# ÚSTAV JADERNÉHO VÝZKUMU
# ŘEŽ

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THEORETICAL APPROACH TO DESCRIPTION OF SOME CORROSION PRODUCT
TRANSPORT PROCESSES IN PWRs PRIMARY CIRCUIT

Report

Řež, October 1990

**informační středisko**

# NUCLEAR RESEARCH INSTITUTE

## ŘEŽ – CZECHOSLOVAKIA

### INFORMATION CENTRE

.

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S U M M A R Y

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# THEORETICAL APPROACH TO DESCRIPTION OF SOME CORROSION PRODUCT TRANSPORT PROCESSES IN PWRs PRIMARY CIRCUIT

## 1. INTRODUCTION

Mathematical modelling of behaviour of corrosion products in NPP primary circuit is significant from the point of view of clarification of effects of various factors on formation of radiation fields and adoption of measures decreasing the doses of operating personnel.

In this contribution, a new approach to some transport processes incorporated into a complex physical and chemical model describing behaviour of corrosion products in PWRs primary circuit is developed.

It is supposed that the corrosion products exist in iont form, colloidal form (size from 0.01 $\mu$m to 0.6 $\mu$m) and in the form of particles and their agglomerates (size from approx. 0.6 $\mu$m to 20 $\mu$m). The whole dispersion spectrum (range of sizes) of colloids and particles is divided into sections characterized by some dimension ($d_{cj}$, $d_{pj}$ - dimension of colloids and particles in the j-th section, respectively). In each section, processes acting as a source of corrosion products or removing corrosion products from the given section (e.g., deposition, detachment) are taking place. Continuity between the sections is secured by the processes of particle coagulation and break-up.

A two-component structure of the oxidic layer is considered: the inner oxidic layer (topotactic layer) is formed as a result of corrosion of structural material; the outer oxidic layer (deposits, epithactic layer) is formed from the corrosion products in the coolant owing to the processes of precipitation and deposition.

## 2. DESCRIPTION OF PRINCIPAL PROCESSES

### 2.1 Release of the corrosion products into the coolant

The process of corrosion is presented as an electro-chemical reaction of the dissolved metal (structural material) in a aqueous environment (coolant) during which the metal is transferred into the iont form. A part of the corroded metal forms the inner oxidic layer (hereinafter the topo-layer) owing to the subsequent oxidation, a part of the corroded metal is released into the coolant in the form of ionts. The topo-layer has a porous structure (with pores going through it) and it is supposed that the concentration of corrosion pro - ducts in the pores is equal to the equilibrium concentration under the given conditions (solubility).

The rate of the electrochemical reaction is not a limiting factor for the release of corrosion products into the coolant. Such processes are represented by molecular diffusion of metallic ionts through the topo-layer pores and mass transfer through the coolant boundary layer.

The transport of corrosion products is described as a diffusion process. The mass flux is directly proportional to concentration gradient between the wall and the bulk of coolant and iversely proportional to the diffusion process "resistance". The "resistance" of the molecular diffusion in the pores of the oxidic layer is given by the relation:

$$R_{MD} \sim \frac{\delta}{D_i} \qquad (s/m) \qquad (1)$$

The "resistance" of the mass transfer through the boundary layer to the diffusion process can be described as:

$$R_{TR} \sim \frac{1}{k_i} \qquad (s/m) \qquad (2)$$

where: $\delta$ - thickness of the oxidic layer, (m)

$D_i$ - coefficient of diffussion of metal ionts in the aqueous environment, $(m^2/s)$

$k_i$ - boundary layer mass transfer coefficient, (m/s)

The flux of mass released into coolant can be then written as:

$$J_r = \frac{D_i \cdot k_i \cdot P \cdot Z \cdot \rho_w \cdot F_i}{D_i \cdot Z + k_i \cdot \delta_{in}} (C_{wi} - C_b) \qquad (kg/s) \qquad (3)$$

where: P   - porosity of the oxidic layer (p = area of pores/total area), (-)

Z   - fraction of given element in the structural material, (-)

$\delta_{in} = S_i / \rho_{ox}$ - thickness of the topo-layer, (m)

$S_i$   - concentration of corrosion products in the topo-layer, (kg/m²)

$\rho_w, \rho_{ox}$ - water and oxide density, respectively, (kg/m³)

$F_i$   - area of corroding surface, (m²)

$C_{wi}$   - solubility of corrosion products near the topo-layer (in pores), (kg/kg)

$C_b$   - concentration of corrosion product in dissolved form in the bulk of the flow, (kg/kg)

The coefficient of transport of ionts through the fluid boundary layer can be determined, e.g., after /1/:

$$k_i = 0.0165 \cdot Re^{0.86} \cdot Sc^{0.33} \cdot \frac{D_i}{d_H} \qquad (m/s) \qquad (4)$$

where: $Re = \bar{U} \cdot d_H / \nu$ - Reynolds number (5)

$Sc = \nu / D_i$   - Schmidt number (6)

$\bar{U}$   - characteristic velocity of a flow system, (m/s)

$d_H$   - hydraulic diameter, (m)

$\nu$   - kinematic viscosity, (m²/s)

## 2.2 Dissolution of the inner and outer oxidic layer

The process of dissolution of the oxidic layer takes place when concentration of corrosion products in the dissolved form near the wall exceeds the concentration in the bulk

of flow (Fig. 1). The rate of the process itself does not play a substantial role in description of this phenomenon since the process is fast in comparison with the transport processes of ionts. The transport of dissolved ionts through the boundary layer of the liquid is the limiting factor in dissolution of the outer oxidic layer (hereinafter epi-layer); in dissolution of the topo-layer, molecular diffusion through the epi-layer is another such factor.

The mass flux owing to the dissolution of the epi-layer is given by the relation:

$$J_{d1} = k_i \; \rho_w \; F_i \; S_c \; \alpha \cdot \left( c_{wc} - c_b \right) \qquad \text{(kg/s)} \qquad (7)$$

The mass flow owing to the dissolution of the topo-layer is given by the relation (Fig. 2):

$$J_{d2} = \frac{k_i \; P \cdot D_i}{D_i + k_i \; \delta_o} \; \rho_w \; F_i \; S_i \; \alpha \cdot \left( c_{wi} - c_b \right) \qquad \text{(kg/s)} \qquad (8)$$

where:  $S_o$    – concentration of corrosion products in the outer oxidic layer, (kg/m$^2$)

$\alpha$    – specific surface of the oxidic layer, (m$^2$/kg)

$\delta_o = \dfrac{S_c}{f_{or}}$ – thickness of the epi-layer, (m)

$c_{wc}$    – solubility of corrosion products near the epi-layer, (kg/kg)

## 2.3 Precipitation on the outer and inner oxidic layer

The process of precipitation on the surface of an oxidic layer takes place when the concentration of corrosion products in the dissolved form in the bulk of coolant exceeds the concentration near the wall (Fig. 1). As in the process of dissolution the precipitation itself has no significant effect on the rate of the whole process. The limiting factor for precipitation on the coolant/epi layer interface is represented by the transport of ionts through the boundary

layer of the liquid. In the case of precipitation on the metal/topo-layer interface the molecular diffusion of ionts through the whole oxidic layer is a further limiting factor.

The flux of mass precipitation on the coolant/epi-layer interface (Fig. 2) is given as:

$$J_{c1} = k_i \cdot \rho_w \cdot F_i \cdot (c_b - c_{wi}) \qquad (\text{kg/s}) \qquad (9)$$

The flux of mass precipitating on the metal/topo-layer interface is given by the relation:

$$J_{c2} = \frac{k_i \cdot D_i \cdot P}{D_i + k_i \cdot \delta_{ox}} \cdot \rho_w \cdot F_i \cdot (c_b - c_{wi}) \qquad (\text{kg/s}) \qquad (10)$$

where: $\delta_{ox} = \frac{S_o + S_i}{\rho_{ox}}$ -total thickness of the oxidic layer, (m)

## 2.4 Process of agglomeration of corrosion products

The interaction of sections of colloids and particles of corrosion products takes place during the process of their agglomeration, that is during the process of collision of two particles and formation of a bigger particle (the same relates also to colloids).

For formation of a particle with the size $d_j$ it is necessary that two particles with sizes $d_l$ and $d_k$ satisfying the condition

$$d_j = \sqrt[3]{d_l^3 + d_k^3} \qquad (11)$$

agglomerate. It is supposed that the agglomeration takes place by means of Brownian and turbulent agglomerations /2, 3/. Probabilistic function for the Brownian mechanism of agglomeration has the form:

$$P_b(d_k, d_l) = \frac{2 k_B T}{3 \mu} \left( d_k + d_l \right) \cdot \left( \frac{1}{d_k} + \frac{1}{d_l} \right) \qquad (\text{m}^3/\text{s}) \qquad (12)$$

The probabilistic function of agglomeration owing to the turbulent mechanism is determined in dependence on the relation of particle size and of microscale of turbulence $\lambda_o$ :

$$P_T(d_\kappa, d_\ell) = 3\pi \left(\frac{\varepsilon}{\nu}\right)^{1/2} (d_\kappa + d_\ell)^3 \quad \text{for} \quad (d_\kappa + d_\ell) < \lambda_o \quad (m^3/s) \qquad (13)$$

$$P_T(d_\kappa, d_\ell) = \frac{\pi}{3 \cdot \bar{\nu}} \cdot \varepsilon^{1/3} (d_\kappa + d_\ell)^{7/3} \quad \text{for} \quad (d_\kappa + d_\ell) > \lambda_o \quad (m^3/s) \qquad (14)$$

The rate of formation of particles with the size $d_j$ will be equal (with consideration of the condition (11) ) to:

$$J_{coag} = \frac{6 \, M \, \rho_w}{\tau \cdot \rho_{ox}} \cdot \left[P_T(d_\kappa, d_\ell) + P_b(d_\kappa, d_\ell)\right] \cdot \frac{d_\kappa^3 + d_\ell^3}{d_\kappa^3 \cdot d_\ell^3} \cdot C_\kappa \cdot C_\ell \quad (kg/s) \qquad (15)$$

where :   $k_B$  - Boltzman constant, (J/K)
          $T$  - temperature, (K)
          $\mu$  - dynamical viscosity, (Pa.s)

$\varepsilon = \dfrac{2 \, \bar{U}^3 \, C_f}{d_\kappa}$ - rate of turbulent energy dissipation per unit of mass, (W/kg)

$\lambda_o = \left(\dfrac{\nu^3}{\varepsilon}\right)^{1/4}$ - Kolmogorov microscale of turbulence, $(m)$

          $C_f$  - Fanning friction factor
          $M$  - mass of coolant, (kg)
          $C_1, C_k$ - concentrations of particles/colloids of corrosion products with sizes of $d_1$, $d_K$, (kg/kg)


## 2.5 Deposition and detachment of colloids

As colloids, the corrosion product particles with sizes in the range from 0.01 to 0.6 $\mu$m and carrying electric charge are understood. Owing to the Van der Waals, electric and magnetic interactions of a colloidal particle with an electrically charged surface a potential barrier is formed with parameters and form determining the processes of deposition of colloids on the outer oxidic layer and detachment from this layer. The shape of

the potential barrier, formed in consequence of attracting Van der Waals and repulsion electric interactions, is outlined in Fig. 3 where those barriers the colloidal particle must overcome during the processes of deposition and detachment are also shown.

The Van der Waals interaction potential between a spherical particle with diameter $d_{cj}$ and a flat plate is determined by the relation /4/:

$$\phi_w = A \cdot \left[ \frac{1}{6} \ell_n \left( \frac{H + d_{cj}}{H} \right) - \frac{1}{12} \cdot \frac{d_{cj}}{H} \cdot \frac{2H + d_{cj}}{H + d_{cj}} \right] \qquad (J) \qquad (16)$$

The electrical double layer interaction potential of a spherical particle and a flat plate can be described in the following manner /5/:

$$\phi_\varepsilon = \frac{\varepsilon \cdot \varepsilon_o \cdot d_{cj}}{8} \left\{ 2 \, \Psi_1 \Psi_2 \, \ell_n \left[ \frac{1 + e^{-kH}}{1 - e^{-\kappa H}} \right] + \left( \Psi_1^2 + \Psi_2^2 \right) \ell_n \left[ 1 - e^{-2\kappa H} \right] \right\} \qquad (J) \qquad (17)$$

The surface interaction potential is given by a sum of the expressions (16) and (17):

$$\phi = \phi_w + \phi_\varepsilon \qquad (J) \qquad (18)$$

where: A - Hamaker's constant, (J)

H - separation between the spherical particle and the plane surface, (m)

$\varepsilon_o$, $\varepsilon$ - permitivity of free space (F/m) and dielectric constant

$$K = \left( \frac{2 \cdot z^2 \cdot e^2 \cdot N(\infty)}{\varepsilon_o \cdot \varepsilon \cdot k_B \cdot T} \right)^{1/2} - \text{inversion diffuse layer thickness,} (1/m) \quad (19)$$

$\Psi_1$, $\Psi_2$ - Stern potentials of the colloid and the surface, (V)

z - valence

e - electronic charge, (C)

$N(\infty)$ - colloid concentration at a distance from the surface, $(1/m^3)$

The surface electrical potential $\psi(0)$ is determined by the difference between the value of the corrosion product point of zero charge and the pH value of the coolant /6/. (The point of zero charge is characterized by such pH value of environment that the corrosion product electrical double layer behaves for the outside as neutral.)

$$\psi(0) = 2,3 \frac{R.T}{F} \cdot \left( pzc - pH \right)$$

(V)    (20)

where:  R, F - universal gas constant, Faraday number, (J/mol.k), (C/mol), respectively

pzc  - point of zero charge

The deposition of colloids on the epi-layer surface consists of two processes:

- transport of colloids through the boundary layer of the liquid;

- capture of colloids on a surface, described by the probability of their penetration through the potential barrier.

The rate of capture of colloids on a surface is determined by the expression /7/:

$$Q_j = \frac{D_{Bj}}{\int_{0}^{\delta} \left[ exp\left( \phi / k_b T \right) - 1 \right] dH}$$

(m/s)    (21)

where:  $D_{Bj}$  - coefficient of Brownian diffusion of colloid with the size $d_{cj}$, $(m^2/s)$

$\phi$  - surface electrical potential, (J)

$\delta$  - maximum extent of surface interaction potential, (m)

The flux of colloids of all sections, depositing on the surface of epi-layer, will be equal to:

$$J_{dc} = \sum_{j=1}^{m} \frac{a_j \cdot k_{pj}}{a_j + k_{pj}} \cdot \rho_w \cdot F_i \cdot C_{cj} \qquad (kg/s) \qquad (22)$$

where : $k_{pj}$ - coefficient of transport of colloids of the
j-th section through the boundary layer of the
liquid, (m/s)

$a_j$ - first order surface reaction rate constant, (m/s)

$C_{cj}$ - concentration of colloids with the size $d_{cj}$,
(kg/kg)

m - number of sections of colloids

During the detachment of colloids from the epi-layer
the colloid particle must (with a help of hydrodynamical effect
of the liquid) penetrate the potential barrier shown in Fig.3.
The rate of escape of the colloids with the size $d_{cj}$, from
the surface can be described by the following expression /8/:

$$b_{pj} = \frac{D_{pj}}{\int_{r \cdot Y_o}^{Y_i} exp\left(- \phi(y)/k_B T\right) \int_{v \cdot Y}^{\infty} exp\left(\phi(v)/k_B T\right) dv \, dy} \qquad (1/s) \qquad (23)$$

where: $l_o$ - separation at minimum of potential, (m)

$Y_i$ - separation at maximum of potential, (m)

The flux of colloidal particles of all sections, which
are detached from the surface of the outer oxidic layer, is
given by the expression:

$$J_{cc} = \sum_{j=1}^{m} b_{pj} \cdot S_c \cdot F_i \qquad (kg/s) \qquad (24)$$

where : $b_{pj}$ - first order constant for escape of colloidal
particles from a surface, (1/s)

## 2.6 Break-up of corrosion products agglomerates

Agglomerates are formed from smaller particles and colloids as a consequence of processes of agglomeration. Their break-up into their individual particles takes place, if the shear stresses $\tau$ acting on the agglomerate from the side of flowing liquids exceed the attracting forces $F_A$ acting between the particles. It is assumed that the agglomerate consists of mono-dispersion particles/colloids with the size $d_M$. The atractive forces among the mono-dispersion particles forming the agglomerate have the nature of the Van der Waals forces and it is possible to describe them by means of the following relation /3/:

$$F_A = \frac{A \cdot d_M}{12 \cdot H^2} \qquad (N) \qquad (25)$$

where: $d_M$   - the size of the mono-dispersion particles forming the agglomerate, (m)

     $H$   - minimum distance of separation, (m),

The general criterion of stability of the agglomerate is as follows:

$$\frac{F_A}{\pi \cdot d_M^2} < \tau \qquad (N/m^2) \quad (26)$$

where : $\tau$ - shear stress acting on the agglomerate from the side of liquid, $(N/m^2)$

The maximum stable size of an agglomerate is determined in dependence on the relation of the size $d_{pj}$ and the turbulent scale in the liquid $\lambda_0$ (27), (28) and is simultaneously a function of the sizes of mono-dispersion particles forming the agglomerate /3/:

$$d_{max} = \left(\frac{\pi \cdot d_n^2}{F_A}\right)^{3/2} \cdot (12\mu)^{3/2} \cdot \varepsilon^{1/2} \qquad \text{for} \quad \lambda_o < d_{pi} < 10\lambda_o \qquad \text{(m)} \quad (27)$$

$$d_{max} = \left(\frac{\pi \cdot d_n^2}{F_A}\right)^{3/2} \cdot \left(\frac{2}{\rho w}\right)^{3/2} \cdot \frac{1}{\varepsilon} \qquad \text{for} \quad d_{pi} > 10\lambda_o \qquad \text{(m)} \quad (28)$$

If the size of the agglomerate is lower than the scale of turbulence, the maximum allowable value of rate of dissipation of turbulent energy is the limiting factor /3/:

$$\varepsilon_{max} = \frac{\nu}{(12\mu)^2} \cdot \left(\frac{F_A}{\pi \cdot d_n^2}\right) \qquad \text{for} \quad d_{pi} < \lambda_c \qquad \text{(W/kg)} \quad (29)$$

It is assumed, that the share of agglomerates with the size $d_{pj}$ formed by the mono-dispersion particles with the size $d_M$ into which the agglomerates break-up is proportional to the share of such particles in the dispersity spectrum $\alpha_{Mj}$ from which the given agglomerate can be formed (that is, it must hold that $d_M < d_{pj}$):

$$\alpha_{Mj} = \frac{C_M}{\sum\limits_{k=1}^{i} C_k} \qquad (30)$$

where: $C_M$ - concentration of particles (colloids) with the size $d_M$, (kg/kg)

$C_k$ - concentration of particles (colloids) with $d_k < d_{pj}$, (kg/kg)

The mass of particles with the size $d_M$ formed as a consequence of break-up of all particles and their agglomerates is described by the expression:

$$J_{bM} = \sum_{j=1}^{n} c_{pj} \cdot Q \cdot \alpha_{Mj} \cdot B_{Mi} \qquad \text{(kg/s)} \quad (31)$$

where :  Q - coolant flow rate, (kg/s)

$\alpha_{Mj}$- the share of particles $d_M$ in the dispersity spectrum (30)

$B_{Mj}$- criterion stability of the agglomerates (27) - (29), ($B_{Mj}$ = 0 or 1)

n - number of sections of particles and agglomerates.


## 2.7 Deposition of corrosion product particles

The deposition of particles can be described by a model of Beal /9/. The flux of mass directed towards tha wall is described here with consideration of Brownian diffusion of particles through the boundary layer of the liquid and of pulsation of particle concentration in the turbulent wind. Supposing that the scales of turbulent viscosity and turbulent diffusion are equal, the flux of mass can be described by the following relation:

$$N = \left(D + \nu_T\right)\frac{dc}{dy} \qquad (kg/m^2.s) \qquad (32)$$

where:  N  - flux of mass towards the wall, $(kg/m^2.s)$

D  - Brownian diffusion coefficient, $(m^2/s)$

$\nu_T$ - eddy diffusivity, $(m^2/s)$

C  - concentration of additions (particles), $(kg/m^3)$

By means of empirical expressions for $\nu_T$ in the laminar, buffer and turbulent layers of liquid it is possible to solve the equation (32). The coefficient of deposition of particles with the size $d_{pj}$ is given by the relation:

$$K_{pj} = \frac{K \cdot p \cdot v}{K + p \cdot v} \qquad (m/s) \qquad (33)$$

where:  K  - transport coefficient, (m/s) (for its detailed determination in the laminar, buffer and turbulent layers, see /9/)

v - radial velocity of particle, (m/s)

p - sticking probability, (-)

The sticking probability of particles on the wall is determined in the following manner /10/:

$$P = \begin{cases} 1 & \text{for } S^+ \leq 2.4 \\ (2.4/S^+)^4 & \text{for } S^+ \geq 2.4 \end{cases} \quad (34)$$

where: $S^+ = S \cdot \dfrac{u \cdot \sqrt{c_j/2}}{\nu}$ — dimensionless stopping distance (35)

$$S = \dfrac{0.05 \cdot \rho_{cx} \cdot d_{pi}^2 \cdot \bar{u} \cdot \sqrt{c_j/2}}{\mu} + \dfrac{d_{pi}}{2}$$ — stopping distance, (m) (36)

The flux of mass directed towards the wall and forming the deposits is equal to:

$$J_{df} = \sum_{j=1}^{n} K_{Dj} \, \rho_w \, F_i \, c_{pi} \quad \text{(kg/s)} \quad (37)$$

where: $K_{Dj}$ - deposition coefficient of particles with the size $d_{pj}$, (m/s)

## 2.8  Erosion of particles from the deposits

Principal factor determining the resuspension (ero - sion) of particles from the deposits (epi-layer) is represented by hydrodynamical effect of flow of liquid. The forces maintaining the particles in this layer have the nature of the Van der Waals forces. The Van der Waals forces between a particle and a surface are given by the relation /6/:

$$F_v = \dfrac{A \cdot d_{pj}}{12 \cdot H^2} \quad \text{(N)} \quad (38)$$

The tangential drag forces acting on the surface
from the side of flow of liquid are given by the relation /6/:

$$F_d = \frac{1}{2} \cdot f_d \cdot C_d \cdot \rho_w \cdot \bar{u}^2 \cdot \frac{\pi \cdot d_{pi}^2}{4} \qquad \text{(N)} \qquad (39)$$

where: $C_d$ – particle drag coefficient

$\bar{u}$ – fluid velocity, averaged over particle projected
area, (m/s)

$f_d = 1.7$ – factor to allow for proximity of surface and velo-
city distribution normal to the surface

The fluid velocity, averaged over the particle pro –
jected area is determined in dependence on the relation of par-
ticle size $d_{pj}$ and the boundaries for the laminar, buffer and
turbulent layers of liquid in which the velocity profile is
determined in different way.

In the hydrodynamical action of the flow on a partic-
le the deposits is higher than the forces binding the particle
to the deposit surface, such particle is resuspended from the
deposit and is carried by the flow of liquid. The rate of par-
ticle erosion (resuspension) can be determined on the basis of
the rate of their deposition. (It is not possible to resuspend
more particles of given size from a surface than is the number
of particles deposited on the surface.) The flux of mass from
the deposits owing to erosion by the flow of liquid is descri-
bed by the following relationship:

$$J_{ep} = \sum_{j=1}^{n} K_{Dj} \cdot \rho_w \cdot F_i \cdot \gamma \cdot C_{pi} \cdot E_j \qquad \text{(kg/s)} \qquad (40)$$

where: $\gamma$ – factor of particle overlapping and screening in the
direction of fluid flow $(0 < \gamma < 1)$

$E_j$ – criterion of erosion of particles from a surface

$E_j = 1$ if $F_d > F_v$

$E_j = 0$ if $F_d \leqslant F_v$

## 3. CONCLUSION

On the basis of the approaches presented above a physical and chemical model of corrosion product behaviour in a PWR primary circuit (computer code DISER) is being developed. The model attempts to consider the transport of corrosion products in coolant in iont, colloidal and insoluble forms and different nature of their transport processes. In description of the individual processes there has been an effort to base the work mainly on the theoretical nature of the phenomena and to minimize the utilization of experimental quantities which can be different for different facilities. Complex approach to the description of corrosion product behaviour can clarify the roles of the individual factors and processes, mainly the role of colloidal particles which effect on formation of radiation fields is very unclear.

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surface

coolant

$C_w$

Dissolution

$C_b$

$C_s$

Precipitation

$C_w$
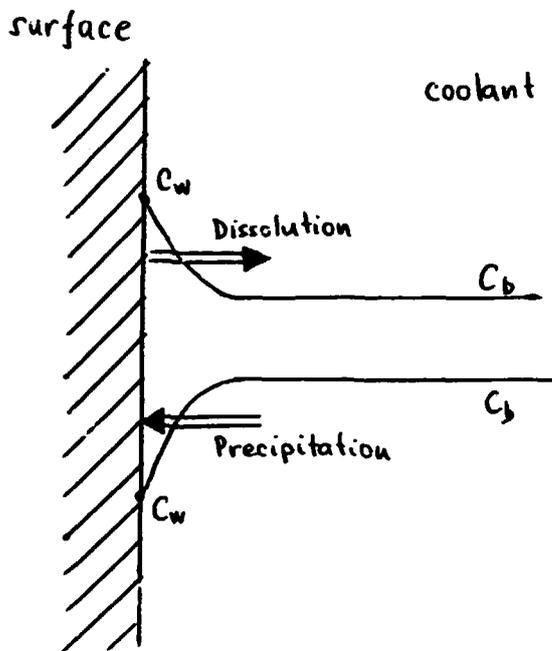
Fig. 1    Processes of corrosion products dissolution
and    precipitation

$C_b$

dissolution          precipitation          bulk of stream

$J_d$                $J_c$

coolant

boundary layer

$J_{d_1}$    $J_{d_2}$          $J_{c_2}$    $J_{c_1}$          oxidic

$C_{w_o}$                                    outer layer
                        layer

$C_{w_i}$                                    inner layer

base metal
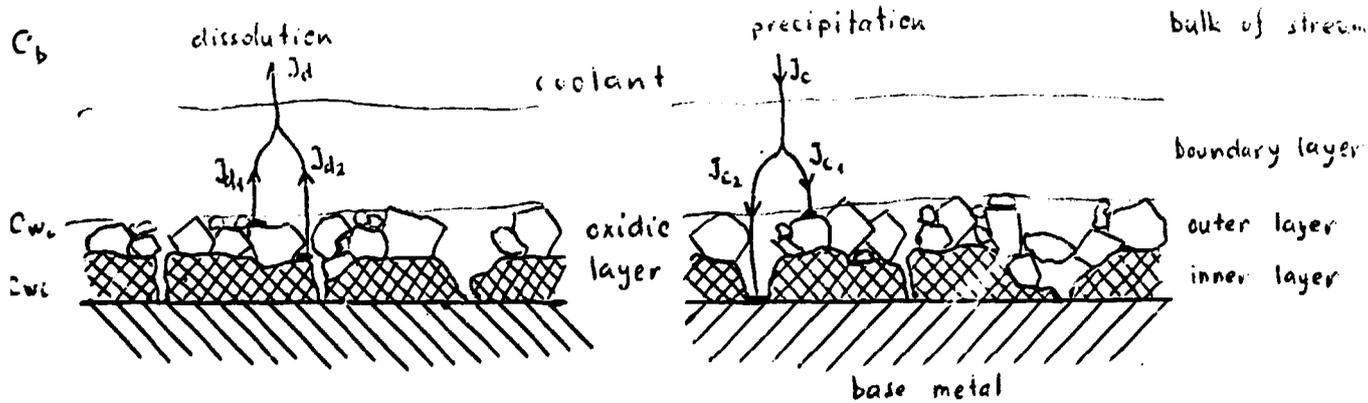
Fig. 2a  Dissolution of inner          Fig. 2b  Precipitation on outer
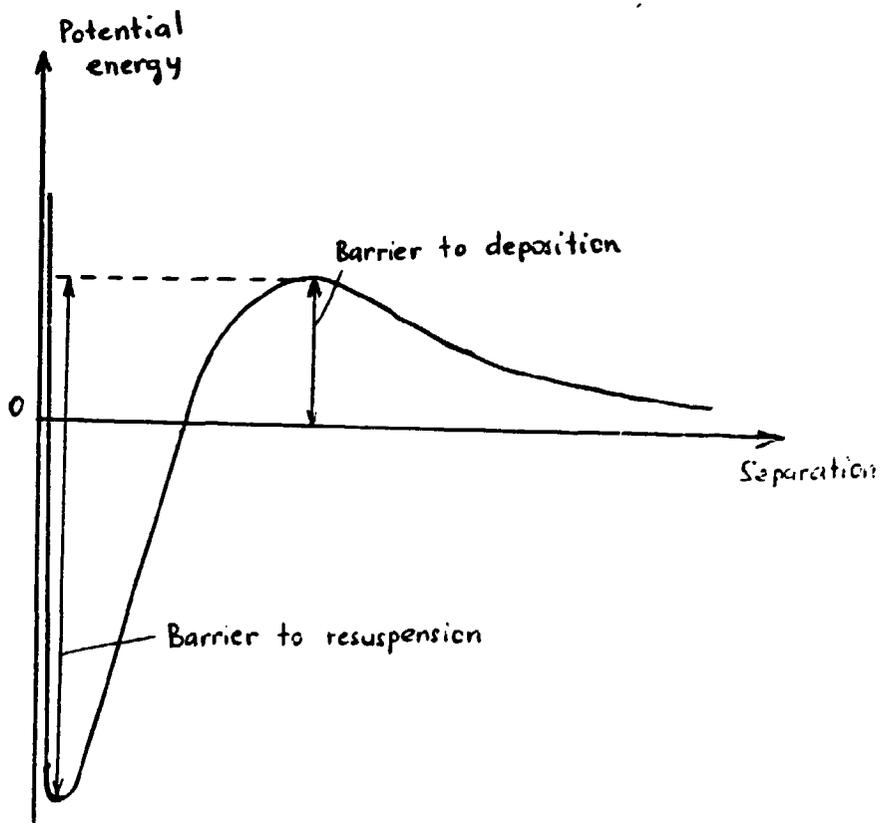and outer oxidic layer          and inner oxidic layer

Fig. 3    Interaction potential for combination of attractive van der Waals and repulsive electrical double layer forces