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Abstract

Atomic Force Microscopy based nanoindentation was conducting in a sample of four different Mexican Composite Portland Cements paste at 28 days curing. The most important mechanical property determined by this characterization technique was the Modulus of elasticity of the different cement products of hydration (mainly C-S-H and Portlandite), using load versus distance curve fitting. At least two types of C-H-S were identified by nanoindentation measurements. A statistical analysis of the information was performed, and the variation of the different identified amounts of C-S-H was empirically correlated against the chemical composition of each cement sample studied.

Keywords: Atomic Force Microscopy, Nanoindentation, Composite Portland Cement

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Introduction

Cement is the building material of greatest economic and social impacts in the world, hence the importance of its study. “Currently, it is known, most of the time, the approach to continuous media results are unsatisfactory for use in real materials. In man-made structures, defects appear during the production stage at nano-, micro-, and macro- scales, which evolve throughout its useful life, generating failures, some of which, can be catastrophic.” (Casanova del Ángel, 2014).

In civil engineering, structural elements are analyzed using generalized models; these can be accurate in two dimensions determined by the mechanics of materials, or approximate models such as the finite element method. These models consider the material as isotropic, homogeneous and linear, so that the results obtained from the analysis do not consider the interactions that occur at the microscopic level, e.g., fractures, dislocations and vacancies among others. According to theories of multiscale modeling, all these interactions are crucial for understanding the behavior at different scales (Liu, Karpov, & Park, 2006).

The paste formed while the hydration process of Portland cement is considered as a multiphase material (Sáez de Ibarra, Gaitero, Erkizia, & Campillo, 2006), which implies that is the subject of study of multiscale modeling. (Karakasidis & Charitidis, 2007)

As a product of cement hydration, specifically of alite $\left(3CaO \cdot SiO_2\right)$ and belite $\left(2CaO \cdot SiO_2\right)$, Calcium-Silicate-Hydrate (C-S-H) phase is formed. Two packing densities of C-S-H have been identified, low density (LD C-S-H) and another high density (HD C-S-H), although recent studies propose an Ultra high-density phase. (Vandamme & Ulm, 2009).

There have been studies using Atomic Force Microscopy on the issue of the microstructure of cement and its behavior. Jones (Jones, Grasley, & Ohlhausen, 2011), makes a comparison between the Modulus of Elasticity obtained by AFM technique against "traditional" nanoindentation. AFM indentation results were distinct from the measured values obtained with nanoindentation in the average value and distribution; this behavior could be due to the differences on contact areas between AFM and nanoindentation probes.

Since the development of C-S-H depends, among other factors, on the amount of alite and belite present in the clinker, it results interesting to study how much the differences in the chemical composition affect the mechanical behavior at microscopic level.

A multiscale model links the behavior of the material in the minor scales with the largest scales. With the development of these models, one has the possibility of simulating the material behavior at different scales in order to monitor, predict and design materials with improved properties. As a result, the materials can be nano-modified; these materials standout as having greater strength, durability, etc.

To achieve the development of multiscale models is necessary to know the mechanical behavior at the microscopic level. In this research work, experimentation and analysis for obtaining Modulus of Elasticity was performed by Atomic Force Microscopy and the mathematical models; Hertz (Hertz, 1881) and Sneddon (Sneddon, Galin, & Moss, 1961). Also, statistical analysis of the information that shows the correlation between the chemical composition against the amount of C-S-H formed and the Modulus of Elasticity of each sample was conducted.

Theory

Physical Chemistry of Cement

Modern Portland cement is a mixture of clinker, gypsum and mineral additions such as fly ash, blast furnace slag and calcium carbonate. Portland cement clinker contains mainly two calcium silicates, tricalcium aluminate and aluminoferrite (European Standard, 2008).

The major products obtained from the hydration process of cement are Calcium-Silicate-Hydrate (C-S-H) and Portlandite (Crystal C-H). At nanoscale, Portland cement paste is mainly a C-S-H phase within which are the other components.

The cementitious properties of Portland cement are derived from the reactions generated when in contact tricalcium and dicalcium silicates with water. Hydration products such as C-S-H and C-H develop creating a matrix that is considered as a continuous, with a certain packing density. This density is critical to the strength of the material; at higher compaction, higher compressive strength.

Hardened cement has a porous structure. This porosity increases with the initial w/c ratio, and decreases with the hydration process. The pore radius is about <1 to 1000nm, the pores with radii smaller than these are considered an integral part of the paste and are called gel pores.

The main property of the hardened cement paste is the compressive strength, which is defined with a stress-strain curve under certain load. This property is that there is a network formed upon hydration, which is subjected to certain stress/external forces, and it is impossible to break it until reaching a maximum value.

The long term strength mainly depends on the chemical composition; relations between the minerals present in the clinker (calcium sulfate and certain oxides).

There is evidence to suggest that cements with higher content of alite are more resistant at early ages and that belite contributes most to the resistance at ages older than 28 days.

Atomic Force Microscopy (AFM)

The basis for Atomic Force Microscopy is the interaction between the tip and the material case of study, so it becomes imperative to study the contact forces between them.

The Lennard-Jones model for the study of contact forces suggests that forces of attraction and repulsion at large separation distances may be omitted; that there are forces of attraction at medium distances; and that there are repulsive forces at short distances; contact (Jones, Grasley, & Ohlhausen, 2011). It assumes that for repulsive forces between two atoms or molecules, the contact among them causes interpenetration of electron clouds but that nothing deforms behind each atom.

Regarding the contact between two solids in which the atoms are in a compact system, there is not only interpenetration of the electron clouds, the material below the surface is also deformed as if there were springs that bind atoms and that they compressed as the distance between the objects is reduced.

There have been developed analytical tools to describe continuous systems under certain assumptions as linear elastic behavior by Hooke's law:

$$\sigma = E \cdot \varepsilon \quad (1)$$

Where:

σ : stress

E : Modulus of Elasticity

ε : strain

Another assumption is that there are not tangential traction forces present (shear strength) during the contact.

There are models that describe the interaction of two objects in contact such as the Hertz' model (Hertz, 1881), which assumes that: 1) no attractive forces are present; 2) the material has no viscoelastic behavior.

This model was generated to describe the contact between two spherical objects, in the case of atomic force microscopy, since the geometry of the sample is nearly flat; it is considered the radius of curvature equal to zero.

This model relates:

$$a = (RF / M)^{1/3} \ldots\ldots\ldots \quad F = \frac{Ma^3}{R} \quad (2)$$

$$F = \frac{4}{3} MR^{1/2} \delta^{3/2} \quad (3)$$

$$\delta R = a^2 \quad (4)$$

where

a: contact radius

F: load applied

δ : Penetration depth

$$R = \left(\frac{1}{R_1} + \frac{1}{R_2} \right)^{-1} \quad (5)$$

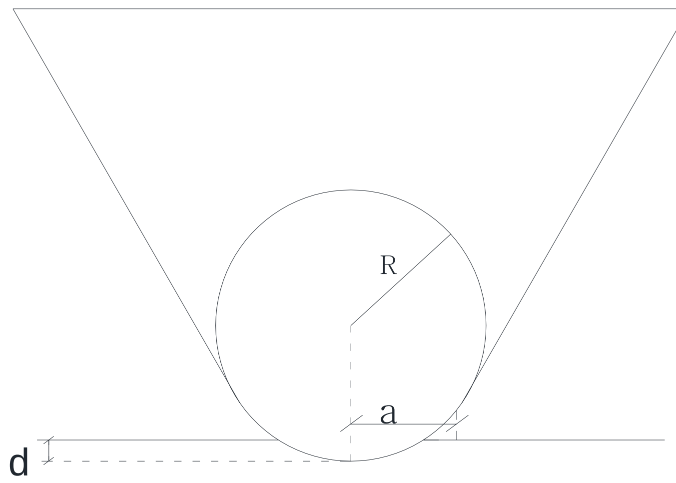
$R_{1,2}$: radii of curvature of the bodies in contact

R_i of the sample, being infinite is neglected

$$\frac{1}{M}=\left[\frac{\left(1-\nu_1{}^2\right)}{E_1}+\frac{\left(1-\nu_2{}^2\right)}{E_2}\right] \tag{6}$$

$$M\approx\left[\frac{E}{\left(1-\nu_1{}^2\right)}\right]\approx 1.5E \tag{7}$$

Figure 1. *Schematic Representation of the Parameters Required to Calculate the Modulus of Elasticity Based on Nanoindentation Tests*



The tip-sample interaction is a function of the separation distance D = -h. The strength increases with distance at a rate of $1/(-D)^{1.5}$

In models of contact, it is assumed that the repulsion happening during contact (penetration of the tip) is due to compression of the "springs" that link atoms. The attractive forces are present between the tip and the sample; there are more complete models than the Hertz model which take into account these forces. Two of the simplest models are the JKR (Johnson-Kendall-Roberts) and DMT (Derjaguin-Muller-Toporov) (Jones, Grasley, & Ohlhausen, 2011).

The JKR model studies attractive forces at the contact interface; while DMT only studies forces outside the contact area. These models complement Hertz model using the relationship between force and radius of curvature, affected by $(2\pi R\gamma)$ this to increase the contact area due to the increasing in the force of attraction between bodies.

Although there are forces that depend on the separation between the tip and the sample, usually the load applied to the tip is greater than the adhesive forces contributing so the latter can be neglected. (Jones, Grasley, & Ohlhausen, 2011)

For this reason, in this work the Hertz model is used to obtain the mechanical properties (Modulus of Elasticity)

Experimental

Materials

Portland Cement Composite CPC 30R was used, from four cement factories located in different states of the Mexican Republic; even though they have the same strength specifications, their chemical composition is different; a common situation in the production of commercial cements.

CPC, as specified by the Mexican Standard (NMX-C-414-ONNCCE-2004) is a combination of Portland cement clinker; calcium sulfate and pozzolanic materials which consist in a mixture essentially of reactive silicon dioxide SiO_2 and Al_2O_3 aluminum oxide, blast furnace slag or limestone. This type of cement is comparable with the European Portland-composite cement CEM II / BM according to EN 197-1 (European Standard, 2008; Arteaga Arcos, Chimal-Valencia, Yee-Madeira, & Díaz de la Torre, 2013).

Table 1 shows the chemical composition of each of the cements used in the analysis:

Table 1. *Chemical Composition of CPC-30 Samples (%wt.)*

Sample control number	L.I.*	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	P_2O_5	BaO	$CaSO_4 \cdot 2H_2O$	$CaCO_3$
1	0.1	19.7	10.0	3.4	42.5	1.0	0.8	0.4	0.2	0.0	0.0	0.3	6.9	11.7
3	0.1	20.6	10.7	3.4	42.2	1.1	1.3	0.4	0.2	0.0	0.0	0.0	5.2	12.0
4	0.4	14.1	3.9	2.2	46.8	1.1	1.2	0.4	0.3	0.0	0.0	0.0	4.8	22.8
7	0.2	20.3	9.5	3.3	43.8	3.3	1.0	0.3	0.3	0.0	0.0	0.0	4.9	11.9
*Lost on ignition														

For the hydrated cement specimens, the mixture was prepared using a w/c ratio of 0.5 according to (ASTM 109/C) standard; it was then poured in 1.2 cm diameter molds. They were allowed to cure for 24 hrs, and then the molds were immersed in a solution of calcium hydroxide and allowed to cure for 28 days.

After curing, they were demolded and immersed in ethanol for 24 hrs, this in order to stop the hydration process. The samples were introduced at 40 °C for 24 hr (Arellano Aguilar, Burciaga Díaz, & Escalante García, 2010) in order to complete the drying oven process.

Specimens were prepared for metallography according to the methodology of KO Kjellsen (Kjellsen, 2003) with some modifications, this preparation consisted of:

- Place acrylic tubes 2.5 cm in outer diameter and 1.5 cm high on a glass pre-lubricated with glycerin.
- In each tube, a cement specimen was placed.
- Epoxy resin was poured to fill the tube
- Then they were allowed to harden for 24 hrs, the first two under a red light.

- The samples were sand with emery paper of different levels of roughness (100, 280, 400, 600, 800, 1200, 1500, 1800, 2000)
- They were then polished on polishing cloths with diamond paste of three different particle sizes (1/4µm, 1 micron, 3 um). For sanding and polishing ethanol was used as a lubricant.

Results

A typical topography from AFM and its lateral force images are presented in Figure 2. A lateral force image can be useful in order to define AFM based indentations position. The contrast in this kind of images could be due to changes in mechanical properties of different material in case of samples that include more than one kind of materials (Haugstad, 2012).

Figure 3 shows a series of load versus displacement lines for different indented points. It can be observed the same behavior for all the tested samples, even though; the particular values of the curves are different among each cement sample. This trend can be interpreted as the variations of the modulus of elasticity for C-S-H (at the micrometric scale) could be identified in different samples by using this technique.

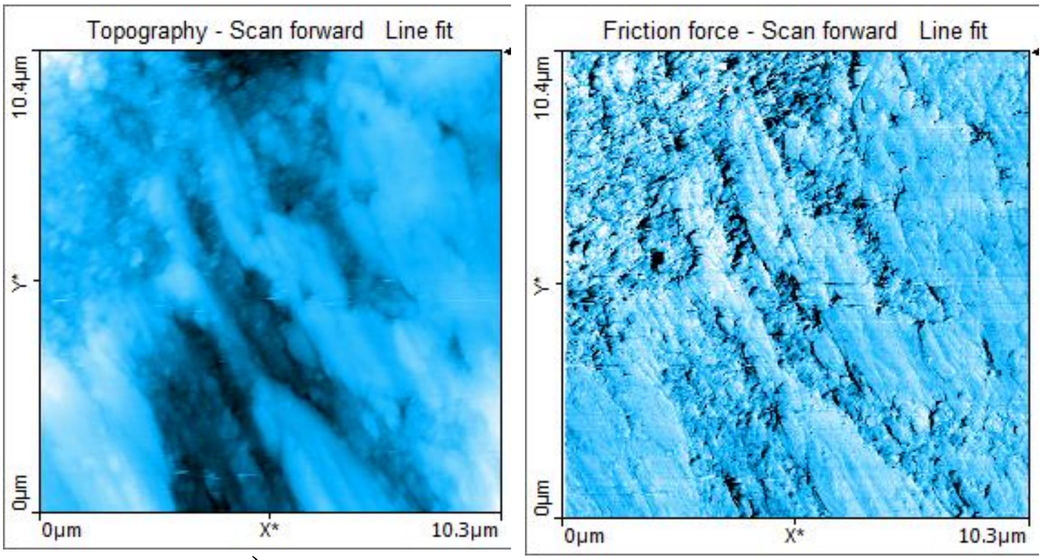
Histograms of calculated values for the modulus of elasticity can be observed in Figure 4. It could notice a bimodal distribution of modulus of elasticity values; this is in accordance with previously reported values and can be associated with low and high packing density C-S-H (Jones, Grasley, & Ohlhausen, 2011).

In one hand, samples 1, 3 and 4 presented the same behavior; the range and the distribution of the values are almost the same, in the other hand, sample 7 showed lower values of the modulus of elasticity. In fact, it can be identified in sample 7 certain points with very low values when compared against the ones found in the other samples, this could be associated with indentation on calcium hydroxide instead of C-S-H (Jones, Grasley, & Ohlhausen, 2011). In sample 4, it could be assumed the formation of the two packing density C-S-H but with lower values when compared against sample 1 and 3, especially the high-density C-S-H.

Sample 1 and 3 virtually have the same chemical composition and the less amount of calcium carbonate content as an addition; this could explain the very similar values of the Modulus of Elasticity approached by AFM based nanoindentation and the higher values of modulus of elasticity found. Sample 4 is the one that has the highest amount of calcium carbonate; this could be the reason of the formation of lower values on high-density packaging C-S-H. Another possible explanation is that perhaps the indentation was conducted over a different compound that C-S-H or portlandite; it is required to conduct further research in combination with other analytical techniques in order to identify the chemical composition of the hydration products in order to correctly identify differently formed phases.

Finally, it is worth to be mentioned that the values of the modulus of elasticity approached in this research work by AFM technique are lower than values reported in technical literature (Ulm & Constantinides, 2007; Plassard, Lesniewska, Pochard, & Nonat, 2004), where typical values are about 50 MPa. It could be due to the particular operation mode of the AFM device used in this research; it is required to conduct more tests in order to correctly calibrate the instrument with different cement paste samples.

Figure 2. *AFM Micrograph of Cements Paste. a) Topography, b) Lateral Force*



a) b)

Figure 3. *AFM Based Nanoindentation for Some Cement Paste Samples*

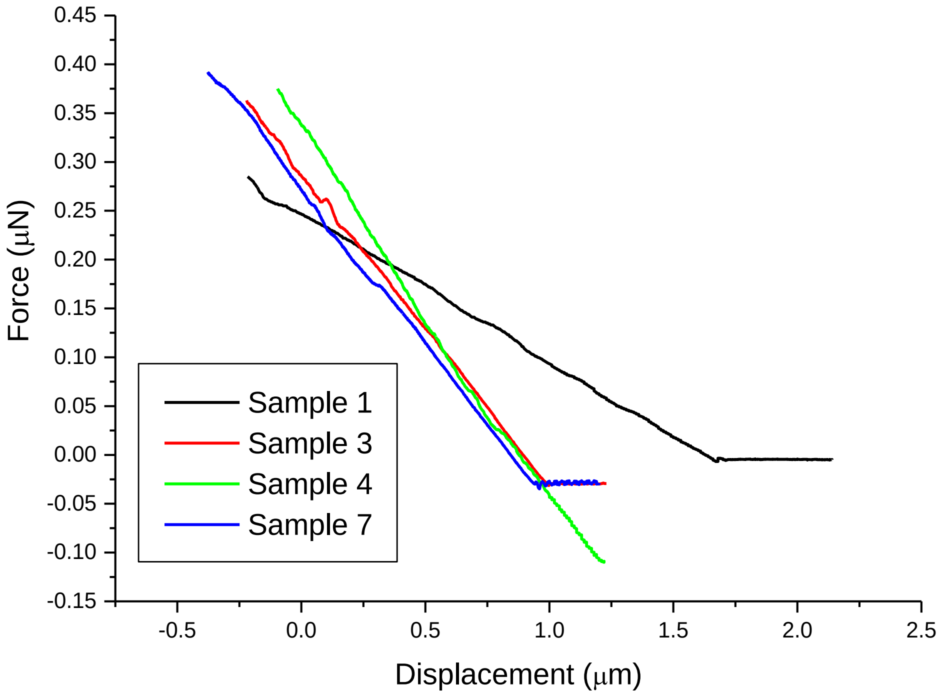
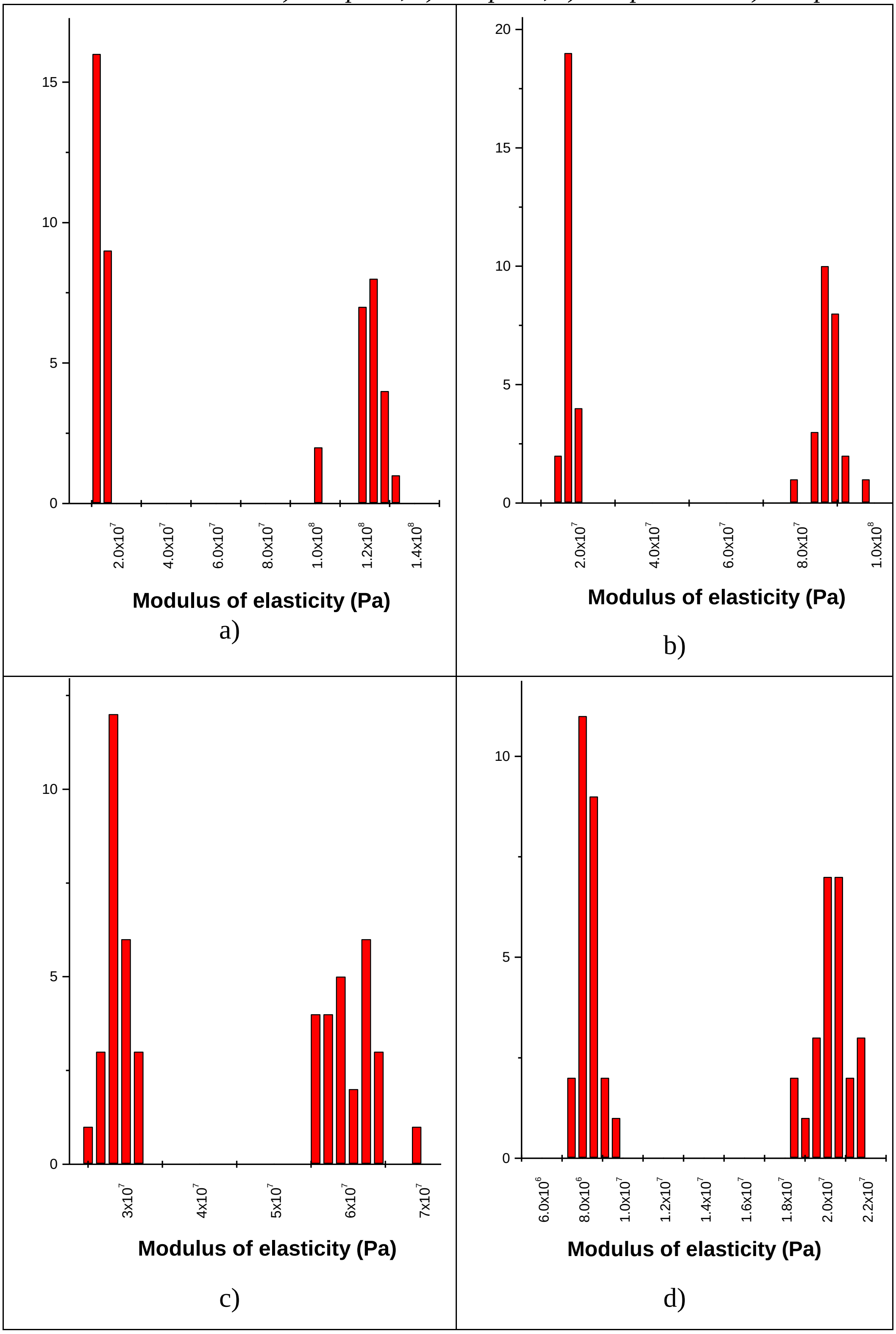


Figure 4. *Histograms of the Modulus of Elasticity Values Calculated by AFM Base Nanoindentation. a) Sample 1, b) Sample 3, c) Sample 4 and d) Sample 7*



Conclusions

Based on the values of the modulus of elasticity found in some of the samples it is worth to be noticed that the cements with higher amounts of calcium carbonate as an addition present low values of the modulus of elasticity of the hydration products formed into the cement paste. Furthermore, it could be assumed the presence of some phases different than C-S-H or portlandite in possible higher amount than the reported in typical values in Ordinary Portland Cement. It is required to conduct further research in order to correctly identify the chemical composition of hardened compounds in order to better understanding of the behavior observed herein.

References

Arellano Aguilar, R., Burciaga Díaz, O., & Escalante García, J. (2010). Lightweight concretes of activated metakaolin-fly ash binders, with blast furnace slag aggregates. Construction and Building Materials , 1166-1175.

Arteaga Arcos, J., Chimal-Valencia, O., Yee-Madeira, H., & Díaz de la Torre, S. (2013). The usage of ultra-fine cement as an admixture to increase the compressive strength of Portland cement mortars. Construction and Building Materials , 152-160.

ASTM 109/C, 1.-9. Standard Test Method for Compressive Strength of Hydraulic Cement Mortars.

Casanova del Ángel, F. (2014). Fractal Effect of Corrosion on Mechanical Behavior of Unprotected Structural Steel. En M. A. (Ed), Developments in Corrosion Protection (págs. 551-565). ISBN: 978-953-51-1223-5, InTech.

European Standard. (2008). EN-191-1. Composition, specifications and conformity criteria for common cements. Brussels, Belgium: European Commitee for Standarization.

Haugstad, G. (2012). Atomic Force Microscopy. Undestanding Basic Modes and Advanced Applications. New Jersey: John Wiley & Sons Inc.

Hertz, H. (1881). On the contact of elastic solids. J. reine angew , 92: p.156-171.

Jones, C., Grasley, Z., & Ohlhausen, J. (2011). Mearurement of elastic properties of calcium silicate hydrate with atomic force microscopy. Cement and Concrete Composites , 468-477.

Karakasidis, T., & Charitidis, C. (2007). Multiscale modeling in nanomaterials science. MATERIALS SCIENCE & ENGINEERING C , 1082-1089.

Kjellsen, K. (2003). Preparation of flat-polished specimens for SEM-backscattered electron imaging and X-ray microanalysis--importance of epoxy impregnation . Cement and Concrete Research , 33(4) p. 611-616.

Liu, W. K., Karpov, E. G., & Park, H. S. (2006). Nano Mechanics and Materials Theory, Multiscale Methods and applications. Chichester : Wiley .

(2004). NMX-C-414-ONNCCE-2004 . México, DF: ONNCCE.

Plassard, C., Lesniewska, E., Pochard, I., & Nonat, A. (2004). Investigation of the surface structure and elastic properties of calcium silicate hydrates at the nanoscale. Ultramicroscopy , 100 ((3-4)), 331-338.

Sáez de Ibarra, Y., Gaitero, J., Erkizia, E., & Campillo, J. (2006). Atomic Force Microscopy and nanoindentation of cement paste with nanotube dispersions. PHYSICA.STAT.SOL , 1076-1081.

Sneddon, I., Galin, L., & Moss, H. (1961). Contact problems in the theory of elasticity. North Carolina : Raleigh, NC Dept. of Mathematics, School of Physical Sciences and Applied Mathematics North Carolina State College.

Ulm, F., & Constantinides, G. (2007). The nanogranular nature of C-S-H. Journal of the Mechanics and Physics of Solids , 64-90.

Vandamme, M., & Ulm, F.-J. (2009). Nanogranular origin of concrete creep. Proceedings of the National Academy of Sciences , 106(26): p.10552-10557.