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Effect of Polycarboxylate Ether on the Grinding and Property of Cement

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SCHOOL OF GRADUATE STUDIES

FACULTY OF CHEMICAL AND FOOD ENGINEERING

(Process Engineering)

MSc Thesis on:

Effect of Polycarboxylate Ether on the Grinding and Property of Cement

By:

Dawit Mamuye

FEB 2023

Bahir Dar, Ethiopia

BAHIR DAR UNIVERSITY

BAHIR DAR INSTITUTE OF TECHNOLOGY

FACULTY OF CHEMICAL AND FOOD ENGINEERING

Effect of Polycarboxylate Ether on the Grinding and Property of Cement

By:

Dawit Mamuye

A thesis submitted in Partial Fulfillment of the Requirement for the Degree of Master of Science in Process Engineering

Advisor: D/r Zenamarkos Bantie (PhD)

FEB 2023

Bahir Dar Ethiopia

Acknowledgement

First, I would like to thank Almighty God for giving me courage and strength to accomplish my study. Then, I wish to give sincerely thank my Advisor Dr. Zenamarkos Bantie for his guidance and support.

Declaration

This is to certify that the thesis entitled "**Effect of Polycarboxylate Ether on the Grinding and Property of Cement",** submitted in partial fulfillment of the requirements for the degree of Master of Science in process engineering under faculty of chemical and food engineering, Bahir Dar Institute of Technology, is a record of original work carried out by me and has never been submitted to this or any other institution to get any other degree or certificates. The assistance and help I received during this investigation have been duly acknowledged.

Dawit Mamuye Date **FEB 2023**

APPROVAL SHEET

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Approval of thesis for defense result

I hereby confirm that the changes required by the examiners have been carried out and incorporated in the final thesis. Name of Student: Dawit Mamuye Signature ______ date FEB 2023,as members of the board of examiners, we examined this thesis entitled "Effect Of Polycarboxylate Either On The Grinding And Property Of Cement". We hereby certify that the thesis is accepted for fulfilling the requirements for the award of the degree of Masters of Science in "Process Engineering".

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v

Abstract

Cement is obtained by heating a mixture of limestone with iron oxide, aluminium oxide and silicon oxides; and grinding the resulting clinker together with calcium sulfates and slag, limestone, or fly ash depending on the cement type. In this study the effect of PCE on cement grinding, compressive strength and water demand of treated cement has been investigated. Response Surface Methodology (RSM) based on central composite design (CCD) experiments was used to optimize process parameters for compressive strength and water demand of mortar. A statistical model with the factor of PCE concentration and blaine was developed using two-level CCD experiments with central and axial points. From the analysis of variance, it was observed that both parameters have a significant effect on compressive strength and PCE concentration has a significant effect on water demand reduction of resulted cement. The maximum and minimum values of compressive strength were 61.56 and 52.9 MPa respectively. The optimum results found to be compressive strength of 60.92 MPa, PCE concentration of 0.15 %, and blaine of 3690 cm^2/g for the given cement type and composition.

The difference between R-squared and Adj R-squared is less than 0.2 in both cases. This implies the experimental data is good fit at linear model for compressive strength and quadratic model for the water demand. Since the experimental result is in accordance with the model predicted value; it shows the reliability of the predicted model.

Keywords: Polycarboxlate Ether, Cement, cement/PCE composite, compressive strength

Table of Contents

List of tables

List of figures

List of Acronyms

ANOVA………............Analysis of Variance

ASTM……….………American Society for Testing and Materials

ACI ……….................American Concrete Institute

CCD…………………Central Composite Design

Al2O3 ……….................Alumina

RSM…………………Response Surface Methodology

ACV ……….................Aggregate Crushing Value

ASTM ……….................American Standard for Testing and Measurement

cm2 ……….................Square Centimeter

AIV ……….................Aggregate Impact Value

CaO ……….................Calcium Oxide

Fe2O3 ……….................Ferrite

CO2………................ Carbon dioxide

ERA ……….................Ethiopian Road Authority

G ……….................Gram

Kg ……….................Kilogram

gm/cm3 ……….................Gram per cubic centimeter

H2O ……….................Water

kg/m3 ……….................Kilogram per cubic meter

MgO………................ Magnesium Oxide

K2O ……….................Potassium Oxide

P2O5………................ Phosphorus pentaoxide

MPa ……….................Mega Pascal

Na2O ……….................Sodium Oxide

MnO ……….................Manganese Oxide

OPC ……….................Ordinary Portland Cement

PCC ……….................Portland Cement Concrete

oC……….................Degree Celsius

SO3 ……….................Sulfate

Psi………................. Pound per square inch

PPC ……….................Portland Pozzolana Cement

SiO2………................. Silicon dioxide

%………................. Percent

SEM………................. Scanning Electron Microscope

Pci ……….................Pound per cubic inch

μm………................. Micrometer

Chapter One

Introduction

1.1. Background

Cement is a manmade fine inorganic powder, in which when react with water acts as a binder for constructions that sets, hardens, and adheres to other materials to bind them together. It is not used on its own, but rather to bind sand and gravel (aggregate) together. When mixed with fine aggregate and water, cement produces mortar for masonry, or with sand, gravel, and water, produces concrete. Concrete is the most important material in the construction world, used to build many types of infrastructures. Buildings, dams, railways, bridges, canals, and many other infrastructures use concrete as one of major raw materials. [1]

Cement manufacturing is a complex process. It starts from mining of raw materials, and then crushing, grinding, milling and pyro-processing which reaches up to $1450^{o}C$. Major raw materials are limestone and clay, which contains CaCO3, SiO2, Al2O3 and Fe2O3. In the pyro-processing, the chemical bonds of the raw materials are broken down, melt and recombined to form a new mineral containing intermediate product called clinker, which are rounded nodules between 1mm and 25mm in diameter. The clinker is then ground with gypsum and/or supplementary cementitious materials like natural pozzolana, fly ash, furnace slag in the case of blended cement, to a fine powder in a cement mill to create cement. Concrete is one of the utmost broadly employed construction materials in the world [2,4].

CO2 emissions from cement production are generated from the decarbonation of limestone (CaCO3), the calcination, and the milling process. About 900 kg of CO2 are released for every ton of clinker produced, producing approximately 5 - 7 % of global anthropogenic carbon dioxide emissions [1-3]. To reduce the environmental impact of CO2 emissions from cement production, a part of the clinker can be substituted with supplementary cementitious materials (SCMs). These are known as blended cements (CEM II/III) that are more environmentally more friendly than Portland cement. However, the disadvantage of blended cements is their slow early strength development, owing to a reduced rate of cement hydration and the slow pozzolanic reaction of SCMs [1,4,5].

Generally, calcium-based salts such as calcium chloride, nitrate or format are used as accelerators to increase the rate of hydration and to boost the early strength of Portland cement [4]. In blended cements, many reports showed an increase of early strength through addition of accelerating admixtures, such as calcium chloride, calcium formate, sodium sulfate, sodium thiocyanate, alkanolamines, and glycerol [5-8]. However, those admixtures sometimes lead to a decreased final strength.

Cement grinding is the most important process in the whole cement production. The grinding process of cement absorbs 60-70% of the total energy employed. Finish grinding accounts for about 38% of specific electric power consumption [5]. The fineness of the cement has strong effect on initial as well as final strength development of cement mortars and concretes. However, while grinding cement to a certain degree, there will be agglomeration of particles, which will negatively affect the production capacity and the power consumption of the process. This is because the cement produces electric charge in the process of grinding, in which positive and negative charges on cement particle's surface attract each other and form agglomeration between the finest particles [5,7,9]. Grinding aid is a good way to avoid the occurrence of this phenomenon. Because of its effect to increase cement fineness, increase specific surface area, optimize the grain size distribution of cement particles, reduce grinding energy, and increase production capacity, cement grinding aid is widely used in cement industry [4-8].

Commercial grinding aids are composed of Triethanolamine (TEA), Triisopropanolamine (TIPA), Dietheleneglycol (DEG), Polyethylenglycol (PEG) and other amines and glycols. Compounds relating to class of amines merely modify particle size of cements neutralized charges arising at rupture valence bond and catalyse hydration process to increase strength, both in initial and late periods of hardening. Glycol compositions mainly prevent agglomeration of cement particles in grinding process, and reduce coatings on the grinding media, but exert little effect on change in particle size [7]. Recently Polycarboxylicether (PCE) powered products are introduced to the market. They have been used with great success for a long time as concrete additives, as a superplasticizer. However, their unique properties as cement additives were only recognized in recent years [7].

Workability and rheological characteristics of the cement mixture is important for the final characteristics of the hardening concrete, and it results from a combination of dissimilar physical spectacles [1-3]. The volume fraction and particle size, shape, the inter-particle forces play a significant character in bringing the rheological features of granular scheme [4-5]. The production of special concretes like high-performance concrete and self-compacting concrete requires the water content reduction in cement paste. This water reduction influences the long-term mechanical characteristics, durability, strength, early age strength, permeability, etc. consequently, the addition of organic admixtures is principal in the production of these concretes to permit such peculiar features. Superplasticizers are water reducing agents, and they are grouped into four clusters based on their chemistry, namely sulfonated naphthalene-formaldehyde condensate, sulfonate melamine-formaldehyde condensate, modified lignosulfonate, polystyrene, sulfonates, sulfonic acid esters, and polyacrylates [6-8]. Polycarboxylate superplasticizers (PCE) are characterised by comb-formed, and the hydrophilic polyethylene oxide comprises the side chain and the carboxylic groups on the main chain form an anionic charged support [8]. The number of carboxylic groups, length and number of side chains are flexible variables that give in various polymer architectures and ensure dissimilar effects on cement hydration and rheology [8-9]. The effect of PCE on mixtures of cement is linked to inter-particle dispersive forces that avoids the agglomerates creation [10] and are broadly used owing to their compliance.

The adsorbed PCE amount on particle surfaces determines the interaction effect between the particle and cement superplasticizer [11-12]. The technique of solution depletion in together with the analysis of total organic carbon permits in evaluating the polymer amount left in solution after water-powder mixtures centrifugation. Diverse reports showed the effect of diverse polymer architectures and their interaction with the cementitious system, indicating that short side chain superplasticizers show high adsorption particularly on positively charged cement phases, such as ettringite [9-13]. On the other side, adsorption of PCE on cement particles increases with the increase of the specific surface area available and decreases with the increase of the sulfate ions concentration [14-15]. In this study the impact of PCE on the grinding and final property of cement has been investigated.

1.2. Statement of the problem

Cement is a hydraulic material when react with water cause a sequence of physicochemical processes known as hydration reaction. The hydration of cement controls the physical and chemical property of hardened cement products. For this reason, studies of cementitious system of hydration and hardening processes are important for the manufacture and use of cement. Higher cement fineness and lower water to cement ratio in a cementitious product plays a vital role by enhancing the durability for the intended application. Superplasticizers such as PCE are chemical employed in concrete to decreasing the water and cement ratio. The working mechanism of such plasticizing/water reducing effect is known to be electrostatic repulsive force and steric hinderance of adsorbed PCE's on the cement particle, which is similar mechanism of cement grinding aids (amines, glycols) [9]. In this study PCE have been added to the cement grinding process to evaluate if it can increase the fineness of the cement and reduce the water demand of the resulting treated cement. Hence, the present study provided employment of PCE on cement grinding and evaluating the fineness improvement on grinding and compressive strength enhancement as a water reducer in a standard mortar.

1.2. Objectives

1.2.1 General Objective

The general objective is to evaluate the effect of polycarboxylate ether on the grinding and final property of cement.

1.2.2 Specific Objectives

- To evaluate the performance of the resulting cement by determining the compressive strength.
- To evaluate the water demand reduction of PCE which will be added in cement grinding.
- To evaluate the chemical and mineral properties of cement.
- To optimize the parameters affecting compressive strength of cement.

1.3. Significance of the study

The significance of the study is evaluating advantages of PCE in cement grinding and final properties, which can be scaled up for commercial applications. Also helps for further study on CO_2 emission reduction and study the contribution to energy and cost reduction of cement and its products.

1.4. Scope of the study

The scope is to study the impact of selected PCE, having known performance in terms of water reduction in concrete, to cement grinding and final property of cement. It includes, determining the contribution to increase the fineness of cement, determining the impact on compressive strength enhancement and water demand reduction of the cement.

Chapter Two

2. Literature Review

Polycarboxylate ether (PCE) superplasticizers are known as high-range water-reducing admixtures in concrete [11], such as ready-mix concrete, self-compacting concrete (SCC), ultra-high strength concrete (UHPC) [12-14], etc. PCEs improve the rheology of concrete through the dispersion of particles [15,16]. Consequently, the water consumption in the mix proportion of concrete is reduced, leading to an improvement of compressive strength and durability of hardened concrete [17,18].

The molecular structure of comb-like PCE copolymers generally consists of a main chain (backbone) to which side chains are attached. The backbone carries carboxylate anchor groups (COO-) that have a negative charge and are responsible for adsorption of the polymer onto the positively charged surface sites of cement particles and hydration products like ettringite [18-22]. The non-ionic side chains grafted to the backbone of PCEs are normally made from polyethylene glycol (PEG) which is accountable for the dispersing ability via a steric hindrance effect [22,23,24].

Currently, several types of PCE superplasticizers are used in the concrete industry, including MPEG-type PCEs, APEG-type PCEs, VPEG-type PCEs, HPEG-type PCEs, IPEG-type PCEs, and PAAM-type PCEs [25].

2.1. Preparation of PCEs

There are two main synthetic routes used for producing PCEs [25,26]. Esterification of carboxylic groups in polyanionic trunk chains with poly (ethylene glycol) can be used to synthesize MPEG-based PCEs. This procedure produces a highly uniform PCE with statistical distribution of the side chains along the backbone. However, this method is less popular in the industry because of high cost, long reaction time, and low conversion rate.

Free radical copolymerization of a monomer carrying carboxylic groups and a monomer bearing the side chain (macromonomer) is normally used in the industry due to its simpler procedure and higher cost-effectiveness. This process produces a gradient polymer with non-homogeneous distribution of the side chains along the main chain. Recently, reversible addition-fragmentation chain-transfer or RAFT polymerization technique has been used to produce specific gradient polymers such as MPEG PCEs with a well-controlled structure [27], and MPEG PCEs with large anionic blocks that can adsorb more strongly on cement

[28]. Several kinds of PCE can be synthesized via free radical copolymerization such as, MPEG, APEG, VPEG, HPEG and IPEG PCE types.

MPEG-type PCEs are prepared from -methoxy poly(ethylene glycol) methacrylate ester macromonomer with methacrylic acid [29]. And APEG-type PCEs are made from -allyl-methoxy or -hydroxy poly(ethylene glycol) ether and maleic anhydride or acrylic acid [30]. VPEG-type PCEs are synthesized by aqueous free radical copolymerization of 4-hydroxy butyl-poly(ethylene glycol) vinyl ether and maleic anhydride or acrylic acid [31]. HPEG-type PCEs are made from the macromonomer -methallyl-methoxy or -hydroxy poly(ethylene glycol) with e.g. acrylic acid [32]. And, IPEG-type PCEs (also called TPEG-PCE) are prepared from isoprenyl oxy poly(ethylene glycol) ether as macromonomer by copolymerization with e.g. acrylic acid [33].

The adsorption of PCE copolymers on the surfaces of cement particles is one of the most important parameters influencing the rheological properties such as fluidity and slump loss of concrete. The charged surfaces of the particles, as measured by zeta potential, are a key factor for PCE adsorption via electrostatic interaction. A highly positive zeta potential leads to a high PCE adsorption [21,22,34]. The various architectural structures in PCE superplasticizers control their adsorption and dispersing effect [25,35] which include length of the backbone, chemical composition of the backbone (acrylic, methacrylic, maleic etc.), length of side chains, grafting density of side chains (polyether/ester to carboxylate ratio), distribution of the side chains along the backbone (random, gradient)

The density of ionic groups in the polymer backbone relates to the anionic charge density of a PCE which can be determined experimentally by titration with a cationic polyelectrolyte such as polydadmac, etc. The anionic charge density of the PCE plays a vital role for its adsorption behavior and, consequently, its dispersing power. Generally, PCE adsorption increases with an increase in the density of ionic groups on the backbone [35]. However, a decreased PCE adsorption can be observed for PCE copolymers possessing a long side chain at the same grafting density [35]. Moreover, the pH value of the aqueous solution and calcium ions present in the cement pore solution affect the anionic charge of the PCE [42]. The anionic charge of PCEs increases with increasing pH values due to a deprotonation of the carboxylate (–COO-) groups in the polymer backbone.

However, a reduction in anionic charge results from the presence of calcium ions that can coordinate with the carboxylate groups, both through complexation and counter-ion condensation. Generally, the –COO- groups can coordinate Ca2+ as a monodentate or bidentate ligand (Figure 14) which depends on the architecture of the PCE. In PCEs possessing a high side chain density, the –COO- group is shielded by the side chains and preferably coordinates with Ca2+ as bidentate ligand, producing a neutral Ca2+–PC complex. Consequently, this type of PCE shows almost no anionic charge in cement pore solution. PCEs exhibiting a high density of –COO- possess anionic character in pore solution due to monodentate complexation of Ca2+.

2.2. Polycarboxylate superplasticizers

High-efficiency polycarboxylate superplasticizer is based on the unique side-chain structure of polyether. Their chemical composition (Figure 2.1) is presented by a main chain of carboxylic groups (n) organized in a comb structure with ethylene oxide (EO) units in the side chain (m). Through the molecular structure design and the polymerization of various functional groups, it shows a good steric hindrance effect and electrostatic repulsion effect. It greatly improves the dispersion and retention performance of concrete and has an excellent water reduction rate and small slump loss. It is adaptable to different building materials and can be widely used in fresh concrete for long-distance transportation, concrete for long-distance pumping in the high-temperature construction environment, etc [29].

2.2.1. Applications (polycarboxylate superplasticizer)

PCE superplasticizers are mainly used for ready-mixed concrete, high slump concrete, self-compacting concrete (SCC), high-performance concrete, precast concrete and other high tech concrete ranges.

2.2.2. Features & Advantages (polycarboxylate superplasticizer):

polycarboxylate superplasticizers gives excellent water reduction/workability, good cohesiveness, thixotropic properties, improves pumpability, good compatibility with active admixtures such as slag and fly ash. Due to different structures and types, it can give different desired properties including slump retention for easy pouring and compaction.

2.2.3 Usage

The content of this product is generally 0.3% -1.5% of cementitious material. It can be used in combination with other types of polycarboxylate superplasticizer, retarder, defoamer, air-entraining agent, and other additives, to make the concrete easier and work better. The dosage should be optimized by trial by using actual building materials to satisfy the project needs.

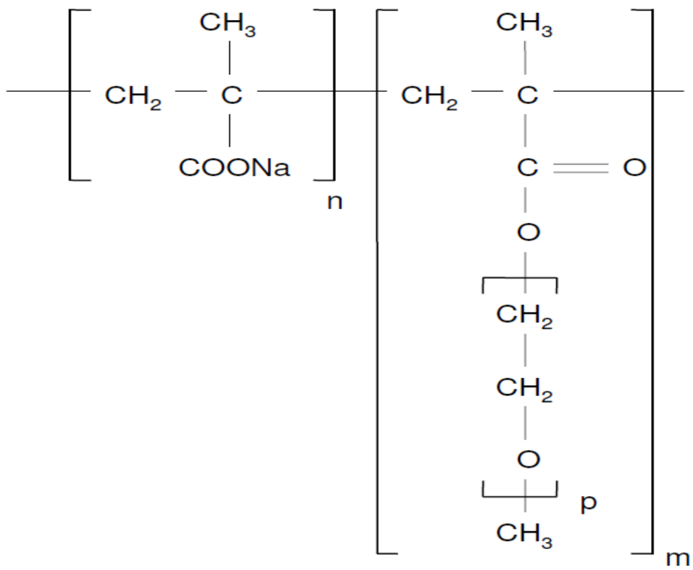

Figure 2.1. Typical chemical structure of polycarboxylate ether (PCE) superplasticizer [21]

2.3. Concrete

It is made of coarse granular material called filler or aggregate that is entrenched in a hard material matrix of binder or cement with water binding and aggregates together and filling the space formed between them. When the elements are mixed with water the concrete hardens and solidifies because of a chemical reaction between the cement and the water called hydration and forms a stone like material by combining and binding the aggregates [18].

2.3.1. Properties of concrete

Mechanical strength, in particular compressive strength: The strength of normal concrete varies between 25 and 40 MPa. Above 50 MPa, the term High Performance Concrete is used (50 MPa corresponds to a force of 50 tonnes acting on a square with sides of ten centimetres).

Durability. Concrete is extremely resistant to the physico-chemical attack emanating from the environment (frost, rain atmospheric pollution, etc...) It is particularly well-suited for structures exposed to demanding and extreme conditions.

Porosity and density. These properties are responsible for the first two. The denser (or the less porous) the concrete the better its performance and the greater its durability.

The density of concrete is increased by optimizing the dimensions and packing of the aggregate and reducing the water content [23-26].

2.4. Cements

Cements are classified according to their early and final strength as well as their composition. In addition to cements that consist of >95% clinker, there are so-called composite cements, in which a portion of the clinker is replaced by alternative raw materials, such as fly ash, ground slag, or limestone. As the production of clinker is energy-intensive and releases large amounts of CO2, the use of alternative raw materials can conserve natural resources and reduce CO2 emissions.

Depending on the desired application, different types of cement each with a specific composition are necessary. Cement characteristics can also be modified using additives [44].

2.4.1. Manufacture of cement

There are four stages in the manufacture of portland cement: (1) crushing and grinding the raw materials, (2) blending the materials in the correct proportions, (3) burning the prepared mix in a kiln, and (4) grinding the burned product, known as “clinker,” together with some 5 percent of gypsum (to control the time of set of the cement). The three processes of manufacture are known as the wet, dry, and semidry processes and are so termed when the raw materials are ground wet and fed to the kiln as a slurry, ground dry and fed as a dry powder, or ground dry and then moistened to form nodules that are fed to the kiln [35].

2.4.2. Types of cement

1. Ordinary Portland Cement (OPC): is a type of cement that is manufactured and used worldwide. It is widely used for all purposes including:

Concrete: When OPC is mixed with aggregates and water, it makes concrete, which is widely used in the construction of buildings.

Mortar: For joining masonry and Plaster: To give a perfect finish to the walls.

Besides the afore mentioned purposes, Ordinary Portland cement is also used to manufacture grout, wall putty, solid concrete blocks, AAC blocks, and different types of cement.

2. Rapid Hardening Cement: Rapid Hardening Cement is made when finely grounded C3S is displayed in OPC with higher concrete. It is commonly used in rapid constructions like the construction pavement.

3. Portland Pozzolana Cement (PPC): To prepared PPC or Portland Pozzolana cement, it needs to grind pozzolanic clinker with Portland cement. PPC has a high resistance to different chemical assaults on concrete. It is widely used in construction such as: marine structures, sewage works, bridges, piers, dams, mass concrete works

4. Low Heat Cement: Low heat can be prepared by keeping the percentage of tricalcium aluminate below 6% and by increasing the proportion of C2S. This low heat cement is used in mass concrete construction like gravity dams. It is important to know that it is less reactive and the initial blaine is greater than OPC [34].

2.4.3. Physical properties of cement

When cement, water, aggregate, and additives are mixed together, a significant heat increase occurs. This is due to the exothermic process in the reaction between cement and water (called hydration). Measuring the concrete temperature over time enables to know how far the concrete is in the hydration process (Concrete Maturity) and thereby also an estimated concrete strength. When water and Portland cement are mixed, the constituent compounds of the cement and the water undergo a chemical reaction resulting in hardening of the concrete. This chemical reaction of the cement and the water is called hydration, and it results in new compounds called hydration products [35].

2.4.4. Physical properties of cement

Different blends of cement used in construction are characterized by their physical properties. Some key parameters control the quality of cement. The physical properties of good cement are based on: Fineness of cement, Soundness, Consistency, Strength, blaine, Heat of hydration, Loss of ignition, Bulk density and Specific gravity (Relative density) [39].

Chapter Three

Materials and Methods

3. Materials and Chemicals

Materials used in this study were PCE, Clinker, TEA and Gypsum. TEA has been used as a reference grinding aid to compare the performance of PCE. In addition to above listed chemicals and materials, the following equipment's in the table 3.1 has been used.

Table 3.1 List of equipment's

No	Equipment's
1	Mortar mixer consists of bowl and blade according EN 196-1
2	Prism molds with dimension of 40mm X 40mm X 160MM
3	Jolting apparatus
4	Compressive strength testing apparatus
5 6	Tempering tool; round, non-absorbing rod, Diameter: 40mm±1mm, Length: 200mm±10mm, Masse, Weight: 250g ±15g.
7	Flow table
8	Caliper
9	Climate 21±2C° and 60±10% rel. humidity
10	Stopwatch accuracy, 1s.
11	Pointed trowel
12	Leveling tool

The methods used to determine its effect upon grinding and final property of cement is to compare the fineness of cement, which is one of the key parameters for the strength development, milled with both PCE and without PCE within a given period of time in a laboratory ball mill, then the final characteristics of both blank cement and treated cement with PCE have been evaluated using EN 191-1 test methods. The time taken to get the specified fineness of cement has been measured. The time taken is used to evaluate treated samples by PCE and TEA and a reference blank sample has been produced for comparison. The cement used in this study is Ordinary Portland cement (95% of clinker and 5% gypsum).

3.1. Methods

Sample preparation

25% dry material content of PCE and TEA was prepared in the lab. Then, clinker and gypsum samples were collected from the mill feed at Mugar cement Ethiopia. The clinker and gypsum samples were crushed in a jaw crusher to reduce the size for milling purpose. After wards, laboratory cement has been prepared milling in a laboratory ball mill using 95% clinker, 5 % gypsum treated with 0.05, 0.10 and 0.15 % PCE and TEA. The sample cement fineness (Blaine and 32 micrometer residue) has been tested; and further properties including compressive strength and flowability has been tested.

Compressive strengths Test

The method used to determine the compressive and flexural strengths of mortar was according to EN 196-1[46]. The reference mortar consists of 450 g of cement, 1,350 g of standard CEN sand and 225 g of water. The consistency (flowability) of the standard (reference) mortar was measured according EN 13395-1:2002-09 [45]. Then, for each sample test the flowability kept constant while varying the water content (w/c). The mixing operation was carried out automatically using automatic mixer according EN 196-1 as follows: [46]

The required amount of water has been added to the mixing bowl first followed by cement, and then the mixer was immediately started at low speed, at 140±5 rotation per minute. After 30 sec of mixing, the sand was added slowly and steadily stirred for further 30 seconds. Then, the mixer was switched to high speed, at 285±10 rotation per minute, and mixing continued for additional 30 seconds. After that, the mixer was stopped for 90 seconds. At this interval the mix has been homogenized manually by plastic scraper to disperse the mortar adhering to the wall and bottom part of the bowl. Then mixing was continued again at high speed for 60 additional seconds. The spread flow of fresh mortar was measured using flow table test according to EN 13395-1:2002-09 [45]. After that, the mortar was casted into 40 x 40 x 160 mm prism steel molds and compacted on a vibrating table for 120 seconds. The specimens were then covered with a plate of glass and cured for

2 and 28 days in a humidity chamber at a temperature of 20 ± 1 ° C and 90 % relative humidity [reference(s)]. For the strength test after 28 days, the specimens were demolded after 1 day in a humidity chamber and then cured in water at 20 ± 1 ° C. After curing, the compressive and flexural strengths were measured using an instrument according EN 196-1 [46].

3.2. Design of experiment

To maximize compressive strength and to minimize the water demand of cement mortar, a Response Surface Methodology (RSM) by Central Composite Design was used. Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes. It also has important applications in the design, development, and formulation of new products, as well as in the improvement of existing product designs. RSM's target is optimization. Central composite design developed a mathematical correlation between two independent variables on compressive strength and water demand of cement mortar. In this case the two factors namely, PCE concentration and blaine for the response surface were used to determine the optimal compressive strength and water demand. For this analysis, a total of 9 experiment runs were required. PCE concentration from, 0.05%-0.15% PCE have been used. This ranges are selected based on practical dosages of commercial grinding aids based on amines and glycols [9,10]. Cement fineness with blaine value has been in a range from 3550 Cm^2/g -3887 Cm^2/g. This values are typical value of OPC type I cemnt in the industry.

Central composite design under RSM was normally performed by using design expert software, which then slightly modified to meet applicable experimental conditions. In this study, design expert (Version 13) was used as optimization software.

Table 3.2 Minimum and maximum values of compressive strength of cement/PCE process variables.

Parameters	Minimum	Maximum	Goal
PCE concentration	0.05	0.15	is in range
Blaine (Cm^2/g)	3550	3710	is in range

Table 3.3 Experimental designs

		Factor 1	Factor 2	Response 1	Response 1
Std	Run	A:PCE Concentration	B:Blaine Value	Compressive Strength	Water Demand
		%	cm2/g		
9	1	0.1	3710		
7	2	0.1	3600		
2	3	0.15	3695		
6	4	0.15	3685		
3	5	0.05	3550		
8	6	0.1	3640		
1	7	0.05	3585		
5	8	0.05	3620		
4	9	0.15	3690		

3.3. Model fitting and statistical analysis

To illustrate the dependence of compressive strength and water demand of cement mortar on PCE concentration and fineness of cement (blaine) in terms of coded values A and B respectively, the results obtained from CCD was adapted to the second order model equation. Using Design -Expert tool used to analyze the experimental results.

Chapter Four

Results and discussion

4. Results and discussion

4.1. Chemical and Mineral compositions

The chemical compositions (Table 4.1) and mineral compositions (Table 4.2) shows the composition of the cement. The physical characteristics of the diluted Polycarboxlate Ether results are presented in the following Table 4.3. These chemical and mineral compositions analysis results were typically among the primary parameters used for assessing the quality of a cement and Polycarboxlate Ether (PCE). Cement and Polycarboxlate Ether (PCE) chemical properties also have a large influence on compressive strength of cement and the quality of the final product. The three primary chemical components of interest in Cement and Polycarboxlate Ether are Chemical compositions of cement, Mineral compositions cement and the physical properties of the Polycarboxlate Ether (PCE) as presented in Table 4.1 to 4.3. The chemical composition of the cement is Al_2O_3 with mass % of 5.95, Fe_2O_3 with mass % of 3.68, MgO with mass % of 1.16, Na_2Oeq with mass % of 0.512, SO_3 with mass % of 1.28CaO, with mass % of 65.5, f-CaO with mass % of 0.62 and SiO_2 with mass % of 20.62.

Table 4.1 Chemical compositions of cement

Chemicals	Al_2O_3	Fe_2O_3	MgO	Na_2Oeq	SO_3	CaO	f-CaO	SiO_2
Mass %	5.95	3.68	1.16	0.512	1.28	65.5	0.62	20.62

Similarly, the mineral composition of the cement is C3A with mass % of 9.55, C_2S with mass % of 15, C_4AF with mass % of 11.19, C_3S with mass % of 58.52. These values are in the range of OPC type I cement. C3A contributes for the early strength, C3S for early as well as final strength and C2S contributes for the latter strength of cementitious products.

Table 4.2 Mineral compositions cement

Chemicals	C_3A	C_2S	C_4AF	C_3S
Mass %	9.55	15	11.19	58.52

Moreover, the physical properties of the Polycarboxlate Ether (PCE) results shown in Table 4.3.

Table 4.3 The physical properties of the Polycarboxlate Ether (PCE)

	units	values
pH	-	5.9
Solid matter	(%)	25
Density	(g/cm^3)	1.06

4.2. Compressive strength and Water Demand

The values are the average of replicates. The standard deviation was less than 10%.

As shown below table 4.4, the maximum and minimum values of compressive strength were 61.56 and 52.9 MPa respectively. Also, it is observed that the highest compressive strength of 61.56 MPa was obtained at experimental run number 3 with PCE Concentration of 0.15% and blaine of 3695 Cm2/g. The compressive strength results are different and the difference in compressive strength produced is affected by the variables manipulated in highest compressive strength, in this case, PCE concentration, and cement fineness (blaine). The influence of PCE concentration on compressive strength is mainly due to water to cement ration reduction [4,5].

The minimum water demand of the mortar was 204g for the given consistency with PCE concentration of 0.15% and blaine 3690 cm2/g.

Table 4.4: Experimental results

		Factor 1	Factor 2	Response 1	Response 2
Std	Run	A:PCE Concentration	B:Blaine Value	Compressive Strength	Water demand
		%	cm2/g	MPa	(g)
9	1	0.1	3710	58.1	209
7	2	0.1	3600	56.9	207
2	3	0.15	3695	61.56	203
6	4	0.15	3685	60.3	203
3	5	0.05	3550	52.9	224
8	6	0.1	3640	57.75	209
1	7	0.05	3585	54.65	225
5	8	0.05	3620	54.28	225
4	9	0.15	3690	60.93	204

4.3. Test results compared to TEA

Effect of PCE with different concentration, the effect of blaine; and their corresponding compressive strength and water demand of cement mortar has been investigated at various conditions. Blank cement and treated with PCE and TEA with different concentration were characterized for setting time, water demand and compressive strength. The fineness of the cement and average compressive strength increases as the concentration of both PCE, and TEA increased.

As we can see from below table 4.5, the fineness of the cement in terms of blaine value, is highly influenced by TEA than PCE; and the water demand of the treated cement is highly influence by PCE than TEA.

Table 4.5. Experimental results using TEA

Additive name	GA dosage	Blaine (CM2/g)	Fresh Feed		Water Demand (mm)for 170mm DF	Compressive Strength
			Clinker	Gypsum		28d
TEA	0.05	3798	95%	5%	225	55.895
	0.1	3887	95%	5%	220	56.06
	0.15	3856	95%	5%	220	60.945

4.4. Analysis of variance (ANOVA)

Optimization of the compressive strength was carried out using a central composite design with two factors (PCE concentration, and Blaine) with two response which was compressive strength (MPa) and water demand (g). Statistical analysis was carried out to determine the correlation coefficients of the model as a function of the responses. The sequential model sum of squares for compressive strength is summarized.

4.4.1. ANOVA for Response Surface

4.4.1.1. ANOVA for Compressive Strength Response Surface Linear model

To determine whether or not the linear model is significantly affected by the Parameters listed in the design, it was crucial to perform an analysis of variance (ANOVA). The Probability values (P-values) were used to perform as a device to check the significance of each coefficient, which also showed the interaction strength of each parameter. The smaller the p-values are, the bigger the significance of the corresponding coefficient.

Table 4.6: Analysis of variance for the linear model for compressive strength in test cement mortar.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	74.87	2	37.43	135.74	< 0.0001	significant
A-PCE Concentration	16.40	1	16.40	59.49	0.0002	
B-Blaine Value	1.65	1	1.65	5.97	0.0503	
Residual	1.65	6	0.2758			
Cor Total	76.52	8				

F- Value is a test for comparing model variance with residual (error) variance. The Model F-value of 135.74 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case PCE concentration ‘’A’’ is a significant model term.

Coefficient of variation, the standard deviation expressed as a percentage of the mean; predicted Residual Error sum of squares, which is a measure of how the model fits each point in the design. The R- squared, measure of the amount of Varian around the mean explained by the model; Adj R- squared, a measure of the amount of variation in new data explained by the model, and Adequate precision, this is a signal to disturbance ratio due to random error. Presented table below, are used to decide whether the model can be used or not.

Table 4.7 Model adequacy measures

Std. Dev.	0.5251	**R^2**	0.9784
Mean	57.49	**Adjusted R^2**	0.9712
C.V. %	0.9135	**Predicted R^2**	0.9465
		Adeq Precision	24.8267

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. This ratio of 24.8267 indicates an adequate signal. This model can be used to navigate the design space. The difference between R-squared and Adj R-squared is way less than 0.2 which is 0.0072. This implies the experimental data is good fit at linear model.

4.4.1.2. Development of regression model equation

A model equation is a mathematical expression in which the whole model was expressed in a single equation that helps to maximize response. The model equation that correlates the response which is compressive strength to the process variables in terms of actual value after excluding the insignificant terms was given below.

4.4.1.3. Final Equation in Terms of Coded Factors

The software recommended a linear model, which was used to explain the mathematical relationship between the independent variables and the dependent response. The regression model was obtained for both coded and actual factors, with a positive sign representing synergistic influence and a negative sign representing antagonistic influence. The final equation in terms of coded actors is given by:

$$Compressive\ strength\ = 57.19 + 2.78A + 0.9458B$$

where A-PCE concentration and B-blaine.

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. Thus, we can see from the equation that, PCE concentration has more significance then the blaine value.

4.4.1.4. Normal probability plot

The normal probability plot, (Fig 4.1), indicates the residuals following by the normal % probability distribution. In the case of this experimental data the points in the plots are in a good fit to the straight line; this shows that the linear model satisfies the analysis of the assumptions of variance (ANOVA) i.e., the error distribution is approximately normal.

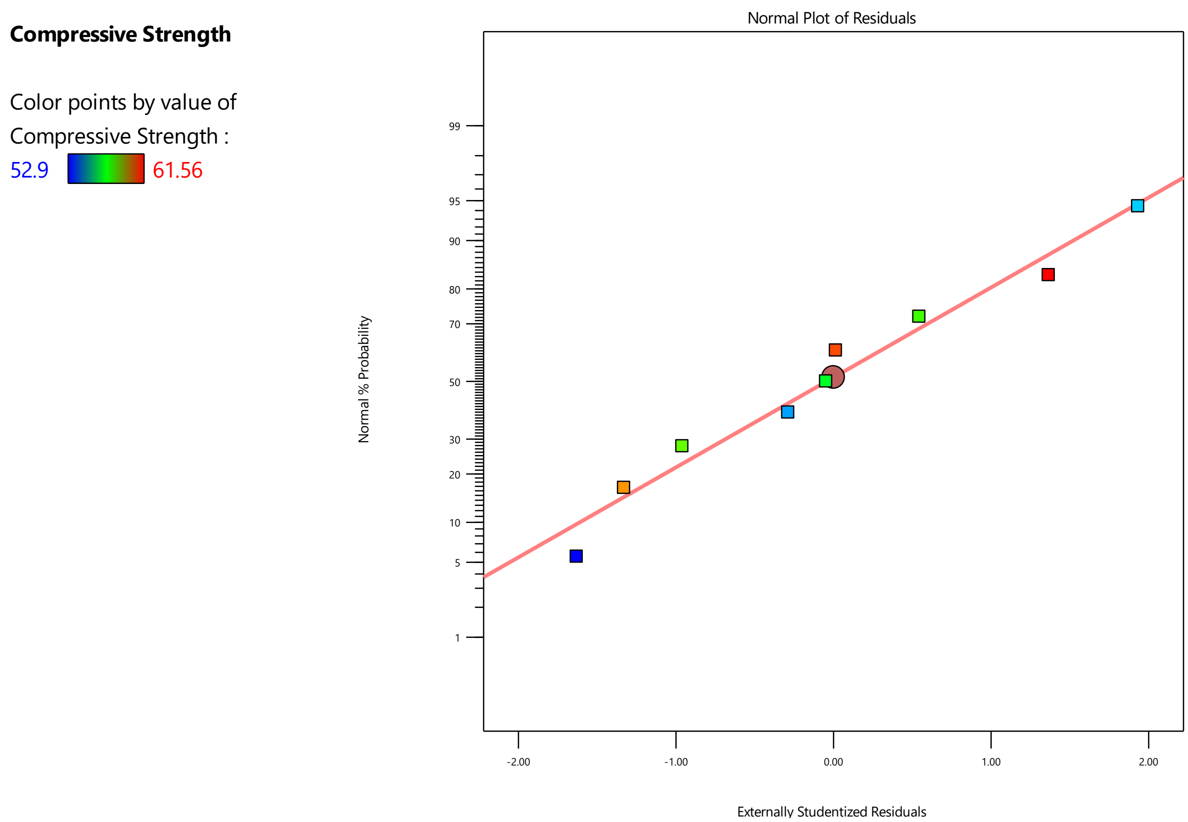

Figure 4.1: Normal probability plot of residuals versus studentized residuals values of compressive strength

4.4.1.5. Residual versus predicted plot

If the model is correct and the assumptions are satisfied, the residuals should be structured less; in particular, they should be unrelated to any other variable including the predicted response. A simple check is to plot the residuals versus the fitted (predicted) values. A plot of the residuals versus the predicted response values tests the assumption of constant variance. The plot shows random scatter which justifying no need for any alteration to minimize personal error (Fig 4.2).

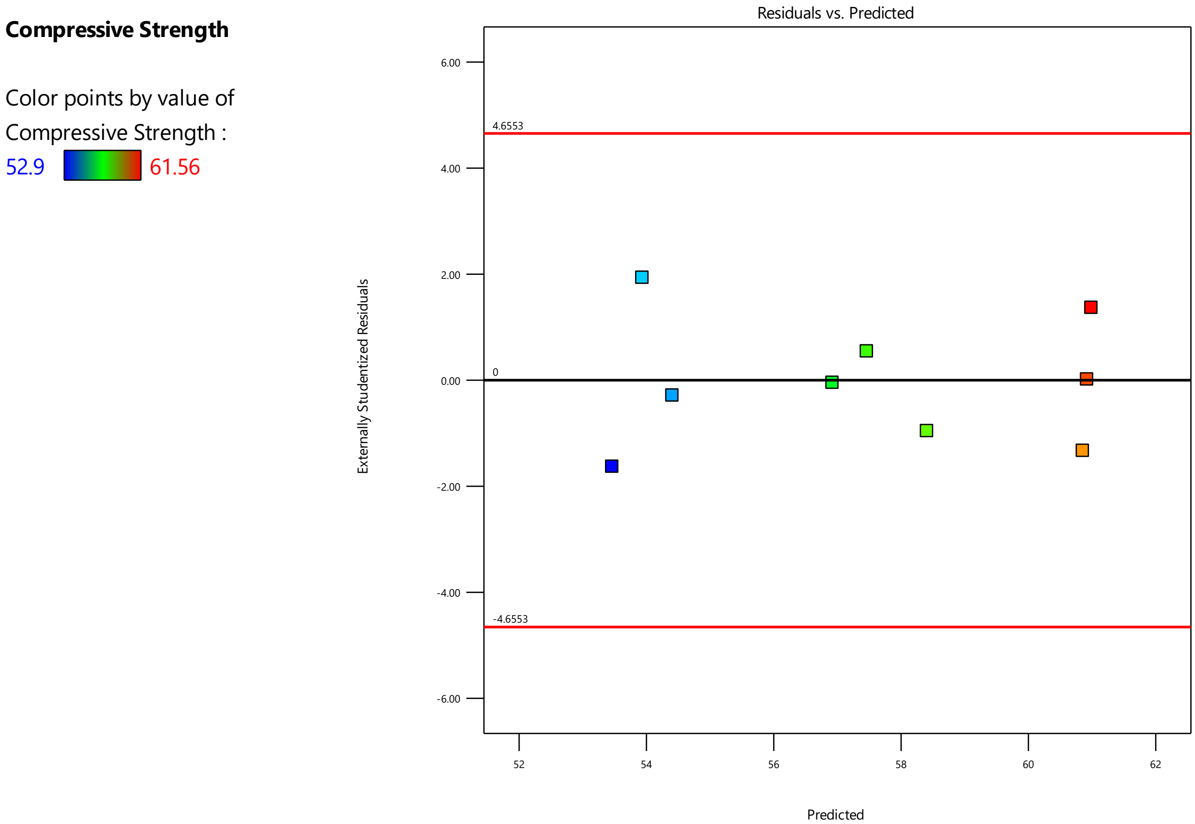

Figure 4.2: Studentized residuals versus predicted values of compressive strength

4.4.1.6. Interaction effect Blaine and PCE concentration

From the interaction plot of blaine and PCE concentration (Figure 4.3) the - compressive strength slightly increased as Blaine increased and highly compressive strength highly increased with PCE concentration increased. The impact of the blaine is due to the fact that the higher the surface area increases the possibility of higher hydration reaction of cement [14, 18]. And the significant impact of PCE concentration on the strength development is highly related to the water cement ratio (water demand) reduction. [9,10]

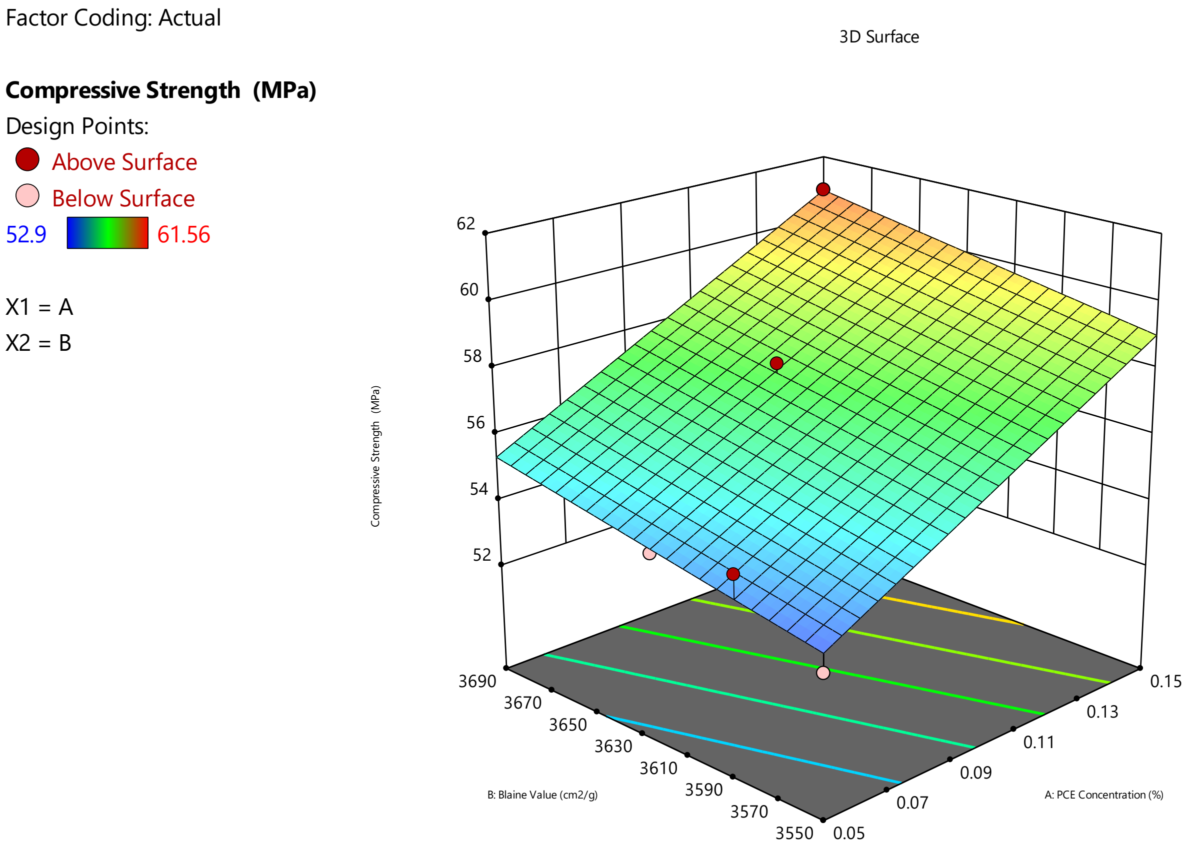

Figure 4.3: Response surface plots of the effect of Blaine and PCE concentration on compressive strength.

4.4.1.7. Determination of the optimum operating conditions

The effects of the operating conditions on the compressive strength from cement/PCE composite were investigated and the optimal values for the given cement composition and type were determined in this study as shown in Table 4.7 and Figure 4.6-4.8. From Table 4.7 and Figure 4.6-4.8 it is observed that the desirability was 0.926 at PCE concentration of 0.15 and Blaine of 3690 cm^2/g and resulted in compressive strength of 60.92 MPa. Figure 4.6 to 4.8 present the desirability and optimized contour plots and they are showing the desirability at the optimized parameters by taking two factors at a time and by keeping other variable at the center point.

Table 4.8: optimized solution of compressive strength from cement/PCE composite

Number	PCE Concentration	Blaine Value	Compressive Strength	Desirability	
1	**0.150**	**3690.000**	**60.923**	**0.926**	**Selected**
2	0.150	3686.672	60.878	0.921	
3	0.150	3681.741	60.811	0.914	
4	0.147	3689.999	60.769	0.909	
5	0.150	3671.915	60.678	0.898	
6	0.150	3668.827	60.637	0.893	
7	0.150	3668.009	60.625	0.892	
8	0.150	3661.812	60.542	0.882	
9	0.150	3655.604	60.458	0.873	

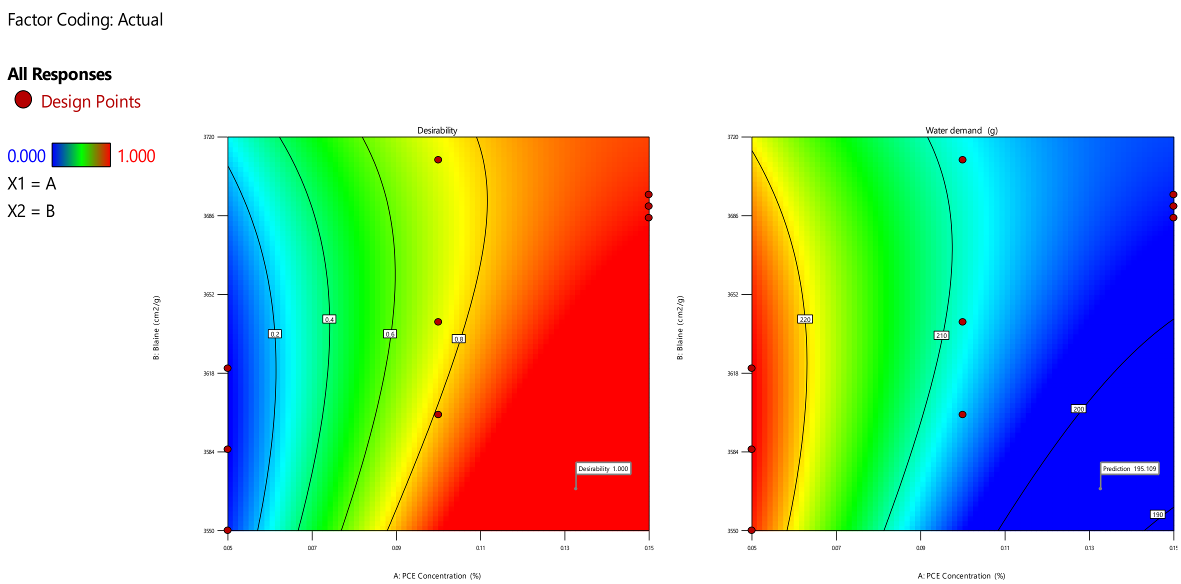

Figure 4.4: Contour plots of the effect of blaine and PCE concentration on compressive strength.

4.4.1.8. Model validation

Using the optimized condition obtained from the central composite design an experiment was conducted for cement/PCE composite and an optimized compressive strength of 60.92

MPa- was obtained and it is possible to say that this is in good agreement with the predicted one. Thus, the model can be considered to be accurate and reliable for predicting the compressive strength of cement/PCE composite of this particular cement. However, cement qualities and compositions highly fluctuated. Thus, the model can only give indications about the significant impact of PCE concentration on the strength development of cement.

4.4.1.9. ANOVA for water demand Response Surface quadratic model

To determine whether the quadratic model is significantly affected or not by the parameters listed in the design, analysis of variance (ANOVA) has been performed. The Probability values (P-values) were used to check the significance of each coefficient, which also showed the interaction strength of each parameter.

Table 4.6: Analysis of variance for the quadratic model for compressive strength in test cement mortar.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	750.11	5	150.02	574.58	0.0001	significant
A-PCE Concentration	87.29	1	87.29	334.31	0.0004	
B-Blaine	2.57	1	2.57	9.83	0.0518	
AB	0.9936	1	0.9936	3.81	0.1462	
A^2	1.44	1	1.44	5.53	0.1002	
B^2	1.12	1	1.12	4.29	0.1302	
Residual	0.7833	3	0.2611			
Cor Total	750.89	8				

F- Value is a test for comparing model variance with residual (error) variance. The Model F-value of 574.58 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case PCE concentration ''A'' is a significant model term.

Residual Error sum of squares, which is a measure of how the model fits each point in the design also evaluated.

Table 4.7 Quadratic model adequacy measures for water demand

Std. Dev.	0.5110	**R^2**	0.9990
Mean	212.11	**Adjusted R^2**	0.9972
C.V. %	0.2409	**Predicted R^2**	0.9941
		Adeq Precision	52.5945

The Adeq Precision result of 52.5945, mach higher than 4, indicates an adiuate signal. measures the signal to noise ratio. The difference between R-squared and Adj R-squared is also way less than 0.2 which is 0.0018. This implies the experimental data is good fit at quaratic model.

4.4.1.10. Final Equation in Terms of Coded Factors

Based on the model fit evaluation results, quadratic model was used to explain the mathematical relationship between the independent variables and the dependent response. The regression model was obtained for both coded and actual factors. The final equation in terms of coded factors is given by:

$$Water\ Demand\ = 208.78 - 12.66A + 2.89B + 5.14AB + 3.29A^2 - 3.02B^2$$

where A-PCE concentration and B-blaine.

From the equation we can see that, PCE concentration (A), has very significant impact to reduce the water demand of cement mortar.

4.4.1.11. Normal probability plot

The normal probability plot, (Fig 4.5), indicates the residuals following by the normal % probability distribution. In the case of this experimental data the points in the plots are in a good fit to the straight line; this shows that the quadratic model satisfies the analysis of the assumptions of variance (ANOVA) i.e., the error distribution is approximately normal.

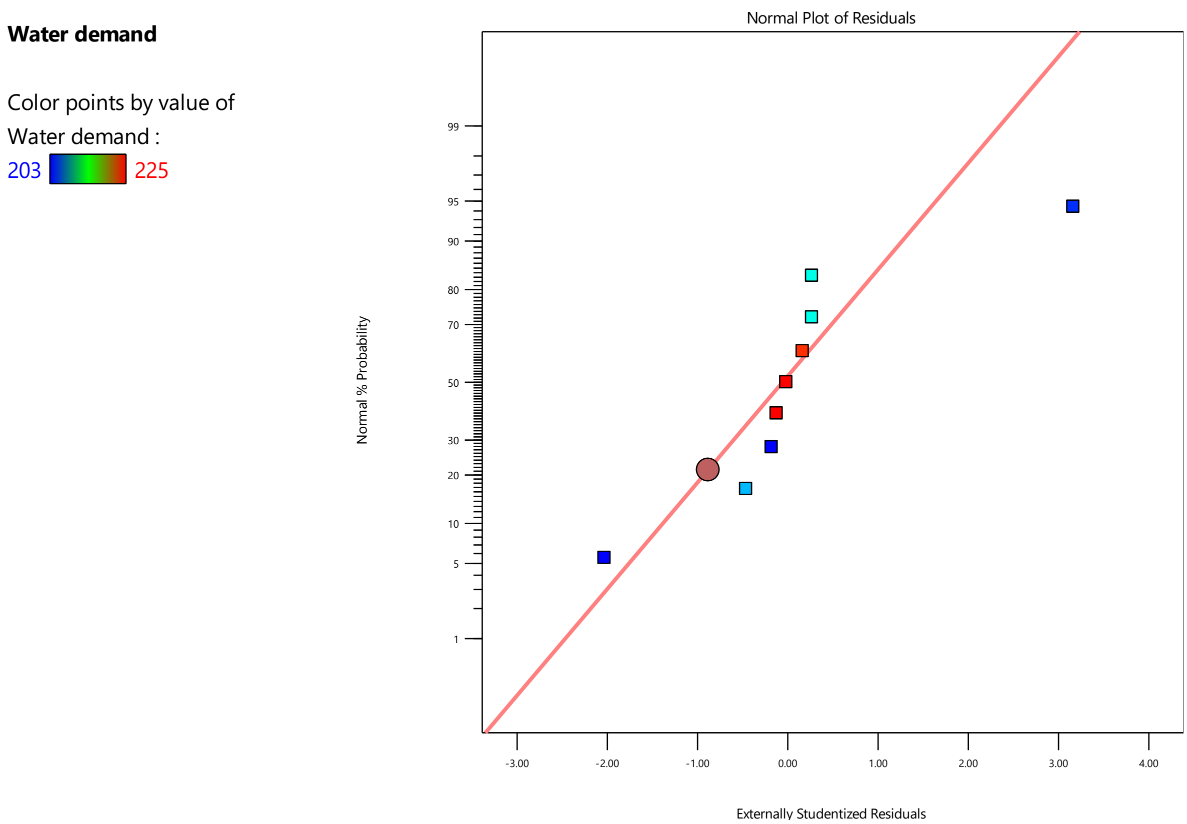

Figure 4.5: Normal probability plot of residuals versus studentized residuals values of mortar model demand.

4.4.1.12. Residual versus predicted plot

As we can see from Fig 4.6 below, the residuals are structured less and unrelated to any other variable including the predicted response. This indicates the model is correct and the assumptions are satisfied. And the plot of the residuals versus the fitted (predicted) values are randomly scattered, which justifying no need for any alteration to minimize personal error.

Water demand

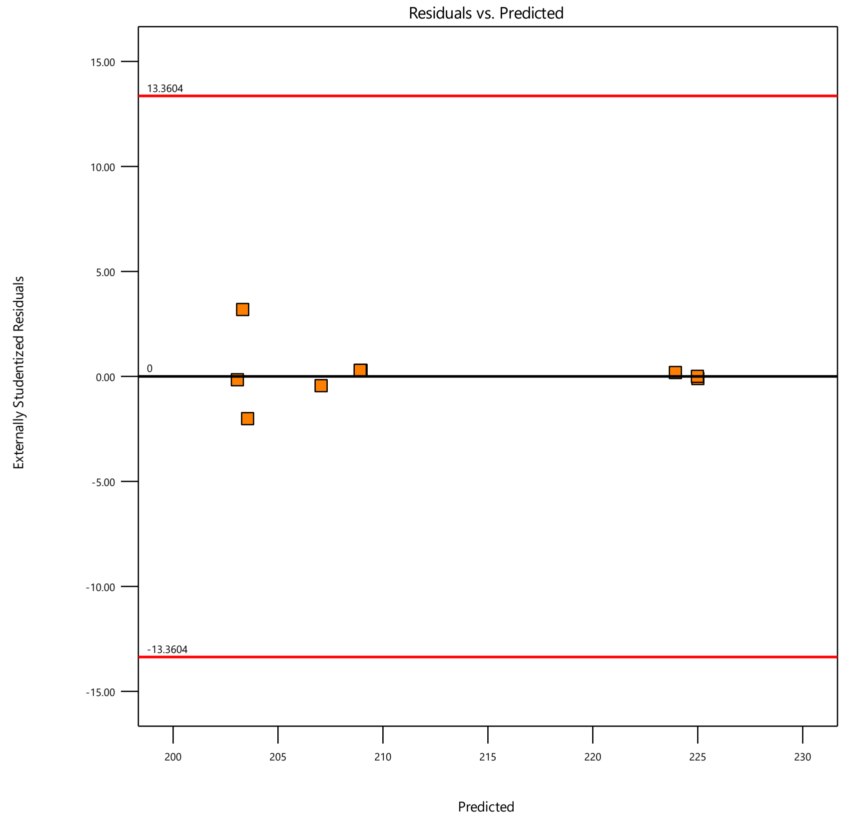

Figure 4.6: Studentized residuals versus predicted values of compressive strength

4.4.1.13. Interaction effect Blaine and PCE concentration

From the interaction plot of blaine and PCE concentration (Figure 4.7) the water demand dramatically decreases with the increase of PCE concentration. This result confirms that the PCE introduced to the cement grinding process still performs as water reducer to the final cement.

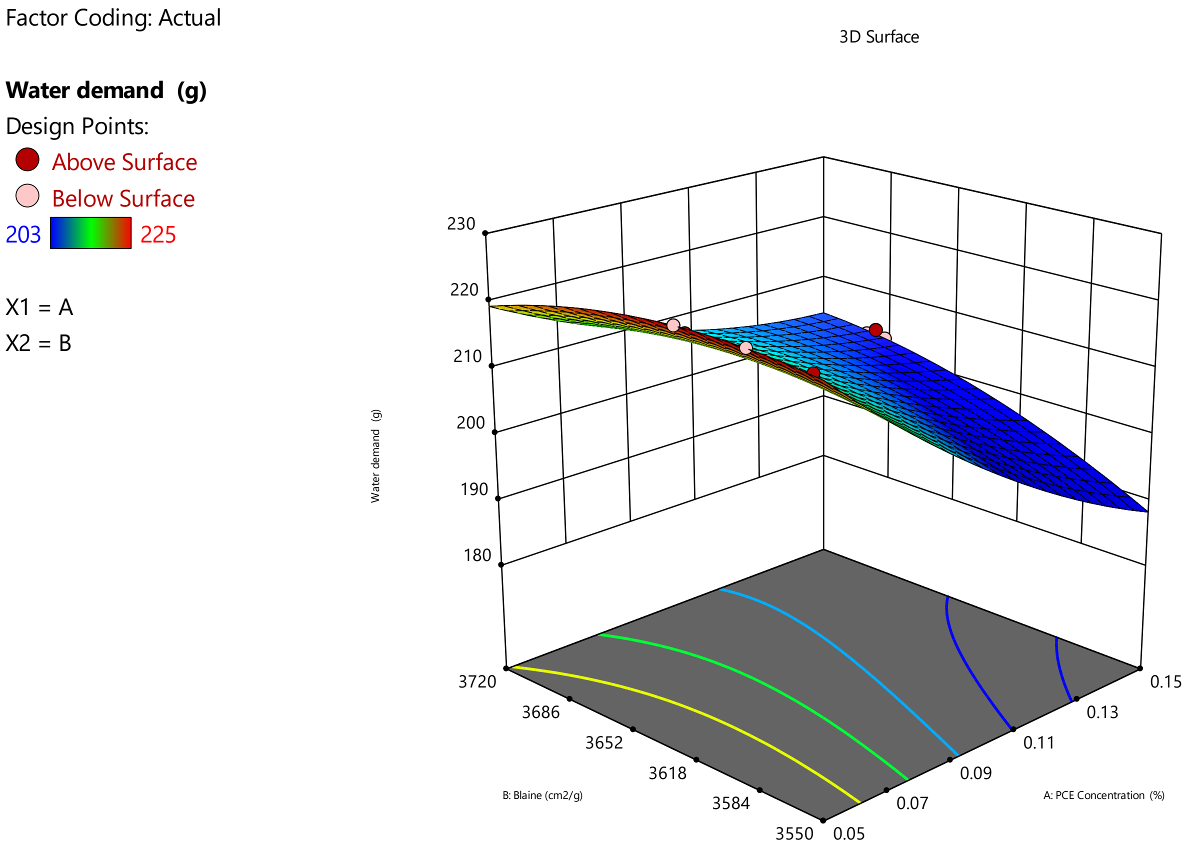

Figure 4.7: Response surface plots of the effect of Blaine and PCE concentration on water demand.

4.4.1.14. Optimization of water demand using response surface methodology

The effects of the operating conditions on the water demand of treated cement were investigated and the optimal values for the given cement composition and type were determined in this study, as shown Figure 4.8. From the figure, it can be observed that the desirability was 1.00, at PCE concentration of 0.149 and Blaine of 3676 cm^2/g and resulted water demand of 202.7g. The desirability and optimized contour plots below are showing the desirability at the optimized parameters by taking two factors at a time and by keeping another variable at the center point.

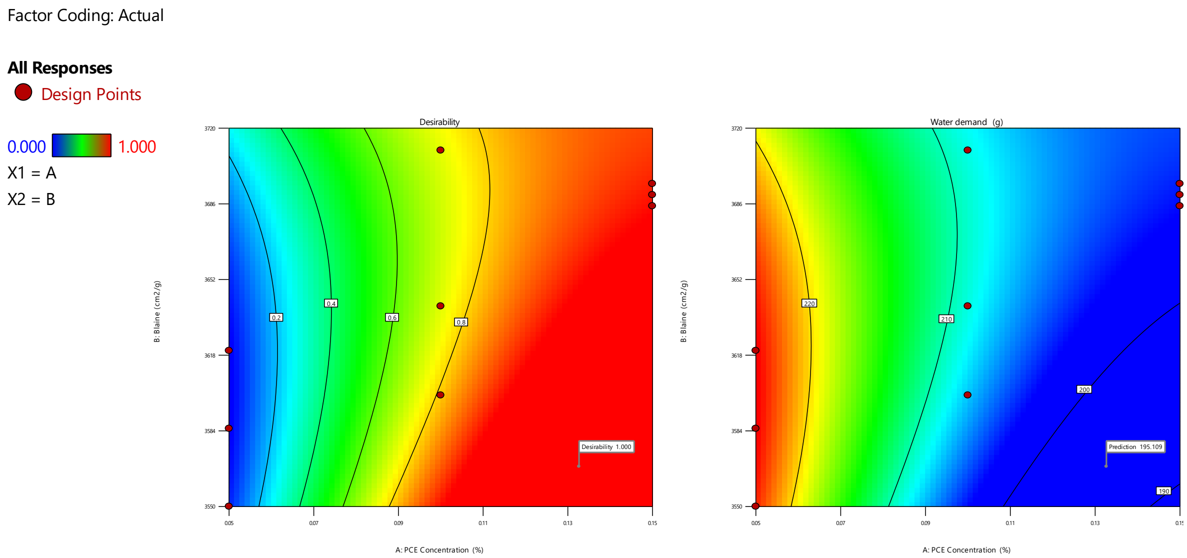

Figure 4.8: Contour plots of the effect of blaine and PCE concentration on compressive strength.

4.4.1.15. Model validation

Using the optimized condition obtained from the central composite design an experiment was conducted for cement/PCE composite and an optimized water demand of 202.7 g was obtained, and it is possible to say that this is in good agreement with the predicted one. Thus, the model can be accurate and reliable for predicting the water demand of this cement. However, cement qualities and compositions highly fluctuated. Thus, the model can only give indications about the significant impact of PCE concentration on the water demand of a given cement.

Chapter Five

Conclusion and recommendations

5. Conclusion and recommendations

5.1. Conclusion

This study investigated the effect of PCE concentration and blaine value on cement mortar compressive strength and water demand. Response Surface Methodology based on central composite design experiments was used to optimize process parameters for compressive strength of PCE treated cement mortar. A statistical model for the compressive strength of PCE/cement conditions such as PCE concentration and blaine was developed using two-level CCD experiments with central and axial points. From the analysis of variance, it was observed that all parameters have a significant effect on compressive strength. The optimum compressive strength of 60.92 MPa was obtained at PCE concentration of 0.15 % and blaine amount of 3690 cm^2/g. Since the experimental result is in accordance with the model predicted value; it shows that the reliability of the predicted linear model.

The laboratory tests have been done using laboratory ball mill, which is a closed batch system, different from plant mill which is a continuous system. PCE will have more impact since it will reduce agglomeration of cement particles in the classifier [7]. Thus, further studies can be done with plant scale to study the full impact of PCE.

Based on the results found in this research and from previous studies, it can be concluded that PCE can slightly improve the fineness of cement while used in cement grinding and the resulting cement will have lower water demand according to the PCE dosage.

One of the challenges for the new developed calcined clay cement is, the higher water demand compared to other cement types. The results obtained in this research would be a starting point for further research on the PCE effects in calcined clay cement.

5.2. Recommendations

Further research work on compressive strength of PCE/cement production should:

- ❖ Study on Sample characterizations using Scanning electron microscope–backscattered electron
- ❖ Investigate microstructure of cement paste/PCE

References

[1] C.A. Hendriks, E. Worrell, D. de Jager, K. Blok, P. Riemer, Emission reduction of greenhouse gases from the cement industry, In: The proceeding of the greenhouse gas control technologies conference. http://www.wbcsdcement.org/pdf/tf1/prghgt42.pdf, **2004** (accessed 23.08.04).

[2] World Business Council for Sustainable Development (WBCSD) and International Energy Agency (IEA), Cement technology roadmap 2009: carbon emissions reductions up to 2050, **2009**, 1-36.

[3] W. Shen, L. Cao, Q. Li, W. Zhang, G. Wang, C. Li, Quantifying CO2 emissions from China's cement industry, Renewable and Sustainable Energy Reviews, 50, **2015**, 1004-1012.

[4] R. M. Edmeades, P.C. Hewlett, Cement admixtures, In: P.C. Hewlett Lea's chemistry of cement and concrete, fourth ed., Butterworth-Heinemann Publishing, Oxford, **2003**, 841-905.

[5] Mishra, R. K.: Simulation of interfaces in construction materials: tricalcium silicate, gypsum and organic modifiers, Ph.D. Dissertation, University Akron, USA, 2012

[6] Mishra, R. K., Flatt, R. J., Heinz, H.: Force field for tricalcium silicate and insight into nanoscale properties: cleavage, initial hydration, and adsorption of organic molecules, J. Phys. Chem. C 2013 (117), pp. 10417–10432

[7] Mishra, R. K., Flatt, R. J.: Understanding the Effectiveness of Polycarboxylates as Grinding Aids 2012.

[8] Choi, H., Lee, W., Kim, S.: Effect of grinding aids on the kinetics of fine grinding energy consumed of calcite powders by a stirred ball mill, Advanced Powder Technology 2009 (20), pp. 350 354

[9] Heller, T., Müller, T., Honert, D.: Cement additives based on PCE, ZKG International 2-2011, and pp. 40–48

[10] Assaad, J. J., Asseily, S. E.: Use of water reducers to improve grindability and performance of Portland cement clinker, ACI Materials Journal November-December 2011 (108, 6), pp. 619-627

[11] T. Hirata, Japanese Patent JP 84 (**1981**) 2022 (S59-018338).

[12] K. Mitsui, T. Yonezawa, M. Kinoshita, T. Shimono, Application of a new superplasticizer for ultra-high strength concrete. In: 4th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, 148, **1994**, 27-46.

[13] H. Okamura, M. Ouchi, Self-compacting concrete - Development, present and future. In: First International RILEM Symposium on Self-Compacting Concrete, 7, **1999**, 3-14.

[14] J. Plank, C. Schröfl, M. Gruber, Use of a supplemental agent to improve flowability of ultra-high performance concrete, Proceedings of Ninth ACI international Conference, Superplasticizers and Other Chemical Admixtures in Concrete SP-262, **2009**, 1-16.

[15] V. S. Ramachandran, V. M. Malholta, Superplasticizers, In: V. S. Ramachandran (Ed), Concrete Admixture Handbook 2nd edition, Noyes Publications, Park Ridge, NJ, **1996**, 410-517.

[16] H. Uchikawa, S. Hanchara, D. Sawaki, The role of steric repulsion force in the dispersion of cement particles in fresh paste prepared with organic admixture, Cement and Concrete Research, 27 (1), **1997**, 37-50.

[17] E. Sakai, A. Ishida, A. Otha, New trends in the development of chemical admixtures in Japan, Journal of Advanced Concrete Technology, 4 (2), **2006**, 211-223.

[18] J. Plank, PCE superplasticizers – chemistry, applications, and perspectives, ZKG International 67, Drymix Special, 1, **2014**, 48-59.

[19] K. Yoshioka, E. Tazawa, K. Kawai, T. Enohata, Adsorption characteristics of superplasticizers on cement component minerals, Cement and Concrete Research, 32 (10), **2002**, 1507-1513.

[20] J. Plank and C. Hirsch, Superplasticizer adsorption on synthetic ettringite, In: V. M. Malhotra (Ed), Seventh CANMET/ACI Conference on Superplasticizers in Concrete (Editor), ACI, Berlin, SP-217-19, **2003**, 283-298.

[21] J. Plank, C. Hirsch, Impact of zeta potential of early cement hydration phases on superplasticizer adsorption, Cement and Concrete Research, 37, **2007**, 537-542.

[22] A. Zingg, F. Winnefeld, L. Holzer, J. Pakusch, S. Becker, L. Gauckler, Adsorption of polyelectrolytes and its influence on the rheology, zeta potential, and microstructure of

various cement and hydrate phases, Journal of Colloid and Interface Science, 323, **2008**, 301-312.

[23] K. Yoshioka, E. Sakai, M. Daimon, A. Kitahara, Role of steric hindrance in the performance of superplasticizers for concrete, Journal of the American Ceramic Society, 80 (10), **1997**, 2667-2671.

[24] A. Ohta, T. Sugiyama, Y. Tanaka, Fluidizing mechanism and application of polycarboxylate-based superplasticizers, In: V. M. Malhotra (Ed), Fifth CANMET/ACI Conference on Superplasticizers in Concrete, ACI, Rome, SP-173, **1997**, 359 – 378.

[25] J. Plank, E. Sakai, C.W. Miao, C. Yu, J.X. Hong, Chemical admixtures – Chemistry, applications and their impact on concrete microstructure and durability, Cement and Concrete Research, 78, **2015**, 81-99.

[26] G. Gelardi, S. Mantellato, D. Marchon, M. Palacios, Chemistry of chemical admixtures, In: P.-C. Aïtcin, R.J. Flatt (Eds.), Science and Technology of Concrete Admixtures, Elsevier (Chapter 9), **2016**, 149-218.

[27] D. Rinaldi, T. Hamaide, C. Graillat, F. D'Agosto, R. Spitz, S. Georges, M. Mosquet, P. Maitrasse, RAFT copolymerization of methacrylic acid and poly(ethylene glycol) methyl ether methacrylate in the presence of a hydrophobic chain transfer agent in organic solution and in water, Journal of Polymer Science Part A: Polymer Chemistry, 47 (12), **2009**, 3045-3055.

[28] S. Pourchet, S. Liautaud, D. Rinaldi, I. Pochard, Effect of the repartition of the PEG side chains on the adsorption and dispersion behaviors of PCP in presence of sulfate, Cement and Concrete Research, 42, **2012**, 431-439.

[29] J. Plank, K. Pöllmann, N. Zouaoui, P.R. Andres, C. Schaefer, Synthesis and performance of methacrylic ester based polycarboxylate superplasticizers possessing

hydroxyl terminated poly(ethylene glycol) side chains, Cement and Concrete Research, 38, **2008**, 1210-1216.

[30] S. Akimoto, S. Honda, T. Yasukohchi, Additives for cement, EP 0,291,073, **1992**.

[31] G. Albrecht, J. Weichmann, J. Penkner, A. Kern, Copolymers based on oxyalkylene glycol alkenyl ethers and derivatives of unsaturated dicarboxylic acids, EP 0,736,553, **1996**.

[32] D. Hamada, F. Yamato, T. Mizunuma, H. Ichikawa, Additive mixture for cement-based concrete or mortar contains a copolymer of polyalkoxylated unsaturated acid and a mixture of alkoxylated carboxylic acid with a corresponding ester and/or an alkoxylated alcohol, DE 10,048,139 A1, **2001**.

[33] M. Yamamoto, T. Uno, Y. Onda, H. Tanaka, A. Yamashita, T. Hirata, N. Hirano, Copolymer for cement admixtures and its production process and use, US 6,727,315, **2004**.

[34] L. Ferrari, J. Kaufmann, F. Winnefeld, J. Plank, Interaction of cement model systems with superplasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements, Journal of Colloid and Interface Science, 347, **2010**, 15- 24.

[35] K. Yamada, T. Takahashi, S. Hanehara, M. Matsuhisa, Effects of the chemical structure on the properties of polycarboxylate-type superplasticizer, Cement and Concrete Research, 30, **2000**, 197-207.

[36] E. Sakai, K. Yamada, A. Ohta, Molecular structure and dispersion-adsorption mechanisms of comb-type superplasticizers used in Japan, Journal of Advanced Concrete Technology, 1 (1), **2003**, 16-25.

[37] Sohoni, S., Sridhar, R., Mandal, G. Powder Technology **1991**, 67, 277-286.

[38] J. Plank, B. Sachsenhauser, Impact of molecular structure on zeta potential and adsorbed conformation of A-allyl-ω-methoxypolyethylene glycol – maleic anhydride superplasticizers, Journal of Advanced Concrete Technology, 4 (2), **2006**, 233-239.

[39] J. Plank, C. Schroefl, M. Gruber, M. Lesti, R. Sieber, Effectiveness of polycarboxylate superplasticizers in ultra-high strength concrete: The importance of PCE compatibility with silica fume, Journal of Advanced Concrete Technology, 7 (1), **2009**, 5-12.

[40] H.F.W. Taylor, Hydrated calcium silicates: part I. Compound formation at ordinary temperatures, Journal of the Chemical Society, 3, **1950**, 3682-3690.

[41] Heinz, H.; Suter, U. W., "Atomic Charges for Classical Simulations of Polar Systems" J. Phys. Chem. B 2004, 108, 18341-18352.

[42] J. Plank, B. Sachsenhauser, Experimental determination of the effective anionic charge density of polycarboxylate superplasticizers in cement pore solution, Cement and Concrete Research, 39, **2009**. 1-5.

[43] Heinz, H.; Lin, T. Z.; Mishra, R. K.; Emami, F. S., "Thermodynamically Consistent Force Fields for the Assembly of Inorganic, Organic, and Biological Nanostructures: The INTERFACE Force Field" Langmuir 2013, 29, 1754-1765.

[44] T. Nawa, Effect of chemical structure on steric stabilization of polycarboxylate-based superplasticizer, Journal of Advanced Concrete Technology, 44, **2006**, 225-232. entation of mixed corn stover and cow dung." Energy 46(1): 644-648.

[45] EN 13395-1:2002-09, Products and systems for the protection and repair of concrete structures - Test methods; Determination of workability - Part 1: Test for flow of thixotropic mortars; EN 13395-1:2002

[46] EN 196-1, Methods of testing cement - Part 1: Determination of strength