Multi-method approach to study the influence of additives in ternary systems: gypsum, water and impurities

Doctoral Thesis

to be awarded the degree
Doctor of Engineering (Dr. –Ing.)

Submitted by
Jazmín Consuelo Aboytes Contreras
Ingeniería Química Administrativva
from Mexico City

Approved by the
Faculty of Natural and Materials Sciences
Clausthal University of Technology

Date of oral examination
March 14th, 2014

Chairperson of the Board of Examiners

Prof. Dr. rer. nat. Wilhelm Oppermann

Chief Reviewer
Prof. Dr. rer. nat. Albrecht Wolter

Reviewer

apl. Prof. Dr. Hans-Ulrich Hummel

The work was carried out at:

- **Institute of Non-Metallic Materials**
  Clausthal University of Technology
  Dean of Faculty: Prof. Dr. rer. nat. Albrecht Wolter
  Zehntnerstraβe 2A, 38678 Clausthal-Zellerfeld, Germany

- **Knauf Gips KG**
  Research and Development Knauf Group
  Am Bahnhof 7, 97346 Iphofen, Germany

- **Sika Deutschland GmbH**
  Research and Development
  Peter-Schuhmacher-Straβe 8, 69181 Leimen, Germany

- **Sika Technology AG**
  Research and Development
  Tüffenwies 16, 8048 Zürich, Switzerland

Name, Vorname Datum:

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ACKNOWLEDGMENTS

Thanks and deep gratitude to my brilliant professor, Prof. Dr. Albrecht Wolter, that by his supervision of my investigation with careful attention and positive enthusiasm, I was inculcated passion for the science of construction chemicals.

I would like to express my heartfelt gratitude to TU-Clausthal, Knauf Gips and Sika Technology for giving me the opportunity to conduct my doctoral work here in Germany.

Special thanks are paid to Prof. Dr. Hans-Ulrich Hummel for his encouragement and constant contributions during the whole project. Also, I would like to express my gratitude to Dr. Norman Blank for his readiness to help and advice whenever I asked for.

Gratitude is paid to Dr. Sebastian Förthner and Dr. Christina Hampel for their endless support during the whole project. I warmly thank Dr. Dieter Honert for his honesty and kind words of advice. Special appreciation and gratitude is well paid to my colleagues Dr. Markus Müller, Dr. Thomas Müller and Mr. Jan Patrick Niklaus for their deep friendship and great support.

Furthermore, I would like to thank my colleagues: Mr. Rexhep Kelmendi, Mrs. Nadine Hust, Mrs. Julia Hillenbrand, Mr. Olaf Kern, Mr. Jakob Taube, Mr. Gerhard Kramer and Mr. Sven Pechwitz for all their help during the practical course. I would also like to express my gratitude to Mrs. Daniela Speer, Mrs. Sabrina Maier, Mrs. Andrea Behfeld and Mrs. Nicole Linsenmeier for their help to come with bureaucracy in an uncomplicated way. I would also like to thank all the colleagues at Sika Deutschland Leimen for one of the nicest working environments I have ever been.

This thesis is dedicated to my parents: Graciela and Alfredo. Without their love, encouragement and support under all conditions, I would not have succeeded. I would also want to thank my sister Constanza and my brother Alfredo for always being there for me even when I am so far away from home. Also, I would like to dedicate this work to Declan, who always had an open a comforting ear for all the problems I met.

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0 ABSTRACT

The production of gypsum wallboard starts with high-quality materials that are obtained from natural and/or industrial sources. The optimization of the manufacture of wallboard is a major target for the building materials industry. Admixtures, such as PCEs, are widely used as additives to decrease the water demand without affecting the workability of the cementitious and gypsum systems. The limiting factors for the use of PCEs in the production of gypsum-based products are impurities of the raw materials. The presence of certain impurities, such as swelling clays, could result on an incompatibility with the admixtures that would affect directly the workability.

The main goal of this thesis was to find a polycarboxylate-type admixture that will avoid the loss of its robustness while in contact with the impurities of natural hemihydrate, specially swelling clays. The fundamental mechanisms in the interaction of methoxypoly(ethylene-glycol)methacrylate type comb polycarboxylate based superplasticizers were investigated by: (1) the influence of the raw material, (2) the influence of the PCE structure and (3) the influence of the bentonite as an impurity. Two model systems were considered: natural beta-hemihydrate and, natural beta-hemihydrate with bentonite, as a contaminant. The experimental data was obtained performing slump tests, setting times, adsorption calculations, calorimetry, as well as rheological studies and zeta potential analysis.

The raw material was studied to understand the compatibility of the PCEs with the different types of gypsum: hemihydrate and dihydrate, synthetic and natural, and alpha and beta hemihydrates. Moreover, the decrease of the PCE performance as an effect of impurities in natural hemihydrate was determined by the decrease of the workability of the slurry and the adsorption of the PCE in raw materials.

To understand the influence of the PCE structure, three main areas were analyzed as follow:

- Effect of the side chain lengths of the polycarboxylates on the workability of the slurry.
- Influence of the backbone type of these copolymers on workability and hydration of the hemihydrate slurry.
- Effect of the side chain density of the polycarboxylate copolymers on their adsorption-workability behavior.

In the pure hemihydrate system, a polycarboxylate possessing long side chains (2000 g/mol) with a methacrylic acid backbone and lower side chain density (C:E 9) is the ideal comb-polymer for the flowability required in the wallboard production.

In the hemihydrate-bentonite model system, experimental data was obtained for the decrease of the PCE performance due to adsorption and intercalation of the PCE into the bentonite-layered structure. The study showed the effect of the side chain lengths and backbone type of the copolymers on their undesired consumption by bentonite contaminants. The investigation revealed that the polymer consumption is dependent on the side chain length and backbone type. Therefore, a polymer with short side chains (59 g/mol) and a MAS backbone was found to be an ideal structure: it would increase the compatibility with the bentonite contaminants in the natural hemihydrate.

1 LIST OF ABBREVIATIONS

The following table describes the significance of various abbreviations and acronyms used throughout the thesis.

Abbreviation	Meaning
AS	Acrylic Acid Backbone
BET	Brunauer, Emmet and Teller (BET theory)
DH	Dihydrate
DSC	Differential Scanning Calorimetry
HH	Hemihydrate
hr	Hours
MAS	Methacryl Acid Backbone
MIX	Mix Backbone (Acryl and Methacryl Acid)
min	Minutes
mmol	Millimol
mm	Millimeters
MPEG	Methoxy Poly(ethylene glycol)
MPEG2000MA	Methoxypoly(ethylene glycol) 2000 Methacrylate
HPMA	Hydroxypropyl Methacrylat
PCE	Polycarboxylate
pH	Pondus hydrogenii
s	Seconds
TGA	Thermal Gravimetry
TOC	Total Organic Carbon
w/g	Water-to-gypsum ratio
wt. %	Weight percent
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence Spectroscopy
ζ potential	Zeta potential

2 INTRODUCTION

"… the people who will succeed fifteen years from now, the countries which will succeed, are those which are most based on a sustainable vision of the world. That is what we should be training people to do."

Rt Hon Charles Clarke MP, Secretary of State for Education and Skills, 25th March 2003.
(cited Forum for the Future, 2004)

One of the most substantial discussions in every industry is sustainability as it has been set as an end-goal to every process. This approach has been proven as a source of innovation, implying an action with manageable impact on the environment and a more effective way on the use of the resources. The significance of sustainability in the construction industry has been recognized in recent years, especially with respect to the consumption of energy and natural resources. With the increase of energy costs, there is a rising need to reduce energy consumption, as well in the wallboard production and of gypsum-based products [1,2,3,4].

The production of gypsum wallboard starts with high-quality materials that are obtained from natural sources, such as quarries or underground mines, or from synthetic production from a flue gas desulfurization plant of the power generation industry. In order to produce wallboard, the material must be calcinated to produce calcium sulfate hemihydrate (known as stucco). In the manufacturing facility, stucco is mixed with water, additives and other different components to obtain the desired characteristics for the final product [5]. The slurry is then spread between two paper sheets; subsequently, the wet boards travel through the conveying line where the calcium sulfate hemihydrate combines with water in the slurry to form calcium sulfate dihydrate (gypsum), developing a rigid panel [6]. Afterwards, the board is cut to length and transported through the dryer to remove moisture. After drying, the wallboard is ready for delivery.

The requirement of water needed to convert the hemihydrate to dihydrate is fairly minor against the amount needed to achieve proper mixing and slurry to flow. The stoichiometric amount of water needed to entirely hydrate the stucco to gypsum results in a water-to-stucco weight ratio (w/s) of 0.18. On the other hand, the w/s required to obtain flowable slurry is approximately 0.7 [7]. A reduction of the w/s ratio means a decrease in the time that the wallboard needs to spend in the drying oven and a decrease on the energy required for the drying process; frequently, the dryer capacity limits the productivity of the plant [8]. Lower drying requirements result in higher productivity and lower specific energy consumption.

Additives can improve the wallboard plant profitability. In the cement industry, for example, the problem of the excessive amount of water required for an increased workability has been addressed by the use of dispersing agents [9, 10]. Admixtures are widely used as additives to decrease the water demand without affecting the workability of the cementitious and gypsum systems; strength and durability are properties that are improved as well. Hence, nowadays, the use of admixtures has increased in the construction industry [11]. In the gypsum industry, traditional admixtures such as sulfonated naphthalene formaldehyde condensates, sulfonated melamine formaldehyde condensates and lignosulfonates are commonly used in the production of wallboard [9, 12]. Nevertheless, the water demand could still be reduced through novel technologies such as polycarboxylate ether-based superplasticizers (PCEs) [13, 14, 15].

However, the limiting factors for the use of PCEs in the production of gypsum-based products are impurities of the raw materials. Regardless of the high-quality material, impurities are always a factor. The purity of the natural stucco varies due to its origin; the type and amount of impurities fully depend on the source location of the quarry or mine, resulting in a unique composition for each kind of stucco [16].

These quality fluctuations could lead to an unexpected behavior that will hinder the performance. This will depend on the kind of impurity and their extent in the gypsum rock. The presence of certain impurities, such as swelling clays, could result on an incompatibility with the admixtures that would affect directly the workability [17]; other common impurities, including quartz and limestone, are generally inert and harmless [18, 19].

The main challenge for the admixture researchers is to develop new polymers that would keep its robustness without being disturbed by the different impurities contained in the natural stucco. Most studies about the effect of impurities on the performance of admixtures in gypsum have only been carried out in a small number of sites and the knowledge obtained usually remains confidential [20, 21]. The research to date has tended to focus in how to eliminate the impurities rather than improving the formulation of the new admixtures. As of today, most publications in the industry report that no “universal” admixture exists for all binder types [22, 14].

This dissertation was undertaken to design and evaluate model systems to understand the interaction between PCE-based superplasticizers and stucco. The capabilities of a series of copolymers were evaluated to determine which formulation would increase the productivity of the manufacture line, without being affected by impurities. This dissertation will be solely focused on bentonite as a minor constituent in gypsum due to its high swelling capacity. Bentonite is a rock formed of highly colloidal and plastic clays, composed mainly of montmorillonite, a clay mineral of the smectite group. Bentonite may also contain cristobalite and crystalline quartz [23, 24]. This expandable clay is considered to be one of the materials that mainly effects the performance of the admixtures because of its ability to adsorb significant amounts of PCA on its surfaces and within its interlayered structure [25, 26].

A systematic approach was developed with polycarboxylates superplasticizers and their interaction with beta-hemihydrate and bentonite systems. Understanding the interaction between the superplasticizers with stucco and bentonite is decisive to develop optimized admixtures with functional application in the building industry. Different tests were performed to determine the working mechanism of the admixtures on several gypsum types and the fluctuations on the performance when the impurity is added [27, 28, 29].

The first section of this dissertation will review the literature concerning the different types of gypsum and their application as well as the nature and effect of the impurities they might contain. It will then go to the description of the design, synthesis, characterization and evaluation of materials tested.

The results and discussion chapter assesses the influence of the bentonite and the decrease in performance of the gypsum-polymer system. In order to remedy this problem, three scenarios were defined (gypsum; gypsum and polymer; gypsum, clay and polymer) to provide a basis for comparison. Finally, the findings obtained have been linked with the literature to provide a solution that will moderate the influence of bentonite in the slurry.

3 STATE OF KNOWLEDGE

3.1 General

One of the oldest materials used in construction is gypsum. By the Neolithic period, calcinated gypsum was starting to be elaborated to join masonry pieces, seal wall joints and starting to replace mud mortar for the lining of walls. In Ancient Egypt, it was used as a coarse mortar and as plaster to seal the joints of the Giza pyramid and also, to prepare surfaces for painting (some of them are still in a good condition). Around Europe in the middle ages, plaster of Paris was used as building material for palaces and monuments [30]. The name "gypsum" comes from the Greek "*gypsos*" and derives from the two words denoting "earth" and "to cook", referring to the burnt or calcinated material [31, 32]. The origin of gypsum rock is inferred from the fractional or entire evaporation on inland seas and salt lakes during several geological periods. When gypsum is in solution, it is held until evaporation causes it to be deposited; this process leads to the formation of different crystalline minerals where gypsum often crystalizes in seams and veins [33]. Natural gypsum or gypsum rock is an easy to mine material thanks to its low hardness.

Gypsum is a naturally occurring mineral composed of calcium sulfate and constitutional water, and its chemical name is calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$). When gypsum is heated at 120ºC, it loses an average of three-quarters of water and becomes hemihydrate gypsum $\left(CaSO_4 \cdot \frac{1}{2}H_2O\right)$, which is a soft material and can be easily ground to a powder. Finally anhydrite ($CaSO_4$) can be prepared by the dehydration of hemihydrate when it is heated at 200ºC and above (Figure 3-1) [34, 35, 36].

3.1.A Dihydrate

Originated from supersaturated aqueous solutions in shallow seas, gypsum deposits exist in many countries. The well-known deposits of the Paris Basin and the areas around the Mediterranean are examples of the formation of primary deposits [37, 38, 39]. Under increased pressure and temperature, anhydrite could have been developed from the original gypsum, converted back in gypsum by the uptake of the surface water [40].

Gypsum usually forms a solid dense rock near the Earth´s surface; therefore, mining is carried out in quarries or underground mines. Variations of the dihydrate are: alabaster, a compact and massive marble-like material with a very fine crystalline structure used for decoration purposes; selenite, a transparent crystalline material, used for windowpanes in antiques; satin spar, a satin-like fibrous material, used as well for decoration; and copy, an efflorescence-like material, found on saline deposits in Australia [41, 42, 43].

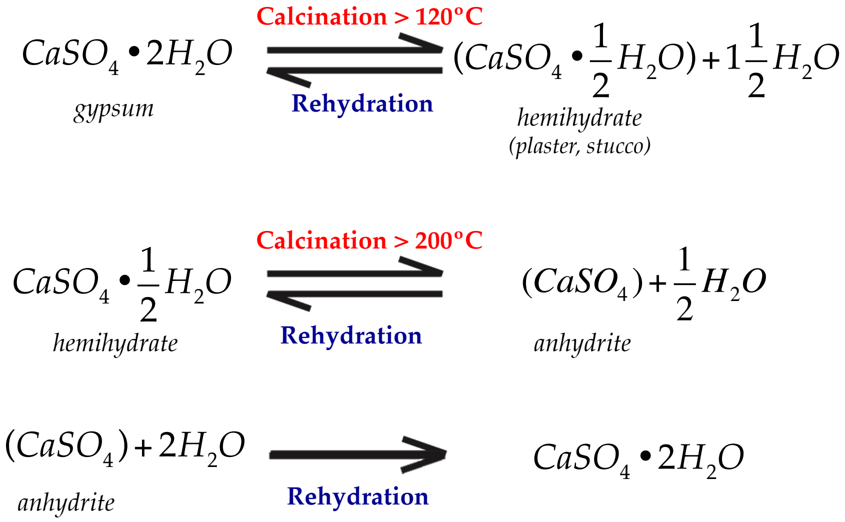
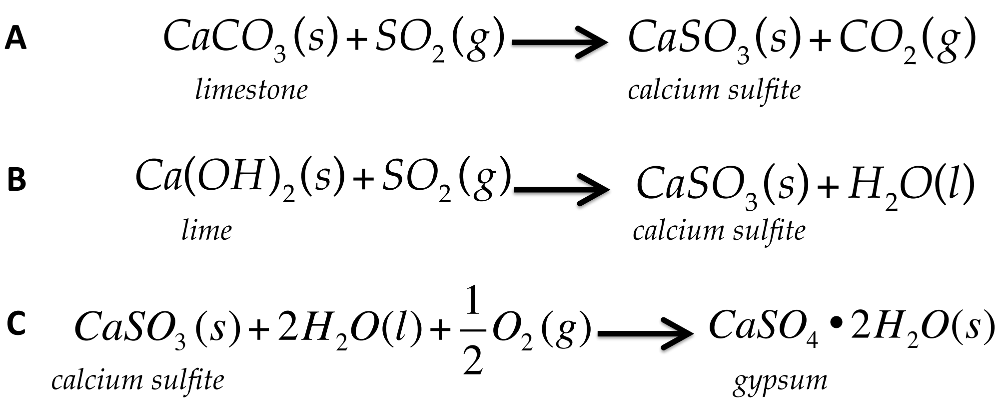


Figure 3-1 Chemistry behind gypsum technology

Approximately 60% of all calcinated gypsum originates from natural gypsum and 40% from synthetic gypsum and the recycling of gypsum products. Most of the synthetic gypsum used in the gypsum industry is flue-gas desulphurization (FGD) gypsum [17].

FGD gypsum is obtained from the desulfurization of combustion gases of fossil fuels, such as anthracite, bituminous coal, lignite, and oil, in large combustion plants, especially power plants [44]. Several methods have been designed, but only a few have been applied in the industry. Most of them operate with the wet scrubbing method where a countercurrent that washes the flue gas to remove the sulfur dioxide (SO_2), producing calcium sulfite ($CaSO_3$) in aqueous solution [45].

Figure 3-2 displays the main reactions for obtaining FGD gypsum. When scrubbing with limestone ($CaCO_3$), the slurry produces calcium sulfite ($CaSO_3$) as expressed in Figure 3-2.A. The reaction, when scrubbing using lime ($Ca(OH)_2$), produces calcium sulfite (Figure 3-2.B). Finally, calcium sulfite is further oxidized with air to produce gypsum (Figure 3-2.C) [44, 46, 47, 48].



A $$\underset{limestone}{CaCO_3(s)} + SO_2(g) \longrightarrow \underset{calcium\ sulfite}{CaSO_3(s)} + CO_2(g)$$

B $$\underset{lime}{Ca(OH)_2(s)} + SO_2(g) \longrightarrow \underset{calcium\ sulfite}{CaSO_3(s)} + H_2O(l)$$

C $$\underset{calcium\ sulfite}{CaSO_3(s)} + 2H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow \underset{gypsum}{CaSO_4 \bullet 2H_2O(s)}$$

Figure 3-2 Main reactions for Flue-Gas Gypsum

3.1.B Obtaining Hemihydrate

Gypsum processing can be divided in two stages: preparation of the raw gypsum and calcination of the material. In natural gypsum, the preparation of the gypsum rock is a main step to make the material convenient for the calcination process. The coarse rock is conveyed to the crushing plant, where jaw, impact and single role crushers followed by impact pulverizers, ball mills and ring-roll mills reduce the size of the material step by step [49].

On the other hand, FGD gypsum differs from natural gypsum in the chemical composition and physical properties. Usually, FGD gypsum has a higher purity and lower level of impurities, such as limestone or dolomite, nevertheless it may have a higher content of deleterious impurities (fly ash and calcium sulfite) [50], requiring a different handling procedure. The crystals obtained are large and compact, allowing its separation from the aqueous suspension with hydrocyclones and vacuum drum filters or centrifuges (dewatering). Dewatered gypsum is stored outdoors on heaps or, on roofed storage sheds to avoid accumulating additional moisture from precipitation and to provide windscreens to prevent dusting [51]. Grinding could be necessary if the particle size needs to be modified, improving the characteristics of the stucco after calcination. The properties of the FGD gypsum allow both, kettle calcination and the usage of rotary kiln.

Calcination is one of the most important operations on the gypsum plant. Calcination is defined as the decomposition of materials that may be broken down by the heat; in the gypsum industry it is used to dehydrate (wholly or partially) gypsum for the manufacture of gypsum-based products [52]. The calcination process is carried out in two main types of kilns: kettle kiln or rotary kiln. A kettle kiln operates with combustion without contact between product and flue gas. On the other hand, a rotary kiln functions thru combustion with contact between product and flue gas [53, 54, 55]. If the gypsum is under-calcinated, the residual gypsum may reduce the setting times and in large amounts, may reduce the strength, as the material would not be uniform. On the other hand, the over-calcination to anhydrite would result in a variable material that would be more difficult to use in a efficient wallboard production: the energy consumption will increase and setting times may be affected as the properties of the material will change [56].

Depending on the production process, the hemihydrate (HH) occurs in two forms: α and β. The β-HH or Plaster of Paris, is the most common binding material produced from gypsum, it is also known in France as ‘plâtre de Paris’, in the USA as ‘calcinated gypsum’, and in Germany as ‘Stuckgips’. Plaster comes from the kettle calcination or other kilns fired with coal, liquid fuel or gas. The alpha-hemihydrate (α-HH) is obtained in an autoclave with high-pressure steam or with superheated water, and is characterized by less acicular crystals. β-HH is obtained from the dihydrate by heating at low water-vapor partial pressure, i.e., in dry air or vacuum, between 45°C and 200°C; α-HH is also obtained from dihydrate at high water-vapor partial pressure, e.g., above 45°C in acid or salt solutions, or above 97.2°C in water under pressure (e.g., 134°C, 3 bar, 4 h). The comparison between the properties of α-HH and β-HH is summarized in Table 3-1[35, 57].

Table 3-1 Properties of α-HH and β-HH

Properties	α -hemihydrate	β -hemihydrate
Mode of production	Autoclave	Rotary kiln or kettle
Crystal structure	Compact, well-formed, prismatic, transparent large primary particles	Flaky, rugged secondary particles made up of extremely small crystals.
Water/Plaster ratio (in 100g water)	0.37-0.38	0.64-0.74

For the manufacture of β-HH, the initial dihydrate content is of prime importance: maximum dihydrate content is desirable since the presence of anhydrite may actually jeopardize the production process or impair the quality of the product. For certain products, such as ceramic gypsum or mould gypsum, an impurity level beyond 1% is prohibitive as the presence of impurities can lead to degradation of the product surface [30, 58].

After calcination, the material should not be stored left open on the air because if the relative humidity is above 70%, hemihydrate will convert to dihydrate and the crystals will act as accelerators shortening the setting time when in contact with the mixing water. If the material is stored for a longer time in a high humidity environment, more conversion will occur leading to a higher lengthening of the setting times as the dihydrate crystals will surround the hemihydrate challenging the mixing water to reach and react with the hemihydrate [59].

3.2 Purity in Gypsum

Gypsum purity is key in manufacturing wallboard and screeds. Wallboard manufacture makes the most stringent demands on the properties of gypsum. Regardless of the high-quality material, impurities are always to be considered. Factors that affect the properties of the slurry or the finished board must be carefully controlled. Among calcinating characteristics, impurities could affect slurry properties (such as flow characteristics and setting rate) and could cause poor bonding of the paper, reduced strength and discoloration [60].

The purity of the mined natural rocks presents a variation between 80-96% [50]. The purity of the stucco varies due to its origin; the type and amount of impurities fully depend on the source location of the quarry or mine, resulting in a unique composition for each kind of stucco [16]. In natural gypsum, high purity is desired to improve the adhesion between paper and gypsum. Wallboard gets its strength from the formation and the consequent interlocking of crystals of calcium dihydrate that form during the rehydration. At the paper core interface, the crystals interlock with the fibers of the paper materials to achieve adhesion (core bond). A certain amount of swelling clay would reduce the water dedicated for slurry fluidity, obstructing the paper to properly core bond [61]. On the other hand, the purity significance of synthetic gypsum is often compared with natural gypsum; the higher the purity of synthetic gypsum, the higher the value [62]. There are several methods to determine the purity of the raw material, including:

- Differential Scanning Calorimetry (DSC). The sample is heated under constant heating rate. Used to obtain the thermal critical points of substances.
- Thermal Gravimetry (TGA). The sample is continuously weighted as it is heated to temperatures up to 2000ºC max. With high temperatures, various components of the sample are decomposed and the weight percentage of each resulting mass can be measured [63, 64].
- X-Ray Fluorescence Spectroscopy (XRF). It is used for the elemental or oxide content of a material. X-Rays are used to excite a sample and generate secondary X-Rays. It provides determination of mayor, as well as minor and trace elements in solids [65].
- X-Ray Diffraction (XRD). The sample is analyzed to identify crystalline compounds or phases. Each chemical compound or phase reflects X-Rays with a different diffraction pattern. To identify compounds, the pattern obtained is compared to a large database of patterns already tested. This technique is considered to be complimentary to the XRF analysis [66].
- SO_3 analysis. Sulfur trioxide is an important parameter to measure the purity of gypsum. This test method is used to determine the quality of the

raw material. Sulfate is precipitated from an acid solution of the gypsum with barium chloride. The precipitate is filtered and weighted as barium sulfate and the sulfur trioxide equivalent is calculated. Calculations using SO_3 analysis are most accurate on samples that are known to be completely hydrated or completely dehydrated [50, 67].

- Inductively Coupled Plasma Spectrometry (ICP). It is a conventional spectroscopic technique that uses inductively coupled argon plasma as the source of atomic emission. It is used to determine trace elements in gypsum. [50]

Gypsum raw material processed by the gypsum industry can be contaminated with other minerals, called impurities. The most common impurities found in gypsum are carbonates, such as limestone and dolomite, clay, quartz, iron oxide and soluble salts [68]. Most of the natural gypsum contains between 10-15% of impurities, while some deposits may have a higher purity (up to 95%) and others a much lower purity (80%). Overall, the tolerance towards impurity depends on the type and quantity of impurity and the product to be manufactured [69].

With certain impurities, like carbonates and quartz, if at least 80% of the rock is gypsum, the production would not be affected as they have minimal effect on the manufacturing of wallboard. However, when detrimental impurities are part of the composition of the raw material, for example swelling clays, certain methods like sieving, washing and precipitation, could partially reduce the amount of impurities but there is a possibility of an amount remaining that may be quite detrimental to the products to be manufactured.

CARBONATES (Calcite $CaCO_3$, Dolomite $CaMg(CO_3)_2$) are the predominant group found in many gypsum sources. Limestone is the main carbonate found in gypsum. Composed primarily of calcium carbonate, it has a fairly little effect on the manufacturing of the wallboard by increasing its weight, affecting the level of installation effort and increasing the transportation costs. If there is a high amount of limestone present in the material, it could affect the processing equipment as well since it is a harder substance than gypsum [70].

SOLUBLE SALTS play an important role in the physical properties of the wallboard, when present in natural and several kinds of synthetic gypsums. Chloride salts (NaCl, KCl) are common in both, natural and synthetic gypsums. Magnesium salts ($MgSO_4{*}7H_2O$), existing in synthetic gypsum, are originated from limestone sources in desulfurization systems [50, 69].

SILICA (SiO_2) is another important impurity from the manufacture and medical perspective. It is common in both, natural and synthetic, gypsum and is one of the components of clay, fly ash or quartz. Crystalline silica (quartz) reduces the life of the process equipment because it is a very hard substance, and high quantities of respirable silica are associated with silicosis [71].

To evaluate the purity of gypsum, it is important to determine the differences between an impurity and a minor constituent in products. The impurities are part of the composition of the raw materials. On the contrary, a minor constituent is defined as a substance amounting less than 1% of total final product [71].

3.2.A Clay minerals

Clay minerals are the second most abundant impurities in the gypsum-based products, while limestone is the most abundant. Depending on the type of clay mineral, the resulting effect would change according to the clay structure. Clay minerals are structured in four main groups according to their properties: kaolinite, smectite, illite and chlorite. In structure terms, clays are divided in two groups: 1:1 or 2:1. Both structures have tetrahedral and octahedral sheets, with the difference that a 1:1 contains one tetrahedral sheet and one octahedral sheet (e.g. kaolinite, serpentine) (Figure 3-3.A) and a 2:1 clay mineral consists of one octahedral sheet between two tetrahedral sheets (e.g. smectites, sepiolite, attapulgite, chlorite) (Figure 3-3.B).

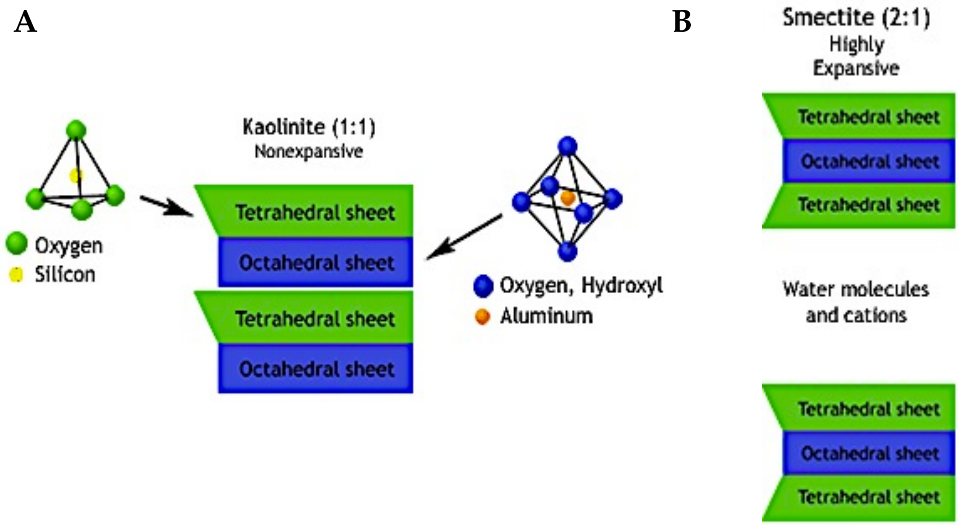


Figure 3-3 Structures of clay minerals [72]

The 2:1 clay minerals have a layered structure, which can be described as constructed from two modular units: a sheet of corner-linked tetrahedral and a sheet of edge-linked octahedral. Each tetrahedron consists of a cation (dominant cation is Si^{4+}, but Al^{3+} and Fe^{3+} could substitute it occasionally) coordinated with four oxygen atoms. The octahedral sheet consists of two planes of closed-packed oxygen ions occupying the octahedral sites between two planes (Figure 3-4.A).

When the centers of the six oxygen ions are connected around an octahedral cation site, an octahedron is formed. The cations are usually Al^{3+}, Mg^{2+}, Fe^{2+} or Fe^{3+} [73, 74].

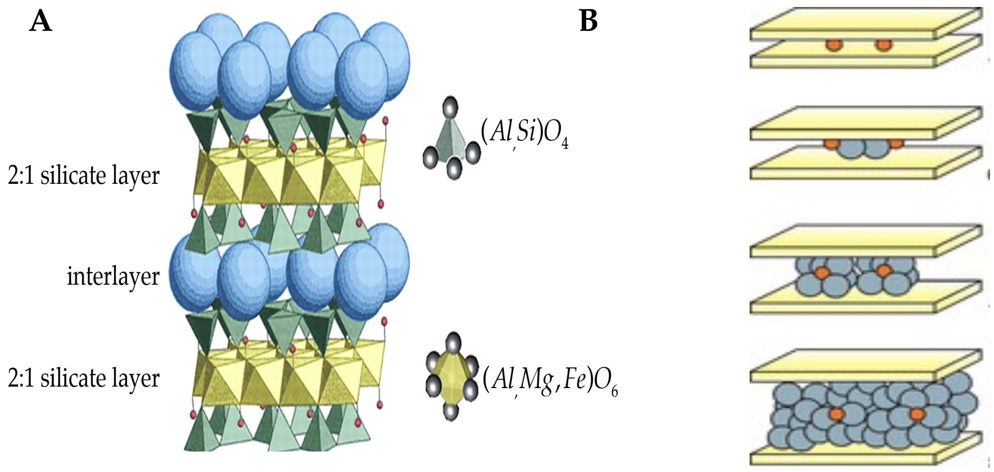


Figure 3-4 The structure of Bentonite [75]

Swellable clays, such as smectites (e.g. sodium montmorillonite, saponite and hectorite, generally referred as main constituents of bentonites), expand when initially wetted by the mix water; are being capable of absorbing 7 to 10 times its own weight in water, and swelling up to 18 times its dry volume (Figure 3-4.B). This affinity of absorbing significant amount of water and other liquids is quite useful in cat litter or oil absorbent, but adverse in gypsum wallboard [76]. A bentonite is a Na montmorillonite clay of the smectite group, which allow the slurry to form a gel-like structure that would change the performance of the admixture by altering the viscoelastic properties at relative low clay concentrations [26].

If a wallboard contains higher percentages of swelling clays and then is installed in a humid environment, the volume of the product would increase and may cause a *humidified split* [77]. This reaction occurs when soluble salts migrate to the gypsum core-paper interface and absorb multiple molecules from the atmosphere, forming complex salts and blisters on the surface of the board.

3.3 Admixtures

With the increase in the energy costs, there is a raising need to reduce energy consumption and increase productivity in the wallboard production and gypsum-based products. The reduction of the water to stucco ratio means a reduction on the drying energy and thus, in the time that the wallboard needs to spend in the drying oven; in many cases, the dryer capacity limits the productivity of the plant. The lower the drying requirements, the higher the plant productivity becomes [8, 9, 10, 11].

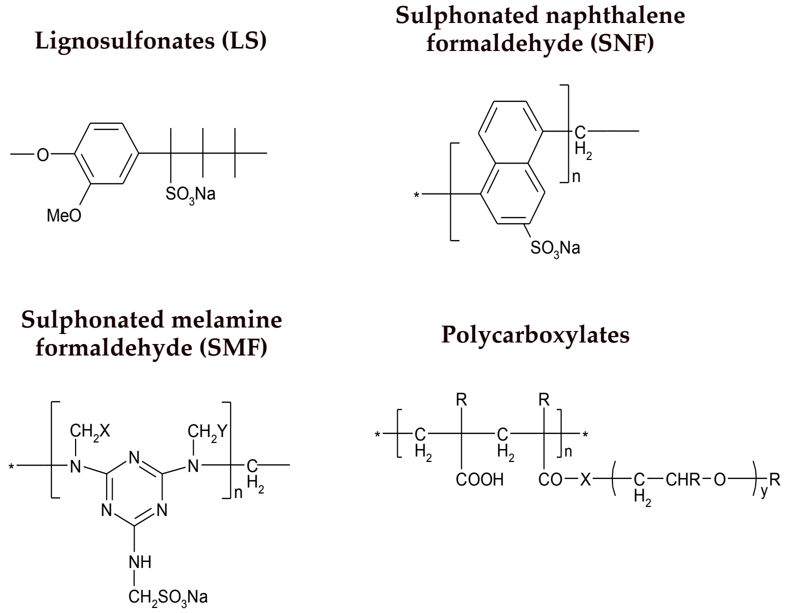
Chemical technology can improve wallboard plant profitability. In the wallboard production there are a number of technological requirements that need to be monitored during the whole manufacture process, to cite a few: the setting of the gypsum occurs within three to four minutes from mixing with water, while no flash setting shall occur in the mixer, good adhesion must be assured between the lining paper and the gypsum core and the mechanical properties of the board must satisfy prescribed standards. To satisfy all these requirements, plasticizers are used in the process. Superplasticizers are surface-active substances; these fluidizing agents are widely used as additives to decrease the water demand without affecting the workability of the cementitious and gypsum systems; strength and durability are properties that are improved as well. Efficacy is the ability to improve the fluidity of a slurry at a constant dispersant dosage or to reduce the amount of water while holding the slump flow. There are four families of plasticizers:

- Lignosulfonates (LS)
- Sulphonated naphthalene formaldehyde condensates (SNF)
- Sulfonated melamine formaldehyde (SMF)
- Polycarboxylates (PCEs)

A **LIGNOSULFONATE** (LS) is a water soluble sulfonate salt generally made from the lignin of sulfite pulp-mill liquors; therefore they are by-products from the pulp manufacturing process [78]. The quality is affected by type of cation, wood types and age, the conditions during the pulp and fermentation process as well as the residual sugar content. Due to their retarding effect, a smaller dosage of accelerator is required when using lignosulfonates. There is no interaction when in contact with foam [79].

SULFONATED NAPHTHALENE FORMALDEHYDE CONDENSATES (SNF) dispersants are effective at lowering the amount of water used in the wallboard manufacturing process [80]. SNF are synthetic polymers produced by naphthalene with sulfuric acid and then polymerizing with formaldehyde, followed by the neutralization with sodium or calcium hydroxide [81]. The quality is affected by the type of cation; the grade of condensation, influence of the length of the chain and molecular weight; and the residual sulfite content. In direct contact with foam, they present defoaming properties, which increase the foam consumption. Independent from their concentration level, they do not show any or minimal retarding effect. The gypsum core is harder in comparison to the usage of lignosulfonates [82]

SULFONATED MELAMINE FORMALDEHYDE CONDENSATES (SMF) are widely employed as flow improving agents in the processing of hydraulic binder containing compositions such as dry mortar mixtures, pourable mortars and other cement bonded construction materials and in the production of gypsum panels. SMF are used in this connection as a representative of s-triazine, causing a tough dissolving effect of the construction chemicals mixture while reducing undesired side effects that occur in the processing or in the functional properties of the hardened building material [83].


Lignosulfonates (LS)

Sulphonated naphthalene formaldehyde (SNF)

Sulphonated melamine formaldehyde (SMF)

Polycarboxylates

Figure 3-5 Different molecule structures of plasticizers

POLYCARBOXYLATES (PCE) are polymers with a "comb-type" structure, in which the backbone is a linear chain (anionic polymer) with carboxylate groups and ether lateral chains (nonionic polymers) forming the side chains or teeth. Due to the easy availability of the monomers and the large variability (backbone, side chains type, side chain length and amount of carboxylate groups) they can be designed to specific products and process conditions. They are, as well, environmentally and ecologically unproblematic because they do not contain formaldehydes [14].

In the 1980s, the first generation of polycarboxylates was developed. These new polymers were used as concrete water reducers [13], presenting a maximal reduction of 40% of the water demand in the system [84]. There is a wide knowledge about PCEs in cement and concrete, proving to have excellent dispersing performance and becoming one of the indispensable materials for high performance concrete [85]; however, the effects are frequently altered when the system is modified and it is very difficult to predict how individual compounds react in different media; occasionally the compatibility of the material with the superplasticizer could change the expected behavior.

3.3.A Mechanism of action of polycarboxylates

PCEs, as innovative technologies, enabled a further breakthrough in the mechanism of action of admixtures. The flocculation of particles can be avoided by the addition of a plasticizer to the slurry (Figure 3-6.*A*): the particles will repel each other (electrostatic stabilization) and a powerful deflocculating action will be presented; resulting in a more uniform distribution of the gypsum particles all through the mix (Figure 3-6.*B*) and an increase of the workability (plasticizing effect) [86].

Superplasticizers have a superior dispersive power as a result of dual forces, both steric and electrostatic repulsion that prevent flocculation and promote fluidity. Steric stabilization is due to configurational limitations produced by the pendant chains extending from the polymer backbone into the solvent (usually water) as particles approach each other [87]. When incorporated into the mix (Figure 3-6.*C*), the admixture particles are adsorbed onto the surface of the gypsum particles and negatively charged ends extend beyond, causing them to become mutually repulsive and therefore having a higher dispersing effect due to the tridimensional shape and chemical composition of the polycarboxylate (Figure 3-6.*D*).

These properties became interesting for the gypsum industry (in which the conventional plasticizers, based on melamine or naphthalene sulfonate condensates are still commonly used) after observing positive results with cement and concrete [88], although they had to be optimized to be usable in the gypsum-based systems to deliver the required performance. As mentioned before, there is a remarkable flexibility when it comes to optimize the structure of this comb polymer dispersants; variations on the polymer architecture include the structure, molecular weight; type, length and composition of the backbone; type and length of side chains, among others.

It was found [17] that the structure of the polymer affects the liquefaction of calcium sulphate phases differently than in cementitious systems, presenting the drawback of a longer setting time on the plasterboard, which will reduce the productivity of the manufacturing line. The degree of retardation depends on the exact formulation of the polycarboxylate dispersant. This performance could be improved by adjusting the additive formulation; some authors believe the shorter the backbone and the longer and more numerous the ether lateral chains, the greater and long lasting is the flow ability [89]. Most publications in the area of data report there is no “universal” admixture, up to date, for all binder types.

In the gypsum industry, there has been some work done with β-HH and α-HH plaster and polycarboxylates. It has been found a relationship between the polymer structure and dispersing mechanism of the polycarboxylate superplasticizer in calcium sulphate systems, affecting set times and hydration reaction of gypsum with water due to the electrostatic repulsion and steric effect [13, 17, 87].

There is a reduction on the efficiency of the polycarboxylates that is linked to the presence of impurities in the raw material. Researchers in the gypsum and chemical industry agree that there is an interaction between the polycarboxylate superplasticizers and the gypsum containing impurities. The impurities (mainly swelling clays) make the natural gypsum incompatible with the polycarboxylate superplasticizer as they affect the mechanism of action of the admixture [50, 90]. Hence, they would interfere with the expected results: leading to poor dosage response and an increasing water demand.

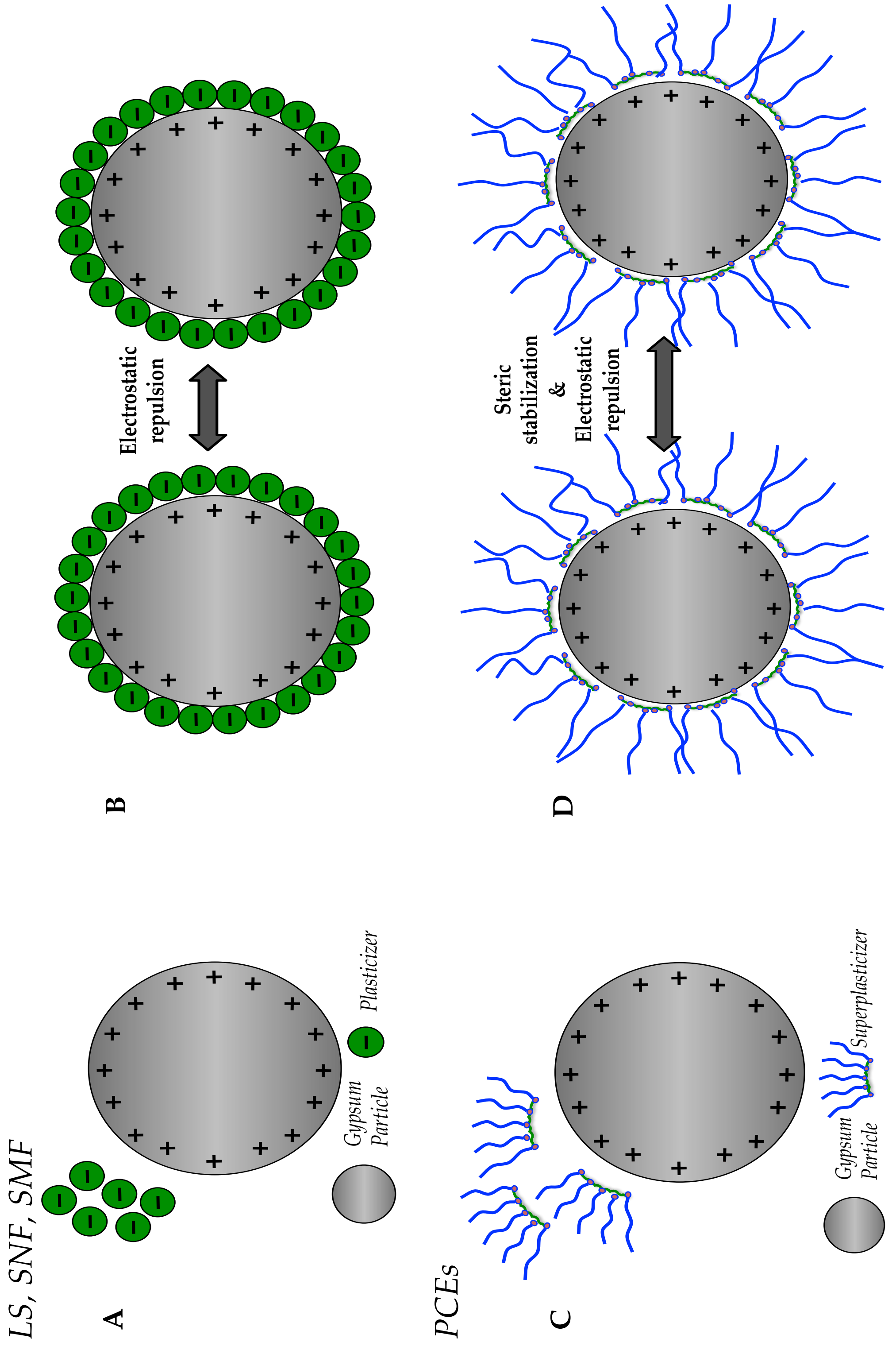


Figure 3-6 Differences between the mechanisms of action of Lignosulfonates (LS), Sulphonated naphthalene formaldehydes (SNF), Sulphonated melamine formaldehydes (SMF) and polycarboxylates (PCEs).

3.4 Application

Gypsum is used extensively in a wide variety of applications. In agriculture it is used as a soil additive; in environmental engineering it is used as an additive in turbid water to settle dirt and clay particles without affecting ecosystems; in medicine, it is used to create surgical and orthopedic casts; in the food industry it is used as a dietary source of calcium, to condition water suitable to produce beer, as an ingredient in white bread, flour, and other food products and in the dental industry it is used to take impressions and make models of dental impressions.

Gypsum has also been widely used as a construction material since ancient times. Around 3000 BC in Egypt, it was used as a mortar in the pyramids and the early Greeks discovered the advantages of the calcination of gypsum. Reports indicate that gypsum mortar was used in Egypt during the construction of the Pyramid of Cheops (1580-1350 BC). In the medieval times, hydraulic gypsum mortar was used for castles and fortresses in Germany [30-33, 69, 91-93].

Nowadays, it is a fundamental construction material in our modern day society; its products are widely used in all construction types, regardless of the complexity of the design. According to the European Gypsum Industry, more than 1,500 million square meters of interior surfaces are covered every year with gypsum products, such as wallboard, blocks or gypsum paste [94].

3.4.A Wallboard production

A gypsum-building panel is produced with stucco and water to form a calcium sulfate dihydrate crystal matrix. The most important factors in wallboard manufacturing are uniformity, speed and efficiency; this is the method to obtain a low-cost construction material [83]. A schematic illustration of the wallboard production is shown in Figure 3-7. The stucco is mixed with the additives and water using a high shear mixer. Water is added in excess to give sufficient fluidity to the slurry, the hydration reaction needs to be completed. Several authors discussed the theory about the requirements of pure β-hemihydrate: its stoichiometric ratio requires 18.62% of its own weight to water to rehydrate to gypsum (water/binder-ratio is 0.1862). The typical water demand of plaster of Paris is above w/b=0.70, resulting in a 65-75% excess water [7, 17, 56]. Reducing the excess of water required for the wallboard manufacture by the addition of a novel PCE, that will keep its robustness in presence of detrimental impurities, is the main interest of the present thesis.

After mixing, the slurry is placed on the paper surface [49], then it is continuously deposited on a moving surface that includes a facing material below and above the slurry; the bond between the paper and the gypsum core is of critical importance to the quality of the gypsum board. A bond failure would be evidenced by the paper peeling away from the core with little force and no evidence of gypsum core particles adhering to the paper surface or the paper separating with various amounts of thickness of the core fragments adhered to the paper [95]. The next step is to smooth it to a constant thickness and shaped into a continuous ribbon, which is conveyed on a belt until the calcinated gypsum is set and subsequently cut to form the panels of desired length. The process concludes in the oven or drying kiln to remove excess moisture. Nowadays, it is particularly expensive to operate those drying devices; by reducing the amount of excess water added, the production cost would decrease in a significant way.

In the wallboard production, the control of setting times is extremely important. In order to enhance the workability, a number of organic and inorganic compounds are used to accelerate or retard the process of setting and hydration.

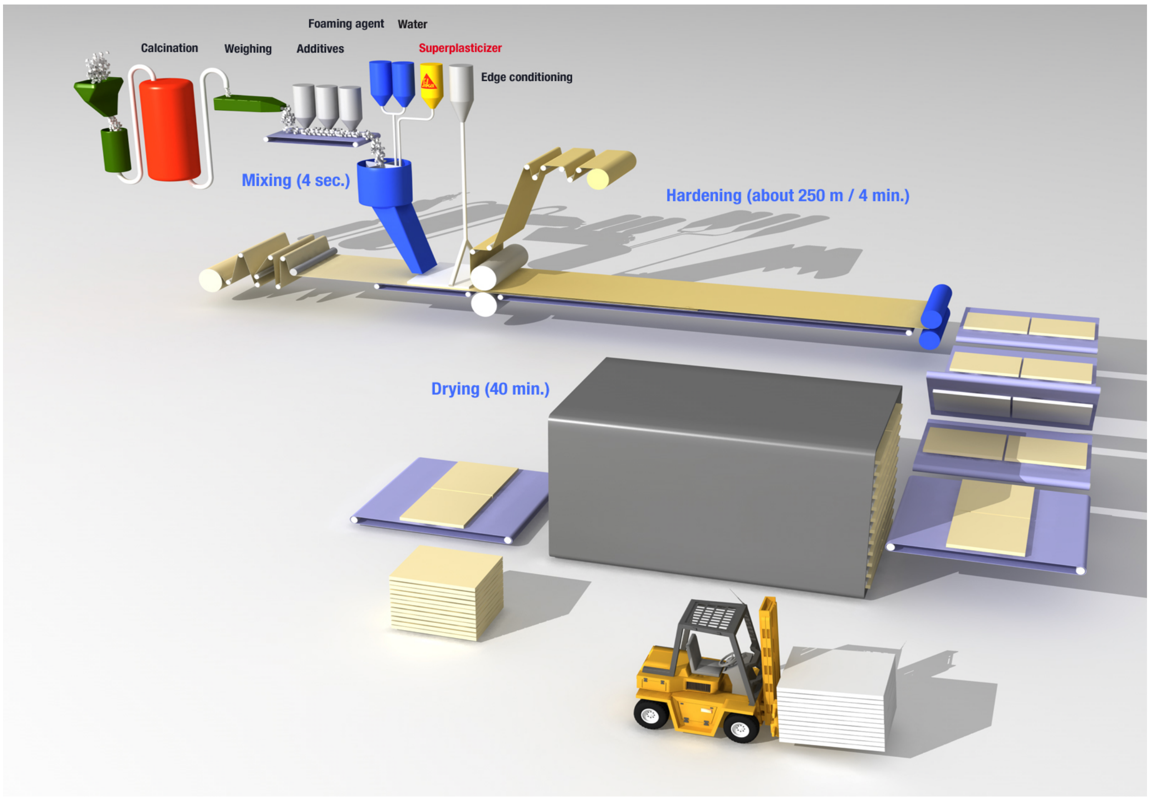


Figure 3-7 Wallboard production

4 EXPERIMENTAL

4.1 Material Characterization

4.1.A Polymer synthesis and characterization

Polycarboxylates are polymers with a "comb-type" structure, in which the backbone is a linear chain (anionic polymer) with carboxylate groups and ether lateral chains (nonionic polymers) forming the side chains or teeth [96]. As shown in Figure 4-1 the backbone of the polymer chain has a negative charge due to the deprotonated carboxylate groups [29]. Modifying the backbone and side chains nature, the side chain number and length, and the charge density would change the structure of the polycarboxylates. These parameters would lead to changes in the application behavior (water reduction, workability, rheology and strength) on each system.

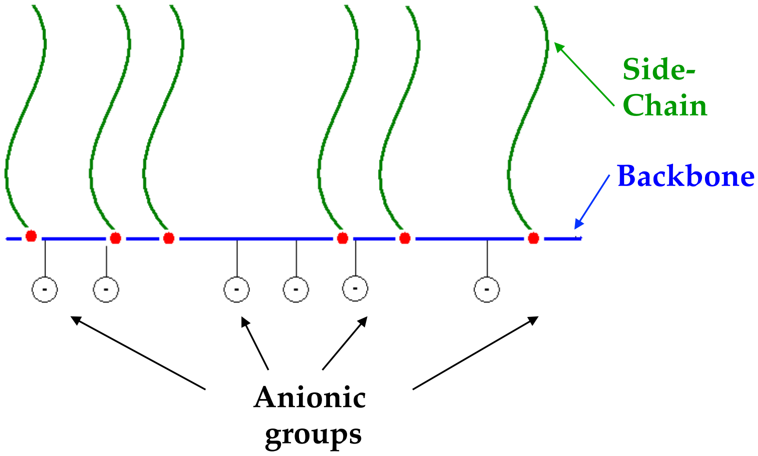


Figure 4-1 Schematic representation of PCE architecture

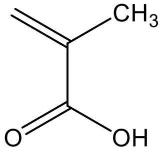
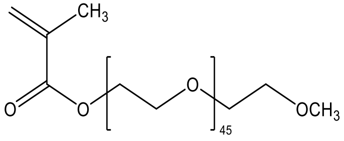
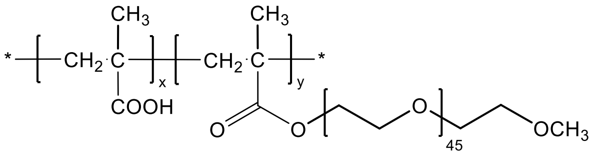
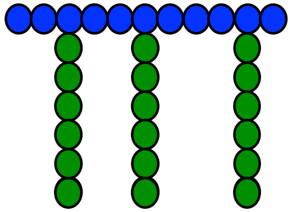
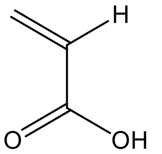
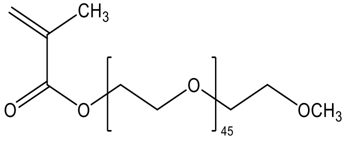
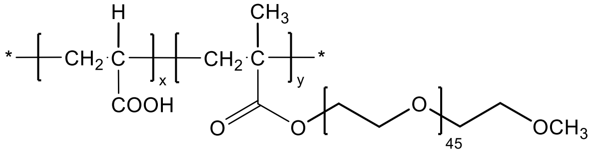
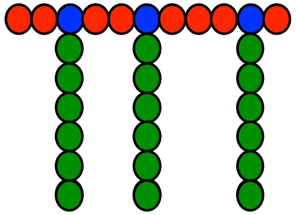
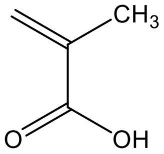
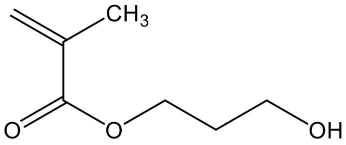
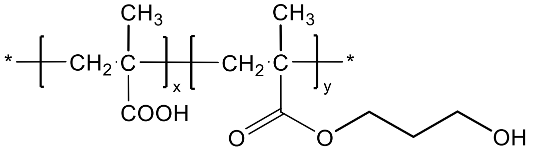
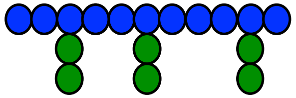
The polymers were synthesized via radical copolymerization. For the different polymer series methacrylic acid (MAS), acrylic acid (AS), methoxypoly(ethylene glycol) 2000 methacrylate (MPEG2000MA) and hydroxypropyl methacrylat (HPMA) were used as monomers. Copolymerization was initiated by sodium persulfate ($Na_2S_2O_8$) and the chain transfer agent used was sodium hypophosphite monohydrate ($Na_2PO_2H_2\cdot$)

For this study, three series of polymers were synthetized. The density of side chains, the side chain length and the backbone structure were varied to understand the influence of the interaction between the PCE and gypsum particles at the solid-liquid interface, in pursuance of capturing the efficiency of different polymer architectures.

The first series of polymers had a pure methacrylic acid backbone with methoxypoly(ethylene glycol) side chains (MPEG2000MA). Polymers were synthesized via copolymerization of MAS and MPEG2000MA. The second series of polymers consisted of a mix backbone (methacrylic and acrylic acid) with methoxypoly(ethylene glycol) side chains. Polymers were synthetized via copolymerization of AS with MPEG2000MA. The polymer architecture in the first and second series, kept the side chain length constant and varied on the side chain density (Acid/Ester). The molecular structures of the experimental superplasticizers are shown on Table 4-1.

Copolymerization of methacrylic acid and hydroxypropyl methacrylat (HPMA) provided the third series of polymers with a pure methacrylic acid backbone. The polymer architecture kept the side chain length constant and varied on the side chain density. The main difference between the polymers synthetized with MPEG2000MA against HPMA is the side chain length. The MPEG2000MA series have a longer side chain length than the HPMA series.

Table 4-1 Chemical structures of polymers test

Series	Monomers		Polymer	Schematic Model
1	 **MAS**	 **MPEG2000MA**	 **MAS 1,3,6,9**	
2	 **AS**	 **MPEG2000MA**	 **MIX 1,3,6**	
3	 **MAS**	 **HPMA**	 **MAS short 1, 3**	

Different polycarboxylate ether-based superplasticizers were tested in this study. Varying the number of acid/ester ratio (C:E), different polymer architectures were obtained. The superplasticizers tested in this work differentiate between C:E = 1, 3, 6 and backbone structure: methacrylic acid (MAS) and methacrylic/acrylic acid mix (MIX). The polymers on the first and second series have methoxypoly(ethylene glycol) as their side chain with molecular weight of M = 2000 g/mol. The polymers on the third series have hydroxypropyl side chains with molecular weight of M = 59 g/mol. Detailed information of the investigated samples is presented on Table 4-2.

Table 4-2 Detailed information of the investigated PCE samples

Series	Name	Backbone	Side chain length [g/mol]	Acid/ Ester [C:E]	Mw [g/mol]	Mn [g/mol]	D= Mw/Mn
1	MAS 1	MAS	2000	1	157 760	54 740	2.88
	MAS 3	MAS	2000	3	104 330	31 270	3.34
	MAS 6	MAS	2000	6	71 170	21 520	3.31
	MAS 9	MAS	2000	9	50 900	15 391	3.31
2	MIX 1	MAS + AS	2000	1	58 310	25 440	2.29
	MIX 3	MAS+ AS	2000	3	44 220	19 160	2.31
	MIX 6	MAS + AS	2000	6	28 120	12 990	2.16
3	MAS short 1	MAS	59	1	27 537	18 146	1.52
	MAS short 3	MAS	59	3	20 596	17 009	1.21

4.1.B Gypsum characterization

Wallboard manufacture has the most stringent demands on the properties of gypsum. Factors that affect the properties of the slurry or the finished board must be carefully controlled. In order to evaluate the performance and adsorption behavior, measurements on the blank gypsum types were performed. In the study, three different gypsum types represent the gypsum materials, currently used in wallboard and screed production: natural beta-hemihydrate, FGD beta-hemihydrate and alpha-hemihydrate.

Gypsum types used in this study were characterized with different methods. In Table 4-3, the properties of each type are summarized. Particle size distributions were obtained by laser diffraction measurements; surface areas were obtained from BET and Blaine methods. Due to specific surface areas, the water-to-gypsum ratios (w/g) used to mix them, varied from type to type. The w/g was determined to be set where the slump flow reached a value between 140-150 mm; this would be considered as the starting point of the series of tests.

Table 4-3 Properties of the gypsum types

Sample	Particle Size Distribution	BET value [m²/g]	Blaine value [g/cm³]	w/g
Turkey Natural β – Hemihydrate	d(0.1): 1.293 µm d(0.5): 6.435 µm d(0.9): 29.919 µm	7.489	2.52	0.71
Lippendorf FGD β – Hemihydrate	d(0.1): 2.271 µm d(0.5): 17.449 µm d(0.9): 73.084 µm	8.554	2.50	0.67
Niederauβem α - Hemihydrate	d(0.1): 2.471 µm d(0.5): 17.056 µm d(0.9): 42.360 µm	1.745	2.61	0.43

4.1.C Clay characterization

For this investigation, three different types of clay minerals were tested where two of them were natural and one was synthetic. Their properties are shown in Table 4-4. Each clay mineral was characterized by different methods: particle size distributions (PSD) were obtained by laser diffraction measurement; surface areas were obtained by BET method. The water requirement (w/g) of the clay minerals was determined in order to be comparable with the w/g of the different gypsum types. It was set where the slump flow reached a value between 140-150 mm.

The three different samples were also characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), X-Ray diffraction (XRD), and X-Ray fluorescence. The analysis of the natural samples ´SS.003´ and ´SS.480´ indicated a relatively small amount of montmorillonite. The third sample is a synthetic bentonite. It is known that montmorillonite can be synthesized with a very similar structure and properties to their natural counterparts [97]. The analysis showed a material with high content of montmorillonite and a minimal content of other phases. Further tests in this investigation were carried on with the sample ´Bentonite SA´ due to its high purity.

Table 4-4 Properties of the clay minerals tested

Sample	Particle Size Distribution	BET value [m²/g]	w/g	HCl insoluble after 850°C	Swelling Percentage*
SS.480 (clay)	d(0.1): 7.6 µm d(0.5): 170.5 µm d(0.9): 577.4 µm	100.089	0.71	57.3%	27.2%
SS.003 (clay)	d(0.1): 12.7 µm d(0.5): 173.7 µm d(0.9): 656.6 µm	20.967	2.5	71.4%	35.6%
Bentonite SA	d(0.1): 2.74 µm d(0.5): 10.796 µm d(0.9): 24.108 µm	29.658	7.94	70.8%	30.2%

4.2 Methods

4.2.A Performance tests

A gypsum paste is prepared by adding 200 g of stucco to the water containing the plasticizer, under mixing for 15 seconds, followed by a 15 seconds waiting time and finally, 30 seconds of mixing. By already established methods, slump flow performance and setting times (knife and thumb pressure) were measured. According to the Knauf method, the slump flow performance consists in filling up a hollow cylinder ($ø_{inside}$=50 mm, height=51 mm) with the mix prepared on a glass plate, and then the cylinder has to be pulled-up. The cylinder is removed until the whole material drops on the glass plate. When there is no more visible flow, the diameter has to be measured at two perpendicular points and the average is the result. After the slump flow is measured, one proceeds to measure the setting times with the same sample. A knife has to be drawn through the sample and the coalescence of the edges has to be observed. The initial setting time is defined, as the time at which there is no flow-back from the edges (DIN EN 13279-2). The final setting time is determined by pressing the sample with the thumb applying a pressure of 5 kg. The value is obtained when there is no surface water released upon pressing.

4.2.B Adsorption

Adsorption of plasticizer was determined by analyzing the concentration of plasticizer present in the aqueous phase, through calculating the Total Organic Carbon (TOC) left in the pore water solution with a Shimadzu TOC Analyzer. To define the amount of the PCE adsorbed on the materials tested, adsorption isotherms were collected. The solution depletion method was used to prepare each sample (Figure 4-2).

The mix solution contains the water and the PCE amount related to the dosage chosen. After the gypsum is mixed with the solution, the suspension was centrifuged. Then, the pore solution was removed through a 0.45 μm nylon filter by pressure filtration from the slurry after centrifugation. The pore solution was first diluted 1:1 with 0.1 mol/l HCl and subsequently, diluted 2:50 with bi-distillate water before the TOC measurements were applied.

In order to detect the carbon content, the combustion catalytic oxidation technique was employed by a Shimadzu TOC-VCPH Analyzer. The instrument was set to reject the first two measured values and to make an average of the remaining three values. Reference solutions with the same concentration (without plasticizer) were set as standard and measured after each 10 samples. The amount of plasticizer bound to the gypsum slurry was calculated from the TOC contents using a reference measurement of the aqueous polymer solution by the difference between the added and the measured content of organic carbon. The TOC content of the plain gypsum mix was taken into account. To obtain the adsorption isotherms, five different PCE dosages were used for each PCE and gypsum type, and each measurement was repeated three times to ensure an accurate result. For these experiments, the same materials as for the performance analysis were used.

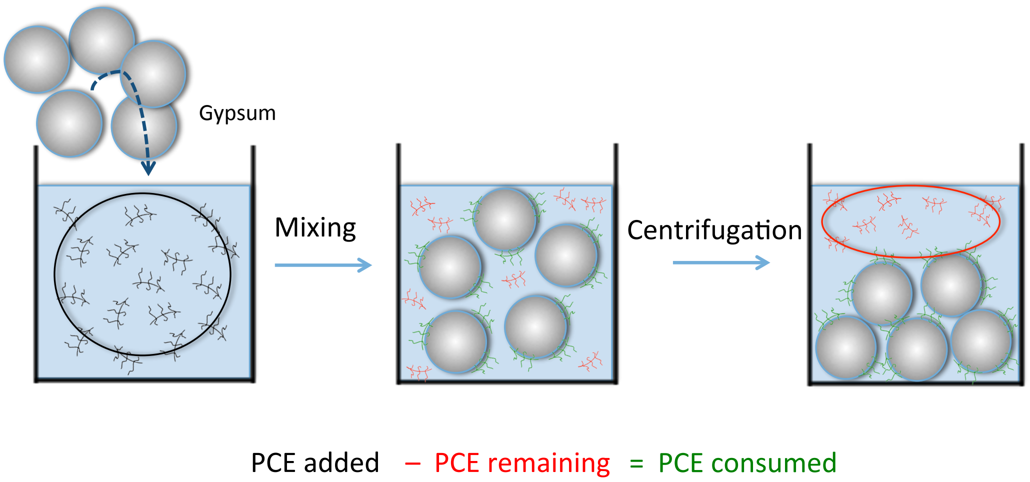


Figure 4-2 Solution depletion method to analyze PCE adsorption

To validate the accuracy of the results of workability and adsorption, each test was repeated five times and a minimal error of 0.2% was obtained.

4.2.C Rheology

Laboratory rheological data were obtained with an Anton Paar rheometer model Rheolab QC, equipped with vane geometry, well adapted for the mixing of gypsum slurry. The vane geometry consisted of two blades around a cylindrical shaft. The blade height and diameter were chosen to optimize the measurement accuracy and to avoid any flocculation. The device used measured the rheological properties of the slurries by recording cycles measuring the shear stress and yield stress at specific shear rates. The testing cycle consisted a series of “single-point” tests at fixed speeds and comparing the results with a reference test. Further details are available in Appendix 8.1

4.2.D Calorimetry

In the hardening progress of the gypsum slurry, the heat evolved in the exothermic reaction can be measured in a calorimeter. Semi-adiabatic calorimetry is based on ´temperature rise´ measurements that are used to understand the effect of the admixture type and dosage on the material; and the impact of impurities on the properties of the gypsum slurry.

A semi-adiabatic calorimeter was used during this study to quantify the hydration development of various gypsum systems. The calorimeter consisted of an insulated container that uses 8 cylindrical samples and one reference. Probes are used to control the slurry temperature. Each tests was performed over a period between 1-4 hours. Semi-adiabatic calorimetry tests were performed on stucco (blank system); stucco with admixture; and stucco with bentonite and admixture. The type and dosage of the admixture were varied. Further details are available in Appendix 8.2.

4.2.E ζ – Potential

Zeta potential is a physical property that is exhibited by any particle in suspension. It can be used to optimize the formulations of suspensions and emulsions. To investigate the interaction occurring between PCE and stucco (with or without bentonite), zeta potential measurements were performed with the Electro kinetic Sonic Amplitude technique. It determines the particle velocity by measuring the sound frequency. The suspension is subjected to an alternating high frequency electric field. The motion of the particles generates a sound wave, which is monitored and delivers the dynamic of the suspended particles. The zeta potential is calculated from the dynamic mobility with the standard software [98, 99].

Prior the sample measurements, pH-meter (4.0, 7.0, 10.0) and zeta flow through cell were calibrated. The titration unit was washed prior to the use with the titrant to insure its purity.

The stucco was suspended in water; the slurry had a pH value of 7. If the pH changed when polymer or bentonite were added to the slurry, the value was adjusted with KOH to kept it constant. PCE titration experiments were carried out on suspensions with natural beta-hemihydrate. Changes on the zeta potential were analyzed when bentonite was added in the system.

5 RESULTS AND DISCUSSION

In the wallboard production, stucco is mixed with water, additives and other components to obtain the structure required by the final products. However, the behavior of the additives could change depending upon several factors, such as the source and composition of the stucco and the type of the admixture used.

In this dissertation, three aspects were studied: the raw material, the PCE structure and the presence of bentonite as a detrimental impurity of the slurry. In section 5.1, the influence of the raw material is analyzed to understand the behavior of the PCE adsorption: where and how it takes place. In section 5.2 the influence of the PCE structure is investigated and three series of polymers were tested to define the ideal structure-relationship for the workability required in the wallboard production. Three polymer parameters were varied: side chain length, backbone type and density of side chains. In section 5.3, a more detailed study on the influence of bentonite, as a detrimental impurity, is presented focusing on the mechanism of its expanding layers and the decrease on the effectiveness of the PCE in the slurry.

5.1 Influence of the Raw Material

Over the last years, due to commercial demand from the building industry, PCEs, acting as High-Range-Water-Reducers, have been the additives to be the most researched upon [100]. Comb polymers are commonly used as dispersants in gypsum suspensions. The effectiveness of such polymeric additives to stabilize these suspensions is determined to a large extent by the reduction of the water demand due to the adsorbed polymer.

In wallboard manufacturing, after the stucco is mixed with water and additives, the slurry is spread between two paper layers. While the board continues along the conveyor belt, the calcium sulfate hemihydrate (HH) reacts with the water in the slurry to form calcium sulfate dihydrate (DH), resulting in a rigid panel.

The first set of analyses examined the adsorption of polymer in both gypsum phases. Figure 5-1 compares the results obtained from the analysis of the adsorption of a PCE between calcium sulfate hemihydrate and calcium sulfate dihydrate. From the graph below it can be seen that the PCE adsorbed significantly more in HH than in DH. The blue graph representing the PCE adsorption in DH shows a minimal adsorption even at high concentration of PCE, while in the HH adsorption takes up to 100% before reaching saturation. The results reveal that the polymer adsorption does not take place in the DH phase; it takes place on the HH phase. As the phase changes from hemihydrate to dihydrate, there is an irreversible loss of surface area. The DH forms at crystalline boundaries, which join neighboring crystals together in such a way as to seal off portions of the surface of the crystals, so the PCE molecules can no longer reach them, hence the reduction on the dispersion power of the slurry [101]. There is no adsorption when the slurry is in-between the paper sheets and prepared to core bond. The tendencies toward adsorption on HH are strong; the present study will further focus on the adsorption of polymer in hemihydrate.

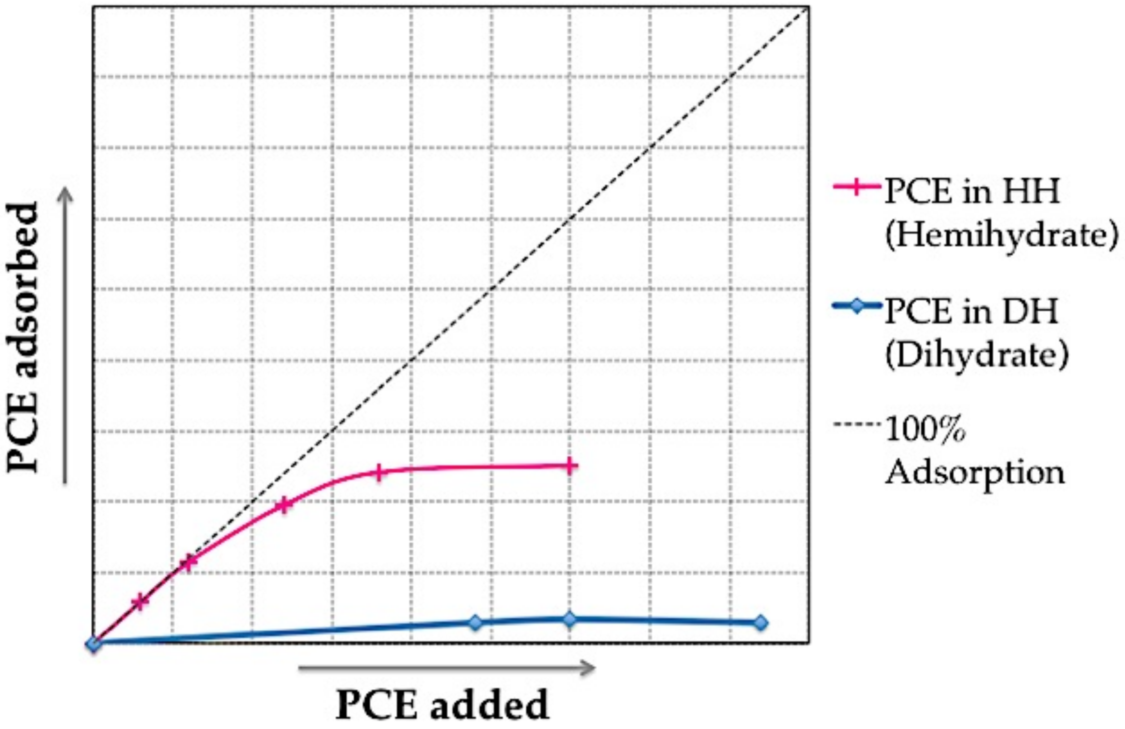


Figure 5-1 Adsorption of PCE in Hemihydrate (HH) and Dihydrate (DH)

The nature of the HH tested is also a factor of importance. As described in Section 3.1.B, hemihydrate can be classified by its origin, natural-HH and FGD-HH, or by its crystal structure, α-HH and β-HH. Natural-HH and FGD-HH are chemically the same, but their physical properties can be significantly different. It is known that there are considerable differences in particle size and shape between natural ground gypsum rock and synthetic gypsums [50]. In general, FGD-gypsum has higher surface area and also, as the free moisture is reduced through mechanical dewatering, the water-soluble impurities are reduced and the purity is increased. The differences between α and β hemihydrate are the result of differences in the crystal size and surface area. The crystals of α-HH are dense and prismatic while the crystals of β-HH are scattered and irregularly shaped. α-HH is conformed of large crystals and β-HH of extremely small crystals. Increasing the size of the crystal leads to a smaller surface area of the powder, leading to a decrease of the water demand (water to plaster ratio). The smaller crystal size of β-HH increases the surface area of the powder, which increases the water demand [102]. The β-HH is almost 80% smaller than the α-HH, which results in a higher specific surface area for the same weight. Hence, α-HH has a water to plaster ratio much smaller than β-HH (≈44%).

As stated in Table 4-3 (section 4.1.B, pg. 30), both β-HHs have a similar surface area (BET: 7.489 & 8.554 m^2/g, respectively) and a comparable water demand (w/g 0.71 & 0.67). α-HH has a drastically smaller surface (1.745 m^2/g), which decreases its water demand accordingly (w/g 0.43). The α-HH forms less acicular crystals than β-HH, allowing the crystals to pack tightly together, making a denser and stronger plaster. The crystal morphology increases the flowability of water, requiring less water to form a flowable slurry [103].

One of the PCEs from the synthetized series (MAS 6) was tested in three different HH types to observe the differences on its behavior. The differences between the gypsum types are highlighted in Table 4-3. It is important to remark that the slump performance of the α-HH was superior to the β-HH due to the nature of crystal size and shape. The crystal shape in α-HH allows a higher dispersion of the slurry due to the flowability of the water. Adsorption is another factor that is strongly influenced by the surface of the gypsum particles in each gypsum type. As observed in Figure 5-2 the α-hemihydrate manifests a lower adsorption of superplasticizer; whereas in the other two gypsum types, the level of adsorption is at a much higher concentration. The behavior of the PCE in Natural β-HH and FGD β-HH are quite similar. Both adsorb the polymer with the same tendency and reach saturation at the same concentration. The β-HHs have a higher surface area of the powder than the α-HH, the increase of the surface area allows more polymer to be adsorbed by the HH particles.

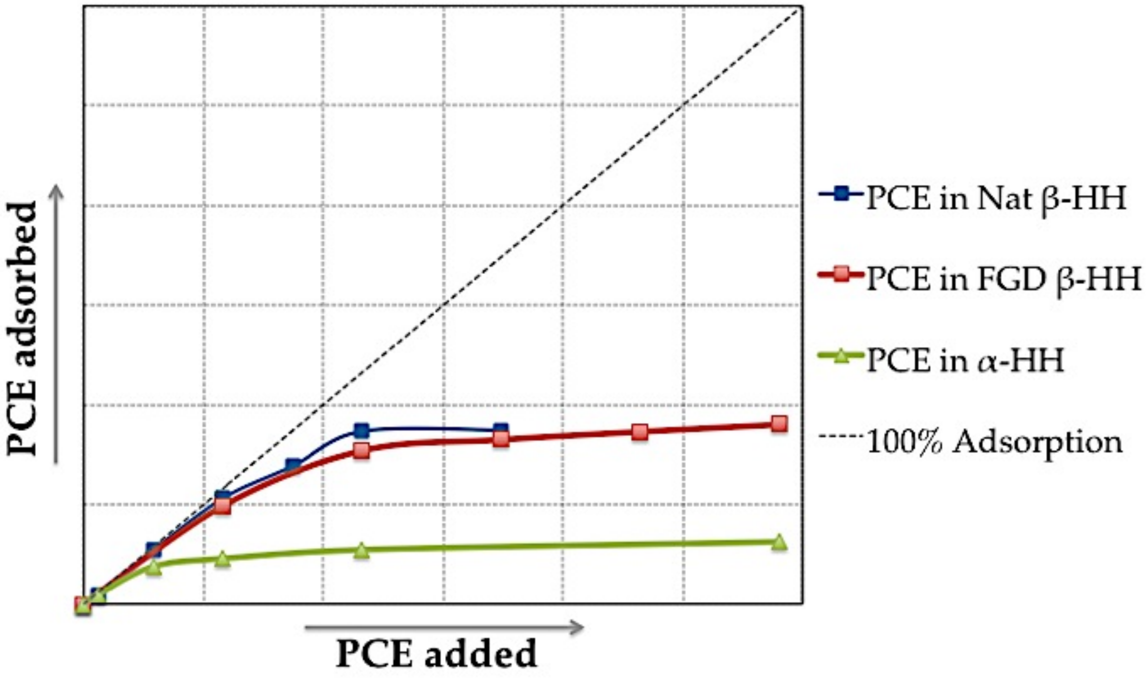


Figure 5-2 PCE adsorption in different types of HH

The adsorption ratio of the PCE changes depending on the differences of the origin and crystal structure of the hemihydrate. The β-HH adsorbs PCE significantly more than the α-HH (up to 60%). The purity of the β-HHs has a strong influence in the adsorption behavior. The β-HHs tested in this study were selected because of its high purity content. Both, natural and FGD β-HHs, show a comparable PCE adsorption. FGD β-HH generally has a higher purity, 96%, while natural β-HH varies between 80-96%.

When working with natural stucco, there is always a chance of detrimental impurities to be existent in the stucco composition. The presence of certain impurities, such as swelling clays, would diminish the dispersing behavior of the PCE. In Figure 5-3 a comparison between a slurry without bentonite and a slurry with 1% bentonite in weight was made by testing a PCE from the synthetized series.

Figure 5-3 is quite revealing in several ways. First, there is a main difference in the slump behavior between the two systems. The bentonite has a strong effect on the flowability of the slurry; therefore the slump flow of the system with bentonite is drastically affected. Second, it leads to a further understanding of the mechanism of action of the PCE. It is known that the workability of the slurry is fully linked to the adsorption of the PCE on the HH particles [104, 105].

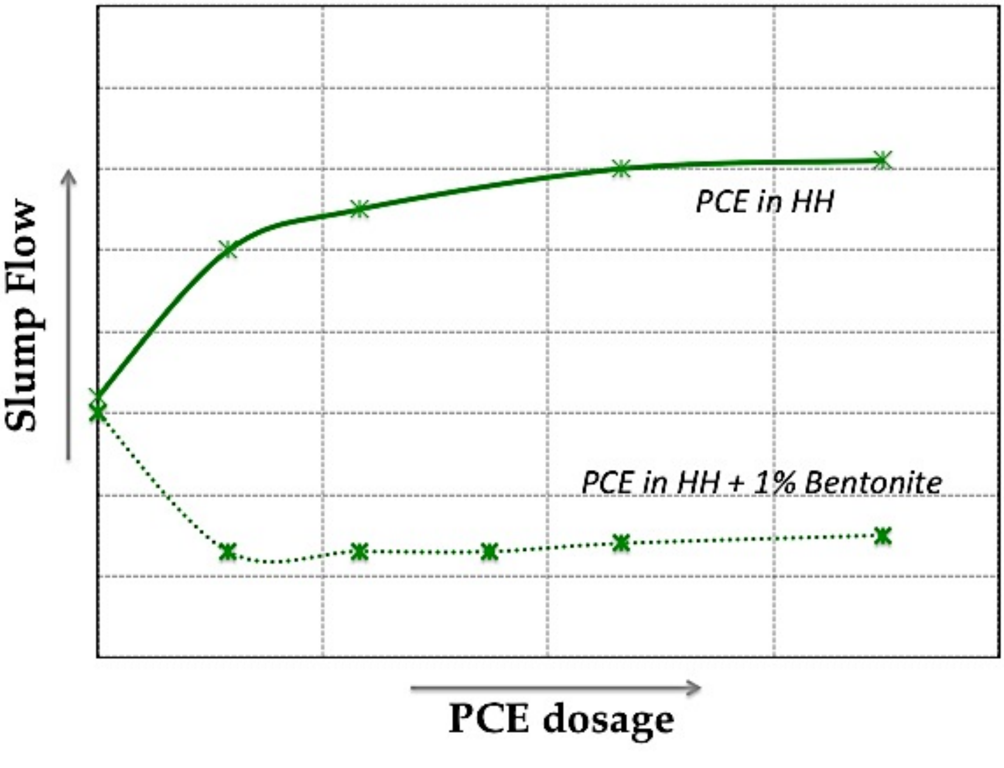


Figure 5-3 Effect of the bentonite in the slurry

When a PCE is adsorbed, electrostatic and steric forces are able to improve the flow of the slurry. Nevertheless, the bentonite possesses a layered structure that allows a variety of interactions with polymers that can affect and can be detrimental for the workability of the slurry [106]. Bentonite particles offer three types of surfaces to the macromolecules: external basal plane, edge surfaces and the interlayered surfaces (Figure 5-4). The polymer can adsorb on the external basal plane or on the edge surfaces, presenting a similar adsorption as the hemihydrate particles. In addition, the bentonite layers are able to expand when in immersed in water, the polymer also adsorbs on the interlayered surfaces. This behavior inhibits the PCE to fully interact with the gypsum particles, hence the reduction on the dispersing power shown in Figure 5-3.

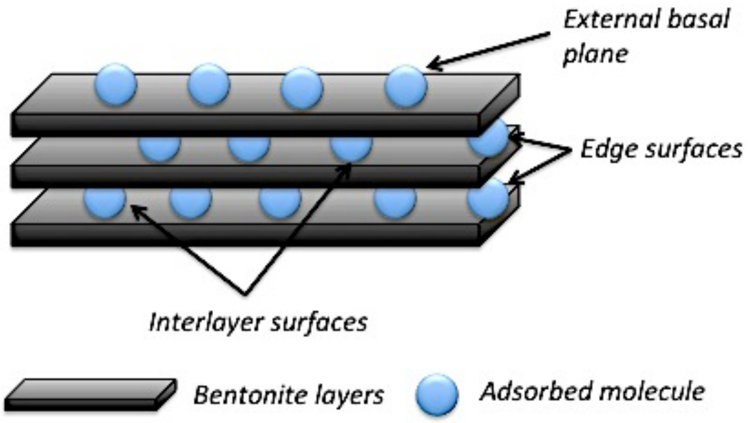


Figure 5-4 Adsorption surfaces of bentonite

Swelling clays, like bentonite, interact through the three surfaces in mainly three different ways: electrostatic interaction, cation-dipole interaction and intercalation [107]. To distinguish the difference between the adsorption of the bentonite and the hemihydrate, pure bentonite and hemihydrate were evaluated with a PCE of the synthetized series on Figure 5-5.

From the data in Figure 5-5, it is apparent that the hemihydrate particles adsorb the PCE until saturation is reached, where no more polymer molecules would be adsorbed when the plateau is reached. On the contrary, the bentonite particles keep adsorbing polymer and saturation is not reached (to the extent of this tests). Interestingly, this finding is related to the structure of the bentonite. A higher polymer adsorption by the bentonite is expected as a result of its expanding lattices and high active surface area. According to several researchers, polymers intercalate into the clay layers, mainly, by ion exchange with organic cations allowing the adsorption of a bigger amount of polymer [107-109].

For the superplasticizers tested in the hemihydrate with bentonite, there was a strong detrimental impact in the workability. Indicating that when natural hemihydrate is contaminated by a substantial amount of bentonite (higher than 1wt%), competing adsorption by hemihydrate and bentonite for the PCE molecules can occur, consequently reducing the PCE effect for dispersion as seen in Figure 5-3.

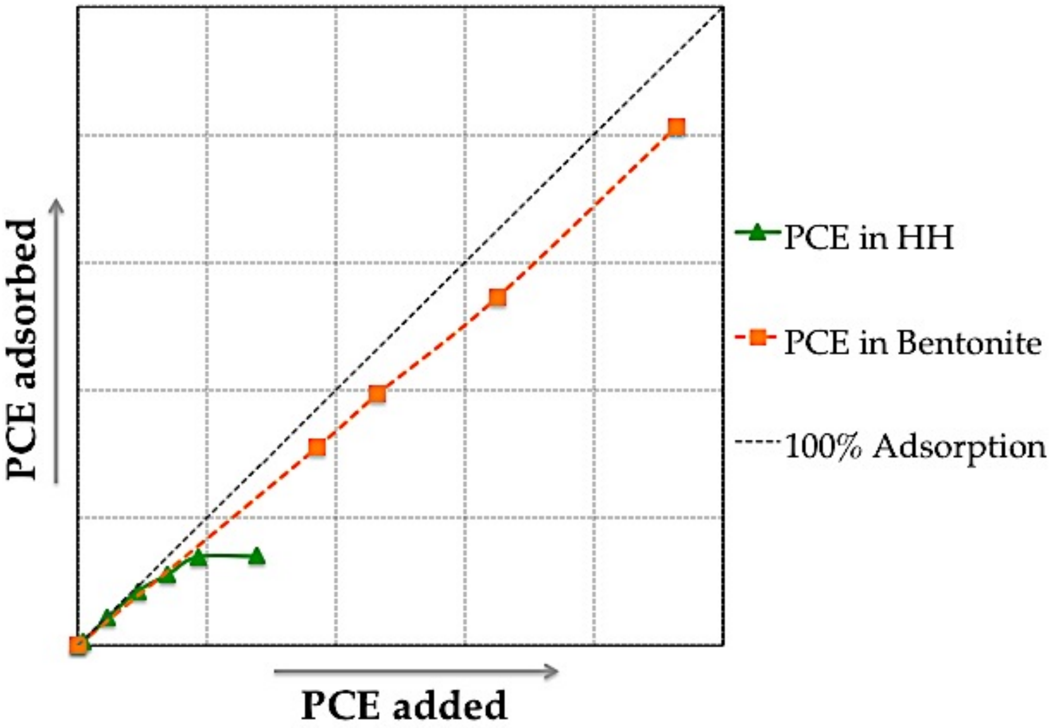


Figure 5-5 PCE adsorption in HH and pure bentonite

The main challenge for this study is to design a PCE that would keep its robustness on systems with and without detrimental impurities, mainly clay minerals. Three different kinds of hemihydrate were tested (Natural β-HH, FGD β-HH and α-HH). This study focused on increasing the efficiency of the wallboard production. The stucco used in the manufacture gypsum wallboard is exclusively in the β-HH form. α-HH is not used commercially due to its slower hydration rate compared to β-HH; it will require a slower line speed [110]. Both Natural and FGD β-HH are used in the wallboard production. Certain impurities occasionally occur with natural β-HH as well as FGD β-HH. However, the impurities, like limestone or dolomite, in the FGD β-HH are generally inert and harmless. To test the robustness of the PCE, the presence of a detrimental impurity, such as swelling clays, is required. Natural β-HH may contain swelling clays up to 5% as a detrimental impurity depending on the source location of the quarry or mine.

To analyze the robustness of the synthetized PCEs, two model systems were defined: (1) pure natural β-HH system and (2) natural β-HH + 1 wt% bentonite system. The investigation started with pure natural β-HH systems to optimize the polymer structure. Afterwards, the polymers were tested in β-HH + 1 wt% bentonite systems.

5.2 Influence of the PCE Structure

PCEs are characterized by an adsorbing backbone unit and side chains that provide the dispersing power. PCEs are widely used owing to their versatility: the backbone, the number and the length of side chains are flexible parameters. Differences in superplasticizer architecture produce different results on adsorption and rheological properties. The gypsum particle affords a direct adsorption of the negatively charged backbone of PCE on its surface, leading to a stronger adhesion [99]. The attachment of the backbone to the particle surface guarantees the presence of the repulsion forces due to the side chains effect [111].

As stated before, superplasticizers are known for their mode of action: they only work when they are adsorbed on the surface of the binder [99, 112]. The suspension could be pictured as a bulk composed by dispersed particles, some of which had adsorbed PCE coating their whole surface, others partially covered and others are not; leading to a system in which the origin of the repulsion forces is different from particle to particle. In a colloidal suspension, PCEs are preferably adsorbed on positively charged particles and with their side chains they avoid positive-negative particle aggregation. Some authors believe that in cement, when particles do not adsorb superplasticizers, the electrostatic interaction becomes dominant, while in other cases it is supplemented by steric repulsion [99, 113]. When PCE is adsorbed at the solid–liquid interface in a particle suspension, it induces a repulsive interparticle force that avoids the formation of agglomerates. Adsorption analysis is necessary to quantify the amount of molecules effectively adhering to the colloidal particles.

When the solution contains superplasticizers, the main forces interacting in the mix are van der Walls attraction, steric repulsion, and electrostatic interaction. To maintain electroneutrality, an equal number of ions with the opposite charge will surround the particles and give rise to overall charge-neutral double layers [114]. The electrostatic force arises because the particle surfaces are charged at the liquid-solid interfaces. It is a mutual repulsive force between the double layers surrounding the particles that stabilize the system. The factors that induce the electrostatic repulsion are: (1) the solvent properties, such as ionic strength, pH and dielectric constant; and (2) particle properties, such as surface charge density, acid-base chemistry of charge groups, adsorption capacity of the surface and shape, size and surface roughness. The electrostatic forces are only present when charged particles are interacting through a polar medium, such as water [115].

The steric hindrance is a repulsive force that stabilizes the system and the main force the PCE effect is based on. The steric interaction is given by the brush formed by the side chains of adsorbed PCE on each gypsum particle. The steric hindrance is achieved by attaching, grafting or chemisorption superplasticizers to the surfaces of the particles [115]. The factors involved are: grafting density, molecular weight and side chain length of the polymer. The steric hindrance parameter is a conformational property of a polymer side chain which reduces or suppresses otherwise attractive interparticle van der Waals forces or ion correlation forces. The steric repulsion is a result of the adsorption of the admixture onto the particle surface, which acts as physical barrier that inhibits particle-particle interactions and enhances particle-particle repulsion leading to increased fluidity [116-119].

In this study, the adsorption characteristics of various comb dispersants containing different polymer structures on surfaces of gypsum particles were investigated. The effect of the structure on their adsorption was also examined in order to elucidate their adsorption mechanism. A detailed analysis is presented regarding the dispersion forces owed to each type of PCE. The parameters compared among the plasticizers led to differences between each sample. Plank et al. mention the influence of different polymer architectures and their interaction on different cement systems [29]. Similar to cementitious systems, changes in the PCE architecture influence its dispersion ability, resulting in different performance behavior. In order to focus on the effect of each PCE on each gypsum type, the results were distributed on three cases: side chain length, backbone structure and C:E ratio.

5.2.A Dispersing effect of different PCE structures

The slump response of the slurry depending on different polymer architectures, first and second series, is shown in Figure 5-6. It is evident that, in most cases, a higher dosage of PCE provides more effective performance properties of the gypsum mix. However, same dosages of polymers show differences in slump performance. Polymers with the same backbone, i.e., MAS 1, MAS 3 and MAS 6, at a dosage of 0.5% PCE show different dispersing power: MAS 1, 150mm; MAS 3, 190 mm; and MAS 6, 200mm. MAS 1, MAS 3 and MAS 6 have a pure methacrylic acid backbone, but they are differentiated by the acid/ester ratio (C:E). MAS 1 has a C:E=1, MAS 3 has a C:E=3 and MAS 6 has a C:E=6. The acid/ester ratio determines the side chain density of the polymer and the side chain density regulates the steric hindrance of the polymers. This structural modification allows the polymer to different behavior even with the same backbone. By increasing the C:E ratio the dispersing power of the PCE increases.

Differences in the dispersing power are also observed when the two backbones are compared at the same PCE dosage. In Figure 5-6, at a 0.5% PCE dosage, a MIX backbone showed a higher workability than the MAS backbone: MAS 1, 150mm and MIX 1, 180mm; MAS 3, 190mm and MIX 3, 215mm; and MAS 6, 200 and MIX 6, 215mm. It is evident that any change in the PCE structure will change the PCE behavior in the slurry.

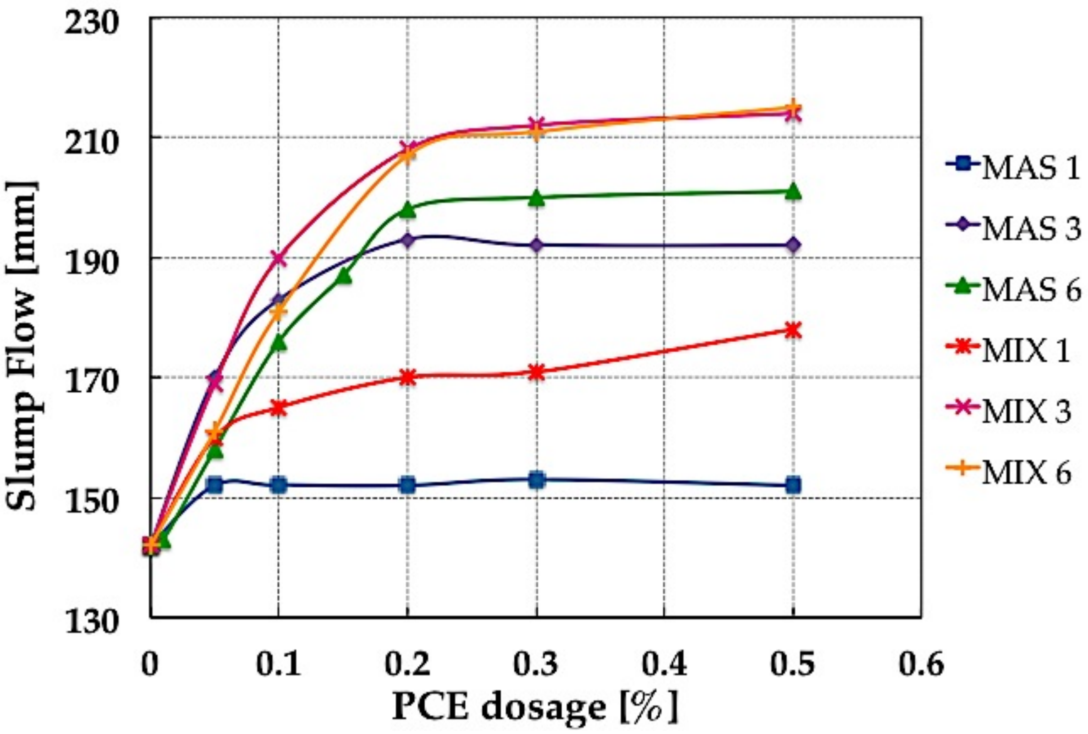


Figure 5-6 Slump response from different polymer architectures

The number of carboxylic groups (COOH-amount) in the polymers is an important factor to fully understand the behavior of the different polymers with the same backbone and different C:E ratios. From Figure 5-6, it is possible to observe that both polymers, MAS 1 (blue) and MAS 6 (green), reach saturation at different polymer dosages. For instance, MAS 1 reaches saturation at an early stage with 0.05% PCE dosage at a 152 mm slump, while MAS 6 reaches saturation with 0.20% PCE dosage at a 200 mm slump. The steric hindrance in MAS 1 is much higher than the one from MAS 6. MAS 1 contains an equal number of COOH groups and side chains (C:E 1 = C:E 6/6), while MAS 6 contains one side chain per six COOH groups (C:E 6 = C:E 6/1). The steric hindrance resulting from the high side chain density of MAS 1 results in a low adsorption of the polymer in the gypsum particle. Further PCE molecules cannot be adsorb on the surface because of the steric force from the molecules adsorbed, not allowing them to adsorb on the surface. Once there are few molecules adsorbed, the dispersion power of the polymer is minimal. This indicates that increasing the C:E ratio will result in an increase on the polymer adsorption and therefore a increase on the dispersing power of the polymer.

To investigate the PCEs tested in this study, the number of COOH groups in mmol per gram polymer was calculated as shown in Figure 5-7 and the number of COOH groups contained by the first and second series of the synthetized PCEs is shown in Table 5-1. The number of COOH groups varies depending upon the side chain density of each polymer (C:E), the lower the steric effect, the higher the number of COOH groups. In order to control the adsorption behavior of the PCEs, the number of COOH groups and steric effect can be varied by increasing or decreasing the C:E ratio. It is believed that polymers with a higher amount of COOH would adsorb better on the particles than the polymers with a lower amount of COOH [99].

$$COOH_{amount}\frac{mmol}{g}=1000*\frac{nCOOH_{mol}}{mPolymer_{g}}=1000*\frac{mAcid}{m(Ester+Acid)}*MAcid$$

Figure 5-7 Calculation of the COOH-amount in PCEs

Table 5-1 Number of COOH groups in mmol per gram PCE polymer

Polymer	COOH*	Polymer	COOH*
MAS 1	0.498	MIX 1	0.499
MAS 3	1.360	MIX 3	1.477
MAS 6	2.512	MIX 6	2.822

**mmol/g polymer*

To observe the influence of adsorption on slump performance, the number of COOH groups for different polymer dosages per 100g of stucco was calculated as shown in Figure 5-8.

$$\frac{Added\ COOH\ mmol}{100\ g\ gypsum}=\frac{Dosage\ polymer\ g}{100\ g\ gypsum}\times COOH\ amount\ mmol/g$$

Figure 5-8 Method of calculation of the number of COOH groups for different PCE dosages per 100g of stucco

Figure 5-9 displays the graphs standardized with the PCE dosage by COOH amount. The results show that the workability of comb polymer dispersants on gypsum conforms approximately to LANGMUIR´s adsorption isotherm. The information suggests that the adsorption of PCEs is dominated by the electrostatic interaction between the COO-groups on the comb polymers and the positive surface of the gypsum. One layer of PCE covers the positively charged surfaces of hemihydrate particles thru the negatively charged COO-groups, resulting in repulsion between the hemihydrate particles with adsorbed polymer. In Figure 5-6, the slump performance is dependent on the PCE dosage added, the behavior of the PCEs on each gypsum type is observed, although the data cannot be compared directly as each polymer has different acid content. On the other hand, Figure 5-9 represents the performance on basis of the COOH amount added and a direct comparison of the behavior can be made.

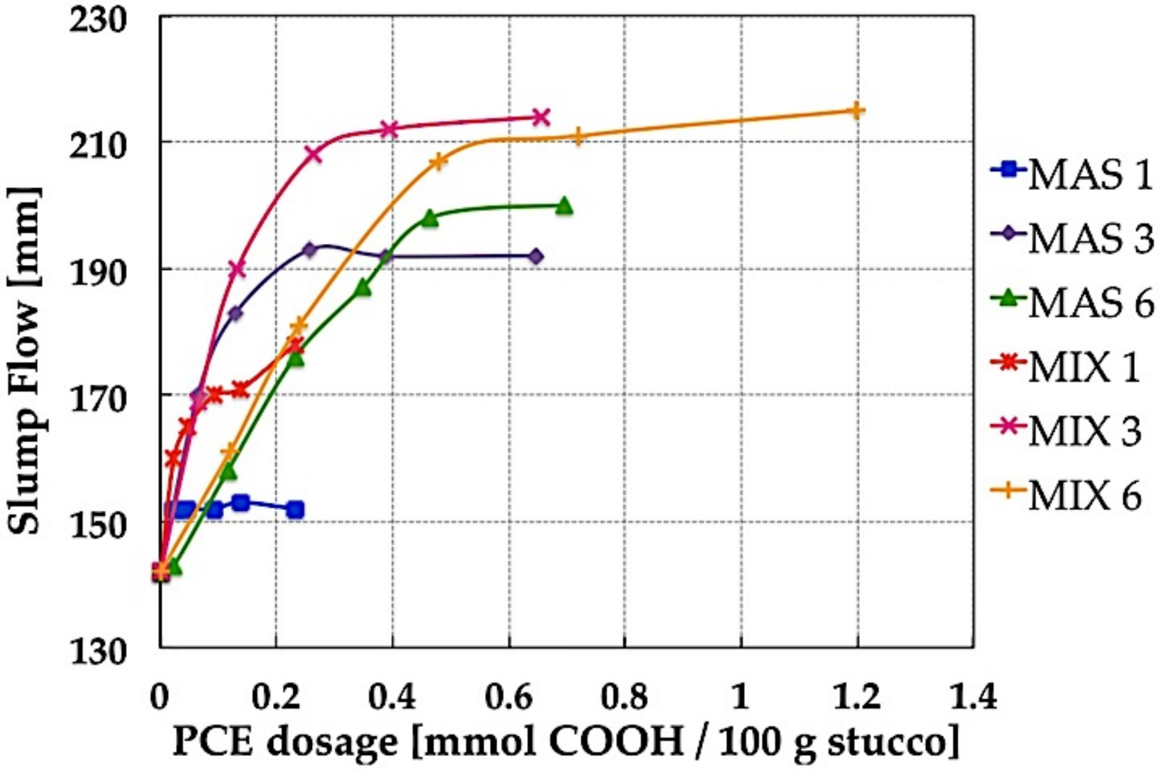


Figure 5-9 PCE dosage (COOH) vs. Slump Flow

Indeed, the quantity of PCE adsorbed on the particle, allows detecting how effective the interaction between PCE molecules and the gypsum particles is. The variable parameters, such as backbone type, carboxylic groups, side chain length and density, have a strong influence on the PCE adsorption, slurry dispersing power and rheology. The dispersive inter-particle forces, electrostatic interaction and steric hindrance avoid the formation of agglomerates. The stability of the particles in suspension and the rheology of the slurry are affected by these forces.

The workability of a liquid-solid suspension is usually characterized by detecting its rheological properties. The shear stress and viscosity are two parameters to describe the fluid internal resistance to flow and the changes presented when the PCE is added. In solid-liquid suspensions, the particles that are in contact with each other create a *weak* solid structure that, in order to flow, needs to be broken. This effect is described as Bingham model [118, 120, 121].

Rheological tests were carried out to observe the effect of superplasticizers on the workability of the gypsum slurry. The results indicate that the PCE reduces the viscosity of the slurry, resulting in good flowability. From the results obtained, it is known that a higher dosage of PCE will improve the rheological properties of the slurry. When the PCE dosage increases, it reduces the shear stress improving the rheological properties of the suspension. As a larger amount of molecules are adsorbed by the gypsum particles, the shear stress is reduced due to the improvement of the flowability of the slurry.

However, when exceeding a certain PCE dosage, the difference on the flowability will not be evident anymore. This approach may be used for the estimation of the saturation point. From this observation, the saturation point was defined as the point where a further addition of plasticizer will not improve the slump flow; neither an increase on the polymer adsorption would be detectable. Despite the effect of the dispersion forces, steric and electrostatic, when the saturation point is reached, the workability will not improve. According to Ferrari, the same behavior is presented in cement pastes when a larger amount of particles is covered by the PCE and this fact may challenge more PCE to be adsorbed [122].

To demonstrate the growth of the polymer saturation, rheological measurements for hemihydrate systems were carried out. The results relay on several rheological properties that can be measured, such as shear stress, viscosity or thixotropic phenomena. The rheometer provided a deeper analysis of the workability behavior of the slurry. Rheological measurements yield direct information on the evolution of the slurry behavior and the performance of HH-PCEs combinations. Figure 5-10 provides the correlation between experimental data from the evolution of the slump flow and shear stress as a function of the polymer dosage.

The shear stress is present when a fluid is in motion. The shear stress, or tangential stress, is a pair of forces applied in opposite directions but in a sliding technique. In response to the shear stress, a material deforms [123]. The changes of the shear stress are associated by the modifications in the slurry induced by the superplasticizer. The shear stress provides information about the viscosity of the slurry. More precisely, each polymer dosage reduces the shear stress until it reaches saturation. The maximum value for shear stress corresponds to the slurry with no superplasticizer added, as the plasticizer is added, the dispersion forces start changing the behavior of it and the workability is increased.

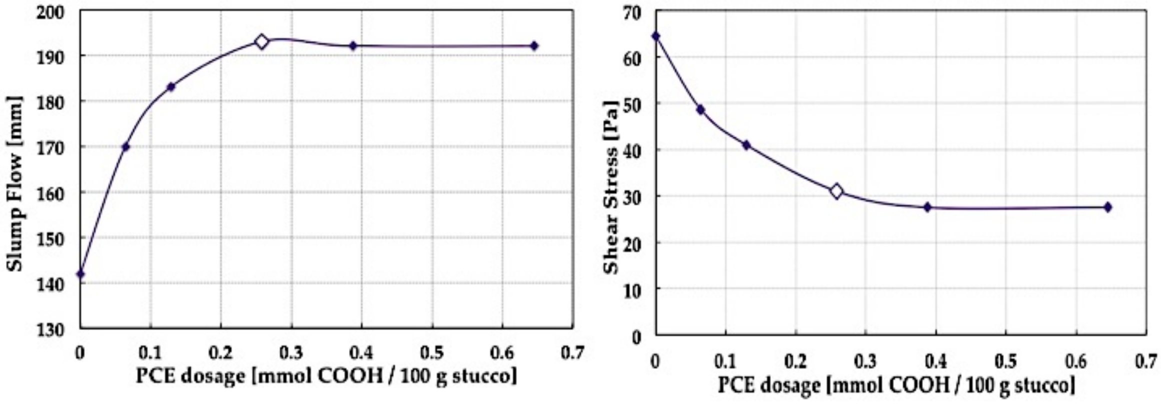


Figure 5-10 Evolution of the slump flow (left) and viscosity (right) as a function of MAS 3 concentration

The highest dosage of polymer tested (0.65 mmol COOH per 100g of stucco), resulted in segregation of HH significative of an over-dosage. The differences between the shear stress are not that significant and the values are similar. This fact is well witnessed by the decrease of the shear rate as a converge towards a limit value (27 PA) is reached up to a dosage of 0.30 mmol COOH per 100g of stucco and that further addition of this PCE would not drop the value anymore. This fully correlates with the slump flow development as it reaches it maximum value at the same dosage. The evolution of the yield stress as a function of plasticizer concentration is a critical issue for the stability of the HH slurry. Only a small concentration range will allow the admixture to fully adsorb and apply the dispersion forces properly: a low shear stress, high dosage, would lead to sedimentation, segregation and bleeding, where as a high yield stress, low concentration, will not allow the proper flow of the slurry [124]. In Figure 5-10 the ideal PCE concentration would be 0.25 mmol COOH per 100g of stucco, right before the slurry reaches saturation (indicated with the hollow point in the graph).

5.2.B Influence of the side chain length

One of the main advantages of PCEs is the flexibility of the design of its structure. The structure can be tailored to fit the technical requirements needed for the application in the market. The length of the side chains is one of the parameters that can be modified to a certain extent. The side chain length is a key parameter that controls the development of the dispersion forces, mainly steric stabilization, on the slurry. The structural characteristic of PCE is an anionic polymer backbone, with expanded lateral graft chains at periodical intervals. These side chains instigate a steric hindrance effect between the hemihydrate particles suspended in water and enable the PCE superplasticizers to exhibit dispersing force comparable to other admixtures.

Three different series of polycarboxylate-based superplasticizers were analyzed in this study. The first and second series of PCEs were synthesized with methoxypoly(ethylene glycol) 2000 methacrylate *(MPEG2000MA, 2000 g/mol)*; the third series was synthetized with hydroxypropyl methacrylate *(HPMA, 59 g/mol)*. Figure 5-11 compares the workability behavior of MAS 3 and MAS short 3. Both polymers have the same backbone and the same side chain density but are different in side chain length.

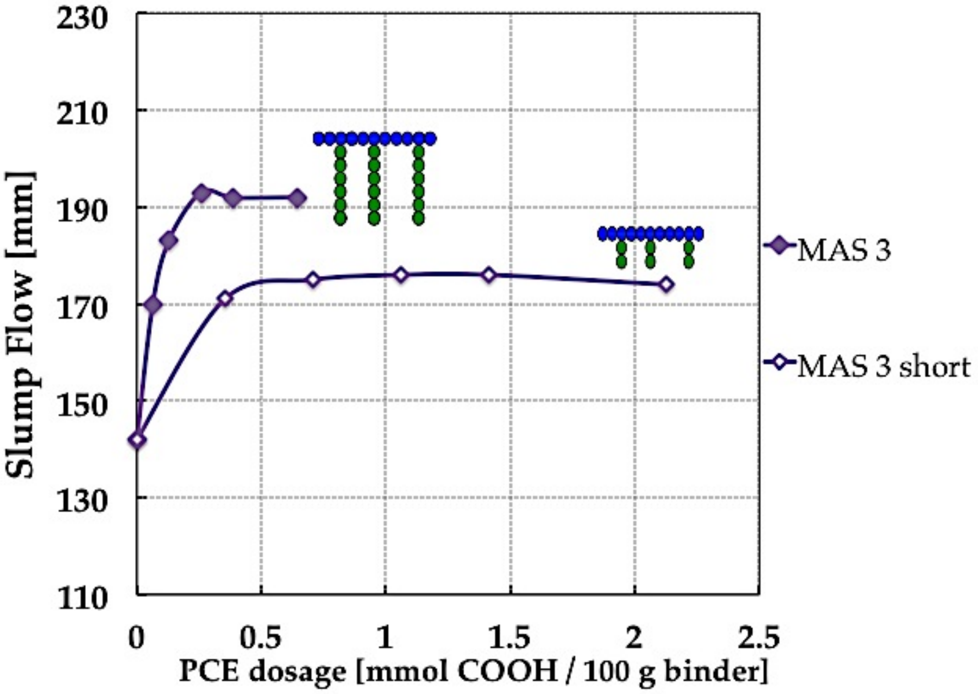


Figure 5-11 Influence of the side chain lenght on the workability

As shown in Figure 5-11, the influence of the side chain length is evident. MAS 3 has a stronger dispersing power in the slurry than MAS short 3. The length of the side chain has a direct influence on the steric hindrance of the molecule. MAS 3 has side chains with molecular weight of 2000 g/mol and MAS short 3 with 59 g/mol. The length of the side chain of MAS short 3 is 97% smaller than MAS 3. The reduction of the length of the side chain decreases the PCE's dispersing power. The molecules of MAS 3 interact with the HH particles and due to their high steric hindrance, reach a high slump flow at low PCE dosages: 0.25 mmol of COOH per 100g stucco result in a 192 mm. With higher dosages, the slurry is saturated and the slump performance remains the same. In the same dosage range, MAS short 3 has a 160 mm slump, resulting in a decrease of the dispersing power (17%). The dosage of MAS short 3 was increased to reach a maximum value of 174 mm at a 0.5 mmol of COOH. Even though the polymer dosage was increased, the slurry did not show a higher flowability. The research indicates that a longer side chain is vital for higher workability, as the steric hindrance force would be stronger than with a polymer with shorter side chains.

5.2.C Influence of the backbone

In the wallboard production, two main important factors have to be considered: the flowability and quick setting and hardening of the slurry. These aspects fully depend on the polymer structure and its adsorption on the gypsum particles.

The flowability of the slurry relays on the electrostatic and steric dispersion forces, which are also influenced by the backbone structure. In the three gypsum types, the results expose a high influence of the backbone structure on the performance of the PCEs on the gypsum tested. As observed in Table 5-2, when comparing the backbone chemistry, the ones with a MIX backbone display a higher saturation point than the ones with pure methacrylic acid backbone. The addition of the acrylic acid demonstrated a strong potential to improve the fluidity.

Table 5-2 Maximum slump reached at saturation

Sample	MAS 1	MAS 3	MAS 6	MIX 1	MIX 3	MIX 6
Turkey Natural β – Hemihydrate	152	192	200	178	214	215
Lippendorf FGD β – Hemihydrate	154	185	190	175	201	209
Niederauβem α - Hemihydrate	160	205	219	189	220	245

**mm*

The difference between the two backbones is explained by the addition of the acrylic acid, which increases the steric hindrance on the molecule [125, 126]. The interaction of the PCEs with pure methacrylic acid backbone and the hemihydrate is weaker in comparison with the MIX backbone. The action mechanism of the acrylic acid is based on the admixture's carboxylic acid group, which is strongly hydrophilic, and, as in cementitious systems, enables dissolution of polymers in water and their adsorption on the surface of the gypsum particles [127]. It is known that the increment of carboxyl groups in the molecular structure increases the adsorption anchorage between superplasticizers and gypsum particles [128]. The polymers with a MIX backbone contain a higher amount of carboxyl groups than the ones with MAS backbone, leading to an increase in the polymer adsorption.

The research states that copolymers containing a methacrylic and acrylic acid backbone have a better dispersing ability than the ones with pure methacrylic acid backbone. Figure 5-12 provides a schematic illustration of the mechanism of adsorption of a PCE with pure methacrylic acid backbone (*MAS 3, COOH amount = 1.360 mmol/g polymer*) and a PCE with a mix backbone, acrylic and methacrylic acid (*MIX 3, COOH amount = 1.477 mmol/g*). In the diagram, it is possible to observe the differences of the adsorption behavior of the these two PCEs with the same C:E ratio. MIX 3 has a better dispersion power than MAS 3. Both reach a maximal slump at a dosage of 0.30 mmol COOH, however MAS 3 has a 10% reduction on the dispersing power compared with MIX 3.

In the structure of MAS 3, the methacrylic acid shows a more rigid structure than the backbone containing acrylic acid. The methyl group in the methacrylic acid prevents further adsorption of PCE molecules by increasing the steric hindrance.

The acrylic acid increases the flexibility of the molecule by the formation of hydrogen-bonding groups, decreasing the steric hindrance. As a result, more PCE is adsorbed [129, 130]. The increase of PCE molecules adsorbed results in a better dispersion power of the slurry. The positive behavior of the MIX backbone maintains being robust in the three gypsum types.

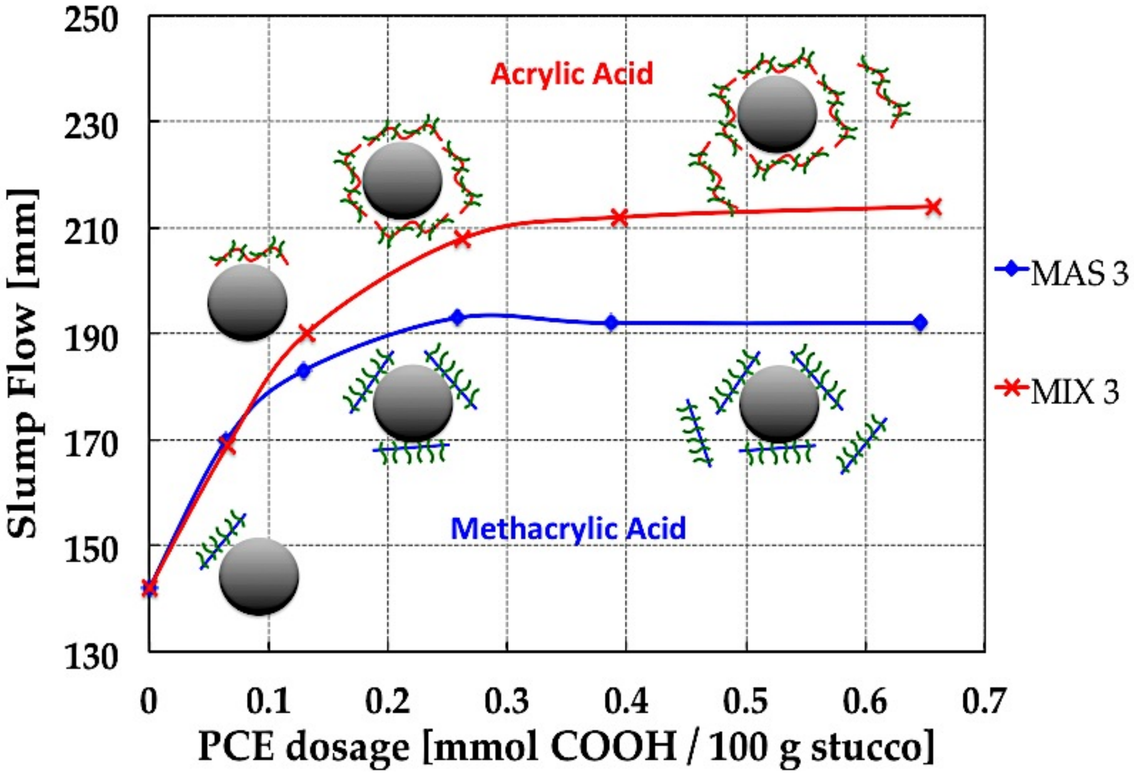


Figure 5-12 Adsorption mechanism of MAS backbone (blue) and MIX backbone (red)

According to the flowability results, a polymer with a MIX backbone will lead to a higher dispersing power. The second important factor to consider, the setting and hardening of the slurry are also of crucial importance to run the wallboard production at a high speed for maximum capacity utilization. A polymer that delays the hardening of the slurry will reduce the speed of the wallboard forming line and decrease the productivity of the plant.

The comparison between the initial setting of MAS 6 and MIX 6 is shown in Figure 5-13. The influence of the PCE adsorbed is evident on the setting times as it increases when more PCE is adsorbed. MAS 6 adsorbs the polymer up to 0.35 mmol carboxyl groups and its longest setting is 25 minutes. MIX 6, in the same dosage delays the hardening to 55 minutes. The PCEs with a MIX backbone, compared with pure methacrylic acid backbones, increase the setting times in the slurry to a higher extent. If the initial setting times were increased to that extent, the slurry would not meet the requirements of the wallboard production. Therefore, for technical requirements, a MAS backbone is defined to fit the manufacture specifications.

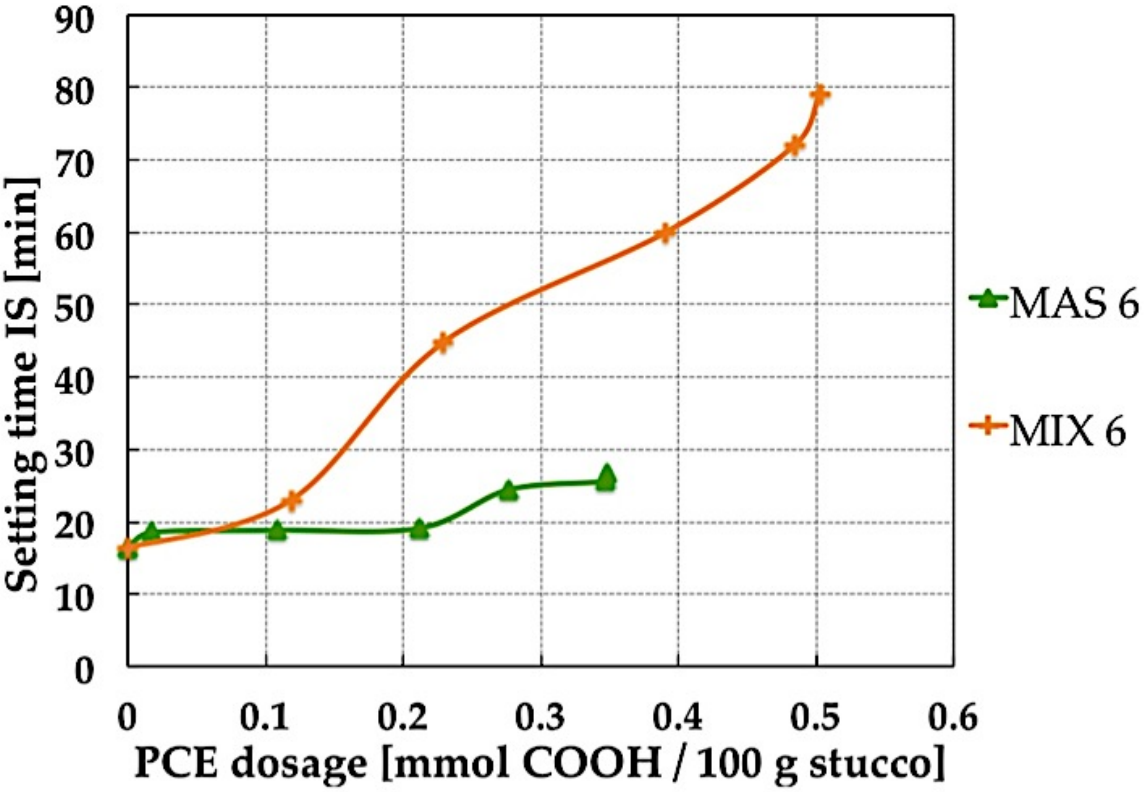


Figure 5-13 Influence of the backbone on the setting time

5.2.D Influence of the C:E ratio

Aforementioned, the backbone of a PCE is dependent on MW of the polyacrylic acid by copolymerization and the side chain length by the number of ethylene glycol repeating units in the ester. The difference in molar ratio between the backbone and the side chains can be regulated by the concentration of monomers, methacrylic acid (MAS), acrylic acid (AS), methoxypoly(ethylene glycol) 2000 methacrylate (MPEG2000MA) and hydroxypropyl methacrylat (HPMA), added from the onset of the synthesis (C:E ratio). Three different concentrations were designed to enhance the performance of the PCEs: 1, 3 and 6.

The C:E ratio plays an important role in the adsorption of the PCEs. The results obtained from the adsorption analysis of the PCEs of the first and second series can be seen as comparison in Figure 5-14. The results suggest a tendency of the PCEs with C:E 1 (MAS 1 & MIX 1) as being the ones with the weakest performance overall. Despite the further addition of PCE, the workability was not improved. On the other hand, the C:E 6 in MAS 6 and MIX 6, led to the highest saturation point. The higher the C:E ratio, the slump flow and the saturation will show a positive increase.

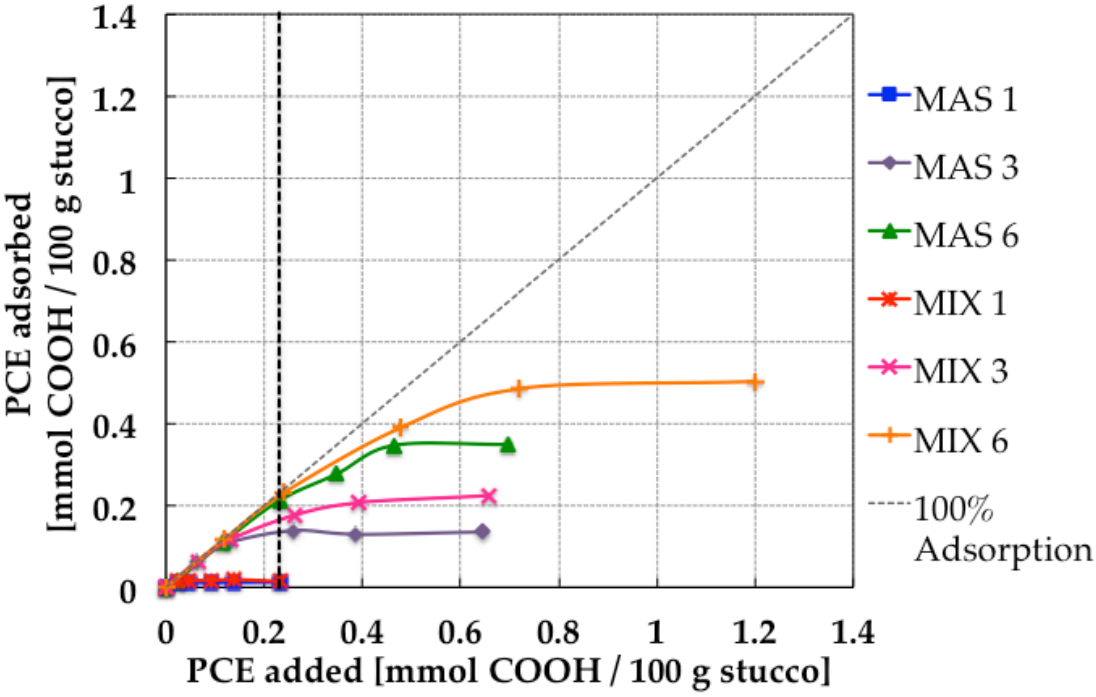


Figure 5-14 Influence of the C:E on the PCE adsorption on natural β-HH

In the three gypsum types, natural β-HH, FGD β-HH and α-HH, the PCEs with the lowest C:E ratio, present the lowest saturation point and a low workability. As observed in Table 5-3, the PCEs with C:E 6 had the highest adsorption in the three gypsum types. For instance, MIX 6 at a 0.23 mmol of COOH per 100g stucco added is fully adsorbed (100%) by the natural and FGD β-HH, on the other hand MIX 6 is 50% adsorbed by the α-HH. As mentioned before, the β-HHs have a higher surface area of the powder than the α-HH, the increase of the surface area allows more polymer to be adsorbed by the HH particles.

Table 5-3 Adsorption of COOH vs. type of gypsum

Sample	MAS 1	MAS 3	MAS 6	MIX 1	MIX 3	MIX 6
Turkey Natural β – Hemihydrate	0.021*	0.131	0.230	0.020	0.176	0.230
Lippendorf FGD β – Hemihydrate	0.011	0.093	0.230	0.018	0.133	0.201
Niederauβem α - Hemihydrate	0.003	0.041	0.092	0.003	0.046	0.103

**Starting concentration of 0.23 mmol COOH/100 g gypsum*

When comparing the evolution of the slump flow of MIX 3 and MIX 6 in Figure 5-15, the results indicate that with the same amount of polymer added, there is a drastic difference in the slump flow. At 0.3 mmol of carboxyl group added, the slump performance of *MIX 3* is higher than *MIX 6* (210 mm and 188mm, respectively). Interestingly, the explanation behind is the amount of carboxyl groups added and the side chains per carboxyl group added (steric hindrance). At 0.3 mmol of carboxyl group from *MIX 3*, would correspond a 0.10 mmol of side chains added; on the other hand, the same amount of carboxyl group added from *MIX 6*, would correspond to a 0.05 mmol of side chains per carboxyl group added. According to the tendencies shown in Table 5-4, the increase of the amount of side chains per carboxyl group added would improve the slump performance as a result of the steric hindrance. Also, it is evident that by adding the same amount of side chains per carboxyl group, it is possible to obtain the same slump performance.

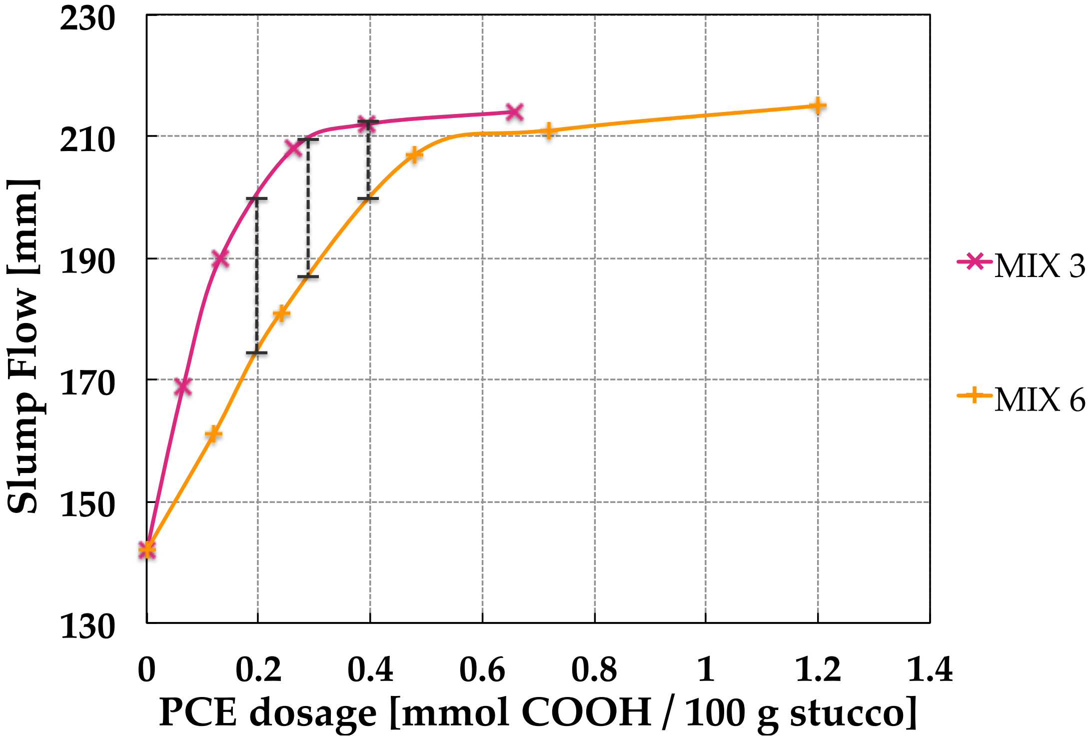


Figure 5-15 Differences in the dispersing efficiency of MIX 3 and MIX 6 in natural β-HH

Table 5-4 Influence of the side chains per carboxyl group added on the slump flow in natural β-HH

COOH added*	Side chains per COOH added*		Slump**	
	MIX 3	MIX 6	MIX 3	MIX 6
0.20	**0.07**	0.03	**200**	175
0.30	0.10	0.05	210	188
0.40	0.13	**0.07**	213	**199**

*mmol/100g HH, **mm *derived by interpolation*

Turning to the adsorption experimental data, the results express a higher polymer adsorption rate by molecules with higher C:E ratio (MIX 6). Figure 5-16 and Table 5-5 compare the adsorption characteristics between MIX 3 and MIX 6. The results indicate that when there is a higher amount of steric hindrance in the PCE, the adsorption of the polymer will decrease. The higher amount of side chains per carboxyl group is the result of a higher density of side chains in the polymer, which leads to an increase of the steric hindrance.

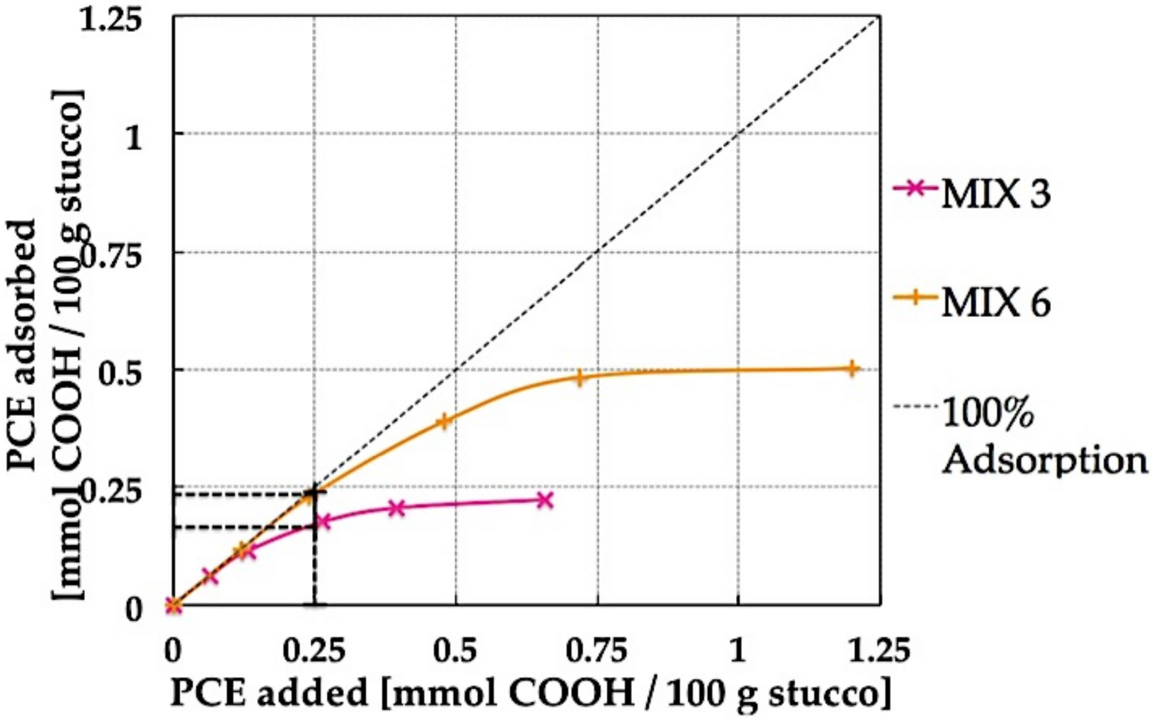


Figure 5-16 Differences in the adsorption of MIX 3 and MIX 6

Table 5-5 Influence of the side chains per carboxyl group added on the PCE adsorption in natural β-HH

0.3 COOH added*	MIX 3	MIX 6
COOH adsorbed*	**0.19**	**0.29**
% COOH adsorbed	63%	99%
Side chains per COOH adsorbed*	**0.063**	**0.048**

*mmol/100g HH

Figure 5-17 describes the differences between the adsorption of MIX 3 and MIX 6 due to the steric hindrance of the PCEs. Starting with 0.3 mmol of COOH added per 100g of stucco, it is possible to observe that the structure of MIX 6 allows a full adsorption of the polymer, when MIX 3 allows only 63%. In this schematic representation, the influence of the side chains is evident: more side chains (MIX 3) will increase the steric hindrance of the polymer, and when another PCE molecule gets closer to the gypsum particle, this will not be adsorbed even if the particle has sufficient surface for the adsorption of another PCE molecule. The addition of further PCE will not improve the adsorption rates and they will remain in solution. For example, 0.8 COOH mmol per 100g of stucco will result in a 25% adsorption of MIX 3 and a 50% adsorption of MIX 6.

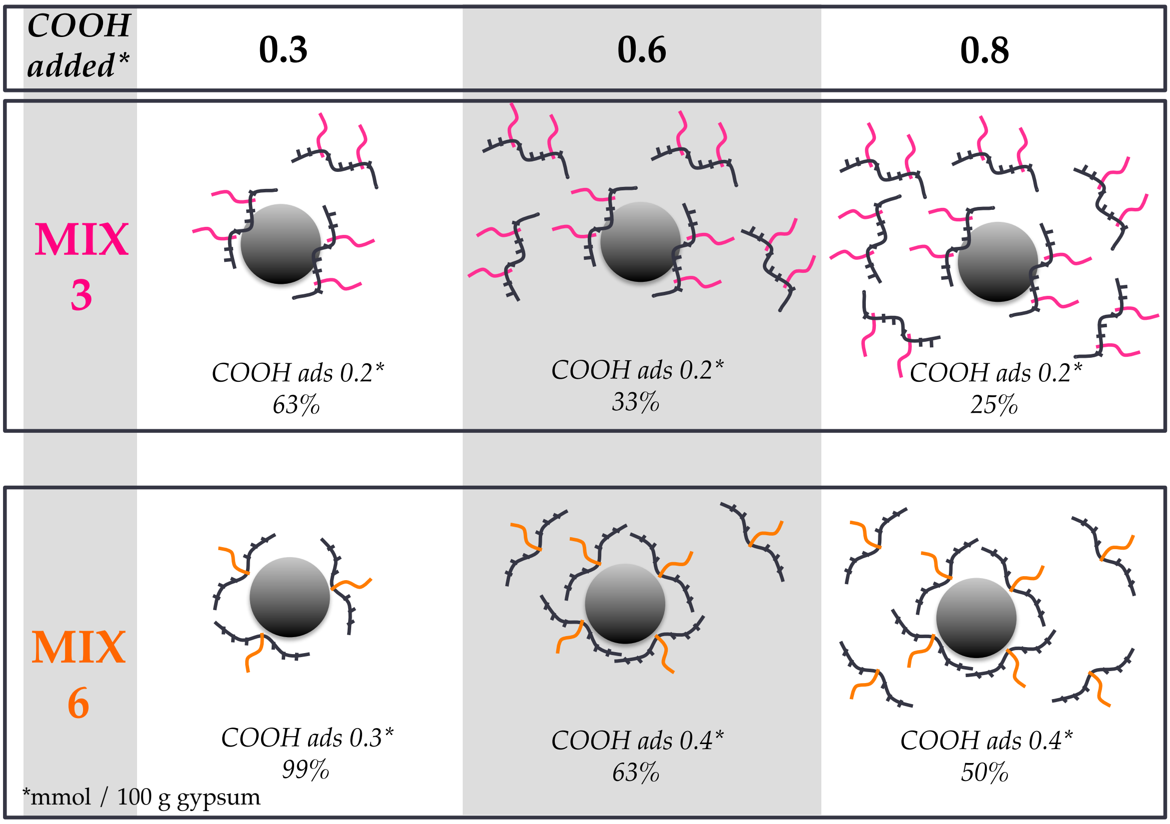


Figure 5-17 Mechanism suggested for the adsorption of MIX 3 and MIX 6

As it can be seen from Figure 5-18, when comparing the slump performance and the carboxylic groups adsorbed of MIX 3 and MIX 6, it is possible to observe that the same slump performance is reached with different amounts of carboxylic groups adsorbed. This behavior corresponds with the amount of side chains per carboxylic group adsorbed. Table 5-6 compares the amount of carboxylic groups adsorbed and the slump of MIX 3 and 6 at a similar slump flow (214 and 215mm, respectively). The different dosages of MIX 3 and MIX 6 contain the same amount of side chains per carboxyl group adsorbed (0.08 mmol); the steric hindrance is similar leading to a comparable dispersion power.

A comparison between the data suggests the idea that the efficiency of the PCE is related to the backbone structure, the length of the side chains and the C:E ratio. As stated before, important changes occur when the acrylic acid is incorporated in the polymer backbone. The acrylic acid has better adsorption and performance in comparison with the pure methacrylic backbone. The drawback of the MIX backbone is the drastic increase on the setting times, which is counterproductive for wallboard production. The length of the side chains is an important factor and needs to be considered, longer side chains would lead to a higher workability in comparison with shorter side chains. The use of a pure methacrylic backbone and a low C:E ratio provides a decrease of the slump performance, which matches the low adsorption of the superplasticizer. In each system, a higher C:E ratio enables stronger adsorption in particle suspensions. Indeed, MAS 1 and MIX 1 afford rather poor adsorption compared to MAS 6 and MIX 6.

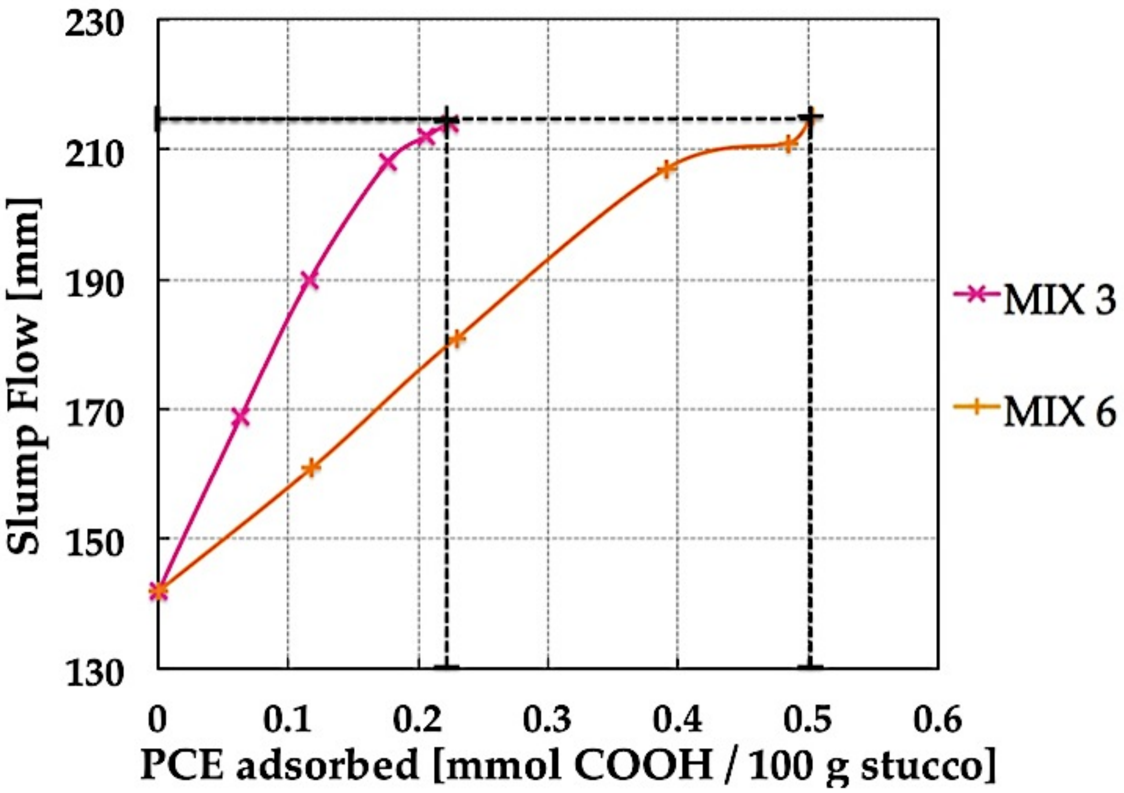


Figure 5-18 Influence of the adsorption of MIX 3 and MIX 6 on the slump performance in natural β-HH

Table 5-6 Influence of the side chains per carboxyl group adsorbed in the slump performance in natural β-HH

PCE	COOH adsorbed*	Side chains per COOH adsorbed*	Slump**
MIX 3	0.22	**0.075**	214
MIX 6	0.51	**0.08**	215

*mmol/100g HH, **mm

The remaining question is how the ideal polymer structure should look like. From the data presented above, the required characteristics for a strong polymer without a dramatic increase on the setting times in the HH system are: long side chains, a lower side chain density (high C:E ratio) and a pure methacrylic acid backbone.

In order to synthetize a more efficient polymer, it is necessary to further analyze the results obtained in more detail. Figure 5-19 compares the influence of the adsorption on the setting times of the polymers from the first and second series. The graph below summarizes the setting times of the slurry and the corresponding polymer adsorption. As mentioned before, a MIX backbone (red circle) increases the adsorption of the PCE and the setting times of the slurry; while PCEs with MAS backbone (black circle) have a minor adsorption and shorter setting times. Also, as stated before, by increasing the C:E, the adsorption will increase. A high polymer adsorption is desired to have a high dispersing power in the slurry. In the first and second series, the polymers with a C:E 1 have the lowest PCE adsorption and the shortest setting times. On the other hand, polymers with C:E 6 have the highest adsorption and longer setting times. The wallboard production requires a polymer that allows a quick setting and hardening. Shorter setting times are due to increase the plant profitability. According to this research, the next polymer should be designed to provide better adsorption rates and shorter setting times, consequently to fit the blue circle in Figure 5-19.

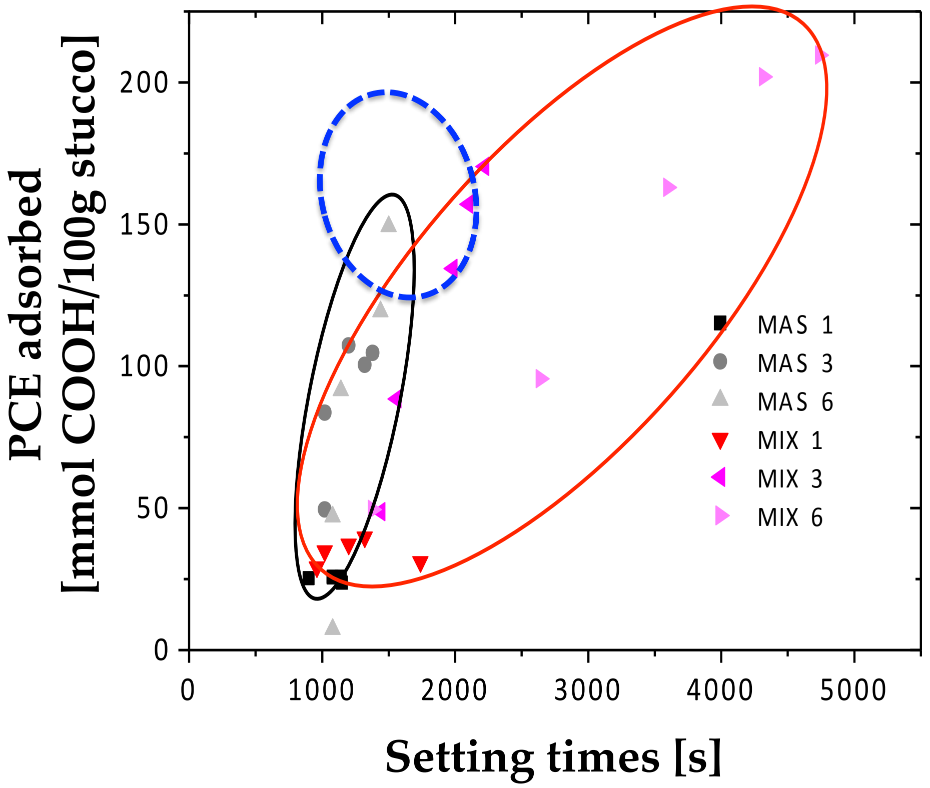


Figure 5-19 Influence of the adsorption on the setting times. MAS series (black circle), MIX series (red circle) and ideal polymer (blue circle).

Based on this hypothesis, MAS 9 was synthetized with a pure methacrylic acid backbone and a C:E 9. MAS 9 contains the highest carboxyl groups of all polymers tested (3.459 mmol/g polymer) and the lowest side chain density (0.384 mmol/g polymer). The low side chain density results in a decrease on the steric hindrance of the molecules allowing more PCE to be adsorbed in the gypsum particles. As analyzed in Figure 5-17, the increase of the C:E will increase the PCE adsorption rate. MAS 9, Figure 5-20 in black, is the polymer that adsorbs the best among all polymers tested in HH systems.

The retardation effect of MAS 9 is compared in Table 5-7. As mentioned in Section 5.2.C, the setting and hardening of the slurry are also of crucial importance to run the wallboard production at a high speed for maximum capacity utilization. Differences in the hardening of the slurry are observed when different PCE structures are compared at the same PCE dosage. It is evident that any change in the PCE structure will change the retardation effect on the slurry. MIX 6 and MAS 9 had the strongest dispersing effect among the polymers tested. However, the retardation of the slurry, up to 85 minutes, will not fit the requirements of quick setting and hardening for the wallboard production. On the other hand, MAS 1 and MIX 1 had quicker setting of the slurry but weaker dispersing power. The use of PCEs with strong dispersing power, the slurry should be enriched with certain additives, such as accelerators, to allow lower drying requirements in the manufacture of wallboard.

Table 5-7 Retardation effect of MAS 9

Dosage / Sample	MAS 1	MAS 3	MAS 6	MIX 1	MIX 3	MIX 6	MAS 9
0.05 %	30*	30	34	30	40	40	43
0.10 %	34	32	35	39	45	66	50
0.20 %	34	35	47	40	53	85	53

**minutes*

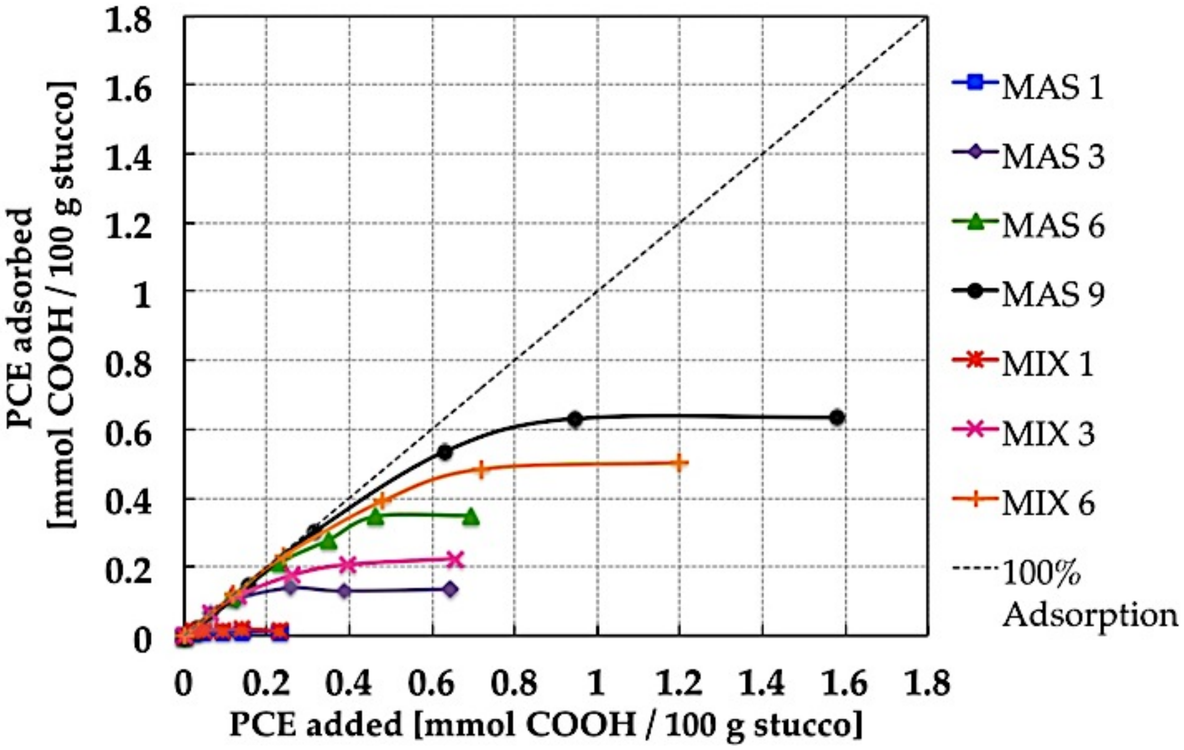


Figure 5-20 Adsorption of MAS 9

The PCE architecture is an important parameter to consider when targeting an improvement in the wallboard production. Synthetizing the ideal PCE is an end-goal to decrease the excess water needed in the manufacture of gypsum boards. As a result, the efficiency in wallboard plants will be increased and the energy costs will be reduced.

Relevant structural parameters influencing the effects of the PCE are the side chain length, the backbone type and the C:E ratio. The adsorption behavior, dispersing power and setting times of the slurry will be modified by the different PCE designs.

Indeed, PCEs with short side chains will not have the same dispersing power than polymers with longer side chains. Research indicates that a longer side chain is vital for higher workability, as the steric hindrance force of the particles with adsorbed PCE would be stronger than with a polymer with shorter side chains. Moreover, the presence of acrylic acid in the MIX backbone will increase the dispersing power in the slurry. A MIX backbone will increase the PCE adsorption on the gypsum particles; however, the acrylic acid in the backbone highly influences the hardening of the slurry. This behavior does not fit the requirements of quick setting and hardening of the wallboard manufacture. Furthermore, the ratio between carboxyl groups and side chains will also influence the steric hindrance of the PCE molecule. A high steric hindrance (low C:E) of the PCE molecules, will not allow the adsorption of further PCE on the gypsum surface. As the carboxyl groups contained in the PCE molecule increase, more PCE is able to adsorb on the surface, thus resulting in an increase of the dispersing power in the slurry. In the pure hemihydrate systems, the performance of MAS 9 correlates with the most suitable structure of the PCE for the wallboard manufacture.

5.3 Influence of bentonite on the System

In the process of wallboard production, swelling clays, as an impurity in stucco, can affect the fluidity of the slurry [69]. In general, admixtures are employed to reduce the excess of water that is required for certain slurry fluidity and to increase productivity. Swelling clays are known to change the properties of the slurry and to decrease the performance of PCEs, when expanding, as they adsorb or entrap the PCEs [131, 132]. There is a possibility to restore the response of the PCEs when clays are presented: by reducing or preventing the clay expansion before the contact with the PCE and/or modifications on the mixing sequence [73, 90]. The construction chemical industry has an increasing interest in developing PCEs possessing enhanced clay tolerance. It is known that one of the biggest compatibility problems between PCEs and natural stucco is intercalation of the PCEs in the interlayer surfaces of the clay [133, 134] and that the intercalation of the PCEs depends greatly on the chemical structure of the PCE [135]. A polymer that would only adsorb on the clay surface would not incorporate into the multi-layer structure of the clay; hence, the swelling clay will not affect the performance [131]. Such optimization of the PCE performance would solve the compatibility problem between certain natural stuccos and comb shaped polymers.

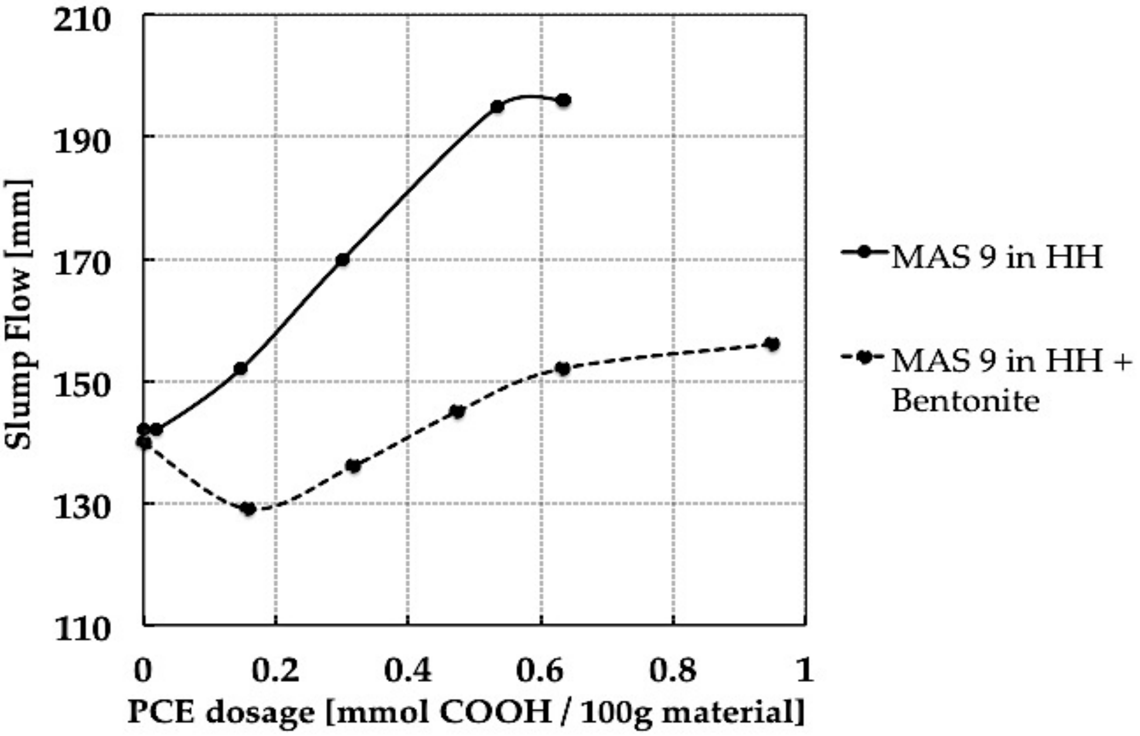


Figure 5-21 Effect of the Bentonite in the behavior of MAS 9

As described in section 5.2, MAS 9 was determined to be the polymer that suits the best the pure hemihydrate system. To prove the robustness of MAS 9, the polymer was tested in the second model system: HH + 1 wt% of bentonite as a contaminant. The results shown in Figure 5-21 show the strong detrimental effect of the presence of bentonite in the slurry. For example, in the pure HH system, at a dosage of 0.5 mmol of COOH per 100 g material, MAS 9 reaches a maximum slump of 195 mm. On the contrary, in the HH-bentonite system, it reaches a maximum of 149 mm. The bentonite reduces the performance by 24%. The improvement of workability by MAS 9 is almost completely suppressed by bentonite. This indicates, as revealed in section 5.1, that when the slurry is contaminated with bentonite, competing demands by HH and bentonite of the PCE can occur, therefore a reduction of dispersion force is evident.

The detrimental behavior of the bentonite in the system can be seen in every polymer from the first and second series. Figure 5-22 shows the impact of the bentonite contaminant on the performance of two different polymers (MAS 3 and MIX 3). Alike previous results, bentonite has a high affinity for PCE and, as expected, bentonite reduces drastically the dispersing performance of the slurry, in both cases by up to 30%. Researchers [136] suggest that PCEs synthetized with longer side chains (first and second series) adsorbed in the clay predominantly via intercalation of the side chains into the interlayer surface of the bentonite structure. The intercalation ability of the side chains is molecular weight dependent; the higher the molecular weight, the more uptake [137, 138].

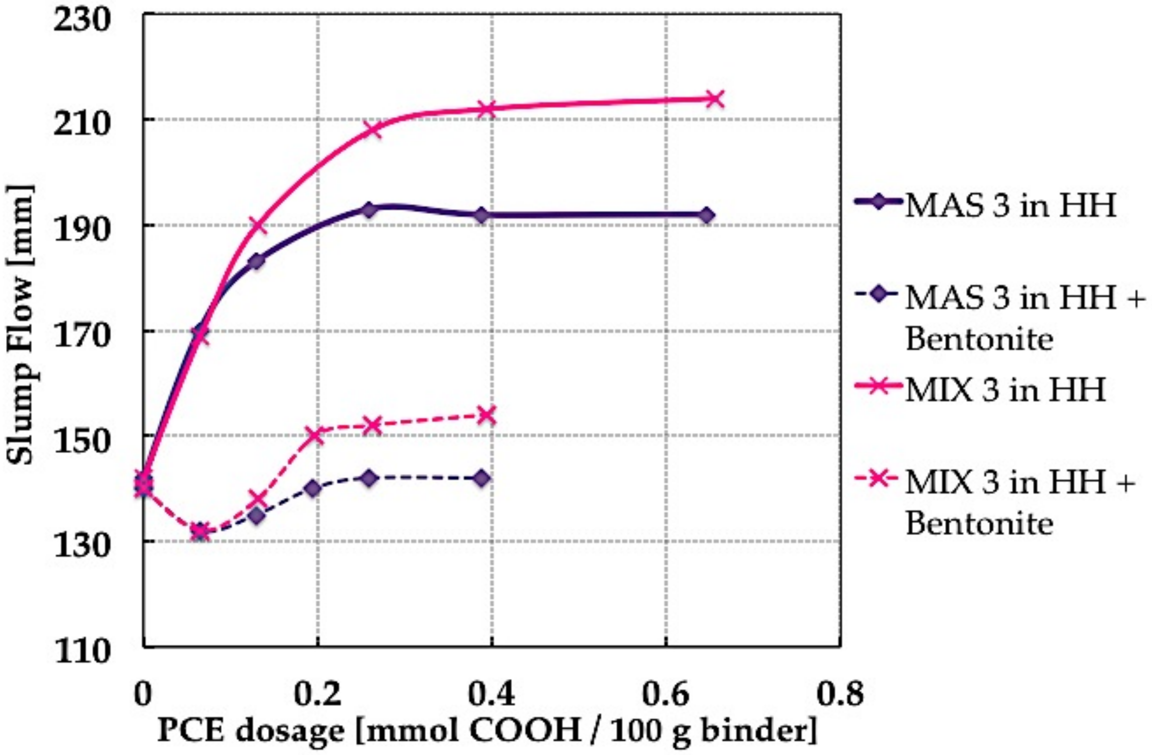


Figure 5-22 Influence of the Bentonite in the HH slurry

In Figure 5-23 a schematic representation of the different mechanisms of adsorption between HH and bentonite is shown. According to Ng and Plank [132], the main driving force behind the decrease on the dispersing power of the PCEs is chemisorption due to the intercalation of the PCE into the multi-layer structure of the bentonite via hydrogen bonding with water. HH particles adsorb the polymer through their surface by electrostatic attraction; however, the multilayered structure of the bentonite allows adsorption on the surface by electrostatic attraction and in-between layers by chemisorption. The existence of PCE in between layers increases the spacing between the bentonite inter-layers, easing water molecules to enter the bentonite structure, and reducing the available water in the slurry. As a result, in lower PCE dosages, the slump performance shows values even lower than the blank samples (Figure 5-22).

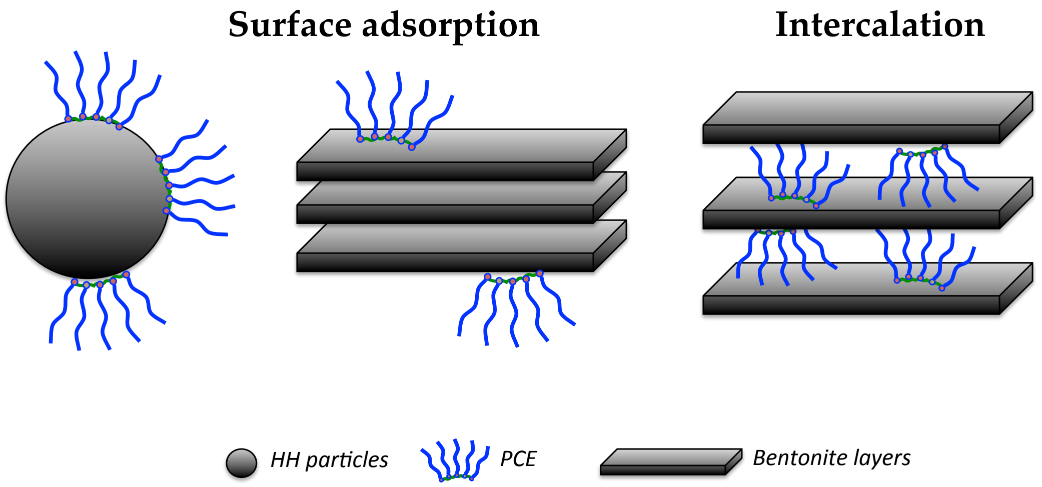


Figure 5-23 Differences on the mechanical mechanism of adsorption between HH particles and Bentonite layers

To better understand the mechanism of action of the PCEs in bentonite, adsorption tests of PCE raw materials, backbone and side chains, were carried out in pure bentonite systems. Figure 5-24 presents the results of the adsorption of pure backbone. It is evident that a pure acrylic acid (AS) backbone has the tendency to adsorb the most compared to a pure methacrylic acid backbone or a mix backbone. The acrylic acid has flexibility properties that allow a higher surface and inter-layered adsorption on the bentonite. Researchers agreed that the gyration radius is one of the main forces that dominate the elasticity of the methacrylic and acrylic acid. The radius of gyration is the distance from the segments of the molecule from its center of mass. The difference between the flexibility of their gyration radius (Rg) is approximately 15 nm (methacrylic acid Rg≈20.5, acrylic acid Rg≈35nm) [139, 140]. Therefore, the interaction of the acrylic acid and the bentonite is increased. MAS and MIX backbones present similar adsorption, however the adsorption of MIX backbone is slightly increased when the polymer dosage is increased. The MIX backbone contains methacrylic and acrylic acid; hence, the acrylic acid contributes to the elastic properties of the backbone allowing a higher adsorption of the backbone as the dosage is increased.

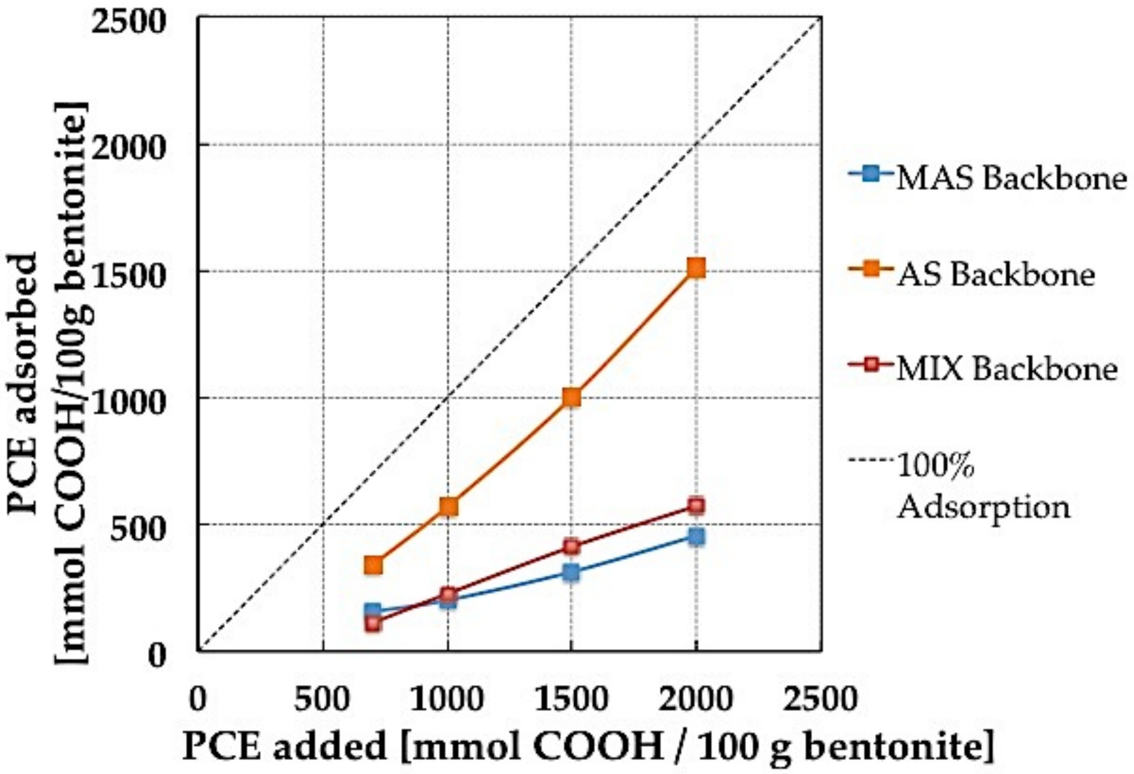


Figure 5-24 Adsorption of pure backbone in Bentonite

As described in section 5.2.B, the PCEs from the first and second series were synthetized with long side chains due to their stronger dispersing power. The results in pure hemihydrate systems showed that shorter side chains in the polymer structure would decrease the dispersing power of the molecule. It is expected that the characteristics of the bentonite structure may affect the adsorption and dispersing performance of the long-side-chain PCEs.

With the purpose of understanding the differences on the adsorption of the side chain length on bentonite, two different side chain lengths were analyzed, using MPEG 2000 and MPEG 350, with side chain length varying from 2000 to 350 g/mol. The results obtained from the adsorption of pure side chains in bentonite can be seen in Figure 5-25. From this data, there is a clear trend of increased PCE adsorption when increasing the side chain length. Interestingly, the longer the side chains are, the higher intercalation is presented. Higher intercalation means higher consumption of polymer by the bentonite structure and a decrease of the dispersion efficiency of the slurry. The results from Figure 5-25 contrast the results from section 5.2.B, where the ideal structure for a polymer in pure natural stucco would be a PCE synthetized with long side chains.

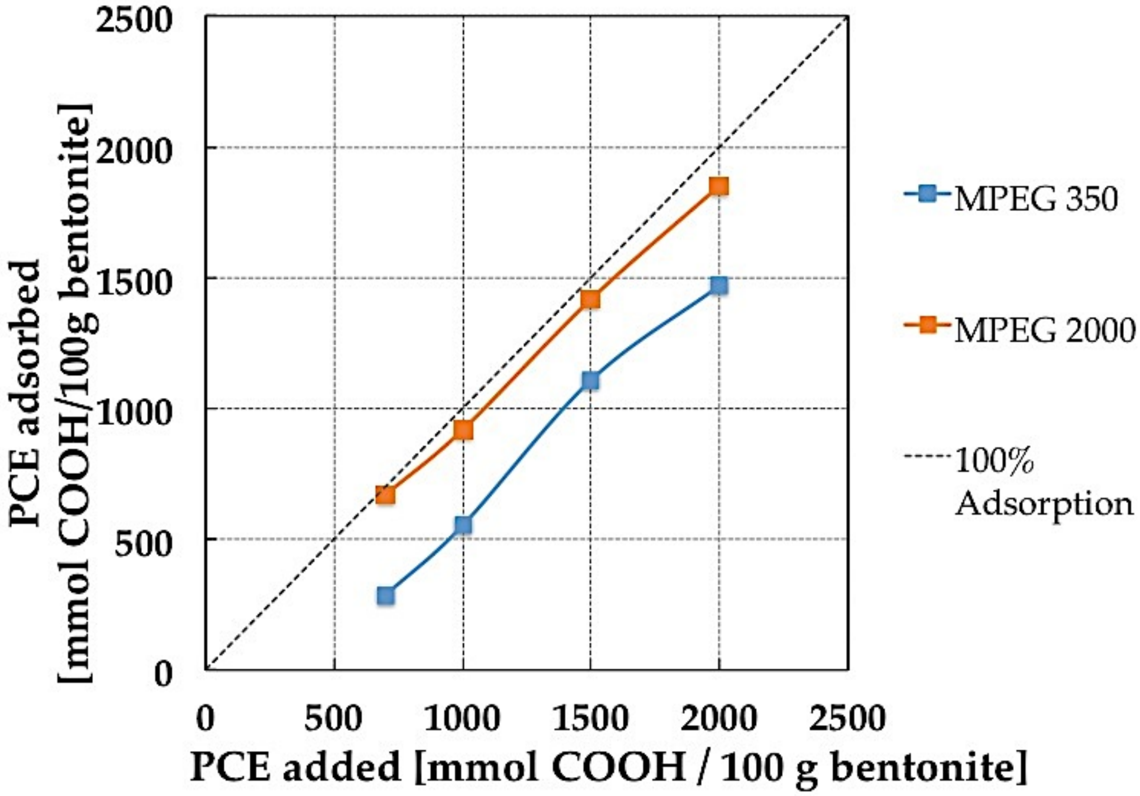


Figure 5-25 Adsorption of pure side chains in Bentonite

According to Ng and Plank, in cementitious systems, the effectiveness of PCEs with longer side chains is more affected than from those with shorter side chains. They suggest that the failure of such PCEs might be correlated to their ease of intercalation [136]. To diminish the problem of intercalation, a third series of polymers was synthetized. MAS 1 short and MAS 3 short, both possess shorter side chains; the length was varied from 2000 to 59 g/mol. The effectiveness of PCEs with shorter side chain is displayed in Figure 5-26.

Due to the high side chain density of MAS 1 (C:E 6/6), the PCE remained adsorbed by the bentonite trough intercalation into the interlayer surfaces. The entire intercalation of MAS 1 in the bentonite structure did not allow electrostatic forces to be present in the slurry. As a result, there are no changes on the slump performance. MAS 3, (C:E 6/2), shows a strong intercalation on the bentonite layers, however the changes of the slump performance indicate that electrostatic and steric forces are existent, resulting in adsorption of the polymer on the hemihydrate particles. Nevertheless, the dispersing power is weaker than of the polymers with shorter side chains.

In contrast, MAS short 1 and MAS short 3 are not as sensitive as polymers with longer side chains. The decrease of the side chain length diminishes the intercalation of the polymer in between the bentonite layers, leading to higher flow dispersion in this system. By diminishing the intercalation, the PCEs possessing shorter side chains allow a higher adsorption of PCE on the hemihydrate particles. Consequently, the steric repulsion increases the flowability of the slurry. According to the results in the HH-bentonite system, the ideal polymers structure should be synthetized with shorter side chains due to its lower sensitivity to clay.

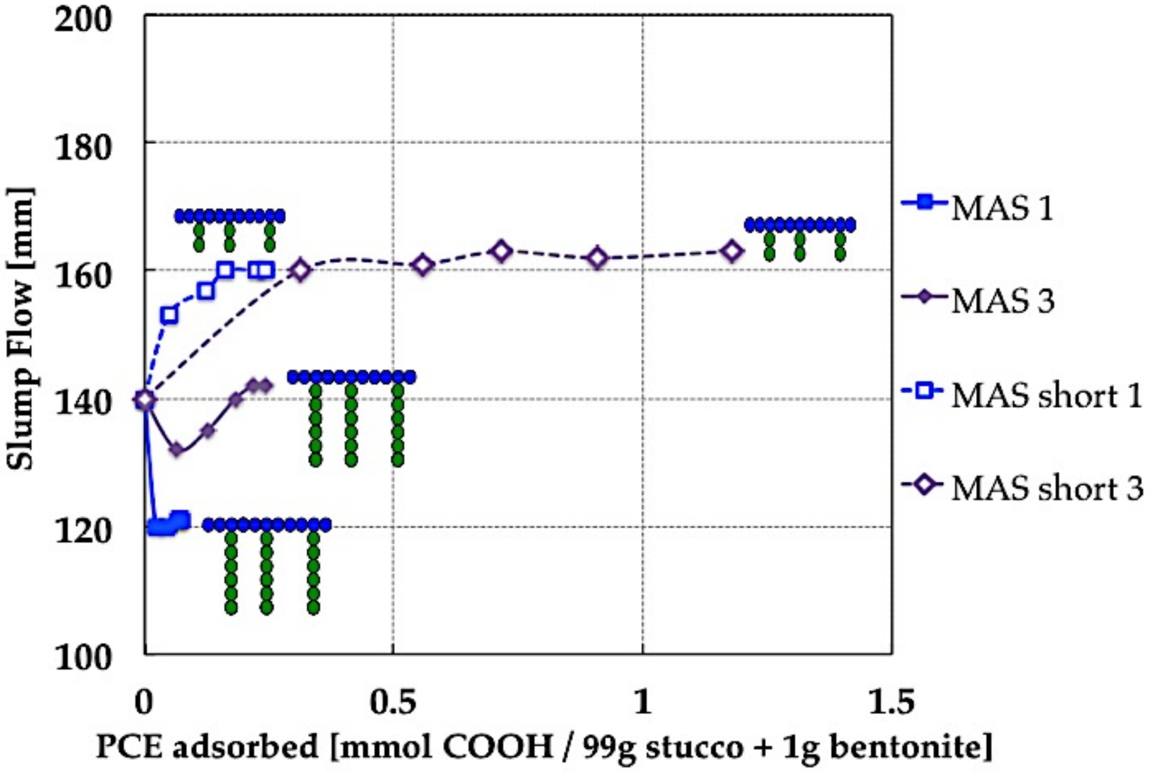


Figure 5-26 Slump response of short side chain polymers in HH-Bentonite systems

The results showed the effect of bentonite on PCE performance on the slurry. The PCE structure has to be modified in order to increase the compatibility of the PCE with bentonite as it affects the adsorption and the dispersing power of the PCE. In section 5.2.C, the PCEs retardation effect in the slurry was observed: the higher the adsorption of polymer, the longer the setting times became. The retardation problem previously mentioned is well demonstrated by the calorimetry curves in Figure 5-27. Calorimetry provides critical insights into the retardation behavior of PCE-HH slurries. In this dissertation, the calorimetry was successfully employed to identify the aggravating effect of the bentonite in the HH slurry. In semi-adiabatic calorimeters, the samples were placed in heat-insulated cylinders where the temperature and heat capacity increase were measured during hydration. The heat capacity data from the different PCE dosages in the slurry were compared to estimate the heat capacity as a function of degree of hydration for the pure hemihydrate system and the hemihydrate-bentonite system.

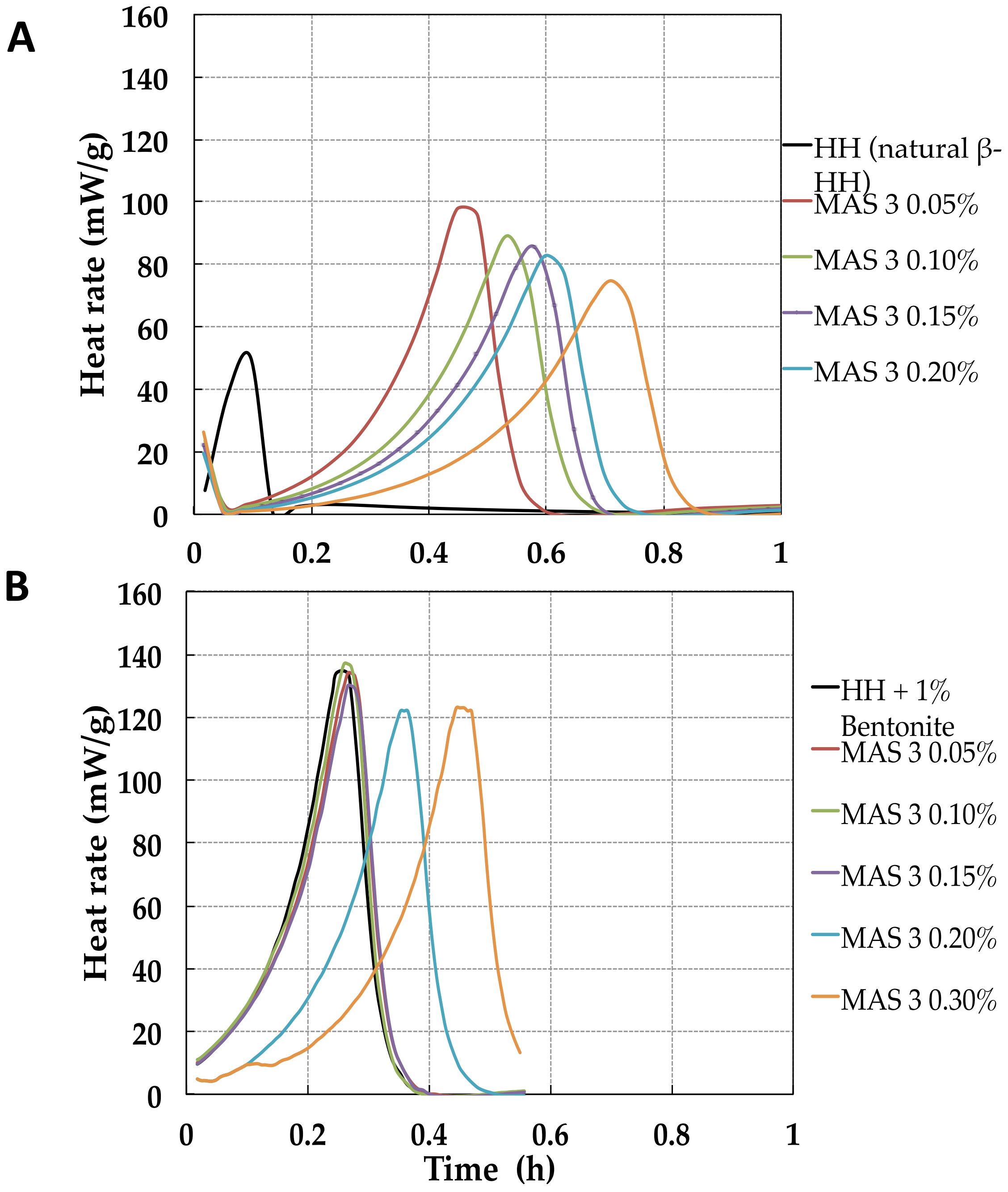


Figure 5-27 Calorimetry curves for pure hemihydrate system (A) or hemihydrate-bentonite system (B)

The results from the retardation effect of the PCEs the slurry can be seen in Figure 5-27.A. The rates of heat realeased are plotted on a per gram of solids basis. A slurry without polymer, blank value in black, will have a heat of hydration of approximately 50 mW/g at 0.1 hr.; when the polymer is added, substantial energy begins to liberate with any PCE dosage. Therefore, retardation of the hydration is observed even with low dosages. The retardation effect increases with higher PCE dosages. In Figure 5-27.B it is possible to observe the effect of the bentonite as a contaminant in the slurry. Contrastingly, when bentonite is contained in the mix, the slurry presents no retardation without any PCE, it maintains during low dosages and the retardation finally increases only at a high dosage of polymer (0.20% & 0.30%). The results can be attributed to the increase of polymer consumption due to the bentonite.

In order to design a PCE that is compatible with hemihydrate-bentonite systems, interactions between hemihydrate, bentonite and different PCE-architectures have been investigated with several methods. Macroscopically, the dispersing power of the PCEs has been analyzed with workability test, slump flow and rheology. Rheological properties are closely associated with the interparticle forces of the suspended materials. The evolution of hydration and the delay of the setting times have been examined through calorimetry. Microscopically, adsorption information quantifies the amount of molecules that are involved in the process. The impact of the molecules adsorbed on the interparticle forces is explained by the changes of the zeta potential of the slurry in presence of PCE. Dealing with hemihydrate-bentonite-superplasticizer interactions raise the questions about the interparticle forces that will increase the polymer's dispersing power.

PCE-particle interface and associated surface properties remain as an interesting field for research. Zeta potential (ζ-potential) provides important information about the colloidal behavior of the slurry. Ionic species disturb the PCE performance behavior in the adsorption on the particle, dispersing power and rheology. The adsorption of ions on positive charged surfaces influences the ζ-potential, which, in theory, influences the PCE adsorption process. The range and intensity of the steric forces depend on the ions in solution, influencing the rheology.

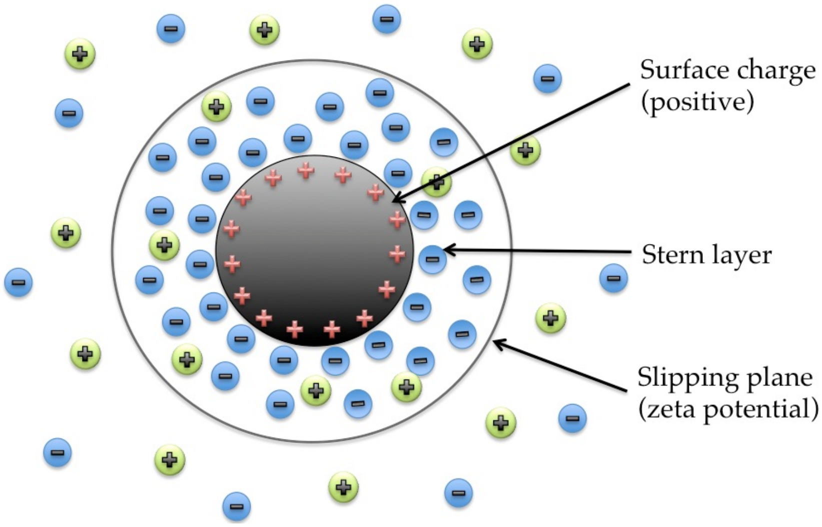


Figure 5-28 Schematic illustration of electric double layer and zeta potential

Zeta potential is the potential difference between the dispersing medium and the stationary layer of the dispersed particle to the surrounding fluid [141]. It is considered the electric potential in the interfacial electric double layer at a location of the slipping plane (known also as shear plane) as illustrated in Figure 5-28. In liquids, the surfaces bind layers of molecules or ions, resulting in a deviation of the hydrodynamic slipping plane from the solid-liquid interface.

It is known [142] that the negatively charged acid groups of the comb-shaped polymers adsorb on the hemihydrate particle, which has a positive charge due to calcium ions. The resulting double layer, and the zeta potential respectively, lead to electrostatic repulsion between the hemihydrate particles. In PCEs, the impact of their adsorption on hemihydrate particles is explained by the displacement of the slipping plane, which strongly depends on the adsorbed polymer. The dispersing power increases when the PCE dosage is increased, due to steric forces induced by the side chains.

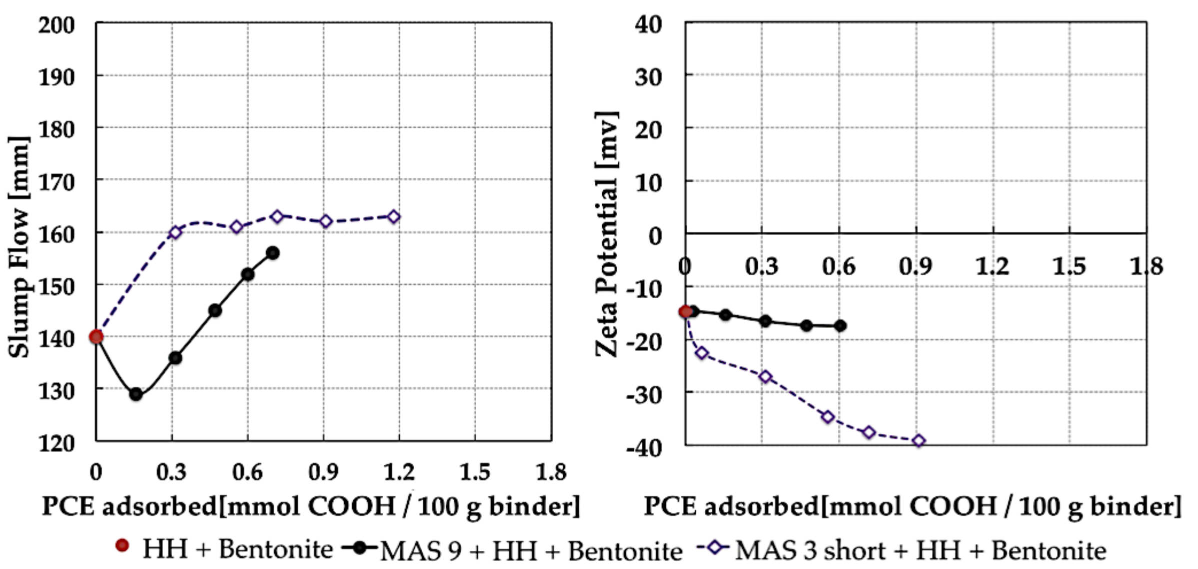


Figure 5-29 MAS 9 and MAS 3 short. Correlation between the slump response (left) and the zeta potential (right) in 100 g of binder (99 g hemihydrate + 1 g bentonite)

Figure 5-29 shows the evolution of zeta potential when increasing the PCE dosage and the results correlate with the dispersing power of the PCEs. MAS 9 and MAS short 3 were the polymers chosen for the zeta potential tests as they were the polymers in each series with the best performance in the pure hemihydrate system (MAS 9) and in hemihydrate-bentonite system (MAS short 3). The negative zeta potential of the slurry is due to the negative zeta potential from the bentonite.

As seen on the left graph from Figure 5-29, the degree of dispersion of the hemihydrate-bentonite suspensions increases when the PCE dosage is increased. As described before, MAS short 3 has better compatibility with clay systems resulting in a higher dispersing power. On the other hand, the dispersing power of MAS 9 decreases as the polymer tends to intercalate between the bentonite inter-layers. The changes of zeta potential when PCE is adsorbed are observed in

Figure 5-29 on the right side. For the comb-type PCE, it was observed that the short side chains (MAS short 3) shift the slipping plane of the zeta potential to greater distances away from the hemihydrate surfaces. The changes in the charge of the slurry (from -15mV to -40mv) represent the interparticle forces that allow the increase of the dispersing power of the slurry. This is linked to the slump performance of MAS short 3 in the left graph. The increase in the conductivity of the slurry increases its workability (shown in Figure 5-29 on the left). On the other hand, MAS 9 maintains a stable zeta potential even when the polymer dosage is increased. The minimal change of the charges in the slurry is related to the bentonite in the slurry. The polymer, due to its long side chains, intercalates in the bentonite inter-layers not allowing polymer to adsorb on the hemihydrate surfaces, thus there is no interparticle forces allowing a dispersion power as high as the one presented by MAS short 3. The mechanism of PCE adsorption on hemihydrate-bentonite systems is favored by lowering of the zeta potential in the slurry. This increase is possible with short side chain polymers only.

6 SUMMARY AND OUTLOOK

This investigation has given an account of and the reasons for the widespread use of polycarboxylate-based superplasticizers (PCE) in the wallboard industry. Usually, the addition of PCE to the slurry will provide a higher workability to the slurry and would satisfy the requirements needed for the wallboard production. Relevant factors influence the effects of the PCEs, such as: the nature of the stucco, the polymer architecture and the adsorption and concentration of superplasticizer.

In this dissertation, different aspects on the properties of the slurry containing PCE superplasticizers are highlighted, with special regard to the effect of impurities on their dispersing power. Suitable materials were tested in order to underline the positive and negative aspects of each PCE design. The research shows that the superplasticizer architecture has a strong influence on the efficiency of the PCE. Any modifications in superplasticizer architecture will produce different results on adsorption and rheological properties. The present study was designed to determine the right structure for a PCE that would keep its robustness even with detrimental impurities. Three series of polymers with different characteristics were evaluated in natural stucco with and without the presence of bentonite (as a detrimental impurity).

One of the more significant findings to emerge from this study is the importance of the backbone in the PCE structure. As described in section 5.2.C, a mixed backbone, acrylic and methacrylic acid, would provide a better workability than a pure methacrylic acid backbone. Nevertheless, the acrylic acid retards the setting of the slurry. For the wallboard production, this would become an issue, as the manufacture requires a fast setting of the slurry.

The results elucidate that a PCE with longer side chains and low side chain density (MAS 9) affords strong adsorption of the superplasticizers, then high dispersion forces, and thus good rheology. PCE architectures with higher side chain density and shorter side chains led to smaller dispersion efficiency even with high concentration of superplasticizers in the solution.

In the model system of natural stucco without bentonite, the results show that MAS 9 is the PCE suitable for a strong workability, fulfilling the requirements for the wallboard production. Surprisingly, MAS 9 was found not to be suitable when tested in the model system of natural stucco with bentonite. These differences can be explained in part by the length of the side chains. The research has shown the effect of the bentonite on the behavior of the PCEs. The bentonite diminished the effective dispersing power of each PCE tested on the first and second series, both with long side chains. The results suggested that the PCEs are intercalated thru their side chains, increasing its adsorption and not allowing its dispersing power to become effective for the slurry rheology.

In order to reduce the intercalation effect, a third series was designed with shorter side chains. When the side chain length is decreased, the intercalation effect was reduced allowing some dispersing power in the slurry. These findings further support the ideas of Ng and Plank (2012) in the concrete industry, who suggested that when working with systems with clay, shorter side chains in PCEs would provide a better dispersing power rather than PCEs with longer side chains. MAS short 3 provided the best workability in the stucco-bentonite systems among all the polymers tested.

However, when MAS short 3 was tested with pure systems, the workability did not fulfill the requirements expected for the wallboard production. In comparison with MAS 9, its dispersing power suffered a considerable reduction. These results are explained by the fact that shorter side chains in the PCEs would present lower dispersion forces, and thus lower workability.

Indeed, MAS short 3, as a PCEs with short side chains, would work better in a stucco-bentonite system, but it will not provide the right dispersing power in a system without bentonite. In contrast, MAS 9 has the best dispersing power in a pure system, but it will not be suitable for a stucco-bentonite system. In the three series of polymers tested, there was no polymer that kept its robustness in both systems.

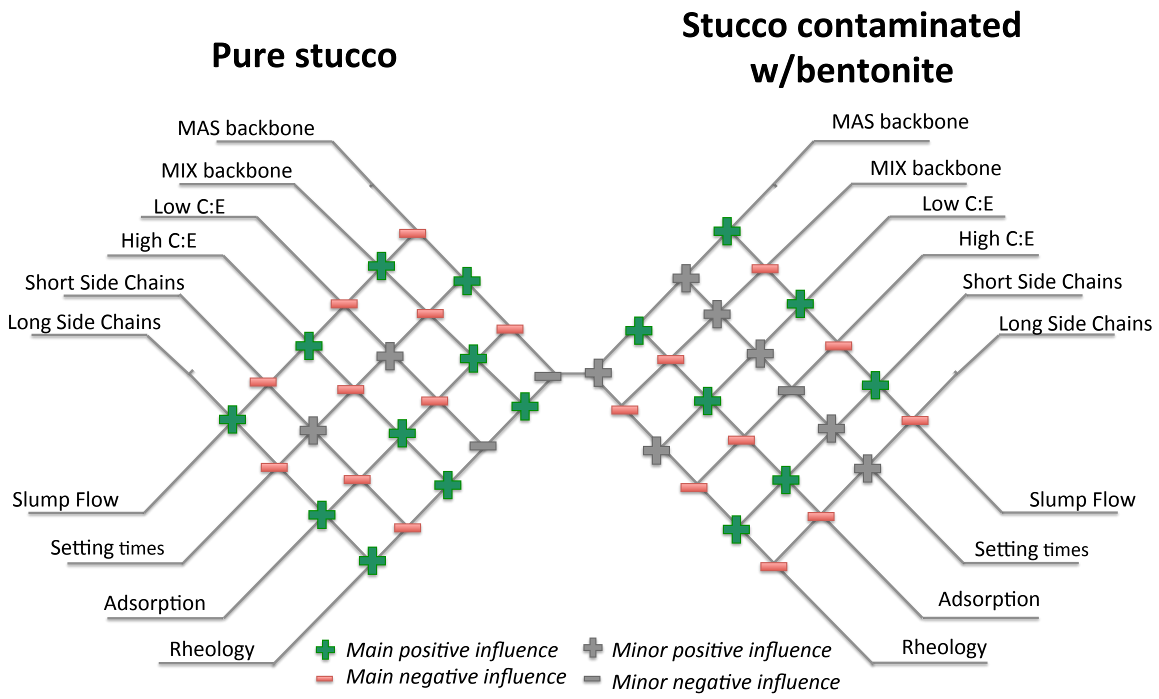


Figure 6-1 Most significant findings of the different PCE structures in pure stucco and stucco contaminated with bentonite

In furtherance of designing a polymer that would keep its robustness in a stucco-bentonite system, the findings shown on Figure 6-1 provide three alternatives for future research:

- A polymer that would have a structure in-between MAS 9 and MAS short 3. The polymer would keep the MAS backbone and the side chain length would be longer than MAS short 3 to increase workability and shorter than MAS 9 to hinder the polymer intercalation in the bentonite layers.
- A "polymer-blend" of MAS 9 and MAS short 3. Ideally, this molecule should decrease the detrimental effect of the bentonite while keeping its dispersing effect.
- Addition of two polymers: a "clay-polymer" and a fluidizing polymer. It can be clearly stated that the intercalation of the PCE is the main reaction between the PCEs and bentonite. In order to decrease the detrimental effect of bentonite in the slurry, certain modifications in the wallboard production are required. The "clay-polymer" should be added in the premixer where the polymer can intercalate in the clay contained, as a contaminant, in the slurry. The "fluidizing polymer" should be added in the high-shear mixer, following the process described in section 3.4.A. It is expected that the fluidizing PCE can effectively increase the workability of the solution by fully adsorbing in the hemihydrate particles.

The results documented in this dissertation include a wide range of investigations on the impact of the quality of the raw material and polymer structure on the adsorption (and/or intercalation) behavior of different PCEs on hemihydrate-bentonite systems. Another aspect emerging from this multi-method analysis concerns the idea that further research with additional techniques is required to fully understand the effects, which are not explainable with the presented methods:

- How to quantify the total amount of polymer adsorbed by the bentonite.
- The distance of expansion of the in-between bentonite layers when polymer is adsorbed.

Techniques, such as X-Ray diffraction of textured specimen enrichment of the clay minerals prior to preparation of the specimen will be essential in the analysis of clay minerals.

For the addition of two polymers, "clay polymer" and fluidizing polymer, in the optimization of the wallboard production, it is necessary to define the right dosages of each polymer to target the requirements needed. The total amount of PCE adsorbed or intercalated by the hemihydrate or clay, would be the result of a delicate balance of PCE dosages added in each production stage, premixer and mixer.

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8 APPENDIX

8.1 Rheometer

Laboratory rheological data were obtained with an Anton Paar rheometer model Rheolab QC (Figure 8-1), equipped with vane geometry, well adapted for the mixing of gypsum slurry.

Figure 8-1 Anton Paar rheometer model Rheolab QC[1]

The rheometer Rheolab QC was employed for measurements under ambient conditions without a temperature control system. The properties which can be analyzed and specifications of the equipment are listed in Table 8-1 and Table 8-2.

Table 8-1 Properties that can be analyzed with the Anton Paar Rheometer model Rheolab QC

Properties which can be analyzed	Dynamic viscosity	η
	Shear rate	γ
	Shear stress	τ
	Speed	n
	Torque	M
	Temperature	T
	Time	t
	Kinematic viscosity	ν
	Yield Point	τ o
	Deformation	γ
	Compliance	J

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[1] www.anton-paar.com

Table 8-2 Specifications from Anton Paar Rheometer model Rheolab QC

Specifications	Speed	0.01 to 1500 1 1/min
	Torque	0.25 to 75 mNm
	Shear Stress	0.5 to 3 x 104 Pa
	Shear rate	10^{-2} to 4000 1/s
	Viscosity measuring range	1 to 109 mPas
	Temperature range	-20 to 180°C
	Internal angle resolution	2 μrad
	LAN-Ethernet interface	PC
	Serial interface RS232	PC, printer
	PS/2 interface	Keyboard, bar code
	Dimensions W x H x D	300 x 720 x 350 mm
	Weight	14 kg

8.2 Calorimeter

A semi-adiabatic calorimeter was used during this study to quantify the hydration development of various gypsum systems. The calorimeter consisted of an insulated container that uses 8 cylindrical samples and one reference. Probes are used to control the slurry temperature.

A new software named SemAment (Semi Adiabatic measurement) was developed by Sika Technology AG to obtain and download accurate data from the calorimeter. The calorimeter is connected to a controller that links the computer with the calorimeter (Figure 8-2). The software is able to measure the temperature evolution, it quantifies the hydration by calculating the heat release in calibrated cells and it represents the information in an excel sheet for further analysis.

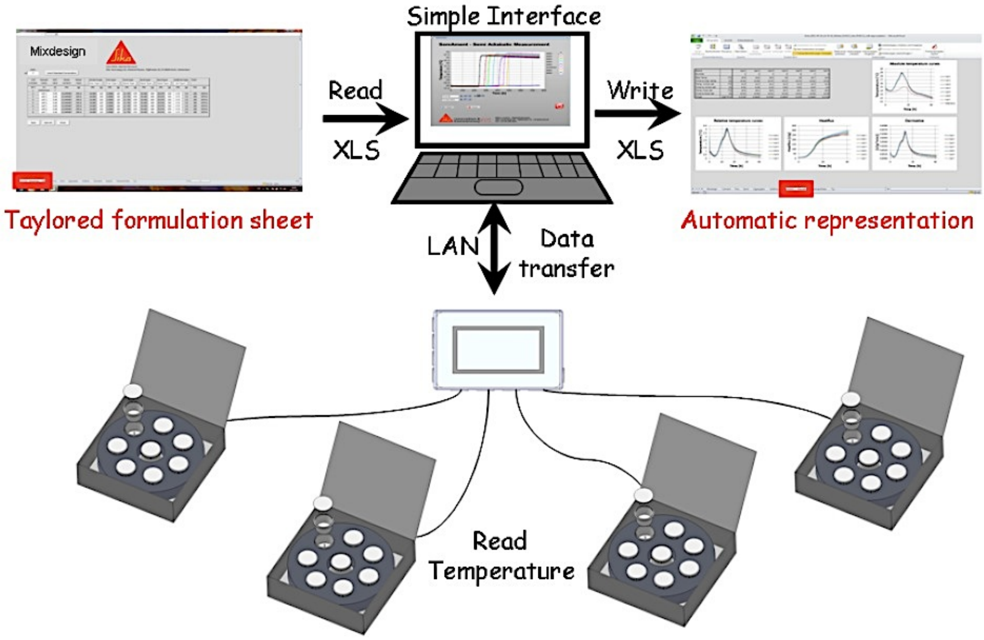

Figure 8-2 From the Mix design to the results: an automatic system [2]

The calorimeter is composed of a PT-100 and of a semi-adiabatic container: a part of the heat generated by the slurry will be dissipated with time due to thermal lost. The total heat induced by the slurry hydration is approximated with the following expression:

$$Q(t) = \rho V C_p (T(t) - T_{e)} + kA \int_{o}^{t} (T(t) - T)dt$$

Where T_e is the room temperature (K), $T(t)$ the instantaneous temperature of the sample (K), A contact surface between sample cell and infinity (m^3), V sample volume (m^3), C_p the calorific capacity of cement ($J.g^{-1}.K^{-1}$), ρ slurry sample ($g.m^{-3}$) and k thermal transfer of the box ($W.m.K^{-1}$).

The temperature is recorded as a function of the time for the cells with sample. There is also a reference cell containing the same material type. The temperature of the reference cell is subtracted to compensate the room temperature fluctuations.

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9 CURRICULUM VITAE

Jazmín Consuelo Aboytes Contreras
E: aboytesjazmin@gmail.com•M: +49 173 565 3001• 69115 Heidelberg. Germany
linkedin.com/in/aboytesjazmin

Meticulous researcher, who undertakes complex assignments, meets tight deadlines and delivers superior performance. Possess practical knowledge in the building material industry. Applies strong planning and analytical skills to produce high impact research in the area of chemical sciences. Operates with a strong sense of urgency and thrives in a fast-paced setting. In an interdisciplinary approach, provides an excellent environment for innovation, allowing her to pursue outstanding research on chemical processes. Fluent in Spanish, English and Italian; conversant in German. Core competences include:

Chemical Engineering • Product Development • Process Optimization • Organization • Team Oriented • Negotiation • Client Relations • Strategic Planning • Detailed Oriented • Project Management • Process Development • Strategic Consulting • Enthusiasm

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EDUCATION

Ph.D. Material Science and Polymer Engineering
The Clausthal University of Technology (TU-Clausthal). Clausthal-Zellerfeld, Germany 03/2011– Expected graduation 03/2014
Dissertation: "Multi-method approach to study the influence of additives in ternary systems: gypsum, water and impurities"

Bachelor of Science in Chemical Engineering with minor in Industrial Engineering
Instituto Tecnológico y de Estudios Superiores de Monterrey (ITESM), Monterrey, N.L. México. 08/2004 – 06/ 2009

WORK EXPERIENCE

Consultant at the Instituto Tecnológico y de Estudios Superiores de Monterrey Jan 09-July 09
(Monterrey, N.L, Mexico)

- Guided new formula and managed center project through all stages of product development.
- Modeled and developed new studies for the feasibility of products.
- Provided innovative ideas for projects in the chemical industry (mainly in beverage and detergent industries)

Researcher at CEMEX, Global Center for Technology and Innovation May 08-Dec 08
(Brügg, Switzerland) Internship

- Assisting in the R&D area and marketing creating presentations in order to meet the client's needs.
- Reviewed and clarified tests discrepancies in order to increase product security.
- Evaluated new products and diagnosed the behavior of additives for the cement industry.
- Collected intensive data in order to identify and extract focus areas for future tests.
- Arranged and classified data into organized summaries, reports and spreadsheets for record tracking

Researcher at the Instituto Nacional de Nutrición Salvador Zubirán Winter 2007
(México City, Mexico)

- Studied the change of genetic expression by means of food in Zuker Rats
- Management of diets and treatment of rats.
- Assisting Master degree students in the development of thesis projects and other nutritional projects.
- Worked as a team member by analyzing data and comparing results with other projects.

TECHNICAL SKILLS

Proficient in Microsoft Office Suite: advanced Excel • Word • Power Poing • Outlook • Access
Lotus Notes • MatLab • Research Methods • Preparing documentation • Verifying data • Report writing • Designing Databases • Statistical analysis • Coordinating studies

ACTIVITIES:

- Volunteer in the construction of houses for unprivileged families in the South of Mexico. Team leader and directly involved with all the building activities.
- Part of a program known as "Heart Beats" were I aided the development of underprivileged children as an English and Chemistry teacher.
- Au Pair during school break in Salt Lake City, California and NYC, USA & Lugano, Switzerland; English teacher in Prague.
- Summer course coordinator supervision of 30 children from 6 – 15 years old, coordination of summer class logistics

PERSONAL INFORMATION

Place and date of birth: Mexico City, August 19, 1985