- Technical Paper -

A SIMPLE APPROACH TO DETERMINE MECHANICAL PROPERTIES OF RUST LAYER ON STEEL SUBSTRATE

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ABSTRACT
Cracking in concrete structure due to corrosion of steel is one of the major factors inducing degradation of its durability and even premature failure. In order to predict crack opening and its propagation based on numerical or theoretical modeling, mechanical behavior of rust between steel and concrete are necessary. A simply approach is presented to determine mechanical properties of rust layer, namely, Young's Modulus, Poisson's ratio and $\sigma - \varepsilon$ relationship by a conventional four-point bending test. Closed-form solutions are obtained for rust in linear and nonlinear range respectively.
Keywords: rust-layer, Young's modulus, Poison's ratio, stress-strain relationship, bending test

1. CONTEXT OF THE STUDY

Damage due to reinforcement corrosion has been recognized as one of the major causes of the deterioration in reinforced concrete structures. Initially, steel reinforcement is embedded in concrete where the high pH(~13) of cement-saturated pore fluid normally passivates the surface by a solid corrosion product, spinel [1]. However, this protection can be broken by aggressive ions such as chlorides or by an acidification of the environment in the vicinity of the steel such as carbonation. Under chloride attack, even low chloride ion concentrations are inimical to spinel formation; the solubility-limiting solid corrosion product is "green rust" instead, a layer-structured hydrate containing both Fe^{2+} and Fe^{3+} and Cl^-. In the range 10-15mM/l chloride, iron solubility increases abruptly from near-zero to 170-180mM/l. The passive film is consequently damaged locally and steel starts to dissolve in the unprotected areas. In case of penetration of carbon dioxide, the pH of the concrete pore solution close to the rebar decreases from 13 to 9 causing general corrosion of steel.

When steel rebars are de-passivated, porous oxide layer are formed at the steel surface, their solid volume is higher than that of the original metal. As this volume increases a pressure is induced around the embedded steel due to the constraint of surrounding concrete. Once the expansive-induced ring-tensile stress is over the concrete tensile strength, cracks initiate at the steel/concrete interface and propagate outwards and eventually spread to the surface of the concrete cover. These cracks in turn provide a path for more rapid ingress of aggressive agents to the reinforcement, which can accelerate the corrosion process. Cracking, spalling or delamination of concrete cover will not only lead to deterioration of durability but also to degradation of safety and serviceability because of the degradation of mechanical properties of corroded steel and loss of bond between concrete and reinforcement as well.

Given the importance and the extent of the problem, research on the corrosion-induced cracking and its development in concrete has attracted a lot of attention over the past decades, for predicting the serviceability and durability of reinforced concrete structures [2-8].

Such as in JSCE 338 Committee report [2], design equation as below is introduced to evaluate propagation period of corrosion in concrete:

$$\gamma_i \frac{W_{cr}}{W_{cr,lim}} \leq 1.0 \tag{1}$$

In which, γ_i is a structural ratio; W_{cr} is the design value of corrosion quantities of steel in concrete(mg/mm^2); $W_{cr,lim}$ is the limitation values of corrosion quantities to induce crack opening(mg/mm^2). However a precise determination of $W_{cr,lim}$ has not yet been given mainly due to the difficulties in modelling corrosion process and choosing right materials parameters.

The work dealing with this problem included ① experimental studies covering laboratory tests and field investigation; ②theoretical studies by means of theory of elasticity or nonlinear fracture mechanics, and ③ numerical analyses using finite element method. All of these efforts have made great contribution in modeling the corrosion happening of reinforcement and predicting the propagation of cover cracking. As an example, Suda et al. [9] has derived a relationship

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between expansion displacement u and expansive pressure p based on elastic thick-walled hollow cylinder theory*1. Equation (2) shows clearly that mechanical properties of rust, such as Young's modulus and Poisson's ratio are necessary parameters. Rust is not only the direct cause for creating cracks in concrete cover but also participating in the stressing and cracking process in concrete cover induced by its volume expansion.

For simplicity, some researchers assumed that rust has the same mechanical properties as that of steel, neglecting the deformation of steel and corrosion products since the Young's modulus of steel is about one order of magnitude larger than that of concrete. Bhargava proposed an analytical model to predict the time required for cover cracking and corrosion weight loss, wherein the stiffness contribution from the combination of reinforcement and expansive corrosion products are assumed to be the same as the reinforcement [5]. On the other hand, Molina et al. assumed that the properties of rust is nearly equal to those of the liquid water, resulting in E_r =0.012GPa [4]; SUDA et al estimated the critical corrosion amount by using the values of elastic modulus of corrosion product in range of 0.1~0.5GPa[9]. Kawamura et al compare their rigid-spring model with experimental results by substituting various E_r with 20, 100, 200, 2000MPa and find 100MPa is consistent[10].

Above all, before attaining to a reasonable prediction of concrete cracking, it is indispensable to make a fully understand on the mechanical properties of corrosion products. A few of researchers have devoted to the determination of Er in the past decades, however, so far a wide range values from 0.1GPa to 200GPa has been obtained by various kinds of testing methods shown in literature review below. Before going further, it is advisable to take a close look at them and trace the sources which resulted in the large discrepancies.

2. LITERATURES REVIEW ON MECHANICAL PROPERTIES OF CORROSION PRODUCT

Since the splitting stress in concrete cover is resulted from the volume expansion of rust and the corresponding deformation restriction of concrete around, most studies focus on the Young's modulus of rust (E_r) together with some on its stress-strain relationships. A brief literature review lists a few typical among them in Table 1. Two groups can be roughly classified from preparation of experimental specimens, viz. one is concrete or motor specimens with steel rebar or steel plate embedded in and the other is corrosion product collected from virgin steel. In each group, two kinds of testing methods can be observed. One is mechanical measurement including ①loading tests, ②static water pressure, ③oedometer tests, and ④ indentation tests; The other is non-mechanical measurement such as expansive displacement field measurement and Ultrasonic measurements. Looking at the results from Group 1 and Group 2, it is difficult to recognize the influence of restriction from concrete on Er , except the relative huge values from indentation tests, although some researches have claimed that

Upon the brief literature review above, the obtained Young's moduli of rust are found to be in a large range from 0.1GPa to 200GPa. Further investigation on mechanical properties of corrosion product is in need. The aim of our study is to explore a simple and general experimental method for determination of stress-strain relationship of rust layer at its original configuration on the virgin steel, without any other possible influential factors and un-avoidable sophisticated testing techniques. This new testing method involves a simply-supported four-point bending experiment of a corroded steel plate. The rust layer originated from the steel plate is taken as a thin film atop the un-corroded steel plate. Based on the load-deflection curve collected from experiment, the stress-strain curve can be obtained. The proposed testing method contains the following merits: (1) the rust layer may keep its original configuration in the midst of testing; (2) steel sample is not necessary to be embedded into concrete/mortar, avoiding the influence coming from concrete/mortar specimen; (3) four-point loading test is a conventional mechanical test, avoiding sophisticated operations.

In this paper, flexural behavior of corroded steel plate and the derivation of stress and strain of rust layer film in linear and nonlinear range are introduced in the first place. They can be expressed not only in terms of load and deflection, but also in terms of load and strain at the bottom of the steel substrate. Meanwhile, Young's modulus and Poisson's ratio of rust within elastic range are deduced by a simpler way.

Before going further, it is indispensable to make a discussion on rust layer structure above steel substrate leading to corresponding assumptions.

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*1

$$\mathrm{u} = \frac{p}{E_2(b^2-a^2)}\left(\frac{4a^2b^2}{((1-\mu_2)a^2+(1+\mu_2)b^2+(1-\mu_1)(a^2-b^2)\,{E_2}/{E_1})} - b(a^2+b^2+(a^2-b^2)\mu_2)\right) \qquad (2)$$

where: $a=\frac{D}{2}-t, b=\frac{D}{2}+t(\alpha-1), t=w/\rho$

D: initial diameter of steel; E_1 and μ_1: elastic modulus and Poisson's ratio of steel; E_2 and μ_2: elastic modulus and Poisson's ratio of rust; t: thickness of lost steel part due to corrosion; w: weight of lost steel part; ρ: density of steel; u: expansion displacement; p: expansive pressure.

Table 1 Literature Review

Authors	Methods	Results	Specimens
S.Care et al[11]	Displacement field measurement by digital correlation technique	$E_r \approx$ 0.13Gpa	Concrete or mortar with steel bar or plate embedded
Yoshioka[12]	Expansive strain measurement with loading tests	$E_r \approx$ 0.2-0.3GPa	
Asuke et al[13]	Loading by static water pressure	$E_r \approx$ 20GPa	
Ouglova et al[14]	Oedometer test and Ultrasonic measurements	E_r= several Gpa	Corrosion product peeled from virgin steel
Yuxi Zhao et al [15-16]	Loading test and Oedometer test	$E_r \approx$ 0.1 GPa	
	Micro-indentation tests	$E_r \approx$ 47~86GPa	
A.Dehoux et al[17]	Micro-indentation tests	$E_r \approx$ 50-200Gpa	

3. DISCUSSION REGARDING RUST-LAYER STRUCTURE

Researches [18-19] indicate that most of the rust layers formed on carbon steel or low alloy steels exposed to atmospheric corrosion are composed of a loose outer rust layer and a dense inner rust layer. The outer layer is composed of goethite (α- FeOOH), lepidocrocite (γ-FeOOH), magnetite (Fe_3O_4) , H_2O, and amorphous ferric oxyhydroxide ($FeO_x(OH)_{3-2x}$, x=0-1), while the inner rust layer is composed of Fe_3O_4 with a little α- FeOOH. Akaganeite (β- FeOOH) is found to be linked with the presence of chlorides in the environment. All these products can coexist partly as crystalline and partly as amorphous structures. Moreover, specific phases in the rust are detected with some alloying elements in the metallic substrate, like copper, phosphorus or chromium. These particular phases have the ability to improve the interface bonding between rust layer and steel substrate and consequently the corrosion resistance of the steel substrate. On the other hand, it is worth noting that corrosion products of carbon steel are porous in nature since they are not enhanced by the alloying elements, and the adhesion is poor at the interface.

Some cracks and voids are distributed randomly within the rust. Fig. 1 and 2 (taken in authors' lab) illustrate two SEM photos showing rust layer on SS400 with and without cracks. These cracks are due to a local volume increase or a stress-free oxidation strain ϵ_{ii}^{T} during the formation of oxides from steel substrate. Large residual stresses can derive from the oxidation strain, especially when the oxide forms on surfaces subject to large curvatures. The ensuing residual stresses influence the mechanical behavior of the oxide and substrate and may locally modify the oxidation rate. Specifically, film cracking or spalling are a frequent consequence of residual stress in oxide films formed on metals and alloys [20].

Summarizing the above discussion regarding rust layer structure, it may concludes that constitution and structure of rust layer would be various depending upon various constitution of steel substrate and environmental condition. To simply the problem, we will not consider the influence on rust layer of steel substrate and environment at this moment. And in a whole, the following assumptions are proposed for employing the theories in section 4 to model the mechanical behavior of rust layer upon steel substrate:

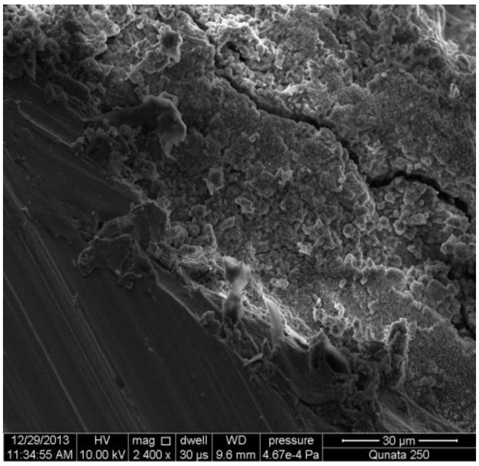

Fig. 1 Rust layer with cracks

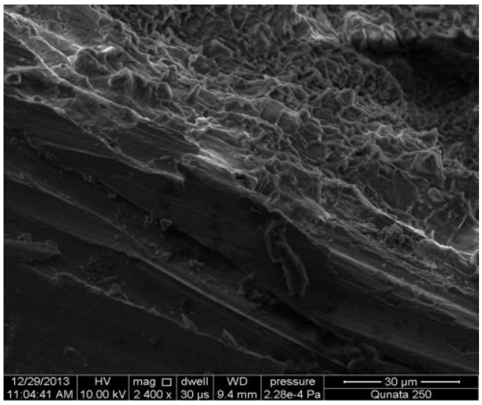

Fig.2 Rust layer with no cracks

①Rust layer is a homogeneous and isotropic material;

②No slip is permitted at the interface between rust layer and steel plate. In other words, rust layer and steel substrate should work together under bending.

4. MECHANCIAL PROPERTIES OF RUST UPON STEEL PLATE

4.1 A bilayer structure modelling the corroded steel plate

Based upon the assumptions in preceding section, the rust layer above a steel plate can be looked upon as a thin film deposited atop an elastic steel substrate, which material properties are well known as illustrated in Fig. 3. Hereinafter, thickness of substrate steel and rust film and elastic modulus of steel are denoted by t_s, t_r and E_s. Subscripts r and s stand for the film and substrate respectively. Upon flexural moment, this bilayer structure tends to bend resulting in a linear strain distribution along the cross section depth. Fig. 3 illustrates a general strain distribution, where the strain (ε) at a point y away from the interface can be expressed in terms of the strain at the top ($\varepsilon_{r,t}$) and curvature of the bilayer structure (κ) as

$$\varepsilon = \varepsilon_{r,t} + \kappa(y - t_r) \tag{3}$$

Referring to the curvature κ in the mid-span, it is a constant since the moment is a constant, and can be expressed in terms of displacement δ of pure bending part in four-point bending beam shown in Fig. 4 by

$$\kappa = -\frac{2\delta}{\left(\delta^2+\frac{d^2}{4}\right)} \tag{4}$$

Alternatively in terms of strain at the bottom of steel substrate, it would be as

$$\kappa = \frac{\varepsilon_{s,b}}{h-h_{na}} \tag{5}$$

h_{na} represents the location of neutral axis (Fig.3),

$$h_{na} = \frac{\frac{t_r^2}{2}+n\left(t_r t_s+\frac{t_s^2}{2}\right)}{t_r+nt_s} \tag{6}$$

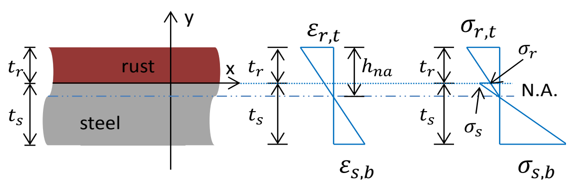

Fig.3 Rust film and substrate: strain distribution and stress distribution

4.2 Stress versus strain relationship of rust layer in nonlinear range

As for the four-point bending beam (Fig.4), the equilibrium conditions are as follows:

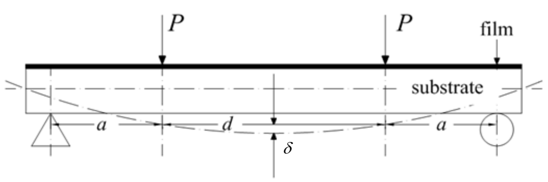

Fig.4 Four-point bending of bilayer structure

$$\int_{-t_s}^{0} E_s \varepsilon dy + \int_{0}^{t_r} \sigma_r dy = 0 \tag{7}$$

$$\int_{-t_s}^{0} E_s \varepsilon y b dy + \int_{0}^{t_r} \sigma_r y b dy = M = Pa \tag{8}$$

As long as the film thickness is below 1/10 of that of its substrate, the stress (σ_r) in the film can be assumed to be approximately uniform [21] in Eqs.7-8. Consequently, a closed-form solution for rust layer can be solved based on Eqs.3-4, 6, 7 and 8 simultaneously:

$$\sigma_r = \frac{-\frac{6Pa(4\delta^2+d^2)}{b}+4\delta E_s t_s^3}{3t_f(t_f+t_s)(4\delta^2+d^2)} \tag{9a}$$

$$\varepsilon_{r,t} = \frac{6Pa(4\delta^2+d^2)/b-4\delta E_s t_s(6t_f^2+9t_f t_s+4t_s^2)}{3E_s t_s(t_f+t_s)(4\delta^2+d^2)} \tag{9b}$$

In the above equations, a, d and P are shown in Fig. 4; b denotes the cross sectional width of the steel plate beam. Thus, as long as δ-P curve (Fig. 5) is given, through Eq.5, the stress versus strain relationship of the atop film of rust layer can be resulted.

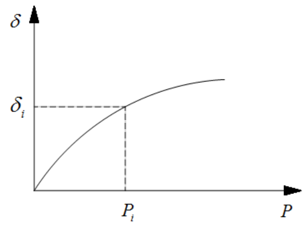

Fig. 5 Load-displacement curve

Alternatively, by taking advantage of Eq.3 and Eq.5-8, stress and strain relationship can also be expressed in terms of P and strain ($\varepsilon_{s,b}$) at the bottom of the substrate as follows.

$$\sigma_r = \frac{-6Pa+E_s b t_s^2 \varepsilon_{s,b}}{bt_s(3t_r+2t_s)} \tag{10a}$$

$$\varepsilon_{r,t} = \frac{12Pa(t_r+t_s)-E_s b t_s \varepsilon_{s,b}(6t_r^2+9t_r t_s+4t_s^2)}{E_s b t_s^2(3t_r+2t_s)} \tag{10b}$$

The derived Eqs.9-10 are especially beneficial for describing behavior of rust in nonlinear range. As far as in elastic range, a simpler way can be resorted to as follows.

4.3 Young's Modules and Poisson's ratio of rust layer in elastic range

Using the slope in the early unloading part of a bending test, one can obtain its Young's Modulus. By measuring the elastic constants in uniaxial and biaxial stress states, one can estimate its Poisson's ratio. Detail procedures to obtain Young's Modulus and Poisson's ratio of rust are explained below.

(1) Young's Modulus

The basic principle to obtain Young's Modulus of rust-layer is based on the rigidity difference ratio (Eq.7) between composite steel plate beam (Beam A) with rust layer upon it and steel substrate beam (Beam B) alone without rust layer upon it(after cleaning the rust away).

$$\frac{(EI)_{com}}{E_s I_{s,unc}} = \frac{E_r I_r + E_s I_s}{E_s I_{s,unc}} = \frac{I_r + nI_s}{nI_{s,unc}} \tag{11}$$

where, $n = \frac{E_s}{E_r}$ (12)

$$I_r = \frac{1}{12}bt_r^3 + bt_r\left(h_{na} - \frac{t_r}{2}\right)^2 \tag{13}$$

$$I_s = \frac{1}{12}bt_s^3 + bt_s\left(h - h_{na} - \frac{t_s}{2}\right)^2 \tag{14}$$

$$I_{s,unc} = \frac{1}{12}bt_s^3 \tag{15}$$

The symbols involved in above equations can be referred to [21].

Given the thickness of rust layer and un-corroded part of steel plate, it is found from Eqs.11-15 and Eq.6 that the rigidity ratio (namely the slope of unloading part) is a function in n alone. Then E_r may be determined by E_s/n.

Alternatively, the rigidity difference ratio can also be expressed in terms of strain at the mid-span bottom of steel substrate as:

$$\frac{(EI)_{com}}{E_s I_{s,unc}} = \frac{\frac{M(h-h_{na})com}{\varepsilon_{com}}}{\frac{M(h-h_{na})s,unc}{\varepsilon_{s,unc}}} = \frac{\frac{(h-h_{na})com}{\varepsilon_{com}}}{\frac{t_s/_2}{\varepsilon_{s,unc}}} \tag{16}$$

Consequently,

$$\frac{\varepsilon_{s,unc}}{\varepsilon_{com}} = \frac{1}{1+\frac{E_r I_r}{E_s I_s}} \cdot \frac{t_s/_2}{h-h_{na}} \tag{17}$$

Given the strain values at the bottom of Beam A ($\varepsilon_{\mathrm{com}}$) and Beam B ($\varepsilon_{\mathrm{s,unc}}$) are collected, E_r can be obtained by Eq.(17).

(2) Poisson's ratio

Since the rust-layer is assumed to work with steel substrate together as a whole, the strain ratio of transverse direction against longitudinal direction at the bottom of Beam A is equal to the strain ratio at the upper side of rust-layer, which is exactly the Poisson's ratio of rust-layer.

$$\nu = -\frac{\varepsilon_{\mathrm{r,t,2}}}{\varepsilon_{\mathrm{r,t,1}}} \tag{18}$$

where, $\varepsilon_{\mathrm{r,t,2}}$ is the strain in the transverse direction; $\varepsilon_{\mathrm{r,t,1}}$ is the strain in the longitudinal direction.

5. CONCLUSIONS

To summarize, we present a simple and generic approach for characterization of rust layer with nonlinear stress versus strain relationship. In addition, expressions for both Young's Modulus and Poisson's ratio are derived for rust-layer in linear range. Only standard testing techniques are required.

Assumptions such as no slip occurring at the interface between steel substrate and rust layer are necessary. In a whole effect, it can be secured especially in case of low-alloy steels. However, further observation is in need.

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