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Mechanical properties of an iron oxide formed by corrosion in reinforced concrete structures

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Abstract. The paper deals with elastic properties of iron oxides formed in reinforced concrete structures. Due to the difficulty to perform mechanical tests on the real oxides presented in the form of (multiple) laminated stratums, the elastic modulus of iron oxides remains unknown. Young's moduli of porous compact "synthetic oxides" in powder form, obtained in laboratory conditions, were measured from both acoustic measurements and oedometric tests. The elastic modulus of the compact polycrystalline iron oxide is deduced with respect to two models, a micromechanical one and a Hertz' theory. The full method is validated on a well-known material, the alumina.

1. INTRODUCTION

The degradation of concrete structures due to the corrosion of the reinforcements is a crucial problem for both the safety and the economical point of view. By nature, the high alkalinity of the concrete pore solution (pH13) provides protection to the reinforcing steel but the penetration of carbon dioxide CO2 decreases the pH from 13 to 9, causing general corrosion. Moreover, chlorides ions can as well break down the passive layer and cause the mix of general and pitting corrosion. Usually, the layer of corrosion products consists of liquid water and hydrated iron oxides. Due to volume expansion of the oxides (with a coefficient between 2.2 and 3, depending on oxide/hydroxide nature), the cracking of concrete lead to dangerous fall of concrete parts and to unprotected steel.

Numerical simulations of mechanical behaviour of concrete structures with corroded rebars need the knowledge of the mechanical behaviour of the iron oxide. Unfortunately, these data are available for the crystal only. As rust in concrete is mixed with the pore solution oome authors [1] simply use the moduli of water K=2 GPa, nu=0.5 for the iron oxide.

The elastic properties of iron oxide crystal can be found in "The Oxide Handbook" [2]. The Young's modulus of Fe2O3 or Fe3O4 ranges from 214 to 350 GPa and cannot be retained for the observed structure, which consists of a powder grain aggregate, more or less laminated. Due to grain-to-grain punctual contacts, these structures exhibit much lower elastic properties on which we have very few knowledge.

Experimental difficulty is linked in one hand to the slowness of the reaction that leads to very few materials to make a specimen. The retained strategy has been to make both ultrasonic and oedometric measurements on synthetic oxide under different compressive loads. It has been verified that the chemical structure of synthetic oxide was relevant to the naturally formed 40 years old one.

The elastic properties of the oxide crystal (not the powder, but the grain itself) can be of interest if it helps us to model more precisely the real oxide (or mix of oxide and water) behaviour in its different possible structure. The Young's modulus of the crystal will be recovered using various inverse analysis based on (i) a simple Hertz's model, (ii) a classical micromechanical approach Hashin Strikman bounds [3, 4] and (iii) a Self Consistent model [5, 6] ((ii) and (iii) are not shown in this paper). Of course, the anisotropy of the crystal will not be taken into account as the available data are the mechanical properties of the powder structure which is supposed to be isotropic: the Young's modulus of the crystal has to be considered as the average one. In order to validate the present approach, experimental tests and numerical modelling has been performed on alumina powder whose mechanical properties are well known [5].

2. IRON OXIDE MANUFACTURING

To simulate the real conditions of oxides formation in carbonated reinforced concrete structure, iron oxides were obtained from low alloy steel samples exposed in an aerated solution containing 100 ppm of Cl- which pH was fixed to 9 by NaOH addition. A half of the oxides was dried in an oven at 50°C during 24 hours and the other one during 48 hours (the temperature was chosen to avoid modification of the chemical composition of the oxide). The weight loss between the oxides dried during 24 hours and those dried during 48 hours is 3.4 %. The oxides were in a powder state.

The chemical composition of the produced oxides was studied by X ray diffraction. The analysis was also performed on the oxides obtained from a real reinforced concrete structure that was attacked by carbonation and chlorides ions during forty years. The chemical composition of these oxides is given in Table 1. A comparison of the chemical compositions shows that the laboratory grown oxides consist of lepidocrocite ($\gamma FeO(OH)$) and the real oxides consist of goethite, lepidocrocite (quite majority) and maghemite. Note, that in both cases, the presence of lepidocrocite is the main observed phase. The density of both oxides was measured using a micro ultrapycnometer, P/N 02112-1 (Table 1). These results show that the density of the laboratory grown oxides (4049 kg/m3) is close to the one of the real oxides (4345 kg/m3). To study the distribution of particles size, the lepidocrocite dried during 48 hours was examined by a scanning electron microscope (SEM) (Figure 1). The size of forty particles was measured and the principal results are given in Table 1. Their size varies from 0.4 µm to 8.7 µm with an average value of 3.6 µm. The particles of alumina, the reference material, are 3 µm in mean diameter.

Table 1: Principal characteristics of oxides used in this contribution.

Oxide	Chemical composition	Average density, kg/m^3	Particle size, µm
Oxide obtained from 40 years old corroded reinforced structures	Goethite (γ FeO(OH)) + Lepidocrocite (γFeO(OH))+ Maghemite (Fe_2O_3)	4345	-
Laboratory grown oxide (dried 24 hours)	Lepidocrocite (γFeO(OH))	4049	-
Laboratory grown oxide (dried 48 hours)	Lepidocrocite (γFeO(OH))	-	min = 0.4 ; max = 8.7 average =3.6
Aluminium oxide	Al_2O_3	3970	3

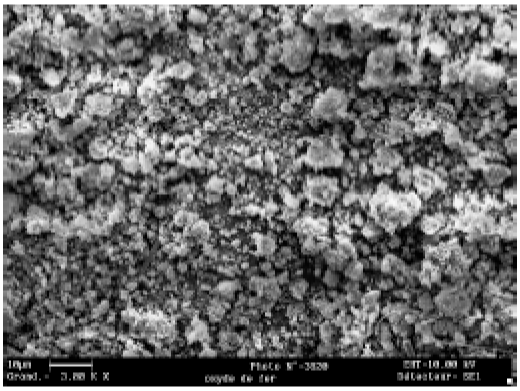

Figure 1. SEM observation of lepidocrocite particles dried during 48 hours at 50°C.

3. OEDOMETERIC MEASUREMENTS

Being a granular material, the iron oxide mechanical properties are supposed to depend strongly on the confinement. Moreover, around the corroded rebar, the oxide is confined between concrete and steel: this state can be assimilated to an oedometric one where the tangential and axial expansions are blocked by the symmetry of the problem. The strain tensor ε writes

$$e = (e_i \otimes e_i)e \quad (1)$$

in which the $\boldsymbol{e}_i$ direction corresponds the radial direction of both the rebar and the axis of the oedometer and ε a loading parameter. The diameter of the oedometer is determined with respect to the diameter of the ultrasonic transducer and its length has the same order of magnitude to insure a good transmission of the wave. The retained material is mild steel for both machinery and wave transmission.

Once the oxide in the oedometer, the system has been compressed respect to a MTS hydraulic device. The load has been released to perform ultrasonic measurements as the oedometer had to be removed from the machine; at these steps, the load and displacements were recorded. The stress is obtained from the ratio between the applied force and the section of the oedometer and the strain is deduced from head displacement while neglecting the deformation of the oedometer (reasonable as soon as the mild steel has a Young's modulus of 220 GPa, much greater than the few GPa of the oxide powder as it will shown later on). In linear elasticity, for such oedometric testing, the stress to strain relationship writes:

$$\varepsilon = \frac{\sigma}{E}\frac{(1+\nu)(1-2\nu)}{(1-\nu)} \tag{2}$$

in which the function of ν varies very few when ν varies from 0 to 0.2 that are common values of ν for such materials. For the 24h-dried lepidocrocite, a full mechanical testing has been performed with a unique unloading path at the end of the test: it exhibits the apparition of permanent strain, revealing the classical behaviour of a powder material and confirming the observations of Lungrend [7] on the iron oxide (Figure 2).

We can observe: (i) That from point O to point A, a strong non linear behaviour (with intense stick and slip phenomena) that can be associated to particles re-arrangement. (ii) From point A to B a linear curve is observed but does not correspond to linear elasticity as shown by the unloading response from point B to point C. (iii) The last path B-C is probably a non-linear elastic regime as observed on granular materials. Indeed, for granular materials we commonly observe unloading-reloading responses that are superimposed (see in Mitchell [12], Bardet [13]). Even if it is not the case, i.e. a small hysteresis exists, it will be of no practical importance in our case because the non linearity is not important.

The tangent modulus for the 24 hours dried lepidocrocite has been measured (using the curve) for different stress states on the branch B-C supposed to be linear elastic and a 6 GPa secant modulus is obtained from Figure 2. A similar global behaviour has been observed in case of lepidocrocite dried during 48h and alumina (Figure 3).

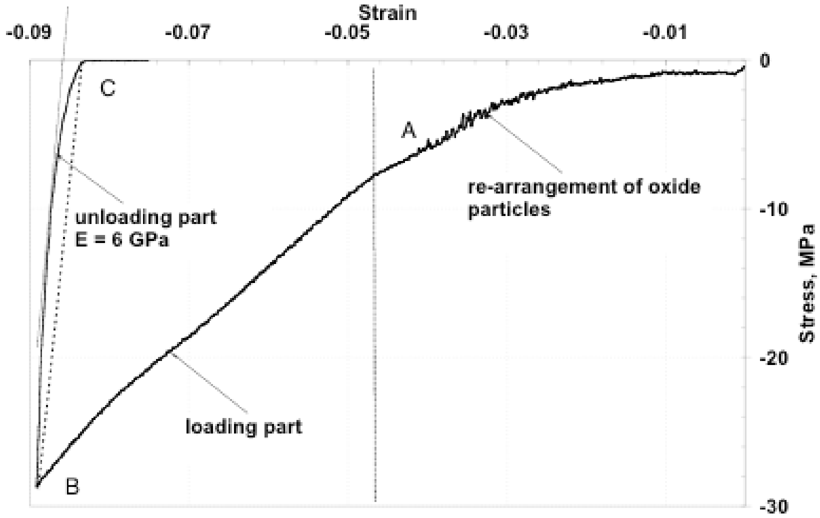

Figure 2. Results of compression test on lepidocrocite dried during 24 hours.

4. ULTRASONIC MEASUREMENTS OF THE OXIDE IN POWDER FORM

Zohdi [3] used successfully the ultrasonic method on ettringite which is also a granular material. The ultrasonic measurements (Figure 3) have been performed respect to a homemade 220V pulse emitter, two 1MHz Panametrics longitudinal transducers and a 200MHz Tektronics numeric oscilloscope. The wavelength to grain size ratio is about 100 leading us to use the continuum approximation for propagation equation. The retained method was the transmission one, the emitter was stuck on one end of the oedometer with some silicon grease and the receiver at the other end. This method insures only one fly across the oxide, in order to keep some power at the receiver (such materials dissipate quickly the mechanical waves, especially at the loose sates). The flying time across the oxide is the difference between measured flying time and the one obtained for the empty oedometer: this eliminates the time origin incertitude relative to the direct contact method. The wave speed is simply the ratio between oxide thickness (oedometer is measured with a slide calliper) and the flying time.

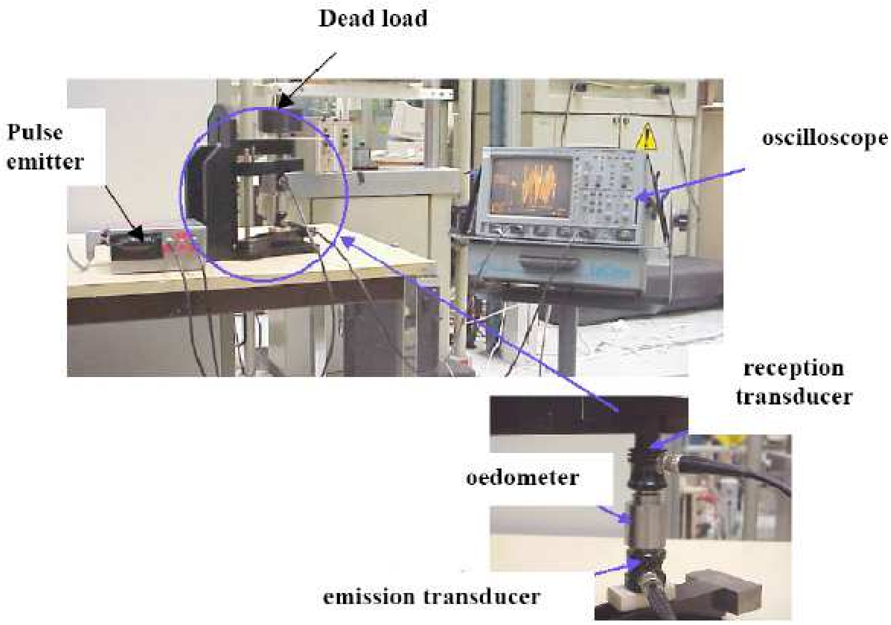

Figure 3. Scheme of the ultrasonic measurement system.

The ultrasonic theory [8] gives the following formula for the propagation of a longitudinal wave in an isotropic medium:

$$\rho(V_1)^2 = E\left(\frac{1-\nu}{1-\nu-2\nu^2}\right) \tag{3}$$

in which E is the Young's modulus and ν the Poisson's ratio of the medium. The missing Poisson's ratio could be determined with shear waves; unfortunately, these ones propagate very poorly in such medium. However, the fraction in ν varies only from 1 to 1.11 when ν varies from 0 to 0.2. As a common Poisson's ratio for granular materials is around 0.2, it has been decided to keep that value for the present study.

We suppose that the procedures in which the load unload sequences are prescribed to ensure the acoustical measurements are of no effect on the state of the material (that is true in the case of an elastic behaviour). During measurement, a 2.5 kg mass was applied onto the transducers in order to ensure a good contact. This load is equivalent to a very small stress around 0.1MPa. Even if this stress is indeed in the strongly non-linear part of the load strain curve, it permits the transmission of the wave and allows the measurement of the velocity. Of course, no measurement of the real elastic modulus of the granular material can be made from the mechanical data as this part of the behaviour is strongly non-linear and include friction, gliding, … It should be mentioned that the compacted powder seemed to be cohesive enough to permits the propagation of waves under a very small stress. A future extension of this work can be to perform *in situ* ultrasonic measurements.

The oedometric compression has been stopped for ultrasonic measurements five times for the 24h dried lepidocrocite and seven times for the 48h dried. As the actual oedometer length gives its volume V and the pycnometer oxide measurements give the oxide volume $f\,V$ the oxide volume fraction f was deduced.

We can observe in figure 4 that the measured Young modulus of 2 GPa is consistent with the value of 1.26 GPa given by the tangent modulus for a low (–5 MPa) applied stress as the ultrasonic modulus is often higher than the mechanical value for a large range of materials.

For the reference alumina, five measurement points were performed. Without any surprise the Young's modulus increases as the compaction increases, with a typical non-linear behaviour for granular materials. A volume fraction of 1, for pure crystal, leads to several hundred GPa: from 215 to 350 GPa for maghemite Fe_2O_3 [2] and 390 GPa for alumina [5]. This point should be added to the measured modulus on Figure 4 and exhibits very high non linearity which can be explained from a micromechanical point of view by the increasing number of contact points when the load increases and from a purely elastic point of view by the non linearity of the Hertz equations for the elastic contact between two ellipsoidal domains.

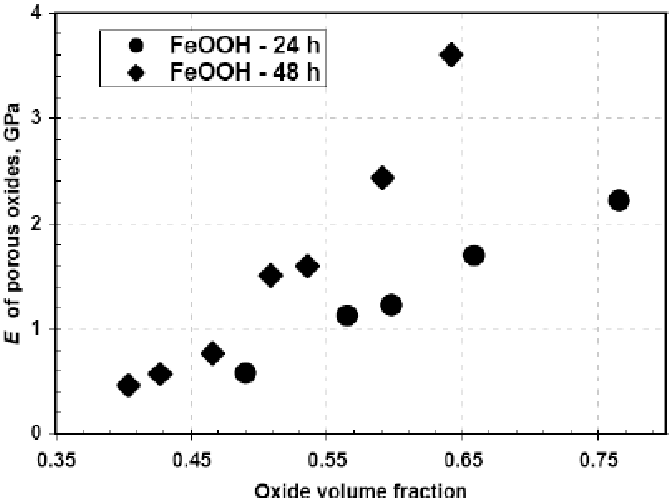

Figure 4. Evolution of the Young modulus derived from the US measurements.

The measured Young's modulus is around some GPa, making the Lundgren [7] assumption of 6 GPa a "reasonable" value.

5. HERTZ' CONTACT MODEL

Grain to grain contact seems to lead to the non-linear elasticity of the powder material. In order to model it, it has been chosen to use the Hertz' elastic contact theory. In such materials, a force network develops, with grain-to-grain transmission by contact forces. Considering a concentrated load, the network develops as a cone whose angle can vary from quite wide in the case of spherical particles without friction [9] to some straight line in the case of square grains [10]. Friction tends also to diminish the angle of this cone, as in the Mohr-Coulomb approach. For the sake of simplicity, we chose to model the limit case of the transmission of the load by grain columns, as shown on Figure 5.

The oedometric stress lead to grain forces whose intensity is given respect to the average surface S_g of the grain:

$$F_g = \sigma S_g \quad (4)$$

Then it was supposed a spherical contact between grains. The load applied to particle surface can be presented as:

$$F_g = \frac{F}{\pi N_{horizontal}} \quad (5)$$

where F_g is the load applied on the surface of a particle; $N_{horizontal}$ is the particles number along the horizontal direction (the diameter of the specimen is equal to 20 mm) and F is the load measured during the manufacturing of a specimen of known porosity. When a mechanical load, F, acts along the z-axis on the surfaces of elastic particles 1 and 2 (Figure 5), the displacement δ, with increasing load can be obtained by:

$$\delta = \frac{\Delta L}{N_{vertical}} \quad (6)$$

where ΔL is the measured displacement (the vertical displacement of the piston) and $N_{vertical}$ is the number of particles calculated with the initial height along the vertical direction.

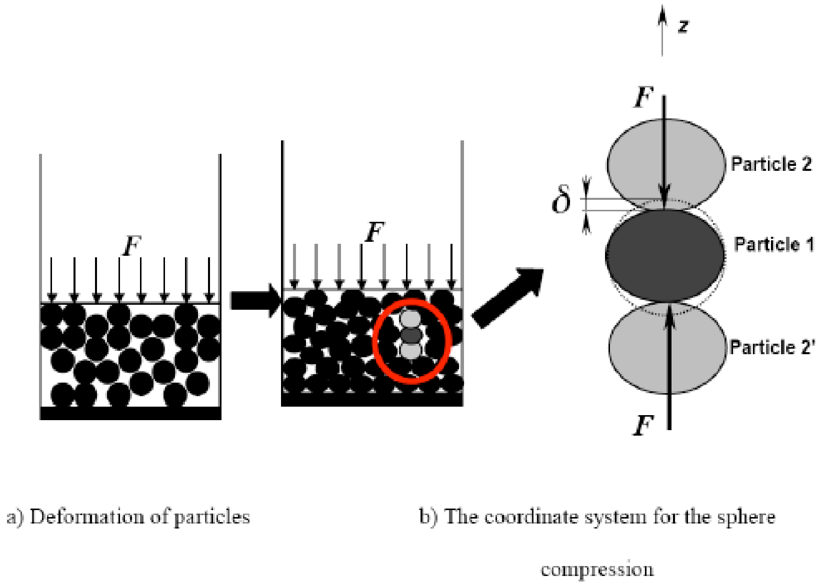

Figure 5. Principle of the Hertz model.

This displacement can be also given by:

$$\delta = \left(\frac{9F_g^2}{16R^* E^2} \right)^{1/3} \quad (7)$$

where $(1/R^*) = (1/R_1 + 1/R_2)$ is the relative curvature and E is the combined Young's modulus which is defined as:

$$E = \left(\frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \right)^{-1} \quad (8)$$

The subscripts 1 and 2 denote the particle 1 and particle 2, respectively. In case of the tested oxides, all the particles are assumed to have the same radius ($R=R_1=R_2$) and the same mechanical properties ($E_1=E_2=E$). The Young's modulus of an oxide particle – supposed to be isotropic - can be found:

$$E = \sqrt{\frac{9F_g^2(1-\nu)^4}{2R\delta^3}} \tag{9}$$

In our case we intend to find the Young's modulus of the particle that matches the Young's modulus of the powder. The Figure 6 give the obtained values for lepidocrocite. The results for oxides are much more convenient to bibliography [2, 5]. For the lepidcrocite of interest the Figure 6 suggests an average value of 400 GPa for the 48h dried lepidocrocite, with grain max size 8.7 µm, very close to the 390 GPa of the reference [2]. For the 3.63 µm grain average size we obtain a higher average value of 600 GPa. The order of magnitude is still correct but this simple model is probably no more applicable to this situation.

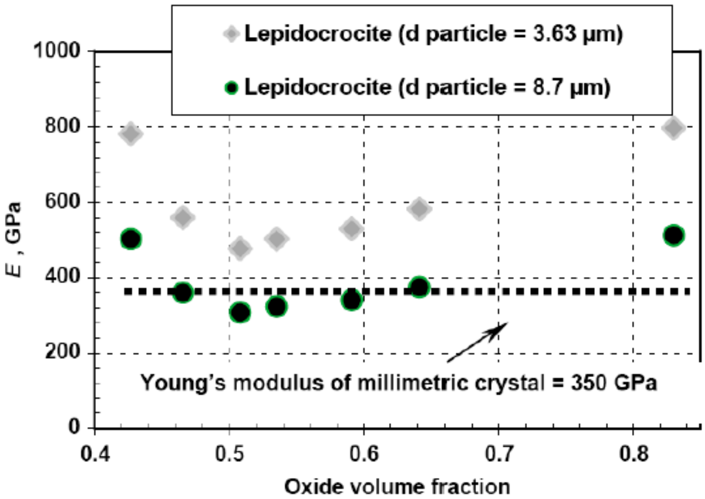

Figure 6. Young modulus derived from the Hertz theory.

6. CONCLUSIONS

Based on the observations made during the experimental investigation and the results of theoretical calculations, the following conclusions can be made:

Mechanical testing performed on iron oxide (lepidocrocite), in a powder state, shows a non-linear behaviour with important permanent strain, revealing the classical behaviour of a powder material and confirming the observations of Lungrend [7]. To avoid any dissipative phenomena the Young's modulus of some GPa has been deduced from elastic discharge branch of stress-strain curve.

The Young's modulus values obtained during mechanical testing were confirmed by ultrasonic measurements. The elastic modulus increases with the compaction and shows also a typical non-linear behaviour for granular material. For oxide volume fraction equal to 1 (pure crystal) the Young's modulus can reach several hundred GPa: from 215 to 350 GPa for maghemite Fe_2O_3 [2] and 390 GPa for alumina [5].

The ultrasonic measurements showed that the oxide dehydration increases the elastic modulus from 1.8 (drying 24 hours) to 3.6 (drying 48 hours) for 0.65 % of oxide volume fraction.

The Hertz contact model leads to results very convenient with results found in bibliography [2, 5]. An average value of 400 GPa for the 48 h dried lepidocrocite with grain max size 8.7 µm is very close to the 390 GPa of the reference [2].
Despite the influence of the friction contact on the estimation of the Young's modulus, it should be advised to use the Young's modulus obtained by ultrasonic measurements to perform a simulation of degradation processes in concrete structures under the expansion of corrosion products. This choice can be justified by the fact that these measurements were carried out on micrometric particles of oxides which is close to the real oxides.

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