

# Formulation and evaluation in ready mix concrete of chemical additives based on molasses, carboxymethylcellulose and polynaphthalenesulphonate

Alejandro Ocampo<sup>1</sup> and Hugo Zea<sup>1\*</sup>

<sup>1</sup>Departamento de Ingeniería Química y Ambiental, Universidad Nacional de Colombia, Bogota, Colombia.

\*Corres.author: hrzear@unal.edu.co

**Abstract:** Globally, large concrete companies have the common purpose of reducing the dependence on additives used in high performance concrete due to the high costs they represent. This study a basic characterization of currently commercial additives is performed upon this characterization substitutes additives locally available are selected and use in the formulation of ready mix concrete evaluating performance in terms of strength, workability, water consumption and temperature profile. Molasses, CMC and PEGMA were identified as potential substitutes additives to get to an industrial tests phase.

**Keywords:** Concrete ready mix, concrete additives, molasses, carboxymethylcellulose, polynaphthalenesulphonate.

## Introduction

One of the highest production costs in the design, development and marketing of concrete mixtures for the construction industry, is related to the purchase of additives, chemicals compounds and are used to bring special properties to the fresh or hardened concrete; these special properties are related to the reduction of water consumption, increased resistance to compression or extension of the setting time, and others, they also can improve the durability, workability and strength of a concrete mixture and also is used to overcome difficult situations construction such as casts in hot or cold weather, pumping requirements, early strength requirements or specifications of a water/cement ratio very low<sup>1</sup>.

## Cement hydration

In cement chemistry, the term hydration denotes all the changes that happen when cement is mixed with water. Actually, hydration is a complex sequence of chemical reactions between the phases of clinker, plaster, additions and water that, in the first place, results in a certain setting (hardening) rate, development of hydraulic properties and resistance to compression. The reactions of hydration depend on whether the cement is blended or not.

Other types of more complex compounds, of the same nature of hydrated siliceous crystals, that normally depend on the presence of substances as calcium sulfate or alkalis like  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  are also produced. In blended cements more complex reactions occur, but the hydration products are similar and, in general, less heat is produced as well. Immediately after water mixing, the sulfates dissolve and react with  $\text{C}_3\text{S}$  forming ettringite. In addition, an oversaturated solution with calcium hydroxide is formed due to water reaction with the  $\text{C}_3\text{S}$ . A layer of ettringite crystals is formed around the aluminate delaying any subsequent reaction. Because of the pressure that the crystals exert, the ettringite layer breaks after some hours of inactivity and the reaction begins again until the whole sulfate has reacted with the aluminate. Cement hydration involves a collection of connected chemical processes<sup>2-5</sup>:

- **Mixing period:** The different ions liberated by several phases enter into the solution. This dissolution is quite rapid and of exothermic nature; two fast reaction hydrates take place. Cement surface particles get partially covered with hydrated calcium silicate, formed by  $\text{Ca}^{2+}$ ,  $\text{H}_2\text{SiO}_4^{2-}$  and  $\text{OH}^-$  ions that originate from silicate clinker phases; and with ettringite, formed by the combination of  $\text{Ca}^{2+}$ ,  $\text{AlO}_2^-$ ,  $\text{SO}_4^{2-}$  and  $\text{OH}^-$  ions.
- **Inactive period:** The rapid increase in  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ions content in water reduces the dissolution speed in the clinker phases. Heat flow lessens the reaction speed. A small quantities of ettringite are formed as well.
- **Initial setting:** Hydration reaction is suddenly activated when  $\text{Ca}(\text{OH})_2$  starts to precipitate. This occurs when there is practically no silicate in the aqueous phase. This sudden consumption of the  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ions accelerates the dissolution of all cement components.
- **Hardening:** In most cements there is less calcium sulfate than what it is needed to react with the aluminum phase, that is why sulfate ions are totally consumed by ettringite formation during the initial setting. This usually occurs between 9 and 15 hours after initial mixing. In that moment, ettringite turns into the sulfate source used to form monosulphoaluminate with the remaining aluminum phase. This reaction generates heat and results in the acceleration of the hydration phases of silicate.
- **Deceleration:** In this hydration phase, cement grains are covered with an hydrate layer that gets thicker and thicker, which is why it is increasingly difficult for water molecules to reach the dehydrated section of cement particles across this thick layer. Cement hydration stops when there is no anhydrous phase, when water cannot reach the dehydrated phase any longer (very dense and deflocculated systems), or when there is no more available water, if that happens (very low water/binder material rate).

### Additives for concrete

Diverse organic and inorganic compounds are added to cement and concrete to facilitate their manufacture, manageability and improve their performance from concrete mixings initial production up to their durability as a finished, harden product. Grinding assistants are the most common additives for cement and they can consist of glycols, alkanolamines<sup>1</sup> and phenolic compounds. Additive compounds for concrete are classified as water reducers (normal and high), accelerators, retarders and air incorporators. Formulations can include hydroxycarboxylic and lignosulphonic acid salts, naphthalene and melanin sulfonates, corn syrup, alkanolamines, nitrates, nitrites and chlorine salts<sup>6</sup>. The more frequently used additives are air incorporator agents, water reducers, retarders and accelerators. Concrete additives are products capable of dissolving in water, which are added during the mixing in percentages not bigger than 5% in cement mass. This definition excludes, for example, metallic fibers and the pozzolanic materials<sup>3,7-9</sup>. Additives can be tentatively qualified according to the properties that they modify in fresh or harden concrete. Additives work or function through one or more mechanisms<sup>10,11</sup>:

- **Chemical interaction** in cement hydration processes; typically causing acceleration or deceleration of the reaction speed of one or more clinker phases or cement.
- **Cement surface adsorption**; typically causing better particle dispersion (plasticizing effect).
- **Modifying water superficial tension**; causing an increase of air present in the mixture, affecting rheology; causing an increase in plastic viscosity or mixture cohesion.

- Introducing special chemicals in hardened concrete body that can affect such specific properties as susceptibility of steel structures corrosion or water repellency.

Additives that reduce water are also called plasticizers or superplasticizers given their capacity to reduce water. According to the international norm, the first ones should reduce 6% minimum and the second ones must reduce a minimum of 12%, regarding a standard, without additive, mixture with the same handling, measured by slumping test<sup>12</sup>. In a microscopic scale, superplasticizer action defers clearly of that of plasticizer for a much more effective deflocculation and very high cement particles dispersion<sup>13</sup>.

Water reducers can be anionic, cationic or even not ionic. Anionic and cationic are composed of molecules that have a loaded side that neutralizes an opposite electrical charge in a cement particle. Not ionic water reducer's molecules act like dipoles joined to the cement grains<sup>13</sup>. Most water reducers tend to act as retardants; therefore, some of the ingredients used in such water reducers, like lignosulfonates and hydroxycarboxylic acids, are also a basic component of setting retardants. Some other important substances used like retardants are sugars and their derivatives<sup>14</sup>.

Water reducer's mechanism is principally based on its ability to be adsorbed in cement particles surface causing deflocculation by electrostatic or steric repulsion; generally, duration of such effect is temporary and variable. Most reducers generate a significant setting delay which causes an early resistances decrease; additionally, slight variations in water/cement relation produce exudation<sup>15</sup>. Retardants additives are known for delaying cement hydration without affecting its long-term mechanical properties<sup>16</sup>.

The effect of sugar in hydrated cement paste properties have been investigated, in general, it has been accepted that the delaying action of sugar and acids derived from sugar is due to its adsorption in hydrated cement particles surface as well as in hydration products. Both sugar and its acid derivatives can be adsorb in  $\text{Ca}(\text{OH})_2$ <sup>17</sup>. To reduce the amount of water in concrete mixture, it was discovered that lignosulfonate molecules, which are obtained as a paper industry residue, act as dispersing agents. It is possible to obtain a 5 to 10% water reduction using lignosulfonate before some disadvantages like strong delay or the air trapping happen, and it increases concrete workability and improves its compaction<sup>18</sup>. Likewise, molasses, a by-product of the sugar industry, increases fresh concrete fluency and handling and it also delays cement paste final setting time. Molasses is the remaining liquor after saccharose crystallization and separation<sup>17</sup>.

## Materials and Methods

### Characterization techniques.

Physical and chemical properties were determined by means of the UV, IR absorption and analysis of thermal decomposition by thermogravimetry.

Thermogravimetric analysis was performed in a TA Instruments TGA 2050. Samples were subjected to drying at 105 °C for 3 h and then heating with a temperature ramp rate of 10 °C / min and 5 °C / min up to 1000 °C in air, each analysis was performed in duplicate.

A UV GENESYS 20 Thermo Scientific spectrophotometer was used to determine the absorbance and wavelength of the absorption bands characteristic of the samples. This analysis was done in duplicate for each sample. For recording IR spectra spectrophotometer was used to apply the FT-IR KBr background technique for measuring transmittance percentage; 80 runs were programmed with a resolution of 4.0 nm in the range of 400 to 4000  $\text{cm}^{-1}$ . A portion of the aqueous solution of the various additives was dried at 60 °C until constant weight. Then it was ground and subsequently homogenized thereon to record the IR spectrum<sup>19</sup>.

Ready mix concrete performance tests were performed according to ASTM's standards C39/C39M (Test method for compressive strength of cylindrical concrete specimens),

C143/C143M (Test method for slump of cement-concrete) and C1064/C1064M (Test method for temperature of freshly mixed cement-concrete).

## Results

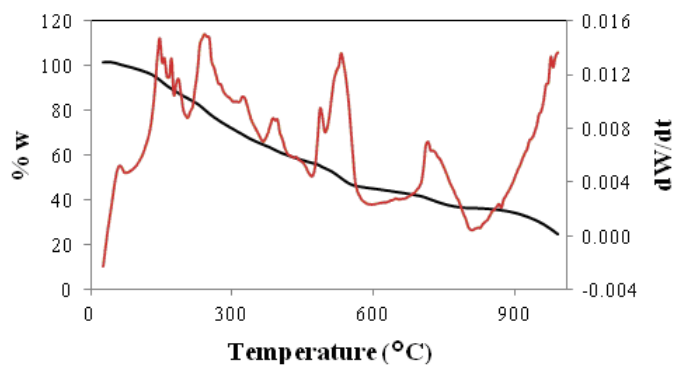
### Characterization of commercial additives.

For purposes of this study, commercial additives will be called as additives. Additives 1 and 2 are used as plasticizers of the second generation and also have effect on setting time and additive 3 is used as superplasticizer. Table 1 shows the pH, density and percentage of solid content of additives 1, 2 and 3.

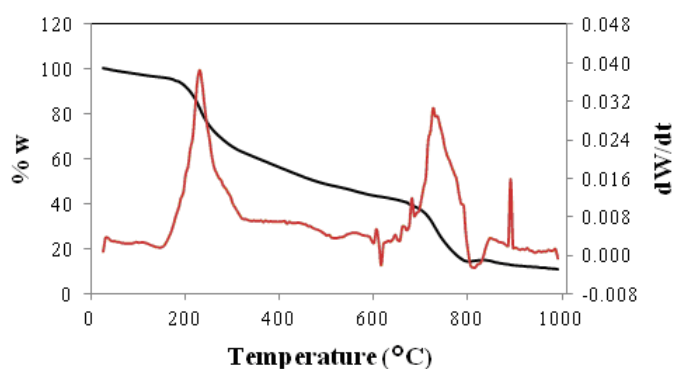
**Table 1.** Physical properties of commercial additives.

	pH	$\rho$ (kg/L)	% solids
<b>Additive 1</b>	5.20	1.32876	50.81
<b>Additive 2</b>	7.57	1.30896	47.41
<b>Additive 3</b>	4.53	1.10298	39.68

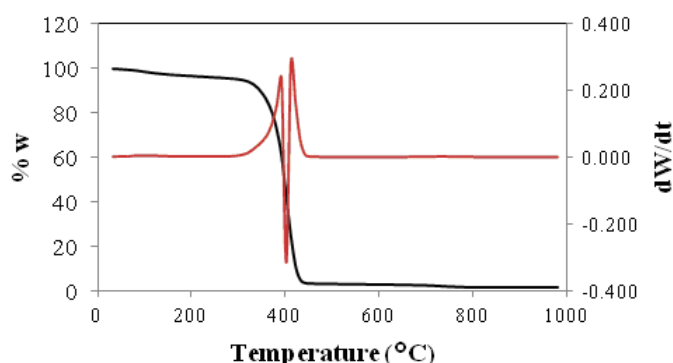
TGA profile of additive 1 (Figure 1) shows an almost constant weight loss, however the differential weight loss profile presents several peaks representing different stages of decomposition; TGA profile and the differential weight loss profile of additive 2 (Figure 2) clearly shows two weight reductions around 200 and 700 °C matched with differential weight loss peaks; TGA profile and the differential weight loss profile of additive 3 (Figure 3) shows a single weight dramatic reduction around 400 °C, typical of material that decomposed under heating.



**Figure 1.** TGA for Additive 1.

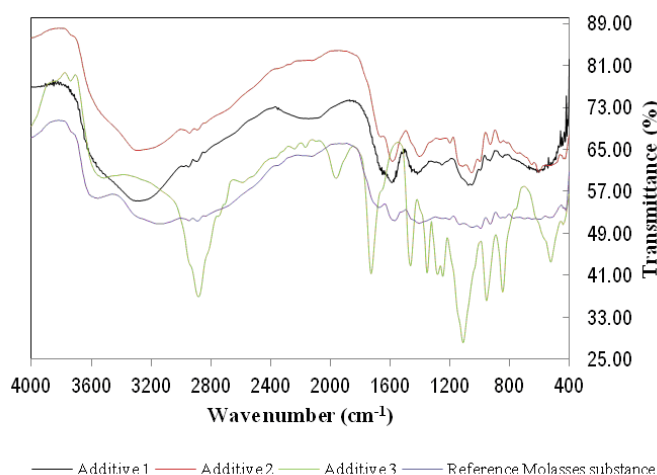


**Figure 2.** TGA for Additive 2



**Figure 3.** TGA for Additive 3

The result of the IR spectrums of additives 1, 2 and 3 are presented and summarized in Figure 4 and Table 2, respectively.



**Figure 4.** Comparison of the FT-IR spectra of commercial additives and molasses reference substance.

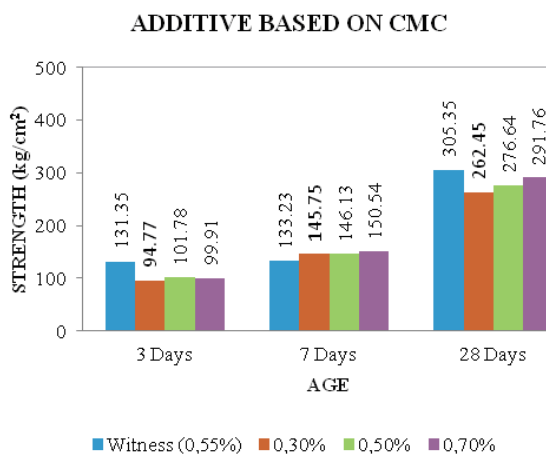
**Table 2.** Commercial Additives characterization by Spectrophotometry UV

Additive	Absorpti on $\lambda$ (nm)	Absorbance	Comments
Additive 1	~205	0.349	Main absorption 180-230 nm; minor absorptions in 230-300 nm. The typical spectrum with PNS (Naphthalene sulfonate condensates) additives presents three absorption peaks at 227, 292 and 328 nm.
	214	0.348	
	322	0.756	
Additive 2	220	1.207	Absorption at 170-205 nm, there is a plateau at 195-215 nm. Absorption band at 260-280 nm. The additive has two absorption zones in unfolded 222nm and a maximum at 300 to 330 nm. This would indicate a mixture of several bases, one of which PMS (Melamine sulfonate condensates). The typical spectrum with PNS (Naphthalene sulfonate condensates) additives present three absorption peaks at 227, 292 and 328 nm.
	274	1.589	
	307	2.623	
Additive 3	None visible in the interval defined	Not detected	It was not possible to detect absorption bands acceptable resolution that identifies species using this technique. The aromatic group-containing polyacrylates and show no visible UV spectra in regions above 200 nm.

**Formulation of substitute additives**

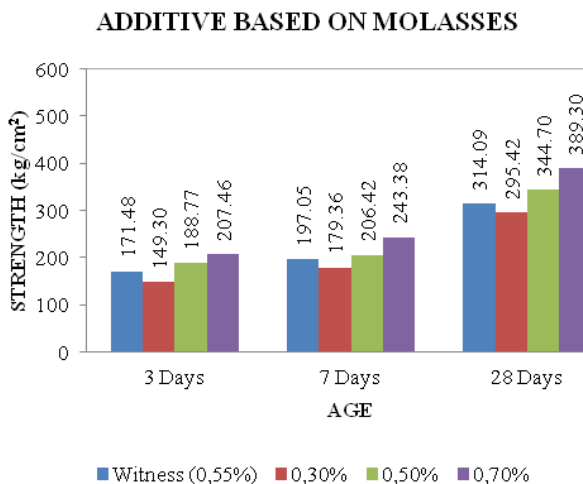
According to the characterization performed by the methods described above, it was proposed to obtain three types of concrete admixtures: a second generation plasticizer with PNS poly(naphthalenesulphonate) as active principle, a retardant polymer with cellulose as the active principle (CMC), a water reducing senior with a polycarboxylate as active (P-ethylenglycol metacrylate, PEGMA) and retardant based on cane molasses. Subsequently, these additives were tested in concrete mixtures.

Figures 5 to 8 shown the results of the concrete compressive strength for the four ready mixtures with 0,3%, 0,5% and 0,7% or 0,2%, 0,6% and 0,8% of substitutes additives respect to cement mass; these samples were tested at aging time that ranges from 3 to 28 days; the witness sample is a ready mixture prepared using usual commercial additive.

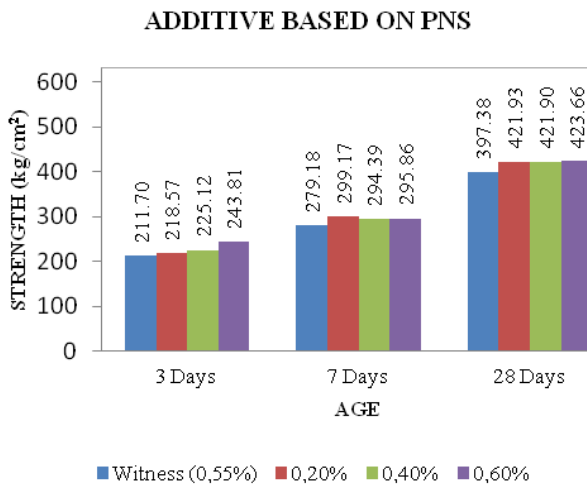


**Figure 5.** Concrete Compressive strength with Additive based on CMC

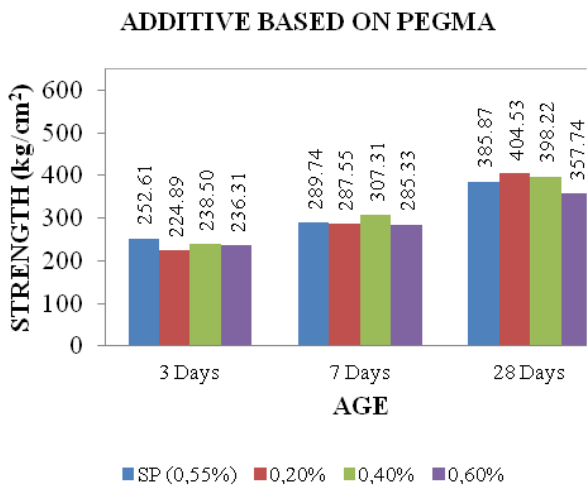
For the mixtures containing CMC there is a detrimental effect in the strength on all mass percentages; in the case of the mixtures containing PNS and PEGMA there is none or little change (less than 10%), on the contrary the ready mixtures containing molasses shows increment in the strength higher to 10% for the composition of 0.07%.



**Figure 6.** Concrete Compressive strength with Additive based on molasses

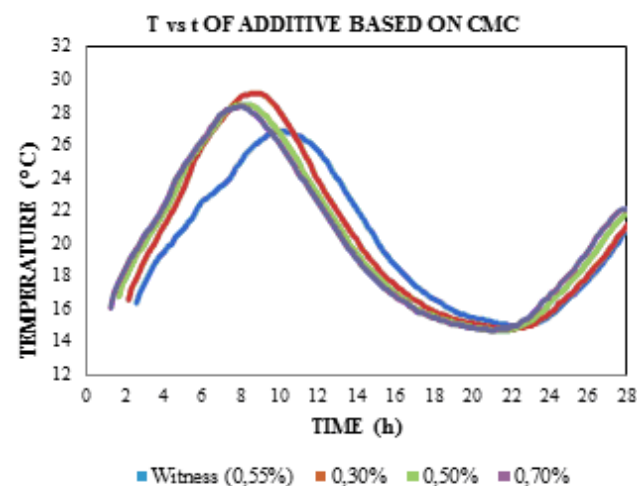


**Figure 7.** Concrete Compressive strength with Additive based on poly(naphthalene sulphate)



**Figure 8.** Concrete Compressive strength with Additive based on polycarboxylate

Figures 9 to 12 shown the results of the temperature profile of the ready mixtures containing substitutes additives.



**Figure 9.** T vs t (h) curve for concrete with additive based on CMC

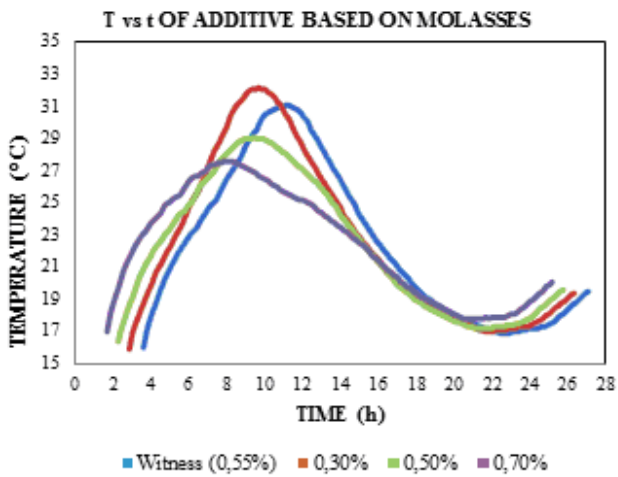


Figure 10. T vs t (h) curve for concrete with additive based on molasses

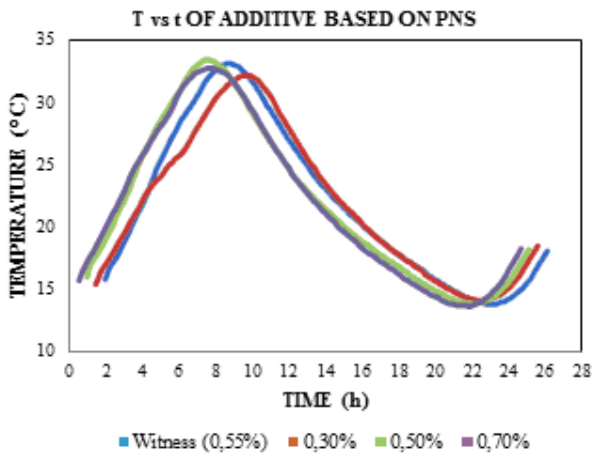


Figure 11. T vs t (h) curve for concrete with additive based on poly(naphthalene) sulphonate

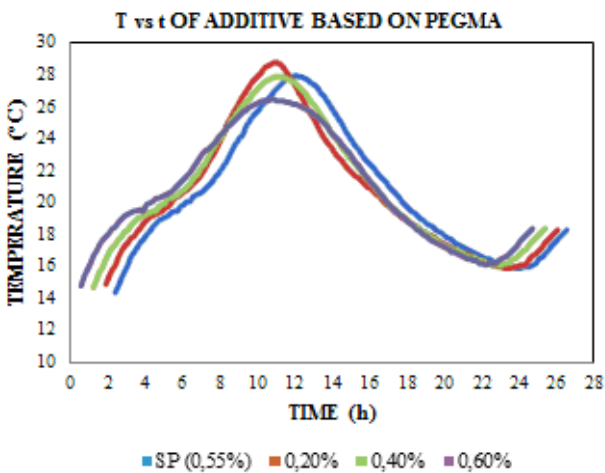


Figure 12. T vs t (h) curve for concrete with additive based on polycarboxylate.

Retardant additives obtained at laboratory level show more elevated temperature peaks regarding commercial additives; it is possible that active principle adsorption over cement particles is more rapid and occurs on a bigger amount of particles, then, when surpassing the additive layer thickness limit on the surface, it yields and



a larger cement quantity its exposed to a bigger amount of water, releasing more heat during initial setting time until the temperature peak presents. Another important consideration is that in the case of additives obtained at laboratory level the active plasticizing beginning principle that disperses cement particles is not formulated, which is why temperature peaks should not coincide even if results demonstrate that laboratory additive action is very similar to commercials.

According to temperature profiles of delaying additives, it is possible to suggest a dose in which the additive must be added to fresh concrete mixture; for example, in the case of molass, it must have a value between 0.3% and 0.5% for final setting to be near 11 h and temperature peak to be between 29 and 32°C. Base molass additive is the additive that possesses a greater potential to carry out an industrial test of a concrete mixture that has a final setting time requirement close to the control sample used in the tests.

In term of the plasticizing effect of the substitutes additives (Figures 13 to 16) there are handling curves similar to standard samples, which is why it is assumed that the delaying mechanism that commercial additive has does not produce meaningful effects on concrete mixture plasticity subsequent to cement dispersion by water reduction. Duplicated plasticizers handling curves show significant differences regarding the standard sample and among themselves; this might suggest that the additive is not stable and that it has a condition in which the active principle has diminished its concentration. This observation is coherent with the need of a stabilizer in the formulation of commercial additives. For the same reason, stability in the retardants additives obtained at laboratory level is observed.

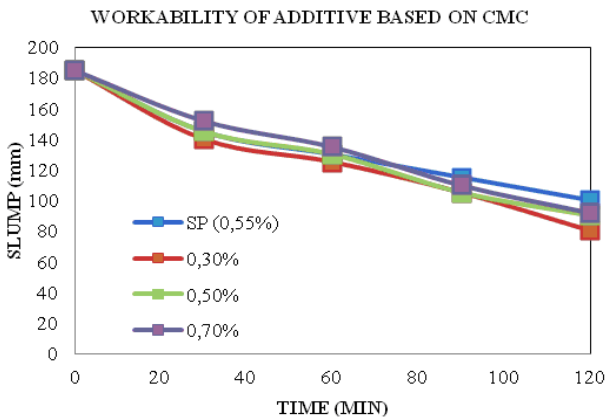


Figure 13. Slump test Additive based on CMC

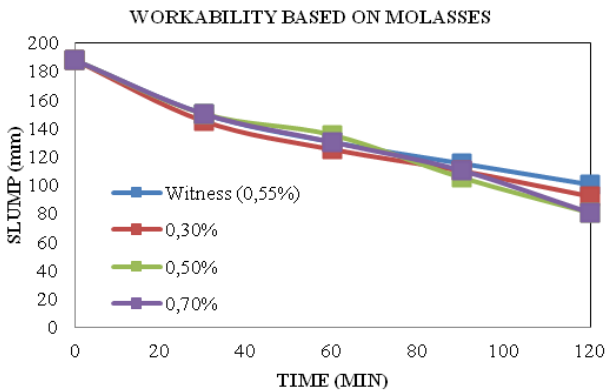
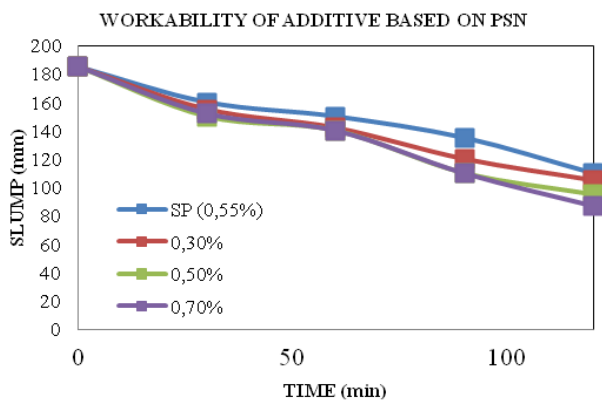
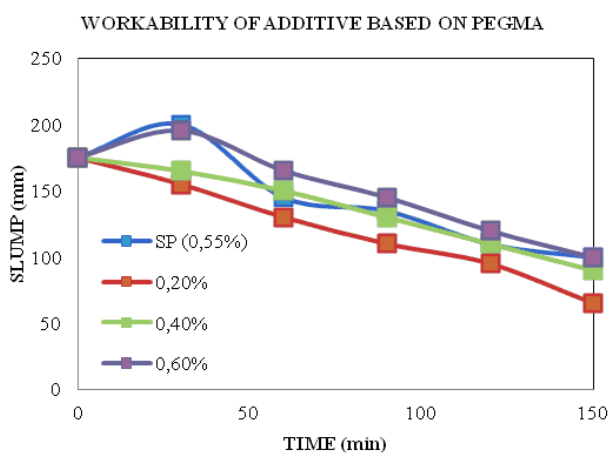


Figure 14. Slump test Additive based on Molasses



**Figure 15.** Slump test with Additive based on poly(naphthalene sulphonate)



**Figure 16.** Concrete slump test with Additive based on polycarboxylate

Some considerations about the obtained results from the obtained additive on concrete mixings are:

- Dose does not have a major effect on the final handling
- A bigger amount of occluded air with the additives obtained at the laboratory is observed. The obtained mixtures produce large quantities of foam which is why it is probable that commercial additives formulation has some anti-foaming agents of unknown nature. Nevertheless, these quantities of air are not sufficiently high as to reject the additive.
- There is a special situation with delaying additives and that is that they have minor setting times (minor delaying effect than the commercial additive) but greater handling.
- The only additives get to the minimal value of compression resistance (i.e. control resistance) to the ages in which it has been practiced to date, are the base molass additive and the CMC 104, that in spite of presenting minor resistances to 3 days, recovers to 7 days, even nearly overcoming the resistance to 7 days of control in doses superior to 0.3%. Plasticizing additives present significant drops in compression resistance.
- Handling curves of plasticizers have lesser variability than delaying additives curves.

#### 4. Conclusions

It was possible to completely characterize a series of commercial additives of periodic use in a concrete production plant. Production of a concrete additive that emulates the action mechanisms of those who are commonly used in a concrete production plant is technically feasible and it might eventually present significant cost saving in the operation associated to the monthly purchase of concrete additives. Additives with a greater

potential to get to an industrial tests phase, because of concrete mixing results in tests, are those of base molass, CMC and PEGMA.

It is necessary to carry out a rigorous kinetic study about the production of the proposed additives that involve chemical reactions; there is no knowledge about the speed with which this products are obtained or the selectivity or conversion towards them. In the eventuality of carrying out the enlargement of any obtaining processes, the reaction(s) speed will determine reactors volume, catalysts presence; need to implement strategies to favor reactions advance, and the subsequent separation operations. It is important to bear in mind those products of condensed production reactions as well as polycarboxylates production has polymeric materials as its main product, which is why that stoichiometry must model the reactions that are occurring.

## References

1. Garrault, S., et al., On the origin of the dormant period of cement hydration. International Congress Chemistry of cement: 2011, p. 7.
2. Bullard, J.W., et al., Mechanisms of cement hydration. *Cem. and Concr. Res.*, 2011, 41(12): p. 1208-1223.
3. Aitcin, P.C., High performance concrete. Holcim Edition, 1998.
4. Stark, J., Recent advances in the field of cement hydration and microstructure analysis. *Cem. and Concr Res.*, 2011, 41(7): p. 666-678.
5. Popovics, S., Model for the quantitative description of the kinetics of hardening of portland cements. *Cem. and Concr. Res.*, 1987, 17(5): p. 821-838.
6. Jeknavorian, A.A., et al., Novel pyrolysis-gas chromatography/mass spectrometric techniques for the characterization of chemical additives in portland cement and concrete. *J. of Analy. and App. Pyro.*, 1998, 46(2): p. 85-100.
7. Institute, A.C., ACI Education Bulletin E4-03, in Chemical Admixtures for concrete. p. 12.
8. ASTM, Standard Specification for Chemical Admixtures for Concrete C494/C494M - 11.p. 10.
9. ASTM, Standard Specification for Chemical Admixtures for Use in Producing Flowing Concrete C1017/C1017M - 07. p. 9.
10. Paulini, P., Reaction mechanisms of concrete admixtures. *Cem. and Concr. Res.*, 1990, 20(6): p. 910-918.
11. Nelson, E.B., J.-F. Baret, and M. Michaux, 3 Cement Additives and Mechanisms of Action, in *Developments in Petroleum Science*, B.N. Erik., 1990, p. 3-1-3-37.
12. De la Peña, B. and R. Vernal A., Nuevos aditivos reductores de agua y su aporte a la tecnología del hormigón, Sika Chile.
13. Diamond, S. and K. Matsukawa, Chemical admixtures of highway concrete: fundamental research and a guide to usage, Part II - Quantitative analysis of interactions between Portland cements and superplasticizers P. e-Pubs, Editor., Purdue University. 1993 p. 308.
14. Young, J.F., A review of the mechanisms of set-retardation in portland cement pastes containing organic admixtures. *Cem. and Concr. Res.*, 1972, 2(4): p. 415-433.
15. Knaus, S. and B. Bauer-Heim, Synthesis and properties of anionic cellulose ethers: influence of functional groups and molecular weight on flowability of concrete. *Carb. Poly.*, 2003, 53(4): p. 383-394.
16. Fattuhi, N.I., Influence of temperature on the setting of concrete containing admixtures. *Constr. and Buil. Mat.*, 1988, 2(1): p. 27-30.
17. Jumadurdiyev, A., et al., The utilization of beet molasses as a retarding and water-reducing admixture for concrete. *Cem. and Concr. Res.*, 2005, 35(5): p. 874-882.
18. El-Mekkawi, S.A., et al., Utilization of black liquor as concrete admixture and set retarder aid. *J. of Ad. Res.*, 2011, 2(2): p. 163-169.
19. Yilmaz, V.T., A. Kindness, and F.P. Glasser, Determination of sulphonated naphthalene formaldehyde superplasticizer in cement: A new spectrofluorimetric method and assessment of the UV method. *Cem. and Concr. Res.*, 1992, 22(4): p. 663-670.