore be different from that in operating nuclear reactors.

Table 2.2 Some characteristics of a PWR fuel crud (after Bergmann [12]).

Element composition (wt%):	Fe 39-47; Ni 19-24; Cr 0.8-2.5; Co 0.11
Phase compositions	Mainly $Ni_xFe_{3-x}O_4$ (x=0.4-0.9); Ni or NiO
Radiochemical compositions (μCi/mg parent)	^{58}Co 800-1 300; ^{60}Co 25 000-100 000
Surface concentration (mg/cm^2)	0.10-3.50
Fuel crud thickness (μm)	0.8-29
Estimated crud density (g/cm^3)	1.2

2.3 Radioactivity

The radionuclides that appear in fuel crud result from activation of core deposits, which may be detached from the fuel rods or dissolve into reactor water and finally re-deposit onto the surfaces of system pipes. Table 2.3 shows some important radioisotopes commonly found in fuel crud and examples of their levels in BWR and PWR.

Table 2.3 Radioisotopes commonly found in PWR and BWR fuel crud*.

Radio-isotope	Half-life (days)	GE reactors BWR (μCi/cm^2) [16]	Point Beach 1 PWR (μCi/cm^2) [16]
^{51}Cr	27.7	-	0.9-16
^{59}Fe	44.6	-	0.1-2.0
^{58}Co	70.8	40-50	0.7-13
^{65}Zn	244	-	-
^{54}Mn	312	15-90	0.1-2.0
^{60}Co	1924	110-180	0.1-2.0

*The data is corrected to the reactor shutdown time.

As shown in Table 2.3 that most of crud radioactivity may diminish substantially after a few months removal. Decay will have to be taken into account for any present-day handling of the older fuel rods. ^{60}Co has, on the other hand, a long half-life and may therefore be the principal isotope present in fuel crud. For the similar reason, the crud radioactivity on older spent fuel may have been higher on reactor discharge than more recently discharged fuel having relatively little crud.

3. Fuel crud deposition

As mentioned earlier, fuel crud originates from two main sources. One is through deposition of solid corrosion products that are suspended and circulated in the reactor water system. The other is through deposition of corrosion products in hydroxide form by a so-called “deposition and dry-out” mechanism. In the following we shall discuss these processes separately.

3.1 Deposition of hematite particles

3.1.1 Interaction with zirconia layer

Deposition of hematite (Fe_2O_3) particles may be considered as a process involving gravity, van der Waals attraction, hydrodynamic interaction, and the electrostatic interaction of the electrical double layers surrounding both particles and hot cladding surfaces. These forces can be described as follows.

Gravity

The gravitational force (F_g) on a spherical Fe_2O_3 particle is given by

$$F_g = \frac{\pi}{6} d_p^3 \left(\rho_p - \rho_f\right) g \qquad \text{(Eq 3.1)}$$

where d_p is the spherical particle diameter; ρ_p is the particle density; ρ_f water density, and g the acceleration due to gravity. The larger the particles, the weaker the gravitational force.

van der Waals interaction

van der Waals force of adhesion (F_v) between a sphere and a flat plate may be expressed as

$$F_v = \frac{A d_p}{12 H^2} \qquad \text{(Eq 3.2)}$$

where A is Hamaker’s constant and H the distance between the sphere and plate. The larger the particles or smaller the distance, the stronger the force of adhesion.

Hydrodynamic re-suspension force

The tangential drag force (F_d) acting on a spherical particle resting on a surface may be written:

$$F_d = f c_d(\mathrm{Re}_p) \frac{1}{2} \rho_f u^2 \frac{\pi d_p^2}{4} \qquad \text{(Eq 3.3)}$$

where f is a factor to allow for the proximity of the surface and the velocity distribution normal to the surface; c_d particle drag coefficient; Re_p particle Reynolds number ($Re_p = ud_p\rho_f/\eta$); u water velocity averaged over the particle projected area in the absence of the particle and η viscosity of water. Apparently, the drag force is stronger on larger particles in a high water velocity environment.

The lift force on a spherical particle in a slow linear shear flow may be estimated from the theory of Saffman [17]. It may be insignificant in magnitude compared with the tangential drag, but it may make a significant contribution to transport away from the surface following detachment. Under reactor water conditions particles with a size of 2 μm or greater would be expected to perturb the bursting process significantly [18].

Electrical double layer interaction

The surface charge of solid oxides and hydroxides may be qualitatively explained in terms of a two-step process: surface hydration followed by either the adsorption of H_3O^+ and OH^- ions, or the dissociation of the surface "hydroxide". As the particles approach the hot metal surfaces (Fig. 3.1) [19], a favourable total potential energy (V_t) (Fig. 3.2) for the interaction between hot metal surfaces and particles and between particles would result in the particle deposition.

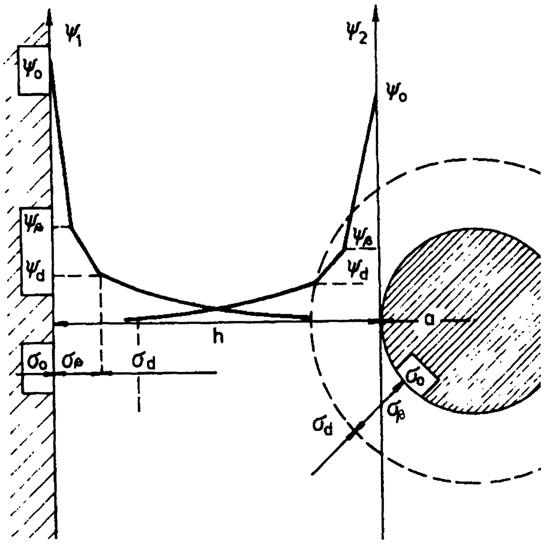
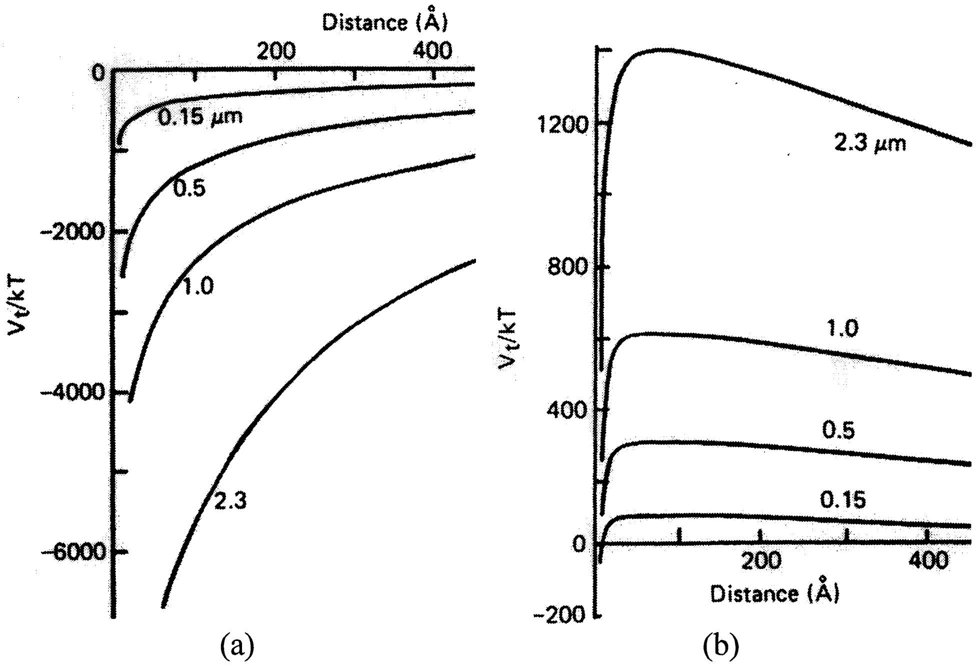


Fig. 3.1 The interaction of the two double layers upon approach of a particle to a flat wall. Typical particle size a is 0.01-10 μm; σ_0 and ψ_0 refer to particle and wall surface; σ_β and ψ_β to the plane of the adsorbed counterions; σ_d and ψ_d to the diffuse part of the double layer as described by Gouy-Chapman's model (after Urrutia, *et al.* [19]).



(a) (b)

Fig. 3.2 The total potential energy (V_t) as a function of the distance (a) between hot ZrO_2 surface and Fe_2O_3 particles and (b) between Fe_2O_3 particles with various sizes. T=285°C, zpc=8.0, pH=7 and Hamaker's constant = $5x10^{-13}$ (after Kawaguchi, *et al.* [20]).

During the initial stage of deposition, the electro-kinetic interaction on the surface is considered to be important. Conditions are favourable for deposition when surfaces of the hot metal and particles have opposite charge, as believed to be the case for ZrO_2 with a negative charge [20,21] and Fe_2O_3 with a positive charge at neutral pH [22]. As shown in Fig. 3.2(a) there is a strong attractive interaction between the Fe_2O_3 particles and the ZrO_2 surface as larger particles are more favourable for deposition.

3.1.2 Interaction between hematite particles

The attractive interaction between hematite particles, as shown in Fig. 3.2(b), may become significant when the distance between particles is small (< 50 Å). Therefore, once a layer of hematite deposit is formed on the fuel surfaces, further particle agglomeration may proceed, in spite of repulsive force between the particles, as a result of collide-and-stick mechanism. In this case, however, the potential well at the deposition site is very shallow. This means that it may be easy for the agglomerated particles to separate again. Moreover, according to this figure the larger particles would be more difficult to agglomerate, which is incorrect as shown by Kawaguchi [20]. This may imply that the shallow potential well may have to be considered when the stability of an agglomerate is concerned.

3.1.3 Deposition rate and influencing factors

At present, the rate of the particle deposition is available solely from laboratory simulations of the reactor water environment without consideration of irradiation effects. The deposition rate (*R*) for hematite particles is, as shown in Figs. 3.3 to 3.5, approximately constant over a relatively heavy deposit range (up to 4 mg/cm^2), and increases linearly with both particle concentration (C_{Fe}) in the simulated reactor water and heat flux (*Q*). The rate is maximised at the particle size of 0.5 μm (Fig. 3.6). But one must bear in mind that the potential well between particles is shallow and these experiments were carried out at a flow velocity that is very much lower than that in nuclear reactors. The higher flow velocity results in less deposition as exemplified in Fig. 3.7 where water flow velocity along the fuel rod is plotted against the amount of crud collected along the rods.

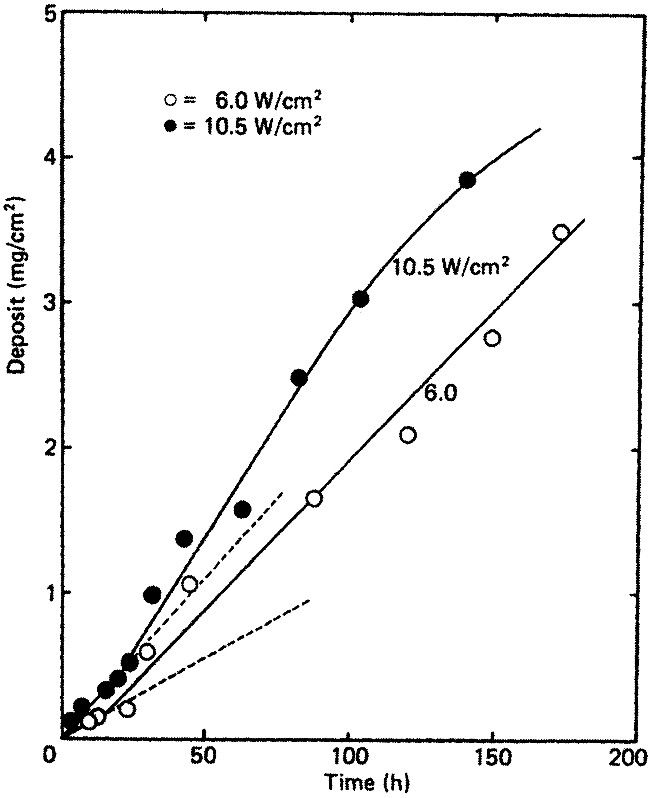


Fig. 3.3 Time dependence of deposition rate of Fe_2O_3 particles with a diameter of 0.5 μm and iron concentration of 1 ppm. Water temperature and linear flow rate were 453K and 1.1x10-3 m/s, respectively (after Kawaguchi, *et al.* [20]).

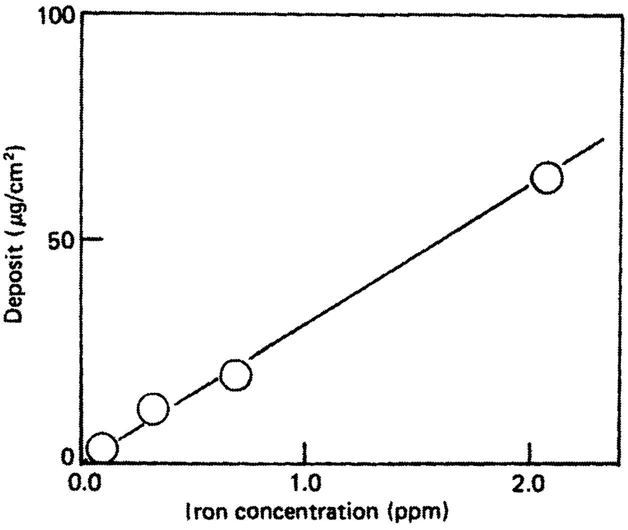


Fig. 3.4 Iron concentration dependence of deposition rate of Fe_2O_3 particles with a diameter of 0.5 μm, heat flux of 6.0 W/cm², and time of 4 h. Water temperature and linear flow rate were 453K and 1.1×10^{-3} m/s, respectively (after Kawaguchi, *et al.* [20]).

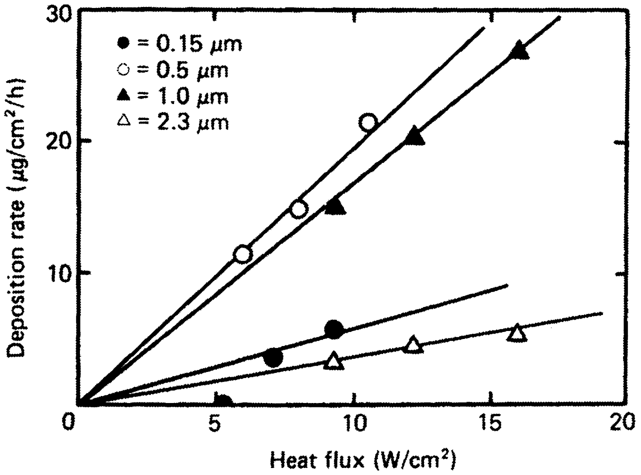


Fig. 3.5 Heat flux dependence of deposition rate of Fe_2O_3 particles of different particle sizes. Iron concentration is 1 ppm. Water temperature and linear flow rate were 453K and 1.1×10^{-3} m/s, respectively (after Kawaguchi, *et al.* [20]).

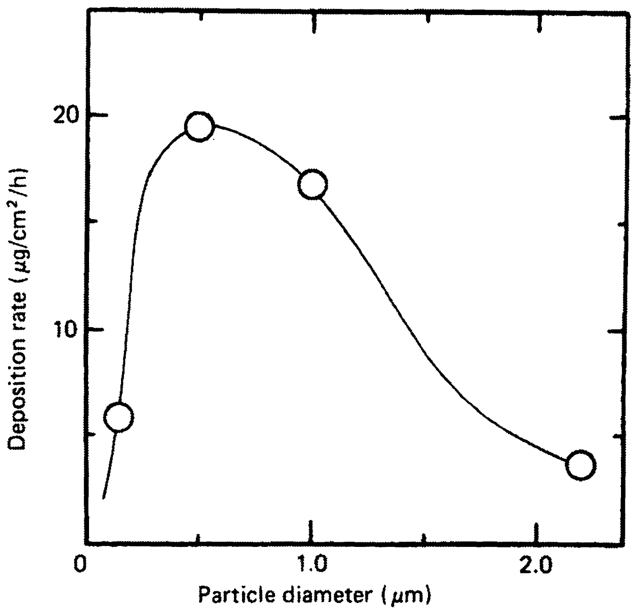


Fig. 3.6 Particle size dependence of deposition rate. Iron concentration was 1 ppm and heat flux 10 W/cm². Water temperature and linear flow rate were 453K and 1.1x10-3m/s, respectively (after Kawaguchi, *et al.* [20]).

The effect of pH on deposition rate was investigated by Kawaguchi, *et al.* [20]. They found that at 453K the deposition rate decreases about 50% with increasing pH from 7 to 8 (Fig. 3.8). This was explained by double-layer interaction upon extrapolation to the high temperature reactor water.

The particle surface charge is established with an adsorption of H^+ and OH^- ions or dissociation of hydrated surface sites. A change in the pH would also change the surface charge of the adherents and electrical double layer. Fig. 3.9 shows the calculated results of total interaction energy at various pH and the distance between an Fe_2O_3 particle and ZrO_2 wall. The calculated result is in a good agreement with the experimental data shown in Fig. 3.8.

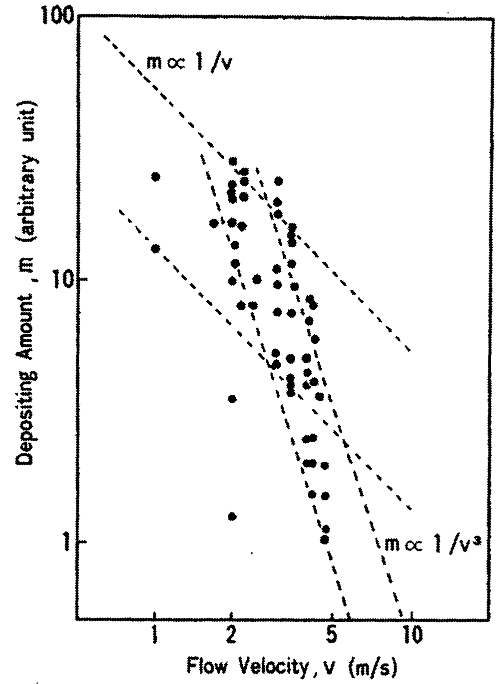


Fig. 3.7 Flow rate dependence of deposition of fuel crud in a BWR (after Uchida, *et al.* [23]).

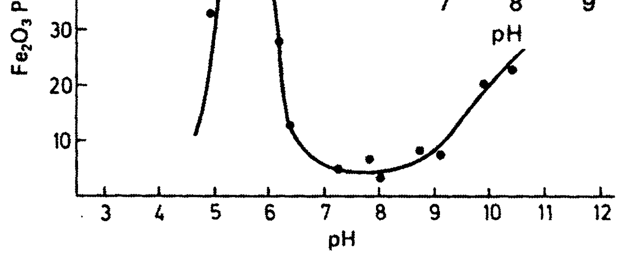


Fig. 3.8 pH dependence of deposition rate of Fe_2O_3 particles at 298K and 453K, respectively (after Kawaguchi [20] and Urrutia, *et al.* [19]).

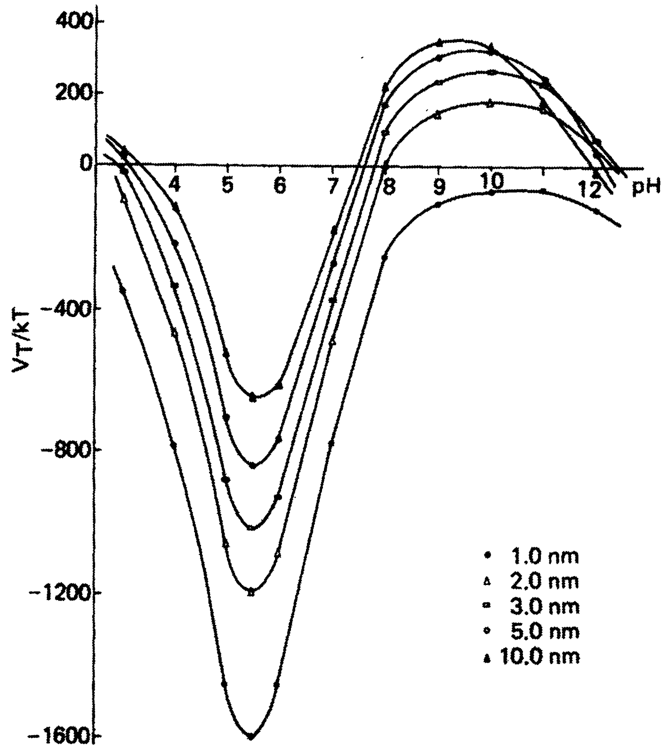


Fig. 3.9 Total interaction energy, V_T as a function of pH, for various fixed distances between Fe_2O_3 particle and ZrO_2 wall. Hamaker's constant is 1.3×10^{-12} erg; T 298 K; and particle radius 0.1 μm (after Urrutia, *et al.* [19]).

3.2 Deposition of ferrite particles

Ferrite is one of the main phases in fuel crud and in reactor water. Unlike hematite, ferrite is ferromagnetic. The particles may exist as single domains up to 0.1 or 1 μm in size. Upon deposition ferrite particles may create a magnetic field around them. The force of adhesion for a uniformly magnetised sphere in contact with the surface of a semi-infinite magnetisable medium is given by

$$F_m \approx \frac{1}{5}\mu_0 \frac{(\mu-1)}{(\mu+1)} M^2 d_p^{\,2} \qquad \text{(Eq 3.4)}$$

where μ_0 is the permeability of free space; μ relative permeability of the semi-infinite medium and M magnetisation of the sphere. This magnetic field can affect not only the further deposition of ferrite particles from reactor water but also the further crystal growth within the crud layer.

Rodliffe [18] calculated the relative sizes of gravity, van der Waals and magnetic forces under reactor water chemistry conditions. The results are shown in Fig. 3.10. One can see that the van der Waals force is dominant for particles of a diameter less than about

200 μm, provided that the geometry is a perfect sphere-plate. Magnetite and nickel ferrite particles of 0.01-1 μm in size may exhibit a magnetic adhesion force that is comparable with or greater than the van der Waals force.

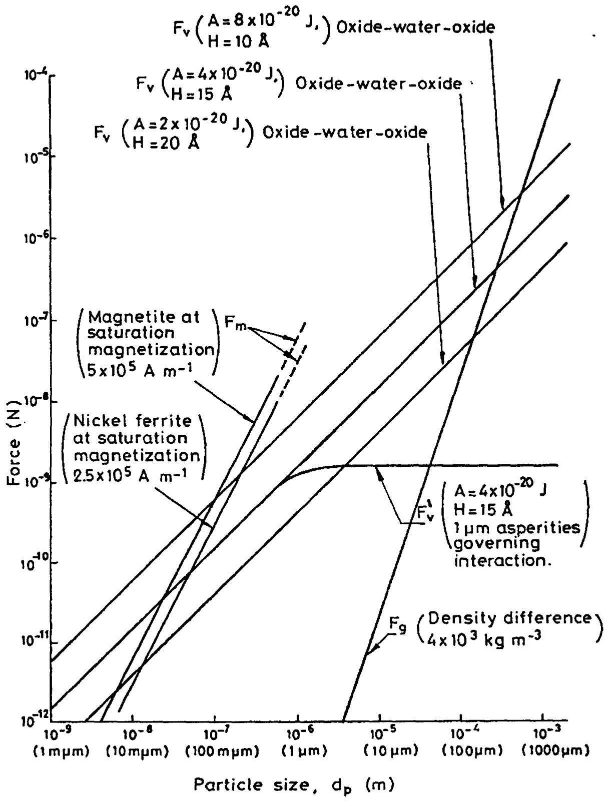


Fig. 3.10 Gravity, van der Waals and magnetic forces in reactor water (after Rodliffe [18]).

A ζ-potential of ~50 mV is capable of inhibiting particle deposition throughout the size range relevant to light water reactors. Only for a ζ-potential of less than ~10 mV does the van der Waals attraction exceed the electrical double layer repulsion for all separations [18].

For a surface exposed to typical water reactor flow conditions, *i.e.* friction velocities of 0.1 to 0.3 m/s, particles smaller than 1 μm will be stable against re-suspension in the absence of electrical double layer repulsion. Those smaller than 100 μm will not re-suspend, provided that their ζ-potentials are less than 400-800 mV for BWR and less than 200-400 mV for PWR in constant potential interaction, respectively [18].

Particles greater than ~10 μm should not be stable against re-suspension even in the absence of electrical double layer repulsion. The behaviour of particles in the size range of 1-10 μm is less well defined but there is certainly little margin to compensate for any electrical double layer repulsion [18].

Nishino *et al.* [24] studied the kinetics of forming nickel ferrite using various iron hydroxides and hematite compounds in high temperature water. The results show that at 488K the formation of $NiFe_2O_4$ from γ-FeOOH is rapid during the first 20 min. but slows down with time (Figs. 3.11 and 3.12). It indicates that the reaction may be a diffusion-controlled process where Ni^{2+} (or Co^{2+}) ions must penetrate through the ferrite shell and react with the hematite core. Moreover, the ferrite may recrystallize to form large crystals with a more regular geometry as shown in Fig. 2.2.

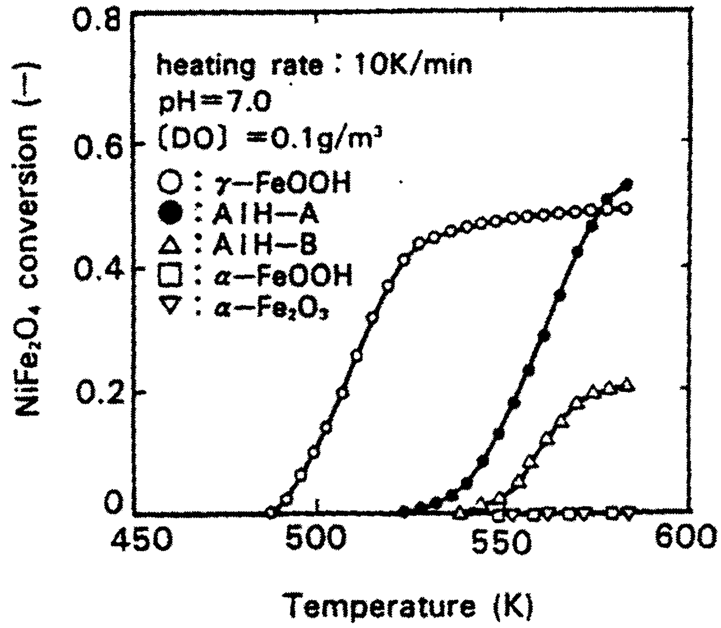


Fig. 3.11 Ferrite conversion rate vs. temperature for various iron-containing species.

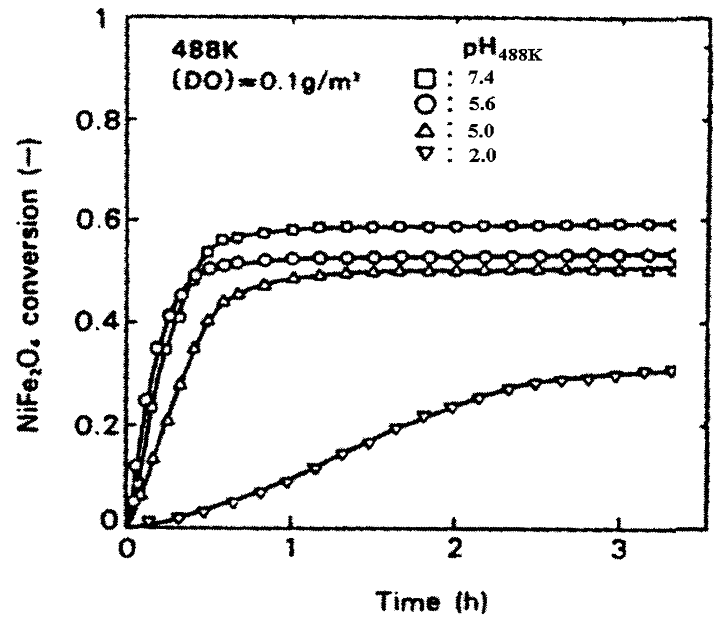


Fig. 3.12 Ferrite conversion rate vs. time and pH. The reaction rates differ slightly (~15%) at pH 5.6 and 7.4 as calculated at 488K. It is attributed to less reactant γ-FeOOH at lower pH [24].

3.3 "Evaporation and dry-out" deposition

The "evaporation and dry-out" model [25-27], as illustrated in Fig. 3.13, describes, under nucleate boiling conditions in a BWR, the deposition proceeding through the precipitation of hydroxides (e.g. FeOOH, $Ni(OH)_2$ and $Co(OH)_2$) on cladding surfaces, followed by dehydration and reaction to form hematite and spinels in the "dry-out region". Heat transfer from the heated surface to water is primarily due to evaporation of a micro-layer of water that is formed between the bottom of a growing bubble and the heated surface. This model is supported by the fact that in some cases oxide deposits are circular in shape [26].

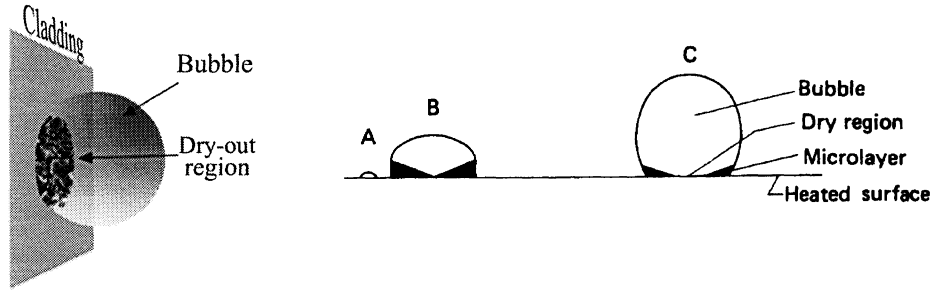


Fig. 3.13 A schematic drawing of "evaporation and dry-out" model.

The deposition rate dW/dt is expressed as follows:

$$\frac{dW}{dt} = \frac{KQC}{L} \tag{Eq 3.5}$$

where Q is heat flux; C concentration of the deposit in boiling water; L latent heat of water and

$$K = (\frac{4}{3})^2 R_b U \rho_G^2 / (\rho_L \eta) \,. \tag{Eq 3.6}$$

R_b is the maximum radius of the bubble; U bubble growth rate; ρ_G vapour density; ρ_L water density and η viscosity of water. K (deposition rate constant) values [26-28] for deposition of α-Fe_2O_3, Ni^{2+} and Co^{2+} are 0.3, 0.1 and 0.02, respectively. The smaller values for Ni^{2+} and Co^{2+} are probably due to higher solubility of their oxides.

4. Fuel crud stability

4.1 Thermodynamic consideration

Thermodynamics may be a powerful tool for predicting the effect of water chemistry on corrosion product transport and the associated radioactivity build-up in nuclear reactors. One of the most studied subjects has been the dissolution behaviour of those solid phases present in reactor water and on the surfaces of fuel rods or system pipes. A large number of autoclave simulation studies, *e.g.* [29-33], have been carried out, aimed at transferring the measured solubility data to the real reactor water system.

Turner [34] claimed that most of the experimental approaches failed to comply with basic thermodynamic principles. The measured data are not thermodynamic solubility and therefore non-transferable. He also pointed out that the data cannot be expected to make reliable predictions, nor to give any direct guidance on the direction of transport of Ni or Co in PWR primary circuits.

In order to understand Turner's arguments, we shall briefly discuss the two basic concepts of thermodynamics, *i.e.* solubility and phase rule.

Solubility is a thermodynamic property of a solid. It can be obtained under certain thermodynamic conditions. Let us take $NiFe_2O_4$ in water as an example. When $NiFe_2O_4$ is in equilibrium with its saturated ideal solution, *i.e.* no more solid $NiFe_2O_4$ will dissolve, its solubility can be defined by the following equation

$$X_{satd\_so\ln} = \exp\left(\frac{\mu_s - \mu^\bullet}{RT}\right) \qquad \text{(Eq 4.1)}$$

where $X_{satd\_so\ln}$ is the mole fraction of $NiFe_2O_4$ in the saturated solution in water at certain temperature and pressure. μ_s and $\mu^\bullet$ are the chemical potentials of solid $NiFe_2O_4$ and its pure, supercooled, liquid $NiFe_2O_4$, respectively. One of the thermodynamic conditions is that Ni^{2+} does not exchange with Fe^{2+}. Since the solubility (in terms of mole fraction) of any specified solid is the same in all solvents with which it forms an ideal solution, the information obtained for one thermodynamic state can be transferred to another less known state.

Gibbs' phase rule is expressed by the following well known equation

$$F = C - P + 2 \qquad \text{(Eq 4.2)}$$

where

F the number of degrees of freedom. It is the number of intensive variables that can be altered without the appearance or disappearance of a phase.

C	the number of components. It is the minimum number of chemical species from which all phases in the system can be prepared. When a system does not react chemically, it is simply the number of chemical species. For a system undergoing R independent chemical reactions among N chemical species $C = N - R$.
P	the number of phases or the number of different homogeneous regions in system.

These may be easily understood by some practical examples given in Table 4.1.

Table 4.1 Solubility and Gibbs' phase rule (after Turner [34]).

Nr	System	C	P	F	Variables F
1	Fe_3O_4, H_2, HCl, H_2O	4	3	3	T, pH, $p(H_2)$
2	$NiFe_2O_4$, NiO, H_2, HCl, H_2O	5	4	3	T, pH, $p(H_2)$
3	$NiFe_2O_4$, $NiCl_2$, H_2, HCl, H_2O	5	3	4	T, pH, $p(H_2)$, $[Ni^{2+}]$

For the first system magnetite does have true solubility under defined T, pH and $p(H_2)$, but the usable thermodynamic property is an equilibrium constant, or rather a set of equilibrium constants which are complex analogues of a solubility product based on the following reaction:

$$Fe_3O_4 + (6\text{-}3x)H^+ + H_2 = 3Fe(OH)_x^{(2\text{-}x)} + (4\text{-}3x)H_2O \qquad \text{(Eq 4.3)}$$

The equilibration between magnetite and a water solution may be rapid and there may be no change in composition of magnetite as dissolution proceeds. Experimentally, one may measure the solubility by assuming that the magnetite phase formed in hot water does not contain water.

From the 2nd system it is seen that two solids ($NiFe_2O_4$ and NiO) must be present before a solubility can be defined. Suppose that $NiFe_2O_4$ and NiO are put into a closed vessel with the pH and $p(H_2)$ buffered at 285°C for a long time. With increasing $p(H_2)$ soluble Fe(II) would increasingly enter the solution and compete with Ni^{2+} for available divalent metal sites in the spinel structure. The extent to which this happens would depend on the total mass of spinel and on how the free energy of formation of spinel varies with the Ni^{2+}/Fe^{2+} ratio. Because the quantities of the cations in the solution depend on the relative masses of the phases, no solubility can be found in such a system. The same is true if additional spinels of other types are brought into consideration in the above system.

Under above conditions, it can be concluded that the mixed spinels of Fe, Ni and Cr do not have any solubility. An equilibrium state can be established in such a system but the dissolved levels of Fe, Ni and Cr, as may be measured experimentally, would not be solubility. In other words, if one adds more solids into the system, a different set of equilibrium levels would be found after re-equilibration. Because of the very different ratio of solid to liquid quantity in the systems of the laboratory simulation as compared to that in reactor water circuits, and for the reason discussed above, the property that is measured in the laboratory has hardly any relevance to what is concerned in the reactor water. Interested readers are directed to the reference [34] for more detailed discussion.

4.2 Kinetic consideration

Crud formation on the cladding surfaces is the result of concurrent deposition and release processes. The dissolution of various spinel phases may be achieved through both slow solid state diffusion mechanism and rapid solution transport. It is believed [34] that final equilibrium would be limited by the former, and the claim that dissolution rate is determined by the surface reaction is incorrect.

The situations in autoclave experiments or reactor water circuits are much more complicated. The factors, such as local water chemistry, varied mechanical and hydrothermal environments can all influence the mass transport processes involved in establishing the equilibrium.

Although the solubility data for those interesting phases are hard to get, many interesting experimental measurements of the ion concentration in various spinel-water system under reactor water chemistry conditions may provide us qualitative picture about crud release and the influencing factors concerned.

Some experimental results, as compiled by Dinov [33], show that under PWR water chemistry conditions, iron concentration in water-magnetite and water-nickel ferrite systems decreases with increasing pH for up to approximately 6.7 and increases thereafter.

5. Transport of radioactivity and counter-measures

5.1 Activation of elements

The origin of radioactivity build-up, as mentioned above, comes from the activation of some elements through neutron capture. The activity may be calculated by

$$A^{\phi} = k\sigma_{ac} fn\left(1 - e^{\lambda t}\right)e^{-\lambda\phi} \qquad \text{(Eq 5.1)}$$

where

A^{ϕ}	measured activity in net counts per second at time ϕ
ϕ	time increment between end of irradiation and the time at which the target is counted
k	efficiency of the counter for measuring the induced radioactivity
σ_{ac}	activation cross-section for neutron capture by the target material, square centimetres per atom per neutron, averaged over the energy distribution of the neutron flux
f	flux of neutrons, neutrons per square centimetre per second
n	total number of target nuclei
λ	disintegration constant of radioactive material
t	time duration of exposure to neutron flux
e	base of natural logarithm

Some relevant data are given in Table 5.1. The elements which make the major contribution to persistent induced activity are chromium, manganese, cobalt, copper, zinc, tantalum and tungsten.

Among various radioactive species in PWR, ^{58}Co accounts for approximately 60%, ^{51}Cr 25%, ^{60}Co 10% and the rest for 5% of the total species. In terms of γ-ray energy, Co-58 and Co-60 account for 90% of the total dose rate. For BWR, ^{60}Co accounts for ~82%, ^{58}Co 6% and ^{54}Mn 8% of the total radioactive species, respectively. It is therefore vital to decrease the dose rate caused by ^{58}Co and ^{60}Co.

For Co it may take long time to become activated to ^{60}Co. Therefore, ^{60}Co found in reactor water or the oxide scales on the system pipes may have stayed on fuel rods for a long time, probably as the inner dense layer of crud as described in chapter 2 of this report. The release of ^{60}Co may occur through release of fuel crud during reactor water cooling, crud detachment due to hydrodynamic processes or spalling of thick ZrO_2 layers, and other interactions between fuel crud and reactor water.

Table 5.1 Induced activities in metals present in structural materials

Element	Isotope mass nr.	Natural abundance (%)	σ_{ac} (barns)	Active species	Half life	γ-ray energy
Titanium	50	5.3	0.04	^{51}Ti	72d	1.0
Chromium	50	4.4	16	^{51}Cr	27d	0.32
Manganese	55	100	13.3	^{56}Mn	2.6h	2.1
Iron	58	0.33	0.8	^{59}Fe	46d	1.3
Cobalt	59	100	37	^{60}Co	5.3y	1.3
Nickel	64	1.9	3.0	^{65}Ni	2.5h	0.93
Copper	63	69	4.3	^{64}Cu	12.8h	1.35
Zinc	64	48.9	0.5	^{65}Zn	250d	1.12
Zinc	68	18.5	0.1	^{69}Zn	138h	0.4
Zirconium	94	17.4	0.1	^{95}Zr	65d	0.92
Molybdenum	98	23.8	0.13	^{99}Mo	67h	0.84
Tantalum	181	100	21.3	^{182}Ta	113d	1.2
Tungsten	186	28.4	34	^{187}W	24h	0.76

5.2 Adsorption and reaction of radioactive ions

The activated fuel crud may release into reactor water and re-deposit onto the surfaces of water circuit pipes. The radioactive ions in solution, on the other hand, can also be absorbed on the surfaces of fuel rods, crud particles in reactor water and system pipes. They contribute to the total radioactivity build-up in nuclear power plants.

The adsorption of Co^{2+} ions on the surfaces of magnetite particles was found [35, 36] to follow the Langmuir isotherm. The adsorbed Co^{2+} ions may react with hydrated crud at the particle surfaces. Permér and Österlundh [37] investigated the diffusion of Co^{2+} ions in monolithic trevorite and chromite samples in simulated BWR water chemistry environments. They found that in the trevorite sample the cobalt concentration depletes rapidly along the length of diffusion path while in the iron chromite sample the change in depletion rate is relatively small. It is, however, not clear to what extent the cobalt ions are adsorbed on the sample surfaces or diffuse into the crystal lattice/grain boundaries to form solid solution with trevorite and chromite. Moreover, the element composition profile should be closely related to the surface morphology and grain boundary structure of their samples.

There is little, if any, reported work on Co^{2+} (or other possible radioactive elements) adsorption on hematite. In high temperature reactor water it is possible that cobalt ferrite forms upon cobalt adsorption and reaction with hematite particles.

For cobalt in the suspended particles and in the ionic form in reactor water, its role in radioactivity build-up on the system pipes may be different. This is due to the fact that the particles in reactor water tend to stay only in the loose and porous layer of the oxide scales on system pipes, while cobalt ions in reactor water may penetrate rapidly into the oxide scales through pores and grain boundaries. Little has been reported concerning the radioactivity distribution in the oxide scales on the system pipes.

5.3 Countermeasures of activity build-up

Tremendous achievements have been made over the years to reduce the activity build-up in nuclear power plants, through some crucial countermeasures during reactor operation. Basically, there are two ways to reduce the dose rate. One is to use corrosion resistant and low or Co-free materials in the water circuit. The other, as will be further discussed in the following, is to improve the operational conditions to decrease the corrosion rate of system pipes and to suppress the build-up of radioactive species in the oxides of both fuel surfaces and system pipes.

5.3.1 BWR

For BWRs, the most effective way so far applied to decrease the dose rate has been to decrease the iron concentration in the reactor water well below 1 ppb. In the new Japanese ABWR (Advanced Boiling Water Reactor) a crud concentration to a level of as low as 0.1 ppb or less is kept to minimise the dose rate [45]. The low iron concentration control is easily understood as the deposition rate of crud on a hot surface is proportional to the crud concentration in the water (see Fig. 3.4).

To reduce the corrosion rate of system piping is an important countermeasure. In Swedish BWRs stainless steel is exclusively used for piping at high temperature. In Japan injecting oxygen into feed water and alkaline pre-filming of carbon steel water pipes are successfully used to suppress corrosion [38]. Fig. 5.1 shows the countermeasures adopted in some Japanese BWR.

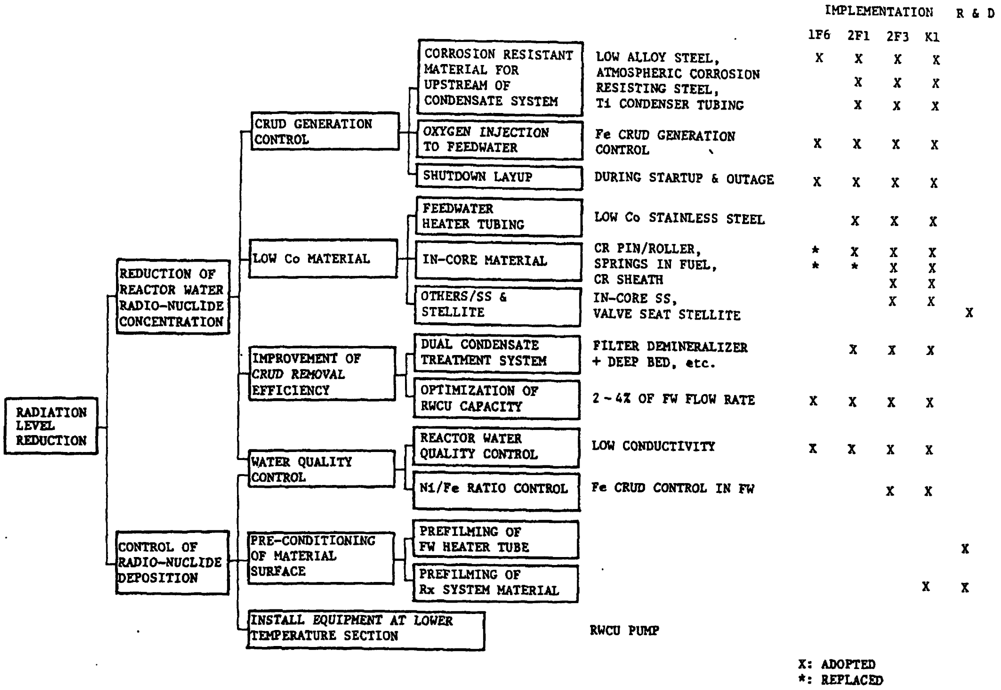


Fig. 5.1 Countermeasures for reducing radiation dose rate in some Japanese BWR (after Nagao, *et al.* [39]).

Fe/Ni ratio control of reactor water has been practising in Japan. It is done during start-up operation by injecting iron-containing species into reactor water, and during normal operation by keeping the iron concentration in reactor water well low 1 ppb. The idea is that during the start-up the nickel concentration is relatively high in reactor water and the formed nickel-rich fuel crud is more soluble. By increasing the iron concentration in reactor water during the start-up operation, less soluble nickel ferrite phase is formed on fuel surfaces.

Iron injection tests in the Swedish Forsmark 3 reactor, which was operated at a low iron level of ~0.05 ppb, showed that in reactor water both ^{58}Co and ^{60}Co were decreased by ~50% but their uptake on vertical piping to reactor water cleanup system was increased [40]. Among various possible reasons to this, that the uptake of Co by the injected iron agglomerates and subsequent removal by the cleanup system may be important.

Hydrogen water chemistry (HWC) is an alternative water chemistry to reduce oxidising species in reactor water. Hydrogen is injected into the feed water and reacts with oxygen and hydrogen peroxide produced in the core region, resulting in a reduction of the electrochemical corrosion potential in the primary system. Moreover, it was found [3] that the phase ratio of nickel ferrite to hematite in HWC fuel crud is much smaller than that operated in neutral water chemistry (NWC). The fuel crud particles are also much smaller in HWC than in NWC.

In contrast with above Ni/Fe control, high nickel ion control, so-called “ultra low crud control”, has been introduced in some Japanese BWRs (Hemmi, *et al.* [46]). They found that a few ppb of nickel ion in primary coolant suppressed not only cobalt deposition onto primary piping surface but also corrosion rate of stainless steel. They explained that high nickel favours the formation of ferrite on the stainless surface and suppress the enclosure of cobalt in the ferrite structure. Moreover, high nickel control makes the ferrite on fuel surface more soluble. Consequently, concentrations of Co-60 and Co-58 remain relatively high in the primary coolant. But the negative effect is limited due to the extremely low cobalt deposition onto piping surfaces.

Hosokawa, *et al.* [47] found in a simulated BWR loop that the hematite layer initially formed on fuel cladding may promote the formation of nickel ferrite phase. Since nickel ferrite phase in which cobalt is often incorporated is more soluble in reactor water, it is desirable to suppress its formation. This may be done by pre-oxidation of cladding materials.

Uruma, *et al.* [48] observed that when their new BWR fuel rods were used, crud deposition rate at the initial stage was increased on the relatively rough cladding surface. However, the effect of surface roughness becomes insignificant after a few hundred hours of exposure in the test loop. They proposed that the preferentially deposited chromium on the cladding in the initial stage re-dissolve very slowly and form local acidic region, leading to the radiation build-up problem. Therefore, re-dissolution of deposited chromium may be a potential mechanism to resolve radiation build-up problem. However, adding chromium ions was found by Inagaki, *et al.* [49] to have no effect on suppression of cobalt deposition. In order to elucidate the behaviour of chromium compounds by thermodynamic method, Hiroishi, *et al.* [50] evaluated the values of hydrolysis constant and standard formation energy of Cr^{3+} ion at high temperature.

Haginuma, *et al.* [51] investigated the effect on cobalt accumulation behaviour in type 304 stainless steel in a simulated BWR loop. They proposed that the mechanisms of the cobalt accumulation suppression by zinc and nickel addition are different. Zinc can reduce both the weight of the corrosion film and cobalt concentration in the corrosion film, while nickel mainly reduces the cobalt concentration in the corrosion film. In the case of calcium, magnesium and manganese additions, no suppression effect on the cobalt accumulation were observed.

A new method has been developed by Hiroishi and Ishigure [52] to treat the thermodynamics of mixed spinels including Fe^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} ions. The method is based on site preference energy of cations in spinel lattice. They have examined (1) distribution of cations in stoichiometric spinel compounds; (2) the free energy of formation of non-stoichiometric mixed spinels; (3) distribution of divalent cations in non-stoichiometric mixed spinels and (4) Co pick-up process of spinel.

5.3.2 PWR

For PWR, it is very important to control pH of primary system during reactor operation at a value at which fuel crud is the least soluble and integrity of fuel element guaranteed. In Japan a pH_{285} 6.9±0.2 has been recommended [41]. Ringhals applies pH_{300} 7.3. In some European countries pH_{300} 7.4 is used. However, operation at high pH may have potential detrimental effect on Zircaloy corrosion and stress corrosion cracking. The pH value has to be optimised individually in different plants.

Garbett, *et al.* [53] described their experiences about the corrosion product behaviour and their relevance to the low radiation fields in PWR since the initial passivation (forming a protective oxide film) of the primary circuit during the hot functional tests (HFT). They suggested that adding H_2 and using start-of-cycle boron/lithium concentrations in HFT is beneficial for later radiation field development. They proposed that nickel and cobalt be released under different redox conditions. Ito, *et al.* [54] presented their experience of HFT to reduce the radiation source. Through low-dissolved H_2 concentration management, the removal of outer oxide layer could also be carried out effectively during plant shutdown.

Takahashi, *et al.* [55] found that in a PWR decreasing feed water hydrazine content and increasing feed water ammonia content to maintain pH are advantageous for the decrease in iron, nickel and other anionic impurities in the secondary circuit.

Hisamune, *et al.* [56] used low dissolved hydrogen (DH) chemistry as an effective countermeasure against the radiation build-up in a PWR. The method does not influence the fuel integrity in high burn-up operation and may be effective in mitigating PWSCC of Inconel 600 in primary system. Ishihara, *et al.* [57], also reported similar results. Based on their thermodynamic analyses, the phenomenon may be due to high solubility of nickel ferrite spinels. Venz and Dinov [58] found, however, that crud coolant activity is rather independent of DH in the PWR examined. Nishizawa, *et al.* [59] examined the thermodynamics of crud composition and its relation to DH. Their calculation showed that, with decreasing DH under the typical PWR condition nickel fraction in nickel ferrite increases and more nickel may be present in reactor water.

During the shutdown operation, it is desirable to remove as much fuel crud as possible and other corrosion products from the primary water circuit. To achieve this, the following straightforward countermeasures have been proposed [41]: (1) decrease pH at an early stage and adjust temperature to increase crud release; (2) keep the water flow to increase the crud release rate and (3) maximise the capacity of the reactor water cleanup system. The injection of hydrogen peroxide or some oxygenating additive, O_2 or air can be used to promote the crud release.

To decrease the dose rates in PWRs, some other countermeasures can also be applied, such as improving materials for both fuel grids and steam generators, polishing channel head surfaces and refining cold shutdown procedures [42].

Zinc chemistry may be a promising alternative to decrease the dose rate in light water reactors [43]. The hypothesis behind Zn-dosage, though not being well developed, is thought to be due to its capability of forming a more stable Zn containing spinel phase than Co containing spinel phase on fuel rods [44].

Beverskog and Mäkelä [60] investigated the long-term effect of zinc addition and its interruption in a PWR loop in Halden. They observed that Co-60 pickups by the pipe materials were low with zinc addition, especially when the pipe materials had fresh surfaces before the experiments. They proposed that zinc addition inhibit the ion transport through the oxide in both ways: inactive cobalt from coming out into the coolant where it can be activated and inhibiting activated corrosion products from incorporation into the oxide. The former transport is the source for cobalt to be activated and the latter the result of neutron activation of cobalt, which forms a radioactive source.

Burrill [61] presented some general ideas about the effects of radiolysis and irradiation on the behaviour of corrosion product on fuel cladding. He proposed that (1) reducing radiolytic species from water radiolysis interfere with magnetite formation on fuel cladding in the reactor core and suppress dissolved iron precipitation, and (2) boiling result in net water radiolysis around the steam bubbles and provide oxidising condition at fuel element surface to enhance precipitation of dissolved iron as magnetite.

Millett and Wood [62] described the shut-down chemistry that is being practised in many US PWRs. The procedure is to maintain acid and reducing conditions during cool-down followed by forced oxidation with hydrogen peroxide. This procedure first removes fuel crud and corrosion products on ex-core surfaces then dissolves the reduced nickel so that they may be removed by the clean-up system.

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SKI Report 00:5

On Fuel Crud and Radioactivity Transport in Nuclear Power Plants

Part 2: A Summary of the Contributions to Water Chemistry'98

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Table of Contents

Abstract

Sammandrag

Abstract

This report has surveyed the major results of the contributions concerning fuel crud characterization and radioactivity transport mechanisms that were presented in Water Chemistry'98, an international conference held on October 13-16, 1998 in Kashiwazaki, Japan.

In order to characterize fuel crud, researchers applied various kinds of analytical techniques, such as scanning electron microscopy equipped with energy dispersive X-ray spectrometer (SEM + EDS), X-ray powder diffractometry (XRD), secondary ion mass spectrometry (SIMS), inductively coupled argon plasma emission spectrometry (ICP), and X-ray photoelectron spectrometry (XPS). Moreover, atomic force microscopy was shown to be a potential alternative for crud topography analysis. In particular, sharp SEM images of fuel crud at the cross-sections of fuel rods were successfully obtained.

Thermodynamics was widely applied to interpret the results of water chemistry control. In particular, the concept of solubilities for various solid phases was used. However, the question about whether or not the phase rule is strictly obeyed in reactor water chemistry environments was not discussed in any detail.

Among various techniques for radiation build-up control, zinc addition, high nickel ion concentration control and low dissolved hydrogen chemistry in PWR are a few interesting examples discussed in the conference.

Sammandrag

Denna rapport utgör en granskning av de viktigaste resultaten av bidragen rörande bränslecrud-karaktärisering och mekanismer för aktivitetstransport, som presenterades vid Water Chemistry'98, en internationell konferens i Kashiwazaki, Japan den 13 - 16 oktober 1998.

Varierande analytiska tekniker för karaktärisering av bränslecrud presenterades: SEM + EDS (Scanning electron microscopy equipped with energy dispersive X-ray spectrometer), XRD (X-ray powder diffractometry), SIMS (Secondary ion mass spectrometry), ICP (Inductively coupled argon plasma emission spectrometry), XPS (X-ray photoelectron spectrometry). Atomkraft mikroskopi för analys av crudtopografi visade sig vara ett potentiellt alternativ. Särskilt skarpa SEM bilder av bränslestavars genomskärning visades.

Termodynamik tillämpades allmänt för att förklara resultat inom vattenkemisk kontroll. Speciellt konceptet för löslighet hos flera fasta faser användes. Frågan om fasregeln gäller eller inte för vattenkemi i reaktormiljö diskuterades inte alls.

Bland varierande tekniker för kontroll av aktivitetsuppbyggnad, som diskuterades på konferensen, märktes zinkdosering, god nickeljonkontroll och låg halt av löst väte (PWR).

1. Introduction

Water Chemistry'98 was an international conference on water chemistry in nuclear power plants. It was organized by Japan Atomic Industrial Forum (JAIF) and held in Kashiwazaki, Japan from October 13 through 16, 1998. Over 300 people worldwide attended the conference. The topics covered operational experience, the scientific basis for water chemistry control, advanced technologies, decontamination and reduction of waste and other topics. Over 160 scientific papers were contributed.

This report will summarize the major results of the contributions concerning fuel crud characterization and radioactivity transport mechanisms that were presented during the conference.

2. Characterization of fuel crud

Characterization of fuel crud or corrosion products from reactor water is generally difficult due to radiation problems. In this conference, however, some researchers presented some interesting methods for structural characterization of fuel crud.

Lai, et al. [1] measured the size distribution of crud particles sampled from PWR coolant by scanning electron microscopy (SEM). They estimated the elemental compositions of the particles of different sizes by energy dispersive X-ray spectrometry (EDS). The results showed that over 70% of the particles had a size from 0.1 to 3.0 μm, and Fe counted for about 95% of the total metal cations in the particles.

Goto, et al. [2] analyzed the elemental composition of two kinds of BWR fuel crud samples. One was the outer loosely bound crud; another was the inner tenacious crud. The loosely bound crud had a slightly higher Fe/Ni ratio (1.8) than the tenacious one (1.5). With XRD they detected only nickel ferrite phase in the specimens. With EDS element mapping, they identified some Ni-rich particles in the crud sample and attributed them to NiO phase.

Rosenberg, et al. [3] examined VVER fuel crud by XRD, SEM, secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectrometry (XPS). The crud particles on the outer surface appeared to have regular crystal forms. The main crystalline phase in the crud was identified as ferrite. A small amount of hematite was also present. Elemental carbon, as identified by SIMS and XPS, were seen on some fuel rod sample, which was probably from the disintegrated ion exchange resins.

Nishino, et al. [4] introduced atomic force microscopy (AFM) to study the effect of irradiation on cladding corrosion. They obtained a sharp topograph of a corroded cladding material. AFM seems to be a potential tool even for structural characterization of fuel crud, since the image quality is not influenced by irradiation emitted from a crud sample.

Hermansson, et al. [5] examined fuel crud from some Swedish BWRs. They developed some simple and effective sampling methods for compositional and microstructural analyses of fuel crud. In particular, they succeeded in obtaining sharp SEM images of fuel crud at the cross-sections of fuel rods. They observed, among other things, that fuel crud particles were small at the bottom end of fuel rods but large at the top end. They also observed that in HWC the fuel crud had a lower ratio of nickel ferrite to hematite than in NWC.

3. Mechanisms of crud deposition and radioactivity transport

3.1 For BWR plants

The common approaches to reduce the irradiation build-up in a BWR have been (1) to minimize the use of cobalt containing material in the system; (2) to increase the capacity of clean-up system; (3) to diminish, through water chemistry control, the deposition of non-activated crud on fuel or release of activated crud into the reactor water; and (4) to reduce the amount of activated corrosion products on out-of-core surfaces through surface treatment and water chemistry control. Many researchers presented their operational experiences covering all these fields. Thermodynamics alone was applied to support water chemistry control.

Takamori, et al. [6] described their experience of water chemistry control in the new Japanese ABWR (Advanced Boiling Water Reactor). Very little crud deposition was achieved by the crud concentration to a level of as low as 0.1 ppb or less. They introduced an improved Fe/Ni control by which more iron crud is required at the beginning of a cycle and less iron crud at the end of the cycle. In this way, cobalt in reactor water is locked up on the fuel surface to form a stable ferrite phase.

In contrast with the above Ni/Fe control, high nickel ion concentration control, so-called “ultra low crud control”, has been introduced in some Japanese BWRs (Hemmi, et al. [7]). They found that a few ppb of Ni ion in primary coolant suppressed not only cobalt deposition onto primary piping surface but also corrosion rate of stainless steel. They explained that high Ni favors the formation of ferrite on the stainless surface and suppresses the enclosure of cobalt in the ferrite structure. Moreover, high nickel ion concentration control makes the ferrite on the fuel surface more soluble. Consequently, concentrations of Co-60 and Co-58 remain relatively high in the primary coolant. But the effect is limited due to the extremely low cobalt deposition onto piping surfaces.

Hosokawa, et al. [8] found in a simulated BWR loop that the hematite layer initially formed on fuel cladding may promote the formation of the nickel ferrite phase. Since the nickel ferrite phase in which cobalt is often incorporated is more soluble in reactor water, it is desirable to suppress its formation. This may be done by pre-oxidation of cladding materials.

Uruma, et al. [9] observed that when their new BWR fuel rods were used, the crud deposition rate at the initial stage was increased on the relatively rough cladding surface. However, the effect of surface roughness becomes insignificant after a few hundred hours of exposure in the test loop. They proposed that the preferentially deposited Cr on the cladding in the initial stage re-dissolves very slowly and forms a local acidic region, leading to the radiation build-up problem. Therefore, re-dissolution of deposited Cr may be a potential mechanism to resolve the radiation build-up problem. However, adding Cr ions was found by Inagaki, et al. [10] to have no effect on the suppression of cobalt deposition. In order to elucidate the behavior of Cr compounds by thermodynamic methods, Hiroishi, et al. [11] evaluated the values of hydrolysis constant and the standard formation energy of Cr^{3+} ion at high temperature.

The experience of addition of zinc and other metal ions to decrease irradiation build-up in the BWR plants was reported by many investigators at the conference. Haginuma, et al. [12] investigated the effect on cobalt accumulation behavior on type 304 stainless steel in a simulated BWR loop. They proposed that the mechanisms of the cobalt accumulation suppression by zinc and nickel additions are different. Zinc can reduce both the weight of the corrosion film and cobalt concentration in the corrosion film, while nickel mainly reduces the cobalt concentration in the corrosion film. In the case of calcium, magnesium and manganese additions, no suppression effect on the cobalt accumulation was observed.

A new method has been developed by Hiroishi and Ishigure [13] to treat the thermodynamics of mixed spinels including Fe^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} ions. The method is based on site preference energy of cations in spinel lattices. They have examined (1) the distribution of cations in stoichiometric spinel compounds; (2) the free energy of formation of non-stoichiometric mixed spinels; (3) the distribution of divalent cations in non-stoichiometric mixed spinels and (4) the Co pick-up process of spinels.

3.2 For PWR plants

Garbett, et al. [14] described their experiences about the corrosion product behavior and their relevance to the low radiation fields in PWR since the initial passivation (forming a protective oxide film) of the primary circuit during the hot functional tests (HFT). They suggested that adding H_2 and using start-of-cycle boron/lithium concentrations in HFT is beneficial for later radiation field development. They proposed that nickel and cobalt are released under different redox conditions. Ito, et al. [15] also presented their experience of HFT through the low dissolved H_2 concentration management to remove the outer oxide layer during plant shutdown.

Takahashi, et al. [16] found that in a PWR decreasing feed water hydrazine content and increasing feed water ammonia content to maintain pH are advantageous for the decrease in iron, nickel and other anionic impurities in the secondary circuit.

Hisamune, et al. [17] used low dissolved hydrogen (DH) chemistry as an effective countermeasure against the radiation build-up in a PWR. The method does not influence the fuel integrity during high burn-up operation and may be effective in mitigating PWSCC of Inconel 600 in the primary system. Similar results were also reported by Ishihara, et al. [18]. Based on their thermodynamic analyses, the phenomenon may be due to the high solubility of nickel ferrite spinels. Venz and Dinov [19] found, however, that crud coolant activity is almost independent of DH in the PWR studied. Nishizawa, et al. [20] examined the thermodynamics of crud composition and its relation to DH. Their calculation showed that, under typical PWR conditions, with decreasing DH the nickel fraction in nickel ferrite increases and more nickel may be present in reactor water.

Beverskog and Mäkelä [21] investigated the long-term effect of zinc addition and also interruptions in a PWR loop in Halden. They observed that Co-60 pickup by the pipe materials was low with zinc addition, especially when the pipe materials had fresh surfaces before the experiments. They proposed that zinc addition inhibits the ion transport through the oxide in two ways: hindering inactive cobalt from coming out into the coolant where it can be activated, and inhibiting activated corrosion products from incorporation into the oxide. The former transport is the source for cobalt to be activated and the latter the result of neutron activation of cobalt.

Burrill [22] presented some general ideas about the effects of radiolysis and irradiation on the behavior of corrosion products on fuel cladding. He proposed that (1) reducing radiolytic species from water radiolysis interferes with magnetite formation on fuel cladding in the reactor core and suppresses dissolved iron precipitation, and (2) boiling results in net water radiolysis around the steam bubbles and provides oxidizing conditions on the fuel element surface to enhance precipitation of dissolved iron as magnetite.

Millett and Wood [151] described the shut-down chemistry that is being practiced in many US PWRs. The procedure is to maintain acid and reducing conditions during cool-down followed by forced oxidation with hydrogen peroxide. This procedure first removes fuel crud and corrosion products on ex-core surfaces, and then dissolves the reduced nickel so that they can be removed by the clean-up system.

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