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Mechanism of reinforcement corrosion

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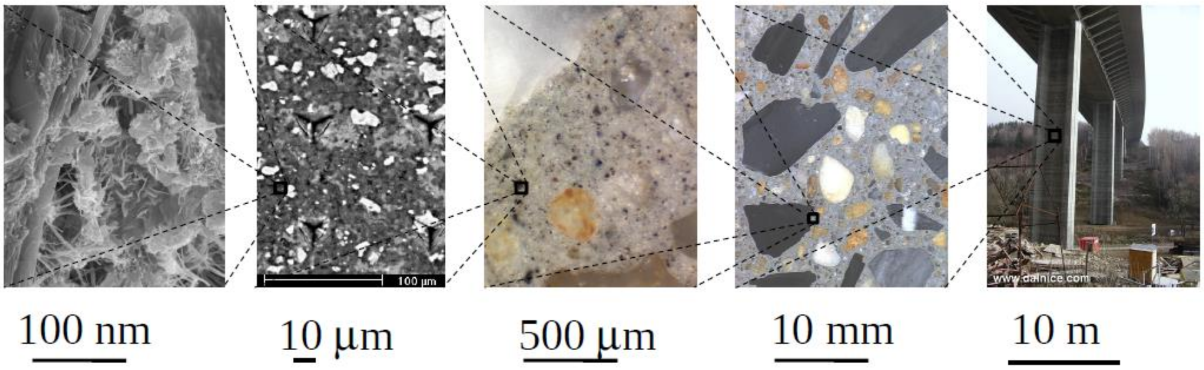
Contents

1 Introduction

Durability of concrete depends on options of transport of aggressive substances after concrete hardening- especially penetrations of liquids (water), gases (carbon dioxide, oxygen) or ions (chlorides, sulfates). Penetration is enable by presence of pores, by their amount, type and size.

Transport processes of concrete
Absorption- suck of substances in to capillary pores of material
Diffusion- expanding of particles by difference of concentration
Penetration- substances enter into concrete and permeate concrete by difference of pressure on surface of materials (water and concrete)

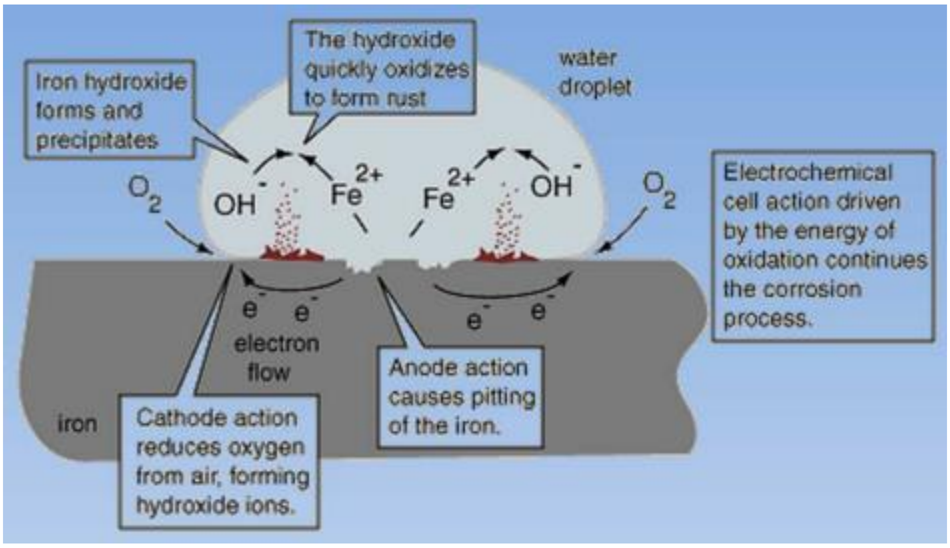
Scales of cement- based materials
We have several scales of observation of concrete.



In scale of construction (10^{-1} m) we can see concrete and reinforcing steel bars, of concrete (10^{-1} - 10^{-2} m) we can see mortar and coarse aggregates (>5 mm), of mortar (10^{-2} - 10^{-4} m) we observe cement paste, fine aggregates (<5 mm), macroporosity, admixtures and additives. In scale of cement paste (10^{-4} – 10^{-6} m) we observe clinker minerals, hydration products (C-S-H), capillary porosity, capillary water, admixtures and additives. In scale of C-S-H (10^{-6} – 10^{-9} m) we observe globule, gel water and gel porosity.

2 Basic principle of corrosion

Corrosion of steel reinforcement is electromechanical process shows on following picture. Corrosion may starts when cover layer is destroyed.



Picture 1[http://concrete.fsv.cvut.cz/~prochazka/YTBK/Prednaska_2_2014.pdf]

During corrosion of metal are going two reactions on the surface of reinforcement. One of them is oxidation also referred to as partial anodic reaction (dissolution of iron) and second is reduction reaction which is also referred to as partial cathodic reaction (reduction of oxygen). The products of electromechanical reaction can reacts witch each other and non-electrochemically to form the rust on iron bar surface. The process can be describe as following reaction:

(1) $2\ Fe + 2\ H_2O + O_2 \rightarrow 2\ Fe(OH)_2$

This reaction includes the dissolution of iron, the reduction of oxygen and formation of rust:

(2) $Fe \rightarrow Fe^{2+} + 2\ e^-$	anodic
(3) $2\ H_2O + O_2 + 4\ e^- \rightarrow 4\ OH^-$	cathodic
(4) $2\ Fe^{2+} + 4\ OH^- \rightarrow 2\ Fe(OH)_2$	chemical

3 Types of corrosion

The known types of corrosions are in this time uniform, pitting, crevice and galvanic corrosions. Article is more focused on uniform and pitting corrosion, which are the most common for corrosion of reinforcement.

3.1 Uniform corrosion

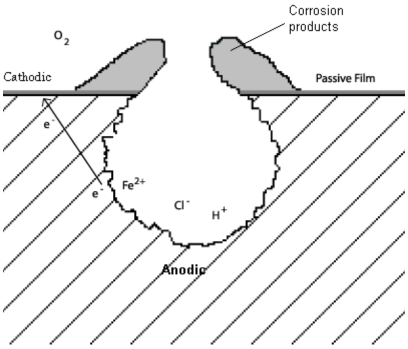
The most widespread form of corrosion that is observed, uniform corrosion is characterized by corrosive attack proceeding evenly over the entire surface area, or a large fraction of the area of the metal under attack.

Picture 2[https://www.nace.org/Corrosion-Central/Corrosion-101/Uniform-Corrosion]

3.2 Pitting corrosion

Pitting corrosion is caused by depassivation of a small area, localized form of corrosion that leads to the creation of small holes (pin holes) in the material. Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to predict and design against. Corrosion products often cover the pits making the detection often very difficult.

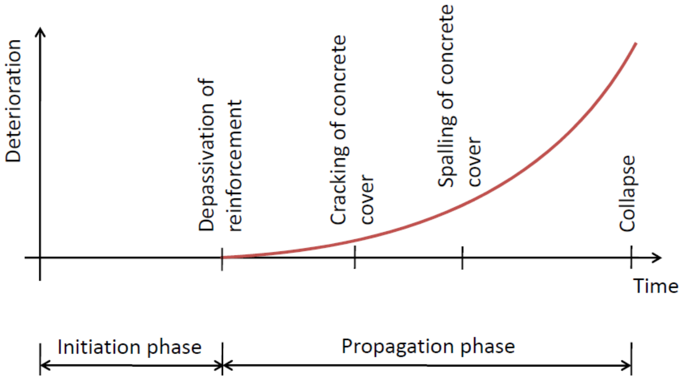
Picture 3: Pitting corrosion [forensic.cc] [octane.nmt.edu]



Picture 4: Pitting corossion

4 Service life

The service life is time period during which a structure or any its part satisfy design performance requirements without unexpected costs or disruption due to maintenance and repair. The service life of reinforced concrete structures can be divided into two time periods. First is named as *initiation period* t_i, i.e. the time from concrete casting to the moment when the reinforcement is no longer passivated. Second, the *propagation period* t_p, during this time the corrosion of the depassivated steel takes place, and consequently, the failure probability is increased for both the load and service ability limit states.

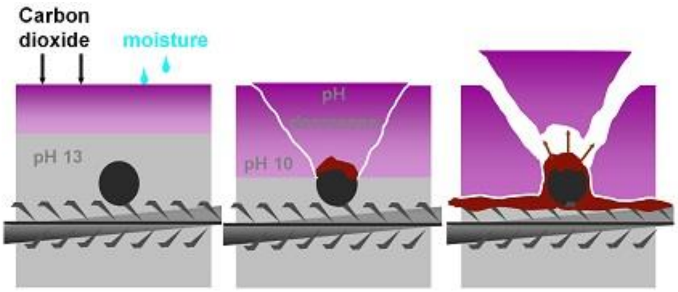


Picture 5: Initiation and propagation phase (Smilauer, 2014)

The most damaging mechanism for steel corrosion in reinforced concrete are carbonation and chloride ingress.

5 Carbonation

A diffusion- driven process is accelerated by presence of cracks. The process is described as follows $Ca(OH)_2+CO_2=CaCO_3+H_2O$. Portlandit reacts with carbon dioxide. Portlandit is divided to the calcium carbonate and water. It decreases Ph under 9, follows depassivation of reinforcement surface and in final corrosion of reinforcement. Products of corrosion causes increasing of reinforcement volume and it causes abruption of concrete cover.



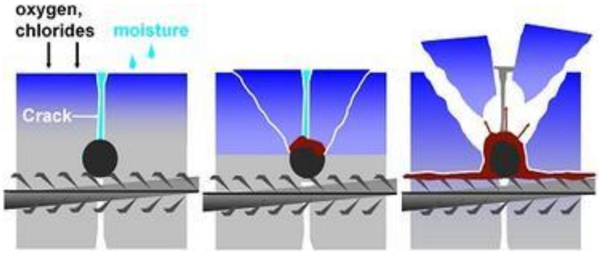
Picture 6[http://failures.wikispaces.com/Concrete+Bridge+Failures+-+Deterioration+and+Spalling]

The main factors for controlling of carbonation are diffusivity of CO_2 and reactivity of CO_2 with concrete. The main factors affecting concrete carbonation are the type and the content of binder, the water/binder ratio, the degree of hydration, the concentration of CO_2 and relative humidity. The rate of carbonation is also affected by content of water and cement, the content of alkali, the type of cement, the fineness of the materials, the temperature and presence of cracks.

6 Chloride ingress

In this thesis is used program documentation of FReET (FReET, 2010): Steel bars are passive, as far as corrosion in the presence of oxygen and moisture is concerned, thanks to a microscopically thin oxide layer which forms in their surface due to the alkalinity of the concrete is lost due to carbonation. However, in marine and coastal environments, or in the presence of deicing salt (NaCl), it can be destroyed by chloride ions dissolved on pore water. Reinforcement corrosion starts when chloride concentration exceeds about 0.6 % of binder mass.

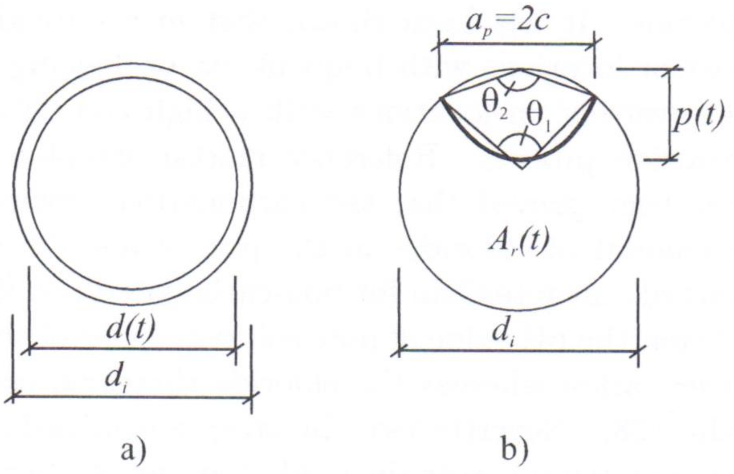
One reason for the lack of agreement among the measured values of the critical chloride concentrations is the influence of several factors such as chloride binding, chloride mobility, steel interface (voidage, pre-rusting), cementitious binder (type of binder, C3A content, pH), concrete barrier (cement type, amount of cement, w/c ration, curing, concrete cover), and environmental factors (relative humidity, temperature, chloride type).



Picture 7[http://failures.wikispaces.com/Concrete+Bridge+Failures+-+Deterioration+and+Spalling]

7 Steel corrosion

Electrochemical process during which coupled anodic and cathodic reactions take place.



Picture 8: a) uniform corrosion b) pitting corrosion

In this chapter will describe steel corrosion models for uniform and localized corrosion.

7.1 Model of corrosion 1

(FReET, 2010): This model is used for the prediction of uniform corrosion. The formula for the time related net rebar diameter *d(t)* in exposure time *t* [years] reads

$$(5)\, d(t) = \begin{cases} d_i & t \leq t_i \\ \varphi[d_i - 0.0116 i_{corr} R_{corr} (t - t_i)] & t_i < t < t_i + \frac{d_i}{0.0116 i_{corr} R_{corr}} \\ 0 & t > t_i + \frac{d_i}{0.0116 i_{corr} R_{corr}} \end{cases}$$

Where φ is the uncertainly factor of the model [-], d_i is the initial bar diameter [mm], $t = t_i + t_p$ where t_i is the time to corrosion initiation, i.e. depassivation, and t_p is the time of corrosion propagation, parameter R_{corr} [-] express the type of corrosion. For uniform corrosion the coefficient R_{corr} equals 2. By the coefficient R_{corr} also the effects of chloride concentration, pH level or other conditions may be described, whenever applicable. i_{corr} is the current density (normally expressed in μA/cm^2). For uniform corrosion, a mean value can be considered as 1 μA/cm^2 or calculated according to (Petersson, 2004). This formula describes the dependence of i_{corr} on time derived on the basis of experiments for RC flexular members as:

$$(6)\, i_{corr} = 0.3686 \ln(t) + 1.1305$$

7.2 Model of corrosion 2

(FReET, 2010): This model is used for localized corrosion. The studies by Gonzales show that the maximum rate of corrosion penetration in the case of pitting corrosion is 4-8 times that of general corrosion. The depth of pit *p(t)*[mm] at time *t* [years] can be estimated by the following equation

$$(7)\, p(t) = \varphi[0.0116 i_{corr} R_{corr} (t - t_i)]$$

Where φ is the uncertainly factor of the model [-],$t = t_i + t_p$ where t_i is the time to corrosion initiation and t_p is the time of corrosion propagation. For $t_i < t_p$, *p(t)* = 0. Corrosion current i_{corr}

is taken as 3 μA/cm^2 to mm/years under the assumptions that steel (Fe) has $n = 2$ (number of electrons freed by the corrosion reaction), $M = 55.85$ g (atomic mass) and $d = 7.88$ g/cm^3.

7.3 Model of corrosion 3

(FReET, 2010): Advanced modelling of localized corrosion. The net cross sectional area of corroded rebar A_r at time t is calculated as

$$(8)\, A_r(t) = \begin{cases} \varphi\left(\pi\frac{{d_i}^2}{4} - A_1 - A_2\right) & p(t) \leq \frac{\sqrt{2}}{2}d_i \\ \varphi(A_1 - A_2) & \frac{\sqrt{2}}{2}d_i < p(t) \leq d_i \\ 0 & p(t) > d_i \end{cases}$$

Where

$$(9)\, A_1 = \frac{1}{2}\left[\theta_1\left(\frac{d_i}{2}\right)^2 - a_p\left|\frac{d_i}{2} - \frac{p(t)^2}{d_i}\right|\right], A_2 = \frac{1}{2}\left[\theta_2 p(t)^2 - a_p\frac{p(t)^2}{d_i}\right]$$

$$(10) \qquad a_p = 2p(t)\sqrt{1 - \left(\frac{p(t)}{d_i}\right)^2}, \theta_1 = 2arcsin\left(\frac{a_p}{d_i}\right), \theta_2 = arcsin\left(\frac{a_p}{2p(t)}\right)$$

Where φ is the uncertainly factor of the model [-] and $p(t)$ is the radius of the pit in time t. It should be noted that pitting corrosion is highly localized on individual reinforcement bars. It is unlikely that many bars could be affected in the same section, hence pitting corrosion will not significantly influence the structural capacity of a cross-section. The value of $p(t)$may be obtained from the model of corrosion 2.

7.4 Model of corrosion 4

(FReET, 2010): The corrosion cracking model where is assumed uniform corrosion, estimate the critical time to cracking $t_c = t_i + t_{p,cr}$ of concrete cover due to stress resulting from the expansion of corrosion products from the reinforcement. t_i is the time to corrosion initiation. $t_{p,cr}$ is the resulting time to cracking on the rust- concrete interface since corrosion initiation. Three stages are considered in this model: 1. *Free expansion*- stresses are not created on the surrounding concrete. The porous zone around the reinforcement is filled by rust products. But amount of corrosion products is less than the amount of corrosion products required to fill the porous zone around the steel-concrete interface W_P. 2. *Stress initiation*- in porous zone is amount of corrosion products needed for to fill the porous zone W_P and on the surrounding concrete affects expansive pressure. 3. *Cracking*- the total amount of corrosion products reaches the critical amount of corrosion products W_{crit} and cracking of surrounding concrete starts.

The critical amount of corrosion products W_{crit} can be divided into two parts: W_P, the amount of corrosion products needs to fill the porous zone around the steel-concrete interface and W_S, the amount of corrosion products that generate the critical tensile stresses. Then W_{crit} is calculated by following formula:

$$(11) \qquad W_{crit} = \frac{\rho_{rust}\pi[d_i(d_s+d_0)+2d_0d_s]}{1-\rho_{rust}\frac{\alpha}{\rho_{st}}}$$

Where d_i is the initial bar diameter, d_o porous zone thickness, ρ_{rust} and ρ_{st} the specific gravities of rust and steel, α is the ratio of steel to the corrosion products molecular weight, and d_s is the thickness of the corrosion products needed to generate tensile stresses, is given by following formula:

$$d_s = \frac{a*f_t}{E_{ef}}\left(\frac{x^2+y^2}{x^2-y^2}+\nu_c\right) \tag{12}$$

Where a is concrete cover, f_t is the tensile strength of concrete, ν_c the Poisson ratio of concrete, E_{ef} is the effective modulus of elasticity, $x=(d_i+2d_o)/2$ and $y=a+(d_i+2d_0)/2$

$$E_{ef} = \frac{E_c}{1+\varphi_c} \tag{13}$$

Where E_c is the modulus of elasticity of concrete, φ_c is the creep coefficient. For a constant corrosion rate can by time $t_{p,cr}$ calculate as:

$$t_{p,cr} = \varphi\frac{{W_{crit}}^2}{2k_p} \tag{14}$$

Where φ is the uncertainly factor of the model and k_p is related to the rate of metal loss and expressed as:

$$k_p = 0.092\left(\frac{1}{\alpha}\right)\pi d_i i_{corr} \tag{15}$$

Where i_{corr} is the annual mean corrosion rate, can be estimated by (6).

7.5 Model of corrosion 5

(FReET, 2010): This model is used for approximate computation of corrosion induced crack width and for prediction of the serviceability of corrosion affected RC structures.

Concrete with an embedded steel bar can be modelled as a thick- wall cylinder. The inner radii of cylinder is $x=(d_i+2d_o)/2$ and outer radii is $y=a+(d_i+2d_0)/2$. The thickness of the rust surface is determined from:

$$d_s(t) = \frac{W_{rust}(t)\left(1-\frac{\alpha\rho_{rust}}{\rho_{st}}\right)}{\pi\rho_{rust}(d_i+2d_0)} \tag{16}$$

Where α is a coefficient related to the type of corrosion products, ρ_{rust} is the density of corrosion products, ρ_{st} is the density of steel and $W_{rust}(t)$ is the mass of corrosion products determined from:

$$W_{rust}(t) = \left(2\int_{t_i}^{t} 0.092\left(\frac{1}{\alpha_{rust}}\right)\pi d_i\, i_{corr}(t)dt\right)^2 \tag{17}$$

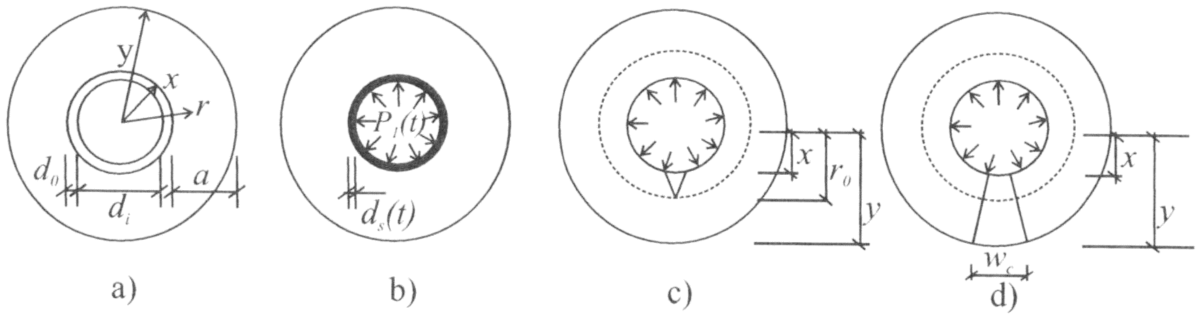
Where i_{corr} is the annual mean corrosion rate, can be estimated by (6). The time is equal $t=t_i+t_p$.

The growth of the ring of corrosion products causes an outward pressure on the concrete at the interface between the rust band (ring of corrosion) and concrete.

The expansive pressure at the interface between the rust band and the concrete is obtained from the radial stress:

$$P_1 = -\sigma_r(x) = \frac{E_{ef}d_s(t)}{x\left(\frac{x^2+y^2}{x^2-y^2}+\nu_c\right)} \tag{18}$$

E_{ef} is the effective modulus of elasticity and ν_c the Poisson ratio of concrete. In phase of no cracking concrete is used the theory of elasticity for determine the radial stress $\sigma_r(r)$ and tangential stress $\sigma_\Theta(r)$ at any point (r) in cylinder because the concrete cylinder is considered to be elastically isotropic.



Picture 9: Scheme of the corrosion induced concrete cracking process

The initial cracking time obtained from tangential stress $\sigma_\Theta(r)$ at $r=a$ can be determined by satisfying the conditions that $\sigma_\Theta(x)=f_t$, where f_t is the tensile strength of the concrete. The crack in the concrete cylinder propagates in the radial direction and stops at r_0, which divides thick wall into to cylinders as you can see on picture c). The theory of elasticity can be apply for the outer uncracked cylinder and for inner in the interval $[x, r_o]$ is the residual tangential stiffness constant along the cracked surface and represented by $\alpha_{stiff}E_{ef}$, the α_{stiff} is tangential stiffness reduction factor and depends on the average tangential strain ε_0 over the cracked concrete and is obtained from:

$$\alpha_{stiff} = \frac{f_t\, exp[-\gamma(\varepsilon_\theta - {\varepsilon_\theta}^c)]}{E_{ef}\varepsilon_\theta} \qquad (19)$$

Where ${\varepsilon_\theta}^c$ denotes average tangential cracking strain, $\gamma=f_t/G_f$, G_f is a fracture energy. The elastic modulus in the radial direction is different from the tangential one. The width of concrete crack picture d) can be calculate by expression:

$$w_c = \frac{4\pi d_s(t)}{(1-\nu_c)(x/y)^{\sqrt{\alpha_{stiff}}} + (1-\nu_c)(y/x)^{\sqrt{\alpha_{stiff}}}} - \frac{2\pi y f_t}{E_{ef}} \qquad (20)$$

The crack width increases with time with the growth of corrosion products.

7.6 Model of corrosion 6

(FReET, 2010): In this mathematical model is developed a relationship between steel mass loss and the internal radial pressure caused by rust growth. The model predicts the time to cracking due to corrosion $t_c = t_i + t_{p,cr.}$

The model used four assumptions:

1. The products of corrosion are created a uniformly around steel bar surface so it caused uniform expansive stress around steel bar on surrounding and a uniform radial displacement at the surface of the rust layer.
2. The porous zone around steel bar have to be fill by corrosion products and after can start to induce internal pressure on the surrounding of concrete.
3. The corrosion caused strain only in concrete.
4. The concrete around steel bar is modelled and named as a thick-walled cylinder with wall thickness which is equal to the cover thickness of concrete. The crack is created when the tensile stress in the circumferential direction in each point on the rust surface reached the tensile strength of concrete.

The relationship between the percentage steel loss and the corresponding radial pressure on concrete is express by:

$$P_{corr} = \frac{100\frac{M_{loss}}{M_{st}}E_{ef}d_i}{90.9(1+\nu_c+k)(d_i+2d_0)} - \frac{2d_0E_{ef}}{(1+\nu_c+k)(d_i+2d_0)} \tag{21}$$

The M_r is mass of rust per unit length of one bar and M_{loss}, the mass of steel per unit length consumed to produce M_r is expressed $M_{loss} = 0.622\ M_r$. And the relationship between the mass density of rust is $\rho_{rust}= 0.5*\rho_{st}$, ρ_{st}=7.85 g/cm^3 (density of steel). But corrosion product starts press on the surrounding after filling porous zone by corrosion products. k is given by following expression:

$$k = \frac{(d_i+2d_0)^2}{2a(a+d_i+2d_0)}, \text{ where } a \text{ is concrete cover} \tag{22}$$

The cracking causes radial pressure so P_{corr} is combined with then.

$$P_{cr} = \frac{2af_t}{d_i} \tag{23}$$

$$\frac{100\frac{M_{loss}}{M_{st}}E_{ef}d_i}{90.9(1+\nu_c+k)(d_i+2d_0)} - \frac{2d_0E_{ef}}{(1+\nu_c+k)(d_i+2d_0)} = \frac{2af_t}{d_i} \tag{24}$$

8 Conclusion

In this thesis are first two chapters about basic principles used for corrosion of reinforced concrete. The third chapter describe the uniform and the pitting corrosion, their calculations and models are described in chapter seven. In this chapter are expressions and equations used for calculation initiations time, time to cracking on the rust- concrete interface since corrosion initiation and expansive pressure at the interface between the rust band and the concrete. Next are three chapters which contain description of service life of the reinforced concrete, carbonation and chloride ingress in the reinforced concrete.

9 Used literature

The following table contains a list of references used in this thesis.

(Metrohm, 2014)	Metrohm, Applivation note 16, 2010-1015, Available from: http://metrohm-aulolab.com
(FReET, 2010)	FReET Deterioration Module, program documentation, 2010
(Petersson, 2004)	Petersson, P.E. (2004) A service life model for scaling resistence of concerete-reflections
(Smilauer, 2014)	Introduction to cementitious materials, Smilauer, 2014
(Fidransky, 2014)	Mechanismy degradace betonu a železobetonu, Fidransky, online: http://concrete.fsv.cvut.cz/~prochazka/YTBK/Prednaska_2_2014.pdf