

Optimization of production and hydration conditions of amorphous hydraulic binders with a C/S ratio of 1.1

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Abstract

This work intended to study several aspects related to the production and hydration of amorphous hydraulic binders with a C/S ratio of 1.1, being particularly focused on the study of the reduction of the melting temperature of this type of clinker. For this study, a melting element (sodium tetraborate decahydrate) was introduced in the clinker production, with different additions being made. The structural differences of the clinkers produced as well as their hydraulic behavior were studied through the techniques of XRD, FTIR, TGA, isothermal calorimetry and ^{29}Si NMR. Regarding the hydration conditions, different W/C ratios and different pH conditions were tested and the impact of these parameters on the hydraulic reactivity of this binders was studied through the techniques mentioned above.

1. Introduction

The cement industry is responsible for about 5% of anthropogenic CO_2 emissions and most of cement CO_2 emissions, about 510 to 712 kg CO_2 /ton cement are related to limestone calcination at high temperatures [1, 2]. The need for the reduction of CO_2 emissions in cement industry drove the development of new alternatives and one of the possible approaches corresponds to the reduction of calcium incorporation in the cement production, however this reduction leads to progressively less reactive calcium silicate phases. This work is dedicated to the study of new amorphous clinkers with low C/S ratios and aims to the study of variations in their production as well as in hydration conditions.

2. Experimental Procedure

2.1. Materials and processing conditions

The amorphous hydraulic binder was produced by using a combination of raw materials common in the cement industry, in such a way that the obtained overall C/S molar ratio was 1.1. Table 1 shows the

composition of the raw materials used and the final theoretical composition of the amorphous hydraulic binder. The production process consisted in the following procedure:

- A. Heating the raw mix at rate $R_1=25^\circ\text{C}/\text{min}$ to a temperature T_1 .
- B. The temperature T_1 (in the liquid region) was maintained constant for 60 minutes, allowing the homogenization of the composition
- C. Quenching by pouring the melt into a tank of water at ambient temperature.

After quenching, the amorphous material obtained was dried in a stove at 105°C for approximately 30 minutes and then ground in a ring mill for 180s with propanol, followed by a drying step at 50°C in a stove for about 30 minutes. The ground powder had a particle size below $35\mu\text{m}$ and was used to produce the pastes which were poured into molds with dimensions of $20\times 20\times 40\text{ mm}^3$ and cured in a moist cabinet with a relative humidity over 95% and a temperature of 20°C . The prisms were demolded at 7 days, just before the compressive strength test.

Table 1- Raw materials and raw mix combinations used to produce the amorphous hydraulic binders with C/S molar ratio of 1.1.

Raw-materials	Composition (wt%)											
	%wt	LOI	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	TiO ₂	P ₂ O ₅
Limestone	49.64	43.9	0.20	0.16	0.14	99.11	0.30	0.04	0.02	0.04	0.02	0.00
Sand	48.45	0.37	97.30	1.29	0.16	0.00	0.02	0.00	0.52	0.11	0.00	0.00
FCC	1.91	0.65	39.48	51.39	0.52	0.13	0.17	0.09	0.02	0.48	0.81	0.22
C/S=1.1	100	-	47.99	1.69	0.16	49.20	0.16	0.02	0.26	0.08	0.02	0.00

Anhydrous clinkers as well as their respective pastes, at the ages of 7, 28 and 90 days, were analyzed to follow structural evolution, phase development and mechanical performance.

3. Results and discussion

3.1. B₂O₃ addition

The amorphous hydraulic binders (C/S ratio of 1.1) were produced with different B₂O₃ wt% by adding sodium tetraborate decahydrate (Borax), in order to obtain clinkers with theoretical compositions of 0%wt, 2.5%wt, 7%wt and 12%wt B₂O₃. It was observed a decrease in the melting temperature with increasing B₂O₃ wt%. Table 2 shows the clinkerization temperatures of the binders produced, considering the different B₂O₃ wt%. It was designated a nomenclature in the form "xB₂O₃y", where x and y indicate B₂O₃ wt% and clinkerization temperature, respectively.

Table 2- Clinker temperatures applied as a function of the B₂O₃ %wt added.

B ₂ O ₃ %wt	Clinkerization temperature (°C)				
	1550	1530	-	-	-
0	1550	1530	-	-	-
2.5	1550	1500	-	-	-
7	1550	1500	1450	1400	-
12	1550	1500	1450	1400	1350

3.1.1. Isothermal Calorimetry

Figure 1 shows the calorimetric results for all samples, where it is possible to observe that the induction period is practically constant, however differences in the intensity of the exothermic peak appear as well as in the time at which it emerges. Samples with 2.5%wt B₂O₃ present a peak with higher intensity than the samples without addition of B₂O₃, however the posterior trend is a lower peak intensity with the increase of B₂O₃ addition. In addition, it is also observed that the higher the addition of B₂O₃, the wider the exothermic peak becomes, that is, later the maximum heat released is reached, becoming more gradual the heat release.

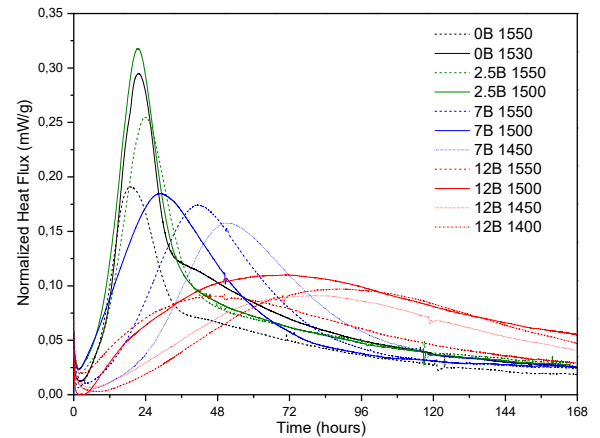


Figure 1- Calorimetric curves related to the hydration of amorphous hydraulic binders of C/S molar ratio 1.1, produced with different additions of B₂O₃ and at different clinkerization temperatures.

3.1.2. Compressive Strength

In table 3 the development of compressive strengths is shown for the samples with different B₂O₃ content. It is observed that there is a tendency for the increase of strength development with an increase of up to 7%wt B₂O₃, while above this value an inverse trend was observed until 12%wt B₂O₃. For a clinkerization temperature of 1550 °C and 1500 °C, identical resistances were obtained for any addition of B₂O₃ up to 7% B₂O₃ at the 7th day of hydration. However, at older stages of hydration there is a higher strength development for clinkers containing 2.5%wt and 7%wt B₂O₃. From Table 3 it is possible to observe that a slight increase in strength development occurs when the temperature is lowered from 1550°C to 1500°C, with additions of 0%wt, 2.5%wt and 7%wt B₂O₃.

3.1.3. TGA

The determination of bound water in the samples was determined through TGA, assuming that the structural water present in the formed hydration products is lost between 105°C and 500°C and knowing that no Portlandite contribution to the weight loss in this temperature range exists. This temperature range was defined in agreement with other published studies [3-5]. From the amount of bonded water determined by TGA and by assuming the data computed in the work of Qomi et al. [6] for the water to silicon ratio (W/S) in calcium silicate hydrates with a varying C/S, an estimation of the CSH %wt produced was performed. A final stoichiometry C_{1.1}SH_{0.82} was obtained, where 1.1 corresponds to the C/S ratio of CSH which was defined as equal to the C/S ratio of the precursor material and 0.82 corresponds to the W/S ratio which was calculated.

Table 3- Compressive Strengths of samples produced with different clinkerization temperatures and different B₂O₃ content.

T (°C)	B ₂ O ₃ %wt	Compressive strength (MPa)		
		7 days	28 days	90 days
1550	0	9.0	12.1	14.7
	2.5	10.7	18.1	25.5
	7	8.7	18.5	30.0
	12	3.5	10.9	12.2
1500	0	10.9	18.1	22.6
	2.5	9.5	20.6	28.1
	7	9.5	21.7	31.1
	12	1.1	2.6	1.6
1450	7	3.0	7.8	10.7
	12	2.0	6.3	8.7
1400	7	7.0	18.4	25.6
	12	1.9	8.6	13.2
1350	12	0.2	0.4	0.1

Calculations were performed according to the equations below.

$$wt\% C_xSH_y = \left(\frac{\frac{wt\% SiO_{2reacted}}{wt\% SiO_{2initial}} + wt\% H_2O_{bound}}{100} \right) * 100 \quad Eq. 1$$

where

$$wt\% SiO_{2reacted} = \frac{wt\% H_2O_{bound}}{\left(\frac{W}{S}\right) * \frac{M(H_2O)}{M(SiO_2)}} \quad Eq. 2$$

Figure 2 plot the calculated wt% C_{1.1}SH_{0.82} against the respective compressive strength for the pastes produced with 7, 28 and 90 days of hydration. It is observed that there is a higher CSH formation for clinkers produced with 2.5%wt and 7%wt B₂O₃ compared to the other samples. It is also possible to observe the dependence of the compressive strength on the amount of CSH produced, indicating that this

phase is the main responsible for the mechanical properties. However, different strength development with %wt CSH is observed for different clinkers, demonstrating different intrinsic mechanical properties of the hydration products formed. However, the results seem to indicate that the incorporation of B₂O₃ (and Na₂O) into the formed CSH, for clinkers with an addition up to 7%wt B₂O₃, translates into an improvement in mechanical properties.

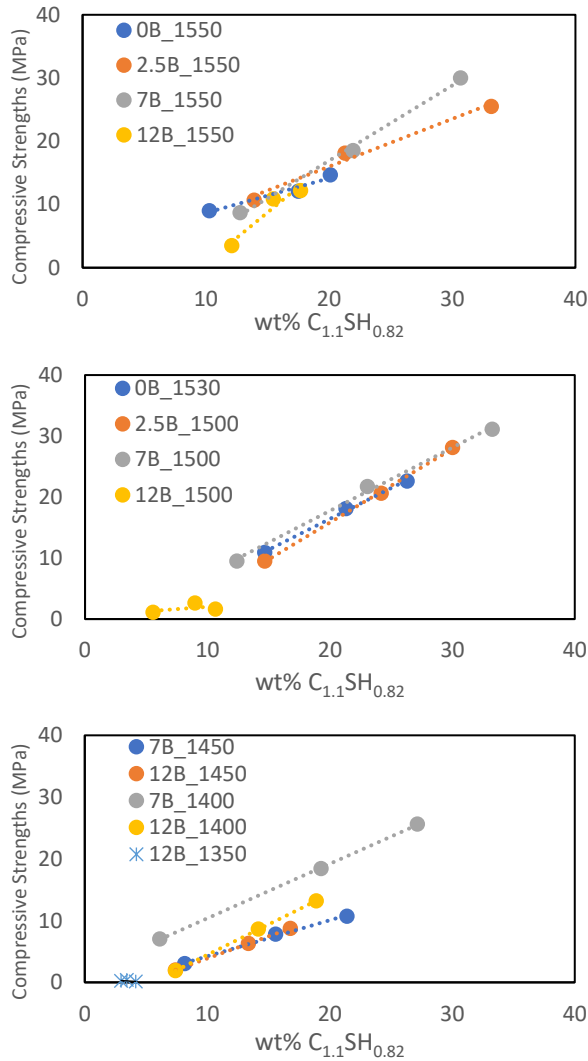


Figure 2- Relation between the compressive strengths obtained and wt% C_{1.1}SH_{0.82} formed.

3.1.4. ²⁹Si MAS NMR

The acquired ²⁹Si MAS NMR spectra of the anhydrous binders produced at 1500°C are shown in figure 3. The center of the bands corresponding to the Qⁿ units in amorphous calcium silicate materials can be found in the work of Zhang et al. [7], where Q⁰, Q¹, Q², Q³ and Q⁴ are approximately centered at -70, -75, -82, -89 and -101 ppm, respectively. In figure 3, it is possible to observe that with the increase of the addition of B₂O₃ the displacement of the spectra for more negative chemical shifts occurs, corresponding to a displacement towards the most polymerized units.

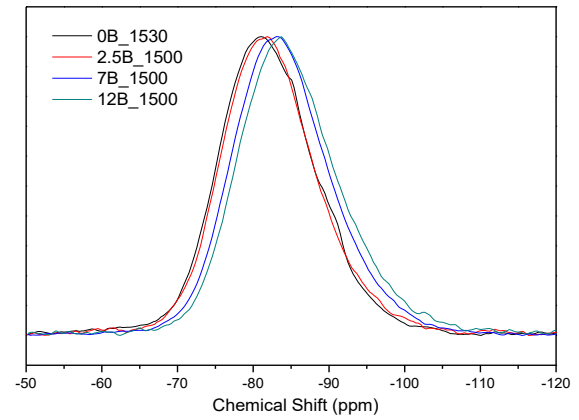


Figure 3- ²⁹Si NMR spectra of anhydrous samples.

3.1.5. Discussion

The ²⁹Si NMR indicate that the addition of B₂O₃ functions as a network former, increasing the polymerization of the network. In addition to the Si-O-Si formation, Si-O-B structures can also be formed in the network. Thus, the introduction of B₂O₃ has the effect of reducing the strength of the structure, since there is a decrease in its uniformity [8]. From the results obtained on the compressive strengths, there seems to be benefits in the addition of B₂O₃ up to 7%wt. Whereas, further increase up to 12%wt B₂O₃, revealed to be deleterious. However, using only the

²⁹Si NMR results it would be expected that the higher polymerization of the structure would always result in lower strength, since it is expected that the Q⁰ units are the most prone to react [9]. The variations in the resistances obtained according to the addition of B₂O₃, demonstrate that there are several effects of the addition of B₂O₃ that may be competing. For example, the progressive increase of the observed resistances at 1550 °C and 1500 °C with the addition up to 7%wt B₂O₃ seems to be indicative that one of the dominant effects of B₂O₃ up to such addition will be its ability to weaken the structure, due to the reduction of uniformity previously explained. This weakening of the structure should ensure an easier incorporation of water, resulting in a greater amount of structural water. Furthermore, the addition of B₂O₃ was performed using sodium tetraborate decahydrate and, therefore, as the addition of B₂O₃ increases, so does the addition of Na₂O. Minority elements, such as sodium, may also function as a network modifier, like B₂O₃, in that they favor the breakage in the glassy matrix of the structure, essentially composed of an interconnected silica network, thus reducing the degree of condensation. Another possible effect of the existence of Na⁺ on the structure corresponds to the displacement of negative charges. Maintaining the clinkerization temperature, the addition of B₂O₃ also promotes an increase in the energy content, since the melting temperature of the clinker will decrease. The decrease in resistance when moving from 7%wt to 12%wt B₂O₃ seems to be indicative of the predominance of other effects than those previously mentioned, which obviously are also plausible in these additions. One of the effects that can lead to

this decrease is the greater polymerization of the structure when B₂O₃ is added, an addition of 12%wt may mean an excessive increase of polymerization of the structure, functioning B₂O₃ as a network former.

3.2. Optimization of the hydration conditions

The impact of the water/cement (w/c) ratio was studied from the point of view of the hydraulic behavior of the hydrated clinker. In this way, 4 different ratios - 0.375, 0.35, 0.325 and 0.3 - were studied to produce the clinker pastes OB_1550 and 2.5B_1500.

3.2.1. Compressive Strengths

Table 4 plots compressive strengths against the w/c ratio for the different ages of hydration, relative to clinker OB_1550 and 2.5B_1500. It is possible to observe the benefit of the addition of B₂O₃ in the clinker structure, since, for any w/c ratio, better compressive strengths were obtained with clinker 2.5B_1500 compared to clinker OB_1550.

Table 4- Compressive strengths in function of w/c ratio for the different ages of hydration, relative to clinker OB_1550 and 2.5B_1500.

Sample	W/C ratio	Compressive strength		
		(MPa)		
		7 days	28 days	90 days
OB_1550	0.375	9.0	12.1	14.7
	0.35	12.2	14.0	19.7
	0.325	13.2	20.4	20.3
	0.3	0.3	0.4	1.1
2.5B_1500	0.375	11.3	20.6	28.1
	0.35	12.1	26.3	28.5
	0.325	13.1	31.9	29.6
	0.3	12.9	26.9	31.2

3.2.2. TGA

Figure 4 shows the thermogravimetric results obtained for the pastes produced with 7, 28 and 90 days of hydration, relative to the samples OB_1550 and 2.5B_1500, with different w/c ratios. A larger amount of structural water is also observed for the 2.5B_1500 compared to OB_1550 for any w/c ratio at the 28th day of hydration, which is accentuated by increasing the hydration time to 90 days.

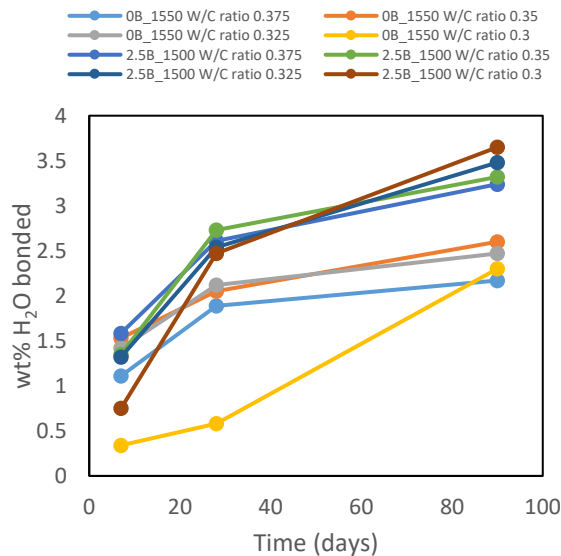


Figure 4- Thermogravimetric results obtained for the pastes produced with 7, 28 and 90 days of hydration, relative to the samples OB_1550 and 2.5B_1500, for which the W/C ratio was varied.

3.2.3. Discussion

In the previous chapter, it was possible to observe the benefit of the addition of up to 7%wt B₂O₃ as well as the reduction of the clinker temperature from 1550°C to 1500°C, observing a higher hydraulic reactivity for the pastes prepared under these conditions, applying a w/c ratio of 0.375. In this chapter, the effect of these two factors on the reactivity of the produced clinker is notorious since any w/c ratio applied in the production of the pastes 2.5B_1500 results in higher

compressive strengths compared to the pastes OB_1550, for 28 and 90 days of hydration.

Figures 5-6 show the relation between the results of the compressive strengths and the respective quantity of C_{1.1}SH_{0.82} obtained, for the variation of the w/c ratio of clinker OB_1550 and 2.5B_1500, respectively. It is observed in figure 5 that the application of the w/c ratios of 0.35 and 0.325 in the hydration of the amorphous clinker OB_1550 leads to an improvement in strength as well as in the CSH formed. For higher w/c ratios, hydration kinetics is delayed, with the excess water decreasing the cohesion of the system due to the creation of pores that are probably formed after the evaporation of this excess water. On the other hand, the use of a w/c ratio of 0.3 results in very low strength and CSH formation at all ages, also affecting the workability, and probably not being able to ensure enough water to promote an ideal hydration process.

Regarding the binder 2.5B_1500, it shows increased resistance at younger ages (7 and 28 days) with decreasing w/c ratio until 0.3. The strength development registered for the transition from 28 to 90 days of hydration for w/c ratios below 0.375 is not very marked, probably due to the low penetration of water resulting from reduced capillary pore size. For the w/c ratio of 0.375 there is a higher evolution of resistances from 28 to 90 days compared to other tested ratios, ending with similar strength. With this, it can be said that lower w/c ratios seem to contribute beneficially for early age strength while higher ratios ensure higher strength development at older ages.

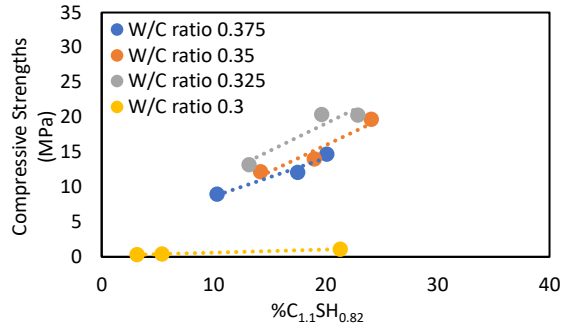


Figure 5- Compressive strengths as a function of wt% $C_{1.1}SH_{0.82}$ formed with respect to the variations applied in the w/c ratio in the hydration of the amorphous clinker OB_1550.

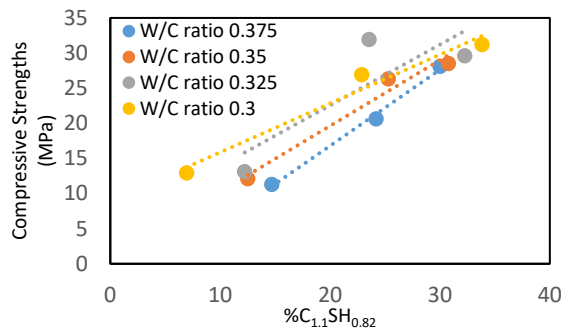


Figure 6- Compressive strengths as a function of wt% $C_{1.1}SH_{0.82}$ formed with respect to the variations applied in the A/C ratio in the hydration of the amorphous clinker 2.5B_1500.

3.3. Amorphous Hydraulic Binder hydration study under variable pH conditions

In order to study the influence of initial pH in the hydration behavior of these amorphous binders, a set of experiments were designed with different aqueous solutions of NaOH with pH 12, 13 and 13.5. At a later stage of the study, pastes with a constant w/c ratio of 0.375 and with pH 13.5 were produced.

3.3.1. Preliminary Study - CaO and SiO₂ Saturation Concentration

In a preliminary study, the impact of the amount of clinker in solution on the concentration of solution ions obtained was investigated. Addition of 5, 10, 15 and 20 g in 50 ml of water at the beginning of the calcium and silica dissolution process was carried out

and calcium and silica concentrations in solution were determined. Table 5 shows the results obtained for the concentrations of CaO and SiO₂ obtained as well as the ratio C/S relative to the solution ions and the %structural H₂O obtained for the residue of the filtration process through the TGA.

Table 5- Concentrations of CaO and SiO₂ in solution, C/S ratio of ions in solution and wt% structural H₂O of filtration process residues.

Addition of clinker (g)	CaO (mmol/L)	SiO ₂ (mmol/L)	C/S	Wt% H ₂ O bonded (residue)
5	4.32	4.34	1.00	0.22
10	4.59	4.47	1.03	0.24
15	3.99	4.03	0.99	0.23
20	4.41	4.50	0.98	0.23

It is possible to verify that the concentration of ions in solution is practically constant regardless of the amount of sample added to 50 ml of distilled water. This observation indicates that these concentrations of SiO₂ and CaO obtained correspond to the saturation of the system. It is also verified that the release of ions into the solution always results in C/S ratios very close to the C/S of the precursor anhydrous, suggesting that there is no preferential release of ions and that the dissolution of the clinker occurs homogeneously. In the case of the water content obtained by TGA for the filtration residue of the various clinker additions, it is observed that a virtually constant value is obtained for all additions (~0.23%). This supports the theory that, in fact, regardless of the mass of amorphous hydraulic binder added, the CaO and SiO₂ concentration values obtained represent the saturation concentrations of these species, since the relative percentage of CSH formed in the experiment period is approximately constant in any of the scenarios tested.

3.3.2. Determination of CaO and SiO₂ in solution

The initial addition of 5g of amorphous clinker in 50 ml of water was chosen, since for these conditions the saturation of the system is guaranteed. To study the evolution of the saturation concentration under higher pH conditions, a solution of NaOH [0.01M] was added to the mixing water until the desired pH was obtained, prior to addition of the clinker. Table 6 shows the concentration of the ions in solution as a function of the pH. The imposition of pH 13.5 results in a decrease in the saturation concentration of the system, suggesting that for these pH conditions the system will reach saturation faster and, therefore, a faster precipitation of hydrated products. Thus, it was decided to monitor the evolution of the hydration of the paste prepared with pH 13.5.

Table 6- Concentration of the ions in solution and compressive strengths as a function of the pH of solution.

		pH			
		7	12	13	13.5
Conc. [mmol]	CaO	4.32	5.63	5.81	4.11
	SiO ₂	4.34	5.66	5.52	4.02
Strength (MPa)	7 days	9	-	11.4	4.7
	28 days	12.1	-	13.8	7.7

3.3.3. Compressive Strengths

Table 6 shows the compressive strengths obtained as a function of the pH of the solution, on the 7th and 28th day of hydration. It is possible to observe a benefit in increasing the pH of the water from 7 to 13, considering the results of the resistance obtained for the same, at both the 7th and 28th day of hydration. The transition from pH 13 to 13.5 results in a considerable decrease of the resistances.

Furthermore, the paste produced without addition of NaOH resulted in higher strengths compared to the pastes with pH of 13.5.

3.3.4. TGA/DRX-Rietveld

Table 7 shows the results of the Rietveld analysis for the pastes with pH 13.5 and pH 7. The results of the Rietveld analysis after hydration do not indicate considerable differences in the formation of the semi-crystalline tobermorite 9Å structure between the pastes produced with pH 7 and 13.5. It is observed in table 7 that for the pastes with pH 13.5 formation of monohydrate calcite occurs at a very early stage of hydration. Structural water determined by TGA is also presented in table 7 for both samples at 7 and 28 days of hydration, with higher values obtained for the sample produced at a pH of 13.5.

3.3.5. Discussion

The experiments performed with variable initial pH revealed that the saturation concentrations of SiO₂ and CaO were constant for pH between 12 and 13 while it decreased for pH of 13.5. This suggested that, in the case of the higher pH condition, the precipitation of CSH would occur earlier. In fact, it was observed that, for the two hydration ages studied, a greater amount of structural water and consequently, of CSH, was obtained for the paste with pH 13.5 when compared to the paste prepared without addition of NaOH. However, lower strengths were obtained for this situation compared to the neutral pH paste. Which may indicate that the nature of the hydration products may be different and dependent on the initial pH conditions or the mechanical properties might be affected by other factors, such as porosity, that can occur during the production of the pastes.

Table 7- Rietveld analysis and wt% structural water relative to the evolution of the hydration of the paste without addition of NaOH (pH 7) and addition of NaOH (pH 13.5).

	pH	%H ₂ O bonded	%Amorphous	%Tob	%W	%PW	%MHC
7	7 days	1.11	93.8	4.7	0.6	0.9	0
	28 days	1.89	93.9	4.3	1	0.8	0
13.5	7 days	1.48	94.0	3.7	1.1	0.6	0.6
	28 days	2.07	92.3	4.7	1.8	0.6	0.6

4 Conclusions

4.1. B₂O₃ Addition

It is concluded that the addition of 7%wt B₂O₃ to the new amorphous clinkers results not only in a beneficial contribution to its hydration development, translated into higher mechanical strength, but also in the decrease of the clinkerization temperature by about 50°C when compared to the situation without B₂O₃.

4.2. Optimization of hydration conditions

In the study of the optimization of the w/c ratio for the two types of clinkers produced, denominated OB_1550 and 2.5B_1500, it is concluded that clinker 2.5B_1500 always has better hydraulic reactivity, presenting a higher formation of CSH and resistances, indicating that the system benefits from the changes imposed in the system.

In clinker OB_1550, system optimization occurs for the w/c ratio 0.325 for younger hydration ages, but at more advanced ages system benefits most with the w/c ratio of 0.35. In clinker 2.5B_1500, it was also observed a benefit in reducing the w/c ratio to 0.35, 0.325 and 0.3 at younger ages, but at more advanced ages the application of the w/c ratio 0.375 confers the optimization of the hydration of this clinker.

4.3. Amorphous Hydraulic Binder hydration study under variable pH conditions

In the study of the hydration of the amorphous hydraulic binder under variable pH conditions, it was observed that the imposition of pH 13.5 on the solution that hydrates clinker represents an increase in the formation of CSH against hydration without addition of NaOH (pH 7). However, this increase in CSH formation did not result in improved strengths, indicating worse intrinsic mechanical properties of CSH formed in the NaOH-added paste (pH 13.5).

5. References

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