New cements with low content in Calcium for sustainability challenge

Production and characterization of CaO-SiO_2-Al_2O_3-Fe_2O_3 amorphous

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Abstract

Cement is one of the most used materials worldwide. However cement industry has always been one of the largest CO_2 emissions responsible. This environmental concern leads to this dissertation - an investigation about the production and characterization of alternative clinkers with low content of CaO. This study focused on amorphous in the CaO-SiO_2-Al_2O_3-Fe_2O_3 system with C/S ratios of 0.8, 1.0, 1.1 and 1.25 (eutectic); this composition of calcium silicate glasses are in the range of Wollastonite, a clinker with a lower content of $CaCO_3$ rather than clinker OPC.

The samples produced were characterized by spectroscopy techniques, FTIR, MNR and XRF. Their structural alterations related to the chemical composition, were determined and compared with the results obtained with molecular dynamics simulation (MD).

The three main techniques used to characterize the samples produced (FTIR, MNR and MD) revealed a decreasing of Q^3 and Q^4 structural units with increasing C/S ratio. It also shown that structural units Q^2 are predominant in all samples. Also verified that a decrease in the C/S ratios lead to an increase of silicate rings in the structure, whereas the increase of the C/S ratio (i.e., increase of calcium content) resulted in structures composed of linear silicates chains.

Keywords: Amorphous, Aluminum silicate, Cement Clinker, Wollastonite, FTIR, MNR, XRF, Molecular Dynamics

Introduction

Portland cement is the most common used cement today. Over the past years, its worldwide production continuously increased. Thus, it proves to be one of the most reliable economical materials and a fundamental ingredient on construction.

Portland cement is a powdered binder composed by calcium silicates, aluminates and ferrites.

Cement industry has been always among the largest CO_2 emission source. Almost 5-7% of global CO_2 emissions are caused by cement plants, for produce 1 Ton of cement 900Kg CO_2 is emitted to the atmosphere.

The strategy of CO_2 reduction is the aim of this study: to reduce the content lime (CaO) present in the clinker.

Clinkerization, is the name given to the firing process due to the transformation of the raw materials in a nodulized material- the clinker.

Clinkerization is responsible for 50% of the CO_2 emission of the process, most of the emissions are in the carbonation of the limestone ($CaCO_3$ -> $CaO + CO_2$).

On Portland clinker, the mineralogical composition is generally within: 50-70% C3A (alite), 15-30% C_2S (belite), 5-10% C_3A (aluminate) and 5-10% C_4AF (ferrite)- percentage by mass. Portland clinker has a C/S ratio about 3.

This dissertation involves producing clinkers 100% amorphous in the range of Wollastonite with C/S ratios **0.8**, **1.0**, **1.1**, **1.25** and the lowest content in aluminum and iron as possible (3% (mass) aluminum and 3%(mass) iron). This amorphous were characterized using three techniques: ^{29}Si NMR, infrared spectroscopy (FTIR) and x-ray fluorescence spectroscopy (XRF). It was modeled and characterized by molecular dynamics simulations of amorphous with the same C/S ratios (0.8, 1.0, 1.1, 1.25) and with 3%(mass) content of aluminum. The experimental amorphous were structural compared to the simulated ones.

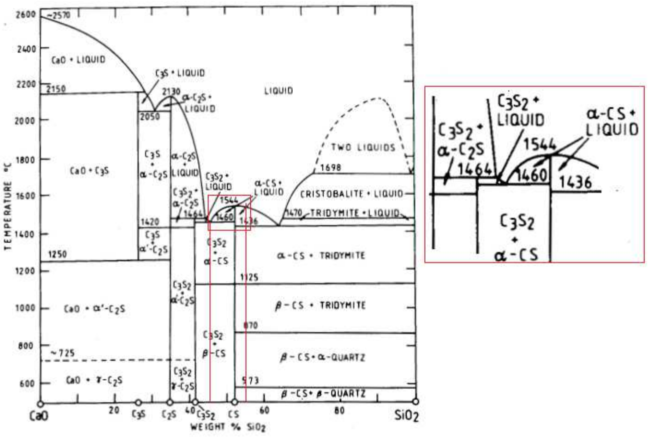

Fig. 1 The CaO-SiO_2 system and the work zone in red.[1]

Silica structure

In cement, silica is the reactive component in hydraulic properties. Silica is formed by SiO_4 tetrahedra, Q^n, nomenclature for the tetrahedrally coordinated cations.

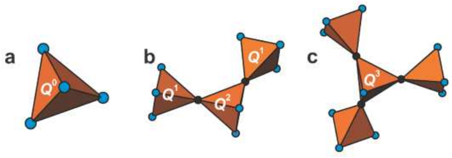

Fig. 2 Illustration of the Q^n nomenclature for tetrahedrally coordination cations.[2]

Silicium in the center of the tetrahedron and oxygen atoms on the vortices, n denote the number of bridging oxygen atoms. (a) An isolated Q^0 tetrahedron. (b) A Q^2 unit bonded to two Q^1 terminal tetrahedral. (c) A central Q^3 tetrahedron connected to Q^1 units.

In this range of wollastonite (CS) we already know the structure of the crystal, a linear chain with Q^2 of SiO_4 tetrahedra.

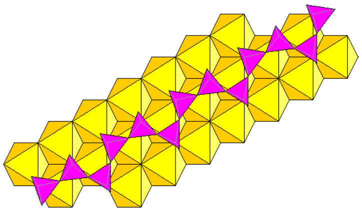

Fig. 3 Crytalline wollastonite.[3]

Amorphous silica exhibits an essentially identical short-range structure as the crystalline SiO_2 polymorph, are formed by SiO_4 tetrahedra and the local structure of calcium is similar to its short-range order, forming a octahedra, calcium in the center and oxygen atoms at the vortices. However on long-rang this tetrahedral has no periodic distribution, forming structural units Q^0, Q^1, Q^2, Q^3 and Q^4 in isolated tetrahedral, simple linear chains or rings….

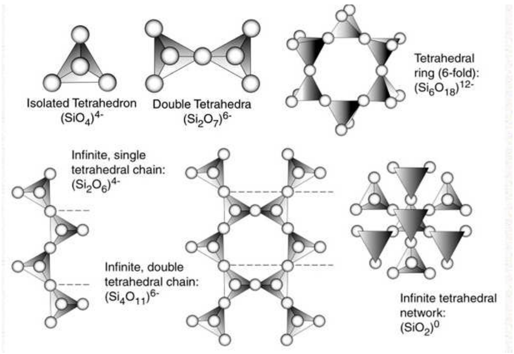

Fig. 4 Possible network tetrahedral structures in silica.[6]

Experimental procedure

The limestone, silica, fly ash and iron slag were grinded and mix, than the raw materials goes to the kiln to a firing process- begins the clinkerization- at the end of this stage we had a nodulized clinker, this clinker was powdered to a 10µm grain, and its ready to be characterized by spectroscopic techniques.

Table. 1 chemical composition of the clinkers.

Série Al 3,0% Fe 3,0%				
	C/S ratios			
weigh (g)	**0.8**	**1.0**	**1.1**	**1.25**
limestone	132,4	145,8	151,3	158,5
silica	92,2	79,6	74,4	67,6
Iron slag	8,9	8,7	8,6	8,4
Fly ash	16,5	15,9	15,8	15,5

Table. 2 work conditions.

C/S ratios(mol)	**Temperature(°C)**	**Time (h)**
0.8	1470	2h30
1.0	1500	3h
1.1	1500	2h30
1.25	1450	2h30

Methods

- **Infrared spectroscopy (FTIR)**

FTIR spectroscopy is a useful tool in the molecular characterization of inorganic species. This vibrational technique which is common in many analytical laboratories has advantages of requiring small quantity of the sample, quick and easy sample preparation and short analysis time. IR spectra are characterized by the wave number (cm^{-1}) of absorbance and its intensity (a.u.).

IR spectroscopy was conducted using a Bruker Alpha Platinum spectrum, with a resolution of 2 cm^{-1} on powdered samples.

- **Nuclear magnetic resonance (NMR)**

Solid state ^{29}Si magic-angle spinning (MAS) NMR offers an efficient method to characterize the structural units in silica. Interpretation of ^{29}Si NMR spectra provides the local silicate tetrahedral environment, designated as Q^n . An increase in the number of SiO_4 units bonded to each Si center produces an increase in the average electron density around the central Si atom, leading to a more negative chemical shift, relative to tetramethylsilane (TMS)- the reference Si.

Solid state NMR analysis was performed using a Tecmag/Bruker 300wb, with 9,4 Tesla magnetic field, operating 59,625MHz for ^{29}Si, a MAS rate about 3100Hz, relaxation delay 40seg with number of scans over 2000, external reference tetrakis (trimethylsylil)silane (^{29}Si=-9,8; -135,64 ppm).

- **X-ray fluorescence spectroscopy (XRF)**

XRF is the emission of characteristic “secondary” (or fluorescent) x-rays from a material that has been excited by bombarding with high-energy x-rays. The phenomenon is widely used for elemental analysis and chemical analysis.

The XRF analysis was performed using a AXIOS^{max} PANalytical instrument.

- **Molecular dynamics simulations**

Molecular dynamics simulations generate trajectories of each atom or particle in a system according to pre-designated interactions potentials via Newton’s second law of motion. These trajectories capture interactions among atoms in the system. In this study we used the well- known Lennard-Jones potentials (describe interactions between two atoms/molecules).

The simulator DL_POLY2.20 has three main input files: FIELD, CONFIG and CONTROL, and there are three main output files: OUTPUT, REVCON and HISTORY.

Table. 3 Lennard -Jones potentials used in the simulation.

Pair interaction	Charge	ε(eV)	σ(Å)
Ca-Ca	2	0,00011	4,1980
Ca-O	2	0,084067	2,4200
Si-O	4	1,167341	1,4990
Al-O	3	0,172881	1,7777
O-O	2	0,014079	3,2530

In file CONTROL it was first defined the temperature at 4000K with constant volume (NVT conditions), with 170000steps and 0,5fs of timestep. Further simulations obtained us a decreasing temperature (100K steps) from 2500K to 300K with 1000 steps which and 1fs of timestep (very common in MD for glasses). At 300K temperature the simulation is made at NPT conditions, 100000 steps and 2 fs timestep, last simulation is made at 300K, 50000 steps, 1 fs timestep and generating the HISTORY file with the atom trajectories.

In file CONFIG we generate a simulation cubic cell with 50 Å of cube edge.

The trajectories that generate molecular structure were produced by the software VESTA®. We also had the results for energy of the system and RDF's of the main atomic bonds.

Results

FTIR spectroscopy

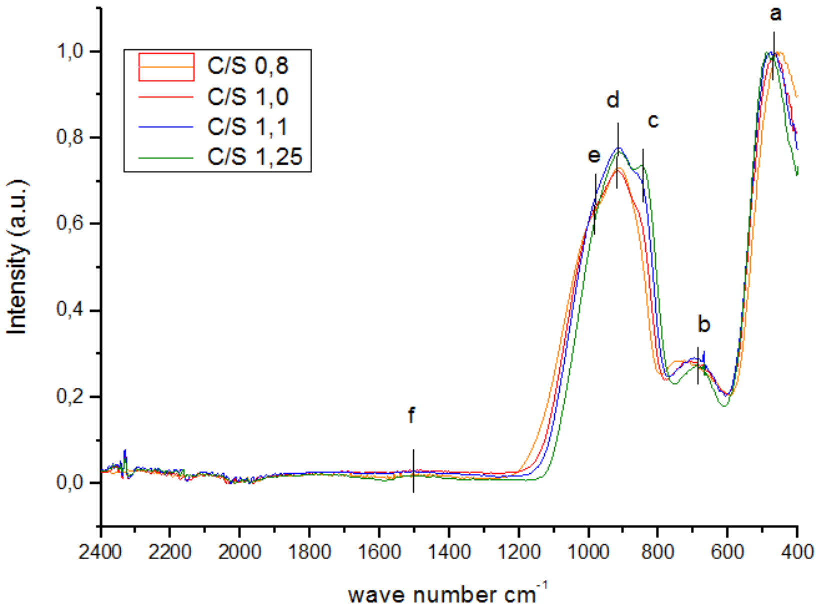

Fig. 5 FTIR spectra obtained for the amorphous.

Table. 4 peaks and respective vibration modes.

Peak	wavenumber	Vibration modes	Reference
a	400-500cm^{-1}	Deformation of SiO_4 tetrahedra (Q^4units)	[10][12][15]
b	~660 cm^{-1}	Si-O-Si bending vibrations	[10][15]
c	Ombro a ~875 cm^{-1}	Bending of CO_3^{2-}; Si-O stretching vibrations (Q^1 and Q^0 units)	[11][12]
d	~970 cm^{-1}	Si-O stretching vibrations (Q^2unit)	[12][15]
e	Ombro ~1065 cm^{-1}	stretching vibrations Si-O-Si; bending Si-O (Q^3 and Q^4units)	[11][12][15]
f	~1500 cm^{-1}	Asymmetric stretching of CO_3^{2-}	[11]

^{29} Si NMR spectroscopy

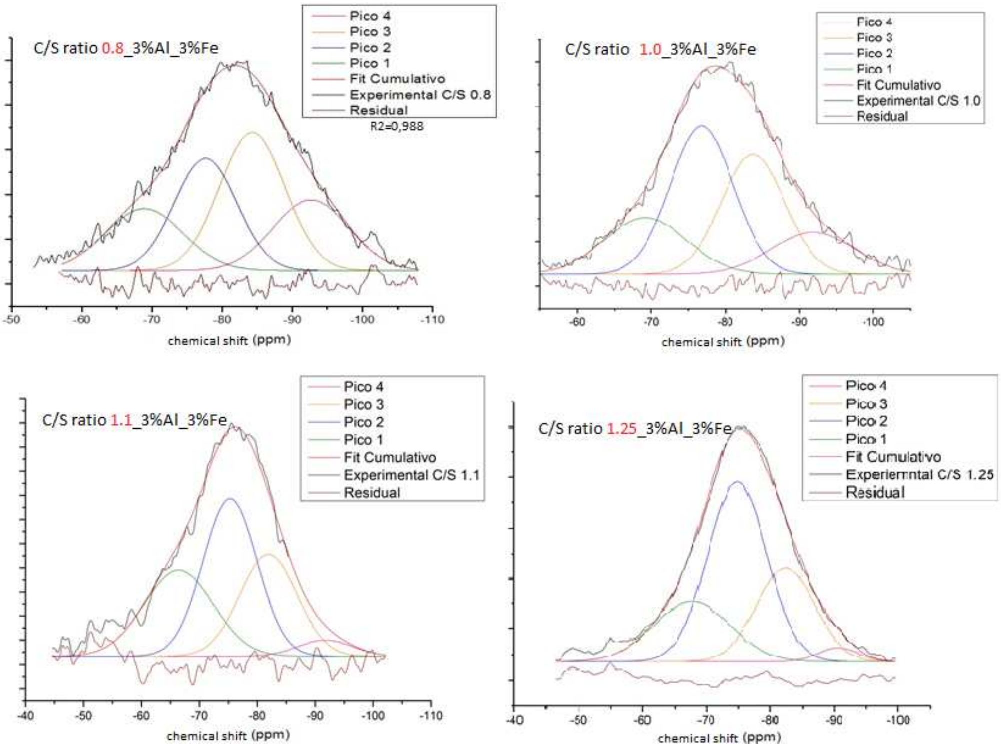

Fig. 6 Deconvolution of ^{29}Si NMR spectra for amorphous samples.

Table. 5 ^{29}Si isotropic chemical shifts and parameters in C/S ratio 0.8_3%Al_3%Fe.

C/S 0.8	center	Area	FWHM	Structural unit	Reference
Peak	(ppm)	(%)	(ppm)	Q^n	
1	- 68,85	18,05	13,00	Q^0	[11]
2	- 77,59	26,83	10,45	Q^1	[5][8] [11]
3	- 84,25	34,73	11,00	Q^2	[5][11][13]
4	- 92,62	20,39	12,65	Q^3	[5][11][13]

Table. 6 ^{29}Si isotropic shifts and parameters in C/S ratio 1.0_3%Al_3%Fe.

C/S 1.0	Posição do centro	Área	FWHM	Grupo associado
Pico	(ppm)	(%)	(ppm)	Q^n
1	- 69,18	18,44	13,00	Q^0
2	- 76,80	37,49	10,00	Q^1
3	- 83,75	30,41	9,99	Q^2
4	- 91,84	13,65	12,99	Q^3

Table. 7 ^{29}Si isotropic chemical shifts and parameters in C/S ratio 1.1_3%Al_3%Fe.

C/S 1.1	center	Area	FWHM	Structural unit
Peak	(ppm)	(%)	(ppm)	Q^n
1	- 66,42	28,08	14,00	Q^0
2	- 75,30	40,24	10,99	Q^1
3	- 81,93	27,62	11,65	Q^2
4	- 91,76	4,06	11,00	Q^3

Table. 8 ^{29}Si isotropic chemical shifts and parameters in C/S ratio 1.25_3%Al_3%Fe.

C/S 1.25 Peak	center (ppm)	Area (%)	FWHM (ppm)	Structural unit Q^n
1	- 67,74	21,51	14,00	Q^0
2	- 74,84	50,13	10,81	Q^1
3	- 82,40	25,80	10,66	Q^2
4	- 90,62	2,55	7,27	Q^3

XFR spectroscopy

Table. 9 Molar composition of the amorphous samples by XRF spectroscopy.

Molar composition	**C/S 0.8**	**C/S 1.0**	**C/S 1.1**	**C/S 1.25**
SiO_2	0,873	0,784	0,753	0,702
CaO	0,702	0,802	0,839	0,886
Real C/S ratio	0,804	1,022	1,115	1,262

Molecular dynamics

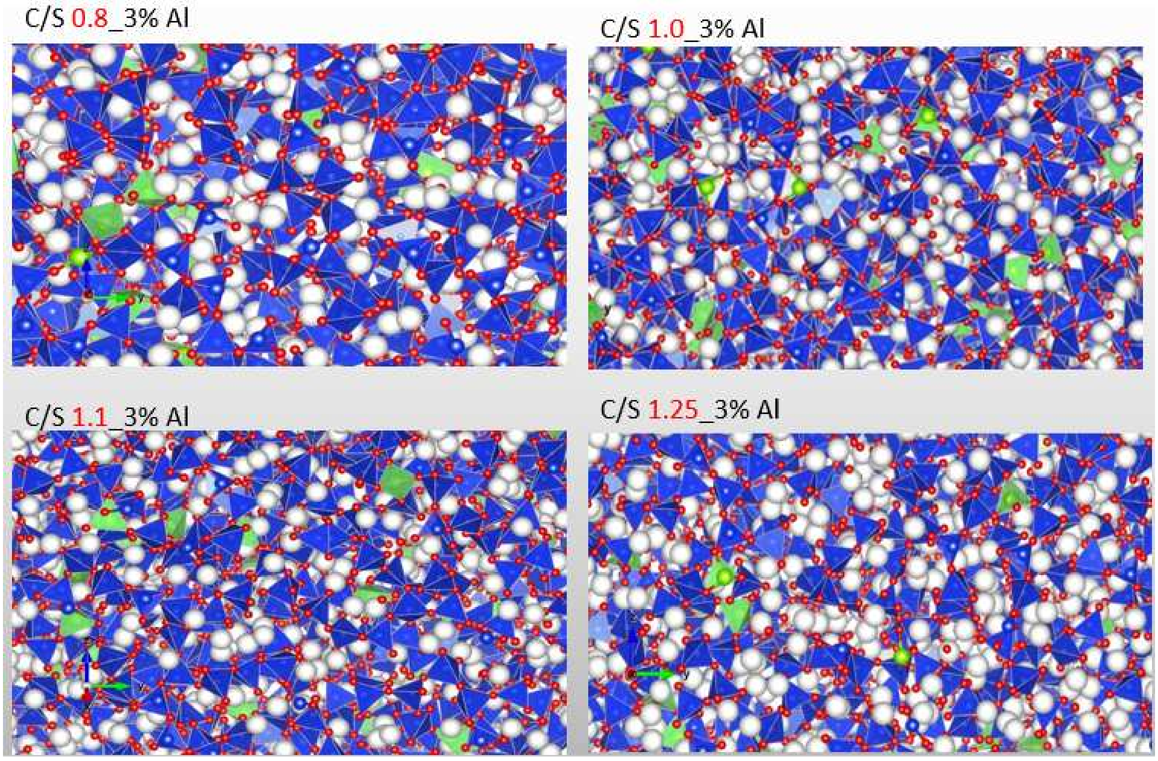

Fig. 7 Molecular model of the amorphous samples: the with spheres are calcium atoms, red spheres are the oxygen atoms, the blue are Silicium tetrahedra and the green are Aluminum tetrahedra.By MD at 300K.

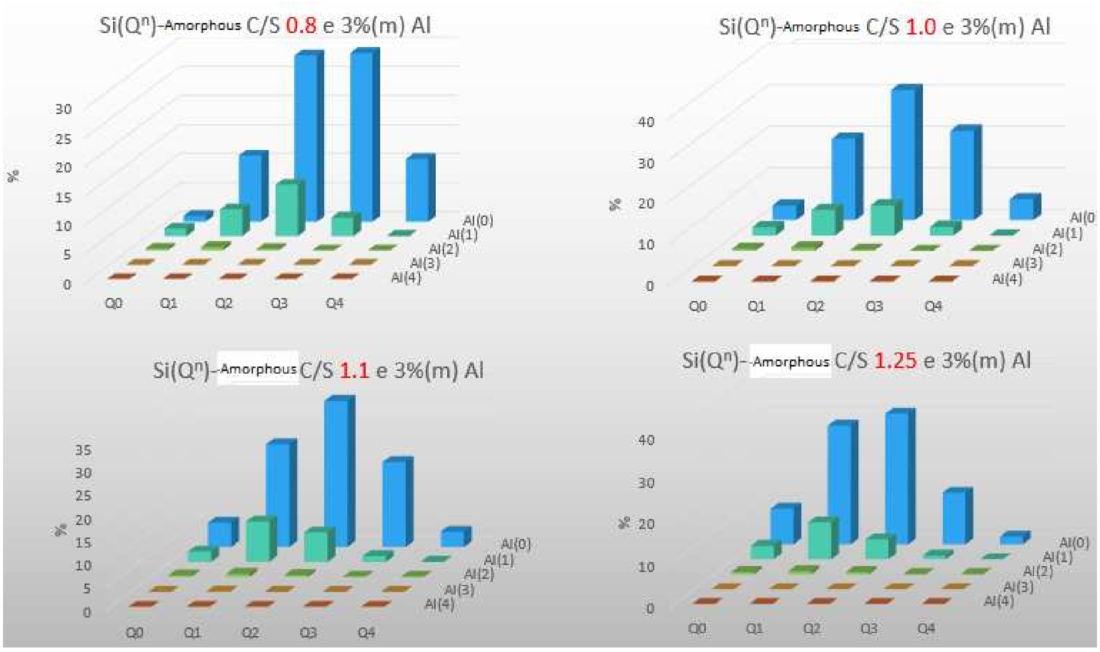

Fig. 8 Structural units obtained in amorphous samples by MD(300K).

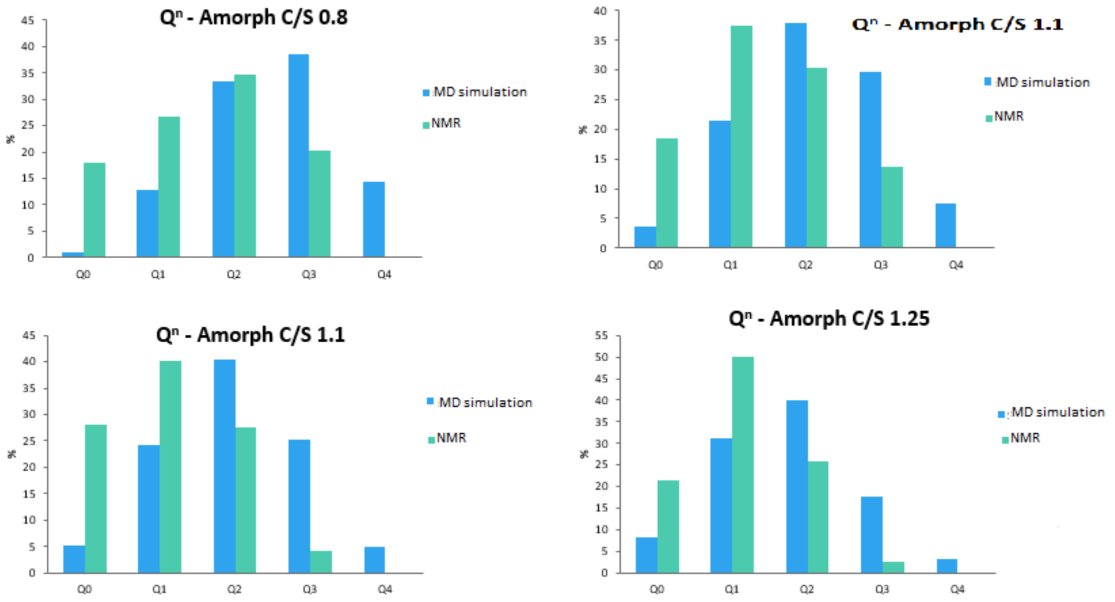

Fig. 9 structural units Q^n : MD simulation VS ^{29}Si NMR.

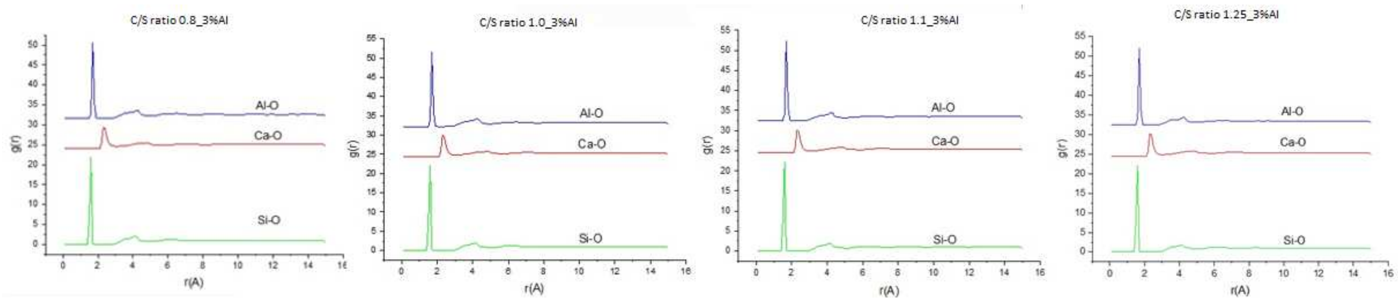

Fig. 10 RDF's obtained by MD simulations for the amorphous sample.Al-O bond 1,7Å, Ca-O bond 2,3Å, Si-O bond 1,6Å.

Table. 10 stability of the systems: Energy and densities.

Amorphous sample	Energy (KJ/mol clínker)	C/S	Experimental density (g/cm^3)	Simulated density (g/cm^3)	deviation
C/S 0.8 (3%mass de Al)	-6976	0.8	2,86	2,79	2,5%
C/S 1.0(3%mass de Al)	-7315	1.0	2,95	2,81	4,9%
C/S 1.1(3%mass de Al)	-7456	1.1	2,98	2,83	5,3%
C/S 1.25(3%mass de Al)	-7697	1.25	2,95	2,86	3,1%

Conclusions

The main purpose of this study is to present the production and characterization of the clinkers 100% amorphous with a low ratio of calcium oxide (CaO) . The four amorphous studied show C/S ratios of 0.8, 1.0, 1.1 and 1.25 with a 3% mass content of aluminum and iron. This compositions are in the range of wollastonite. The samples were structurally analyzed trough the infrared spectroscopy techniques (FTIR),magnetic nuclear resonance (NMR-MAS) and x-ray fluorescence (XRF). The amorphous produced experimentally were correlated to those simulated by molecular dynamics. FTIR spectra confirmed typical amorphous spectra with large bands. Spectra shown two major absorption types: tetrahedra SiO_4 angular bend vibrations (400-800cm^{-1}) and Si-O stretching vibrations (~1000cm^{-1}). The study showed that the predominant structure is the Q^2 unit on every sample. The C/S lower ratios showed Q^3 and Q^4 units while the major C/S ratios showed Q^0 and Q^1 units. Polymerization increases while the ratio decreases.

Si NMR spectra showed Q^0 , Q^1, Q^2 and Q^3 units (there weren't any Q^4 units on the samples) .The mainly structure is the Q^1 unit (exception for CS ratio 0.8_3%Al_3%Fe sample with the Q^2 predominance). Once again this research shows a polymerization with the ratio decrease. The C/S lower ratios showed Q^2 and Q^3 units while the major C/S ratios Q^0 and Q^1 units are more significant. This technique presents satisfactory results with the predominance of the Q^1 unit, as well the crescent increase of Q^0 units, ideal for the raise of the hydrated clinker reactivity. However we can't ignore the complexity of the spectra deconvolution .

XRF results present sample molar ratios CS 0.8, 1.0, 1.1 and 1.26. All samples present a mass content of 3% Al and 3% Fe. Those values were later used directly on the computational simulation to obtained simulated amorphous as much as identical to those produced experimentally.

Molecular dynamics revealed an identical tendency to the FTIR and MNR spectroscopy: polymerization increases while the ratio decreases. For molecular dynamics the main structure was Q^2 unit. 3D microstructure snipe shoots of the simulation shows tetrahedral structures of SiO_4 and AlO_4 interconnected. The MD results are reliable compared with other studies and my experimental results. The method stability checked trough the quick stabilization of the four systems energy. The RDF's results are reliable to the crystallographic studies. Comparing experimental densities to simulated ones the deviation is not significant.

The three main techniques FTIR MNR and MD used to characterize the samples revealed a increasing of Q^0 and Q^1 structural units with increasing C/S ratio.

References

1. Taylor,Harold F.W.; *Cement Chemistry*; Academic Press London **1990.**
2. Edén, Mattias; *NMR Studies of oxides-based glasses* Annu.Rep.Prog.Chem.,Sect:C:Phys.Chem.,**2012**,108,177-221.
3. http://www.uwgb.edu/dutchs/petrology/WollastoniteStructure.HTM [citado em Julho 2014]
4. Schneider, M. et al. *Sustainable cement production-present and future*, Cement and concrete research vol.41,issue7, (**2011**) ,642-650.
5. Schneider,J. *et al*.; Jornal of Non-Crystalline *Solids* 273(**2000**)8-18.
6. httpwww4.nau.edumeteoriteMeteoriteBook-GlossaryS.html [citado em Dezembro 2014]
7. Zachariasen, W.H*.,* J.Am.Chem.Soc.,**1932**,54,3841-3851.
8. P.Zhang, P.J. Grandinnetti, J.F. Stebbins, J.Phys. Chem. B 101 (**1997**) 4004.
9. D.De Sousa Meneses *et al.* Journal of Non-Crystalline Solids 352 (**2006**) pp 5301-5308.
10. B.Mihailova, L.Kontantinov, E.Dinolova, J.Non-Cryst.Solids 191 (**1995**)79.
11. Mendes,A et al; *NMR,XRD,IR and synchrotron NEXAFS spectroscopic studies of OPC and OPC/slag cement paste hydrates;* Materials and Structures **(2011)** 44:1773-1791
12. I.Lecomte *et al.;*Jornal of the European Ceramic Soc. 26 (**2006**) 3789-3797.
13. Hansen et al.; *29Si MAS NMR Spectroscopy in calcium silicates* Inorg.chem**.2003**,42,2368-2377.
14. Zanotto, E.D.; Muller, E.*;* J.Non-Cryst.Solids 130 (**1991**) 220.
15. Nunes,Teresa; (Outubro **2014**) *Introduction to Solid State NMR- Part I* IST.
16. S.A.MacDonald, C.R.Schardt, D.J.Masiello, J.H.Simmons,J.Non-Cryst.Solids 275 (**2000**) 72.
17. Cormack,A.N., Cao,Y., *Molecular Dynamics simulation of glasses*, Molecular engineering 6:183-227, Kluwer Academic Publishers **(1996).**
18. Bauchy,M., *Structural,vibrational and elastic properties of a calcium aluminosilicate glass from molecular dynamics simulations: The role of the potential***(2014)** Massachusetts Institute of Technology.