SOLUBILITY Zr-OXIDE AND EFFECT OF WATER CHEMISTRY ON Zr-1%Nb CLADDING CORROSION[1]

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ABSTRACT

A model was developed to describe the influence of physical and chemical parameters on zirconium alloys corrosion in power nuclear reactors.

The model is based on the correlation between the zirconium oxide solubility in high-temperature water under the influence of the chemical parameters and the measured values of fuel cladding corrosion under LWR conditions. By using the apparatus of equilibriums modelling and thermodynamic information calculations were performed to optimise the detailed chemical composition of solutions and Zr corrosion products ZrO_2 and $Zr(OH)_4$ solubility in the primary reactor circuits. In order to get the results, authors used empirical methods for calculation of standard entropy and enthalpy of formation of mononuclear and polynuclear hydrolysis products of zirconium (Zr^{4+}, $Zr(OH)^{3+}$, $Zr(OH)_2^{2+}$, $Zr(OH)_3^{+}$, $Zr(OH)_4^{o}$, $Zr(OH)_5^{-}$).

The influence of coolant quality, as well as temperature and radiation components of corrosion kinetics has also been assessed. The model can be applied for calculating the reliability of nuclear fuel operation.

1. INTRODUCE

Corrosion of Zr alloys is characterised by complex mechanism and depends on many factors [1]. In our opinion, process of corrosion can be described by a model that is based on the correlation between the zirconium oxide solubility in high-temperature water under the influence of the chemical parameters and the measured values of fuel cladding corrosion under LWR conditions.

The total corrosion gain in the case of Zr could be represented by:

$$\mathbf{W = W_T + W_\phi} \quad (1)$$

where W_T and W_ϕ - thermal and radiation weight gain components, respectively.

Empirical studies showed that under constant oxygen pressure in the environment the temperature dependence of the Zr oxidation rate can be described by equation:

$$\mathbf{k_T = k_o \cdot exp(- Q/RT)} \quad (2)$$

The equation serves as a basic for the majority of models predicting Zr-alloys corrosion under LWR conditions and yet it doesn't account for coolant water chemistry.

Table 1. Corrosion rates of Zr+1%Nb alloy under various water chemistry conditions in LWR reactors (average of 3-10 tests) [2]

N°	Water Chemistry Type	pH_{25} measured	pH_{290} calculated	Corrosion rate (x 10^3, mm/h)
1	No stability	4,5-7,0	4,5-5,5	19,4
2	Neutral	6,5-7,0	5,7-6,2	5,6
3	NH_4OH	10,0-10,5	6,5-6,9	2,3
4	K-NH_4OH-B	7,0-8,0	6,5-7,5	0,67
5	Strong alkaline	9,0-10,0	≈ 8-9	38,7

The following experimental facts revealed the influence of water chemistry on Zr-alloys corrosion:

- influence of water pH (Table.1);

- diminution of corrosion film thickness in the transient phase before turning to linear oxidation (i.e. practically partial dissolution of the black film during brief period [3]);
- morphology of > 3-5 m films (the film is formed from grains and has pores of various sizes but of similar geometric form).

The model that considers the influence of water chemistry on Zr alloys corrosion under LWR conditions has been developed in 2 steps which include:

1. Calculation of Zr corrosion products solubilities and
2. Accretion of unified data base on Zr+1% Nb alloys corrosion.

2. CALCULATION OF Zr CORROSION PRODUCTS SOLUBILITIES IN WATER

It is well known that the oxide solubility depends on T, pH and the concentrations of impurities in solution. For some components of Zr water solutions most notably aqua-polymers, experimental thermodynamic data available are very contradictory and unreliable. In some cases such information is missing at all.

Therefore, when it was necessary and possible, the data examination was fulfilled with the use of well-established laws and empirical correlations obtained for wide categories of reactions and compounds: correlations between entropy effects in water solution, empirical dependencies of thermodynamic functions of solid compounds on their composition and temperature, laws of step hydrolysis constants change, their dependence on ions parameters, a.o. The Baes and Messmer method [4] was widely applied in this study.

The fragmentary nature of reliable experimental information on the aqua equlibria at high temperatures poses the question of extrapolating the values of ion thermodynamic functions from the low to the high temperature zone. The current modeling methods such as the Criss and Cobble (1984), Khodakovsky (1968), Breazgalin (1985) and Helgeson (1988) methods are applicable only for a narrow range of chemical species and up to 500-550 K. This study has used the Puchkov and Zarembo method [5], which does

not resort to any empirical parameters and is applicable up to ~ 900 K and ~ 500 MPa without restrictions on any possible aquaspecies.

This method (realised for GIBEN program) calculates the temperature increments of Gibbs energy of formation for ions and changed and neutral ion associates by using merely the values of Gibbs energy of formation and entropies under standard (298,15 K and 0,1 MPa) conditions.

The non-ideality of the solutions was accounted for by generalising the Debye-Huchel relationships (3-rd approximation).

For a series of aqua-species, polynuclear in particular, the thermodynamic functions were estimated for the first time both under standard (298,15 K, 0,1 MPa) and high temperature (up to 623,15 K) conditions.

The above-mentioned examination and calculations give the values of thermal constants under standard conditions for all compounds concerned in the study (see Table 2).

Table 2. Thermal constants for Zr compounds under standard conditions

Compound	$\Delta_f G^0_{298}$ (kJ/mole)	S^0_{298} (J/mole·K)
ZrO_2	-1042,82	50,38±0,4
$Zr(OH)_4$	-1489,8	133,5
Zr^{4+}	-519,7	-338,9
$ZrOH^{3+}$	-761,2	-121,8
$Zr(OH)_2^{2+}$	-999,4	26,7
$Zr(OH)_3^{+}$	-1235,3	124,2
$Zr(OH)_4^{0}$	-1467,9	170,7
$Zr(OH)_5^{-}$	-1652,3	166,1
$Zr_3(OH)_4^{8+}$	-2504,3	-548,9
$Zr_3(OH)_5^{7+}$	-2765,9	-431,7
$Zr_4(OH)_8^{8+}$	-4010,2	-419,4

The results of the examination are given starting with solid compounds of Zr having only one degree of oxidation - (IV). The temperature dependence of the metal Zr heat capacity has been well-studied, and the S^0_{298} value for metallic Zr can be determined with reasonable accuracy. The main solid Zr products in water solutions are ZrO_2 and $Zr(OH)_4$. ZrO_2 has been studied more extensively. The data on the enthalpy of its formation are particularly plentiful while the reliable data on ZrO_2 heat capacity at $T < 298,15$ K are rather limited in number. Studying the thermodynamic properties of zirconium hydroxide is hampered by its instability.

The majority of experimental studies devoted to Zr(IV) thermodynamics in water solutions have been carried out either with strong basic or strong acidic solutions, and the chemical properties ions have been investigated from the standpoint of Zr-Hf separation. The experimental studies of Zr water chemistry are noted for numerous examples of nonreproductivity and conflicting results under similar conditions. Noteworthy also are the facts that some data obtained for solutions with Zr macroconcentrations, where polymerisation processes occur, can't be extended to the solutions with tracer quantitives of Zr where monomers prevail.

Examining homo- and heterogeneous equilibria has allowed to select the values of the hydrolysis constants for Zr^{4+} ion up to the 5th oxidation degree. The data on polymer hydrolysis of Zr are ambiguous, yet the presence of two trimer types and a tetramer type is a well-established fact. Moreover, the formation constants have been also obtained for these species. Literature (original articles and reference sources alike) doesn't contain standard values of formation enthalpies and entropies for mono- and polynuclear products of Zr hydrolysis. Therefore, wide use has been made of empirical and semiempirical methods.

The set of data in Table 2 is most probable although these data need testing and refinement in each case. This is particularly true for the enthalpy and entropy characteristics, since direct experimental measurements are unavailable. Of the wealth of

evidence obtained in numerous calculations of equilibria in the systems of our interest this work reports only the results for solubilities.

The features of monomer hydrolysis of Zr are most noticible at trace metal concentrations (~ 10^{-9} m) when polymerisation is absent through a whole pH range studied (Fig.1). Under these conditions the extent of Zr hydrolysis is very high even in strong acidic media and rises when shifting to the neutral zone occurs. “Base” Zr^{4+} ions are practically absent even at pH ≈ 0,75 and in the range of pH ≈ 1÷9 $Zr(OH)_4^0$ is a prevailing form.

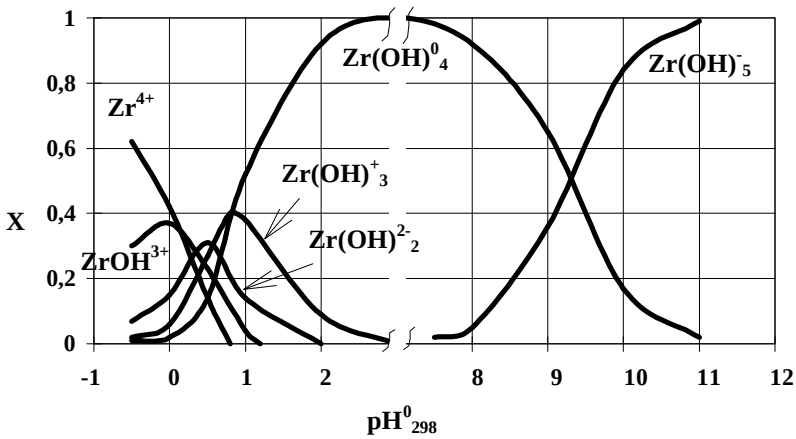

Fig.1. Influence of acid-base properties of water solutions on Zr (IV) mononuclear hydrolysis at 298,15 K, [Zr] = 10^{-9} mole/kg, X - Zr mole fraction

The family of “U”-curves in Fig.2 represents ZrO_2 solubility behaviour as a function of acidic-basic properties of solution. The shift of the curves to the basic zone with temperature growth is clearly seen. The temperature growth to 473 K induces sharp rise of the oxide solubility (almost by a factor of 10^2 compared to that at 298 K). Further growth of temperature substantially raises the oxide solubility in a more acid zone. Hence it follows, that the minimum solubility of zirconium oxide occurs in neutral and moderately acidic media at a minimum temperature concerned.

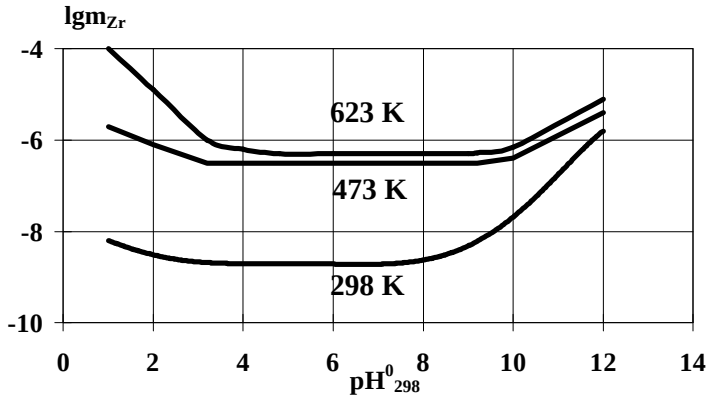

Fig.2. Influence of acid-base properties of water solutions on ZrO_2 solubility at various temperatures: T = 298,15 K; 473,15 K; 623,15 K; m_{Zr} - mole/kg

3. MODEL OF CORROSION

Fig.3 shows the calculated solubilities of ZrO_2 under WWER and PWR primary circuit conditions. Comparing the data in Table 1 and Fig.3 shows that the change in the corrosion rate with pH is adequate to that of the sum of $Zr(OH)_3^+$ and $Zr(OH)_5^-$ concentrations. This fact has been used in our model. At the linear phase kinetics of the corrosion the thickness of the corrosion reaction zone remains constant and no accumulation of corrosion products occurs there.

In this situation the flow of corrosion products through the film pores becomes limiting. At the quasistationary regime general flow (i.e. oxidation rate $\delta h/\delta t$ cm/s) through equipotential surfaces can be written as

$$\mathbf{dh/dt = D_{H2O}\Delta C(V/x) = K_S, \text{ and } K_S \sim K_T} \qquad (3)$$

where D_{H2O} - water selfdiffusion coefficient, cm^2/s; ΔC - concentration gradient, $mole/cm^3$; V - specific oxide (ZrO_2) volume, $cm^3/mole$; x - reaction zone thickness at the (ZrO_{2-x}/ZrO_2) interface, $x \leq 10^{-4}$ cm; K_T - as defined in Eq.2. Since the data on the coefficient of $Zr(OH)_4^{4-n}$ diffusion in water are not available it's been assumed that in

Eq.3 $D_{H2O} \approx D_{Zr(OH)4}^{4-n}$ to an accuracy of a constant coefficient. In the boundary case, when ΔC_x is maximum, it is equal to the equilibrium ion concentration in water (C_{eq}). According to the calculations the temperature dependence of solubility is described by an equation similar to Eq.2, with Q/R dependent both on T and pH_T. That is why Eq.3 describes corrosion process more accurately than Eq.2, which is applicable but in narrow ranges of temperatures and pH.

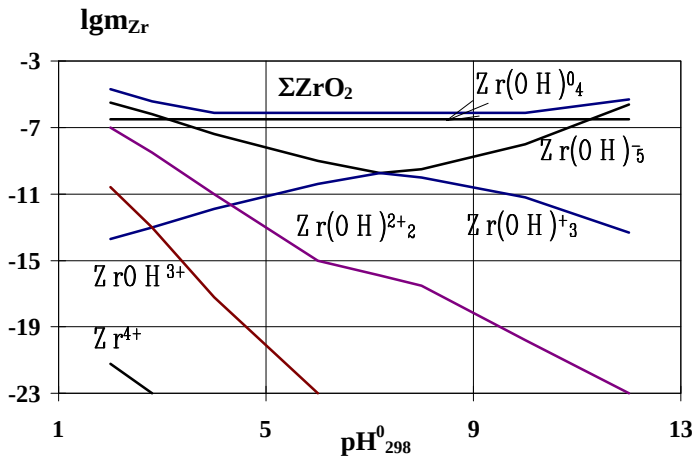

Fig.3. Influence of acid-base properties of water solutions on ZrO2 solubility and its aquaforms distribution at 623,15 K

We assume that irradiation influences on the Zr alloys corrosion rate by changing the coolant chemistry in the above conditions (concentrations of O_2, H_2, H_2O_2, NH_4OH, LiOH, KOH, pH_T , ets.). The activation energy of the radiation corrosion is very small, so that $Q_\phi \approx 0$ [1]. The concentration of dissolved oxygen is one of the important factors that influences the radiation corrosion. Other products of water radiolysis also produce strong effect [6]. Of all long-lived radiolysis products peroxide radicals show the maximum diffusive mobility. In this case

$$\mathbf{k_\phi = f[H_2O_2]_{st}}\ , \qquad (4)$$

where $[H_2O_2]_{st}$ - stationary concentration of H_2O_2. In the case of two-phase flow the coolant (BWR and RBMK conditions) solving the material balance equation, by applying

the stationary concentrations of radiolysis products produced by a simplified radiolysis scheme gives

$$\mathbf{k_{\Phi}^{RBMK} = N\frac{K_G^{H_2}}{p}\Phi^n\alpha} \qquad (5)$$

where N - constant; Φ - neutron fluency, n = 0,5 - 1; $\mathbf{K_G^{H_2}}$ - Henry constant for hydrogen; p - pressure; α - mass vapour content in coolant (α = 0-1).

Theory and experiment points to a very small value of $[H_2O_2]_{st}$ in the PWR and WWER core (< 10 p.p.b), hence as the first approximation for PWR and WWER one can assume $k_{\phi}^{PWR} \approx 0$.

Thus, the thermal component (Eq.2) is common for BWR and PWR alike.

Zr+1%Nb alloy used as RBMK fuel cladding material shows a tendency to nodular corrosion. In compliance with the calculations [7] the maximum H_2O_2 concentration in the BWR coolant water is achieved precisely in the region of initial steam generation. By analogy with Eq.2 for uniform corrosion the linear kinetics equation for nodular corrosion takes the form:

$$\mathbf{V^{loc} = k_T^{loc} + k_{\phi}^{loc}} \qquad (6)$$

The thermal component of the nodular corrosion is most frequently described on the base of CILC-effect (CILC - CRUD Induced Localised Corrosion). The physical meaning of this effect consist in the temperature growth on the outer surface of fuel cladding due to the deposition of corrosion products [8]. From this viewpoint and in compliance with Eq.2 we can write:

$$\mathbf{k_T^{loc} = k_o \cdot \exp[-Q/R(T+\Delta T)]} \qquad (7)$$

where $\Delta T = qh/\lambda$ - growth of cladding temperature under the oxide layers; λ - coefficient of thermal conductivity for oxide layers; h - thickness of the oxide layers.

The model describes the radiation component of the nodular corrosion equation as the combination of several effects, i.e. boiling, irradiation, coolant, impurities, local change

of heat flux. It is also assumed that local boiling provokes the nodular corrosion at the locus of boiling.

In the end the general equation of the nodular corrosion takes the form:

$$V_{BWR}^{loc} = k_T^{loc} + k_\Phi^{loc} = k_0 \exp[-\frac{Q}{R(T + \bar{q}_S \frac{C_{Fe}}{\lambda_C} \tau_i)}] + \alpha\Phi^n \qquad (8)$$

where C_{Fe} - current concentration of ferric products in the coolant; τ_i - time.

Our studies have shown that the local deposition of a rather thin layer of corrosion products or other impurities may induce local overheating as great as 30-70 ^oC and, with considering the "temperature allowance" before coolant boiling in the reactor core may result in local boiling on the fuel rod surface. According to [8] fuel failure almost certainly occurs at surface film overheating above $\Delta T > 50 \div 70$ ^oC. The calculated and experimental results are compared in Fig.4.

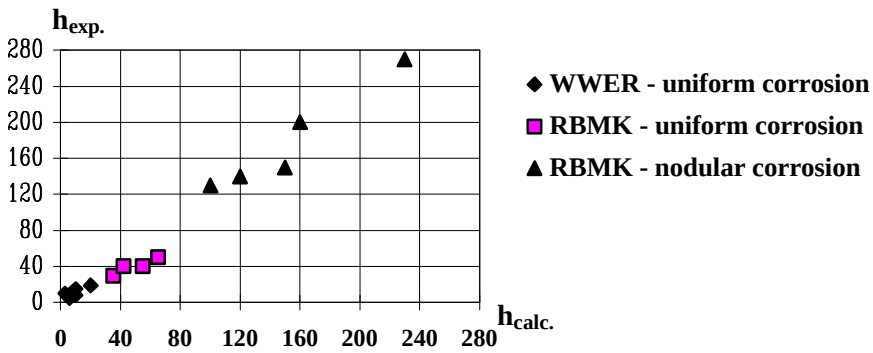

Fig.4. Theoretical (with use of Eq.(8)) and experimental data

4. FUEL FAILURE MODELING

During operation of LWRs fuel reliability may decrease and corrosion of fuel cladding may be responsible for this phenomenon.

To describe the situation we have chosen a model of proportional risks used in the reliability theory [9]. For every set of data the model offers an equation to define the impact of an additional parameter on the fuel failure intensity.

$$\mathbf{n_i = n_0 \exp \sum_{a=1}^{K} b_a V_a} \ , \qquad (9)$$

where n_0 - a nominal number of defective fuel rods discharged from the reactor; n_i - number of fuel rods discharged in i-series; V_a - yearly variation of the corrosion rate determined for a series of data observed or calculated by Eq.8; b_a - coefficient to define the extent of corrosion impact on fuel failure intensity; K - number of parameters considered (corrosion rate included).

Calculations fulfilled by Eq.9 for several RBMK reactor gave the coefficient of the correlation between the observed and predicted fuel failure intensities in the range of 0,63-0,77 (see Fig.5).

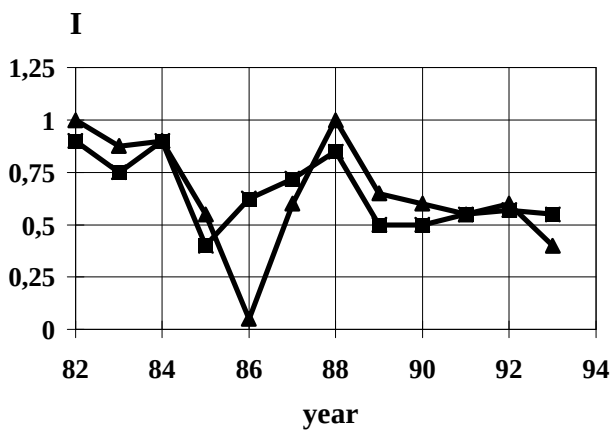

Fig.5. Intensity of fuel leakage (n) at Unit 1 of Leningrad NPP. $I = n_i/n_{max}$

observed results **calculated results**

CONCLUSION

The model has been developed for predicting the influence of water chemistry on Zr alloys corrosion under LWR conditions. This model include calculation of Zr corrosion products solubilities and the correlation with data base on Zr+1% Nb alloys corrosion.

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