

UNIVERSIDADE DE LISBOA INSTITUTO SUPERIOR TÉCNICO

Development and characterization of an amorphouswollastonitic hydraulic binder.

A contribution to carbon neutrality in the cement industry

Mónica Sofia Hoyos Antunes

Supervisor: Doctor Rogério Anacleto Cordeiro Colaço

Co-supervisors: Doctor Rodrigo Manuel Lino dos Santos

Doctor Ricardo Manuel Simões Bayão Horta

Thesis approved in public session to obtain the PhD Degree in Materials Engineering

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Resumo

É esperado que o uso e a procura de cimento Portland (OPC) aumente a nível global aumentando também a sua necessidade de produção. No entanto, o processo de fabrico de OPC contribui significativamente para as emissões antropogénicas de CO₂, devido à descarbonatação de calcário e à combustão de combustíveis fosseis. Uma proposta alternativa é a produção de um ligante hidráulico com uma composição de cálcio semelhante à wollastonite e um elevado teor de amorfização. As emissões de CO₂ relacionadas com o seu processo de fabrico são, inferiores às do OPC. Esta tese, é uma continuação na investigação deste ligante e tem como objetivo compreender as reações do material, melhorar as condições de produção e aplicação, e testar a influência do uso de materiais cimentícios suplementares (SCM) com o ligante.

No estudo da reação hidráulica, foi proposto um mecanismo de hidratação, tendo em conta os princípios de dissolução, e foi calculada a energia de ativação da reação. Os resultados indicam que a ativação do ligante com uma solução de silicato de sódio é essencial para obter resultados competitivos na resistência à compressão a idades jovens. Portanto, nesta tese foi analisada a otimização do rácio SiO₂/Na₂O no ativador e estudada uma via alternativa para a sua síntese e aplicação. Os resultados de energia de ativação indicam que o produto de hidratação deste ligante é estruturalmente diferente aos produtos de hidratação dos principais componentes do OPC. A influencia do armazenamento devido à carbonatação superficial do ligante anidro foi também investigado.

De modo a melhorar a produção do material, foram realizados estudos sobre a influência do aumento do teor de Al₂O₃ e MgO no clinker. Foi possível aumentar o teor até 12 e 8%wt, respetivamente, sem comprometer o desempenho do ligante. Este aumento de materiais fundentes permitiu a redução na temperatura máxima de produção de 1550 para 1450°C.

Finalmente, foi estudado a influencia de 25% wt de substituição de clinker por diferentes SCMs. Os resultados indicam que a solução alcalina ativou a escoria moída de alto forno, resultando numa sinergia entre o ligante e o SCM

Este trabalho tem como objetivo aprofundar os conhecimentos das propriedades deste ligante e melhorar o seu método de produção e ativação, de modo que uma futura transição para uma escala industrial possa ser realizada.

Palavras Chaves

Ligantes Amorfos Hidráulicos Wollastoniticos, Ativação Alcalina, Cimento, Emissões de Carbono, Materiais cimentícios suplementares

Abstract

The continuous demand for essential infrastructure increases the need for Ordinary Portland Cement (OPC) production. However, OPC significantly contributes to CO_2 emissions due to the limestone decarbonation and fossil fuel combustion associated with its production. A solution proposed is a slag-based hydraulic binder with a calcium composition similar to wollastonite and a high amorphous content. This alternative has lower process-related CO_2 emissions than OPC. This thesis is a continuation of previous research and aims to understand the material reactions, refine production and application, and test the influence of using supplementary cementitious materials with the binder

The study of hydraulic reaction of this binder involves proposing a hydration mechanism based on dissolution principles and the calculation of apparent activation energy. The apparent activation energy results suggest the formation of structurally different hydration products than the primary components of OPC. Since the results indicate that a sodium silicate activator is essential to obtain competitive compressive strength at early ages, this thesis also proposes a SiO₂/Na₂O ratio optimization and a cost-effective route for activator synthesis and application. Furthermore, the aging effects due to superficial carbonation of the anhydrous binder were also assessed.

To improve production, in this thesis, a study on the increase in Al_2O_3 and MgO content in the clinker, up to 12% and 8%wt, respectively, without compromising the binder performance was achieved. The increase of these fluxing materials also allowed the decrease in process temperature from 1550°C to 1450°C.

Finally, the influence of replacing 25% of the binder with different SCMs was investigated. The results showed that the alkaline solution activated the ground granulated blast-furnace glass, resulting in synergy between the binder and the SCM.

This work aims to further understand the properties of this binder and improve its production method and activation process so that a transition to an industrial scale can be performed.

Key- words

Amorphous hydraulic binders, alkaline activation, cement, carbon emission, supplementary cementitious materials

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Contents
Abstract
A sknowledgmente
Acknowledgments
CHAPTER 1 Introduction
1 1 Problem statement
1.1 The Chemistry of the CoO-SiO-System 7
1.1.1 The Chemistry of the CaO-SiO ₂ System \dots 7
1.1.2 ACTS. Alternative Clinicer rechnologies
1.1.2.1 Delite-Rich Cliffkers
1.1.2.2 Calcium Suitoaiuminate Cements and Beile-Te einnite-Femile Cements13
1.1.2.3 The Solida Cement Approach
1.1.2.4 The Centement Approach (AWH) 17
1 1 3 Summary of the Alternative Clinker Technologies
1.1.4 Electrification of the Cement Production Process
1 1 4 1 Plasma Technology 22
1 1 4 2 Resistive Electrical Heating
1 1 4 3 Electromagnetic Heating
1.1.4.4 Induction Heating
1.1.4.5 Microwave Heating
1.1.5 Benefits and Difficulties of Electrification
1.1.6 Final Remarks
1.2 Thesis objectives and outlines27
1.3 List of publications
1.4 References
CHAPTER 2. State of the art
2.1 Production of AWH Hydraulic Binders43
2.2 Characterization of the AWH
2.2.1 Anhydrous Material44
2.2.2 Hydrated Material47
2.2.2.1 Isothermal Calorimetry47
2.2.2.2 FTIR and NMR Analysis48
2.2.2.3. HR-TEM and XRD50
2.3 Relationship between the Tobermorite and Pseudowollastonite Content and the Mechanical Performance52
2.4 Influence of Water/Solid Ratio, Granulometry, and C/S Ratio on the Mechanical Performance54

2.5 Alkaline Activation of the Binder	55
2.6 Correlation between Bound Water and Compressive Strength	59
2.7 Conclusions	62
2.8 References	64
CHAPTER 3. A model for the hydration mechanisms of an amorphous-	
wollastonitic hydraulic binder	69
3.1 Introduction	72
3.2 Experimental Procedure	76
3.2.1 Binder production	76
3.2.2 Production of pastes	76
3.2.3 Isothermal Calorimetry	77
3.2.4 Determination species solubility	77
3.2.4.1 Determination of the calcium species solubility	78
3.2.4.2 Determination of the silica species solubility	78
3.2.5 Compressive strength tests in pastes	79
3.2.6 Fourier-transform infrared spectroscopy (FTIR)	79
3.2.7 X-ray Diffraction analysis	79
3.2.8 Scanning Electron Microscopy	
3.3 Experimental Results	
3.3.1 Isothermal calorimetry	
3.3.2 Dissolution tests	
3.3.3 Compressive strength results in pastes	
3.3.4 XRD analyses	
3.3.5 FTIR analyses	
3.3.6 SEM analyses	
3.4 Discussion	92
3.5 Conclusion	
3.6 References	97
CHAPTER 4. Calculation of the apparent activation energy	
4.1 Introduction	
4.2 Experimental procedure	109
4.2.1 Binder production	109
4.2.2 Production of pastes	109
4.2.3. Isothermal Calorimetry	109
4.2.4. Production of mortars	110
4.2.5 Compressive strength tests in mortars	110
4.3 Experimental results	111
4.3.1 Isothermal Calorimetry	111
4.3.2 Compressive strength results in mortars	
4.4 Discussion	

4.5 Conclusions	119
4.6 References	120
CHAPTER 5. On the influence of storage time on the reactivity of an amount wollastonitic hydraulic binder	orphous 123
5.1. Introduction	
5.2 Experimental Procedure	
5.2.1 Binder production	
5.2.2 Isothermal calorimetry analysis	129
5.2.3 Compressive strength tests	
5.2.4 Fourier-transform infrared spectroscopy (FTIR)	129
5.2.5 X-ray photoelectron spectroscopy (XPS)	129
5.2.6 Scanning electron microscopy (SEM)	130
5.2.7 Thermal analysis	130
5.3 Experimental Results	130
5.3.1 Calorimetric results	130
5.3.2 Compressive strength results	131
5.3.3 SEM results	132
5.3.4 FTIR results	134
5.3.5 XPS results	
5.3.6 Thermal analysis	140
5.4 Discussion	141
5.5 Conclusions	144
5.6 References	145
CHAPTER 6. The use of solid sodium silicate as activator for an AWH bi	nder
6.1 Introduction	
6.2 Materials and Methods	
6.2.1 Production of the Binder	154
6.2.2 Production of the Alkaline Activator	155
6.2.3 Analysis of the Activators: Fourier Transform Infrared Spectroscop	(FTIR)
6.2.4 Analysis of the Activators: X-ray Diffraction (XRD) Analysis	157
6.2.5 Production of the Activating Solution	157
6.2.6 Production of Pastes	157
6.2.7 Isothermal Calorimetry	158
6.2.8 Production of Mortars	158
6.2.9 Thermogravimetric Analysis (TGA)	158
6.3 Experimental Results	159
6.3.1 Characterization of the Activators by FTIR	159
6.3.2. Characterization of the Activators by XRD	161

6.3.3 Isothermal Calorimetry Results	162
6.3.4 Compressive Strength Results	163
6.3.4.1 Pastes	163
6.3.4.2 Mortars	164
6.3.5. TGA	165
6.4 Discussion	167
6.5. Conclusions	169
6.6 References	170
CHAPTER 7. Influence of silica modulus on the activation of AWH binders with different alumina content: study of hydration reaction and paste performance	า 175
7.1 Introduction	178
7.2 Materials and Methods	180
7.2.1 Binder production	180
7.2.2 Production of the pastes: activation conditions	182
7.2.3 Isothermal Calorimetry	182
7.2.4 Compressive strength results in pastes	182
7.2.5 FTIR analyses	183
7.2.6 XRD analyses	183
7.2.7 Thermogravimetric analysis	183
7.3. Experimental Results	184
7.3.1 Isothermal Calorimetry	184
7.3.2 Compressive strength results in pastes	186
7.3.3 FTIR Results	188
7.3.4 XRD Results	190
7.3.5 TGA results	193
7.4 Discussion	195
7.5 Conclusion	199
7.6 References	200
CHAPTER 8. Influence of magnesium oxide content on the hydration characteristic and strength development of mortars prepared with the AWH	
binder	207
8.1 Introduction	210
8.2 Experimental Procedure	213
8.2.1 Binder production	213
8.2.2 Laser granulometry	214
8.2.3 Raman analysis of the anhydrous samples	215
8.2.4 Production of pastes	216
8.2.5 Isothermal calorimetry analysis	216
8.2.6 Fourier Transform Infrared Spectroscopy (FTIR)	217
8.2.7 X-ray Diffraction (XRD) analyzes	217

8.2.8 Production of mortars	217
8.2.9 Compressive strength tests in mortars	217
8.3 Experimental results	219
8.3.1 Raman results	219
8.3.2 Isothermal calorimetry	220
8.3.3 FTIR analysis	221
8.3.4 XRD analysis	222
8.3.5 Compressive strength results in mortars	223
8.4 Discussion	224
8.5 Conclusion	226
8.6 Reference	227
CHAPTER 9. Enhancing Sustainability of Amorphous-Wollastonitic Hydraul Binders through Incorporation of Supplementary Cementitious Materials	lic 231
9.1 Introduction	234
9.2 Experimental procedure	237
9.2.1 Binder production	237
9.2.2 Supplementary cementitious materials, chemical composition and mixt specification	ures 238
9.2.3 Laser granulometry analysis	239
9.2.4 Paste production	242
9.2.5 Mortars production	242
9.2.6 Isothermal calorimetry analysis	243
9.2.7 Compressive strength tests in pastes and mortars	243
9.2.8 X-ray Diffraction analysis	244
9.2.9 Thermogravimetric analysis	244
9.3 Experimental Results	244
9.3.1 Calorimetric results	244
9.3.2 Pastes and Mortars compressive strength tests	245
9.3.3 X-ray Diffraction analysis	248
9.3.4 TGA analysis	250
9.4 Discussion	252
9.5 Conclusion	257
9.6 Reference	258
CHAPTER 10. Conclusions and future work	265
10.1 Conclusions	267
10.2 Future Work	272
ANNEX I	273

List of Figures

Figure 2-2. (A) FTIR spectra results of AWH samples produced with a C/S ratio in a range between 0.8 and 1.25; (B) 29Si MAS NMR spectra of AWH samples produced with a C/S ratio in a range between 0.8 and 1.25. Adapted from [4]......46 Figure 2-3. Normalized heat flow (solid) and normalized cumulative heat (dotted) curves as a function of time of hydration of an AWH paste with a 0.325 water/binder ratio and a specific surface area of 5135 cm²/g, adapted from [2]. The calorimetric curve was divide divided into 3 sections: (I) initial period; (II) acceleration period; (III) deceleration period. Figure 2-4. Comparison of the anhydrous AWH FTIR spectra with a 28- and 90-day hydrated sample. The tests were performed on binders with a C/S ratio of either (A) 1.1 Figure 2-5. Comparison of the anhydrous AWH ²⁹SiMAS NMR spectra with a 28- and a 90-day hydrated sample. The tests were performed on binders with a C/S ratio of either Figure 2-6. Selected area electron diffraction of TEM observations of a hydrated AWH sample. Adapted from [23]. (A) HR-TEM image (B) experimental SAED pattern along the Figure 2-7. Comparison of Rietveld XRD analysis with a 7- and a 90-day hydrated AWH sample. P-Pseudowollastonite; T-Tobermorite; *-internal standard Al2O3. Adapted Figure 2-8. Correlation between the pseudowollastonite (PW, blue) and tobermorite (T, orange) content with the compressive strength of AWH paste at 7, 28, and 90 days of hydration. The studied binders had a C/S ratio of 1.1 (top row) or 1.25 (bottom row) were produced with a melting temperature between 1485 and 1530 °C. Adapted from [11].53 Figure 2-9. Compressive strength evolution as a function of the time of hydration for the AWH paste with (A) different w/s ratios and (B) different specific surface areas. Adapted Figure 2-10. Comparison of the compressive strength of OPC (black squares) at 7, 28, and 90 days of hydration with the compressive strength of AWH with different Ca/Si ratios. Blue dots indicate Ca/Si 1.1, and green dots represent Ca/Si 1.25. Adapted from Figure 2-11. Evolution of pseudowollastonite (PW, blue) and tobermorite (T, orange) content, as well as its respective compressive strength at 7, 28, and 90 days of hydration, for pastes produced with AWH. The studied binder was produced at 1500°C and was alkali- activated with a Na₂SiO₃ solution. Based on [9]......56 Figure 2-12. Hydration degree as a function of the curing time of type I OPC (black line), based on [40] and activated AWH binder (red line), water-hydrated AWH binder (blue Figure 2-13. (A) Normalized heat flow and (B) normalized cumulative heat curves as a function of time of the hydration of AWH samples with different amounts of Na₂SiO₃. Figure 2-14. Compressive strength evolution over time for paste samples with different Na₂SiO₃ content. Adapted from [10].....58 Figure 2-15. Plot of weight percentage of C-S-H formed versus compressive strength for

water- hydrated OPC pastes and AWH pastes hydrated with either water or Na_2SiO_3 solution. Adapted from [5,10,11] The green trend line represents the relationship between the percentage of C-S-H formed and the compressive strength of AWH pastes, while the black trend line represents the same relationship for OPC......60

Figure 3-1. Schematic representation of the dependence of the activation energy barrier required for the formation of etch pits ΔG_{crit} and vacancy islands ΔG_{crit} as function of undersaturation, based on [7]73 Figure 3-2. Schematic representation of a tobermorite-like structure, based on [15]...74 Figure 3-3. Schematic representation of the procedure used to test the calcium and silica Figure 3-4. A) Calorimetric results of pastes hydrated with, water, blue line, water+ NaOH_pH 12, black line, and water+ NaOH_pH 13, green line B) Calorimetric results of pastes hydrated with a sodium silicate (SS) solution, red line, water, blue line, and water+ Figure 3-5. Calcium concentration in function to silica concentration in solution: The tested pastes were initially hydrated using water (w/s 0.5, represented by cross characters), an alkaline solution with a pH of 12 (w/s 0.5, represented by triangle characters), and a sodium silicate solution (w/s 0.5, represented by diamond characters). Blue and red icons indicate ion concentrations before and after the exothermic peak, respectively. Circle characters represent the results obtained for a w/s paste of 0.25, hydrated with water for 3.5 years (gray circles) or with sodium silicate solution for 2.5 Figure 3-6. Calcium concentration in function to silica concentration in solution: cross character represents the results obtained for a w/s paste of 0.25, hydrated with water for 3.5 years, and diamond shape-character with sodium silicate solution for 2.5 years...85 Figure 3-7. Correlation between the pseudowollastonite (PW grey) and tobermorite (T orange) content with the compressive strength of AWH paste at 7, and 28 days of hydration, using either water (A) or a sodium silicate activator (B) as a hydrating solution. Figure 3-8. XRD spectra of the phase development of the anhydrous sample (black) with pastes hydrated with either water (blue line), or Na2SiO3 solution (red line), after 7 days of hydration (A), and 28 days of hydration (B). The "t" identifies the C-S-H phase with a Figure 3-9. FTIR spectra of the anhydrous sample (black) compared with the spectra of the paste hydrated with water (blue) and hydrated with Na2SiO3 solution (red), at Figure 3-10. SEM image of the 2.5-year cured paste and the respective EDS line analysis of the blue line. Ampliation 1350x.90 Figure 3-11. SEM image of the 2.5-year cured paste and the respective EDS line analysis Figure 3-12. Schematic representation of the initial hydration of the AWHB. A) displays the initial Ca preferential dissolution and hydrolyzation of the surface and B) the ionization of the silanol group and Si dissolution......95 Figure 4-1. Heat release (A1,B1) and accumulated heat release (A2,B2) in function of time at different temperatures, with different hydration solutions: water (A1,A2) and Figure 4-2. Heat release of a paste activated with Na₂SiO₃ and a water/solid ratio of 0.35 Figure 4-3. Graphic representation of ln(k) in function of 1/T for the temperatures 20, 25,

XV

Figure 5-1. Calorimetric test of the samples FG,7d, and 30d, hydrated with either A) Figure 5-2. Compressive strength of pastes after 7 and 28 days of curing. The pastes were made with different time-stored samples, freshly ground (without storage), 7 and 30 days, and hydrated with either water (blue circles) or with an alkaline solution (orange Figure 5-3.SEM images of the anhydrous samples A) FG sample 800x magnification B) 7d sample 800x magnification, C and D) 270d sample with a 1000x and 3000x Figure 5-4. SEM images of the alkaline activated hydrated pastes after >1 year of storage. Top row (E and F) paste made with binders stored for 7 days. Magnifications: E 3000x; F 4000x. Bottom row (G and H) paste made with an FG sample. Magnifications: E 3000x; F 4000x. Bottom row (G and H) paste made with an FG sample. Magnifications: Figure 5-5. A) Comparison of the FTIR spectra of the FG material (blue) with the 7d (brown), 30d (green) and 270d (red) samples; B) close up of the FTIR spectra. 135 Figure 5-7. A) C 1s and B) O 1s spectra subtractions: "After 7 days" = (7d – not exposed Figure 5-8. Plot of wt% CaCO₃ vs. days of exposure for the samples FG, 7d and 270d. The dashed line is just a guide for the eye and do not represent any theoretical fit... 140 Figure 5-9. Presumed O 1s peak which, when added to the 270d spectrum would produce a difference between 270d and 7d similar to the difference between 7d and FG

Figure 6-1. Lab-made activator before and after the heating process. (A) Glass based Figure 6-2. Comparison of the FTIR results of the synthesized activators with a standard, commercially available EastChem powder.....159 Figure 6-3. Comparison of the XRD results of the synthesized activators with a powder bought from EastChem. 1-Na₆Si₂O₇, 2-Na₂SiO₃, 3-CaAl₂O₄, and 4-Na₂CO₃. Q-Figure 6-4. Isothermal calorimetry results of the AWH pastes hydrated with sodium silicate activators produced with different raw materials. Activators were added either as Figure 6-5 Paste compressive strength results, activated either with the lab-made activators or with the commercial solution......163 Figure 6-6. Comparison of the compressive strength results of the mortar activated using the standard alkaline solution (grey bars) with those of the mortars activated using the Figure 6-7 Correlation between the wt. % C-S-H formed and the compressive strength, for both pastes (blue line) and mortars (orange line). The blue crosses represent the results for the 28-day hydrated pastes that underperformed in the compressive strength

Figure 7-1. Comparison of isothermal calorimetry results of the AWH pastes, varying the

Al content (Blue line 4%wt, Pink Line 7%wt, Green Line 10% Al, and Red Line 12%wt.), and the activating conditions; A- Si/Na of 1.20 B- Si/Na of 0.90, and C- Si/Na of 0.75. Figure 7-2. Compressive strength of AWH in relation to the AI content of the binder pastes after 2, 7, and 28 of hydration. The activating conditions were A- Si/Na of 1.20; Figure 7-3. FTIR spectra of the anhydrous Al4% and Al 12% samples, blue and red line respectively......189 Figure 7-4 FTIR spectra of the Al4 pastes, activated with the MS075, MS09, and MS1.2 activators, down, middle and top line respectively......190 Figure 7-5. FTIR spectra of the Al12 pastes, activated with the MS075, MS09, and MS1.2 Figure 7-6. XRD scans of the AWH binders produced with an Al₂O₃ wt% content from 4% to 12%. P – pseudowollastonite; * - Corundum, introduced as an internal standard to Figure 7-7. Quantitative results obtained by XRD-Rietveld analysis, in weight Figure 7-8. Correlation of compressive strength with the amount of C-S-H formed for the pastes hydrated with an MS075 activator (cross characters) an MS09 activator (circle characters) and an MS1.2 activator (triangle characters). The binders with an Al₂O₃ content (with an Al₂O₃ content (%wt) of 4,7, 10 and 12 are displayed in blue, purple, Figure 7-9. Hydration reaction process of a slag activated with a SS solution with a high Figure 7-10. Hydration reaction process of a slag activated with a SS solution with a low

Figure 8-1. MgO-CaO-SiO₂ ternary phase diagram with a constant content of Al₂O₃ of 10%wt, adapted from [22]. The AWH and AWH 8Mg composition are displayed as a Figure 8-2. Produced clinkers A) amorphous wollastonitic hydraulic binder AWH binder Figure 8-4. Production methods and characterization of the AWH and the AWH 8Mg Figure 8-5. Specification and analysis of the pastes and mortars produced in this study. Figure 8-6. Deconvolution of Raman spectra of the anhydrous samples A) AWH; and B) Figure 8-7. Calorimetric results of the produced pastes: A) Calorimetry results of the activated pastes prepared using either AWH or AWH_8Mg binder (blue and green line respectively) and standard water-hydrated OPC paste (black line); B) pastes with AWH 8Mg used as supplementary cementitious material in AWH pastes (blue dotted Figure 8-8 FTIR spectra of the 28 days alkaline-activated AWH and AWH_8Mg pastes Figure 8-9. 28 days activated paste XRD spectra of an AWH binder (blue line) and an AWH_8Mg binder (green line). P= pseudowollastonite; +=tobermorite; *= internal Figure 8-10. Comparative analysis of compressive strength development of mortars. The blue bars represent AWH, the green bars represent AWH_8Mg and the black bars standard OPC mortar. The striped bars, indicate the mortars that use AWH 8Mg to

Figure 9-2. Comparison of particle size distribution of the SCMs with the ground clinker. Figure 9-3. Flowchart with the origin and characterization process of the AWH binder and each of the SCM. The AWH is represented as black, and the clay, GBFS, FA and L Figure 9-4. Flowchart of paste and mortar production and respective sample Figure 9-5. Visual aspect of the 28 days cured mortar made with AWH, 25FA, 25L and Figure 9-6. Isothermal calorimetry curves of the AWH binder (black line) and of each of the mixtures made with the SCMs, Fly ash (blue curve), GGBFS (red curve), limestone Figure 9-7. Compressive strength of the pastes at the ages of 2, 7, and 28 days 246 Figure 9-8. Mortar results after of 2, 7, and 28 days, for A) compressive strength and B) Figure 9-9. Example of sample failures for the tested mortars after 28 days of curing. Figure 9-10. XRD-Rietveld analysis for the weight percentages of the phases present in Figure 9-11. Correlation between the weight percentage of C-S-H formed with the compressive strength for pastes (cross markers) and mortars (circle markers). The AWH sample and the mixtures 25L, 25CC, 25FA, 25GGBFS are depicted as black, green, Figure 9-12. Trendline analysis of the C-S-H weight percentage vs compressive strength. Mortars from the present study are depicted as full blue circle characters, while mortars from previous studied are displayed as empty black circles. Paste result from previous studies are denoted as cross black characters, where the 24L+25FA+25GGBFS pastes are shown as cross blue characters. The 25CC paste is indicated as orange cross

List of Tables

Table 1-1.Technology-related and binder characteristics of the ACTs reviewed. 26
Table 2-1. Deconvolutions results of the NMR spectra. Adapted from [4]
Table 3-1. Chemical composition of the AWH.76Table 3-2. Summary of the tests performed in this work: conditions studied, hydrationsolutions, curation time, and methodologies81Table 3-3. pH after 2 days of hydration82
Table 5-1. Composition of the AWH binder.128Table 5-2 XPS quantification for anhydrous binders with different storage time136Table 5-3. Carbon released of the FG, 7d, and 270d anhydrous samples.140
Table 6-1 Chemical composition of the AWH clinker produced wt. %.154Table 6-2. Composition of the raw material used in the production of the activator, wt.155
Table 6-3. TGA results for pastes and mortars tested at 2, 7, and 28 days, indicating LOIat specific temperature steps (250°C, 500°C, and 950°C)
Table 7-1. Chemical composition of the produced binders181Table 7-2. Nomenclature of the sodium silicate solutions used as activators182Table 7-3. Rietveld analysis of the AWH binders produced with variable Al2O3 wt%191Content from 4% to 12%191Table 7-4. TGA experimental results obtained for the studied specimens. LOI indicates191the loss in ignition at specific temperature steps. Values are shown in weight193
Table 8-1. Production Specification and chemical characteristics of the binders.213Table 8-2. Qn distribution area ratio obtained from a Gaussian deconvolution of Ramanspectra.219Table 8-3. Quantitative results obtained by XRD-Rietveld analysis for the weightpercentages of the phases present in 28- days-activated pastes.222
Table 9-1. Chemical analysis results of the AWH clinker.237Table 9-2. Chemical analysis results of the SCM.239Table 9-3. Composition and nomenclature of the produced mixtures.241Table 9-4. TGA experimental results obtained for the studied specimens. LOI indicates241Table 9-5. Compressive strength ratios obtained for the SCM mixtures at all ages,250Table 9-5. Compressive strength ratios obtained for the SCM mixtures at all ages,253Table 9-6. Trendline parameters and minimum wt.% C-S-H required for the sample to255

List of symbols and abbreviations

Cement nomenclature

А	AI_2O_3
Ċ	CO ₂
С	CaO
F	Fe_2O_3
Н	H ₂ O
Ν	Na ₂ O
S	SiO ₂
\$	SO₃

List of abbreviations

AWH	Amorphous Wollastonitic Hydraulic binder
C ₂ S	2CaO·SiO ₂ - Belite
C ₃ A	3CaO·Al ₂ O ₃ - Tricalcium aluminate
C ₃ S	3CaO·SiO ₂ - Alite
C_3S_2	3CaO-2SiO ₂ - Rankinite
СН	Ca(OH) ₂ - Portlandite
CS	CaO·SiO ₂ - Wollastonite
C-S-H	Calcium Silicate Hydrate without a well-defined stoichiometry
FTIR-ATR	Fourier Transform Infrared with Attenuated Total Reflectance
OPC	Ordinary Portland Cement
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

CHAPTER 1. Introduction

This chapter contains parts of a peer-reviewed journal:

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Contents

CHAPTER 1. Introduction	1
1.1 Problem statement	3
1.1.1 The Chemistry of the CaO-SiO ₂ System	7
1.1.2 ACTs: Alternative Clinker Technologies1	0
1.1.2.1 Belite-Rich Clinkers12	2
1.1.2.2 Calcium Sulfoaluminate Cements and Belite-Ye'elimite-Ferrite Cements1	3
1.1.2.3 The Solidia Cement Approach14	4
1.1.2.4 The Celitement Approach1	6
1.1.2.5 The C/S≈1 Amorphous Approach (AWH)1	7
1.1.3 Summary of the Alternative Clinker Technologies	8
1.1.4 Electrification of the Cement Production Process	1
1.1.4.1 Plasma Technology2	2
1.1.4.2 Resistive Electrical Heating2	2
1.1.4.3 Electromagnetic Heating23	3
1.1.4.4 Induction Heating23	3
1.1.4.5 Microwave Heating23	3
1.1.5 Benefits and Difficulties of Electrification23	3
1.1.6 Final Remarks24	4
1.2 Thesis objectives and outlines2	7
1.3 List of publications	9
1.4 References	0

1.1 Problem statement

The history of cement has had a major impact on the progress of our civilization during the last century [1]. This cheap mineral binder, when in contact with water, goes through a set of relatively complex physicochemical reactions, that result in a stone-like hard material. This allows the production of mortars, cement mixed with water and sand, and concrete, cement mixed with water, sand, and aggregates such as limestone or granite gravel [2]. Concrete is not only extremely resilient and durable but can also bear heavy compressive loads and resist severe environmental conditions. These set of properties combined allowed concrete to position as the man-made most widely used material in the world [3]. Due to the high demand for concrete, 4.3 Gigatons of cement were estimated to be produced globally during the year 2020 [4].

However, the amount of CO₂ released during the production of OPC has a very strong environmental impact. The production of one ton of clinker releases about 0.83 tons of CO₂ and the production of one ton of cement releases about 0.54 ton of CO₂ [5] making this industry responsible for 5% to 8% of total anthropogenic greenhouse gases [6] The two main sources of CO₂ emissions resulting from cement production are: (i) the decarbonation of limestone since CaCO₃ is decomposed into CaO and CO₂ at temperatures above 550°C, with this contribution representing about 60 to 65% of the total CO₂ emissions [7] and (ii) the fossil fuel combustion to heat the cement kiln, which is responsible for the remaining 35 to 40% of the emissions.

Hence, within the scope of the 2030 United Nations (UN) agenda [8] and also driven by the increasingly higher CO₂ emission taxes it has become a target and a challenge for the cement industry to develop new binders with a lower ecologic footprint, that can be produced at a large scale, so that it can be used as a commodity, without compromising the technical, economic and durability qualities characteristic of OPC. As it became clear from the 26th UN Climate Change Conference of the Parties (COP26), held in Glasgow in November 2021, managing the pressure for the unavoidable need of social development together with the agendas of environmental sustainability and climate change control will be the challenge of the century, and the cement industry itself is a relevant key player in this fundamental discussion. Until now, the methods that have been studied to mitigate CO₂ emissions in cement production follow five main approaches [9]:

- Reduction of the cement-to-clinker ratio, by replacing clinker with supplementary cementitious materials (SCM's);
- The use of alternative fuels in the production of clinker together with the increase of energy efficiency of the kiln process;
- Development of alternative clinker technologies (ACTs), that lead to lower CO₂emissions.
- Carbon capture, use and storage (CCUS), i.e., the sequestration and use of the emitted CO₂ for specific applications;
- Electrification of the clinker production process, especially if renewable electricity produced from non-fossil energy sources is used;

CCUS technologies consist of the capture, transport, use and storage of CO_2 [10]. More interestingly, a number of research projects have also explored the CCS possibility, bringing insights into the use of CO_2 for other applications, namely the production of hydrocarbons or alcohols, through the reaction of CO_2 with H₂ [11]. Yet, in general, CCUS technologies are still costly and in a demonstration stage of Technology Readiness Level (TRL) [12]. On the other hand, the cement kiln main stack flue gases have high amounts of impurities such as N₂, SOx, NOx and CO [13], which make difficult the capture and direct use of pure CO_2 . Further research and development will therefore be needed to reduce the cost of the capture step and to increase the TRL of CCUS technologies to render them an economically viable solution to be applied in the cement industry. The work of Plaza et al. [10] provides a comprehensive and interesting overview of the CCUS technologies that have been evaluated in the cement industry at the pilot scale and also the plans for further industrial implementation.

Regarding SCMs, it is worth mentioning the main conclusions of the working group initiated by the United Nations Environment Program-Sustainable Building and Climate Initiative (UNEP-SBCI) published in 2018 [14]. The group concluded that Portland-based cement approaches will dominate in the near future due to economies of scale, levels of process optimization, availability of raw materials and market confidence, but that two product-based approaches can deliver substantial additional reductions in their global CO₂ emissions, over the next 20–30 years: increasing the use of low-CO₂ additives, or supplementary cementitious materials

4

(SCMs), as partial replacements for Portland cement clinker and more efficient use of OPC clinker. Several types of SCMs may be added to cement during concrete production, including: rice husk ash, silica fume, fly ash and ground granulated blast furnace slag (GGBFS) [15]. For rice husk, the recommended replacement level is 30%, this SCM densifies the concrete matrix and reduces the volume of voids [16]. For silica fume, previous results showed that a replacement of 5% produces the best performance, with an increase of workability, strength and durability of the material [17]. Fly ash may replace up to 70% of the cement, allowing the production of so-called high-volume fly ash concrete (HVFA) [18]. Finally, GGBFS can replace up to 40% of cement without the need for a superplasticizer [19]. However, a major disadvantage of SCMs, pointed out by the (UNEP-SBCI) [14] working group, is that high blended cements may exhibit slow early-age strength development and uncertainty on the long- term durability [20]. Also, the concrete produced with OPC+SCM may present lower flowability [12], hampering the pumping, spreading, molding and compaction of the material [20]

The mix of fossil fuels commonly used to heat the cement kiln (e.g., petcoke, coal, natural gas, fuel oil, mazut, etc.) are already being replaced, to some extent, with alternative fuel such as waste tires, sewage sludge, animal meal, waste oil, waste paper, plastics, textiles, agriculture and biomass wastes, amongst other. Nevertheless, these alternative fuel solutions only represent up to 10% of the reduction of the total CO₂ emissions in cementproduction [21]. According to CEMBUREAU's Roadmap to Carbon Neutrality in 2050, altogether, the replacement of fossil fuels by non-recyclable and biomass waste, and the use of alternative raw materials, will deliver 15% of the CO₂ emissions reduction in the cement industry in 2050 [22].

A much more interesting approach in what concerns energy supply is the electrification of the process, especially if the electricity comes from low-carbon or non-fossil sources [23]. We will come to the topic of electrification at the end of this chapter due to the key importance that it may represent in the near future, particularly having in consideration the European Green Deal agenda and the ongoing green agendas in the rest of the world. Nevertheless, we must take into consideration two fundamental aspects regarding the electrification of the cement industry:

The best available technology (BAT) of OPC production cannot be easily converted into a fully electrified process, since it would require very significant changes not only in the technology itself but also in the dimensioning of the industrial installation. At least 60% of the released CO_2 comes from the decarbonation stage, while only 35 to 40% of the remaining CO_2 emissions come from the energy needed to promote the high-temperature reactions that characterize the clinkering stage. Thus, acting in the material composition stage is mandatory to achieve a significant reduction of CO_2 emissions in cement production. Therefore, at the present point, other emerging technologies or alternative materials will also play an important role in emissions mitigation in the medium/longer term.

This chapter intends to provide a critical review on this last topic: the use of alternative binders, focusing on the threats and opportunities that can be open in a long-term vision, at a moment in which the cost of CO₂/ton almost reaches the production cost of one ton of clinker.

Concerning ACTs, these approaches have to be able to generate, not only a similar economic value to that of OPC, accomplishing the necessary reduction of CO_2 emissions, but at least, present a similar competitive performance. Some of the most critical properties, which must be taken into consideration are:

- Mechanical performance, both at early ages and later ages;
- Rheological performance, enabling an adequate pumping, spreading, molding and compaction of the material [20];
- Reduced chemical shrinkage, since this phenomenon causes serious loss on the durability and bearing capacity of concrete structure, increasing the risk for cracking and decreasing the lifespan of the structures [24],
- Chemical stability, which will be translated into structure durability when submitted to the natural elements.

The fulfillment of the before mentioned requirements is the basis for the development of new alternative clinker technologies, however, any emerging technological solution should be able to compensate for the substitution of the existing OPC production BAT interms of replacement investment. This is clearly a difficult path. However, it is also clear that the actual level of CO₂ emissions related to OPC production is not compatible with the neutrality goals set by the authorities for the cement sector. Therefore, the development of new types of binders as alternatives to OPC may play a role of paramount importance in the quest for cement sector carbon neutrality. Before deepening into some of the new binders commonly presented as alternatives to OPC, we should revisit the CaO-SiO₂ system, which is the chemical base of OPC and the reason for its own success during the last century.

1.1.1 The Chemistry of the CaO-SiO₂ System

To frame the question of CO_2 emissions in the production of hydraulic binders, it is important to shortly revisit the binary CaO-SiO₂ system [25] (Figure1-1), which is the chemical base of OPC and, to some extent, the ACTs that we will discuss further on.



Figure 1-1.Detail of the CaO-SiO₂ equilibrium phase diagram (adapted from [25]).

There are two important characteristics of this system that impact the CO₂ emissions related to the production of hydraulic binders, such as OPC.

The first one is that CaO does not abundantly exist in the earth's crust and must be synthesized from limestone (CaCO₃), according to the reaction 1-1:

$$CaCO_3 \rightarrow CaO + CO_2$$
 (1-1)

Reaction (1), the decarbonation of limestone, is the cause behind the largest source of CO_2 emissions in cement production. Thus, reducing the amount of CaO in the binder results directly in a reduction of CO_2 emissions.

The second one is the hydraulic ability, or reactivity, of the phases that are present in the CaO-SiO₂ system. Besides the main oxides, CaO and SiO₂, in their different allotropic forms, there are four monophasic domains in this system: alite or $(CaO)_3SiO_2$, belite or $(CaO)_2SiO_2$, with five allotropic forms: α , α'_{H} , α'_{L} , β and γ , rankinite or $(CaO)_3(SiO_2)_2$ and wollastonite or CaO.SiO₂, which has two allotropic forms, α and β .

OPC clinkers are formed essentially by alite, with smaller proportions of belite. However, from the binary diagram above, it is evident that producing clinkers in the rankinite or wollastonite domains would result in a decrease in CO₂ emissions. It happens that only alite and belite are hydraulically active [26], with alite presenting higher reaction kinetics when compared to belite. That is, as the amount of SiO_2 increases, the hydraulic reactivity of the calcium-silicate phases decreases. The reason for that is the fact that there are significant modifications in the structure of the calciumsilicate crystalline phases as the C/S ratio decreases, from 3 (alite) to 1 (wollastonite). These changes are essentially related to the organization of the SiO_x units in the crystals, as well as to the spatial distribution of the Ca atoms in the crystal network [27]. Whereas in alite and belite polymorphs, the $[SiO_4]^{4^-}$ groups are isolated and present some degree of disorder in the superstructure, in rankinite, the Si and O atoms are arranged in sorosilicate groups $[Si_2O_7]^{6-}$, in which a central O connects with two SiO₃ units, whilst in wollastonite polymorphs, Si and O atoms are arranged in long parallel dreierkette-type chains of $\{[SiO3]^{2^{-}}\}_{n}$ units and there is an increase in the number of the bridging oxygen atoms in comparison to rankinite [27]. This structural shift among the four types of calcium silicate crystals (alite, belite, rankinite and wollastonite) can be summarized using the Qⁿ terminology, that designates how a

given silica tetrahedron is connected to another silica tetrahedron in a given crystal, as shown in Figure1-2: Q^0 (black), Q^1 (green), Q^2 (orange), Q^3 (blue) and Q^4 (yellow), depending on how many O-Si species are connected to the central silicon atom. While in the hydraulically active phases, alite and belite, the coordination is Q^0 , in the non-hydraulically active phases, rankinite and wollastonite the coordination is Q^1 and Q^2 , respectively. Experimental NMR results indicated that the Q^0 units dissolve preferentially during the hydraulic reactions, resulting in C-S-H structures, predominantly formed Q^1 and Q^2 units [28].



Figure 1-2. Coordination of different silica species in the CaO-SiO₂ system.

Alite constitutes 50–70% of OPC and, upon hydration, is responsible for the strength development up to 28 days [29]. Belite may constitute 15–30% OPC and its contribution to the compressive strength can only be seen at later ages [29]. Both alite and belite, when hydrated, form a non-stoichiometric calcium silicate hydrate phase (C-S-H) and, as a secondary product, calcium hydroxide Ca(OH)₂ or portlandite.

The C-S-H typically obtained from the hydration of alite or belite presents a C/S ratio of approximately 1.7 [30], with the excess of calcium, inevitably producing around 15–20%wt of portlandite [31]. However, the C/S ratio theoretically depends on the concentration of Si and Ca ions that are in the solution and can change from 0.8 to 2.1 [32]. Furthermore, through computational calculations, Pellenq et al. [33], reported that a binder with a C/S ratio between 1 and 1.1 would present crystalline domains characterized by improved mechanical performance.

The hydraulic reaction of OPC is an exothermic process that releases approximately 250 J/g of cement during the first 72 h of hydration [34]. This reaction starts with an induction period, characterized by an initial dissolution of species that are released into the aqueous solution. The species continue to dissolve until their concentration reaches a saturation condition, further leading to the nucleation and growth of the hydrated phases. At this point, there is an accelerating period in which occurs an extensive heat release, corresponding to the massive precipitation and growth of C-S-H and portlandite phases [35]. The precipitation and growth of these phases will result in the setting of the binder and in the increase of its mechanical strength with time. This is the basis of the alite/belite-based binders, the group to which OPC belongs.

The next section will briefly describe the binders that, although in different stages of development, have the potential to become alternatives to OPC in a perspective of CO_2 emissions reduction.

1.1.2 ACTs: Alternative Clinker Technologies

The seek for carbon neutrality in the cement industry in the medium to long term will certainly depend on the possibility of scaling-up alternative clinker technologies (ACTs) encompassing new binder formulations and also new technological processing routes. The reason for that is the fact that hydraulic binders are a commodity whose demand will increase in the next decades, namely with the economic development of large population countries in Asia, South-America and Africa [36]. Therefore, the cement industry cannot depend only on the availability of SCMs for large mass production of hydraulic binders or on the development of affordable CCS, it should pursue also the possibility of developing hydraulic binders with near to zero CO_2 emissions. This long- term goal in the cement industry can only be obtained by reducing substantially the calcium content of the binder and by combining it with processing technologies that enable the full electrification of the processes. In the next points, we will revisit the state-of-the-art in view of the possible answers to this question, having in mind that the main requirements for ACTs that can replace OPC as a widespread commodity material are:

10

- I. The capacity to mimic OPC properties, namely the production of mortar, concrete and reinforced concrete.
- II. A reduction of CO₂ emissions large enough to justify the substitution of the BAT for cement production, since this represents a widespread technology with thousands of dedicated plants all over the world.
- III. A small impact on the need for modifications of national and international standardsfor cement use.

According to some authors [14], it will be difficult to turn around these requirements in order to develop a binder completely different from OPC in a short-term period, adapting it to environmental needs. In fact, to be able to achieve a significant breakthrough in this area, a large investment in research and large-scale demonstration projects is necessary. In addition, it will also be necessary to educate and train the consumers for the acceptance of these novel binders in the construction market [12]. However, even after facing all these difficulties for a long period of time, the hope of producing cement with near-zero CO_2 emissions still remains, with a considerable number of ACTs continuously emerging. Thus, the investigation on this topic has significantly increased in the last two decades and, as a result, a number of alternative binding materials, different from OPC not only in formulation but also in their production routes and even application, have emerged and have been reported in the literature.

At the time this chapter is written, it is difficult to say which of these ACTs, if any or all of them, can become an alternative to OPC in the near future, but certainly, the need for substantial CO₂ reduction in cement production, together with the increasing demand for cement in the world, will bring this forward as a key question. The next paragraphs will be dedicated to a review of the alternative binder technologies that presently exist, with some of them being reported in the scientific literature as possible alternatives to common OPC [37]. This chapter will be focused only on ACTs, without considering activated slags and geopolymers, since we believe that this is a sufficiently broad field to justify a focused review (e.g., for a recent deep review on this topic, see Provis et al. [38]).

1.1.2.1 Belite-Rich Clinkers

Belitic binders are not a recent discovery. In fact, they have been used since the times of the Roman Empire [39]. This type of clinkers has essentially belite in its constitution and, therefore, its reaction process requires 10% less limestone, as it results from the analysis of Figure1-1. Also, the synthesis of belitic clinkers requires lower processing temperatures, compared with the alitic-based clinkers, which also translates into a reduction of the CO₂ emissions resulting from the furnace heating [39]. In addition, its lower heat of hydration [40], its better rheological properties and its improved durability at later ages, due not only to the smaller proportion of CH that is formed in the hydration but alsobecause of its densely packed structure are advantages of belitic clinkers when compared to alitic ones.

Nevertheless, belite clinkers present a low early-age strength, due to their slower hydraulic kinetics. In fact, Kotsay et al. [39], reported, that after 28 days, the degree of hydration of the belite can be four times lower compared to the alite phase and, only after one year of hardening the strength of alite and belite hydrates are comparable. There are two main reasons for the lower hydraulic reactivity of belite at early ages: one is that the H₂O molecules have more difficulty in penetrating the belite lattice, due to its densely packed structure [39], the other is that the Ca²⁺ ions attached to the SiO₄ tetrahedron are less easily dissolved [41]. Therefore, the first step of the hydraulic reaction, the dissolution step, is slower in belite, as compared with alite. It has been disclosed that the incorporation of metal oxides into the lattice of belite, as substitutes of Si, increases the hydraulic reactivity at early ages of belite-rich clinker due to a higher infiltration of H₂O molecules into the lattice, accelerating the dissolution of the material [42].

A completely different approach to belitic clinkers was proposed some years ago in which hydraulic binders with C/S = 1.4 were produced by inducing the formation of a dendritic belite phase embedded in an amorphous calcium-silicate phase [43]. These hydraulic binders were produced by a process involving heating the raw materials with a specified C/S ratio to a temperature below the liquid's surface, followed by a two-step cooling ramp, in order to obtain during solidification a dendritic morphology of the crystalline phase. After milling the clinker obtained by this process, and by adding up to 25% of water, the paste set, showing mechanical performance that went up to four times higher than the values obtained for a reference round shape belite clinker, opening the possibility of developing a novel belite-based clinker with increased reactivity.

Therefore, belitic-rich clinkers can be used in conditions when factors such as low heat release and high later age strength are important parameters, for example in high-performance concrete, or large volume structures [40]. Nevertheless, although the substitution of alite by belite may reduce CO₂ process-related emissions by up to 10%, it is still far from the goals defined for the cement industry in the global agenda for climate change.

1.1.2.2 Calcium Sulfoaluminate Cements and Belite-Ye'elimite-Ferrite Cements

Calcium sulfoaluminate cements (CSACs) are a belitic type of cement, which were developed in the 1970s [44] with the intention of compensating for the lower early-age strengths typically observed in belite-rich cements [44]. Typical raw materials used in the production of CSACs are limestone, calcium sulfate and aluminum-rich minerals or industrial by-products. Its production is carried out at temperatures around 1250°C, approximately 200°C lower than the necessary to produce OPC clinker [44], and is generally easier to grind [45].

The main clinker phases in CSACs are ye'elimite, $Ca_4(AlO_2)_6SO_4$, belite and calcium sulfate $CaSO_4$ [44]. Since ye'elimite rapidly hydrates, it compensates for the loss in early-age strength in belitic clinkers [46]. As ye'elimite dissolves it enables the reaction with calcium sulfate and water and allows the formation of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$ 26H₂O) and microcrystalline aluminum hydroxide $Al(OH)_2$ [45]. Ye'elimite contains about 50%wt. of Al_2O_3 thus, the required alumina content in the raw materials to produce CSACs is above 20%, which can come from sources such as bauxite or industrial by-products, such as the ones proposed in the work by Canbek et al., namely red mud and sulfate-rich/high-lime fly ash [46]. However, the availability of low-cost sources of alumina-rich raw materials is certainly a limitation for the generalized use of CSACs [46].

Cement with high ye'elimite contents (>50%wt) can be used in combination with OPC to produce a fast-setting, rapid hardening cement [45]. CSACs cements with less ye'elimite (25–50% wt) contain significant amounts of belite (30–50%wt) and ferrite (5–20%wt) and can be a sustainable replacement material for OPC [45]. When compared to OPC, in some areas, the use of CSACs has been shown to have better performance when applied to concrete. They present lower shrinkage, lower cracking and higher resistance to freeze-thawdamage [45].

Another alternative to the CSACs is belite-ye'elimite-ferrite cement (BYFC), which presents a lower cost than CSACs, achieved by reducing the use of the most expensive aluminum-rich raw materials, resulting in a higher proportion of silicate and ferrite phases [47]. The ferrite phase, 4CaO AI_2O_3 Fe₂O₃ has a slower hydration process than Ca₄(AIO₂)₆SO₄, therefore, ye'elimite, anhydrite and gypsum are the first phases to react, followed by ferrite and belite [48] Since the hydration of ye'elimite is faster than that observed for belite, the increase of compressive strength is similar to OPC [49].

Both CSACs and BYFCs can be produced in common clinker plants, essentially by changing the raw materials that are used to feed the kiln [47]. This is a major advantage in terms of investment cost since it would allow the production of both types of material within the same facilities without the need for substantial process modifications. However, both CSACs and BYFCs present susceptibility to the carbonation process, caused by the dissolution of the atmospheric CO_2 into the pore paste. This reacts with the hydrated products causing an increasing CO_3^{2-} ion concentration. The formation of this anion has severe consequences facilitating the deterioration of ettringite [45], and raising the acidity of the system leading to the corrosion of steel rebar, used to reinforce concrete [44].

1.1.2.3 The Solidia Cement Approach

Solidia Cement patented in 2016 [50], is a non-hydraulic binder produced using the same raw materials as OPC, but with a lower amount of $CaCO_3$ and a kiln temperature around 1200°C, which allows a reduction of the CO_2 emissions by 30% [50,51]. This binder has an overall C/S molar ratio of ~1 and it is formed essentially by wollastonite/pseudowollastonite, with smaller amounts of rankinite (13%wt), and belite (~3%wt) [52]. This mixture of calcium silicate phases has the ability to harden by a carbonation process and, consequently, there is no need for water consumption for the reaction to occur [51].

This cement is produced by feeding the granulated raw material into a natural gasfired rotary kiln. The calcium silicate compositions created in the rotary kiln emerge in a "clinker" form, that is, in small granules with diameters of approximately 1 to 4 mm. The clinker is then ground to a powder with a mean particle size of approximately 12 μ m.

To produce concrete, this material is mixed with aggregates, sand and water. The

cure of the concrete takes place when the mixture is exposed to a high-concentration gaseous CO_2 environment (60–90%) [53] which allows the reaction of the binder phases and the production of CaCO₃ and SiO₂.

One of the most interesting characteristics of this binder is precisely the fact that the curing process can capture up to 300 kg of CO₂, per ton of binder [51] and is only limited by the ability of gaseous CO₂ to diffuse throughout the particles [51]. To speed up the curing process heat may be applied, these temperatures, if needed, can even be higher than 60 °C since there is no formation of ettringite [53]. The CaCO₃ that is formed fills the pore space within the concrete, creating a dense microstructure and, the SiO₂ is formed at the outer surface of the reacting cement particle [51].

Although Solidia Cement does not hydrate, water plays an important role in its forming and curing mechanism. Water contributes to the good flowability of the material and also acts as a permeating agent contributing to the cure development that occurs through a counter diffusion process where water molecules are replaced by CO₂ molecules [53]. However, since the water is not consumed, 90% of it can be recovered, while the remaining is retained in the cured concrete [52]. The mechanical properties of the concrete are equivalent to those of OPC, and they are achieved within a shorter curing period [52]. Another characteristic of this binder is that the carbonation process only releases about 87 kJ/mol of heat during curing which is dissipated through the evaporation process of the water that is used in the concrete preparation [53].

Even though this is a promising cement, its application and use are limited, since its curing process must be conducted under very controlled CO_2 concentration conditions, which, so far, can only be provided in a ready-mixed concrete plant [12] impairing to some extent the generalized use of Solidia cement as a substitute of OPC.
1.1.2.4 The Celitement Approach

Celitement[®] is a patented hydraulic binder, developed by the Karlsruhe Institute of Technology (KIT) in collaboration with the SCHWENK Zement KG industry [54]. Its concept is to synthesize and stabilize a short-time precursor of C-S-H to produce a hydraulic binder [55]. This material is characterized by its low energy demand during its production process, which enables a reduction in CO₂ emissions [55]. The Celitement[®] production relies on the formation of an intermediate phase that is prior to the development of the C-S-H. This intermediate phase has a similar structure to C-S-H, but a slightly different chemical composition and is referred to as hydraulic Calcium Hydro Silicate (hCHS) [56].

The production method of Celitement, uses CaO as raw material, in the simplest case, or Ca(OH)₂ and quartz sand [57]. It requires a calcination stage (around 1000°C) that is applied only to the CaCO₃-rich raw-material, and hydrothermal processing of the raw mix that takes place in an autoclave at a temperature of 200°C and at a saturated steam pressure of 12 bar, which facilitates the full electrification of the process. The product that results from the autoclave is stabilized by a strong hydrogen bond which makes it non-hydraulically active [55]. In a second step, this product goes through a special grinding operation [55] that enables the destruction of the hydrogen bonds [57] and, around the cores of the non-reactive co-milled silicates, a new amorphous calcium hydrosilicate (hCHS) is produced [55–57]. The final produced material is mainly amorphous, with highly disordered phases and high specific surface, containing in its composition Q⁰ and Q¹ silicate species [57,58]. After 17–20 h of hCHS hydration, a well-ordered C-S-H phase is formed, releasing a very low heat of hydration (120–150 J/g) and promoting an early-age strength comparable to OPC [55].

The Celitement[®] approach is based on a technology that completely differs from the one known today for the production of Portland cement, leading to what may be a significant drawback in its industrial implementation. Nevertheless, this new technology is already under the demonstration phase, with a recent expansion to the pilot plant, constructed in 2011, allowing the production of approximately 700 kg per day [59].

1.1.2.5 The C/S≈1 Amorphous Approach (AWH)

Another alternative, developed and patented internationally by CIMPOR and Técnico-Lisbon, is an amorphous wollastonitic hydraulic (AWH) binder characterized by a raw mix containing 33% less CaCO₃ than the typical OPC, and an overall C/S ratio of 1, allowing for a reduction of more than 25% of the usual OPC clinker process-related CO₂ emissions [60,61]. The production process of this binder allows the use of traditional raw materials, such as limestone, clay, marl, sand, etc., and consists in fully melting the raw mixture, at a temperature of 1550°C, followed by a rapid cooling [59]. The resultant product is mostly amorphous (~94% wt), with the presence of a small amount (<10%) of pseudo-wollastonite [60]. It should be pointed out that the full melting of the mixture may facilitate the electrification of the process through plasma or electrical arc melting, which may lead to a scenario where the effluent gas stream is solely fed by the CO₂ generated by the calcination of the raw meal. Such a highly concentrated CO₂ gas stream could potentially be combined with green H₂ to produce methanol and other hydrocarbons [62,63].

The reactivity of this novel binder comes, mostly, from its amorphous phase, yet even though existing in a small amount, the presence of pseudo-wollastonite has been shown to have some influence on the hydrated product performance [64]. Better compressive strength results were obtained when this phase was produced in an amount of ~6% wt [64]. An investigation on the hydration of this binder observed, by ²⁹SiMAS-NMR spectroscopy, that the least coordinated Qⁿ units, Q⁰ and Q¹, play a very important role in the hydration since they appear to be very prone to polymerize and convert into C-S-H structures that are similar to tobermorite [60]. By changing the structure from crystalline to amorphous, the arrangements of Si–O bonds become more disordered, which favors their dissolution [60] and, consequently, the further formation of equilibrium hydration products [65].

The behavior of this novel amorphous binder was further studied by Santos et al. [28], which investigated the effect of different alkaline activators (Na₂CO₃ and a mixture of NaOH and Na₂SiO₃) on the mechanical strength and structural characteristics of hydrated pastes. It was observed that, when activated, those pastes presented increased hydration kinetics, allowing for an improvement in their mechanical performances. Furthermore, the most competitive results were obtained when the pastes were activated with Na₂SiO₃, with a 3 wt% total content of Na₂O, obtaining pastes with strengths comparable with those of traditional OPC [28].

17

In terms of technological development, this approach presents as main drawbacks: the need for a pyro-processing step that is 100°C superior to that of OPC and, the requirement of a sodium silicate solution for activation, in order to present competitive early-age strength.

In addition, since the processing conditions require the formation of 100% liquid phase, some adaptations to the usual BAT of clinker production may be required in order to industrially implement this type of technology.

1.1.3 Summary of the Alternative Clinker Technologies

Figure 1-3 shows a simplified flow chart containing the stages considered for the production of the alternative binders mentioned in the present review, evidencing the differences of the process in the various ACTs approaches. From Figure1-3, it becomes clear that in the present state, research should be pursued in all the presented solutions. From the several technological proposals contained in Figure1-3, it should be noted that only the Celitement[®] and the AWH binder approaches presently consider a scenario of full process electrification, while the other approaches essentially follow a fuel combustion-based design, similar to the existing BAT. The proximity to the BAT for clinker production is certainly an advantage for the industrial implementation of some of the alternative binders mentioned above. However, when looking forward through a perspective of cement industry decarbonization, full or partial conversion of the existing fuel-based technology to electricity-based technology may be required, especially in the first stages of low-temperature decarbonation processes.



*The grinding stage is considered to be similar in all the cases presented **Mortar and concrete curing should be performed under controlled conditions

Figure 1-3. Simplified schematic representation of the stages considered within the production processes of the alternative binders reviewed

Figure 1-4 shows a detailed description of the various sources of CO_2 emissions within the production processes considered for the ACTs reviewed, evidencing the separation of the contributions for the thermal and material-related emissions. The CSA, AWH and Celitement[®] approaches lead to material-related CO_2 emissions smaller than 0.35 tons per ton of clinker. If full electrification of the process for these ACTs with green electricity is achieved, a target for CO_2 emission in cement production smaller than 0.25 tons of CO_2 per ton of cement is within reach of the cement industry in the upcoming years.



Figure 1-4. CO₂ contributions for the energy- and material-related emissions of the various alternative binders reviewed.

NOTE: (*) indicates the technologies that already consider a fully electrified production process and therefore, depending on the nature of the electricity used, the thermal component of CO₂ emissions can be completely eliminated.

1.1.4 Electrification of the Cement Production Process

Certainly, the reduction in the ecological footprint in the cement industry encompasses the substitution of fossil fuel in the cement kiln for electrification in the heating process. In fact, as the cost of solar photovoltaics, wind power and battery storage decreases, the coupling of industry electrification with renewable electricity supply has become a potential solution for industrial decarbonization [66]. In particular, the electrification of the cement production has become a more feasible alternative to the current method of combustion, and unlike gas furnaces, electric furnaces have very low direct emissions of CO₂, NOx and SOx, however electric furnaces may have shorter lifetime periods than conventional furnaces [67]. According to the work of Madeddu et al. [68], the cement industry has the potential for 36% electrification, which essentially considers the calcination of limestone, whilst the energy necessary for clinker burning is not considered electrifiable at this stage of technology development. However, in the 2018 report of the CemZero project [69], it is referred that the production of cement clinker by means of plasma technology appears to be technically possible. This CemZero project is being conducted in Sweden, as a collaboration between Cementa and Vattenfall, and aims to test different technologies for the total or partial electrification of the cement production process.

Their study indicated that the production costs of cement in an electrified process appear to be doubled in comparison to today's technology but could be competitive compared to other technological options for radical emission reductions [70].

Another project that points to an electrically powered calcination process is the LEILAC, which is being developed by a large consortium of companies and foresees to implement a fully operational plant by 2023 [71]. This project assesses, through a direct separation perspective, the feasibility of CO_2 capture and storage, by means of the generation of a highly concentrated CO_2 gas stream from the calcination stage.

Within these important development is the electrochemical approach that converts $CaCO_3$ in $Ca(OH)_2$ and may represent a real alternative solution to overcome the CO_2 emissions from the decarbonation process in cement industry. This technology is able to capture excess power and, through electrolysis, convert limestone into hydrated lime, working similarly to a battery. This process was already tested at the laboratory scale, and they reported that a future implementation on a larger scale could allow for a decentralized, automated, easy to deploy, easy to start-up and shut down cement

plant [72]. Processes of combining calcination and CO_2 capture by using electricity were also reviewed recently by Tokheim et al. in a conference paper [73]. Due to the critical importance of the topic of electrification in the framework of ACTs a short review of these processes is presented in the following points.

1.1.4.1 Plasma Technology

This technology can produce temperatures above $2000^{\circ}C$ and is currently used as waste treatment and in some niches in the steel industry [74]. Its implementation in the cement industry may open the possibility of using recycled CO₂ as plasma gas [75], which further benefits the goal of CO₂-free cement industry. The main disadvantage of using thermal plasma is the overheating of the reaction media [76], which can impair the clinker performance by changing the phases present at room temperature, and also the short lifetime of the electrodes. As referred above, the use of plasma was one of the technologies that CemZero tested on a laboratory scale, being reported that it is possible to produce cement clinker of regular quality by using plasma gas as a heat source. Nevertheless, a larger-scale test must be performed, since one concern with the use of this technology ishow to maintain the rate of heat transfer in a rotary kiln [69].

1.1.4.2 Resistive Electrical Heating

In this approach, a metal surface is heated by running a current through a resistive element, which usually is protected by a shroud. Then, the heat can be transferred either by gas, through high-velocity convection, or directly to the material, through radiation or conduction, if it is possible to promote the direct contact between the raw meal and combination with another heating method, acting as a boost in gas-fired furnaces [77], or as a complete replacement of the traditional heating method, providing a completely electrified production [78,79]. Typically, electric glass furnaces use a vertical melting process [80]. The furnace is continuously fed at the top side and the melted material leaves the furnace through the bottom. The heating provided by running a high current into molybdenum electrodes [80] whose configuration arrangement influences the homogenization capacity of the mixture [81]. Jebava et al. [81] reported that by distributing the electrode into a longitudinal central row, there is an optimization on the utilization of space and the highest melting performance. These types of furnaces (82].

1.1.4.3 Electromagnetic Heating

By using electromagnetic waves, the electromagnetic heating technologies are able to provide high temperatures, with an efficiency of up to 90% [82]. Furthermore, it has the advantage of being able to generate rapid heat within a target material [82]. Some examples of these technologies include:

1.1.4.4 Induction Heating

Induction heating occurs when an electrically conducting object is placed in a varying magnetic field. The friction between molecules when the material is magnetized first in one direction, and then in the other is converted into heat [83]. To cool the induction furnace, water-cooled coils are used. This technology allows almost instantaneous heating or cooling of the calciner. However, there is a risk of overheating the product when the heat necessary for the calcination is inferior to the heat provided by the induction system [84]. This type of technology is able to reach high temperatures fast and is currently applied in induction furnaces used for metal melting [85]. However, it is not currently seen as a potential solution for processing ceramic materials [82].

1.1.4.5 Microwave Heating

The heat necessary for calcination can be delivered by microwave through a radiation form, by transferring direct energy in the form of electromagnetic waves into the material. Corrêa et al. [86], investigated the use of a microwave oven in the calcination process reaching a temperature of 1160 °C. The team reported that this method provides better results in terms of reaction time, energy consumption and emission of polluting gases when compared with traditional methods. Furthermore, the use of a refractory ceramic coated with copper oxide reduced the energy expenditure and accelerated the process to be twice as fast. Microwave heating is currently used in the conversion of biomass and by-products and also, in waste processing, although mostly at the laboratory scale [87]. Even though this technology is able to provide a rapid internal heating of large volumes, large production scales presents high operation costs, which presently hinder its use in a generalized form [82].

1.1.5 Benefits and Difficulties of Electrification

It has to be taken into consideration that the electrification of any industry is highly influenced by energy and environmental policies [74]. Not only, can the electrification cost be challenging, but also the electricity prices must be competitive. Moreover, industry electrification only reduces greenhouse gas emissions if renewable-generation capacity is added to meet its electricity demand. Nevertheless, in the current conditions of climate change, a complete shift from an oil and gas economy to a green energy source has been associated with the future of energy [88]. In fact, the global renewable energy generation capacity has progressively been increasing, and it is estimated that by 2050, more than 80% of electricity will come from renewable sources [89]. Currently, in the EU-27, renewable sources already make 34% of electricity consumption, with the majority coming from wind and hydropower and a small part from solid biofuels and solar power [90]. Hence, as the prices of renewable electricity and electric equipment continue to drop [66,91], the electrification of the cement industry can be an important option to achieve a high reduction CO_2 emissions.

1.1.6 Final Remarks

To be able to seek neutrality in the cement industry, the current method of cement production must change. There are many potential routes to lower CO₂ emissions, and some are more prone to succeed than others. This chapter reviewed and discussed a variety of alternative clinker technologies for the partial or complete substitution of OPC. The performance of these materials is largely dependent on their physical and chemical characteristics, which have a major influence on its curing process and, consequently, on the binder's mechanical performance. In some of the cases, further studies for a complete characterization of materials properties are needed.

Nevertheless, the goal of CO₂ neutrality in the cement industry can only be reached through an extended replacement of OPC by green alternative binders, as well as through a transition from fossil fuel technology to a green energy-based technology.

The CO₂ process-related emissions, assuming that the main calcium source is limestone, are shown for different ACTs, and very significant differences among these materials can be observed. It should be noted that, if one considers that limestone is the source of Ca in the clinker, this is an absolute limit. As it can be observed, the production of alite or belite-based clinkers will always result in CO₂ emissions above 500 kg/ton of clinker, while the CSA, BYF and Solidia[®] cements allow a reduction of the CO₂ process-related emissions below 400 kg/ton, keeping the same clinker production technology. Still, below the 400 kgCO₂/ton of clinker, it is possible to find the alternatives AWH binder and Celitement[®], with both technologies being based on fully electrified processes. Concerning "wollastonitic" clinkers, two radically different approaches exist: the Solidia Cement approach, in which the setting of near-wollastonite phase specimens is achieved via carbonation, and the AWH binder approach, in which instead of a crystalline structure, the reactivity with water is achieved through the amorphization of the material

The direct emission of CO_2 arising from materials decarbonation is an important factor but not the only one. In fact, the CO_2 emissions arising from the firing process also play an important role in clinker production, which in the case of alite-, belite- and aluminatebased clinkers represent about 40% of the total CO_2 emissions. In this way, the possibility of process electrification is also a key factor in what concerns the reduction of CO_2 emissions in clinker production since this CO_2 contribution could drop to zero if nonfossil sources are used for electric energy production. Under this scenario, the lower limit for the total CO_2 emission would be defined by the own chemistry of each binder, as a result of the calcination of its raw materials.

Table 1-1 presents a summary of the potential impact of each ACT regarding energyand process-related CO₂ emissions, as well as some important characteristics of the alternative technologies and binders. In this table, it was considered that the Celitement[®] clinkers are prone to electrification since they do not need a rotary kiln or considerably high temperature, which facilitates the implementation of resistive electrical or microwave heating. Likewise, the AWH binder procedure does not implement a rotary and, even though there is the needfor high temperatures, there is also a complete melting, which makes the overheating of the reaction media less problematic in the production of clinker. Therefore, processes such as plasma heating or electrical arc are viable. All the other clinkers need a controlled high temperature and a rotary kiln, which makes the implementation of an electrification process challenging

	Technology-Related Characteristics					Binder Characteristics		
Clinker	Process- Related CO ₂ (kg/ton)	Energy-Related CO ₂ (kg/ton)	Total CO ₂ (kg/tonne)	High Abundance of Raw Materials	Electrification Feasibility	Heat of Hydration (J/g)	Early and Late Age Strength	Curing Can Be Performed in Non- Controlled Conditions
OPC clinker	535 [92]	270 [92]	805	Yes	Challenging	250–350 [34]	Both competitive	Yes
Belite-rich clinker	512 [14]	251 [47],[92]	763	Yes	Challenging	175–250 [93]	Long-time strength is competitive [39]	Yes
Calcium sulfoaluminate (CSA) clinker	305 [92]	245 [92]	550	No	Challenging	130 [94]	Both competitive [45]	Yes
Belite-ye'elimite-ferrite (BYF) clinker	362 [14]	208 [95]	570	No	Challenging	523 [96]	Only competitive at early ages [97]	Yes
Celitement [®] clinker	231 [56]	252 [56]	May go from 231 to 483	Yes *	Accessible	120–150 [55]	Both competitive [55]	No
Solidia [®] clinker (crystalline CS)	375 [52]	190 [52]	565	Yes	Challenging	150 [53]	Both competitive [52]	No
X-Clinker (amorphous CS)	340 [98]	247 [92,98]	May go from 340 to 587	Yes	Accessible	125 [28]	Both competitive ** [28]	Yes **

Table 1-1.Technology-related and binder characteristics of the ACTs reviewed.

* Even though the main raw material of Celitement[®] are lime and quartz, their use was conducted under laboratory conditions, with high purity raw materials [56,57]. ** Tests performed on pastes showed that the strength of the AWH binder, compared with OPC, is competitive at all ages [27]. However, tests performed on mortars showed that, for the AWH to be competitive at early ages (2 days), a cure at temperatures around 35 °C may be required [99].

1.2 Thesis objectives and outlines

The main goal of this thesis is to advance the development of an amorphous wollastonitic hydraulic binder (AWH) and evaluate its application in both pastes and mortars. Initially, the mechanical strength was only tested in the paste with a $20 \times 20 \times 40$ mm³ dimension. Subsequently, as binder production became more accessible, tests on mortars were also performed, according to the EN 196-1 norm [100]. By the end of the thesis, it was possible to perform a standardized test with five mortars per age in order to reinforce the robustness of the experimental data. These results are shown in **Annex I**.

Summarizing the main objectives of this work are as follows:

1- Investigate the hydration reaction of the binder and study the importance of an alkaline activation

2- Assess the impact of exposing the anhydrous material to atmospheric conditions.

3- Optimize clinker content and production, which includes reducing the maximum production temperature and broadening the range of Al_2O_3 and MgO content that can be used in the raw materials.

4-Optimize the sodium silicate activator, including the synthesis route and final application

5- Assess the viability of using SCM with the binder.

This thesis is organized into ten chapters. **Chapter 1** consists of an introduction to this work and is divided into three parts: a contextualization of the problems and proposed solutions regarding CO_2 emissions in the cement industry, a description of the thesis's main objectives, and a list of publications and communications resulting from this work. In **Chapter 2**, state of the art on the latest research on the AWH production physico-chemical and mechanical characteristics is reviewed.

Both **Chapter 3** and **Chapter 4** focus on the hydration reaction of the binder. Specifically, in **Chapter 3**, a model for the mechanism responsible for the formation of C-S-H is proposed based on solubility and calorimetric tests, and the importance of using a sodium silicate activator is discussed. In **Chapter 4**, the temperature influence on the compressive strength of mortars at early ages is studied, and the apparent activation energy of the hydration reaction is calculated. This parameter was determined using

experimental results and applying two different approaches.

In **Chapter 5**, the consequences of exposing the anhydrous binder to atmospheric conditions were investigated. The properties of different time-stored samples were compared to non-exposed binders, specifically the surface of the anhydrous grains and hydraulic reactivity with either water or a sodium silicate solution.

Due to the importance of the sodium silicate activator, in **Chapter 6** the synthesis and application of three lab-made Na₂SiO₃ powders were assessed. The powders were made using low-cost raw materials, and the synthesized product was confirmed by FTIR and XRD. Each powder was used to activate the AWH binder, either as a solid or predissolved into a solution. Finally, compressive strength tests were performed in pastes and mortars, and the results were compared to a standard activated sample.

In **Chapter 7** and **Chapter 8**, the influence of the raw material composition on the performance of the binder was investigated. **Chapter 7** focuses on the increase of AI_2O_3 content in the clinker from the typical ~1%wt to up to 12%wt. This change in composition would allow a 100°C decrease in the maximum process temperature. The hydration of each sample was followed by calorimetry, and the pastes underwent a compressive strength test. In this chapter, an optimization of the activating solution was investigated, in order to promote a more controlled kinetic and overall higher performance, regardless of the AI_2O_3 content in the clinker a decrease. Similarly, in **Chapter 8**, the possibility of increasing the MgO content in the clinker from the typical ~1%wt to 8%wt was investigated, specifically, the influence on reactivity and mortar performance. Furthermore, the binder with higher MgO content was also used as an SCM in both AWH and OPC-based mortars.

Chapter 9 focuses on the use of SCM as a partial AWH binder replacement in both pastes and mortars. Four types of SCM were used to replace 25% of the binder: fly ash, lime, calcinated clay, and ground granulated blast-furnace slag. The hydration reaction of each mixture was followed by calorimetry, and the compressive strength was tested in mortars.

In the final chapter, **Chapter 10**, an overall discussion of the main results is presented, focusing on the conclusions of the experimental chapters (from 3 to 9), specifically main achievements and contributions to the development and understanding of the AWH binder. Finally, suggestions for future work are proposed, aiming to enhance the research in this material

1.3 List of publications

All presented works and papers, focused on the properties of an eco-sustainable, hydraulically active, amorphous binder developed by a joint effort of IST and CIMPOR characterized by .an overall C/S ratio of 1.1. Overall, seven papers were published/submitted in peer-reviewed journals and two oral communications, and two posters were presented at national or international conferences.

Papers

- Antunes, M.; Santos, R.L.; Pereira, J.; Horta, R.B.; Paradiso, P.; Colaço, R. The Apparent Activation Energy of a Novel Low-Calcium Silicate Hydraulic Binder. Materials 2021, 14, 5347. https://doi.org/10.3390/ma14185347
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- Antunes, M.; Santos, R.L.; Horta, R.B and Colaço, R Novel Amorphous-Wollastonitic Low-Calcium Hydraulic Binders: A State-of-the-Art Review. Materials 2023, 16, 4874. https://doi.org/10.3390/ma16134874
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- Antunes, M.; Santos, R.L.; Horta, R.B and Colaço, R., Enhancing Sustainability of Amorphous-Wollastonitic Hydraulic Binders through Incorporation of Supplementary Cementitious Materials. Accepted in Case Studies in Construction Materials 2024
- Antunes, M.; Santos, R.L.; Horta, R.B and Colaço, R. Influence of silica modulus on the activation of Amorphous Wollastonitic Hydraulic binders with different alumina content: study of hydration reaction and paste performance. Materials, 2024, 17, 3200 doi:10.3390/ma17133200
- Antunes, M.; Santos, R.L, Ferraria A. M, Botelho de Rego A.M, Pereira J., Horta, R.B and Colaço, R. On the influence of storage time on the reactivity of an amorphous wollastonitic hydraulic binder Submitted in Journal of the American Ceramic Society, 2024

Oral communications

- Antunes, M.; Santos, R.L.; Horta, R.B.; Paradiso, P. Colaço, R. Synthesis of sodium silicate powders to be used as activators in an amorphous low-calcium binder TEST&E2022 3rd conference on Testing and Experimentation in Civil Engineering Oral presentation June 2022 FCT Nova de Lisboa
- Antunes, M.; Santos, R.L.; Horta, R.B.; Paradiso, P. Colaço, R. The apparent activation energy of a novel low-calcium silicate hydraulic binder FIB Symposium; Oral presentation June 2021, Lisbon Portugal, online format

Paper communication

- Antunes, M.; Santos, R.L.; Horta, R.B.; Paradiso, P. Colaço, R. Chemical shrinkage of novel low-calcium hydraulic binders International Union of Laboratories and Experts in Construction Materials, Systems, and Structures; Rilem 74th edition Poster September 2019, Sheffield UK.
- Antunes, M.; Santos, R.L.; Horta, R.B.; Colaço, R. Addition of Supplementary Cementitious Materials (SCMs) on low calcium hydraulic binders: contribute to the carbon neutrality of the cement industry. PhD open days, Poster November 2022 Instituto Superior Técnico Lisboa

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CHAPTER 2. State of the art

This chapter contains parts of a peer-reviewed journal:

Antunes, M.; Santos, R.L.; Horta, R.B and Colaço, R Novel Amorphous-Wollastonitic Low-Calcium Hydraulic Binders: A State-of-the-Art Review. Materials **2023**, 16, 4874. https://doi.org/10.3390/ma16134874

Contents

CHAPTER 2. State of the art	41
2.1 Production of AWH Hydraulic Binders	43
2.2 Characterization of the AWH	44
2.2.1 Anhydrous Material	44
2.2.2 Hydrated Material	47
2.2.2.1 Isothermal Calorimetry	47
2.2.2.2 FTIR and NMR Analysis	48
2.2.2.3. HR-TEM and XRD	50
2.3 Relationship between the Tobermorite and Pseudowollastonite Content and the Mechanical Performance	e 52
2.4 Influence of Water/Solid Ratio, Granulometry, and C/S Ratio on the Mechanica Performance	l 54
2.5 Alkaline Activation of the Binder	55
2.6 Correlation between Bonded Water and Compressive Strength	59
2.7 Conclusions	62
2.8 References	64

Due to the severe environmental impact of the CO₂ emissions associated with the production of ordinary Portland cement (OPC) and the increasing demand for this commodity material, the development of alternative products has become a global concern. One alternative to OPC, or alitic-based clinkers, are amorphous-wollastonitic hydraulic binders (AWHs). This material, described in the literature for the first time in 2015, may significantly reduce the CO_2 emissions associated with its production, resulting from its lower calcium content, but also from the fact that its production technology can be fully electrified. Several studies have been conducted to characterize the properties and hydraulic activity of AWHs. The chemical composition and microstructure of AWHs and their respective hydration products were determined using X-ray fluorescence (XRF), nuclear magnetic resonance (NMR), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and high-resolution transmission electron microscopy (HR-TEM) [1-4]. The hydration of the binder with water was characterized by measuring the compressive strength of pastes at various ages [2,5-7] and its chemical reaction was followed using isothermal calorimetry and computational work [8]. More recent works explored the impact of an alkaline activation [9,10]. Therefore, in this chapter a state-of-the-art review concerning the production, characterization, and optimization of AWHs, as well as perspectives for future developments, is presented.

2.1 Production of AWH Hydraulic Binders

The first studies on AWH binder focused on the influence of the following properties: C/S ratio [4,11], melting temperature [3,4,6,11], and quenching method [2]. In all of these studies, the production process was carried out in small quantities, less than 450g, and under laboratory conditions, following a three-step procedure [5].

I. Heating the raw mixture at a rate $R1 = 25 \circ C/min$ to reach the required melting temperature (T1);

II. Maintaining temperature (T1) in the liquid region for a period of t1 = 60 min to allow for the homogenization of the composition;

III. Cooling the system to room temperature.

For the production of larger batches, an intermediate step between (I) and (II) was implemented by keeping the mixture at 900°C for 1 h [10]. This implementation was required to allow an efficient decarbonation of the mixture and to avoid gas accumulation in the batch [10]. After quenching, a material with a density of 2.94 0.5 g/cm³ [4] was

obtained. Finally, the obtained product was ground in a ring mill with propanol followed by a drying step at 50 \circ C for 1 h [10]. Figure 2-1 depicts a schematic representation of the production process.



Figure 2-1. Schematic representation of the production process.

2.2 Characterization of the AWH

2.2.1 Anhydrous Material

- Figure 2-2 shows the FTIR and NMR analyses of samples of AWH, with the C/S ratios ranging from 0.8 to 1.25 (taken from [4]). An FTIR analysis of AWH binders shows five main regions:
 - 400 to 500 cm^{-1;}
 - 600 to 750 cm⁻¹
 - 780 to 850 cm⁻¹
 - 870 to 900 cm⁻¹;
 - 900 to 1200 cm⁻¹;

The peak identified as **a**, located at approximately 450–490 cm⁻¹, can be attributed to Si-O-Si bending [12], and was similar in all samples. The bands at **b** are caused by the tetrahedral Si-O-Si vibration of amorphous silica [13], and they increased as the C/S ratio increased, indicating the presence of Q^1 and Q^0 structures in the sample [5]. The peak at **c** can be attributed to an isolated tetrahedra's nonbridging Si-O stretching mode [13] The bands *d* and *e* are related to the stretching vibrations of nonbridging Si-O bonds, indicating the presence of Q^2 and Q^3 units [5,13]. The shoulder at *e* was more prominent in samples with a lower C/S ratio, indicating the formation of a more structured sample.

The deconvolutions spectra and results of the ²⁹Si MAS NMR are shown in Figure 2-2, and Table 1, respectively. It can be observed that contrarily to what occurs with wollastonite, which is essentially formed by Q^2 structures [14]. AWH is formed by the dispersion of Q^n connectivity, with a prevalence of Q^1 units with a dispersion of Q^0 , Q^2 , and Q^3 . It can be observed that as the C/S increased from 0.8 to 1.1, there was an increase in the proportion of Q^0 units, and then the Q^0 proportion decreased again. Hence, with the increase in the Ca content from 0.8 to 1.1, there was increasing depolymerization of the silicate chains [4].



Figure 2-2. (A) FTIR spectra results of AWH samples produced with a C/S ratio in a range between 0.8 and 1.25; (B) ²⁹Si MAS NMR spectra of AWH samples produced with a C/S ratio in a range between 0.8 and 1.25. Adapted from [4].

C/S ratio Q ⁿ Area (%)	0.8	1	1.1	1.25
Q ⁰	18.05	18.44	28.08	21.51
Q ¹	26.83	37.49	40.24	50.13
Q ²	34.73	30.41	27.62	26.80
Q ³	20.39	13.65	4.06	2.55

Table 2-1. Deconvolutions results of the NMR spectra. Adapted from [4]

2.2.2 Hydrated Material

2.2.2.1 Isothermal Calorimetry

Since understanding the kinetics of the hydration reaction is crucial for evaluating the binder's compressive strength, isothermal calorimetry measurements were used to track the hydration evolution of the material.

Figure 2-3 illustrates the three regions that can be observed in AWH calorimetric experiments:

I. A first stage of the hydration, characterized by slow reaction kinetics, also observed in OPC, is usually attributed to species ionic dissolution [15]

II. An acceleration period characterized by a high rate of heat release [16,17]. In OPC, this stage is usually attributed to the precipitation of C-S-H products and portlandite. Since in AWH there is no precipitation of portlandite, this second stage should correspond to the formation of C-S-H and, most probably, to the formation of tobermorite, which is present in the hydrated product [18], as we will see in the following points;

III. A deceleration period in which the rate of the reaction decreases, probably due to the inability of C-S-H to keep forming on the surface of the grains. In this period, a gradual densification of the microstructure occurs, as described for OPC [17,19].



Figure 2-3. Normalized heat flow (solid) and normalized cumulative heat (dotted) curves as a function of time of hydration of an AWH paste with a 0.325 water/binder ratio and a specific surface area of 5135 cm²/g, adapted from [2]. The calorimetric curve was divided into 3 sections: (I) initial period; (II) acceleration period; (III) deceleration period.

The activation energy (Ea) of AWH pastes was calculated using the Arrhenius equation and calorimetric results in a range of temperatures from 20 to 35°C [18]. The experiment procedure and a detailed discussion of these results can be found in Chapter IV. The main findings of this study showed that the AWH had an experimental Ea in the 82–85 kJ/mol range[18], which is almost 50% higher than the Ea of alitic and belitic clinkers (51 and 55 kJ/mol [19,20]. This higher activation energy of the AWH material compared to conventional clinkers was attributed to the formation of structurally different hydration products, with a higher C-S-H mean chain length, low C/S ratio, and higher crystallinity [5].

2.2.2.2 FTIR and NMR Analysis

Santos et al. [5] performed FTIR and NMR analyses on anhydrous samples and compared them with 28- and 90-day water-hydrated pastes to assess the structural development upon hydration. Both binders were melted at 1550 °C and had a C/S ratio of either 1 or 1.25. Figure 2-4 and Figure 2-5 depict the FTIR and NMR spectra, respectively. Upon hydration, the FTIR spectra of both samples (C/S of 1.1 and 1.25) revealed the development of a narrow band centered at 445 cm⁻¹, indicating the formation of a more organized structure and a similarity between the hydration products [5]. All hydrated samples exhibited features at ~670 cm⁻¹ and ~960 cm⁻¹. The first peak is characteristic of the Si–O–Si bending mode related to C-S-H gels with a low C/S ratio [5] and the peak at 960 cm⁻¹ to the stretching vibrations of the Q² tetrahedra [21]. In the range of 1400 to 1500 cm⁻¹, the presence of an asymmetric stretching of CO₃²⁻ is shown [22]. Finally, at 1640 cm⁻¹ and 2800 to 3600 cm⁻¹, two broad features can be assigned to the H–O–H bending vibration of molecular water and the stretching vibrations of O–H [22].



Figure 2-4. Comparison of the anhydrous AWH FTIR spectra with a 28- and 90-day hydrated sample. The tests were performed on binders with a C/S ratio of either (A) 1.1 or (B) 1.25. Adapted from [5].



Figure 2-5. Comparison of the anhydrous AWH ²⁹SiMAS NMR spectra with a 28- and a 90-day hydrated sample. The tests were performed on binders with a C/S ratio of either (A) 1.1 or (B) 1.25. Adapted from [5].

The evolution of the normalized ²⁹Si MAS NMR spectra reveals that as the hydration progressed, the resonances moved to more negative chemical shifts, indicating an increase in the degree of polymerization achieved by the rearrangement of the least coordinated Q^n units (Q^0 and Q^1) [5]. Furthermore, the authors reported that the well-defined peaks of the hydrated sample at 79 and 85 ppm indicate the formation of a C-S-H structure, because these peaks are characteristic of end-chain Q^1 groups (79 ppm) and middle-chain Q^2 groups (85 ppm) with nonbridging Si-O-Si linkages. The presence of the Q^2 component increases with age, reaching ~75% after 90 days of hydration, while Q^0 groups disappear after this time of hydration [5].

2.2.2.3. HR-TEM and XRD

Paradiso et al. [23] performed selected area electron diffraction in HR-TEM observations of the hydrated product. It was observed that the C-S-H that formed upon hydration presented well-ordered nanocrystals with dimensions of the order of 10–20 nm and whose diffraction pattern is compatible with 9Å tobermorite (Figure2-6). The presence of C-S-H and the tobermorite phase were also confirmed with Rietveld XRD analysis, which also showed that the proportion of 9Å tobermorite increased with the hydration time (Figure2-7).



Figure 2-6. Selected area electron diffraction of TEM observations of a hydrated AWH sample. Adapted from [23]. (A) HR-TEM image (B) experimental SAED pattern along the [123] zone axis.



Figure 2-7. Comparison of Rietveld XRD analysis with a 7- and a 90-day hydrated AWH sample. P—Pseudowollastonite; T—Tobermorite; *—internal standard Al2O3. Adapted from [23].

Computational simulation studies have previously shown that a low C/S ratio promotes a C-S-H with a more well-ordered lamellar structure that enhances the mechanical stiffness and hardness of the material [24]. The HR-TEM and Rietveld observations by Paradiso et al. show that within the binding phase of C-S-H, densely packed tobermorite 9Å nanocrystals formed in the AWHs. Tobermorite is a layered structure composed of stacked Ca-O layers supported by silica tetrahedra, arranged according to the Dreierketten rule [25]. Depending on the degree of hydration, tobermorite can be categorized into three types, with a basal spacing of 9Å, 11Å, and 14Å [24]. The presence of tobermorite has also been documented during the hydration process of OPC [26]. Previous studies proposed mechanistic pathways for its formation, including the formation of amorphous and semi- crystalline C-S-H, followed by the growth of semicrystalline tobermorite and, finally, the recrystallization of solid tobermorite [27]. The growth of this structure is facilitated by a mixture of heterogeneous nucleation and internal restructuring [28]. The ultra-confined interlayer of water within the tobermorite molecular structure influences the uniaxial tensile and compressive response of the structure [28,29]. In the case of the AWHs, the observed tobermorite 9Å presented layers that were slightly inclined in the axial direction, and the structure did not contain any water molecules within its interlayer spaces. Previous studies reported that the tilting of the tetrahedra in the silicate chains and the shortening of the axial Ca-O distances allow
for better dissipation of energy under compression, thereby improving the mechanical resistance of the material [29].

2.3 Relationship between the Tobermorite and Pseudowollastonite Content and the Mechanical Performance

Different melting temperatures were used to produce AWH clinkers with different pseudowollastonite proportions [6,11]. Pseudowollastonite is a polymorphous wollastonite consisting of isolated trisilicate ring structures in which the calcium cation is ionically linked to oxygen atoms [30] this crystal has a pseudohexagonal structure, whereas wollastonite has a triclinic crystal structure [31]. Wollastonite, which is characterized by its high thermal stability, low thermal expansion, and low thermal conductivity, has a chain structure and a density of 1.75 g/cm³ [32]. With an increase in temperature, wollastonite undergoes a reaction to form pseudowollastonite at 1125 °C [31]; this crystallization can be observed up to 1250 °C, increasing the density of the material to 1.98 g/cm³ [32]. The use of the pseudowollastonite phase has already been studied on low-calcium binders because of its carbonation capabilities, yielding CaCO₃ and SiO₂ as reaction products [33–36]. Plattenberger et al. [37] even proposed that the exposure of this phase to aqueous CO₂ results in the formation of both CaCO₃ and calcium silicate phases, which have been shown to be the more stable phases under low pH conditions.

The samples tested in [6,11] were hydrated with water using a water/solid (w/s) ratio of 0.375 and submitted to microstructural and mechanical characterization [11]. Figure 8 resumes the obtained results. The results indicate that at early ages the compressive strength is more or less independent of the initial content of pseudowollastonite. However, at later ages (28 and 90 days), the samples with an initial pseudowollastonite content between 3.5% and 7.6% show better mechanical performance. In particular, samples with 7.6% pseudowollastonite show a significant evolution of the compressive strength, increasing from 8.5 MPa at 7 days to 34.5 MPa at 90 days. A decrease in the initial pseudowollastonite content and an increase in the tobermorite content for up to 90 days of curing time were also observed.

Therefore, this set of experiences shows that a higher pseudowollastonite content can be obtained by a lower melting temperature due to the equilibrium obtained in the liquid phase with the pseudowollastonite + liquid region of the CaO-SiO₂ phase diagram, and the presence of small amounts of pseudowollastonite (up to 7.6%) in the AWH may be beneficial in terms of mechanical performance. During hydration, the proportion of

52

pseudowollastonite decreases, which may be a consequence of its carbonation process and at later ages could improve the compressive strength of the sample. Finally, it was possible to observe the presence of crystalline tobermorite during hydration, with its content increasing, at least, until 90 days of hydration.



Figure 2-8. Correlation between the pseudowollastonite (PW, blue) and tobermorite (T, orange) content with the compressive strength of AWH paste at 7, 28, and 90 days of hydration. The studied binders had a C/S ratio of 1.1 (top row) or 1.25 (bottom row) were produced with a melting temperature between 1485 and 1530 °C. Adapted from [11].

2.4 Influence of Water/Solid Ratio, Granulometry, and C/S Ratio on the Mechanical Performance

The influence of the water/solid (w/s) ratio and the granulometry on the mechanical behavior is shown in Figure 2-9 [2]. It can be observed that both the w/s ratio and the particle fineness affect the strength of AWH pastes, and the increase in the w/s ratio from 0.325 to 0.425 results in a significant decrease in the compressive strength of the material (Figure 2-9A). Furthermore, increasing its specific surface from 3242 to 5135 cm2/g results in a significant increase in the compressive strength. Nevertheless, Mendes et al. [10] reported that the effect of the particle fineness begins to fade at later ages (90 days) for binders with higher amorphous contents.



Figure 2-9. Compressive strength evolution as a function of the time of hydration for the AWH paste with (A) different w/s ratios and (B) different specific surface areas. Adapted from [2]

The compressive strength of the paste is influenced by both the specific surface area and the w/s ratio. These two conditions impact the exposed area of the particle and the distance between the binder particles, influencing the reactivity of the sample. When the specific surface area is high, indicating a larger exposed area, and the w/s ratio is low, indicating a shorter distance between particles [38,39] the conditions favor a higher reactivity of the sample. This increased reactivity promotes the production of more hydration products, specifically calcium silicate hydrate (C-S-H), resulting in higher compressive strength. The Influence of the C/S ratio on the compressive strength of AWH pastes was analyzed in [5]. The results are shown in Figure 2-10, using OPC pastes as reference material. It was observed that the samples with a C/S ratio of 1.1 had better mechanical performances than the samples with a C/S ratio of 1.25.



Figure 2-10. Comparison of the compressive strength of OPC (black squares) at 7, 28, and 90 days of hydration with the compressive strength of AWH with different Ca/Si ratios. Blue dots indicate Ca/Si 1.1, and green dots represent Ca/Si 1.25. Adapted from [5].

2.5 Alkaline Activation of the Binder

The use of alkaline activation to improve the compressive strength and performance of AWH with a C/S ratio of ~1.1 was studied by Santos et al. [9] and Mendes et al. [10]. The alkaline activators studied were Na₂CO₃, Na₂SO₄, CaSO₄, and a mixture of Na₂SiO₃ and NaOH. The main observation of these works was that the AWH activated with Na₂SiO₃ solution presented, by far, better performances. When Na₂SiO₃ solution is used as an activator, the mechanical strength of AWH can overcome that of OPC. In this way, in this review, we refer only to activation with Na₂SiO₃.

Santos et al.[9] tested the compressive strength after 7, 28, and 90 days of hydration of pastes with a w/s of 0.375 activated with Na_2SiO_3 . The compressive strength together with the evolution of the respective pseudowollastonite and tobermorite contents are shown in Figure 2-11. By comparing these results with those in Figure 8, for water hydrated pastes, it can be observed that the activation of the AWH with Na_2SiO_3 promotes an increase in the compressive strength of up to 300%. Furthermore, the

results indicate that the formation of tobermorite is related to the development of the mechanical properties of the pastes [1].

Since the degree of hydration (α) quantifies the extent of hydration of a binder over time, the experimental data from [18] (Chapter IV) was used to calculate the degree of hydration between water-hydrated AWH and Na₂SiO₃-activated AWH. Using the methodology proposed by Poole et al. [40], this parameter was calculated by obtaining the ratio of heat at each hydration time, H(t), over the total amount of heat available, Hmax, $\alpha = H(t)/Hmax$. The results were compared with a typical type I OPC, as shown in Figure 2-12. The results in Figure 2-12 indicate that when the AWH binder was hydrated with water, the degree of hydration remained below 0.1 for the first 100 h. However, by activating the material with Na₂SiO₃, a considerable increase in the degree of hydration of C-S-H/tobermorite structures, particularly at earlier ages, as observed using HR-TEM and XRD-Rietveld (Figure 2-6 and Figure 2-7).



Figure 2-11. Evolution of pseudowollastonite (PW, blue) and tobermorite (T, orange) content, as well as its respective compressive strength at 7, 28, and 90 days of hydration, for pastes produced with AWH. The studied binder was produced at 1500 °C and was alkali- activated with a Na₂SiO₃ solution. Based on [9].



Figure 2-12. Hydration degree as a function of the curing time of type I OPC (black line), based on [40] and activated AWH binder (red line), water-hydrated AWH binder (blue line).

To reduce the amount of Na₂SiO₃ and optimize the Na₂O content in the hydrating solution, Mendes et al. [10] used a Na₂O and Si/Na modulus of 1.2, followed by a successive reduction of 25% wt. of Na₂SiO₃ until a combination of just NaOH and water was reached (0% of Na₂SiO₃). The activation properties of each mixture were studied with calorimetry and compressive strength tests on pastes with a w/s ratio of 0.25. The calorimetric results and the compressive strength of each studied condition are shown in Figure 2-13 and Figure 2-14, respectively. The isothermal calorimetry analysis obtained by the authors showed a delay in the maximum hydration peak with the increase of Na₂SiO₃ on the activator. However, the increase of the Na₂SiO₃ content also promoted a more controlled kinetic after the peak; consequently, these samples released more heat after 7 days of hydration. As a result, after 7 days of hydration, the amount of heat released with the increase in Na₂SiO₃ concentration. The compressive strength results on pastes activated with the studied solutions showed that the samples with a higher heat released originated higher compressive strength results at later ages.



Figure 2-13. (A) Normalized heat flow and (B) normalized cumulative heat curves as a function of hydration time of AWH samples with different amounts of Na₂SiO₃. Adapted from [10].



Figure 2-14. Compressive strength evolution over time for paste samples with different Na_2SiO_3 content. Adapted from [10]

2.6 Correlation between Bound Water and Compressive Strength

Thermogravimetric analysis was used to calculate the amount of bond water (BW) on the hydrated phases by measuring the weight loss of each sample in the temperature range of 110 \circ C to 500 \circ C [5,10,11]. Considering that the strength development of the samples is directly related to their hydration process, it is possible to correlate the compressive strength with the chemical BW content. Furthermore, assuming the model of Richardson and Qomi [26], a relationship between the bound water and the amount of C-S-H can be established, as displayed in equation (2-1):

$$\frac{H_2 O}{Si} = \frac{19\frac{Ca}{Si} - 7}{17}$$
(2-1)

Using these data, it is possible to compare the percentage of C-S-H on the sample with its compressive strength, as shown in Figure 2- 15. It can be observed that AWHs require a lower amount of C-S-H to obtain compressive strength values similar to OPC. This may be due to the presence of hydration products with a lower C/S ratio, which allows the formation of a C-S-H structure with better mechanical properties [24]. Moreover, the linear correlation between C-S-H formed and the respective compressive strength on all experimental pastes, hydrated with water or with an alkaline solution, suggests that the resulting hydration product is similar in all cases.



Figure 2-15. Plot of weight percentage of C-S-H formed versus compressive strength for water- hydrated OPC pastes and AWH pastes hydrated with either water or Na_2SiO_3 solution. Adapted from [5,10,11] The green trend line represents the relationship between the percentage of C-S-H formed and the compressive strength of AWH pastes, while the black trend line represents the same relationship for OPC.

Finally, Table 2 summarizes the main characteristics of the AWH binders compared with OPC. Other physicochemical characteristics of AWHs compared with alite, α -belite, rankinite, α -wollastonite, mayenite, krotite, grossite, and gehlenite are presented and discussed in detail in Freitas et al.[14]

Table 2-2. Comparative summary of the main features of the AWH binder with OP	Ċ
[4,10,18,24,41]	

	OPC	AWH
Production Method	The raw mix is fed into a kiln and fired to a temperature of 1400– 1450ºC	Melting at ~1500°C of the mixture followed by a fast quenching
Process-Related CO ₂ (kg/ton)	535	340
The density of the material (g/cm ³)	3.1	2.94±0.05
Main phases of the binder	Alite (50-70%) Belite (15-30%) aluminum and aluminum ferritic phase (<20%)	Amorphous (90%) Pseudowollastonite (< 18%)
Activation Energy (kJ/mol)	51-55	82-85
Cumulative Heat after 72h (J/g)	250	53 when activated with Na ₂ SiO ₃ solution with 1.8%wt Na ₂ O content
Hydration products	C-S-H and portlandite	C-S-H and tobermorite 9A
C/S ratio of C-S-H	1.7	1.1
Paste compressive strength 2 days (MPa)	33	11 when activated with Na ₂ SiO ₃ solution with 1.8%wt Na ₂ O content
Paste compressive strength 28 days (MPa)	65	63 when activated with Na ₂ SiO ₃ solution with 1.8%wt Na ₂ O content

2.7 Conclusions

The development, optimization, and use of low-calcium amorphous hydraulic binders with C/S 1 as an alternative to Portland cement-based materials aiming to reduce the carbon footprint associated with its production have made relevant progress since 2015. In summary, the main achievements are as follows:

(a) To obtain a binder with good mechanical performance, the raw materials used in the reviewed studies, should be heated to at least 1500°C, and the quenching should be performed preferentially in water;

(b) With the increase in the calcium content of the raw material, with C/S between 0.8 and 1.25, an increase in the Q⁰ structures was observed, reaching a maximum value at a C/S ratio of 1.1. Moreover, pastes prepared with this ratio showed an increase in compressive strength;

(c) The tests performed on the hydrated product revealed that the only products formed during the hydration of this AWH were an amorphous C-S-H with a C/S ratio of 1.1, and a crystalline tobermorite 9 Å phase. Furthermore, no portlandite was identified;

(d) With the increase in hydration time, a reduction in pseudowollastonite and an increase in tobermorite were observed. On water-hydrated pastes, the optimum content of pseudowollastonite on the anhydrous binder was ~7.6%;

(e) The degree of hydration of the AWHs binder was established and compared with type I OPC, and the results show that even though the hydration rate of the binder was lower than that of OPC, by activating the material a significant enhancement in the degree of hydration was observed, suggesting a potential improvement in its performance;

(f) Competitive strength on pastes was only obtained when the binder was hydrated with a Na_2SiO_3 solution with at least 1.8 $Na_2O\%$ wt. content. When activated, the pseudowollastonite content does not seem to be relevant to the performance of the binder. An important parameter observed was that the AWH binder exhibited a much lower heat release than traditional type I OPCs, even when activated;

(g) Finally, a correlation between bound water and the formation of C-S-H chains with compressive strength was established by different authors.

62

In this chapter, the studies performed for the production and characterization of AWH binders were reviewed. The main results showed that unlike OPC, which predominantly contains crystalline phases (e.g., alite and belite), AWH binder has an amorphous structure that allows for its chemical hydration. When hydrated with the proper alkaline activator the hydration product exhibits a compressive strength that can overcome those of OPC. In addition, the reduction of the calcium content in the AWH binders leads to a significant decrease in CO₂ emissions associated with its production process. However, to fully understand the potential of AWH binders, further investigations are necessary. The production of the material on larger scales, as well as its testing in mortars and concrete, are crucial to evaluate its performance under real-world conditions.

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To be submitted to peer review journal

Contents

69
80
81
81
83
85
86
87

In this chapter, a model for the hydration mechanism of an amorphous-wollastonitic hydraulic binder (AWH) is proposed. The binder was hydrated with water, water+ NaOH, and sodium silicate+ NaOH (SS) solution. The hydration process was monitored by calorimetry, and the concentration of calcium and silica in solution was measured by titration and photometry, respectively. The resulting hydrated product was analyzed by X-ray diffraction Rietveld analysis (XRD), Fourier-transformed infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The calorimetric results indicate that the reaction of the AWH binder has a high sensitivity to the pH of the solution. When water hydrated, the system displays slow kinetics with a long induction period, while the hydration with an alkaline solution significantly increases the reactions kinetics. The addition of a sodium silicate activator resulted in a short induction period, and a higher heat released. Moreover, the results and the literature review suggest that the species dissolution influences the kinetics of the reaction, and depending on the hydrating condition, saturation or undersaturation environment may be promoted, leading to different types of dissolutions.

3.1 Introduction

To enhance the production, performance, and sustainability of a binder material, it is fundamental to understand the mechanism responsible for its setting and hardening. In the case of Ordinary Portland Cement, the globally recognized standard binding material [1–3], although the precise reaction mechanisms are not yet fully understood, it is widely accepted that the hardening is essentially the result of the hydration reaction with water [1] involving processes from the dissolution/dissociation of molecular species to their saturation and precipitation [1,4–9], that allow the formation of hydrated mineral phases that bind together the mixture. Based on OPC heat of hydration measurement it is possible to divide the reaction process into four main stages [7,8], the initial period, the induction period, the acceleration period, and the deceleration period [4,7].

The hydration mechanism starts with the initial period, which involves the wetting of the hydraulically active phases and is characterized by a significant heat release [9]. This is followed by a rapid deceleration, leading to the induction period [6,7,9]. During this stage, the reaction rate slows down, with ionic species gradually dissolving from the anhydrous phase [6]. Juilland et al [7] categorized the dissolution process into three main regimes depending on the undersaturation of the system, (I) step retreat, (II) etch pit opening, and (III) vacancy islands [7]. In the initial phase, there is a high undersaturation in the system and a low activation energy [7], resulting in a fast dissolution and the formation of etch pits on plain surfaces, forming vacancy islands (regime III). As the dissolution continues and the undersaturation decreases, etch pits can only be formed at the surface of crystallographic defects on the particle surface (regime II) [7]. As the system approaches equilibrium and the dissolution becomes slower, the activation necessary increases, restricting the process to step retreat at pre-existing steps (regime I) [7]. Figure 3-1 displays the dependence of the activation energy barrier required for the formation of etch pits and vacancy islands as a function of undersaturation. In this figure the three dissolution regimes are also schematized.



Figure 3-1. Schematic representation of the dependence of the activation energy barrier required for the formation of etch pits ΔG_{crit} and vacancy islands ΔG_{crit}^n as function of undersaturation, based on [7]

At the end of the induction period, when ions in the solution reach a critical concentration, a hydration product with lower solubility than the initial precursor precipitates [6]. This stage is called the acceleration period and is known for having a high heat release [6]. The primary hydration product is calcium silicate hydrate (C-S-H), crucial for the setting and hardening of the material [6]. Depending on the C/S ratio in the solution, the presence of additional minor phases can also be observed [10–12]. For C/S ratios in the 0.6 and 0.8 range, the thermodynamic model predicts the presence of amorphous silica, while for higher ratios, C/S of 1.6, portlandite precipitates [10–12].

The C-S-H is mainly amorphous with varying stoichiometry depending on the C/S ratio and water content [1,13,14]. This hydration product can be described using a defect tobermorite structure, composed of calcium oxide layers in between silicate chains [1,14], as represented in Figure 3-2, based on [15]. The silica tetrahedra are organized in sets of three, with a "dreierketten" arrangement. Two tetrahedra share the O-O edges with the Ca in the calcium layer [14], while the third is the bridging site that links the other two units and is oriented to the interlayer. The higher the organization level of the structure the higher the presence of bridging tetrahedra [14]. Between the layers of the CaO sheets and silicate chains an interlayer composed of water, Ca²⁺, and alkali ions, such as Na⁺ and K⁺, is present [12,14]. According to Gartner et al [15], the initial C-S-H formed is a metastable anhydrous basal sheet that has a negative charge localized in the silicate groups, promoted by the deprotonation of the silanol group at high pH [12,15], This negative charge is then balanced by the adsorption of calcium cations with at least six water oxygens in the inner ligand sphere, hence, allowing the rapid growth of C-S-H. [15].



Figure 3-2. Schematic representation of a tobermorite-like structure, based on [15].

The acceleration period is followed by a deceleration period, in which the progress of the reaction is slow and limited, due to the reduction of available surface area and free water. This phase mainly consists of the densification of the microstructure [16].

Given the high CO₂ emissions related to OPC production [17], alternative such as the alkaline activation of ground-granulated blast furnace slag have been studied [18–21]. Similarly, to OPC, slag hydration also exhibits an induction period followed by an acceleration peak that reflects the formation of a hydration product [22–24]. However, the calorimetric response depends on the nature and concentration of the alkaline activator [12,25] and the composition of the initial precursor [19,26,27]. The alkaline activator influences the pH of the system and consequently the calcium and silica solubility, since higher pH increases silica dissolution [28] but decreases calcium solubility [29]. Furthermore, the basicity of the solution also influences the negativity of the silicate chains, with higher pHs promoting the deprotonation of the silanol group and

increasing the negative charge [12]. To compensate for the negative charge, calcium cations are preferred over monovalent cations. However, compared to higher C/S ratio systems, in systems with a low C/S ratio, alkalis, such as sodium, start to compete with the calcium ions. This results in a higher incorporation of alkali groups in the hydration product structure [12].

In this chapter, the hydraulic reaction of an amorphous slag-like binder with a C/S~1 is investigated. This binder has a Ca/Si ratio of ~1, corresponding approximately to the chemical composition in which wollastonite crystallizes in equilibrium conditions, but is processed in a way that promotes the formation of an amorphous phase upon cooling. The resultant product is mostly amorphous, with the presence of a small amount of pseudowollastonite [30]. This material, an amorphous-wollastonitic low calcium-silicate (AWH), is hydraulically active [31] and, after activation, can reach strengths similar to or higher than those of OPC [32]. However, many aspects of its behavior, starting with the hydration mechanisms, remain poorly understood, being however known that in these systems there is an absence of Ca(OH)₂ in its hydration products and the formation of nanocrystalline 9Å tobermorite, and of an amorphous C-S-H, with a stoichiometry closer to $C_{1,1}SH_n$ than from the standard $C_{1,7}SH_n$. [31,33,34]. Furthermore, conversely, to the main OPC phases, alite and belite, which contain only Q⁰ silicate units, the quenching process required for the formation of the AWHs leads to a wide distribution in Qⁿ silicate connectivity [34] resulting in a lower availability of Q⁰ units and complicating silica dissolution. Therefore, in this work the evolution of the hydration process was monitored by calorimetry, and the concentration of species in the solution was measured before and after the hydration peak. To obtain further insights into the performance of the binder and its hydration process, compressive strength tests were performed on water-hydrated and sodium silicate-activated pastes after 7 and 28 days of hydration. Furthermore, Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction Rietveld analysis (XRD) were performed on each paste to provide information about the chemical and mineralogical changes that occur during the hydration process.

3.2 Experimental Procedure

3.2.1 Binder production

Common raw-cement materials used in the production of Portland cement clinker, but with a lower overall C/S molar ratio of 1.04 were used in the production of the binder. The raw materials were ground, mixed, and compressed. The compressed disc was broken into four pieces and placed in a silicon carbide crucible. The filled silicon carbide crucible was placed in an electric furnace and heated, at a rate of 25°C/min, to 900 °C, maintaining this temperature for 1 hour, to ensure the full decarbonation of the raw meal. Then, the furnace temperature was raised to 1550°C and kept for 1h to guarantee the complete melting of the powder mix and its chemical homogenization. Finally, the material was quenched by pouring the molten mixture into a water container, resulting in an amorphous content above 97%. The amorphous hydraulic binder produced was then ground with a ring mill for 3 minutes, obtaining a final blaine fineness between 5500 and 6500 cm²/g. Wavelength dispersive x-ray fluorescence (WD-XRF) analysis, was made on the material fused beads, prepared by an Eagon 2 from PANalytical (Axios cement, United Kingdom). The chemical composition is shown in Table 3-1.

Table 3-1. Chemical composition of the AWH.

	SiO ₂	CaO	AI_2O_3	Fe ₂ O ₃	MgO	K ₂ O	Other metallic oxides
Wt%	49.6	46.6	2.32	0.73	0.35	0.34	< 0.02

3.2.2 Production of pastes

The paste preparation involved two different water-to-solid (w/s) ratios: 0.5 for solubility tests, and 0.25 for compressive strength tests. The AWH binder was hydrated with 4 different hydrating solutions, namely: distilled water (W); a sodium hydroxide solution with a pH of 12 (NaOH_12), a sodium hydroxide solution with a pH of 13 (NaOH_13) (both made with NaOH pellets , \geq 99 % Prolab, Canada), and a sodium silicate solution with a 1.2 silica modulus and a NaO concentration of 2%wt (SS). This sodium silicate solution was made by incorporating NaOH pellets into a Na₂SiO₃ solution.

3.2.3 Isothermal Calorimetry

Isothermal calorimetry tests were performed on a TAM Air instrument (Waters Sverige AB, Sollentuna, Sweden), and were run at a constant temperature of 20°C. Pastes prepared with the AWH binder and hydrated with a w/s ratio of 0.5 were inserted into vials *ex-situ*, therefore, the first exothermic peak, characteristic of the wetting of the amorphous binder is not displayed.

3.2.4 Determination species solubility

The calcium and silica content were analyzed in two types of samples.

In the first type, solubility tests were performed on samples with hydration periods, between eight hours and four days. For this experiment, the binder was hydrated using a w/s ratio of 0.5, and the samples were stirred magnetically during the entire procedure. Three different solutions were tested: water, water + NaOH (final pH of 12), and sodium silicate (SS) solution with 2%wt of Na₂O.

For the second type, the solubility was analyzed on pastes cured for a period longer than 2.5 years. The samples were prepared using a w/s ratio of 0.25 by hydrating the binder with either water or an SS solution containing 2%wt of Na₂O. The pastes were then molded into inox steel molds with 20×20×40 mm³ dimensions and cured at 20 °C under relative humidity (HR) conditions above HR95%. After two days, the pastes were removed from the molds and left to cure under the same conditions. The water-hydrated sample was stored for 3.5 years, and the SS-hydrated sample for 2.5 years. Then, compressive strength tests were performed, and the resulting debris was manually ground and dried at 100°C for one hour. The dried powder was mixed with distilled deionized water using a water/powder ratio of 0.5 and stirred for a 48-hour period.

Finally, all solutions were filtered with the help of a vacuum pump and diluted with distilled deionized water. A schematic representation of the procedure is presented in Figure 3-3.



Figure 3-3. Schematic representation of the procedure used to test the calcium and silica solubility.

3.2.4.1 Determination of the calcium species solubility

The determination of the Ca²⁺ concentration was performed by titration with an EDTA solution (0.03 mol/L). The titration procedure was made with the help of a photometer (662 Photometer Metrohm Switzerland) with a wavelength of 620 nm.

3.2.4.2 Determination of the silica species solubility

In the presence of water, the siloxane bonds are hydrolyzed and proceed to give a watersoluble species, a monosilic acid as represented in reaction (1) [35]

$$SiO_2 + 2H_2O \leftrightarrow Si(OH)_4$$
 (1)

Since Si(OH)₄ is able to react with acidified ammonium molybdate solution to form yellow molybdosilicic acid, the determination of Si(OH)₄ can be performed using a photometry technique. In this work the expression soluble silica represents the monosilicic acid determined using the photometry method as described below.

The determination of silica concentration in the solution was performed by photometry using a wavelength of 400nm. First, a calibration curve was made with 4 standard solutions with different silica concentrations: 0g/L, 0.005g/L, 0.015g/L, and 0.030g/L, to each sample a buffer solution of sodium acetate with a pH of 4.2 and an ammonium molybdate solution (30g /L) was added. The absorbance of the standard solution was measured by photometry and a calibration curve that relates absorbance with silica concentration 3-1.

Abs=a+b×C [3-1]

Similarly, the unknown silica concentration solutions were prepared by mixing a known amount of the experimental sample with the buffer solution of sodium acetate (pH 4.2) and the ammonium solution (30g /L). The absorbance of the sample was then measured and using expression [3-1], the Si concentration calculated.

3.2.5 Compressive strength tests in pastes

The compressive strength tests of the paste prisms with dimensions of 20x20x40 mm³ were performed at 7and 28 days of hydration in an Ibertest Autotest 400/10 instrument using a constant force rate of 2.4 kN/s during the test. The material resultant from the compressive strength test was then characterized by FTIR and XRD, being this material ground by hand and then dried at 105°C to ensure that all the unbound water was removed.

3.2.6 Fourier-transform infrared spectroscopy (FTIR)

After the compressive strength test at 7 and 28 days of curing time, the samples were milled and analyzed by FTIR-ATR and DRX.

The FTIR analysis was performed on a Bruker 400MHz, model Avance III, USA, with 4 cm-1 resolution and 128 scans.

3.2.7 X-ray Diffraction analysis

The X-ray diffraction was performed in an X'Pert Pro (PANalytical) diffractometer using monochromatic CuK α 1 radiation (λ = 1.54059 Å) and working in reflection geometry (θ /2 θ). The optics configuration was a fixed divergence slit (1/2°), a fixed incident antiscatter slit (1°), a fixed diffracted anti-scatter slit (1/2°), and X'Celerator RTMS (Realtime Multiple Strip) detectors, working in scanning mode with maximum active length. Data for each sample were collected from 5° to 70° (2 θ). The samples were rotated during data collection at 16 rpm to enhance particle statistics. The X-ray tube worked at 45 kV and 40 mA. The amorphous content of the samples produced, both anhydrous and hydrated, was determined by adding 20% in weight of corundum (99.9% α-Al2O3 from Alfa Aesar) Phase quantification was performed through Rietveld analysis using the Panalytical software Highscore.

3.2.8 Scanning Electron Microscopy

A paste hydrated with an SS solution with an MS 0.9 and MNa 3.516 molar and cured for 2.5 years was analyzed using Scanning Electron Microscopy (SEM). Sample preparation consisted of drying the paste at 100°C for 24h, followed by a horizontal cut using a diamond saw. The sample was then introduced into a mold with an epoxy resin and left to cure for 24h at 40°C. After the curing process, the sample was removed from the mold and further sectioned into smaller pieces using the diamond saw. Surface polishing was performed using silicon carbide papers graded at 800 and 400. Finally, a 6-micra diamond spray was applied to the surface and polished using a polishing cloth. During the cuts and polishing steps, an ethanol-based solution from TESTA was used as a lubricant

For SEM observation, the samples were placed on an AI stub using double-sided carbon tape and sputter coated with a thin Au/Pd film in a Quorum Technologies coater, model Q150T ES. They were then analyzed in a ThermoScientific desktop scanning electron microscope (SEM), model Phenom ProX G6, with a CsB6 filament and equipped with a light elements energy dispersive spectroscopy (EDS) detector.

In Table 3-2, a summary of the experimental procedure and conditions performed for each paste is displayed.

Table 3-2. Summary of the tests performed in this work: conditions studied, hydrationsolutions, curing time, and methodologies

	Paste W/S 0.5	Paste W/S 0.25		
Conditions Studied	Influence of different solution on the hydration reaction	Influence of different solution on the performance and phase evolution	Impact of lo hydrat	ong term tion
Tested solutions	Water NaOH SS MS1.2	Water SS MS1.2	Water	SS MS0.9
Curing time	3 days	7 and 28 days	3.5 years	2.5 years,
Analysis Performed	- Calorimetry - Dissolution	-Compressive strength - XDR - FTIR	-Dissolution - FTIR	-Dissolution - FTIR - SEM

3.3 Experimental Results

3.3.1 Isothermal calorimetry

The hydraulic reaction was followed by calorimetry in pastes with a 0.5 w/s ratio, the results are displayed in Figure 3-4. The results show that with the increase of alkalinity, there is an anticipation of the reaction peak and an increase in the amount of heat released. Moreover, It can be observed that the activation with sodium silicate leads to a more intense peak than that of the pastes produced with water or with the sodium hydroxide water solutions. However, the reaction peak of the paste activated with sodium silicate displays an induction period longer than the pastes activated with sodium hydroxide.

Moreover, the pH of the pastes in Figure 3-4B was measured after 2 days of hydration, using a pH indicator. The results are displayed in Table 3-3.



Figure 3-4. A) Calorimetric results of pastes hydrated with, water (blue line) water+ NaOH_pH 12 (black line), water+ NaOH_pH 13 (green line), and a sodium silicate (SS) solution (red line)

Table 3-3. pH after 2 days of hydration

Sample	pH of the	pH of the mixture after
	hydrating solution	2 days of hydration
W_05	7	11
NaOH13_05	13	13
SS_05	13	13

3.3.2 Dissolution tests

In Figure 3-5 the experimental results of the solubility tests are displayed. The calcium and silica solubility were studied in mixtures with a w/s ratio of 0.5, hydrated with either water, represented by cross characters, alkaline solution with a pH of 12 (NaOH hydrated), represented as triangle characters, and a sodium silicate solution (SS hydrated), represented as diamond characters. The data in blue refers to the CaO and SiO₂ concentration before the exothermic peak, and in red after the peak.

For comparison purposes, solubility tests were also performed on long-term hydrated pastes with a w/s ratio of 0.25, the results are displayed in Figure 3-6. The pastes were hydrated with either water or a SS solution and cured for a period of 3.5 years and 2.5 years, this data is represented as a grey and a black circle, respectively.

The solubility results indicate that incorporation of silica in the system by activating the binder with an SS solution results in a high content of Si and a low Ca concentration in the solution. The first sample, tested after 10h of hydration, displayed a Si content of 184 mM, that decreased to ~20 mM, after the 22h.



Chapter 3. A model for the hydration mechanisms of an amorphous-wollastonitic hydraulic binder





Figure 3-6. Calcium concentration as a function to silica concentration in solution: cross markers represents the results obtained for a w/s paste of 0.25, hydrated with water for 3.5 years, and diamond shape- markers with sodium silicate solution for 2.5 years.

3.3.3 Compressive strength results in pastes

Figure 3-7 shows the compressive strength and the evolution of pseudowollastonite and tobermorite content on AWH pastes after 7 and 28 days of hydration, using either water or a sodium silicate activator as hydrating solutions. The results show that the compressive strength and the amount of tobermorite content on the pastes increased over time, indicating ongoing hydration. Moreover, the sodium silicate solution had a significant impact on the compressive strength of the pastes, particularly at early ages, obtaining higher results than those hydrated with water.



Figure 3-7. Correlation between the pseudowollastonite (PW grey) and tobermorite (T orange) content with the compressive strength of AWH paste at 7, and 28 days of hydration, using either water (A) or a sodium silicate activator (B) as a hydrating solution.

3.3.4 XRD analyses

In Figure 3-8 the XRD spectra of the anhydrous sample (black) are compared with the spectra of paste hydrated with water (blue) and a SS solution (red), after 7 and 28 days of hydration. The spectra indicate the presence of a pseudowollastonite phase in all samples and the formation of a crystalline phase, tobermorite 9Å which is indicative of the hydration process. The intensity of the tobermorite 9Å peak is influenced by the hydration time and the type of hydrating solution used since higher values are observed when the sample is activated. After 7 days of curing, the sodium silicate-activated paste presented the formation of a tobermorite-like phase. The water-hydrated paste also showed the presence of this phase, but the peaks were less intense. After 28 days of hydration, the intensity of the tobermorite peaks on both samples increased





Figure 3-8. XRD spectra of the phase development of the anhydrous sample (black) with pastes hydrated with either water (blue line), or Na2SiO3 solution (red line), after 7 days of hydration (A), and 28 days of hydration (B). The "t" identifies the C-S-H phase with a tobermorite-like structure, while "P" denotes pseudowollastonite

3.3.5 FTIR analyses

Figure 3-9 shows the FTIR spectra of the anhydrous sample (black) compared with the spectra of the paste hydrated with water (blue) and hydrated with SS solution (red), at different hydration times: 7 days, 28 days and \leq 2.5 years. Each spectra was dived into the following five main regions.

- A. 1700-1300 cm⁻¹, Characteristic bands of CO_3^{2-} at 1450 cm⁻¹ attributed to asymmetric stretching mode [36]
- B. 1100-1050 cm⁻¹, bands characteristic of stretching Si-O-Si bond [37–39]
- C. 1000-900 cm⁻¹, in this region the main peaks are characteristic of the stretching vibration of non-bridging Si-O [39], the band at ~973 cm-1 can be attributed to the Si-O symmetric stretching vibration, [36], and the bands at ~980 cm-1 [40] and ~900 cm⁻¹ [41,42] to the Si-O-Si asymmetric stretching vibration, specifically Q² and Q¹ structures, respectively. The band at 850 cm⁻¹ can be attributed to the Si-O-Si asymmetric stretching vibration of Q⁰ units and the 875 cm⁻¹ band to the in-plane bending mode of CO₃²⁻ [32,43,44].
- D. 750-650 cm⁻¹ The band at 680 cm⁻¹ can be attributed to the bending motion of oxygen bonds [42] and the band at 712 cm⁻¹ is characteristic of the CO₃²⁻ in-plane
bending modes [32,43,44] and the peak at 714 cm⁻¹, corresponds to the stretching bridging Si-O(Si) characteristic for the presence of a three-membered ring structure [45]

E. 500-400 cm⁻¹ band associated to silica deformation [40], ~455 cm⁻¹ can be associated to the to the Si-O in plane bending [39]



Figure 3-9. FTIR spectra of the anhydrous sample (black) compared with the spectra of the paste hydrated with water (blue) and hydrated with Na2SiO3 solution (red), at different hydration times: 7 days, 28 days and ≤ 2.5 years.

The anhydrous sample displays bands at 922 and 985 cm⁻¹, characteristic of Si-O stretching vibration at Q².[40], due to the pseudowollastonite phase present in the sample. In the 7 and 28 days hydrated samples the spectra exhibit characteristic CO_3^{2-} bands (A and B), indicating the carbonation of the binder. Furthermore, the hydration

reaction caused a narrowing of the C and E regions, suggesting a higher degree of polymerization.

In the water-hydrated sample cured for 2.5-year, the FTIR results suggest an extensive carbonation of the sample due to the high band intensity at ~1450 cm⁻¹ and 875 cm⁻¹. Moreover, the spectra display a broadening of the E region and the presence of bands at 470, 799, and 1100 cm⁻¹, characteristic of the stretching and bending modes of the Si–O–Si siloxane bonds present in amorphous silica [37,46]. These results indicate that instead of an organized silicate structure, the main resulting products from long-term curing of a water-hydrated sample are calcium carbonate and amorphous silica.

3.3.6 SEM analyses

The SEM images of the 2.5-year cured paste and the respective EDS line analysis, are displayed in Figure 3-10, and Figure 3-11. Both images exhibit a heterogeneous matrix, with unreacted particles of different shapes and sizes surrounded by a binding matrix. The EDS line profiling was made across the hydrated phases limited by anhydrous phases. While in the anhydrous area the calcium/silica ratio is ~1, in the hydrated region the calcium content decreases (green line) and the sodium and oxygen content increases, purple and black line, respectively. The increase in oxygen from the grain to the matrix suggests the formation of a C-S-H product, due to the integration of -OH in the calcium silicate structure.





Figure 3-10. SEM image of the 2.5-year cured paste and the respective EDS line analysis of the blue line. Ampliation 1350x.





Figure 3-11. SEM image of the 2.5-year cured paste and the respective EDS line analysis of the blue line. Ampliation 4000x.

3.4 Discussion

The results of this study show that the reaction of the AWH binder has a high sensitivity to the solution pH. When the binder is hydrated with water, the reaction kinetics is slow and displays an induction period of over 2 days, this period is characteristic for species dissolution. The CaO dissolution results in the formation of aqueous calcium hydroxide and pH increase, as displayed in reactions (3-1) and (3-2) [29]. However, since the AWH binder has a lower Ca content when compared with OPC, the solution pH only reaches a value of 11 instead of pH ~13 [47]. Furthermore, the lower calcium content also inhibits $Ca(OH)_2$ saturation and consequent precipitation, and promotes the formation of C-S-H structures with lower C/S content.

 $Ca^{2+}_{(aq)} + OH^{-}_{(aq)} \leftrightarrow CaOH^{+}_{(aq)}(3-1)$ $Ca^{2+}_{(aq)} + 2OH^{-}_{(aq)} \leftrightarrow Ca(OH)_{2(aq)}(3-2)$

Hence, in systems with a lower pH value, such as the water-hydrated AWH case, the system is close to equilibrium and displays a low solubility, characteristic of a type I dissolution regime. Moreover, due to the lower alkalinity there is a lower deprotonation of the silanol group and fewer negative charges in the silicate chain, which decreases the capability of silicate tetrahedra to accommodate cations [48]. This factor inhibits the formation and growth of C-S-H structures. Hence, the system displays a higher induction period, as the formation of the hydration product is delayed, and the ions continue to solubilize. Furthermore, the presence of unreacted calcium and silicon in solution may promote the formation of calcium carbonate and amorphous silica structures instead of C-S-H structures, as was observed in the FTIR spectra of the long-term water-aged paste, Figure 3-9.

The hydration of the AWH binder with a NaOH solution increases the alkalinity of the system which promotes three phenomena 1) decrease of calcium solubility [29]. 2) increase Si solubility [28], and 3) ionization of the silanol group [15].

In this system the Si undersaturation is very high, hence, the energy required for dissolution is low, allowing for all three solubility regimes to take place [49], and leading to a rapid dissolution. Furthermore, the pH is high enough to promote the ionization of the silanol group and allow the formation and growth of C-S-H structures, and the Na cation acts as a catalyzer in C-S-H formation [50]. These contributions result in an increase in kinetic and a reduction in the induction period, as observed by the rapid heat releases in Figure 3-3A. However, this rapid formation and uncontrolled growth of hydration products around the grains, lead to an unorganized accumulation of reaction products, inhibiting the hydration reactions at later ages and leading to a more porous microstructure [26].

With the addition of a sodium silicate activator, there is an introduction of Si into an alkaline system. This introduction decreases Si undersaturation and increases the energy required for dissolution, characteristic of a type I regime. The slower dissolution delays the kinetics of the reaction and promotes the formation of an induction period as observed in Figure 3-3B [49]. However, unlike the water-hydrated paste, in the SS activated system, the pH is high enough to allow the formation and growth of C-S-H structures. Furthermore, the added soluble Si can also act as a nucleation site [49]. The controlled kinetics and the presence of nucleation sites allows for the hydration products to be form evenly around the grain, promoting the formation of more hydration products and resulting in a higher heat release, compared to the other system, Figure 3-3.

The free calcium and silica content of three SS hydrated samples were analyzed at different hydration times. The results show that all samples exhibited a low Ca content and a high Si concentration, attributed to the introduction of a silicate-based activator. Moreover, the 22-hour and 2.5-year activated pastes presented a similar trend, with a small increase in calcium content and a significant decrease in silica.

What is proposed in this work is that, similarly to the slag hydration mechanism proposed by Zuo et al [49], the water-hydration of the AWH binder leads to the stabilization of the silicon surface through the adsorption of dissociated water. This process leads to the formation of a hydrophilic surface at the water-binder interface, as displayed in Figure 3-12A.

The dissolution of the ionic species is promoted by ionic undersaturation in the solution [7] and OH- attack [51,52], which results from water dissociation or the introduction of an alkaline activator. This dissolution gradually exposes the interior of the anhydrous grain. Although Ca and Si dissolution is chemically independent, it is also electrically coupled, similar to the dissolution mechanism of silica in aqueous solutions [53]. Hence, at equilibrium, the anion dissolution is proportional to the cation removal rate.

Due to the presence of coordinated silica layers inside the anhydrous particle [32,33], the penetration of OH- may result in the formation of tobermorite 9 Å. Tobermorite 9 Å does not have crystallographic water in its structure and is typically formed from tobermorite 11 Å dehydration under high temperatures and pressure conditions [54,55]. Since these conditions are not met in the current system, a possibility for the formation of tobermorite 9 Å could be OH- penetration in areas of the anhydrous material with lower calcium content. Moreover, the alkalinity increase in the system promotes silanol group ionization and the formation of C-S-H structures.

The initial hydration products formation, amorphous C-S-H, and tobermorite 9 Å, are schematized in Figure 3-12B.



Introduction of OH- into the anhydrous grain resulting in a tobermorite-like structure

Figure 3-12. Schematic representation of the initial hydration of the AWHB. A) displays the initial Ca preferential dissolution and hydrolyzation of the surface and B) the ionization of the silanol group and Si dissolution.

This initiates a self-sustaining process, where the silica solubilization is promoted until Si saturation is reached, followed by the formation of C-S-H species due to the presence of an alkaline medium and Ca in solution. The C-S-H formation reduces Si saturation, allowing for further dissolution until equilibrium.

Therefore, the following is proposed for each type of hydration investigated during the study

- When hydrated with water, the system is close to equilibrium promoting a slow dissolution, and a delay in C-S-H formation due to the low alkalinity in the medium.
- In the presence of NaOH, both silica dissolution and C-S-H formation are promoted, resulting in a rapid reaction and the formation of an unorganized C-S-H structures around the grain.
- In the case of SS activation, the dissolution of Si is slow due to the decrease of Si undersaturation. However, the high alkalinity of the system facilitates C-S-H formation. The formation and growth of this hydration product exposes the surface of the grain, allowing for further interaction with the aqueous medium and promoting additional dissolution.

3.5 Conclusion

In this work, the hydration reaction of an amorphous wollastonitic hydraulic (AWH) binder under different hydrating solutions was followed by calorimetry. Moreover, calcium and silica content in the solution was measured during different curing times. The main results and the literature review suggest that the Ca and Si dissolution is electrically coupled, and at equilibrium, the anion dissolution is proportional to the cation removal rate. Furthermore, the alkalinity increase in the system promotes the silanol group ionization and consequent C-S-H formation.

A hypothesis was proposed for the formation of tobermorite 9Å, suggesting that it results from OH- penetration in areas of the anhydrous material with lower calcium content.

The species dissolution influences the kinetics of the reaction, with different hydrating conditions promoting various types of dissolution.

• When water hydrated, the undersaturation of the system is low and near equilibrium, leading to a very slow dissolution, slow pH increase, and a high induction period (2 days).

- When hydrated with an alkaline solution, the high pH causes an increase in Si undersaturation, leading to a fast dissolution and rapid formation and growth of unorganized C-S-H structures around the grain. This results in a severe decrease in the induction period.
- When activated with a sodium silicate solution, the pH in the system is high, but the Si undersaturation is low due to the addition of free Si species from the activator. Hence, an induction period of ~14 h was observed. The high pH and the slow and controlled dissolution lead to the formation of an organized C-S-H structure around the grains. Furthermore, the added soluble Si can also act as a nucleation site, resulting in a higher extent of the hydration reaction and, consequently, higher heat release

The hydration reaction allows a self-sustaining process, where silica solubilization is promoted until saturation is reached, followed by the formation of C-S-H species due to the presence of an alkaline medium and Calcium in solution. The C-S-H formation reduces Si saturation, allowing for further dissolution until equilibrium.

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CHAPTER 4. Calculation of the apparent activation energy

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Contents

CHAPTER 4. Calculation of the apparent activation energy	103
4.1 Introduction	106
4.2 Experimental procedure	109
4.2.1 Binder production	109
4.2.2 Production of pastes	109
4.2.3. Isothermal Calorimetry	109
4.2.4. Production of mortars	110
4.2.5 Compressive strength tests in mortars	110
4.3 Experimental results	111
4.3.1 Isothermal Calorimetry	111
4.3.2 Compressive strength results in mortars	114
4.4 Discussion	116
4.5 Conclusions	119
4.6 References	120

Chapter 4. Calculation of the apparent activation energy

In this chapter, the apparent activation energy (Ea) of an amorphous wollastonitic hydraulic (AWH) binder was, for the first time, experimentally determined, using a calorimetric approach. Additionally, a correlation between the Ea, measured at the acceleration period with the C/S ratio of the hydration product is proposed. The Ea of the prepared pastes was determined through isothermal calorimetry tests by calculating the specific rate of reaction at different temperatures, using two different approaches. When comparing the Ea, at the acceleration period of this binder with the one published for alite and belite, we observed that its value is higher, which may be a result of a different hydration product formed with a distinct C/S ratio. Finally, to study the temperature effect on the compressive strength at early ages, a set of experiments with mortars was performed. The results showed that the longer the curing time at 35 °C, the higher the compressive strength after 2 days of hydration, which suggests a higher initial development of hydration products. This study also indicated that the AWH binder has a higher sensitivity to temperature when compared with ordinary Portland cement (OPC).

4.1 Introduction

In order to better understand the properties and the hydration mechanisms of this binder, an important parameter to study is the activation energy of the pastes either hydrated with water or with the activating solution.

When a hydraulic binder comes in contact with water or an activating solution, it undergoes a series of reactions that causes heat release and the hardening of the material. The study of this rise in temperature can give important information about OPC pastes and concrete, as well as alkali-activated materials. For example, it can help to understand the sensitivity of concrete hydration processes in relation to temperature and allows the estimation of compressive strength of cement pastes at an early age [1]. Additionally, its study on alkali-activated materials such as slag allows the prediction of how high-temperature curing can affect the acceleration of the reaction [2].

Therefore, to capture the temperature sensitivity of a particular mixture, the Arrhenius equation, Equation (4-1), can be used.

$$\boldsymbol{k} = \boldsymbol{A}\boldsymbol{e}^{\frac{-Ea}{RT}} \qquad (4-1)$$

where "k" represents the reaction velocity constant, "A" the pre-exponential constant, "Ea" the apparent activation energy, "R" the perfect gas constant, and "T" the temperature.

This equation correlates the kinetics of the mixture (k) with the apparent activation energy (Ea), which refers to the minimum amount of energy required for the occurrence of a particular reaction, which, in this case, is the hydration reaction.

The Ea represents an important parameter to characterize the sensitivity of the concrete hydration processes to temperature and allows the prediction of the compressive strength of OPC concrete. If both the Ea and the effect of time in temperature are taken into account, the physical and mechanical properties of OPC can be predicted [3]

Typical Ea values for the aqueous dissolution of oxide and hydroxide minerals range from 19 to 86 kJ/mol [4], whereas studies on the Ea of blast furnace slag with different compositions of alkaline activators indicate that Ea can range from 39.2 kJ/mol [5] to 75.2 kJ/mol [2].

Ea can be calculated by using the method of the single linear approximation of reaction

rate, in which the reaction rate of the mixture is calculated by applying a best-fit line of the linear acceleration period on the isothermal test [6].

Linearizing Equation (4-1), we obtain Equation (4-2).

$$\ln(k) = \ln(A) - \frac{Ea}{R} \frac{1}{T} (4-2)$$

Huang et al. observed that by mixing 4% of portlandite (CH) with alite (C₃S), there is an increase in the Ea, from 35 kJ/mol to 36 kJ/mol, which indicates that the CH presents a higher energy barrier for nucleation of hydration products than alite. On the other hand, when mixing C₃S with calcium silicate hydrates (C-S-H), the Ea is reduced to 34 kJ/mol; this occurs because the C-S-H has an auto-catalytic effect on the nucleation of hydration products; therefore, less energy is required for the precipitation of the specimen [7].

Thomas et al. [8] studied the kinetic mechanisms and activation energy for belite (C₂S), observing that the activation energy for neat pastes of β -C₂S was 32 kJ/mol, while for a more reactive form of belite, the activation energy increased to 55 kJ/mol. This difference was related to distinct rate-controlling steps for the hydration process. While the lower value was attributed to the dissolution of C₂S, the higher value was suggested to be related to the nucleation and growth of the hydration products. In the same study, Thomas et al. [8] studied how the presence of sodium silicate in the hydration solution of a paste made of neat belite influenced the belite hydration mechanism. A two-step behavior was observed, which included an initial stage, before the peak of maximum heat release, where the Ea was approximately 50 kJ/mol, and a second stage after the peak, when the activation energy dropped and stabilized around 32 kJ/mol, thus indicating that the hydration process was controlled initially by nucleation and growth mechanism, and finally, by dissolution.

Mehdizadeh et al. [5] investigated how the presence of sodium affected the Ea of activated phosphorous slag. The tests were performed with activators with different ratios of SiO₂/Na₂O and Na₂O/Al₂O. They reported that by decreasing the silica content and increasing the alkaline ratio, there is a decrease in the Ea, from 44.5 kJ/mol to 39.2 kJ/mol. Joseph et al. [2] performed a similar study on the apparent activation energy of ground granulated blast furnace slag and class F fly ash, using NaOH and Na2SiO3 as activators; they observed that the reaction mechanism is governed by chemically controlled reactions and reported an Ea that ranged from 48.2±5.9 kJ/mol to 75.2± 6.7 kJ/mol, depending on the method used to calculate it. Previous studies [9] with blast furnace slags activated with a solution with a silica modulus (SiO₂/Na₂O molar ratio) of

1.5 and a Na₂O concentration of 4%wt also reported similar values.

The aim of this work is to calculate the Ea of the AWH binder, to better understand its hydration reaction and temperature dependence. Additionally, to consolidate these results, an experimental study on the temperature effect in the compressive strength at early ages of mortars was performed. The Ea calculations were achieved by using the Arrhenius equation, implementing two different approaches.

Therefore, for the first time, the activation energy of the AWH binder was calculated. The binder was hydrated with either water or an activating sodium silicate solution at different temperatures, ranging from 20 to 35°C. The results were compared with previous works in order to be able to relate the C/S ratio of the hydrated product with the Ea of the reaction.

4.2 Experimental procedure

4.2.1 Binder production

Common Portland cement clinker raw materials were used in the production of the AWH binder, with the overall chemical composition being adjusted to a total C/S molar ratio of 1.1. The raw materials were ground, mixed, and compressed in a disc. The compressed disc was broken into four pieces and placed in a silicon carbide crucible. The filled silicon carbide crucible was placed in an electric furnace and heated at a rate of 25 °C/min, to 900°C, maintaining this temperature for 1 h, to allow full decarbonation of the raw meal. Then, the furnace temperature was raised to 1550 °C and kept for 1 h to guarantee the complete melting of the powder mix and its chemical homogenization. Finally, the material was quenched by pouring the molten mixture into a water container, resulting in an amorphous content above 95%. The amorphous hydraulic binder produced was then ground with a ring mill for 3 min, obtaining a final Blaine fineness around 6000 cm²/g.

4.2.2 Production of pastes

The pastes were hydrated with a sodium silicate solution using a water/solids ratio of 0.35. The sodium silicate solution was obtained by equilibrating a solution of Na_2SiO_3 (Na_2O : 7.5–8.5% SiO2, 25.5–28.5%, Chem Lab, Zedelgem, Belgium) with NaOH (98.2%, VWR-Prolabo, Matsonford, PA, USA) to achieve a SiO₂/Na₂O modulus of 1.2. The overall content of Na_2O in solution, with respect to the binder, was defined as 2%wt. All pastes were stored under relative humidity (HR) conditions above HR90%.

4.2.3. Isothermal Calorimetry

The isothermal calorimetry tests were performed on a TAM Air instrument (Waters Sverige AB, Sollentuna, Sweden). Pastes prepared with the amorphous binder, and a water/solids ratio of 0.35 were inserted into vials ex situ; therefore, the first exothermic peak characteristic of the wetting of the amorphous binder is not displayed, and the correct heat released was only considered after the first 45 min to allow for the equipment to stabilize. The experiments were performed at 20, 25, 30, and 35 °C. These temperatures were chosen according to the characteristics of the equipment and the qualities of the binder.

4.2.4. Production of mortars

Five different mortars were prepared with this new binder. Four of them were cured at $35 \circ C$ for 2 h, 6 h, 22 h, and 44 h under relative humidity (HR) conditions above HR90% and then transferred to another cabinet at 20°C and HR95% until they were mechanically tested. The other mortar was cured at 20°C and HR95% during the entire period of the experiment. All mortars were alkali activated with sodium silicate, using a water/solid ratio of 0.365; SiO₂/Na₂O modulus of 0.9; Na molarity of 3.5 M and overall content of Na₂O in solution, with respect to the binder, of 3.2%wt.

4.2.5 Compressive strength tests in mortars

After 48 h, compressive strength tests were performed on all mortars. Furthermore, mortars cured at 20 \circ C and those cured at 35 \circ C for the first 44 h were also tested at 7 and 28 days of hydration.

4.3 Experimental results

4.3.1 Isothermal Calorimetry

The heat development rate of the pastes was studied at 20, 25, 30, and 35 °C in order to correctly employ equation (4-2). For pastes hydrated with either water or an alkaline activator, the calorimetric curves and the accumulated heat in the function of time are presented in Figure 4-1.



Figure 4-1. Heat release (A1,B1) and accumulated heat release (A2,B2) in function of time at different temperatures, with different hydration solutions: water (A1,A2) and alkaline solution (B1,B2).

A best-fit line was adjusted to the acceleration period in order to obtain the "k" term of equations (4-1) and (4-2) through the slope of the fitting equation. The fits were performed in all the experiments made either with pastes hydrated with water or with alkali-activated pastes. Figure 4-2 presents an example of a calorimetric curve with the respective best-fit linear analysis for the 35 °C alkali-activated sample.



Figure 4-2. Heat release of a paste activated with Na₂SiO₃ and a water/solid ratio of 0.35 at 35 ∘C, with a best-fit line on the linear acceleration period (blue line).

Figure 4-3 correlates ln(k) with 1/T for each temperature and hydration condition. The fit for alkali-activated pastes at different temperatures is depicted as a red dashed line, while the fit for pastes prepared with water is shown as a blue dashed line. The activation energy values were determined by using the equation (4-3) and (4-4), which represent the fitting equations obtained from Figure 4-3, and the values of 82 kJ/mol and 85 kJ/mol were obtained for the alkali-activated pastes and for the pastes prepared with water, respectively.

Alkali-activated (red line): ln(k) = -9818.9 (1/T) + 16.068 Ea = 82 kJ/mol (4-3)

Water (blue line)
$$ln(k) = -10255 (1/T) + 14.969 Ea = 85 kJ/mol$$
 (4.4)



Figure 4-3. Graphic representation of ln(k) in function of 1/T for the temperatures 20, 25, 30, and 35 °C. The blue dots correspond to the pastes hydrated with water, while the red triangle corresponds to the alkali-activated pastes. The best fit is showed as dashed lines

Another method that can be applied to calculate the Ea, previously used by Joseph et al. [2], is the rearrangement of the Arrhenius equation, Equation (4-1) to obtain the instantaneous activation energy. This is carried out by writing the Arrhenius equation at two different temperatures, T1 and T2, and then subtracting them.

Then, to obtain the same behavior of the system at different curing temperatures, the concept of equivalent age is used. This represents the time at which both systems have the same degree of reaction (α) [10]. The α can be calculated using the expression (5), where Q(t) is the cumulative heat released, and Q $^{\infty}$ is the heat release at an infinite time.

$$\alpha = \frac{Q(t)}{Q_{\infty}} (4-5)$$

Therefore, if we define (T_1) and (T_2) as the equivalent age at which the degree of reaction is identical in both systems, we obtain an expression (4-6) as follows:

$$\tau(T_2) = \tau(T_1) \cdot \exp\left\{-\frac{E_a}{R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right\} (4-6)$$

Hence, to be able to apply Equation (4-6), the equivalent age in the activated binder systems of

25°C and 35 °C, was calculated using Equation (4-5), at different times of the acceleration period. Since the remaining parameters of Equation (4-6) are known constants (R, T_1 , and T_2), it is possible to relate the E_a to α . The results are presented in Figure 4-4.



Figure 4-4. Evolution of the Ea of the activated binder determined by equation 4-5, at the set of temperatures 25° C and 35°C.

To experimentally observe the impact that the temperature has on the compressive strength of the binder, five mortars were prepared with a sodium silicate solution and, cured during different times at 35°C followed by a curing at 20°C, until being tested. The results obtained after 2 days of hydration are presented in Figure4-5.

4.3.2 Compressive strength results in mortars

Compressive strength tests at 7 and 28 days of hydration were performed on 2 mortars, initially cured during 0h and 44h at 35°C, and then at 20°C. The results are presented in Figure 4-6.



Mortars compressive strength 2 days hydration

Figure 4-5. Compressive strength of alkaline activated mortars at 2 days of hydration. The curing times at 35°C were 0h, 2h, 6h, 22h and 44h, followed by a curing at 20° C to complete the 2 days.



Figure 4-6. Compressive strength of alkaline activated mortars at 7 (light blue and light orange) and 28 days (dark blue and dark red) of hydration. The curing times at 35° C were 0h and 44h, followed by a curing at 20° C to complete the 7 and 28 days.

4.4 Discussion

It is broadly accepted by the scientific community that cement hydration is a reaction that undergoes a dissolution–precipitation process [11]. In the first stage of hydration, the slow kinetic observed is related to the ionic dissolution, which represents the initial rate controlling step. During this period, the ionic concentration in solution increases until it reaches a saturation point and an equilibrium phase, less soluble than the precursor phase, starts to precipitate, which, in this case, are the C-S-H products. This stage occurs at the acceleration period, measured by isothermal calorimetry, in which the controlling step is the heterogeneous nucleation and growth of C-S-H [7,12]. This type of exothermic reaction is responsible for a large amount of heat release, which can be deleterious on large volume concrete structures, such as dams, since the self-generated head accumulates within the structure, causing fractures due to localized thermal expansion and decreasing its lifespan [13].

Traditional OPC, after 72 h of hydration, releases more than 250 J/g of cumulative heat [14]. In contrast, in this work, we observed that the hydration of the AWH binder, for the same period of time, releases a cumulative heat that is only one-sixth of this value, when hydrated with water, and one-third when activated with the alkaline solution, as seen in Figure 4-1; however, the strength developed by this binder is still competitive with OPC from the 7th day of hydration and further [15].

Two different approaches were used in the present work to calculate the Ea of the nucleation and growth mechanism at the acceleration period of the reaction. In the first approach, based on Equation (4-2), which relates the rate of the reaction with the temperature, values of 82 kJ/mol and 85 kJ/mol were obtained for the activated and non-activated pastes, respectively.

For the second method, based on Equation (4-6), which correlates the Ea with the degree of the reaction, a range of values from 63 to 80 kJ/mol were obtained in the region of the acceleration period. The small discrepancy in the calculated Ea, when compared to the first approach, has been already reported by Joseph et al. [2], who correlate Ea with the use of different methods of calculation. Furthermore, we can observe that the range of Ea calculated stands above the dissolution Ea of wollastonite (54.7 kJ/mol [4]), which further indicates that this value is not correlated with a dissolution mechanism. This assumption results from the knowledge that wollastonite is a non-hydraulic phase [11] contrary to the present amorphous binder, which dissolves to further form C-S-H products [15,16], hence, its Ea for dissolution should be lower than that presented for

wollastonite. Therefore, the obtained Ea values can be translated as the energy necessary to provide to the system so that the nucleation and growth of C-S-H can occur [7].

When comparing the Ea, at the acceleration period of this novel binder with alite and belite, 51 [17] and 55 kJ/mol [8], we can observe that the values of 82–85 kJ/mol are considerably higher. This may be due to the formation of structurally different hydration products. In fact, previous works have reported that this material, instead of producing a C-S-H with a C/S ratio of 1.7 [18], such as alite and belite, produces a C-S-H with a ratio of 1.1 [19]. It is known that the mean silicate chain length of a C-S-H structure increases as the C/S ratio decreases. Hence, we hypothesized that the higher the polymerization degree required to form those C-S-H structures, the higher the energy input necessary, translating into higher values of Ea. Additionally, because this binder has the particularity of producing tobermorite 9 Å, [19], more energy will be required in its growth, since this material has highly polymerized silica chains.

The addition of the activating solution, which causes an increase in alkalinity, showed a considerable impact on the first hours of reaction, decreasing the slow reaction period, characteristic of dissolution. This is a consequence of the influence of pH since its increase causes a rise in the solubility of $[SiO_4]^{4-}$ ions [20] and promotes the formation and growth of C-S-H structures.

The addition of sodium silicate also decreases the Ea from 85 to 82 kJ/mol. This small decrease may be a result of the presence of $[SiO_4]^{4-}$ that facilitates the nucleation of the C-S-H, similar to what was reported by Thomas et al. [8], which showed that the Ea of belite decreased from 55 kJ/mol to 50 kJ/mol when preparing pastes with water or with a solution of sodium silicate, respectively.

The proximity of the Ea values (for the nucleation and growth rate-controlling step) in the studied systems may indicate that a similar C-S-H is formed by using either water or the alkaline solution. In fact, this theory can be sustained by the work of Santos et al. [15], which reported the main hydration product for both pastes resulted in a C-S-H type phase with a semi-crystalline nature, with the crystalline part of this hydration product resembling an ordered tobermorite-like structure.

Finally, to discuss the temperature effect on the early age compressive strength of the binder, first, we need to compare it with the experimental results obtained by Ezziane et al.[21]. In this study, mortars made with OPC were cured under constant temperatures

Chapter 4. Calculation of the apparent activation energy

of 20, 40, and 60°C, and no significant changes were found by the authors. In contrast, the AWH binder mortar's compressive strength (Figures 4-5 and 4-6), displayed a higher sensitivity to temperature, which was expected due to the binders higher Ea. In fact, the longer the curing times at 35°C, the higher the compressive strength results obtained. This increase in early age mechanical performance suggests a higher development of hydration products, which may be a result of the increase in solubility enhanced by the higher temperatures. Since the dissolution process is the initial rate-controlling step, by facilitating this process, the ionic concentration in the solution that is necessary to reach saturation point and start C-S-H formation is anticipated, which translates into higher initial strengths.

Therefore, the higher temperature sensitivity that this novel binder presents can be used to adjust and optimize the reaction mechanism and kinetics of the hydration reaction to a given situation, such as increasing the rate of cement hydration, decreasing setting time, or even accelerating its compressive strength performance. With this purpose, further temperature sensitivity tests must be performed to be able to optimize the amount of time that the hydration should occur at higher temperatures and correlate it to the physical properties shown on the hydrated binder.

4.5 Conclusions

In this work, the activation energy of a novel low-calcium hydraulic binder was experimentally obtained using calorimetric experiments at 20, 25, 30, and 35°C. The obtained results revealed the following conclusions:

- The Ea correlates with the acceleration period and can be translated as the energy necessary to provide to the system so that the nucleation and growth of C-S-H can occur;
- The experimental Ea, calculated for this new amorphous hydraulic binder (82–85 kJ/mol) is higher than that of alite or belite (51 and 55 kJ/mol). This difference in Ea may result from the formation of structurally different hydration products, with a lower C/S ratio of 1.1;
- 3. It was hypothesized that a higher Ea at the acceleration period may translate into a higher mean silicate chains length of C-S-H with a lower C/S ratio;
- 4. The similarity of the activation energy value determined for the alkali-activated the non-activated pastes may indicate the formation of similar C-S-H products. The small decrease may be a result of the high alkalinity in the system and the presence of [SiO₄]⁴⁻ species, which facilitates the nucleation and growth of the C-S-H;
- 5. The compressive strength tests on mortars cured for different periods of time at a higher temperature suggest that this novel binder has a higher sensitivity to temperature when compared with OPC;
- 6. The increase in temperature promotes a faster dissolution of the binder, which allows for the formation of a more hydrated product at early ages;
- 7. A low amount of released heat after 3 days of hydration was reported in this novel binder, i.e., (45 J/g, when hydrated with water, and 100 J/g when hydrated with the activating solution). Previous studies have confirmed that, even with this low amount of heat release, the binder is able to obtain competitive strengths, which opens the possibility of producing a hydraulic binder with a compressive strength comparable to that of OPC but with a lower CO₂ footprint and improved hydration heat properties

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CHAPTER 5. On the influence of storage time on the reactivity of an amorphous wollastonitic hydraulic binder

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Contents

CHAPTER 5. On the influence of storage time on the reactivity of an a wollastonitic hydraulic binder	amorphous 123
5.1. Introduction	126
5.2 Experimental Procedure	127
5.2.1 Binder production	127
5.2.2 Isothermal calorimetry analysis	128
5.2.3 Compressive strength tests	129
5.2.4 Fourier-transform infrared spectroscopy (FTIR)	129
5.2.5 X-ray photoelectron spectroscopy (XPS)	129
5.2.6 Scanning electron microscopy (SEM)	129
5.2.7 Thermal analysis	130
5.3 Results	130
5.3.1 Calorimetric results	130
5.3.2 Compressive strength results	131
5.3.3 SEM results	132
5.3.4 FTIR results	134
5.3.5 XPS results	136
5.3.6 Thermal analysis	140
5.4 Discussion	141
5.5 Conclusions	144
5.6 References	145

The exposure of calcium-silicate hydraulic binders to ambient conditions causes changes, due to physical and chemical interactions between the binder's surface and the water and carbon dioxide molecules present in the atmosphere. As a result, the binder may partially lose its reactivity and, consequently, compromise its strength after hydration. In this chapter, changes in the surface chemistry, due to atmospheric interaction, and their consequences in the hydraulic activity of amorphous wollastonitic hydraulic binders (AWH) are investigated. The binder was ground and then stored and exposed to atmospheric conditions for a period between 7 days and 270 days and the changes at the surface of the grains were studied by scanning electron microscopy, Fourier-transform infrared spectroscopy – attenuated total reflection and X-ray photoelectron spectroscopy. The influence of storage time on the binder's reactivity was studied by hydrating the binder with either water or a sodium silicate solution. The reaction was followed by calorimetry and compressive strength tests were performed on the pastes. The results indicate that, contrary to OPC, the aging of this binder is not mainly caused by its interaction with air moisture, but through the carbonation of the particle's surface. However, activating the binder with an alkaline Na₂SiO₃ solution mitigated this aging effect, allowing for a shelf life of up to 30 days without compromising early age strengths of the hydrated binder.

5.1. Introduction

Understanding cement aging is crucial, not only to ensure the reliability of laboratory test result, but also to inform end-users about potential loss in mechanical performance due to storage time. Therefore, in order to achieve consistent and predictable behaviors, the ageing mechanism and shelf-life of a binder need to be understood and its consequences explored [1–4].

For Ordinary Portland Cement (OPC), the most widely used binding material [5–7], the ageing mechanism has been extensively studied and its consequences investigated [4]. During storage, OPC undergoes transformative changes impacting its chemical, physical, and mechanical properties, consequently influencing the properties of the concrete and mortars it produces [8–11]. Previous research reveals that the aging process involves a delay in hydration reactions and influences the water/cement ratio necessary to maintain standard consistency. In general, it is observed that with the increase in storage time, there is a delay in the hydration reaction [8], a need to increase the water/cement ratio to obtain standard consistency, and a reduction of compressive strength at all ages [10,11]. Popovics [12] measured specifically a 20 % reduction in the compressive strength after three months of storage, escalating to 28 % and 40 % after six months and a year, respectively.

The aging of OPC is intricately linked to alterations in the surface characteristics of cement powders when exposed to ambient conditions [8,10,13]. Scanning Electron Microscopy (SEM) studies followed the evolution from a smooth surface to pre-hydration products with needle-like structures after prolonged exposure, suggesting interactions with water and the formation of calcium-silicate hydrate (C-S-H) structures [8,14]. These changes arise from either physical adsorption of water molecules or chemical reactions between anhydrous OPC minerals with H₂O or CO₂ molecules present in the atmosphere. The resulting products include calcium-silicate hydrate phases, portlandite (Ca(OH)₂), magnesite (MgCO₃), and calcium carbonate (CaCO₃) [8,10,13]. These irreversible changes on particles surfaces act as barriers during binder hydration, reducing cement solubility and enhancing resistance to water diffusion into the interior of the powders [9,10]. Strategies to mitigate aging include airtight storage conditions, enabling a 3-month storage without compromising its compressive strength, or the introduction of hydrophobic coatings during clinker grinding [4,9,15].

Due to its ubiquity, much research has focused on the storage impact of OPC [4]. However, with the growing use of alternative binders with lower CO_2 emissions

associated with their production [16], understanding the impact of storage on their performance is also required [1–4].

In alkaline-activated materials (AAM), small variations in the precursors can lead to significant changes during early hydration [17–21], therefore, pre-carbonation during storage impacts its hydraulic reactivity [2,3]. Mutti et al, [3] reported that extended aging periods in slags could lead to calcite and aragonite precipitation around the grains' surface, compromising its dissolution, and reducing its hydration kinetic and reactivity. However, these effects can be mitigated by keeping the samples in sealed conditions [2] and by increasing the alkalinity of the activating solution [3].

Amorphous wollastonitic hydraulic (AWH) binder is a slag-like material with a mainly amorphous structure and a Ca/Si ratio of ~1 [22–25]. This material is hydraulically active [23] and, after activation, can reach strengths similar to or higher than that of OPC [25]. However, one parameter that still needs to be explored is the influence of storage time on the surface chemistry of the binders' grains and its reactive capabilities. Due to its hydraulic nature and relatively high calcium content [26], a possible pre-carbonation and/or pre-hydration phenomenon during storage may significantly influence its performance. Hence, through calorimetric and compressive strength tests, along with comprehensive spectroscopic and microscopic analyses, we investigate the impact of air exposure on the aging dynamics of this binder and its influence on its hydraulic capabilities, both in water hydrated and alkaline activated solutions. The findings presented in this work shed light on the underlying processes, emphasizing the carbonation-induced passivation layer as a key factor influencing hydraulic reaction kinetics in such calcium-silicate binders.

5.2 Experimental Procedure

5.2.1 Binder production

The AHW binder was produced by using common OPC raw materials, namely sand, limestone, and fly ash, with the overall chemical composition being adjusted to a total Calcium/Silicate molar ratio of 1.1. The raw materials were ground, mixed, and compressed in a disc, which was then broken into four pieces and placed in a silicon carbide crucible. The filled silicon carbide crucible was placed in an electric furnace and heated, at a rate of 25 °C/min, to 900 °C, maintaining this temperature for 1 h, to fully decarbonate the limestone. Then, the furnace temperature was raised to 1550 °C and kept for 1 h, to guarantee the complete melting of the powder mix and its chemical homogenization. Finally, the material was quenched by pouring the molten mixture into a water container, resulting in a binder with an amorphous content above 97%.

The granulated material produced was then ground with a ring mill for 3 minutes, obtaining a final particle size distribution where where 90%wt of the sample is below 45 μ m. The chemical composition of the binder is indicated in Table 5-1 and it was determined by X-ray fluorescence (XRF), using the fused bead method. XRF beads preparation consisted in melting at 1200°C a mixture of 0.8 g of the material to be analyzed together with 4.8 g of Fluore-X 65® (containing 66% LiB₄O₇ and 34% LiBO₂ at 99.995%, from ICPH), 0.5 g of NH₄NO₃ (99.0%, from VWR) and an NH₄I tablet (as a non-wetting agent, from PANalytical) in an Eagon2 fusion instrument from PANalytical. The XRF measurements were then performed in a PANalytical Axios Cement instrument.

Table 5-1. Composition of the AWH binder.

	SiO ₂	CaO	AI_2O_3	Fe ₂ O ₃	MgO	K ₂ O	Other metallic oxides
Wt%	49.6	46.6	2.32	0.73	0.35	0.34	< 0.02

After grinding, the material was stored in sealed plastic bags for a period of 7, 30, and 270 days. A freshly ground sample (FG) and samples stored for a period of 7 (7d) and 30 (30d) days were used to perform compressive strength tests as well as isothermal calorimetry, in order to follow their hydration reaction.

The anhydrous samples stored for 7 and 270 days (270d) were analyzed by FTIR, XPS, and SEM. The results were compared with those obtained from a freshly ground material (FG).

5.2.2 Isothermal calorimetry analysis

The calorimetric tests were performed on a TAM Air instrument (Waters Sverige AB, Sollentuna, Sweden), and ran at a constant temperature of 20°C. Pastes with a solid/water ratio of 0.25 were prepared by mixing the amorphous binder either with water or with a sodium silicate solution, with an Si:Na ratio of 1.2 and a Na molarity of 3.52 M. Finally, the pastes were inserted into vials *ex-situ*, therefore, the first exothermic peak, characteristic of the wetting of the amorphous binder is not displayed. The alkaline activator was made by mixing a sodium silicate solution (Na₂O: 7.5-8.5 %, SiO₂: 25.5-28.5 %, Chem Lab, Belgium) with NaOH powder (98.2 % Prolabo, USA).

5.2.3 Compressive strength tests

Compressive strength tests were performed in pastes (20x20x40 mm³) in an Ibertest Autotest 400/10 equipment. For the compressive tests a 2.4 kN/s force rate was applied. Three types of pastes were prepared by mixing different time-stored samples (FG, 7d, and 30d) with either water or a sodium silicate solution, with an a Si/Na ratio of 1.2 and a Na molarity of 3.52 M. Finally, the pastes were tested after 7 and 28 days of hydration.

5.2.4 Fourier-transform infrared spectroscopy (FTIR)

The Fourier-transform infrared spectroscopy- Attenuated Total Reflection (FTIR- ATR) test was performed on all the anhydrous sample materials on a Bruker 400 MHz, model Avance III, USA, with 4 cm⁻¹ resolution and 24 scans.

5.2.5 X-ray photoelectron spectroscopy (XPS)

The bonding state of the Si in the hydrated calcium silicate binder was determined by X-ray Photoelectron Spectroscopy (XPS). Experiments were performed on a non-monochromatic spectrometer: XSAM 800 from KRATOS, Manchester, UK with an X-ray source of aluminum. The operating conditions, in FAT mode, were V=12 kV, I=10 mA; The analysis angle, TOA was 45° and the peak-fitting was performed with an XPSPeak4.1 freeware. Finally, the charge shift was corrected taking as reference the binding energy (BE) of Ca $2p_{3/2}$ from Ca²⁺ centered at 346.8 eV and the sensitivity factors acquired from Windows Vision 2 software library.

5.2.6 Scanning electron microscopy (SEM)

The SEM analysis on the anhydrous samples was made using a Hitachi S2400, Bruker (USA) operating at 20 keV. Before the observation, the powders were glued to the specimen stubs with carbon adhesive tape and sputtered with Pt/Au for 30 seconds using (Quorum Technologies, United Kingdom) to improve the conductivity of the surface.

The SEM analysis of the hydrated pastes was performed on a a ThermoScientific desktop scanning electron microscope (SEM), model Phenom ProX G6, with a CsB6 filament and equipped with a light elements energy dispersive spectroscopy (EDS) detector. The samples preparation consisted of drying the paste at 100°C for 24h, followed by a horizontal cut using a diamond saw. The pastes were then introduced into a mold with an epoxy resin and left to cure for 24h at 40°C. After the curing process, they were removed from the mold and further sectioned into smaller pieces using the diamond saw. Surface polishing was performed using 800 and 4000 grade silicon carbide papers from Struers. Finally, a 6-micra diamond spray was applied to the surface and polished using a polishing cloth. During the cuts and polishing steps, an ethanol-based solution from TESTA was used as a lubricant. For the SEM observation, each sample was placed on an Al stub using double-sided carbon tape and sputter coated with a thin Au/Pd film in a Quorum Technologies coater, model Q150T ES.

5.2.7 Thermal analysis

The content of total inorganic carbon of the anhydrous samples was analyzed by combustion at 950 °C under an oxygen atmosphere using an RC 612 elemental analyzer (LECO Corporation, Mönchengladbach, Germany). The temperature ranged from 80 °C to 950 °C at 20 °C/min.

5.3 Experimental Results

5.3.1 Calorimetric results

Calorimetric tests were performed in the FG, 7d, 30d, and 270d samples. The pastes were hydrated with either water (W) or with the alkaline solution of sodium silicate (A). The results are presented in Figure 5-1. The 270d sample did not present any reactivity, therefore the results are not shown. Both FG and 7d stored binders display a dormant period, followed by an acceleration and deceleration period. This behavior upon hydration, with the initial dormant period, is characteristic of AWH binders and was reported and discussed previously [25]. The results show that the pastes activated with

the alkaline solution have higher kinetic and higher values of heat released than the water-hydrated pastes. The results also show that the storage time influences the reactivity of the binder, which is more evident in the samples hydrated with water, where a delay in the reaction peak and the decrease of the amount of heat released with increasing storage time is observed. On the other hand, all activated samples presented a similar kinetic, showing a hydration peak after ~10 h. However, a decrease in the heat released is also observed on 270 days sample.



Time (davs) Figure 5-1.Calorimetric test of the samples FG,7d, and 30d, hydrated with either A) water, or B) sodium silicate solution.

5.3.2 Compressive strength results

To evaluate the mechanical performance with increasing storage time, compressive strength tests were performed with the binders stored for 7 days (7d) and 30 days (30d) and compared to a freshly ground (FG) sample. The pastes were hydrated with either

water or with the alkaline sodium silicate solution and compressive strength tests were performed after 7 and 28 days of curing, the results are shown in Figure 5-2.

It can be observed that after 30 days of storage, a significant decrease in compressive strength is observed, particularly in the water-hydrated pastes, suggesting a complete loss in reactivity in these samples. The alkaline activated paste also displays a loss in compressive strength with increasing storage time, nevertheless they still maintain competitive results even after 30 days of storage.



Figure 5-2. Compressive strength of pastes after 7 and 28 days of curing. The pastes were made with samples stored at different times, freshly ground (without storage), 7 and 30 days, and hydrated with either water (blue circles) or with an alkaline solution (orange triangles).

5.3.3 SEM results

The surface morphology of three anhydrous samples (FG, 7d and 270d) was observed using scanning electron microscopy (SEM) and is shown in Figure 5-3. No significant changes in the morphology of the surface could be observed [8,10].

Figure 5-4 displays the SEM images of alkaline activated pastes hydrated for over a year.

The pastes were made with either a 7d stored binder or an FG material. Both samples exhibit a heterogeneous surface, with unreacted particles of different shapes and sizes surrounded by a binding matrix. However, only the 7d stored sample paste displayed calcite crystals on its surface.



Figure 5-3.SEM images of the anhydrous samples A) FG sample 800x magnification B) 7d sample 800x magnification, C and D) 270d sample with a 1000x and 3000x magnification, respectively.



Figure 5-4. SEM images of the alkaline activated hydrated pastes after >1 year of storage. Top row (E and F) paste made with binders stored for 7 days. Magnifications: E 3000x; F 4000x. Bottom row (G and H) paste made with an FG sample. Magnifications: E 3000x; F 4000x. Bottom row (G and H) paste made with an FG sample. Magnifications: G 500x; H 2000x

5.3.4 FTIR results

The FTIR spectra of three anhydrous samples, 7d, 30d, and 270d, are compared with a freshly ground (FG) sample in Figure 5-5A and Figure 5-5B. The spectra of Figure 5-5A shows an absence of water in both samples, since the bands at 3390–3408 and 1640–1650 cm⁻¹, caused, respectively, by the stretching and bending vibration of H₂O, are not present. In the close-up spectra, Figure 5-5B, the 270d sample shows the following $CO_3^{2^2}$ characteristic peaks; 1550-1458cm⁻¹ attributed to asymmetric stretching mode and the signals at 875 and 712 cm⁻¹ caused by the in-plane bending modes [25,27,28]. In the region between 800 and 1100 cm^{-1,} there is a combination of symmetric and asymmetric stretching vibrations of the Si-O bands [25,29,30]. The Si-O typical vibrations are present in all the samples with a shoulder at 916 cm⁻¹, which corresponds to a stretching vibrations [29]. For the Si-O-Si structure, characteristic peaks present at

1082cm⁻¹, 719 cm⁻¹, and 455 cm⁻¹, correspond to a symmetric stretching vibration [30], a stretching vibration of a 3-member ring structure [25], and a bending rocking vibration [30], respectively.



Figure 5-5. A) Comparison of the FTIR spectra of the FG material (blue) with the 7d (brown), 30d (green) and 270d (red) samples; B) close up of the FTIR spectra.

5.3.5 XPS results

X-ray photoelectron (XPS) analysis was performed to better understand the storage impact on the chemical composition of the binder. The three samples under study (FG, 7d, 270d) displayed a similar chemical composition in calcium, silicon, and, in a small amount, aluminum. Residual amounts of potassium, sodium, and/or iron were also detected in some samples, although they were not quantified and are not shown. In Table 5-2, the quantification of each element in each sample is presented.

Floment	At. Conc. (%)						
Liement	FG	7d	270d				
С	25.2	29.4	35.3				
0	51.2	50.0	49.1				
Са	9.8	6.5	6.2				
Si	12.6	13.0	7.9				
AI	1.3	1.1	1.4				

Table 5-2 XPS quantification for anhydrous binders with different storage time

In Figure 5-6 the XPS spectra for the regions C 1s, O 1s, Ca 2p, and Si 2p, are displayed, respectively as A), B), C), and D). The C 1s spectrum was fitted with a minimum of 3 components, centered at 284.4 ± 0.1 eV, 286.7 ± 0.4 eV, and 289.2 ± 0.1 eV, assigned, respectively, to graphitized carbon, carbon singly bonded to oxygen (C-O and/or epoxides) and carbonates.



Chapter 5. On the influence of storage time on the reactivity of an amorphous wollastonitic hydraulic binder

Figure 5-6. XPS regions (A) C 1s; (B) O 1s; (C) Ca 2p; and (D) Si 2p.

The identification of the different oxidized species is clearer after the spectra subtraction in Figure 5-7, the difference between the 7 days stored sample and the freshly ground sample is shown as a black line, and the difference between the 270 days stored sample and the 7 days, as an orange line. In Figure 5-7A, C 1s difference plot, the black line indicates that after 7 days of exposure to ambient conditions, there is an increase in the

amount of graphitic carbon as well as carbonate groups. The orange line shows that the relative amount of carbonate continues to grow after 270 days. This is compatible with CaO being transformed into $CaCO_3$, which is also seen in the O 1s differences plot of Figure 5-7B.

In the O 1s difference plot (Figure 5-7B), the black line shows the change after 7 days: a decreasing amount of CaO (negative peak corresponding to oxygen in the oxide centred around 530.0 eV) accompanied by an increasing amount of $CaCO_3$ (positive peak assigned to oxygen in carbonate groups peaking around 532 eV). These two peaks present a relative ratio between their areas of approximately 1:3, which fairly represents the transition of the oxygen from CaO to the three oxygens existing in the CO_3^{2-} group. After 270 days, the difference between the O 1s spectra for 270 days and 7 days (orange line) shows that the decrease of the component at 530 eV is, within the experimental error, the same as for the period from 0 to 7 days exposure (black line). Therefore, the rest of the difference should also be identical. In Figure 5-7B), the orange line, representing the difference in the signals of the samples exposed for 7 days and 270 days, reveals a negative peak at binding energies between ~532 and 533 eV. This may indicate that, besides the increase of oxygen that should appear in that binding energy range due to the increase of the CaCO₃ amount, there is a decrease of oxygen involved in another type of oxygen bonding at later ages. A good candidate is the oxygen bonded to silicon (which appears in the same binding energy range) since Table 5-2 shows a large decrease of silicon from the sample 7d to the sample 270d.





Figure 5-7. A) C 1s and B) O 1s spectra subtractions: "After 7 days" = (7d – not exposed (FG) black line; "After 270d" = (270d-7d), orange line.

5.3.6 Thermal analysis

The thermal analysis results are shown in Table 5-3, from which it can be observed that the carbon release increases with storage time. Assuming that all carbon comes from the carbonation of the binder it is possible to quantify the percentage of $CaCO_3$ that was formed at the surface of the anhydrous powder particles. Figure 5-8 plots the evolution of the carbonated sample fraction with time, where it is possible to see that the carbonation rate tends to rapidly decrease for later ages, possibly indicating a lack of CaO available to react or the limited access of atmospheric CO_2 to continue the carbonation reaction.

Table 5-3. Carbon released of the FG, 7d, and 270d anhydrous samples.

Sample	%wt of carbon released	%wt of CaCO ₃ in the sample
FG	0.009	0.080
7d	0.051	0.425
270d	0.130	1.082



Figure 5-8. Plot of wt% $CaCO_3$ vs. days of exposure for the samples FG, 7d and 270d. The dashed line is just a guide for the eye and do not represent any theoretical fit.

5.4 Discussion

The results of this study indicate that, similarly to OPC, the storage and aging of the slaglike binder influence its properties, delaying the hydration reaction and reducing its mechanical performance, especially when only water is used for its hydration. In OPC this decrease of reactivity is a consequence of the formation of pre-hydration products on the anhydrous grains, mainly caused by the reaction of atmospheric water molecules with OPC.

This study indicates that, even though the AWH binder is hydraulicaly active, the decrease in reactivity is essentially caused by the carbonation reaction that occurs on its surface, and not due to the interaction with water molecules. This is suggested by the FTIR results, due to the absence of the characteristic bands associated with the H₂O bonds and by SEM images, due to the round aspect of the surface grains, instead of the needle-like structure characteristic of the product between water and the binder (C-S-H). Moreover, both FTIR and XPS techniques were able to identify the presence of CO₃²⁻. Although, while FTIR was only able to detect CO₃²⁻ in the 270 days stored sample, in the XPS analysis it was possible to detect it after 7 days of storage. Furthermore, the attenuation of the signals of chemical species such as silicon on the XPS results suggests that a layer of CaCO₃ covered the particle's surface and consequently decreased its signal. The existence of the layer can be inferred by the decrease of the amount of silicon after 30 days, Table 5-2, and in the O 1s spectra subtractions negative peak, between 532 and 533 eV on the 270 days stored sample, Figure 5-7 B).

It was expected that the differences in the spectra from 7 days to 270 days stored samples could be only attributed to the reaction CaO + CO₂ \rightarrow CaCO₃. This would imply that, since the difference between 270d and 7d is the same as the difference between 7d and FG, in the region assigned to O in CaO, the differences in the region assigned to O in CaO₃ should also be the same. However, the experimental results showed that the differences are similar in the CaO BE range and very different in the CaCO₃ range as displayed in Figure 5-6. Figure 5-9 shows the spectrum that should be added to the 270d O 1s spectrum to obtain similar differences between the two pairs of conditions (270d vs 7d and 7d vs FG sample= in the entire BE range. Therefore, it is clear that, in the O 1s region of sample 270d, besides the expected increase of the signal assignable to the O in CaCO₃, there is a simultaneous decrease of the signal corresponding to the O in aluminosilicates and silicon hydroxides and also in a small amount of O in water. The decrease of the signals coming from the silicon-based compounds (O 1s and Si 2p regions) may be explained by the growth of CaCO₃ on the surface that attenuates the signal from the underneath layers. Since the signal is attenuated but not decreased to 0,

it means that the layer has an island-like structure or, if continuous, it has on average a thickness less than 10 nm, the escape analysis length in XPS for these photoelectrons' kinetic energy range.



Figure 5-9. Presumed XPS O 1s peak which, when added to the 270d spectrum would produce a difference between 270d and 7d similar to the difference between 7d and FG in the entire BE range.

In Figure 5-10 it is presented a schematic representation of the observed aging process in the AWH binders. The formation of the CaCO₃ layer around the surface grains caused a decrease in the chemical reactivity of the binder, as demonstrated in the calorimetric test results with the delay of the hydration peak and the decrease of the heat released with the increase of storage time. The XPS and FTIR results strongly indicate that this is due to the decrease of solubility of the sample caused by the CaCO₃ layer that forms around the surface. This layer inhibits the dissolution of the [SiO₄]⁴⁻ and Ca²⁺ ions, causing a decrease in reactivity of the binder, resulting in lower compressive strength.

Even though the pastes hydrated with the alkaline Na₂SiO₃ solution were able to obtain competitive results, allowing a higher shelf-life, they also registered a decrease in the compressive strength, highlighting the importance of proper storing of alkali activated precursors. The pre-carbonation of the sample led to slower hydration kinetics and to the formation of calcite crystals on the surface of the alkaline activated pastes, as

observed on the SEM images in Figure 5-4.



Figure 5-10. Schematic model for the aging mechanism of a binder's grain.

5.5 Conclusions

This work investigates the aging of an AWH binder, shedding light on its impact on chemical reactivity and strength in pastes. The primary outcomes of our study are as follows:

- Despite its hydraulic ability, the anhydrous stored binder exhibits no reactivity with ambient moisture; instead, exposure to atmospheric conditions initiates a reaction with CO₂ present in the atmosphere. This result was expected, as the AWH binder exhibits lower reactivity during water hydration than OPC. Consequently, it decreases the tendency to form pre-hydration products due to the lower hydraulic capabilities of the material.
- The interaction between CO₂ and the anhydrous stored material triggers the carbonation on the surface of the powder, leading to the gradual prevalence of a CaCO₃ layer over time.
- 3. Our experimental findings strongly indicate that the formation of the CaCO₃ layer hinders binder dissolution, consequently delaying the hydration reaction. This reduction in reactivity manifests as a decline in compressive strength with prolonged storage.

In summary, this study suggests that the aging process in this binder is primarily induced by the carbonation reaction occurring on particle's surfaces. The resulting CaCO₃ layer acts as a barrier during binder hydration, decreasing its solubility and increasing resistance to water diffusion into the grain bulk. Notably, the activation of the binder with an alkaline Na₂SiO₃ solution effectively mitigates these aging effects.

These findings not only contribute to the fundamental understanding of the AWH binder behavior but also hold practical implications for enhancing the durability and performance of cementitious materials in real-world applications.

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CHAPTER 6. The use of solid sodium silicate as activator for an AWH binder activator

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Contents

CHAPTER 6. The use of solid sodium silicate as activator for an AWH binder activator	. 149
6.1 Introduction	. 152
6.2 Materials and Methods	.154
6.2.1 Production of the Binder	.154
6.2.2 Production of the Alkaline Activator	.155
6.2.3 Analysis of the Activators: Fourier Transform Infrared Spectroscopy (FTI	R) . 157
6.2.4 Analysis of the Activators: X-ray Diffraction (XRD) Analysis	. 157
6.2.5 Production of the Activating Solution	. 157
6.2.6 Production of Pastes	. 157
6.2.7 Isothermal Calorimetry	158
6.2.8 Production of Mortars	158
6.2.9 Thermogravimetric Analysis (TGA)	158
6.3 Results	159
6.3.1 Characterization of the Activators by FTIR	. 159
6.3.2. Characterization of the Activators by XRD	. 161
6.3.3 Isothermal Calorimetry Results	. 162
6.3.4 Compressive Strength Results	. 163
6.3.4.1 Pastes	. 163
6.3.4.2 Mortars	. 164
6.3.5. TGA	. 165
6.4 Discussion	. 167
6.5. Conclusions	.169
6.6 References	. 170

To ensure an acceptable mechanical strength of amorphous wollastonitic hydraulic binders (AWHs), activation with a sodium silicate solution is necessary. However, the use of this type of activator increases the final cost and the complexity of the products' overall use. This chapter focuses on enhancing the manufacturing of the alkaline activator by producing three Na₂SiO₃ powders using cost-effective raw materials. The procedure consisted of heating a mixture of NaOH pebbles with either sand, glass, or diatomite to a temperature of 330 °C for 2 h. After synthesis, the powders were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD) techniques. Finally, mortars made with AWHs were activated using the synthesized powders that were added either as a solid or dissolved in an aqueous solution. The compressive strength results in these mortars show that the lab-made activators are competitive with the traditional sodium silicate activators. Furthermore, the synthetized activators can be added in either solid form or pre-dissolved in a solution. This innovative approach represents a more economical, sustainable and easy-to-use approach to enhancing the competitiveness of AWHs.

6.1 Introduction

The carbon dioxide emitted in the production of Ordinary Portland Cement (OPC) is responsible for a significant part of global CO_2 emissions [1]. An alternative that has been studied since the 1960s is the substitution of OPC for Alkaline Activated Materials (AAMs) [2,3], which can reduce CO_2 emissions by up to 55–75% [2–5]. AAMs are formed in an alkaline environment that promotes the dissolution of the aluminosilicate precursors, which can originate from either natural or industrial waste materials [5,6]. Glukhovsky et al. [7] classified the alkaline activators into the following six categories, in which M represents an alkali group:

- 1. Alkalis, MOH;
- 2. Weak acid salts, M₂CO₃, M₂SO₃, M₃PO₄, and MF;
- 3. Silicates, M₂O.nSiO₃;
- 4. Aluminates, M₂O.Al₂O₃;
- 5. Aluminosilicates, M₂O.Al₂O₃. (2–6) SiO₂;
- 6. Strong acid salts, M₂SO₄.

The activation process involves breaking the covalent bonds Si–O–Si and Al–O–Si due to the alkaline pH of the solution, leading to the formation of a colloidal phase, followed by coagulation, which eventually results in a condensed structure [2]. Research on these binders has shown not only good mechanical and durability properties, but also low heat of hydration, high impermeability, and resistance to extreme temperatures, sulfates, sea spray and acid attacks [8]. These promising features make them attractive for various applications.

Previous studies showed that sodium silicate (Na_2SiO_3) solutions are efficient activators for amorphous wollastonitic hydraulic binders (AWHs) [9]. However, the use of Na_2SiO_3 can be challenging due to its corrosiveness [10] and significant environmental impact caused by its high embodied energy [11,12]. Hence, the production of a green, low-cost, and easy-to-use activator is necessary.

Several studies have focused on the synthesis of this activator [13,14] using different silica-rich sources as raw materials. These sources include low-value, silicate-rich wastes [15–18], and bio-derived materials [19,20]. There are two main routes of synthesis that can be applied [21], a thermochemical method and a hydrothermal method. The thermochemical method consists of mixing the silica-rich powder with a sodium hydroxide powder using a temperature of 450–600 °C [14,19,21], and the

hydrothermal method consists of dissolving the silica-rich materials in an alkaline solution at a temperature $100 \circ C$ [15–18]. Therefore, products produced using the hydrothermal method are liquid and require less energy for production [21]. In both cases, the concentration of the alkaline material [21], the particle size distribution, and the amorphous content of the silica source influence the reaction process [14], since smaller particles have higher SiO₂ extraction capabilities and amorphous phases display higher solubility [14]. Finally, to analyze the formation of condensed and uncondensed silica [18] and to confirm the characteristic bands associated with the sodium silicate spectra [17], the final product can be characterized by FTIR.

The different routes and raw materials used in the production of the activator may affect its application with the binder, since these factors influence the rate of silicate release in the system [14], and consequently the hydration kinetics, compositions, crystalline phases, and mechanical strength of the AAM [14].

Sasui et al. [11] synthesized an alkaline activator by dissolving waste glass powder in a 4M NaOH solution and successfully enhanced the properties of class-C fly ash and ground granulated blast furnace slag. Moreover, they also reported that by increasing the amount of dissolved waste glass powder in the alkaline solution, a higher silicon concentration and increased reactivity was observed. According to Toniolo et al. [22], increasing the amount of waste glass and the molarity of the NaOH solution leads to the formation of zeolite crystalline phases, which in turn enhances the mechanical strength of the final product. However, when using a solution with high NaOH content, it is necessary to balance the reactivity and the structural integrity of the hydration product, since, even though high values (e.g., 10 M) accelerate the dissolution rate of the aluminosilicate precursors, they also promote the disintegration of the network structure after 28 days of curing [22].

Another innovative approach was proposed by Vinai et al. [23]. These authors produced a sodium silicate powder by mixing glass powder, sodium hydroxide powder and water. This mixture was heated at temperatures ranging from 150 to 330 °C for 2–4 h.The results show that the binder hydrated with the lab-made activator obtained similar compressive strength results to those binders activated with commercial solutions. This represents a significant cost reduction in activator production, depending essentially on the cost of the NaOH, which accounts for 95% of the activator cost [23].

This study is focused on the synthesis of a Na_2SiO_3 powder using various raw materials. To this end, the method proposed by Vinai et al. [23] was implemented, while also exploring alternative raw material sources such as sand and diatomite as replacements for glass powder. The synthesized powders were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD). The reactivity of the powders was assessed by isothermal calorimetry in activated pastes made with the AWH binders. The synthesized powders were introduced either as a solid or in a solution. Finally, the performance of the activators, both as a solid and in solution, was tested in AWH-based mortars by measuring their compressive strength after 2, 7, and 28 days. This chapter aims to present a cost-effective and environmentally friendly alternative for the production and application of Na₂SiO₃ alkaline activators, and to enable the activation of the AWH binder using a more affordable, environmentally sustainable, and user-friendly approach.

6.2 Materials and Methods

6.2.1 Production of the Binder

The AWH binder was made using common cement clinker raw materials, with adjustments in the overall chemical composition to obtain a total C/S molar ratio of 1.05. The raw materials were ground, mixed, and compressed into a disc, which was then broken into four pieces and introduced into a silicon carbide crucible. The filled crucible was first heated in an electric furnace to 900°C, using a rate of 25°C/m, and in order to fully decarbonate the raw meal, this temperature was maintained for 1h. Then, the temperature was increased to 1550°C and kept for 1 h to ensure the complete melting of the mix and its chemical homogenization. Finally, the molten material was quenched into a water container. The final product was characterized by XRD analysis, and it displayed an amorphous content of 91.8% and 8% of pseudowollastonite. In Table 6-1, the chemical composition of the produced clinker is displayed. The AWH clinker was then ground with a ring mill for 3 min, obtaining a final Blaine fineness around 4580 cm²/g.

Table 6-1 Chemical composition	of the AWH clinker	produced wt %.
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wt. %	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	Others
AWH	48.7	2.1	0.7	47.4	0.3	0.1	0.3	0.1	0.1

6.2.2 Production of the Alkaline Activator

Three activators were produced using either glass, sand or diatomite as a source of silica. A recycled glass cullet was crushed in a jaw crusher, followed by 3 min of milling in a ring mill. Regarding the sand, AFNOR sand was milled for 3 min in a ring mill, while diatomaceous earth from Rio Maior, Portugal was first crushed in a jaw crusher, followed by 3 min of milling in a ring mill.

To all silica-rich raw materials, commercial-grade NaOH pebbles (98.2% Prolabo, Matsonford, PA, USA) and 10 mL deionized water were added to obtain a final product with a Si:Na ratio of 1 and to facilitate the mixture of the raw materials. The mixture was then stirred with a laboratory rod until a homogeneous paste was obtained. To prevent overflowing, the samples were introduced into the furnace at room temperature and then heated to 330 °C and left for 2 h. After removing from the furnace, the material was cooled to room temperature. Before being mixed with the binder, the solid activators produced were manually milled. The chemical composition of the raw materials used in the production of each activator is shown in Table 6-2. Figure 6-1 depicts each of the mixtures before and after the heating process.

wt. %	SiO ₂	AI_2O_3	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	Others
Glass	72.4	1.8	0.3	8.0	4.1	0.1	0.7	13.1	
Sand	94.9	2.2	0.7	0.0	0.0	0.0	0.8	0.1	<0.05
Diatomite	80.5	7.9	2.4	0.2	0.2	0.1	0.7	0.1	

Table 6-2. Composition of the raw material used in the production of the activator, wt.



Figure 6-1. Lab-made activator before and after the heating process. (A) Glass based activator, (B) sand- based activation, (C) diatomite-based activator.

6.2.3 Analysis of the Activators: Fourier Transform Infrared Spectroscopy (FTIR)

The produced activators were analyzed using FTIR-ATR and X-ray diffraction tests and compared to a standard anhydrous sodium silicate (EastChem, Qingdao, China). The FTIR tests were performed on a Bruker 400 MHz, model ALPHA, operating with a Platinum ATR module, with 4 cm-1 resolution over 24 scans.

6.2.4 Analysis of the Activators: X-ray Diffraction (XRD) Analysis

The XRD analysis was performed using an X'Pert Pro (PANalytical, Overijssel Netherlands) diffractometer with monochromatic CuK α 1 radiation (λ = 1.54059 Å) and working in reflection geometry (θ /2 θ). The optics configuration was a fixed divergence slit (1/2°), a fixed incident anti-scatter slit (1°), a fixed diffracted anti-scatter slit (1/2°), and X'Celerator RTMS (Realtime Multiple Strip) detectors, working in scanning mode with the maximum active length. Data for each sample were collected from 5° to 70° (2 θ). The samples were rotated during data collection at 16 rpm to enhance particle statistics. The X-ray tube worked at 45 kV and 40 mA.

6.2.5 Production of the Activating Solution

For this study, we prepared three types of solutions, with a SiO₂/Na₂O modulus (MS) of 1 and a Na₂O molarity of 3.516 M. The first solution was a standard sodium silicate solution, obtained by mixing Na₂SiO₃ (Na₂O: 7.5–8.5%, SiO₂: 25.5–28.5%, Chem Lab, Zedelgem, Belgium) with NaOH (98.2%, Prolabo, Matsonford, PA, USA). The second solution was made using anhydrous sodium silicate (EastChem, Qingdao, China) combined with solid NaOH (98.2%, Prolabo, Matsonford, PA, USA); this mixture was then dissolved in deionized water. Lastly, the third type of solution was made by dissolving the lab-made activator powder into deionized water.

6.2.6 Production of Pastes

Pastes were prepared with a water/solid ratio of 0.25. The lab-made activators were introduced in two ways: either as a solid directly mixed with the anhydrous binder, or predissolved into a solution. To the aqueous solution the solids were introduced and mixed for 90 s using a bench-top mixture. The resulting pastes were molded into inox steel molds with 20x20x40 mm³ dimensions and cured at 20°C under relative humidity (HR) conditions above HR95% during the entire experiment. The samples were demolded after 2 days and left to cure under the same conditions. Finally, one compressive strength test per age was performed at 2, 7, and 28 days of hydration in an Ibertest Autotest 400/10 instrument using a constant force rate of 2.4 kN/s during the test.

6.2.7 Isothermal Calorimetry

For the isothermal calorimetry tests, pastes made with the AWH binder, and with a water/solid ratio of 0.25, were introduced into vials via ex situ in an A TAM Air instrument (Waters Sverige AB, Sollentuna, Sweden). The tests were run at a constant temperature of 20 °C.

6.2.8 Production of Mortars

Mortars were prepared by mixing the binder with the solution using a water/solid ratio of 0.365, and by adding 1350 g of AFNOR sand. The lab-made activators were introduced in two ways: either as a solid, directly mixed with the anhydrous binder, or pre-dissolved into the solution. The mixing was performed in a Tonimix mixer from ToniTechnik according to the procedure defined in the EN 196-1 standard; the resulting mortar was introduced in 40x40x160 mm³ inox steel molds and left to cure at 20°C under HR conditions above HR95% during the entire experiment. The samples were demolded after 1 day and left to cure under the same conditions, and one replica per age was teste. Finally, one replica per age was tested, which included one flexural test and two compressive strength tests after 2, 7, and 28 days of hydration in an Ibertest Autotest 400/10 instrument. For comparison purposes, a mortar made with a standard sodium silicate solution was also prepared.

6.2.9 Thermogravimetric Analysis (TGA)

The material obtained from the compressive strength test was manually ground and dried at 105°C to eliminate any residual evaporable water. Then, to calculate the amount of bound water (BW) in the hydrated phases, thermogravimetry analysis was performed by calculating the weight loss of the pastes and mortar over time at specific temperature intervals. The analysis was made in an ELTRA multichannel TGA device, with constant heating rates at fixed temperatures of 105, 250, 500, and 950°C until a stable mass was reached. The heating rates varied: 4°C/min from room temperature to 105°C, 10°C/min from 105C to 250°C, and 15°C /min from 250°C to 500°C and between 500°C and 950°C. Finally, the amount of BW was calculated according to the mass loss between 105 and 500°C.

6.3 Experimental Results

6.3.1 Characterization of the Activators by FTIR

The FTIR results of the lab-made activators are compared with a standard solid sodium silicate (EastChem), as shown in Figure 6-2.



Figure 6-2. Comparison of the FTIR results of the synthesized activators with a standard, commercially available EastChem powder.
The principal bands of the FTIR spectra are identified as follows:

- A. Broad band between 2500 and 3800 cm⁻¹ associated with O–H stretching vibration [24,25];
- B. CO₃²⁻ characteristic bands at 1450 cm⁻¹ attributed to asymmetric stretching mode [25];
- C. Bands 1050–1100 cm⁻¹ characteristic of stretching Si–O–Si bond [20,24,26];
- D. Band at 973 cm⁻¹ attributed to the Si–O symmetric stretching [25];
- E. Band associated with Si–O–Si asymmetric stretching vibration, specifically Q⁰ and Q¹ at 850, 900 cm⁻¹ [14,27];
- F. CO₃²⁻ characteristic bands at 712 cm⁻¹ caused by the in-plane bending modes [28–30].
- G. The band at 680 cm⁻¹ can be attributed to the bending motion of oxygen bonds [27];
- H. Al–OH bending vibrations at ~590–570 cm⁻¹ [31] and bands associated to Si–O– Al–O bonds at 459–572 cm⁻¹ [16].

The broad band observed between 2500 and 3800 cm⁻¹ (A) in the glass and diatomitebased activators suggests either water adsorption [24,25] or a more complex structure, since an increase in these bands is also linked to an increase in OH– groups at the surface of polymerized silica [24]. The results also reveal the presence of CO_3^{2-} bands in the glass and diatomite-based samples at 1450 and 712 cm⁻¹ [25].

The strip highlighted as (D) reveals that all spectra exhibit a band at 950 cm⁻¹, indicating the presence of the Na–O–Si bond [20], suggesting an effective reaction [20]. In the diatomite-based sample, the band is broader, possibly due to the higher amount of Si–O–T (T = Si, Al) structures (946 cm⁻¹) [32].

The doublet at ~890 indicates the presence of Q^0 structures at 850 cm⁻¹and Q^1 structures at 900 cm⁻¹ [27]. The bands at 875 cm⁻¹ and 712 cm⁻¹ can be attributed to the in-plane bending mode of CO₃²⁻ [28–30].

All samples exhibit characteristic bands of Al–O bonds at 580 cm⁻¹ [31]; however, the diatomite-based sample has a broader band compared to the other spectra, displaying a band at 572 cm⁻¹, which can be attributed to Si–O–Al–O bonds [16]. This may be a result of a higher Al content on the raw material of the activator.

6.3.2. Characterization of the Activators by XRD

In Figure 6-3, the XRDs of the lab-made activators are compared with those of the commercially available EastChem sodium silicate powder. All samples displayed a crystalline structure, and the following nomenclature was given to the identified peaks: $1-Na_6Si_2O_7$ [23], $2-Na_2SiO_3$ [20], $3-CaAl_2O_4$ [23], $4-CaAl_2O_4$ [23] and $5-Na_2CO_3$ [33]. The samples produced with sand and diatomite presented a peak at 26.6° (20) (Q), which is indicative of the presence of unreacted silica [16]. Both activators were prepared using silica-rich raw materials with a higher crystalline content than glass, which is predominantly amorphous. This difference may have affected the SiO₂ solubility and, consequently, the reaction process.



Figure 6-3. Comparison of the XRD results of the synthesized activators with a powder bought from EastChem. 1—Na₆Si₂O₇, 2—Na₂SiO₃, 3—CaAl₂O₄, and 4—Na₂CO₃. Q— unreacted silica.

6.3.3 Isothermal Calorimetry Results

The calorimetry results for activated pastes prepared with different activator types, introduced as liquid or solid, are shown in Figure 6-4, which displays the normalized heat flow and cumulative heat for each of the tested pastes.



Figure 6-4. Isothermal calorimetry results of the AWH pastes hydrated with sodium silicate activators produced with different raw materials. Activators were added either as a solid (top row) or as a solution (down row).

The experimental heat evolution curves can be divided into three main stages —a first stage, where a slow kinetic reaction can be observed, followed by an acceleration period, characterized by a high release of heat rate, and finally a deceleration period, where a decrease in the rate of the reaction is observed. Traditionally, in OPC, these stages are related to the dissolution of ionic species, the formation of C-S-H, and the densification of the matrix [9,34,35].

With the exception of the glass-based activator, which already contained absorbed water (see FTIR results), all samples displayed two exothermal peaks. This corresponds to different phenomena, such as the water adsorption by the precursor [36] and the formation of different hydration products beside C-S-H, such as C-A-S-H gel [36], since the diatomite-based activator has a higher Al content. Amongst the lab-made activators,

the sand-based samples exhibited the highest cumulative heat released after 2.5 days of hydration, suggesting a more extensive reaction. On the other hand, the diatomitebased sample displayed the lowest cumulative heat released, indicating a lower formation of hydration products. This may be attributed to the higher complexity of the raw materials and a higher level of impurities in the activator.

6.3.4 Compressive Strength Results

6.3.4.1 Pastes

After 2, 7, and 28 days of hydration, compressive strength tests were performed on the pastes. The results are displayed in Figure 6-5. At early ages, 2 and 7 days, the compressive strength was similar in all tested samples, ranging from 15 to 23 MPa and 57 to 73 MPa, respectively. Notably, the lowest compressive strength observed at 2 days corresponds to the diatomite-based activated sample, which also registered the lowest cumulative heat, as determined by isothermal calorimetry, suggesting the formation of a lower amount of hydration products at this age.



Figure 6-5 Paste compressive strength results, activated either with the lab-made activators or with the commercial solution.

However, a significant discrepancy is observed in the 28-day results, particularly for the pastes prepared with a solution of sand-based activator and the solid form of diatomitebased activator. In these samples, the compressive strength was 67 and 70 MPa, respectively, which contrasts with the values obtained for the other systems prepared, which achieved compressive strength values of 96–97 MPa in the case of solid-form activators, and over 100 MPa when considering the solution-form activators.

6.3.4.2 Mortars

After 2, 7, and 28 days of hydration, compressive strength tests were performed on the mortars, and the results are displayed in Figure 6-6. After 7 and 28 days of curing, all tested samples displayed similar compressive strengths. However, similarly to the paste results, the diatomite-based sample exhibited the lowest value after 2 days of hydration.



Mortar Compressive strength after 2, 7 and 28 days

Figure 6-6. Comparison of the compressive strength results of the mortar activated using the standard alkaline solution (grey bars) with those of the mortars activated

6.3.5. TGA

Table 6-3 displays the experimental TGA data obtained for pastes and mortars tested after 2, 7 and 28 days of curing. It includes the respective loss on ignition (LOI) during the 105–250°C, 250–500°C, and 500–950°C steps. The step from room temperature to 105°C is not included, as it only relates to the humidity in the sample. To obtain the amount of BW in the sample, only the results at 105–250°C and 250–500°C were considered.

Type of	Activating	2 days			7 days			28 days		
Sample	Conditions	LOI 250°C	LOI 500°C	LOI 950°C	LOI 250°C	LOI 500°C	LOI 950°C	LOI 250°C	LOI 500°C	LOI 950°C
	Solid Glass	1.55	0.96	0.42	1.64	1.32	0.76	1.72	1.99	0.60
	Solution glass	1.75	0.94	0.39	1.75	1.10	0.49	1.95	2.28	0.56
	Standard	1.18	0.90	0.24	1.89	1.15	0.35	1.99	2.24	0.56
Pastes	Solid diatomite	1.55	0.90	0.34	1.45	1.97	0.51	1.94	2.02	0.59
1 00000	Solution diatomite	1.50	0.92	0.11	1.59	1.69	0.45	1.84	2.21	0.57
	Solid sand	1.80	1.01	0.25	1.56	1.81	0.53	2.32	1.74	0.74
	Solution Sand	1.72	1.06	0.30	1.60	1.85	0.74	1.86	2.35	0.81
	Solid sand	0.51	0.49	0.22	0.65	0.40	0.18	0.94	0.86	0.65
	Solution sand	0.57	0.08	0.14	0.52	0.52	0.15	0.70	0.46	0.43
	Solid glass	0.53	0.26	0.02	0.62	0.73	0.11	0.76	0.45	0.26
Mortars	Solution glass	0.57	0.23	0.22	0.63	0.46	0.09	0.82	0.57	0.26
	Solid diatomite	0.38	0.30	0.05	0.62	0.43	0.34	0.64	0.67	0.60
	Solution diatomite	0.46	0.21	0.11	0.44	0.59	0.27	0.83	0.57	0.25

Table 6-3. TGA results for pastes and mortars tested at 2, 7, and 28 days, indicating LOI at specific temperature steps (250°C, 500°C, and 950°C).

Since the strength development of the samples is directly related to the hydration process, it is possible to relate the compressive strength with the chemical BW. Furthermore, assuming the model of Richardson and Qomi [37,38], a relation between the bound water and the amount of C-S-H can be established, according to Equation (6-1).

$$\frac{H}{S} = \frac{19}{17} \times \frac{C}{S} - \frac{7}{17}$$
(6-1)

Where the H/S ratio is considered for a tobermorite-like C-S-H gel structure and a C/S ratio of 1.1 is assumed, resulting in a C_xSH_y approximated structure with x = 1.1 and y = 0.82 [9,39]. Therefore, by considering the chemical composition of the hydrated product and the BW content of each sample, determined by the weight loss between 250 and 500 °C in the TGA results, the wt. % C-S-H can be determined.

Using these data, it is possible to plot the weight percentage of C-S-H against the compressive strength of every sample, as shown in Figure 6-7 for pastes (blue line) and mortars (orange line); the obtained correlations are displayed in Equations (6-2) and (6-3).

Compressive strength mortars (MPa) = 6.7(%C-S-H) - 32.1 R² = 0.8 (6-2)



Compressive strength paste (MPa) = 4.6(%C-S-H) - 79.4 R² = 0.8 (6-3)

Figure 6-7 Correlation between the wt. % C-S-H formed and the compressive strength, for both pastes (blue line) and mortars (orange line). The blue crosses represent the results for the 28-day hydrated pastes that underperformed in the compressive strength tests, the solid diatomite-based and solution sand-based activated pastes.

6.4 Discussion

In this work, different sodium silicate powders were synthesized by mixing NaOH with different silica sources as raw materials. To assess the degree of reaction and understand the composition and structural characteristics of the resulting powders, FTIR and XRD analyses were performed. The XRD analysis showed that the powders have different crystalline phases; the identified peaks can be attributed to sodium silicate with different SiO₂:Na₂O ratios, with Na₆Si₂O₇ and Na₂SiO₃, calcium aluminum oxide CaAl₂O₄, and sodium carbonate Na₂CO₃. These results indicate a successful synthesis of the material; nevertheless, the diatomite- and sand-based activators exhibited a peak at 26.6° (2θ), indicating the presence of unreacted silica in the final product. Furthermore, when analyzing the FTIR spectra on both the glass- and diatomite-based activator, evidence of -OH bonds was found. In the glass-based activator, this band is broader, stretching between 3700 and 3100 cm-1, indicative of the hydration of the powder. In the diatomite-based powder, this band is narrower and centers around 3400 cm-1, which is characteristic of the OH in NaOH [40], revealing a residual presence of the raw materials and an incomplete reaction. The lab-made activators were then used to activate the AWH binder. Both were added in solid form and in aqueous solution form. Their reactivity was followed by calorimetric analysis, and the results show that the state at which the activator was added did not significantly influence the hydration reaction. After 2.5 days, all tests indicated a comparable cumulative heat, ranging from 47 to 61 J/g. Nevertheless, the sand- and the glass-based activators presented a slightly higher cumulative heat when added as a solid, while the remaining activators showed better results when introduced as a solution.

The influence of different forms of sodium silicate introductions in the compressive strength is an area of ongoing investigation [36,41]. In this study, the pastes' compressive strength results show that the main difference was observed at 28 days in the pastes prepared with a solution of diatomite-based activator and the solid form of the sand-based activator.

Nevertheless, when observing the amount of C-S-H formed in these two pastes (blue crosses in Figure 6-7), the results are similar to those of the other tested samples. Therefore, this underperformance might be related to some defects in the test specimens, since, in both cases, their respective activating conditions (solid or aqueous solution) present compressive strength values within the expected range, and comparable with commercially available activators.

167

Similarly, Gong et al. [36] also reported that when solid sodium silicates are introduced, mechanical properties comparable to the standard method of activation are obtained. These results also allow one to discard any influence of the activator form from the results obtained in this study, suggesting that both forms can be used without compromising mechanical performance.

Considering all the results from the mortar tests, mean compressive strength values and their respective standard deviations were calculated for each age, and the results are displayed in Table 6-4. The higher discrepancy at early ages may be linked to variations in the silica release rates of the activators and the differences observed in the kinetic rate in the calorimetric results. Nevertheless, the standard deviations obtained at 7 and 28 days are within the experimental error [42], indicating that at later ages all samples exhibited similar behaviors.

Table 6-4.	Mean	compress	ive strei	ngth of a	all teste	d mortars,	and	respective	standa	ırd
		dev	viation a	t differe	nt hydra	ation times	6.			

Hydration	Mean Compressive Strength	STD
Time	(MPa)	Deviation
2 days	8.4	4.0
7 days	36.0	1.6
28 days	59.5	2.8

In conclusion, when tested on mortars, the compressive strength results show that all the lab-made activators were competitive with traditional sodium silicate solution, regardless of the state in which the activator was incorporated. These results also point to the possible defects of paste test specimens that underperformed at 28 days.

Finally, a strong correlation between the amount of C-S-H formed and the compressive strength was established for both mortars and pastes (Figure 6-7), strongly suggesting that the mechanical properties of the sample depend on the formation of this hydration product. These results correlate well with those from a previous work [43], wherein mortars were prepared with a similar hydraulic binder under alkaline activation conditions, showing that similar C-S-H gels were produced in both studies.

Furthermore, by analyzing the trend lines obtained in Figure 6-7, it is possible to identify the minimum amount of C-S-H required for the sample to develop compressive strength: ~17 wt. % for pastes and 5 wt. % for mortars. Nevertheless, when compared to previous results for OPC pastes [9,43], we observed that the minimum wt. % C-S-H required for this material was ~35 wt. %. This low limit for the minimum amount of C-S-H in the

AWH sample maybe related to the presence of hydration products with a lower C/S ratio. Previous studies reported that the hydration products of this binder are characterized for having a C/S ratio of 1.1 and have the particularity of producing tobermorite 9 Å [44,45]. This characteristic allows the formation of a C-S-H structure with improved mechanical properties, specifically in terms of hardness and stiffness [38,44].

6.5. Conclusions

In this work, different lab-made Na_2SiO_3 powders were synthesized by using low- cost raw materials, such as diatomite, sand and glass waste. FTIR and XRD analysis confirmed the successful synthesis of these materials. Each synthesized powder was used to activate pastes, and the calorimetric analysis revealed comparable reactivity among the activators, whether added as solids or pre-dissolved into solutions. Furthermore, the compressive strength tests of pastes and mortars demonstrated that the lab-made activators are competitive with traditional sodium silicate solutions, regardless of the form in which they are added. Finally, the C-S-H gels formed from the activation of the AWH binder with the lab-made activators presented similarities with previous studies on the activation of AWH with commercial activators, where a strong correlation between the amount of C-S-H formed and the compressive strength for both mortars and pastes was observed. Furthermore, the minimum amount of C-S-H required for the AWH to develop compressive strength was determined to be 17 wt.% for pastes and 5 wt. % for mortars. This result is lower than the amount of C-S-H required while hydrating OPC, which may be due to the presence of hydration products with a lower C/S ratio in the AWH binder. In conclusion, the synthesis of the activator presented in this paper may represent a cheaper, more environmentally sustainable and easy-to-use alternative for the production and application of alkaline activators.

6.6 References

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CHAPTER 7. Influence of silica modulus on the activation of AWH binders with different alumina content: study of hydration reaction and paste performance

This chapter contains parts of a peer-reviewed journal:

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Contents

CHAPTER 7. Influence of silica modulus on the activation of AWH binders with different alumina content: study of hydration reaction and paste performance 175 7.2.4 Compressive strength results in pastes 182

This chapter investigates the influence of how different sodium silicate with SiO₂/Na₂O ratios (MS) of 0.75, 0.9, and 1.2, affect the hydration behavior of amorphous wollastonitic hydraulic (AWH) binders containing various amounts of Al₂O₃ content 4, 7, 10, and 12% wt. The reaction was followed by calorimetry, and the paste's compressive strength performance was tested at different curing times, 2, 7, and 28 days. The hydrated pastes were characterized by FTIR, thermogravimetry analysis, and X-ray diffraction. The calorimetric results show that a higher Al₂O₃ content and higher MS ratio results in longer induction period. In terms of paste performance, an increase of the Al₂O₃ coupled with an activation with a 1.2 MS ratio results in lower compressive strength, after 28 days of hydration, the results range from 76 to 52 MPa. The decrease of the MS to 0.9 allowed to obtain a narrower range of results, from 76 to 69 MPa. Even though the decrease of the MS ratio to 0.75 led to higher hydration kinetics and high compressive strength results at early ages, at 28 days of curing a decrease in compressive strength was observed. This may be a consequence of the fast kinetic of the mixture, since the rapid growth of hydration products may inhibit the dissolution at later ages and increase the porosity of the paste. Moreover, the results indicate a high AI intake in the hydration product, facilitated by the high sodium content of the activator, which promoted the formation of a higher amount of C-A-S-H structures instead of C-S-H, decreasing the compressive strength of the samples. The TGA results suggest that the samples hydrated with the MS075 solution resulted in a higher content of hydrated products at early ages, while the samples hydrated with the MS09 and MS1.2 solutions exhibit a steady increase with curing time. Hence, an equilibrium in the hydration kinetic promoted by Si saturation-undersaturation appears to be fundamental in this system, which is influenced by both the MS and the AI(OH)⁴⁻ content in solution. The results of this study suggest that for this type of binder, optimal performance can be achieved by decreasing the MS ratio to 0.9. This composition allows for a controlled kinetic and overall higher compressive strength results in pastes produced with this AWH precursor.

7.1 Introduction

Since the raw materials used in Ordinary Portland Cement (OPC) production are economically accessible [1], cement plants are typically located near limestone quarries to avoid the need for transportation of raw materials at larger distances [1,2]. However, variations in the Earth's crust can lead to changes in the raw materials' chemical composition, namely in aluminum, iron, and magnesium oxide content [3]. These variations affect the composition of the produced clinker and may result in changes of its performance [4–7]. Hence, it is important to study the influence of these variations when considering a large-scale production of a binder [3].

In this work the studied binder is an amorphous wollastonitic hydraulic (AWH) binder, a slag-like binder that has been investigated as an OPC alternative due to its lower CO₂ production emissions [8]. Previous works reported a competitive compressive strength in pastes when hydrated with a sodium silicate solution [9,10]. Until now, the binder production maintained a specific chemical composition, with a low content of Al₂O₃, MgO, and Fe₂O₃ elements (<2%wt). However, due to the known variability of natural raw materials, this chapter focused on the variation of Al₂O₃ content that can be incorporated into the clinker without compromising its performance, within the range from 4 to 12%wt.

The Al₂O₃ content influences the hydration reaction of the binder by acting as a network former and a network modifier [11–13]. Typically, AI replaces Si in bridging position [14] and leads to an increase in the mean chain length in the hydrated product [14,15]. This chain length can increase from 3- 5 tetrahedra (C-S-H of OPC) to up to 11 tetrahedra, as observed in the C-A-S-H of alkali activated materials [14]. The charge imbalance caused by the Si⁴⁺⇔Al³⁺ replacement is compensated by Na⁺ incorporation [14]. Nevertheless, in systems with a Ca/(Si+Al) ratio above 0.9 and under suitable activation conditions [14,15], replacement in tetrahedral positions is also possible [14,15]. The final hydrated material consists of a mixture of Si-O-Si and Si-O-Al bonding with a structure that ranges from semi-crystalline to amorphous [7].

Due to the importance of Na⁺ in Al incorporation, the Na/Al ratio is of particular relevance as it affects the structure integrity of the resulting matrix [16] and the occurrence of efflorescence [17]. Larger Na/Si ratios lead to a higher pH and facilitate Al leaching from the precursor materials [18]. However, it can also result in a surge in sodium ion concentration. According to Degefu et al [16], ratios above one may result in a continuous diffusion of the alkali ions, and a ratio of 1.2 results in low durability of the sample. The high sodium concentration can lead to an accumulation of ions on the surface of the

samples, which leads to its carbonation due to the exposure of the alkalis to atmospheric conditions [17]. This efflorescence phenomenon reduces the durability and quality of the material [17].

Conversely, lower Na/AI ratios result in a higher amount of bridging $AI(OH)^{4-}$ in the gel and in a larger mean chain length [17], integrating more Na⁺ ions in the matrix, which promotes a chemically steadier sodium species [17]. However, an excess of AI_2O_3 can also cause a pH decrease which influences the dissolution of the precursor, and the polymerization of the hydration products [16]. Thermodynamic models developed by Yan et al. [19] highlight the importance of the alkalinity of the mixture, as the surge of alkali hydroxide increases the concentration of AI and Si in solution, since with the pH increase there is a preference of AI to form $AI(OH)^{4-}$ complexes and Si to form $SiO(OH)^{3-}$ and $SiO_2(OH)_2^{2-}$. [20]

Other characteristics that also influence properties such as chain length [14] and morphology [21] of the hydration product are the Ca/(Si+Al), Si/Al, and Si/Na ratios [21,22]. Hence, due to the high sensitivity of the system to these ratios, when alkaline activation is required, it is important to consider both the binder and activator chemical composition [7,12,14,23–31].

Notably, sodium silicate (SS) solution has shown to be an effective activator, giving rise to fast hardening and high compressive strength results [10,32–34]. Furthermore, the use of this activator has been correlated to a higher AI integration in tetrahedra position within the C-A-S-H gel and a higher intertwining between chains [14]. Two variables that strongly influence the performance of this activator are the SiO₂/Na₂O (MS) ratio, which impacts the amount of soluble Si content in the system [32,35], influencing the dissolution and absorption of the species [22], and the Na₂O molar concentration, which affects the alkalinity of the solution [36] and the erosion of the grains [22]. Hence, a balance between these two parameters allows better strength results.

Previous research focused on the impact of the MS ratio on the properties of the materials [27,37–39]. Sun et al. [38] studied the influence of MS ratio ranging from 0.5 to 2.0 in pastes, the results indicated that an increase in MS ratio prolonged the setting time, reduced workability, and refined the pore structure of the activated material. Similarly, Caron et al. [40] characterized slag pastes activated with a MS ratio of 0.5 and 2.2 and reported that higher modulus led to slower dissolution rates and a lower C/S ratio in the final product. Additionally, Cihangir et al. [39] reported that for slag activation, MS values of 1.0-1.25 resulted in higher compressive strength at both short and later ages,

moreover, the increase of the ratio promoted the formation of a more condensed and polymerized C-S-H structure. The findings of Aydin et al. [27] indicated that a raise in MS ratio led to microcrack formation in the matrix, while low modulus results in higher compressive strengths at early ages.

Even though the MS ratio has been extensively investigated, there is still a need to understand how the available silicate added by the activator influences the hydration reaction of the mixture. Moreover, the effect of increased alumina content in the precursor's activation requires further research. Hence, the understanding of this phenomena and the effects between the MS ratio of the activator and the Al₂O₃ content of the sample on the hydration reaction and paste performance were investigated. This study allows the optimization of the activator to a specific precursor and consequently improve the performance of the material.

In this chapter, the influence of increasing the Al₂O₃ content up to 12%wt on the AWH was tested on alkaline activated pastes. A sodium silicate solution was used as activator and its composition was optimized in terms of MS ratio and Na2O molarity. The hydration reaction was followed using as isothermal calorimeter and the performance of pastes was tested at 2, 7, and 28 days by assessing its compressive strength into the sample. Each sample was then analyzed by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA).

7.2 Materials and Methods

7.2.1 Binder production

The binder production procedure was similar to previous studies [10,41–43]. In this work, four AWH binders were produced using common OPC clinker raw materials (limestone, marl, sand and fuel cracking catalyst waste to adjust Al_2O_3 content). The chemical composition was adjusted so that the overall C/S molar ratio was of ~1.0 and the theoretical %wt Al_2O_3 content was of 4%; 7%; 10% and 12%. The chemical composition of the four binders is presented in Table 7-1.

% wt	Al_4%	AI_7%	Al_10%	Al_12%
SiO ₂	47.51	45.74	44.58	43.09
Al ₂ O ₃	3.74	6.52	9.67	12.49
Fe ₂ O ₃	0.58	1.14	1.02	1.07
CaO	46.04	44.47	42.73	40.3
MgO	0.67	0.62	0.57	0.52
Other elements	<1.50	<1.50	<1.50	<1.50
C/S (molar)	1.04	1.04	1.03	1.00

Table 7-1	. Chemical	composition	of the	produced	binders
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The clinker of each binder was produced using the same process treatment. First the raw materials were ground, mixed, and compressed in discs to facilitate its introduction in a silicon carbide crucible. The filled crucible was heated in an electric furnace using the following steps:1) increase of temperature to 900°C at 25°C/min rate 2) the 900°C temperature was maintained for 1 hour to ensure full decarbonation 3) increase of temperature to 1550°C at 25°C/min 4) the temperature was maintained at 1550°C for 1h to allow for a complete melting and chemical homogenization. Finally, the resultant material was quenched into a container filled with water.

The AWH clinker produced was dried at 100°C for 1h, to remove the water from the quenching process, and ground for 3 minutes using a ring mill, obtaining a Blaine of approximately 6000 cm²/g and a 45 μ m residue below 20%wt.

7.2.2 Production of the pastes: activation conditions

The pastes were hydrated using a Na₂SiO₃+NaOH activator, with water/solid ratio of 0.3. The alkaline solution was prepared using a standard sodium silicate solution, Na2O: 7.5-8.5%; SiO₂: 25.5-28.5%, Chem Lab, Belgium, equilibrated with NaOH pebbles, 98,2% Prolabo, USA. The prepared pastes were introduced into molds with a 20x20x40 mm³ dimension and cured at 20°C under relative humidity conditions over 90%. After 2 days of curing the samples were removed from the molds and left to cure under the same conditions.

Three sodium silicate activators with different conditions, MS ratio, and Na₂O molarity were used to activate each sample. The characteristic of each solution is displayed in Table 7-2.

Nomenclature	Si/Na	Na ₂ O (M)	pН
MS1.2	1.20	3.52	13.3
MS0.9	0.90	3.52	13.3
MS0.75	0.75	4.92	13.8

Table 7-2. Nomenclature of the sodium silicate solutions used as activators

7.2.3 Isothermal Calorimetry

The hydration reaction of the pastes was followed using an isothermal calorimeter (TAM Air instrument, Waters Sverige AB, Sollentuna, Sweden). The tests were performed using a constant temperature of 20°C.

7.2.4 Compressive strength results in pastes

To assess the pastes performance after 2, 7, and 28 days of curing, compressive strength tests were performed in an Ibertest Autotest 400/10 instrument using a constant force rate of 2.4 kN/s during the test. The paste debris resultant from the test was ground by hand and dried at 100°C to remove evaporable water and avoid further hydration of the samples were then characterized by FTIR and XRD.

7.2.5 FTIR analyses

The FTIR-ATR analysis was performed on a bench-top Bruker, model ALPHA, operating with a Platinum ATR module, with the following conditions: 4 cm⁻¹ resolution; 24 scans.

7.2.6 XRD analyses

The X-Ray Diffraction analysis was performed in an X'Pert Pro (PANalytical) diffractometer using monochromatic CuK α 1 radiation (λ = 1.54059 Å) and working in reflection geometry (θ /2 θ). The X-ray tube worked at 45 kV and 40 mA. The configuration used was the following; optics configuration fixed divergence slit (1/2°), a fixed incident anti-scatter slit (1°), fixed diffracted anti-scatter slit (1/2°),X'Celerator RTMS (Realtime Multiple Strip) detectors, working in scanning mode with maximum active length. For all samples the data was collected from 5° to 70° (2 θ). To enhance particle statistics the samples were rotated during data collection at 16 rpm.

7.2.7 Thermogravimetric analysis

The TGA analysis was performed on an ELTRA equipment. The heating rate of the test was fixed at four temperature intervals, 105°C, 250°C, 500°C, and 950°C, and maintained until a stable mass was reached. The initial step (room temperature-105 °C) was performed at a 4°C/min rate in order to remove evaporable water that could still remain in the sample, the second step (105-250°C) was performed at 10°C/min rate and, the third and fourth steps (250-500°C and 500°C-900°C) at a 15°C/min a rate. The mass loss from the 105-250°C and 250-500°C was used to estimate the amount of bound water in each paste.

7.3. Experimental Results

7.3.1 Isothermal Calorimetry

For each sample the hydration reaction was followed for five days through isothermal calorimetry. The results are displayed in Figure 7-1.

After five days of hydration, independently of the MS of the activating solution, all Al12%wt samples displayed an accumulated heat of 80 J/g. However, for the samples with lower Al content, 4%, 7%, and 10%wt, the results were influenced by the MS content of the solution. The highest values were obtained by the pastes hydrated with a MS0.75 activator.

The results of the pastes hydrated with the MS0.9 and MS1.2 solutions (Figure 7-1A and Figure 7-1B) indicate that an increase in AI_2O_3 content leads to a broadening of the hydration peak and a decrease in its intensity. Moreover, the MS1.2 solution displayed an accumulated heat that ranged from 76 to 85 J/g, while the samples hydrated with the MS0.9 solution ranged from 83 to 90 J/g. This increase of accumulated with the reduction of the MS ratio suggests a higher extent of the hydration reaction. Finally, the calorimetric results in Figure 7-1C show the influence of further reducing the MS ratio to 0.75. All samples displayed an anticipation of the hydration peak, indicating an increase in the kinetic reaction and an increase of heat released after five days of hydration (~110 J/g).



Chapter 7. Influence of MS on the activation of AWH binders with different alumina content: study of hydration reaction and paste performance.

Figure 7-1. Comparison of isothermal calorimetry results of the AWH pastes, varying the AI content (Blue line 4%wt, Pink Line 7%wt, Green Line 10% AI, and Red Line 12%wt.), and the activating conditions; A- Si/Na of 1.20 B- Si/Na of 0.90, and C- Si/Na of 0.75.

7.3.2 Compressive strength results in pastes

The performance of the produced pastes was tested after 2, 7, and 28 days of hydration through compressive strength tests. The results are presented in Figure 2.

The results indicate that the performance of the pastes is influenced by the binders AI_2O_3 content, as samples with 4%wt AI_2O_3 displayed similar results at all ages regardless of the activator used, while samples with higher AI_2O_3 content exhibited higher susceptibility to the activating solution. Furthermore, when the Na_2O was increased and the MS ratio was reduced to 0.75, an initial increase in compressive strength at 2 and 7 days of curing was observed, followed by a decrease after 28 days of curing.



Figure 7-2. Compressive strength of AWH in relation to the AI content of the binder pastes after 2, 7, and 28 of hydration. The activating conditions were A- Si/Na of 1.20; B- Si/Na of 0.90, and C- Si/Na of 0.75.

7.3.3 FTIR Results

In Figure 3 the FTIR results of the Al4 (blue line) and Al12 (red line) anhydrous samples are displayed. Figure 4 and Figure 5 show the FTIR results for the Al4 and Al12 pastes, respectively, activated with the MS075, MS09, and MS1.2 activators, after 28 days of curing.

The FTIR spectra can be divided into eight main band identified as follows:

- A. 3800-2500 cm⁻¹, broad band associated with the O-H stretching [44,45]
- B. 1700-1300 cm⁻¹, CO₃²⁻ characteristic bands at 1450 cm⁻¹ attributed to asymmetric stretching mode [45]
- C. 1100-1050 cm⁻¹, bands characteristic of stretching Si-O-Si bond [44,46,47]
- D. 1000-900 cm⁻¹, the band at ~973 cm⁻¹ can be attributed to the Si-O symmetric stretching vibration, [45], and the bands at ~980 cm⁻¹ [48] and ~900 cm⁻¹ [49,50] to the Si-O-Si asymmetric stretching vibration, specifically Q² and Q¹ structures, respectively.
- E. 900-800 cm⁻¹ the band at 850 cm⁻¹ can be attributed to the Si-O-Si asymmetric stretching vibration of Q^0 units and the 875 cm⁻¹ band to the in-plane bending mode of $CO_3^{2^-}$ [10,51,52].
- F. 750-650 cm⁻¹; the band at 680 cm⁻¹ can be attributed to the bending motion of oxygen bonds [50] and the band at 712 cm⁻¹ is characteristic of the CO_3^{2-} in-plane bending modes [10,51,52].
- G. 650-500 cm⁻¹, band at 521 cm⁻¹ characteristic of the O-Si-O out of plane bending [53] Al-OH bending vibrations at ~590-570 cm⁻¹ [54] and bands associated to Si–O–Al–O bonds at 459–572 cm⁻¹ [55].
- H. 500-400 cm⁻¹ band associated to silica deformation [48], ~455 cm⁻¹ can be associated to the to the Si-O in plane bending [47].

In both anhydrous samples, there is an absence of bands characteristic of hydration and carbonation. The main difference between these samples can be observed in the D and G bands. In the D band, the Al4 sample displays a sharp band at 985 cm⁻¹ and ~900 cm⁻¹, characteristic of Si-O stretching vibration at Q² that can be attributed to the pseudowollastonite phase present in this sample [48].





Figure 7-3. FTIR spectra of the anhydrous Al4% and Al 12% samples, blue and red line respectively.

Figure 7-4 and Figure 7-5 display the FTIR spectra of the 28-day hydrated pastes for the Al4 and Al12 samples, respectively. All samples exhibit characteristic OH and $CO_3^{2^-}$ bands (A and B areas) indicating the hydration and carbonation of the binder. In all samples, the hydration reaction caused a narrowing and a shift of the C, D, and E bands towards higher wavenumbers, suggesting a higher degree of polymerization. Furthermore, all samples displayed a band at ~ 970 cm⁻¹, typical of the Si–O stretching vibrations in C-S-H gel [39,47]. In the H region, a narrowing of the bands and a shift to lower wavenumbers is observed indicating a more organized final structure.

In both hydrated Al4 and Al12 samples FTIR spectra, the MS1.2 and MS0.9 samples exhibit the main Si-O symmetric vibrations (area D) at higher wavenumber than the MS075 sample, suggesting an increased degree of polymerization in the hydrated paste

Chapter 7. Influence of MS on the activation of AWH binders with different alumina content: study of hydration reaction and paste performance.



Figure 7-4 FTIR spectra of the Al4 pastes, activated with the MS075, MS09, and MS1.2 activators, down, middle and top line respectively.



Figure 7-5. FTIR spectra of the Al12 pastes, activated with the MS075, MS09, and MS1.2 activators, down, middle and top line respectively.

7.3.4 XRD Results

The XRD diffractogram and Rietveld analysis of the anhydrous sample produced are displayed in Figure 7-6 and Table 7-3, respectively. The results indicate that the Al4 sample displayed the lowest amount of amorphous material (96%) and the presence of pseudowollastonite crystals.

To investigate the phase development after 28 day hydration with different activating solutions the results obtained through quantitative XRD-Rietveld analysis, in weight

percentage are displayed in Figure 7-7. The results indicate that all samples, regardless of activation method and Al_2O_3 content, exhibited a tobermorite content above 4%wt. Furthermore, the Al4 sample continued displaying a pseudowollastonite content of ~2%wt.



Figure 7-6. XRD scans of the anhydrous AWH binders produced with an AI_2O_3 wt% content from 4% to 12%. P – pseudowollastonite; * - Corundum, introduced as an internal standard to allow for the calculation of the amorphous wt% content.

Table 7-3. Rietveld analysis of the anhydrous AWH binders produced with variable AI_2O_3 wt% content from 4% to 12%.

AWH binder Al ₂ O ₃ %	Pseudowollastonite	Wollastonite	Amorphous
Al4	3.2	0.15	96.65
Al7	0	0.2	99.8
Al10	0	0.3	99.7
AI12	0	0.2	99.8



Figure 7-7. Quantitative results obtained by XRD-Rietveld analysis, in weight percentage, of the phases present in each of the samples studied

7.3.5 TGA results

Thermogravimetric analysis on the pastes cured for 2, 7 and 28 days was performed, in order to calculate the amount of bound water (BW) in the hydrated samples, by analyzing the weight loss in in the temperature range of 105-250°C, and 250-500°C. In Table 7-4 the main experimental TGA data obtained is displayed.

Table 7-4. TGA experimental results obtained for the studied specimens. LOI indicates
the loss in ignition at specific temperature steps. Values are shown in weight
percentages.

	2 days		7 days			28 days				
	LOI	250°C	500°C	950°C	250°C	500°C	950°C	250°C	500°C	950°C
	Al4	2.67	1.56	0.08	2.46	2.60	0.46	2.33	3.05	0.57
MS	Al7	2.80	1.84	0.08	2.42	2.21	0.71	2.98	2.16	0.88
0.75	Al9	2.51	2.03	0.11	2.08	2.66	0.56	2.47	2.35	0.68
	Al12	2.32	1.40	0.09	2.29	1.75	0.44	2.56	2.20	0.88
	Al4	1.90	1.23	0.20	2.67	1.24	0.19	2.47	2.94	0.38
MS	Al7	2.19	1.33	0.27	2.65	1.34	0.40	2.54	2.61	1.95
0.9	Al9	2.01	1.17	0.25	2.15	1.83	0.54	2.47	2.32	1.13
	Al12	2.14	1.26	0.39	2.18	1.63	0.40	2.38	2.31	0.74
	Al4	1.88	1.02	0.22	2.45	1.18	0.24	2.32	4.09	0.49
MS	Al7	1.97	1.07	0.31	2.38	1.57	0.88	3.06	2.33	1.40
1.2	Al9	2.02	1.12	0.21	2.15	1.54	0.89	2.25	2.64	2.80
	Al12	1.85	1.31	0.36	2.24	1.40	0.68	2.45	2.39	2.16

Similarly to previous works [10,41–43], the model of Richardson and Qomi [57] and a C/S ratio of 1.1 was assumed, allowing to establish a relation between the BW and the amount of C-S-H formed. In Figure 7-8, a correlation between the %C-S-H calculated, and the compressive strength obtained for each sample is displayed.

The obtained results suggest that the activation of the binder with an MS075 solution leads to a rapid formation of C-S-H during the early stages of hydration. However, the formation of hydration products appears to stagnate at later ages. In contrast, the samples hydrated with the MS09 and MS1.2 solutions exhibited lower C-S-H formation at early ages but continuous growth in C-S-H content with curing time.

Moreover, when comparing the amount of C-S-H content with the compressive strength obtained, the results indicate that the pastes activated with the MS075 solution presented a higher content of bound water at the early ages, which correlated well with the higher

compressive strength obtained, however, for later ages, the relationship between C-S-H formed and compressive strength seems to differ from the other two conditions tested in this study (MS09 and MS1.2), especially due to the decrease in compressive strength at 28 days for the samples Al10 and Al12 under MS075 activation.



Figure 7-8. Correlation of compressive strength with the amount of C-S-H formed for the pastes hydrated with an MS075 activator (cross markers) an MS09 activator (circle markers) and an MS1.2 activator (triangle markers). The binders with an Al_2O_3 content (with an Al_2O_3 content (%wt) of 4,7, 10 and 12 are displayed in blue, purple, green and red color, respectively

7.4 Discussion

In this work, four AWH clinkers were produced with different Al₂O₃ wt% content, 4, 7, 10, and 12%wt. Each anhydrous clinker was analyzed by XRD Rietveld phase quantification, revealing a high amorphous content (from 96 to 99%). The clinker with the lowest Al₂O₃ content exhibited the lowest amount of amorphous material (96%) and evidenced the presence of pseudowollastonite crystals. This phenomenon may be attributed to the fact that, for this system, alumina acts as a melting agent, hence, the clinkers with lower alumina content present higher melting temperatures. Since all samples were melted at the same temperature (1550°C), the melting of the lowest alumina content sample shows a higher viscosity and density, which may influence the quenching process and promote the formation of pseudowollastonite crystals.

Each binder was activated with three different sodium silicate solutions with MS ratios of 1.2, 0.9, and 0.75, and the hydration reaction of each sample was followed by calorimetry. Comparing the results of the Al4, Al7, and Al10 samples, an increase in the induction period for higher Al_2O_3 content is observed. This result may be attributed to the reduced dissolution of $[SiO_4]^{4-}$ in the presence of Al_2O_3 in the solution [58]

Moreover, the results indicate that the MS ratio and Na₂O molarity of the activator influence the heat release profiles of the hydrated sample. With the decrease in MS ratio a more extensive hydration reaction and an increase in kinetics is promoted.

Analyzing the 28 days paste compressive strength results, Figure 2, it is possible to see that the pastes activated with the MS1.2 solution presents a decrease in strength with the increase in Al_2O_3 content, with a minimum point on the Al10 sample. The compressive strength of the pastes activated with this solution ranged from 52 to 76 MPa. Conversely, samples hydrated with an MS0.9 activator showed a narrower range of results, from 69 to 76 MPa. Hence, when the binder is activated with the MS0.9 solution, the influence of the Al_2O_3 content on the sample's performance seems to be mitigated.

The decrease of the MS ratio to 0.75 led to a higher hydration kinetics and high compressive strength results at early ages on the samples with an Al2O3 content higher than 7%wt. However, after 28 days of curing a decrease in compressive strength was observed. These results may be a consequence of the high NaOH molarity in solution. At early ages the increase of pH facilitates the solubility of $[SiO_4]^{4-}$ ions from the binder [59], promoting the hydration reaction. Moreover, the increase of Na₂O also allows a

195
higher aluminum incorporation into the C-S-H gel, since the sodium cations are able to stabilize the silicon-aluminum exchange. However, the rapid reaction of the system can lead to a localized increase int the matrix density, resulting in an overall more porous microstructure [11]. Moreover, the high aluminum incorporation leads to a higher extent of formation of C-A-S-H structures in detriment of C-S-H. Since the compressive strength of C-A-S-H is lower than that of C-S-H, this leads to a reduction of compressive strength [60]

Similar to the activation of blast furnace slag (BFS) [22,61], the results of this study indicate that the SS activation of the AWH binder can be categorized into four main stages as displayed in Figure 7-9.

In stage I) The introduction of free Si species from the activator promotes a very low undersaturation of this species, causing a low Si dissolution from the binder [61]. Consequently, the Si ions remain at the grain surface, while the undersaturation of Ca and Al is high, allowing the release of these elements into solution, [61,62].

In stage II) the surge of Si in the grains surface gradually increases the thickness of the Si layer [22,61]. Hence, while the dissolution of Ca and Al is possible, the Si dissolution is very slow. This stage is associated with the formation of an induction period [22,61,62].

In stage III) the Ca and AI in solution react with Si, forming a C-A-S-H gel [22], with the consumption of these ions, the Si undersaturation increases promoting the dissolution of the Si layer [22,61].

Finally, in stage IV) the accumulated reaction products inhibit further dissolution of unreacted particles, leading to a deceleration period. [22,61,62].

In systems with a high MS ratio the high $[SiO_4]^{4-}$ concentration can result in the formation of H₂SiO₃ structures [22], which when oversaturated, crystallize as a hydrated sodium metasilicate [22] and result in the precipitation of a gel [63]. Moreover, high MS ratios promote the absorption of Ca²⁺ and Al³⁺ by the soluble $[SiO_4]^{4-}$ [22], leading to higher degree of polymerization, a higher extent of reaction products [22,37], and a denser microstructure [22,37]. However, this denser structure around the grains can also prevent further dissolution [22], inhibiting the hydration reaction [22], consequently, decreasing the performance of the hydrated material at later ages [64]. In addition, the excess of $[SiO_4]^{4-}$ can also promote the SiO₂ precipitation [22].



Figure 7-9. Hydration reaction process of a slag activated with a SS solution with a high MS ratio.

The decrease of the MS ratio is associated to a higher pH, a faster dissolution, a shorter setting time, and a higher flowability [30,55]. As the MS ratio decreases, the $[SiO_4]^{4-}$ undersaturation increases, promoting the release of both Ca²⁺, Al³⁺, and $[SiO_4]^{4-}$ ions into the solution during the dissolution step, and the production of a C-S-H gel on the particles surface [17]. As the reaction continues, the Al³⁺ replaces the Si⁴⁺ in the structure [14] and the Na⁺ is incorporated to balance the C-A-S-H gel formed [14]. The increase of the C-S-H/C-A-S-H layer decreases the OH- diffusion into the particle and the Ca²⁺ and $[SiO_4]^{4-}$ diffusion into the solution [17], leading to the deceleration period. In Figure7-10 a schematic representation of this mechanism is displayed.



Figure 7-10. Hydration reaction process of a slag activated with a SS solution with a low MS ratio

Therefore, the results of this study indicate that to allow the formation of an organized C-(A)-S-H structure a balance of Si saturation-undersaturation is required. A high Si undersaturation (e.g activation with a MS075 solution) leads to an increase in the kinetics and the rapid formation of hydration products. However, this rapid growth inhibits the

dissolution at later ages and increases the porosity of the hydrated product. Both phenomena result in a decrease in compressive strength at 28-days of hydration

Furthermore, low Si undersaturation promotes the increase of an induction period due to the low silica solubility. The low Si undersaturation may compromise the formation of C-S-H products, decreasing the performance of the binder. This is the case for systems with a high AI_2O_3 content and activated with a high MS ratio sodium silicate solution.

TGA results confirm this trend, compared to the other solutions, the samples hydrated with the MS075 solution resulted in a higher amount of C-S-H structures at early ages. However, the formation of hydration products appears to stagnate at later ages. In contrast, the samples hydrated with the MS09 and MS1.2 solutions lead to a steady increase in hydration products with curing time, particularly in the low Al_2O_3 content samples.

In conclusion, obtaining an equilibrium in Si saturation-undersaturation is fundamental in this system. The Si solubility must be low enough to promote the formation of a Si layer and allow a controlled kinetic and the formation of an organized C-(A)-S-H structure and must be high enough to promote the dissolution of the Si layer and allow the hydration reaction to continue. The increase of $AI(OH)_4$ content in solution and the increase of MS ratio increase Si saturation, decreasing its solubility, delaying the reaction and inhibiting the formation of hydration product. Nevertheless, by reducing the MS ratio to 0.9 the Si solubility increases and compensates for the negative effect of $AI(OH)_4^-$, while still maintaining a controlled reaction kinetic.

Therefore, the decrease of the MS ratio from 1.2 to 0.9 led to a more extensive hydration reaction, which translated into higher compressive strength results at later ages. Additionally, in all cases, the presence of sodium is fundamental for AI incorporation in the structure.

7.5 Conclusion

In this chapter, the influence of the activator on the hydration reaction of AWH samples with different AI_2O_3 content was studied by decreasing the MS modulus from 1.2 to 0.75 and increasing the Na₂O molarity. Moreover, the performance in pastes was investigated.

The main results indicate that the kinetic of the system is influenced by silica undersaturation in solution, which decreases for higher Al_2O_3 content and MS ratio in solution. In systems where silica undersaturation is too low, the kinetic of the mixture is delayed, and the formation of more hydration products at later ages is inhibited, due to the low Si solubility. As a result, if the silica undersaturation is excessively high, it promotes an uncontrolled rapid growth of C-S-H structures which can compromise the compressive strength at later ages.

For this specific binder composition, the experimental results suggest that an activator with an MS ratio of 0.9 and a Na₂O molarity of 3.516M leads to a more controlled kinetic mixture and overall higher performance, even on binders with a higher Al₂O₃ content. Since a further reduction of the MS ratio had a negative impact in the long-term performance of paste, we concluded that a MS0.9 may represent the optimized composition of the activator

Hence, in this study the activator was optimized to the precursor, allowing the increase in the range of Al_2O_3 content that can be incorporated into the clinker which could potentially allow a reduction in the melting temperature of the material

7.6 References

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Contents

CHAPTER 8. Influence of magnesium oxide content on the hydration characteristic and strength development of mortars prepared with the AWH
binder
8.1 Introduction
8.2 Experimental Procedure
8.2.1 Binder production
8.2.2 Laser granulometry
8.2.3 Raman analysis of the anhydrous samples
8.2.4 Production of pastes
8.2.5 Isothermal calorimetry analysis
8.2.6 Fourier Transform Infrared Spectroscopy (FTIR)
8.2.7 X-ray Diffraction (XRD) analyzes
8.2.8 Production of mortars
8.2.9 Compressive strength tests in mortars
8.3 Experimental results
8.3.1 Raman results
8.3.2 Isothermal calorimetry
8.3.3 FTIR analysis
8.3.4 XRD analysis
8.3.5 Compressive strength results in mortars
8.4 Discussion
8.5 Conclusion
8.6 Reference

This chapter investigates the influence of increasing magnesium oxide (MgO) content from 1wt% to 8%wt on the production process, reactivity, and performance of an amorphous wollastonitic hydraulic binder (AWH). The reactivity of the binder was followed by isothermal calorimetry in pastes activated with a sodium silicate solution. The results indicate that a higher MgO content increases the amount of heat released and accelerates the reaction kinetics. To assess the influence of MgO on the binder performance, two sets of studies were conducted in sodium silicate-activated mortars. In the first set, the compressive strength of an AWH sample with 8wt% Mg content (AWH_8Mg) was compared to a standard AWH sample at 2, 7, and 28 days of curing. In the second set, the AWH_8Mg was incorporated as a supplementary cementitious material in both OPC and AWH-based mortars. The results showed that the AWH_8Mg exhibited similar results as the typical AWH mortars at all ages. Furthermore, the results also indicate that the AWH_8Mg can be used to replace up to 10% of the binder, in both OPC and AWH-based mortars, without compromising mechanical performance.

8.1 Introduction

Due to its binding capabilities, high reliability and low-cost production, Ordinary Portland Cement is one of the most used materials worldwide [1]. OPC is mainly formed by calcium and silicon oxides, with smaller amounts of iron, magnesium, and alumina oxides [2,3]. The magnesium oxide (MgO) content significantly influences different properties in the clinker [4], including burnability, phase composition, mineral crystal polymorphism, cement strength, and volume stability [4]. However, while a precise MgO amount enhances the hydraulic reactivity, [4,5] the presence of free MgO in the binder promotes the formation of periclase [4]. This phase is responsible for the subsequent expansion of the material, compromising the integrity and safety of concrete structures. Consequently, in OPC clinker, the MgO content is limited to 5% [6]. The MgO content also influence the performance of alkali-activated binders and the reactive ground granulated blast furnace slags (GGBFS) when used in cementitious systems with OPC clinker [5,7].

Several studies investigated the partial replacement of calcium oxide (CaO) with MgO [4,8–11], due to its lower calcination temperature (~ 600° C), and improvement of compressive strength [4]. Nevertheless, when analyzing the carbon cycle emission of magnesia cement compared to OPC, Shen et al [12] reported that even with the lower calcination temperatures, reactive magnesium oxide cement could increase direct CO₂ emission by 79-395 kg/ton. This increase is attributed to the higher CO₂ released during the MgCO₃ decomposition compared to CaCO₃.

Both magnesium and calcium are abundant in the earth's crust [13], and belong to the alkaline earth metals, known for their relatively high reactivity [14]. In the binder, MgO has a similar role to CaO [15], and a minimum content of these elements is required to ensure good performance [16]. The proportional amount of these elements relative to silicon dioxide (SiO₂) can be expressed as the basicity index (equation 8-1). This ratio influences various properties, including melting temperature, crystallization mechanism, microstructure, binder reactivity, chemically bound water, hydration degree, coarse capillary, and compressive strength [2,15–17].

Basicity index =
$$\frac{(CaO+MgO)}{SiO_2}$$
 (eq.8-1)

The increase in the basicity index can lower the melting point of the raw material [18,19] and decrease the viscosity of the mixture [19]. This is caused by the rise of Ca^{2+} and Mg^{2+} cations in the system, which facilitate particle movement and accelerate the breaking of the bridging oxygen bond within the silicate network, gradually transforming

the structure into isolated $[SiO_4]^{4-}$ ions [15,19].

Winnefeld et al. [20] reported that replacing CaO with MgO, while simultaneously increasing Al_2O_3 content, enhances the slag reactivity, resulting in higher compressive strengths, particularly at younger ages. In their study, the hydration product consisted of C-(A)-S-H and a hydrotalcite-like phase. However, increasing the MgO content from 8% to 13% led to a rise of hydrotalcite and a decrease in the Al uptake by C-S-H. Other authors [21] also reported that a high content of MgO (>10%) led to a decrease in the performance, due to the dilution effect [21].

Considering the crucial role of MgO content in both clinker production and binder reactivity, this chapter investigates its influence on an amorphous wollastonitic hydraulic binder (AWH). In this study, the MgO content in the binder was increased from 1 wt% to 8%wt (AWH_8Mg) to assess the impact on the production, reactivity and application.

In Figure 8-1, based in [22], the tested clinkers composition is displayed in an MgO-CaO-SiO₂ phase diagram with a constant content of Al_2O_3 of 10%wt, approximately the same as in the tested clinkers. As the MgO content increases the phase composition changes from Wollastonite to Melilite, which has a melting point of 1390°C.



Figure 8-1. MgO-CaO-SiO₂ ternary phase diagram with a constant content of AI_2O_3 of 10%wt, adapted from [22]. The AWH and AWH_8Mg composition are displayed as a blue and green ball respectively

Both binders were tested in pastes and mortars to assess the influence of MgO content on the hydraulic reaction and in mortars performance. The hydraulic reaction was followed through calorimetric analysis, Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analysis. Compressive strength tests were performed on mortars after 2, 7, and 28 days of curing and compared with standard OPC samples.

8.2 Experimental Procedure

8.2.1 Binder production

Two binders with the chemical composition shown in Table 8-1 were produced. A mixture of raw materials typical from Portland cement industry was used, namely marl and sand. For the binder with higher amount of MgO, dolomitic limestone was used to partially replace marl in the mixture. The raw materials were ground, mixed, and compressed in a disc. The compressed disc was broken into four pieces and placed in a silicon carbide crucible, which was then placed in an electric furnace and heated, at a rate of 25°C/min, to 900°C, maintaining this temperature for 1 hour, to ensure full decarbonation of the raw materials. Then, the furnace temperature was raised to the melting temperature and kept for 3h to guarantee the complete melting of the powder mix and its chemical homogenization. Finally, the melt was quenched by pouring it into a water container and a material with an amorphous content above 98.5% was obtained. The chemical composition, maximum process temperature, and Ca/Si (C/S) ratio and basicity index of both clinkers are displayed in Table 8-1.

	AWH	AWH_8Mg
Process temperature (°C)	1550	1450
SiO ₂ (%wt)	45.0	42.5
Al ₂ O ₃ (%wt)	8.41	6.8
Fe ₂ O ₃ (%wt)	0.54	1.16
CaO(%wt)	42.8	40
MgO(%wt)	1.28	7.69
Other elements(%wt)	<1.50	<1.50
C/S (molar)	1.04	1.04
(C+M)/S	1.06	1.28

Table 8-1. Production specification and chemical characteristics of the binders.

The decrease of the maximum temperature in the production of the AWH_8Mg resulted in a more viscous material and a lower heat exchange rate during the quenching process. This contributes to an increase in the apparent density and a decrease in the amount of trapped air in the final clinker, as observed in Figure 8-2.



Figure 8-2. Produced clinkers A) amorphous wollastonitic hydraulic binder AWH binder and B) amorphous wollastonitic hydraulic binder with an 8% MgO content.

8.2.2 Laser granulometry

The clinker produced was then ground in a ball mill until a residue at 45 µm below 12%. The sample particle size distribution was obtained via light scattering using laser diffraction. Figure 8-3 displays the results of the tests performed on a HORIBA Scientific Laser Scattering Particle Size Distribution Analyzer, using the dry measurement mode.



Figure 8-3. Particle size distribution of the binders used in this study.

8.2.3 Raman analysis of the anhydrous samples

Raman analysis was performed on the anhydrous samples. The spectra were obtained at room temperature using a wavelength of 532nm, covering a range from 100 to 1900 cm⁻¹. Quantitative peak deconvolution was performed using Origin Pro 8 within the range of 750 to 1150 cm⁻¹. Gaussian functions were applied to fit the spectrum data with the assistance of the 'PeakFit' routine. The relative quantity of Qⁿ units was then calculated based on the area fraction of the best-fit curve, taking into consideration the characteristic frequency of each Qⁿ unit.

In Figure 8-4, a flowchart summarizing the production methods and characterization of the AWH and the AWH_8Mg clinkers are displayed.



Figure 8- 4. Production methods and characterization of the AWH and the AWH_8Mg clinkers

8.2.4 Production of pastes

Activated pastes were prepared using the AWH binder and AWH_8Mg binder and compared to a standard water-hydrated OPC paste. Then the AWH_8Mg was used as a supplementary cementitious material, replacing 10% of the binder in both activated AWH pastes and water hydrate OPC pastes. The activation was performed using a sodium silicate solution (Si: Na ratio of 0.9; Na molarity of 3.516 M). A water/solid ratio of 0.4 and 0.278 was maintained in the water-hydrated and activated pastes, respectively. All pastes were stored under relative humidity (HR) conditions above HR90%.

8.2.5 Isothermal calorimetry analysis

Each paste underwent calorimetric tests on a TAM Air instrument (Waters Sverige AB, Sollentuna, Sweden) at a constant temperature of 20°C. The pastes were inserted into vials *ex-situ*, therefore, the first exothermic peak, characteristic of the wetting of the amorphous binder is not displayed.

8.2.6 Fourier Transform Infrared Spectroscopy (FTIR)

After 28 days of hydration the paste samples were dried and analyzed by Fouriertransform infrared spectroscopy (FTIR) and X-ray diffraction (DRX). The FTIR tests were performed on a bench-top Bruker, model ALPHA, operating with a Platinum ATR module, with 4 cm-1 resolution and 24 scans.

8.2.7 X-ray Diffraction (XRD) analyzes

The XRD was performed in an X'Pert Pro (PANalytical) diffractometer using monochromatic CuK α 1 radiation (λ = 1.54059 Å) and working in reflection geometry (θ /2 θ). The optics configuration was a fixed divergence slit (1/2°), a fixed incident antiscatter slit (1°), a fixed diffracted anti-scatter slit (1/2°), and X'Celerator RTMS (Realtime Multiple Strip) detectors, working in scanning mode with maximum active length. Data for each sample were collected from 5° to 70° (2 θ). The samples were rotated during data collection at 16 rpm to enhance particle statistics. The X-ray tube worked at 45 kV and 40 mA.

8.2.8 Production of mortars

The samples AWH and the AWH_8Mg were used to make mortars, by mixing the binder with a sodium silicate solution. The samples were then compared to a conventional water hydrated OPC mortar. Furthermore, the AWH_8Mg was used as a supplementary cementitious material, replacing 10% of the binder in both activated AWH and water hydrate OPC mortars. A water/solid ratio of 0.5 and 0.365 was maintained in the water-hydrated and activated mortars, respectively

8.2.9 Compressive strength tests in mortars

The compressive strength tests of the mortars were performed in a Ibertest Autotest 400/10 instrument after 2, 7, and 28 days of hydration.

Figure 8-5 displays a flowchart with the specifications of the pastes and mortars produced and the respective analysis performed.



Figure 8-5. Specification and analysis of the pastes and mortars produced in this study.

8.3 Experimental results

8.3.1 Raman results

Figure 8-6 shows the deconvolution result performed on the spectra of the anhydrous samples. The bands correspond to the Q_0 (850-880 cm⁻¹), Q_1 (900-920 cm⁻¹), Q_2 (950-1000 cm⁻¹), and Q_3 (1050-1100 cm⁻¹) units, respectively. In Table 8-2 the relative quantity of Q^n units is displayed.



Figure 8-6. Deconvolution of Raman spectra of the anhydrous samples A) AWH; and B) AWH_8Mg

	Amorphous component Qn distribution			
Sample	Q ⁰	Q ¹	Q ²	Q ³
AWH	10	25	55	10
AWH_8Mg	18	23	51	8

Table 8-2. Qn distribution area ratio obtained from a Gaussian deconvolution of Raman spectra.

8.3.2 Isothermal calorimetry

In Figure 8-7 calorimetric results of the first 3 days of hydration of the produced pastes are displayed. The activated AWH and AWH_8Mg binders are compared to a standard water-hydrated OPC paste in Figure 8-5A. The calorimetric results of the pastes made with AWH_8Mg as a SCM are displayed in Figure 8-5B.



Figure 8-7. Calorimetric results of the produced pastes: A) Calorimetry results of the activated pastes prepared using either AWH or AWH_8Mg binder (blue and green line respectively) and standard water-hydrated OPC paste (black line); B) pastes with AWH_8Mg used as supplementary cementitious material in AWH pastes (blue dotted line) and OPC pastes (black dotted line).

8.3.3 FTIR analysis

The 28-day FTIR spectra of the AWH and AWH_8Mg pastes are displayed in Figure 8-8. In both spectra, bands related to the presence of CO_3^{2-} and silica tetrahedra can be observed. The presence of CO_3^{2} can be assigned to the following characteristic peaks, 1550-1458 cm⁻¹, attributed to asymmetric stretching mode, and the signals at 875 and 712 cm⁻¹ caused by the in-plane bending mode [23,27,28]. In the region between 800 and 1100 cm⁻¹, there is a combination of symmetric and asymmetric stretching vibrations characteristic of a Si-O-T structure, in which "T" can be either AI or Si [29], being known that within this band, the signal at higher wavenumbers indicates the formation of a product with a higher network or a denser structure [29]. The Si-O typical vibrations are present in all samples with a shoulder at 916 cm⁻¹, which corresponds to a stretching vibration [30] and at 985, 938, and 922 cm⁻¹, which corresponds to non-bridging vibration [31]. For the Si-O-T structure, the characteristic peaks present are 1082 cm⁻¹, 719 cm⁻¹, and 455 cm⁻¹, which correspond to a symmetric stretching vibration [30], a stretching vibration of 3-member ring structure [23] and a bending rocking vibration at [30], respectively. The peaks at 564 and 666 cm⁻¹ are assigned to the AI-O stretching mode [32].



Figure 8-8 FTIR spectra of the 28 days alkaline-activated AWH and AWH_8Mg pastes

8.3.4 XRD analysis

In Figure 8-9, the XRD spectra of 28 days pastes are displayed, with the respective results of the Rietveld analysis being shown in Figure 8-7.



Figure 8-9. 28 days activated paste XRD spectra of an AWH binder (blue line) and an AWH_8Mg binder (green line). p= pseudowollastonite; +=tobermorite; *= internal standard Al2O3 (20% wt added); o= quartz.

Table 8-3. Quantitative results obtained by XRD-Rietveld analysis for the weightpercentages of the phases present in 28- days-activated pastes.

Sample	Calcite (%wt)	Pseudowollastonite (%wt)	Amorphous content (%wt)	Tobermorite (%wt)	Quartz (%wt)
AWH	0.6	0.3	94.4	4.6	0.2
AWH_8Mg	1	0.2	94.4	4.3	0

8.3.5 Compressive strength results in mortars

The development of compressive strength of the activated mortars made with either AWH and AWH_8Mg is compared to a standard water-hydrated OPC mortar in Figure 8-9. Furthermore, the influence of replacing 10 % of the AWH binder and OPC with AWH_8Mg is also displayed.



Figure 8-10. Comparative analysis of compressive strength development of mortars. The blue bars represent AWH, the green bars represent AWH_8Mg and the black bars standard OPC mortar. The striped bars, indicate the mortars that use AWH_8Mg to replace 10 % of either AWH or OPC

8.4 Discussion

In this work, the influence of increasing the MgO content from 1% to 8 %wt in an amorphous wollastonitic hydraulic binder (AWH) was tested. The main parameters studied were production condition, hydraulic reactivity, and mortar application. The AWH with 8% MgO (AWH_8Mg) was produced at 1450°C using the same procedure as the standard AWH. Figure 8-2 shows that the resulting clinker presented a higher apparent density and lower trapped air when compared to the standard AWH produced at 1550°C. This is likely due to the higher viscosity of the melt in AWH_8Mg, which slows down the heat exchange rate during the quenching process. Nevertheless, both clinkers achieved an amorphous content above 98 %wt.

Raman analysis showed that the increase in MgO promoted a decrease in the formation of highly polymerized structures, resulting in a sample with a lower content of Q^3 structures and an increase in Q^0 structures.

The calorimetric results showed that both activated binders, AWH and AWH_8Mg, displayed a lower amount of heat released after 3 days of hydration compared to water hydrated OPC. In the activated binders, the increase in MgO content led to an anticipation of the hydration peak and a higher heat released, indicating enhanced reactivity in the sample. When AWH_8Mg was used as a supplementary cementitious material, replacing 10% of the AWH binder, the heat release increased from 80 J/g to 100 J/g. This increase in reactivity in the AWH_8Mg sample can be attributed to its higher basicity index which facilitate the production of C-S-H structures, due to the higher availability of Ca/Mg ions and of free Si in the system, since there is a higher amount of Q^0 structures.

Analyzing the FTIR spectra of the hydration products a higher intensity in the O-H bond is observed in the AWH_8Mg, which can be related to a higher amount of hydration products formed. Furthermore, the slight shift of the band around 960 cm⁻¹ to higher wavenumbers in the AWH products may indicate the presence of a higher network and denser structure. The phases identified in the XRD show that both binders have the same hydration products and the increase of MgO did not promote the formation of periclase, which could lead to late expansion and compromise the future performance of the material.

The results presented in Table 8-4 show the ratio between the mortar's compressive strength values of the OPC + AWH_8Mg mixture and the reference OPC at different hydration ages. When analyzing these results, it is possible to realize that the alkalinity of the medium developed by the hydration of OPC was sufficient to activate the reaction or to develop pozzolanic effect in the AWH_8Mg binder. Initial strength did not benefit from the addition of the 10%wt of AWH_8Mg. However, at 7 days of hydration the performance was comparable to the reference cement and at 28 days it even surpassed it. Furthermore, when comparing the compressive strength values of the AWH, AWH_8Mg, and the 90% AWH +10%AWH_8Mg mixture we observed that all binders presented similar results, indicating that the increase in MgO content did not influence the performance of the binder. In conclusion, even though a higher heat of hydration was observed in the sample whit higher MgO content, this did not translate into higher compressive strength results in mortars.

Tabel 8-1. Ratio between the mortar's compressive strength values of the OPC + AWH_8Mg mixture and the reference OPC at different hydration ages.

	Mixture (MPa) OPC (MPa)		
Mortar	2 days	7 days	28 days
90%OPC+10%AWH_8Mg	93%	100%	105%

8.5 Conclusion

In this study, the increase of MgO content to up to 8 %wt in an amorphous wollastonitic hydraulic binder (AWH) binder was investigated, the main results are as follows:

- Raman results show that the increase of MgO content led to the formation of less polymerized structures. This resulted in a lower content of Q³ structures and an increase in Q⁰ structures.
- 2. Calorimetric results show that the alkaline-activated binders release less heat compared to water-hydrated OPC.
- 3. A higher MgO content in the AWH binder leads to increased reactivity, observed through earlier hydration and larger heat release. The enhanced reactivity may be attributed to the higher basicity index, which promotes the formation of Q⁰ structures, as observed in the Raman analysis, and allows the use of either Ca²⁺ or Mg²⁺ cations to be incorporated into the hydration products.
- 4. XRD results verify similar hydration products in both binders and the increase of MgO did not promote the formation of periclase.
- 5. On the water-hydrated OPC mortar the replacement of 10% of OPC with AWH_8Mg displayed potential benefits without compromising strength. The results suggest that AWH_8Mg may be used as a SCM
- 6. In the activated mortars, the compressive strength results were similar at all ages independently of the binder used, AWH, AWH_8Mg, or a mixture of 90% AWH and 10% AWH_8Mg. This suggests that even though the increase of MgO content leads to an increased heat release this did not translate into higher compressive strength values.

In conclusion, understanding the influence of MgO content can improve the optimization of the binder's composition, and allow for a wider range of MgO content in AWH production. The overall results of this study indicate that the increase in MgO content may lead to a decrease in the clinker melting temperature, increase the Q⁰ silica structures in the clinker and enhance the binder reactivity without compromising the compressive strength in mortars.

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CHAPTER 9. Enhancing Sustainability of Amorphous-Wollastonitic Hydraulic Binders through Incorporation of Supplementary Cementitious Materials.

This chapter contains parts of a peer-review journal:

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Contents

CHAPTER 9. Enhancing Sustainability of Amorphous-Wollastonitic Hydra Binders through Incorporation of Supplementary Cementitious Materials.	iulic 231
9.1 Introduction	234
9.2 Experimental procedure	237
9.2.1 Binder production	237
9.2.2 Supplementary cementitious materials, chemical composition and m specification	ixtures 238
9.2.3 Laser granulometry analysis	239
9.2.4 Paste production	242
9.2.5 Mortars production	242
9.2.6 Isothermal calorimetry analysis	243
9.2.7 Compressive strength tests in pastes and mortars	243
9.2.8 X-ray Diffraction analysis	244
9.2.9 Thermogravimetric analysis	244
9.3 Experimental Results	244
9.3.1 Calorimetric results	244
9.3.2 Pastes and Mortars compressive strength tests	245
9.3.3 X-ray Diffraction analysis	248
9.3.4 TGA analysis	250
9.4 Discussion	252
9.5 Conclusion	257
9.6 Reference	258

In cement industry the use of supplementary cementitious materials (SCMs) play an important role in the reduction of CO₂ emissions by allowing a decrease in clinker content. The present chapter investigates the incorporation of four different SCMs into an amorphous wollastonitic hydraulic (AWH) clinker, which requires alkaline activation with a sodium silicate solution. This alkaline activation process could potentially allow the use of some SCMs as precursors within the SCM+AWH mixture. Hence, besides physical, pozzolanic, or latent hydraulic capabilities, the SCM incorporation would also enhance the system reactivity at early and later ages due to their alkaline activation. In this study, pastes and mortars were made by individually replacing 25%wt of the AWH clinker with fly ash (FA), limestone filler (L), calcined clay (CC), and ground granulated blast furnace slag (GGBFS). The influence of the SCM incorporation on the hydration kinetic, phase development, and compressive strength was assessed and compared to 100% AWH samples. The first seven days of the reaction were followed using isothermal calorimetry, and compressive strength tests were performed after 2, 7, and 28 days of hydration, the hydrated samples were characterized using thermogravimetry and X-ray diffraction analysis. The main results indicate that in mortars, both FA and the CC acted as fillers, displaying similar results as the L mixture mortar. However, the high compressive strength of the FA blend pastes, and the high heat release of the CC blend reveal a potential for alkaline activation. With the incorporation of the GGBFS, a synergy between the AWH binder and this SCM was observed, this addition led to an increase in the reaction kinetics, heat released, and compressive strength results at all ages. The positive results were attributed to the GGBFS activation with the alkaline solution, causing a rise in temperature and enhancing the dissolution of the AWH binder. Moreover, on mortars at 28 days of hydration, the compressive strength ratio AWH/(AHW+SCM), was superior to 0.75 on all samples, suggesting a positive interaction between the clinker and the SCM. Overall, the findings presented in this work contribute up to a 25% reduction in CO₂ content associated with AWH cements, resulting in material-related CO₂ emissions of approximately 255kg/ton cement.

9.1 Introduction

Due to the high CO₂ emission related to Ordinary Portland Cement (OPC) production, the partial replacement of the clinker with supplementary cementitious materials has been extensively investigated [1–10]. The use of SCMs influences the hydration reaction of the blended cement, both at early and later stages. In the beginning, it influences the dissolution of the binder due to changes in pH and chemical composition of the solution [5]. At later stages, the SCM may improve binder's properties due to its pozzolanic and hydraulic capabilities [5]. The use of SCMs is cost-effective and may improve the cement and concrete performance, in addition SCMs typically contain a lower CO₂ related emission when compared to OPC clinker. Hence, their use has proven to be an efficient strategy for the decarbonization of the cement industry [11].

Hence, this work investigates the viability of partially replacing the AWH binder with an SCM, to further reduce the CO_2 emissions associated with the use of the clinker. Moreover, due to the clinker's alkaline activation requirements, the incorporation of aluminum-silicate based SCMs may enhance the system reactivity through activation of the SCM, taking full advantage of the physical and hydraulic capabilities of the material.

The SCMs studied in this work were limestone filler (L), calcined clays (CC), fly ash (FA), and ground granulated blast furnace slag (GGBFS) since these materials are commonly used as clinker replacement. Besides these SCMs, some other materials that have also been investigated in previous works include agro-industrial wastes [6,12–14] or recycled construction materials [9,15,16].

The incorporation of L and CC is of particular significance, given their abundant global availability [17]. Moreover, the SCMs CC, FA, GGBFS have potential for alkaline activation.

Limestone powder (CaCO3) is obtained as a secondary product from limestone quarry [18]. Its incorporation in cement-based materials influences both physical and chemical interactions in the system. Dhandapani et al. [19], divided the physical interactions into the following three categories: filler action, shearing action, and improved packing. These properties allow a refinement of pore structure and a decrease in material porosity [18]. Furthermore, the chemical interactions promote a nucleation effect on the filler's surface, which enhances the kinetics of binders' reaction [19].

When heated, limestone can be used to obtain lime (CaO) [20], and the presence of this material in an SCM influences the plastic [21], hydraulic [9], and hardened properties

[21–23] of the mortars' mixture. Specifically, its initial and final setting times [23], flowability [21,23], and compressive strength of the samples [21–23]. Moreover, taking into consideration the water/binder ratio, lime replacement percentage, and curing age, a correlation for the mortars' compressive strength can be estimated [24].

Clay minerals are a globally abundant aluminosilicate-rich material with a diverse mineralogical composition [17]. Besides its low cost and high availability, it can also display pozzolanic activity when calcined between 700 and 850 °C [25]. Moreover, in the case of low-grade clays, the reactivity can be improved through alkali thermal fusion, a process involving the co-calcination of clay with an alkali hydroxide [26]. The thermal activation promotes the dehydration of the water in the interlayers, followed by the removal of hydroxyl groups, which triggers the collapse of the layers, causing an amorphization of the structure [5]. When alkali-activated, calcined clays may form geopolymers, known for their binding capabilities [27]. The geopolymerization reaction can be divided in three steps [28][29]: i) dissolution, characterized by the solubilization of aluminates and silicates into solution, which depends on chemistry of the pore solution, namely its pH, water activity and the dissolved ions concentration; ii) polycondensation when the condensation of the monomers to form a stable threedimensional polymer network occurs, and finally iii) the solidification and hardening of the material, caused by the formation of small solid particles that favors the precipitation and growth of the product [28,29]. Furthermore, previous studies showed that the use of CC can increase both early and long-term mechanical properties and reduces the bleeding and shrinkage of the blended material [30].

Fly ash (FA) is a secondary product of thermal power plants based on coal fire and can be used to partially replace OPC due to its filler and pozzolanic properties [31]. Previous studies reported that FA addition enhances the workability [31] of the mixture while decreasing the hydration heat, [32]and, consequently, thermal cracking. Its incorporation also allows the reduction of cement permeability and, the improvement in the mechanical and durability performance at later ages [31]. Depending on the plant and its location, the chemical, mineralogic and physical composition of FA may vary [33], influencing its reactivity, which essentially depends on the particle size distribution, and the vitreous phase and reactive silica content [34]. Although moderate incorporation of fly ash can be advantageous to the system, e.g 25%wt [35], high volumes, above 70%, may decrease the quality of the mixture [36]. Nevertheless, this issue can be overcome through chemical [34,37–39] or mechanical activation [36,39]. While mechanical activation impacts the availability of chemical components at initial hydrations periods, chemical

activation influences the entire hydration reaction, by shortening the induction period, intensifying the C-S-H formation and increasing the total heat released [36,39]. Moreover, using previous models obtained through statistical analysis of the hardness of cement with high-volume fly ash, the compressive strength of mortars can be estimated [40]. For example, under the specific conditions used in the present work, w/c 0.365, 25% SCM replacement, and 28 days of curing time, and using the equation obtained through statistical analysis by Salih et al. [40], a cement-based mortar mixed with FA would obtain a compressive strength of 46MPa.

Ground granulated blast furnace slag (GGBFS) is produced during iron smelting as a secondary product [41,42]. The composition of this SCM depends on the fluxing material and contaminants in the coke used in the furnace [42]. Its main components are silica, calcium, aluminium, magnesium, and oxygen [4,42]. Nevertheless, the quality of the slags depends on the proportion of these elements, since a higher basicity index, (CaO+MgO)/SiO₂, result in higher hydraulic activity [42,43]. Depending on the cooling method and initial temperature of the slag, more than 95% of amorphous content can be obtained in a GGBFS, which contributes to the high reactivity of the material when alkali activated [43,44]. As a SCM, the slag incorporation influences the workability [4,45], volume stability [4,45], and durability performance of the mixture [4,45], it also improves mechanical properties, specifically compressive strength [45,46] and electrical resistivity [46].

In conclusion, SCM incorporation significantly influences the system reactivity and has high environmental advantages associated with clinker factor reduction in cements. Therefore, this study focuses on the replacement of 25% of the AWH clinker with FA, L, CC, or GGBFS in pastes and mortars. The mixtures were compared with a 100%AWH sample, and all specimens were activated with a sodium silicate solution.

Besides the standard benefits of SCM incorporation, the potential activation of the alumino-silicate-based SCM was also taken into consideration. The influence of the SCM incorporation on the hydration kinetics of the AWH binder was followed by isothermal calorimetry, the phase development and hydration products formed by XRD and TGA analysis, and compressive strength was assessed after 2,7 and 28 days of curing.

9.2 Experimental procedure

9.2.1 Binder production

The production of the AWH binder consisted of grinding and mixing typical raw-materials used in OPC production: sand, limestone, and marlstone, but with a final molar C/S ratio of 1.1. The blended mixture was compressed into discs to facilitate the introduction into a silicon carbide crucible, an then heated using an electric furnace. The mixture was first heated to 900 °C, using a rate of 25 °C/min, and kept for 1 hour to allow the decarbonation of the raw meal, followed by a temperature increase to 1550 °C, which was maintained for 1 h to allow a complete melting and homogenization of the mixture. The produced molten mixture was quenched into a water container. The amorphous content of the AWH material was confirmed by X-Ray Diffraction to be higher than 99%. The average chemical composition was determined by X-ray fluorescence (XRF) using the fused bead method. The experimental results are displayed in Table 9-1

To prepare the XRF beads a mixture of 0.8 g of the AWH, with 4.8 g of Fluore-X 65® (containing 66% LiB₄O₇ and 34% LiBO₂ at 99.995%, from ICPH), 0.5 g of NH₄NO₃ (99.0%, from VWR) and a NH₄I tablet (as a non-wetting agent, from PANalytical) was melted at 1200°C using an Eagon2 fusion instrument from PANalytical. The XRF measurements were performed in a PANalytical Axios Cement instrument. Finally, the clinker was ground in a ball mill for a period of 5h, Figure 9-1.

Table 9-1. Chemical analysis results of the AWH clinker.

C/S molar	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	TiO ₂	Others (<1%)
0.99	45.17	8.35	0.75	41.61	1.09	0.14	1.43	0.17	0.33	0.1



Figure 9-1. Ball mill used for clinker grinding.

9.2.2 Supplementary cementitious materials, chemical composition and mixtures specification

In this work, four different SCMs were used to replace the clinker: limestone filler (L), calcined clays (CC), fly ash (FA), and ground granulated blast-furnace slag (GGBFS).

Limestone was provided by CIARGA, fly ash was sent from CIMPOR Souselas plant, while the granulated blast furnace slag was provided from a Turkish cement plant located in Bolu. The specification of these materials conforms to the NP EN 197-1 – 2012 standard [47]. The limestone and the fly ash were used as received while the slag was ground in a ring mill until a 45 μ m residue content below 20%wt. In Table 9-2 the obtained chemical composition of each SCM is displayed.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na₂O	TiO ₂	P ₂ O ₅	MnO	SrO
Filler	1.50	0.39	0.51	97.39	0.35	0.09	0.04	0.09	0.04	0.00	0.02	0.02
Clay	50.80	18.40	6.48	2.74	6.87	2.27	3.77	0.17	0.78	0.19	0.06	0.02
FA	61.90	21.52	7.25	2.98	1.49	0.30	1.75	0.80	1.00	0.60	0.05	0.08
GBFS	36.32	13.58	0.44	40.28	4.15	0.91	0.65	0.31	2.76	0.00	0.62	0.05

Table 9-2. Chemical analysis results of the SCM.

9.2.3 Laser granulometry analysis

The sample particle size distribution was obtained via light scattering using laser diffraction. The tests were performed on a HORIBA Scientific Laser Scattering Particle Size Distribution Analyzer using a dry mode measurement. The particle size distribution of the clinker and the SCM used in this study is displayed in Figure 9-2.



Figure 9-2. Comparison of particle size distribution of the SCMs with the ground clinker.

In Figure 9-3, a flowchart summarizing the origin and characterization of the AWH clinker and each of the SCM used in this work is provided.



Figure 9-3. Flowchart with the origin and characterization process of the AWH binder and each of the SCM. The AWH is represented as black, and the clay, GBFS, FA and L as orange, red, blue and green respectively

After the characterization of each sample, pastes and mortars were prepared by replacing 25% of the AWH binder with an SCM and compared with a standard 100% AWH test material. Table 9-3 displays the specification and nomenclature of each mixture, and in Figure 9-4 a flowchart of the procedure is exhibited.

Cor		
AWH	SCM	Nomenclature
100%	0%	Clinker
75%	25% Limestone	25L
75%	25% Fly ash	25FA
75%	25% GGBFS	25GGBFS
75%	25% CC	25CC
0%	100% GGBSF	100GGBSF

Table 9-3. Composition and nomenclature of the produced mixtures



Figure 9-4. Flowchart of paste and mortar production and respective sample characterization.

9.2.4 Paste production

All pastes were prepared using a water-to-solid ratio (w/s) of 0.25. The mixture was hydrated with a sodium silicate activator with a Si:Na ratio of 0.9 and Na molarity of 3.516M. The alkaline activator was made by mixing a sodium silicate solution (Na2O: 7.5-8.5% SiO₂, 25.5-28.5%, Chem Lab, Belgium) with a NaOH solution (98,2% Prolabo, USA). The pastes were introduced into inox steel molds (20x20x40mm3) and cured under relative humidity (HR) conditions above HR90% at 20°C. After 2 days the samples were demolded and continued curing under the same conditions. The compressive strength of the pastes was assessed using a sample per age at 2,7 and 28 days of hydration.

9.2.5 Mortars production

The mortars were prepared by mixing 450g of AWH binder+SCM with 1350g of sand (AFNOR) according to the EN 196-1 standard [48]. A visual representation of the prepared mortars is exhibited in Figure 9-5. All samples were activated with a sodium silicate solution (Si:Na ratio of 0.9 and Na molarity of 3.516 M) using a w/s ratio of 0.365. The mixture was blended with a Tonimix mixer from Toni-Technik following the procedure described in the EN 196-1 standard. The produced mortars were then introduced into inox steel molds (40x40x160mm³) The curing was performed under relative humidity (HR) conditions above HR90% at 20°C. After 1 day the samples were demolded and continued curing under the same conditions. The flexural and compressive strength tests was assessed in one specimen per age after 2, 7 and 28 days of hydration.



Figure 9-5. Visual aspect of the 28 days cured mortar made with AWH, 25FA, 25L and 25GGBFS.

9.2.6 Isothermal calorimetry analysis

In this study, isothermal calorimetry analysis was used to follow the reaction rates during the hydration process and to determine the total heat of hydration after a seven-day period. The tests were conducted using a TAM Air instrument (Waters Sverige AB, Sollentuna, Sweden) at a constant temperature of 20°C.

This technique measures the heat provided or removed within the sample to maintain a stable temperature throughout the experiment. The setup consists of two identical cells: a reference cell and a sample cell containing the paste. The heat exchange between these cells is monitored through time and allows to assess the heat generated or consumed by the reaction.

9.2.7 Compressive strength tests in pastes and mortars

The pastes and mortars compressive strength tests were performed at the ages of 2, 7 and 28 days in an Ibertest Autotest 400/10 equipment. The tests on mortars were performed, according to the EN 196-1 norm [48]. The resulting debris of the pastes was hand milled and dried at 100°C for 1h in order to analyze the samples by X-Ray Diffraction (DRX) and Themogravimetric Analysis (TGA).

9.2.8 X-ray Diffraction analysis

To characterize the structure of the anhydrous binder and the hydrated pastes at different ages, the samples were analyzed using XRD. The measurements were obtained using an X'Pert Pro (PANalytical) diffractometer with a monochromatic CuK α 1 radiation (λ = 1.54059 Å) and operated in reflection geometry (θ /2 θ). The set up was the following: optics configuration was a fixed divergence slit (1/2°), a fixed incident anti-scatter slit (1°), a fixed diffracted anti-scatter slit (1/2°), and X'Celerator RTMS (Realtime Multiple Strip) detectors, working in scanning mode with maximum active length. Data for each sample were collected from 5° to 70° (2 θ). During the collection the samples were rotated at 16 rpm to facilitate particle statistics. The X-ray tube operated at 45 kV and 40 mA.

To quantify the amorphous content of the binders a spike technique was used in the XRD analysis by adding 20% wt of an internal reference crystalline phase (Alfa Aesar 99.9% α -Al₂O₃ Corundum) to each analyzed sample.

9.2.9 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed to obtain weight loss measurements during pre-determined temperatures under inert atmosphere conditions. In this work, the measurement was made in an ELTRA equipment, and the heating rates were fixed at four temperature intervals (105 °C, 250 °C, 500 °C, and 950 °C) and maintained until a stable weight was reached. The initial step, from room temperature to 105 °C was performed at a 4°C/min rate; the second step, 105-250°C, at a 10°C/min rate; and the third and fourth steps 250-500°C and 500°C-900°C at a 15 °C/min a rate.

9.3 Experimental Results

9.3.1 Calorimetric results

The calorimetric tests results of the pastes produced with AWH and in systems containing AWH and SCMs, are displayed in Figure 9-6. The results indicate that the pastes prepared with GGBFS released a higher amount of heat, suggesting that the GGBSF may have been activated by the alkaline activator. Furthermore, the pastes prepared with the calcined clay displayed a delay of the hydration peak, and a cumulative heat similar to the AWH sample (~93 J/g). The pastes prepared with limestone and fly ash showed a similar amount of heat released after 7 days of hydration (~82 J/g), indicating that both SCM had a similar effect on the paste.



Figure 9-6. Isothermal calorimetry curves of the AWH binder (black line) and of each of the mixtures made with the SCMs, Fly ash (blue curve), GGBFS (red curve), limestone (green curve), and calcined clay (orange curve).

9.3.2 Pastes and Mortars compressive strength tests

The performance of the samples was assessed at 2, 7, and 28 days of hydration. The obtained results for compressive strength results of pastes and the flexural and compressive strength results of mortars are displayed in Figure 9-7 and Figure 9-8, respectively. The results show a linear relation between the increase in compressive strength with hydration time.

At early ages, the results show that on pastes, the 25%L incorporation resulted into a high compressive strength (38 MPa), due to nucleation effect and filler capabilities of the material. The GGBFS displayed the highest compressive strength at early and later ages, which can be attributed to the activation of the SCM. Similarly, the FA sample exhibited comparable values after 7 days of curing, suggesting a delay in activation of the SCM.

On mortars, the 25GGBFS mixture displayed similar results to the AWH binder, while the other mixtures, 25CC, 25L, and 25FA, exhibited lower compressive strength values. Furthermore, the results of these three mixtures are similar, which indicates that, in mortars, calcined clay and fly ash presented an influence in the system similar to

limestone. All samples displayed a sample failure similar to the failure exhibited in Figure 9-9.

Due to limitations in material production, only one sample per age was tested in this study. However, to validate these experimental data, standardized tests were performed with five mortars and ten compressive strength tests in a posterior work. The results of the test indicate a coefficient variation inferior to 2.7% at all ages. Additional details and results of the standardized tests are available in the supplementary material of the present work.



Pastes, 2, 7 and 28 days of hydration Compressive Strength

Figure 9-7. Compressive strength of the pastes at the ages of 2, 7, and 28 days







Figure 9-8. Mortar results after of 2, 7, and 28 days, for A) compressive strength and B) flexural strength



Figure 9-9. Example of sample failures for the tested mortars after 28 days of curing.

9.3.3 X-ray Diffraction analysis

The weigh percentage of each phase in the pastes produced after 2, 7 and 28 days of hydration was determined using quantitative XRD-Rietveld. The obtained results are displayed in Figure 9-10. All pastes displayed the presence of tobermorite even at early ages. The AWH paste exhibited tobermorite after 2 days of hydration, which increased after 7 days and then stabilized at later ages. The CC sample displayed presence of phengite, dehydroxylated muscovite, quartz and calcite, while the FA sample exhibited quartz and calcite. In both samples the tobermorite content increased with hydration time. On the other hand, the GGBFS pastes displayed a similar phase composition at all ages.



Chapter 9. Enhancing Sustainability of AWH binders through Incorporation of Supplementary Cementitious Materials.

Figure 9-10. XRD-Rietveld analysis for the weight percentages of the phases present in each of studied system after 2, 7 and 28 days of curing.

9.3.4 TGA analysis

The content of bound water (BW) in pastes and mortars was assessed by analyzing the loss on ignition (LOI) within the 110°C-250°C and 250°C-500°C temperature range steps from the TGA results. Table 9-4 displays the main experimental TGA data obtained for pastes and mortars tested.

Table 9-4. TGA experimental results obtained for the studied specimens. LOI indicates
the loss in ignition at specific temperature steps. Values are shown in weight
percentages.

		2days			7days			28ays		
San	nple	LOI								
		250ºC	500ºC	950°C	250ºC	500ºC	950°C	250ºC	500°C	950°C
AWH	Mortars	0.47	0.40	0.07	0.62	0.43	0.18	0.87	0.68	0.38
251	Mortars	0.39	0.49	2.30	0.75	0.54	2.98	0.88	0.61	2.77
202	Paste	1.42	1.22	10.07	1.64	1.73	10.13	2.17	2.45	10.56
2500	Mortars	0.40	0.32	0.13	0.77	0.56	0.31	0.83	0.61	0.33
2000	Paste	1.42	0.85	0.35	2.34	1.26	0.73	2.02	2.38	1.99
25FA	Mortars	0.36	0.45	0.16	0.62	0.48	0.46	0.94	0.60	0.31
2017	Paste	1.38	1.25	0.72	1.86	1.60	1.00	2.24	2.25	1.73
25	Mortars	0.44	0.45	0.03	0.73	0.50	0.20	1.04	0.71	0.24
GGBFS	Paste	1.69	1.23	0.35	1.90	1.75	0.33	1.95	2.46	0.61

Following the methodology of previous studies [49–52], the weight percentage of C-S-H content in each sample was calculated using the experimental BW content and applying the Richardson and Qomi [53] model, assuming a 1.1 C/S ratio. Figure 9-11 displays the correlation between the wt% C-S-H formed and the compressive strength of both pastes (cross markers) and mortars (circle markers) after two, seven, and twenty-eight days of curing.

The pastes and mortars results suggest a positive correlation between C-S-H content and compressive strength, which increases with hydration time. Moreover, at early ages (2 days), the 25CC paste exhibited the lowest amount of C-S-H formed, while the 25GGBFS paste exhibited the highest. This trend continued after seven days of curing, and after 28 days all samples displayed similar C-S-H content.





Figure 9-11. Correlation between the weight percentage of C-S-H formed with the compressive strength for pastes (cross markers) and mortars (circle markers). The AWH sample and the mixtures 25L, 25CC, 25FA, 25GGBFS are depicted as black, green, orange, blue and red colors, respectively.

9.4 Discussion

The calorimetric results displayed in Figure 9-6 show that, compared to the 25FA sample, the 25L sample exhibited a higher main hydration heat peak as well as a higher 7-day cumulative heat. This slightly superior heat release may be attributed to a higher proportion of finer particles in the limestone filler, as shown in Figure 9-1. The incorporation of calcined clay (CC) into the AWH resulted in a reduction of cumulative heat released during the initial stages of hydration. However, it led to an increase after 3 days of hydration resulting in a cumulative heat higher than the AWH sample after 7 days. In the case of the GGBFS mixture, it exhibited the highest cumulative heat released and the earliest peak of hydration among all samples, which may indicate a synergy between both materials or an effective activation of the GGBFS under the alkaline activation conditions used.

When looking to the compressive strength results in mortars, both L, FA and CC added systems present similar performances, indicating that CC and FA act essentially as a limestone filler under these alkaline activation conditions. However, their impact in the mechanical performance cannot be unvalued since their 28 days compressive strength results surpass the strength limit of equivalent clinker incorporation, meaning that a value of, at least, 75% of the compressive strength attained after 28 days for the 100% AWH system can be achieved by any of these systems containing 75% AWH + 25% SCM. The ratio between the compressive strength values obtained for the systems containing SCMs and the value obtained for the system comprising only AWH, at all the ages, are displayed in Table 9-5. These results indicate that the initial compressive strength values obtained in the systems containing L, FA and CC are well below the 75% limit. However, at 28 days this limit is surpassed in all the systems tested.

On the other hand, the system containing GGBFS rapidly reaches a performance above the referred limit, which indicates that this SCM is active under the tested conditions. In fact, its initial reaction seems to occur at a faster kinetics than the system containing only AWH (Figure 9-6), which could be related to the similar C/S ratio combined with a higher MgO content in the GGBFS added, which leads to a higher basicity index (CaO+MgO)/(SiO₂). In addition, the higher heat released in the 25GGBFS system may also contribute to the higher earlier strength development, as was confirmed in a previous study [54] on the temperature sensitivity of the AWH binder, which showed that an increase in temperature promotes a higher dissolution of the AWH, resulting in higher compressive strength, particularly at early ages.

Regarding L, this SCM is not expected to be chemically active and its contribution to strength performance may occur merely through the filler physical effect of pore reduction and structure densification. Interestingly the behavior of the 25FA pastes differ from the observed in mortars, as it was observed a larger compressive strength growth in paste specimens when compared to mortars. Moreover, the calorimetric results of the 25FA and 25L exhibit a similar behavior with an induction period of ~0.5 days. However, while the 25L sample displays a sharper peak, the 25FA peak is broader, and at the third day of hydration exhibits the highest heat flow rate, suggesting a possible activation of the SCM. In fact, the later ages performance observed for the pastes of 25FA are similar to the obtained for the system containing GGBFS, which may indicate that FA may also benefit from an additional activation contribution to its mechanical strength, being this effect more evidenced from the 7th day on.

An opposite behavior was observed for the 25CC system where the strength development in pastes at later ages presented a deceleration when compared to the mortars. There is no apparent reason for this observation and further tests should be conducted in order to identify the real cause for this deceleration. Probably, an existing defect in the test specimen could be the reason for the difference found in the behavior of the

Table 9-5. Compressive strength ratios obtained for the SCM mixtures at all a	iges,
using the mechanical performance of the AWH as reference	

Mortar Mixture	Mixture (MPa) AWH (MPa)	Mixture (MPa) AWH (MPa)	Mixture (MPa) AWH (MPa)
	2 days hydration	7 days hydration	28 days hydration
25F	52%	75%	83%
25CC	34%	64%	78%
25FA	35%	66%	85%
25GGBSF	118%	99%	97%

To provide better insight into the mechanical properties in relation to hydration products formed, a linear trendline correlating the wt% C-S-H with compressive strength data was established for mortars and pastes, shown in Figure 9-12, and compared to data from previous studies [49]. While all mortar data exhibited a correlation, the 25CC sample in paste displayed a different behavior, requiring separate analysis. Considering the trendline parameters, the minimum amount of C-S-H for the sample to develop strength was calculated. The main results are summarized in Table 9-6.

The results obtained are consistent with previous research [49,50], suggesting a significant correlation between the formation of C-S-H and compressive strength for both pastes and mortars, with a minimum amount of C-S-H of 17wt.% for pastes and 5wt.% for mortars. The outline of the 25CC sample may suggest the formation of different hydration products.



Figure 9-12. Trendline analysis of the C-S-H weight percentage vs compressive strength. Mortars from the present study are depicted as full blue circle characters, while mortars from previous studied are displayed as empty black circles. Paste result from previous studies are denoted as cross black characters, where the 25L+25FA+25GGBFS pastes are shown as cross blue characters. The 25CC paste is indicated as orange cross markers.

Table 9-6.	Trendline parameters	and minimum	wt.% C-S-H	required for the	sample
	to	develop resist	tance		

Sample	Slope	y-intercept	R ²	Minimum wt.% C-S-H
Mortars	7.1	37.8	0.8	5.3
Pastes 25FA+25GGBFS+25L	4.5	78.2	0.8	17.3
Paste 25CC	2.2	37.8	0.9	16.9

The replacement of a clinker with an SCM significantly reduces the total emission of the produced cements by decreasing the overall amount of clinker required [55–57]. For the AWH material, assuming full electrification with green energy source for both the production process and the lab-made activator production [49], previous results estimated the material-related CO_2 emissions at 340kg/ton clinker [58]. Hence, a 25% reduction in clinker would lead to a decrease in CO2 emissions to 255kg/ton cement, excluding potential carbon capture and storage. Moreover, the high ratio between the compressive strength values obtained for the SCM+AWH/AWH systems (Table 9-5) suggests the potential for higher replacement levels of all SCMs. For comparison, previous studies on OPC replacement, calculated that a 75% clinker substitution in (CEM III) would result in CO₂ emissions higher than 260kg per ton of cement produced [57,59,60].

In conclusion, in the present study, the reduction of AWH clinker in pastes and mortars without compromising compressive strength was achieved, and the activation of the GGBFS as an SCM was accomplished. Nevertheless, some limitations were faced during the execution of this worknamely:

-The use of the same sodium silicate solution optimized for this specific AWH clinker. The activator composition may require further investigation to ensure a proper activation of all SCM in the mixtures.

-The anhydrous material has a high amorphous content, and the main hydration product (C-S-H) is also amorphous. These characteristics challenge the study of composition development of the samples with hydration time.

-The low number of specimens tested per age. This issue was subsequently addressed by performing a standardized test with five mortar samples per age. The results and details of the additional data are provided in the supplementary materials.

9.5 Conclusion

The use of supplementary cementitious materials (SCMs) is an important strategy to help mitigate CO₂ emission in the cement industry by allowing a reduction in clinker content. Thus, in this work, the replacement of 25% of amorphous wollastonitic hydraulic (AWH) clinker with four different SCMs was investigated. The chosen SCM were fly ash (FA), limestone powder, calcined clay, and ground granulated blast-furnace slag (GGBFS). The main results, implications and future work of this study are summarized as follows:

Main results

- 1. On mortars, fly ash and calcined clay acted as fillers, contributing to mortar performance mainly through physical effects.
- The high heat released in the calcined clay mixture and the high compressive strength of the fly ash mixture pastes suggest potential alkaline activation of both SCMs. However, this effect did not increase compressive strength in mortars, likely due to a dilution effect.
- 3. GGBFS demonstrated effective activation in both pastes and mortars, enhancing the performance of the AWH binder. The calorimetric results indicate that the activation of the GGBFS resulted in an increase in heat released. Due to the high temperature sensitivity of the AWH, studied in previous works, the heat released by the SCM, activation may contribute to the dissolution and reaction of the AWH binder
- 4. After 28 days of hydration, all mixtures obtained more than 75% of the compressive strength of mortar made with 100% clinker, either due to the filler effect of the SCM or its activation with the alkaline solution.
- 5. Despite SCMs' inability to develop a pozzolanic reaction with the AWH binder, they can significantly influence the mixture performance through alkaline activation.
- 6. The results obtained are consistent with previous research suggesting a significant correlation between the formation of C-S-H and compressive strength for both pastes and mortars. However, the results obtained for the 25CC sample paste may suggest the formation of different hydration products.

Main implications

- 1. Reduction of CO₂ emissions per ton of AWH clinker to a minimum of 255kg/ton.
- 2. High compressive strength results even with a 25% clinker replacement.

3. Successful activation of GGBFS as an SCM and positive interaction between this material and the AWH clinker.

Future work

- 1. The sodium silicate solution used with the AWH clinker may require further optimization to ensure proper activation of all SCMs in the mixtures.
- 2. Investigate the implications of further clinker replacement levels.

In conclusion, the results of this chapter indicate that the AWH binder partial replacement with an SCM can improve the materials performance due to physical and/or chemical interaction. Moreover, the SCMs can also be considered as alkali-activated precursors, taking full advantage of the physical and hydraulic capabilities of these materials.

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CHAPTER 10. Conclusions and future work

Contents

CHAPTER 10. Conclusions and future work	
10.1 Conclusions	
10.2 Future Work	273

10.1 Conclusions

The use of cementitious materials is fundamental in our society, and its necessity, and consequently, production is expected to increase. Nevertheless, the production of the most commonly used cementitious material, OPC, is associated with high CO_2 emissions. Therefore, this thesis aimed to investigate a binding material produced with the same raw materials as OPC, accessible production, and high compressive strength at early and late ages but with a lower ecological footprint. The alternative binder studied in this work was first proposed in 2015 and consists of an amorphous slag-like material with a C/S content similar to wollastonite instead of the crystalline phases C_3S and C_2S found in OPC. The use of this composition reduces the process emissions related with $CaCO_3$ decarbonation due to its lower calcium content.

Typically, phases with a C/S ratio~1 are not hydraulically active. However, the amorphization of the structure increased the materials' reactivity, allowing its use as a hydraulic binder. Since the production of this binder requires a complete melting of the raw materials to obtain an amorphous product, a liquid-phase technology would replace part of the traditional solid-phase technology.

Moreover, the feasibility of full process electrification with green energy sources (discussed in Chapter 1) would contribute to CO₂ neutrality in the cement industry. This transition allows for:

- The elimination of CO₂ emissions related to fossil fuel combustion.
- Facilitate the capture and storage of pure CO₂ that results from the chemical process, which can be used as raw materials in other industries.

Due to the environmental advantage in the production process of this binder, the present thesis investigated different properties associated with its hydration and refined its production and activation methods to optimize its reactivity.

In Chapter 3, the hydration of the binder was investigated by performing calorimetric analysis and solubility tests. The main parameters tested were the pH influence in the system and the use of a sodium silicate activator in the hydrating solution. Based on the experimental results and literature review, mechanisms and kinetics affecting the AWH dissolution and C-S-H formation are proposed in this chapter.

The hydration of the binder first leads to the stabilization of the silicon surface through
the adsorption of dissociated water. This process leads to the presence of a hydrophilic surface at the water-binder interface. At equilibrium, the Ca and Si dissolution is electrically coupled, and the anion dissolution is proportional to the cation removal rate. Furthermore, the alkalinity increase in the system promotes the silanol group ionization and consequent C-S-H formation. In this chapter, a mechanism for the formation of tobermorite 9Å was proposed. The results suggest that it results from OH⁻ penetration in areas of the anhydrous material with lower calcium content.

The lower Ca content of the AWH binder, compared to OPC, causes two phenomena, 1) the solution pH only reaches a value of 11, an 2) Ca(OH)₂ saturation and consequent precipitation in inhibited. The lower alkalinity causes lower deprotonation of the silanol group and inhibits the development and growth of C-S-H structures. Hence, the system displays a higher induction period, as the formation of the hydration product is delayed. Furthermore, the presence of unreacted calcium and silicon in solution may promote the formation of calcium carbonate and amorphous silica structures.

In the presence of NaOH, silica undersaturation increases, and the high pH promotes its dissolution and C-S-H formation, resulting in a rapid reaction and, consequently, an unorganized C-S-H structure formation around the grain.

In the case of sodium silicate activation, free Si species decreases Si undersaturation, resulting in the presence of an induction period. However, the high alkalinity of the system facilitates C-S-H formation. Hence, in this system, the high pH and the slow and controlled dissolution lead to an organized C-S-H structure around the grain's surface

The formation and growth of the hydration product exposes the surface of the grain, allowing for further interaction with the aqueous medium and promoting additional dissolution. This initiates a self-sustaining process, where the silica solubilization is promoted until Si saturation is reached, followed by the formation of C-S-H species due to the presence of an alkaline medium and Ca in solution. The C-S-H product reduces Si saturation, allowing for further dissolution until equilibrium is reached.

In Chapter 4, the binder's temperature sensitivity was assessed by calculating the activation energy of the hydration reaction during the acceleration period. The results revealed that the minimum required energy for the occurrence of AWH binder hydraulic reaction is higher than alite or belite, indicating increased temperature sensitivity. Furthermore, the tests performed in mortars cured at different temperatures showed a positive correlation between higher curing temperature and increased compressive

strength at an early age. This result may be a result of a faster dissolution promoted by higher temperatures. Finally, it was proposed that the high activation energy is caused by the formation of structurally different C-S-H hydration products than those produced through the hydration of alite and belite, with a lower C/S ratio of 1.1.

In Chapter 5, it was analyzed the influence of short and prolonged exposure of the anhydrous binder to atmospheric conditions. This study was performed to understand the binder storage influence on its hydraulic reactivity. The results indicate that, similarly to OPC, the surface grains of the anhydrous material go through surface changes. However, in OPC, these changes come from the physical adsorption of water molecules or by chemical reactions between the anhydrous OPC minerals with water and CO₂. In the case of the AWH, the results indicate that the grain does not react with air moisture. Instead, when exposed to ambient conditions, the surface of the grains reacts with atmospheric CO₂. This interaction leads to the formation of a discontinuous CaCO₃ layer that inhibits the dissolution of the binder when exposed to a hydrating solution, decreasing its reactivity with the increase in storage time. Nevertheless, the aging effects can be mitigated by activating the material with a sodium silicate solution due to the pH increase and the addition of free silica units into the system that highly promote the formation of C-S-H structures, as discussed in Chapter 3.

In Chapter 6 the possibility of replacing the commercial sodium silicate solution with synthesized, lab-made sodium silicate powders was explored. This study was conducted to mitigate the disadvantages associated with the standard sodium silicate solution activation. In all mixtures, NaOH pallets were used as sodium sources, while different silica sources were tested, specifically glass, sand, and diatomite. These materials were chosen due to their high availability and low cost.

The mixture was heated to 330°C for two hours, resulting in sodium silicate powders. Even though the diatomite and the based sand activators displayed an incomplete reaction, as seen by the residual presence of raw material in the FTIR and DRX spectra, all synthesized samples successfully activated the binder, resulting in mortar compressive strength similar to the mortar hydrated with the traditional sodium silicate solution. Furthermore, to simplify the material's final use, the solid lab-made activators were mixed with the AWH binder. This approach aimed to obtain a single-component alkali-activated mixture, which allows preparing a solution with just the addition of water for ease of application by the end user. In all cases, the lab-made activators were competitive with traditional sodium silicate solutions, regardless of their physical state during addition.

In Chapter 7 and Chapter 8, the influence of the AWH binder raw material composition was investigated, particularly by increasing the Al_2O_3 content from 1%wt up to 12%wt and the MgO content from 1%wt to 8wt%.

The paste results in Chapter 7 indicate that when activating the AWH binder with a solution with a MS of 1.2, an increase in Al₂O₃ content in the clinker leads to a delay in the hydration kinetic. Additionally, a decrease in the amount of heat released after five days of hydration and a decrease in compressive strength at later ages were also observed. Therefore, knowing that an increase in sodium content could facilitate the incorporation of Alumina in the C-S-H structure and taking into consideration the importance that the pH and the silica saturation have in the hydration of the binder (Chapter 3), the decrease of MS in the activating solution was studied.

The paste hydrated with solutions with a lower MS ratio showed a faster kinetic increase in the heat released after five days of hydration and higher compressive strength results, particularly at early ages. However, the results also indicate that a very low MS can promote an uncontrolled rapid growth of C-S-H species, leading to more porous microstructure and inhibiting continuous densification of the structure with C-S-H, compromising the compressive strength at later ages. Therefore, it was proposed that when the activating solution has a high silica content, it decreases the undersaturation in the system, delaying the solubility of the binder resulting in a lower kinetic of the mixture. Conversely, decreasing the silica content increases the undersaturation resulting in an uncontrolled rapid growth of C-S-H, compromising the compressive strength at later ages. Hence, an optimum point for the silica and Na₂O concentration, that corresponds to an MS of 0.9 in the activator, was proposed. The high Al_2O_3 clinkers (AI 10%wt and AI 12%wth) hydrated with this solution obtained competitive results after 28 days of hydration, compared with the low Al_2O_3 clinker samples. Hence, using this activating condition allows the increase in Al_2O_3 content in the clinker without compromising the performance of the binder, which not only extends the raw material composition but also allows a reduction in the process temperature. Since the Al₂O₃ content influences the phases formed in the binder and decreases the melting point of the system until the eutectic point at $18.5 \text{ wt}\% \text{ Al}_2 \text{O}_3$ is reached, it is possible to reduce the process temperature from the traditional 1550°C to at least 1450°C.

In Chapter 8, the influence of increasing MgO content was observed from the typical \sim 1%wt to 8%wt was investigated. This increase raised the basicity index of the clinker, promoting a shift in the Qⁿ distribution of the resulting material to lower coordination numbers. The higher Q⁰ content promoted an increase in reactivity due to the higher

270

solubility of the silicon species. However, even though the calorimetric results indicate an increase in kinetic and a rise in heat released, this did not translate into higher compressive strength in mortars,. Furthermore, it is important to note the absence of periclase in the hydration product, which could compromise the performance of the binder at later ages.

Finally, in Chapter 9 the influence of blending the AWH binder with different supplementary cementitious materials was investigated by replacing 25%wt clinker in both pastes and mortar. At 28 days of hydration, all mixtures revealed an improvement in compressive strength, indicating the positive contribution of the SCM either due to physical or chemical interaction. Compared with the use of SCM in OPC, in the AWH binder, the SCM cannot show a pozzolanic effect due to the absence of Ca(OH)₂ in its hydrating products. However, the AWH binder's requirement for a sodium silicate alkaline activation can also promote the activation of the blended SCM, improving the overall performance of the mixture. This particular phenomenon was observed in the blended GGBFS mixture. Furthermore, knowing that the activation of the SCM leads to an exothermic reaction and knowing the high sensitivity that the AWH binder has to temperature (Chapter 4), the activation of the SCM leads to a synergy between these two components. The hydration of the SCM increases the system temperature, which in turn, promotes the hydration reaction of the AWH binder.

Overall, the work performed during this thesis led to an understanding and improvement of the AWH binder activation and production conditions, meeting the main objectives of the study. The material exhibited a mechanical performance that compares, and even exceeds, that of OPC both in pastes and mortars at early and later ages. Furthermore, the study of the importance of the activating solution allowed the optimization of the sodium silicate activator, which in turn allowed the incorporation of higher Al₂O₃ content into the clinker, lowering the melting point of the mixture and, consequently, decreasing the maximum process temperature from 1550°C to 1450°C. This work further validates the use of this material as a partial, or complete, replacement to OPC and contributes to establishing the necessary conditions for a scale-up of the production and use of the material.

10.2 Future Work

Although a significant contribution to the understanding of the performance of the binder was achieved in this work, a validation of the proposed hydration model through simulation dynamics would allow its corroboration. Furthermore, since the goal of this product is its large-scale production and commercialization, the performance of the binder according to standardized tests should be assessed, for example, by performing aging studies in hydrated samples. Additionally, a scale-up in the production process is necessary to allow the study of the AWH binder in concrete and reinforced concrete. Another interesting approach would be to investigate the possibility of carbonation of the binder in carbonation chambers instead of its hydration, and the optimization of the sodium silicate activator when added to a SCM+AWH mixture.

ANNEX I

Due to limitations in material production only one sample per age was tested in the study of AWLC-based mortars. Therefore, in this annex a standardized test with higher number of mortars was performed after 2, 7 and 28 days of curing

For this study, the AWH was produced at two different temperatures, 1450°C and 1550°C and then ground until the sieve residue over 45µ was below 4%. The performance of the binders was tested on both pastes and mortars by hydrating the samples with a sodium silicate solution. On pastes, the initial and final setting time of pastes was determined, and the hydration reaction was followed by isothermal calorimetry. On mortars, the spreadability and the compressive strength at different curing times were measured. For each age, five different mortar samples were tested, leading to a total of ten compressive strength measurements. This approach allowed for a statistical analysis to be performed on the obtained data.

The following sections provide a detailed account of the production method, the experimental results, and analysis of the data collected. The main goal of this annex is to complement the main body of the thesis, reinforcing the robustness and validation of the experimental data.

Production method

Preparation of the binder

Common raw cement materials used in the production of Portland cement clinker, but with a lower overall C/S molar ratio of ~1 were used in the production of the 3 AWH binders. The raw materials were ground, mixed, and compressed. The compressed disc was broken into four pieces and placed in a silicon carbide crucible. The filled silicon carbide crucible was placed in an electric furnace and heated, at a rate of 25°C/min, to 900 °C, maintaining this temperature for 1 hour, to allow the decarbonation of the raw materials. Then, the furnace temperature was raised to the melting temperature of either 1450°C or 1550 °C and kept for 3h to guarantee the complete melting of the powder mix and its chemical homogenization. The material was quenched by pouring the melted mixture into a water container resuting in a material with an amorphous content above 98%. The chemical composition of each clinker is shown in Table *1*.

Before grinding, the bulk density of the clinker was determined by measuring the mass required to fill a one-litre container. It was observed that the decrease in melting temperature caused a viscosity increase in the mixture, resulting in less air being trapped in the clinker after quenching and decreasing the volume of the final product, resulting in a clinker with higher density. After grinding, the fineness of the resulting powder was assessed by measuring the Blaine the medium particle size diameter, and the sieve residue over 45µ. Due to its higher density, to obtain a sieve residue over 45µm similar to the 1550C sample, the 1450°C Clinker needed more grinding energy, resulting in a powder with a larger medium-sized diameter and higher Blaine numbers.

Finally, the specific gravity was measured using the test method for density of hydraulic cements (ASTM C188-14). The main results of these experiments are shown in Table 2.

AWH binder	Melting temperature	SiO₂ %wt	Al ₂ O ₃ %wt	Fe ₂ O ₃ %wt	CaO %wt	MgO %wt	K₂O %wt	Other metallic oxides %wt
1550C	1550ºC	42.69	8.52	0.69	44.42	1.04	1.80	0.79
1450C_A	1450ºC	44.28	9.64	1.19	40.00	1.43	1.99	0.72
1450C_B	1450°C	42.87	10.39	0.85	40.64	1.44	2.16	0.73

Table 1- Melting temperature and chemical composition of the produced binders.

AWH binder	Grinding Time (min)	Bulk density (g/cm ³)	Blaine (cm²/g)	Medium particle size diameter (µm)	Sieve residue over 45µm%	Relative density (g/cm ³)
1550C	75	0.71	5810	11	0.64	2.90
1450C_A	90	1.474	6400	25	3.3	2.93
1450C_B	135	1.490	7500	19	2.1	2.93

Preparation of the sodium silicate solution

The sodium silicate solution was obtained by equilibrating a solution of Na_2SiO_3 (Na2O: 7.5–8.5% SiO2, 25.5–28.5%, Chem Lab, Zedelgem, Belgium) with NaOH (98.2%, VWR-Prolabo, Matsonford, PA, USA) to achieve a SiO₂/Na₂O modulus of 0.9 and a Na molarity of 3.516.

Preparations and characterization of pastes

Pastes were prepared by hydrating the amorphous binder hydrated with the sodium silicate solution using a water/solids ratio of 0.2781. The reaction was followed by isothermal calorimetry at 20°C on a TAM Air instrument (Waters Sverige AB, Sollentuna, Sweden) by inserting the paste into a vial *ex-situ*. The initial and final setting time was measured using a needle and assessing its ability to penetrate the paste. It was considered that the initial setting time was the interval in the middle of activating the binder with the alkaline solution and when the needle remains 5mm above the mould bottom, and the final setting time is the period between the mixing of the binder with the solution and when the paste its plasticity.

Preparations and characterization of mortars

The mortars were prepared by activating the binder with the sodium silicate solution, using a solid/water ratio of 0.365. To evaluate mortar's plasticity, spreadability tests were performed according to the requirements of BS EN 1015-3. The samples were stored under relative humidity (HR) conditions above HR95% at 20°C. After 2, 7, and 28 days of hydration flexural and compressive strength tests were performed. For each age five mortars were tested, resulting in five flexural tests and ten compressive strength tests.

Pastes experimental results

To evaluate the performance of the binder the initial and final setting time of pastes was determined and the hydration reaction was followed by isothermal calorimetry, the results are presented in Table 3 and Figure 1 respectively. The calorimetric results show that the sample with the highest Blaine value, 1450C_B, presented the earliest hydration peak and the highest amount of heat released, indicating a faster reaction kinetic compared to the other two samples. Similarly, this paste also presented the earliest initial setting time. Even though the 1550C sample displayed a more intense hydration peak than 1450C_A and exhibited the earliest initial setting time, after 7 days of hydration the amount of heat released was similar to the 1450C_A.

AWH binder	Initial setting time (min)	Final setting time (min)
1550C	90	125
1450C_A	115	245
1450C_B	68	150

Table 3- Initial and final setting time of the produced pastes with each binder.



Figure 1- Isothermal calorimetry results of the hydrated binders.

Mortars Experimental results

For each binder, a total of 5 mortars were made by mixing the binder with sand and the alkaline solution. Following the mixing, spreadability tests were performed, and the results are shown in Table *4*. After 2, 7, and 28 days, flexural and compressive strength tests were performed, the results are displayed in Figure 2. Five mortar samples were tested for each age and underwent a flexural test, which broke the mortar into two. On each half of the sample compressive strength tests were performed, resulting in 10 compressive strength tests per age, the results are show in Figure 3.

AWH binder	Spreadability (mm)		
1550C	165		
1450C_A	180		
1450C_B	168		

Table 4- Spreadability results of the mortars produced with different binders.

In Figure 2 A, B, and C the individualized flexural tests performed at 2,7 and 28 days of curing are presented. Figure D shows the average value and standard deviation of the results obtained. The 1550C sample presented the highest flexural strength at 28 days of hydration, this may be attributed to the increased carbonation of the sample, as the calorimetric results suggest that its hydration kinetics was slower than the 1450C samples. The main difference between carbonation and hydration reactions is caused by their different mechanisms, whereas the hydration reaction occurs evenly throughout all the hydrated samples, the carbonation is influenced by the external penetration of CO₂. This carbonation phenomenon promotes the densification and enhancement of the sample [1]. Hence, the formed coating on the 1550C sample may act as a thick protective layer of decreased porosity on the mortar surface, allowing higher flexural strength at later ages [2,3].



Figure 2- Individual results of mortar's flexural strength test results (A,B and C) and average flexural strength with standard deviation at 2, 7, and 28 days of hydration (D).

In Figure 3 A, B, and C the individualized compressive strength tests performed at 2,7 and 28 days of curing are presented. Figure D shows the average value and standard deviation of the results obtained



Figure 3- Individual results of mortar's compressive strength test results (A,B, and C) and average compressive strength with standard deviation (D) at 2, 7, and 28 days of hydration.

To summarize the database of Figure 3 the average strength, standard deviation, and coefficient of variation (ratio of the standard deviation to the mean) are displayed in Table 5.

Curing time	Samples	Number of specimens	Average Strength (MPa)	St Dev	CV%
2 days	1550C		33.4	0.9	2.6
	1450C_A		18.35	0.7	3.8
	1450C_B		43.5	1.8	4.1
7 days	1550C		60	1.6	2.6
	1450C_A	10	60.3	2.4	3.9
	1450C_B		71.0	1.2	1.7
28 days	1550C		76.0	1.6	2.2
	1450C_A		82.2	3.0	3.7
	1450C_B		90.2	0.9	1.0

Table 5. Database, average strength, standard deviation, and coefficient of variation (CV) of the tested samples

Analyzing Table 5 we observe that all results displayed a low coefficient of variation (CV) indicating a low variation around the average value and a high degree of homogeneity in the dataset. Furthermore, the sample 1450C_B obtained the highest average strength results at all ages.

In each set of results statistical analysis was performed using GraphPad Prism tools. The normality of the tests was assessed with the Shapiro-Wilk test. The comparisons of three or more groups was tested using ANOVA, one-way analysis of variance. To compare two independent groups, the t-Student test was applied. The chosen level of significance was set at 0.05. The results show that the mortars 1550C and the 1450C_A at 7 days of hydration show similar compressive strength results (p-value>0.8). However, significant differences were observed among all the other samples (p<0.05). Furthermore, at all ages the 1450C_B sample exhibited a significant increase in strength when compared to the other 2 samples. (p <0.001).

Conclusion

In conclusion, the experimental results show that heating the mixture at 1450°C instead of 1550°C increases the compressive strength of the material at later ages (28 days). However, the lower hydration kinetic of the 1550C binder allows further carbonation of the samples, resulting in an increase in flexural strength. Statistically significant differences were observed in the compressive strength between the 3 samples at 2 and 28 days of hydration, indicating that the observed differences were due to binder processing parameters, specifically melting temperature and ground fineness of the binder. Furthermore, the 1450C_B sample consistently outperformed the other samples. Finally, between the same dataset, a low coefficient of variation (CV) was obtained, indicating that the test of one sample per age can be representative of the performance of the mortar, reinforcing the validation of the experimental data obtained in the main body of this work.

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