Eindhoven University of Technology

MASTER

The smart use of waste nano-silica rich sludge from photovoltaic production process as a sustainable cement replacement

survey of self-compacting concrete (SCC) adaption for smart and special building constructions by waste nano-silica rich sludge (from the PV industry)

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Beton
Bewust

Kijlstra
Betonmortel

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Graduation Thesis

Written in the graduation atelier Slimbouwen IV (2012) at the Department of the Built Environment, Unit Building Technology with collaboration of the Unit of Building Physics & Services

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This report is the final report of a study that was done for the master's degree for the master track Architecture, Building and Planning. The report has also served as a touchstone for assessing the Master Degree in Architecture, Building and Planning. Common conclusions in the report, results and calculations may require further investigation before for external use is suitable.

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In loving memory of Bert van der Putten, my dad.

I. Preface

Graduating, that's a real challenge. Finally the time is there to close this chapter with writing this thesis. After a long way of studies now for almost 10 years MBO, HBO, and University I can say I took this challenge. My study was just like a concrete plant from every silo you get a additive and at the end you have your mixture. In the beginning, I didn't know if it is a challenge but now can I say, "A challenges it is", but challenges are the way of growing to that one point in life where you can say, "I did it, and not many can say that" I am very grateful for this chance and this experience that is given to me. A long period of intensive work, research, health problems and the social life can only be appropriately handled with a lot of help, support and input of friends and the help of several partners with guide me to the end. Some people I want to address individually.

On the first place George Quercia Brianchi my daily supervisor, He gave me the opportunity to join the Self-Compacting Concrete field, together with Kijlstra Betonmortel. He provide me with all the necessary input, guidance, discussions and time in guiding me to write this thesis.

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My sincere thanks go to all my former colleagues students from the Department Built Environment, where I studied until December, 2012 on this Thesis. In particular:

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Koen Arts, you truly deserve an own paragraph. I thank you for being a good colleague, study mate and friend, for the last years. I owe you so much. Your patience with me (That was not always easy), your help and input, the fruitful discussions and the spare time and all the trips we shared they are greatly appreciated. I wish you all the best for your personal and professional future.

Finally, I am deeply indebted to my family that supported my during this year, in particular to my mom and sisters, who have always supported and encouraged me to go further. To you I owe the most mom standing by my side when I needed it ruff times, when we lost dad on young age. Ever since I we where little kids you tried to open the right doors for us and gave good advice which way to go. This Thesis is a fruit of your continuous support. As the very last I want to thank all of my friends I didn't mentioned above for believing in me and have the patience and the respect for me.

Thank you!
Jeffrey van der Putten
Heesch augustus 2012

**‘Only when the last tree
has died, the last river been
poisoned, and the last fish
been caught will we realize
we cannot eat money’**

19th Century Cree Proverb

II. Summary

Concrete material has been a serious aspect of civilized progression and can be examined throughout history, for example early progressions toward a more sophisticated form of building and use of building materials can be seen in early Egyptian and Roman communities. Concrete is a material can transform a civilization and bring communities toward a more developed and progressive state of living. The use of concrete provides people with the opportunity to create logistical structures that are stronger and more resistant to all sorts of external influence such as weather. The influence of concrete material on sate of civilization has been a significant topic of interest throughout the past and continues to play a fundamental role in our current global state of civilized progression. There is a vast array of prevalent issues surrounding the production and use of concrete materials. In particular, pivotal research is being done in regards to the workability of concrete as well as more concerning research on environmental issues stemming from the emissions being released into the atmosphere during the production of concrete materials. With this in mind it is important to note that this thesis research contributes to the growing interest in the development and effects of concrete material on civilization today. This thesis addresses several current and leading issues within the concrete industry, and provides specific research on the redevelopment of the concrete material using nano-Silica rich Sludge (nSS) as a replacement raw material. The research done in this thesis pays particular attention to the use and effects of nSS as a replacement material in concrete, however, the results of the research study have also provided insight directly related to the global environmental effort in reducing the amount of environmental damage being done by the concrete industry.

This research is completed in cooperation with Kijlstra Betonmortel B.V. Kijlstra Betonmortel Vianen is focused on delivering concrete products and related services for factory and construction. Kijlstra Vianen is specialized in Self-Compacting Concrete (SCC) for the manufacture of prefabricated elements, all strengths and environmental class's. The subject of this research was to investigate the possibility of the partial replacement of the raw material in Self-Compacting Concrete, Portland Cement (CEM I 52,5R) that abides by the current process constraints. SCC is produced with the combination the ingredients including cement, lime, gypsum, quartz and superplasticizers that are all mixed together with water. SCC has special recognition as a valuable concrete product due to the superior ability SCC has to flow and fill all cavities of formwork without defects only under the influence of gravity. As a result of the combined high ability to flow and stability, SCC encapsulates steel reinforcement without blocking aggregates. SCC can save up to 50% in labor costs due to 80% faster pouring and reduced wear and tear on formwork. As of 2005, self-consolidating concretes account for 10-15% of concrete sales in some European countries. In the US precast concrete industry, SCC represents over 75% of concrete production

In this study, a waste product from the photovotalic industry in South Korea called nano-Silica rich Sludge (nSS) was used as an additive to the SCC concrete mixture for research purposes aimed at the possible recycling of waste materials in concrete mixtures. A literature review was conducted prior to the experimental work to determine the impact of the partial substitution of additives on the SCC performance. Nano-Silica rich Sludge is a material involved with the

creation of solar panels. The process of creating a solar panels typically starts by cutting crystalline silicon into tiny disks less than a centimeter thick. These thin, wafer-like disks are then carefully polished and treated to repair and gloss any damage from the slicing process. After polishing, do pants (materials added to alter an electrical charge in a semiconductor or photovoltaic solar cell) and metal conductors are spread across each disk. The conductors are aligned in a thin, grid-like matrix on the top of the solar panel, and are spread on a flat thin sheet on the side facing the earth. All the materials on the panel that are abraded are part of the nSS.

Concrete is the most widely used artificial construction material in the world. Unfortunately, the production process of Portland cement an essential constituent of concrete leads to a significant release of CO_2 a greenhouse gas. The production of one ton of Portland cement clinker generates one ton of CO_2 emission due to raw material calcinations and fuel consumption according to the Cement&BetonCentrum (2011). Global cement production is responsible for 5-8% of the world's carbon dioxide emissions; environmental issues will play a leading role in the sustainable development of the cement and concrete industry in this century. The emission of $CO_2$and the scarcity of raw materials make it desirable to find alternatives to reduce the amount of Portland cement needed in concrete production. Cement is made of limestone which is becoming a scarce resource. There is a serious depletion of limestone in the Netherlands, and in 2015 the only Dutch limestone mine (ENCI) in the Sint Pietersberg is going to be closed permanently. The Dutch market will be depending on the foreign market to get enough cement in the future, which means that the currently limited resource should be used wisely. Furthermore economic implications involved with the overall shortage of resource materials in the future will be an expensive issue for many countries in need of resource materials.

The two most essential properties of SCC are a high flow ability and a high segregation resistance. The use of admixtures in combination with a high concentration of fine particles makes it possible to combine these apparently incompatible properties. However, the high concentration of cement and fillers with puzzolanic properties, can lead to the development of a high heat of hydration. This might induce rather high thermal stresses in the hardening concrete element, possible causing early age thermal cracking

The replacement of CEM I with nSS seem highly relevant to the higher amount of chloride in SCC. This high presence of chlorides could lead to corrosion of the reinforcement by destroying the passive layer on the steel surface. While modern standards impose restrictions on the amount of chloride that may be introduced to the fresh concrete mix, penetration of chloride into hardened concrete is currently the major cause for pitting corrosion in concrete structures.

In general, it is understood that the usage of nSS has an impact on the quality and performance of compressive strength, while it is of major importance to have a constant composition and a constant compressive strength value due to the early demolding time of the precasted elements. The influence of SP due to the amount of replacement on the chloride content is negligible. In the case of early age strength development superplasticizers have a major influence.

The replacement of CEM I with nSS is relevant with respect to sustainability (immobilizing solid waste, reducing landfill).However, nSS is a potential substitute for CEM I, and it is advisable when optimizing the transfer to the full scale production. Conversely, this could be an issue due to the amount of waste nano-siilca and the necessary plant adaption as a result of the high shear energy mixture and a basin that keeps the produced slurry in constant motion. With all these conditions in in required, nSS is still considered a beneficial option and it is still recommended to use nSS as a replacement material in SCC. The results found in the laboratory and in the pilot test are convincingly demonstrated within the thesis to further demonstrate the successful use of nSS in SCC. Finally, the research on the durability of the SCC with nSS unfortunately could not be investigated due to the restricted time frame surrounding this thesis study. Possible tests that can be conducted in the future in regards to durability could include freeze and thaw tests as well as observation study on the effects of SCC with nSS as it is exposed to a highly aggressive environment for a long period of time.

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VI. Proem

Join something “a mixture with strength”

Over hundreds of years, concrete has become the primary material of choice for constructing residential buildings, commercial buildings, infrastructural facilities, highways, dams, bridges, canals, ports and other important facilities. The popularity of concrete owes to its economy, ability to be cast into any shape, ability to be fabricated practically anywhere and last but not the least, its inherent durability. Innumerable historical landmarks made of concrete speak volumes about the durability and versatility of the concrete material itself.

The principal component that makes concrete possible is cement, which has developed into a well-engineered and processed material from its relatively humble beginnings early in history. The word ‘cement’ means to join something. Cementing materials has an interesting history. The oldest structures relied on the sheer mass of the stone blocks for stability – an example is the set of pyramids in Egypt. With the progress of time, Egyptians switched over to smaller blocks and bricks which needed some cementing material. There is evidence of the use of bitumen as a cementing material by the Babylonians and Assyrians, as well as of burnt gypsum in Egypt. The first uses of lime mortar for binding are attributed to Egyptians, Greeks and Cretans, and some of the structures built by them are still standing today. The use of pozzolanic additives is also an age old practice – this is evident by the use of burnt powdered brick (surkhi) in Bengal and Santorin Earth (volcanic tuff) in Greece. In fact, the use of volcanic ash that spewed from Mt. Vesuvius near Pozzuoli in Italy, by the Romans, led to the coining of the word ‘pozzolana’.

It was in 1756 that John Smeaton, a British engineer, while planning the building of Eddystone lighthouse tower, discovered that the best limes for mortar contained a high degree of clayey matter. Ultimately, such a lime was used along with pozzolana in equal quantities. This was one of the first documented examples of application of a binding material that was similar in composition to modern Portland cement. In the early 19th century, Vicat prepared artificial hydraulic lime by calcining an intimate mixture of limestone (chalk) and clay – this is the principal forerunner to Portland cement. The development of ‘Portland’ cement is actually attributed to Joseph Aspdin. In 1824, Aspdin, while obtaining a patent for his hydraulic cement, termed it as Portland cement, upon Portland stone (limestone from Dorset, UK), which had a high quality and durability and a similar appearance. The patent has long since run out, but the name ‘Portland’ has lived on.

In the last fifty years, there has been significant progress in concrete technology, mainly owing to the revival of the interest in supplementary cementing materials, as well as the advent of new generation chemical additives for concrete. With the selection of materials available today, it is possible to design tailor-made concretes for any type of construction. The progress in concrete technology also owes partial credit to the change in research outlook – modern researchers try to learn about concrete from an interdisciplinary viewpoint, combining chemistry and material science with civil engineering. The emphasis on fundamentals has paved the way for many important breakthroughs within the research field surrounding concrete. These advances have ensured that concrete will be a material of choice for many decades into the future.

The most current and innovative technique that is presently receiving the most attention within the concrete industry, is without a doubt, the self-compacting concrete product. This type of concrete is so liquid that without vibrating it can be cast it in the most complex shapes. This technology has spilled over from Japan to Europe and continues to spread in both prefabrication and ready-mixed concrete industries. This thesis aims to change the amount of raw material used in Self-compacting concrete by combining it with a waste material, in collaboration with Kijlstra Betonmortel B.V., which will be explained in full detail within this thesis paper.

In regards to the urgency of research in regards to the development/redevelopment of the concrete industry—it is absolutely essential since it is now time for change, attention must be paid to the environmental damage that has been done, and revitalization of our environment is necessary in order for future generations to survive. For a structural adjustment in the production and consumption behavior, the construction sector can and must play a leading role therein. New materials, innovative production processes, and new progressive thinkers, is what will allow for change and growth within the concrete industry.

VII. List of abbreviations

SCC	Self-Compacting Concrete
HPC	High Performance Concrete
CVC	Conventional Vibrated Concrete
EFNARC	European Federation of Producers and Contractors for Specialist Products for Structures
EN-…	European Concrete Standard
VMA	Viscosity Modifying Admixtures
SP	Superplasticizer
SCM	Supplementary Cementious Materials/ Self Compacting Mortar
CEN	European Committee for Standardization
DiBt	German institute of Technical Approvals
ERMCO	European Ready Concrete Organization
OPC	Ordinary Portland Cement
EU	European Union
CEM I 52,5 R	Portland Cement 95% 5% additives, 52,5 Strength after 28 days, R rapid
CEM III 42,5	Portland Cement <34%, <80% Blast furnace slag, 42,5 strength after 28 days
CMP	Chemical Mechanical Polishing
PV	Photovoltaic
nSS	nano-Silica Sludge
GGBFS	Ground Granulated Blast Furnace Slag
GGBF	Ground Granulated Blast Furnace
XC.. – XF..	Exposure Class
MPa	Mega Pascal
FA	Fly ash

1 Self-Compacting Concrete Introduction (SCC)

1.1 Introduction

“the most revolutionary development in concrete construction for several decades”

Since the first appearance on the Japanese market in the late eighties, Self-Compacting Concrete (SCC) has become increasingly popular, and continues to be in demand across Europe. SCC presently offers a variety of advantages, and presumably will continue to grow in the future. SCC offers a wide range of application advantages, especially within the domain of the prefab concrete industry; as well as the deposited concrete in situ. When the construction industry in Japan experienced a decline in the availability of skilled labor in the 1980s, a need was recognized for a type of concrete that would eliminate the problems with defective workmanship. After the development of self-compacting concrete, a committee was formed to study the effectiveness and properties of the product, which included a fundamental investigation by Ozawa on the workability of concrete at the University of Tokyo (Ozawa et al., 1986). The first usable version of self-compacting concrete was completed in 1988, which was originally named, “High Performance Concrete” and was later renamed, “Self Compacting High Performance Concrete”.

The production of self-compacting concrete, also known as SCC, has stimulated significant progressive development in the market of concrete construction, and is often described as “the most revolutionary development in concrete construction for several decades” (Calmon et al., 2005; EFNARC, 2002). This recognition is due to the superior ability SCC has to fill all cavities of formwork without defects only under the influence of gravity. Without any compaction process, the concrete also has the ability to self-ventilate (de-air). The name SCC was derived from the characteristics described above. However, SCC’s ability to flow inside formwork, partly to a degree of complete leveling, resulted in the alternative name self-consolidating concrete, and an additional, more seldom used title of, self-leveling concrete. The names self-consolidating concrete, and self-leveling concrete, are interestingly both more frequently used in North America. Use of SCC can also help minimize hearing-related damages on the worksite that are induced by vibration of concrete, and the time required to place large sections is considerably reduced when using SCC.

1.2 A general classification

There are several characteristic key properties about SCC in a fresh state that are notable, (i) superior ability to flow, (ii) self-de-airing, (iii) passing ability, and (iv) a sufficient resistance to segregation. As a result of the combined high ability to flow and stability, SCC encapsulates steel reinforcement without blocking of aggregates; SCC fills all cavities of formwork and gives a smooth surface finish. All the above elements is what makes SCC an ideal type of concrete for congested reinforcement and geometrically demanding structures, or more generally, for all the construction elements and applications where sufficient compaction requires extreme efforts.

1.2.1 SCC: Ability to Flow

A great influence on the excellent workability of SCC is through the high powder content and the use of high-range water-reducing admixtures, and if required the use of Viscosity Modifying Admixtures (VMA).The latter allows for the manufacturing SCC with a reduced volume of fine materials. Accordingly, SCC can be classified into three types (Holschemacher and Klug, 2002)

- Powder type (increase of fines ≤ 125 μm)
- Viscosity-agent type (use of viscosity modifying additives)
- Combination type (combination of 1. and 2.)

Firstly SCC as a powder type will be addresses, as shown later on, the use of optimized continuous grading, including the powder range results in sufficient segregation resistance and low yield stress. This is required for good filling ability; however, it also makes VMAs redundant and eliminates a source of uncertainty given the VMAs' performance time. In addition, the impact on the yield stress of mixes, and the unpredictable interaction with the superplasticizer (SP), high powder contents are needed in SCC to increase the cohesiveness. That mostly results in elevated cement contents of SCCs compared to Conventionally Vibrated Concretes (CVCs), which is disadvantageous for environmental reasons, economic reasons, and after-effects of high cement loads such as thermal cracking and increased drying shrinkage. As a result it is an essential common practice to use substantial amounts of mineral Admixtures (Supplementary Cementitious Materials, SCM), such as fly ash, ground granulated blast-furnace slag or limestone powder in SCC concrete mixtures. Such an increased use of powder materials demands the exact knowledge of their properties; moreover, it is also important to consider the use waste materials for such mass applications, such as waste silica of the photovoltaic industry.

1.2.2 Technology advances

A number of special features where quickly recognized within the first years of SCC's existence on the market; these features made the SCC superior to CVC. Due to the self-compaction feature of SCC, the manpower required to lay concrete was reduced at the construction site as no compaction processes is required anymore. This feature led to a shorter period of construction and also the saving of electric power. Effects on the direct surroundings are reduced, as the compaction results in a high noise level. For many precast companies the influence to switch to SCC was the element of efficiency through an absence of the compaction process. Other benefits for precast companies include a reduction in required labor, savings in labor costs, reduced noise levels, reduced dust levels (quartz), and a longer life of molds (Walraven, 2002).

The production of SCC eliminated the possibility for precast companies to incorrectly compact concrete, since SCC self ensures proper implementation. Provided that the SCC mixture satisfies the four key properties mentioned earlier in paragraph 1.2, the mixture is guaranteed to almost entirely fill the formwork of any enclosed reinforcement structure without difficulty. The concrete industry was dramatically improved as a result of SCC's production especially in regards to surface finish as well as elements durability and longevity. The possibility and freedom to cast any structure shape was born as a result of SCC's existence. Structures that could not be casted by CVC in the past were thus available for construction with the use of SCC. Freedom of design in architecture way a groundbreaking element of SCC's success in regards to structural design becoming fully possible. Thinner concrete sections was also an important element of SCC's success due to the ability to fill formwork entirely. Many comparative cases were reported in literature during the early years of SCC's existence documenting the superiority of the SCC product in comparison to CVC. For example SCC superiority was evaluated through the erection of 2 buildings in France (Nanterre) by two companies, one using the CVC and the other SCC. The company using SCC completed their tower two and a half months prior to the company building the tower using CVC. In addition the company using SCC had notable savings, since costs were reduced by 21.4% (Goodier, 2003).

1.2.3 Barriers to acceptance SCC

Despite of the advantages mentioned above and the list of successful applications, SCC was not quickly accepted by the concrete industry. The slow acceptance of the wide range of usage features had a few reasons, which have been summarized in the following points:

- In fresh state the material performances were so good that the existing testing methods for CVC's were no longer suitable for SCC. Moreover, the absence of experience, existing specific measures like funnel time, and slump flow could not be related to characteristics that are actually needed at the building site (Walraven, 2002). The preparation efforts that are needed are too high, and the parameters with which most practitioners were not familiar with this kind of material.
- According to the first point, the standards did not classify SCC. The European Norm 206 (EN 206) divided six flow classes (F1 – F6), because of the filling ability, SCC belongs to class F6 (slumpflow > 630 mm). But due to the different theology of SCC mixes the standards could not be used to specify SCC.
- The mentioning of SCC in a standard written by the European Committee for Standardization (CEN) was not available until March 2007. The time it took to standardize SCC made it difficult to put SCC into practice. One of the reasons was the absence of on-site tests, to agree the quality and in the next instance to control it on site. Until 2004 SCC required special technical approval in Germany before it could be used on site. The German Institute of Technical Approvals in Berlin (DIBt) had to deal with official approval on request by each contractor, which was a time consuming and expensive procedure.
- Lastly, increased sensitivity of SCC mixes to changes of mix proportions, of changes of the environment such as temperature variations. This increased sensitivity formed an additional obstacle to the broad use of SCC as it demands an optimized recipe and precise working on site

1.2.4 Abstract SCC history

In the early eighties, development projects in Japan were focused on the poor compaction of concrete, which was identified as a major cause of poor durability of concrete structures in Japan (Ouchi, 1998). The motivation to develop a new type of concrete was a decline in the availability of skilled labor in the 1980s, a need was felt for a concrete that could overcome the problems of defective workmanship. This problem led to the development of self-compacting concrete, primarily through the work by Okamura in 1986. This development of concrete can be compacted into every corner of a formwork, only using it own weight and without the need of vibrations to compact the concrete (Okamura and Ozawa, 1995).

This overview about flowing and unsegregable superplasitcezed concrete mixes will focus on the significance of SCC as well as its development to the current state of effectiveness. There is a noteworthy extension of literature that follows the driving forces behind the development, production, and importance of SCC in the concrete industry. Interestingly, in opposition to the common standard literature on SCC, researcher Nagataki (1998) promotes the super plasticized, anti-washout, underwater concrete mixtures, developed in Germany during the 1970s. However, it is significant to note that Collepardi (2001) determined that, underwater concrete, and SCC are functionally related in that they both have a high segregation resistance and high fluidity. When analyzing the history of SCC it is important to note that the overall development of SCC was significantly reliant on the production of an equally effective SP; without this combination the superior concrete could not have been possible. Development of this combination started in the “early-SCC-era” of the 1970s until the first casting of the prototype of SCC in Japan in 1988 (Ouchi 1998).

Okamura and Ouchi did not give the name Self Compacting Concrete to the mixture in the early stage, instead they called it “High Performance Concrete” (HPC). The name followed out of three requirements in the different stages (fresh state, early age state, hardened state) of concrete:

- Self-compactable: provided in the fresh state;
- Avoidance of defects and initial defects: during the early age state;
- External influence and protection against these factors: hardened state.

The development of Okamura and Ouchi’s HPC was announced around the same time that Aïtcin (1988) developed a different HPC with a low water-cement ratio and (Ouchi,1998) with a high durability. Aïtcin’s development made it necessary to give Okamura and Ouchi’s HPC an alternative name. When considering the most important features of Okamura and Ouchi’s concrete, a new name essentially suggested itself: Self Compacting Concrete. The first publishing with the new name was in 1995, and after this time the term “self-compacting” was officially established in literature (Goodier, 2003).

1.3 Development History 1980’s until 2012

The scope of this thesis was developed through the reviewing the latest developments in concrete standardization and practical application; when reviewing literature it can be seen that the development and acceptance of SCC is broadly introduced. To receive a detailed review one is required to refer to Goodier (2003), especially when looking at European countries and research on standardization attempts in the first stages of SCC development. As mentioned in the previous paragraphs there was not a wide acceptance of SCC in the different companies during the early stages of existence on the market. Today SCC is produced in considerable amounts in the prefab industry, since companies have changed their production process for using SCC. Looking at the data given by the European Ready

Concrete Organization (ERMCO, 2007-2010) one can conclude that the Scandinavian countries as well as the Netherlands are leading in the usage and acceptance of SCC. When looking to Table 1-1 it is clear see the essential role that Scandinavian countries like Denmark and Sweden play, however it shows the increased use of SCC in other countries.

Countries	**2007**	**2008**	**2009**	**2010**
Austria	2	1	1	2
Belgium	0,5	1	1	1
Czech Republic	0,2	1	4	1
Denmark	**30**	**32**	**34**	**35**
Finland	1	1	1	1
France	**3**	**4**	**5**	**5**
Germany	1,3	2	2	2
Greece/Switzerland	0	0	0	0
Ireland	1	1	1	1
Italy	0	1	1	1
Netherlands	**1**	**1**	**1**	**1**
Poland	5	1	1	1
Portugal	0	0	2	1
Slovakia	1	1	0	0
Spain	0	0	0	0
Sweden	**7**	**7**	**7**	**7**
United Kingdom	2	2	2	2
Average EU	1,3	2	2	2
Israel	0	0	1	1
Norway	**4**	**4**	**4**	**4**
Turkey	2	1	1	1
Average ERMCO	2	1	2	2
Russia	3	1	1	1
USA	2	2	2	2

Table 1-1; Share of SCC (%) on total amount of Ready Mixed Concrete (Source; ERMCO 2007-2010)

Table 1-1 is based on the SCC share of the total ready-mixed concrete production. Following this data the average is deployed in a pi-chart (Figure 1-1) where the data underscored are referred for consistence evaluate classes (flow table test): S1=F1, S2-S3=F2-F3, S4-S5=F4-F5, SCC=F6+SCC, from these values the increased use of SCC is also visible.

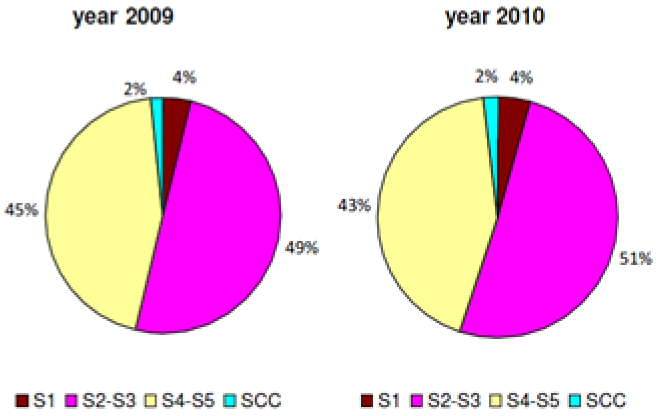


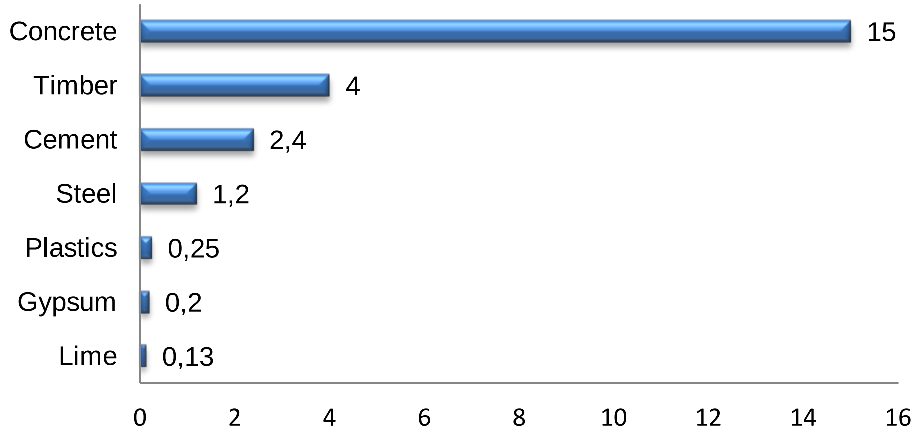
Figure 1-1; Production per consistency class (Source; ERMCO www.ermco.eu/documents/ermco-documents/statistics.xml , 2011)

1.3.1 Standardize the standardization

Since the development of SCC in Japan now about 30 years ago, many organizations across the world have carried out research projects on properties of SCC. One such project was the Brite-Euram SCC project (Brite-Euram Project, 1998) which was set up to promote the use of SCC in some of the European countries. A state-of-the-art report on SCC was compiled, which summarizes conclusions from the research studies sponsored by the Brite-Euram project on SCC (Skarendahl and Peterson, 2000). A recent initiative in Europe is the formation of the project –Testing SCC– involving a number of institutes and research studies on various test methods for SCC. In addition, the participation from the specialty concrete product industry –EFNARC– (European Federation of Producers and Contractors of Specialist Products for Structures) has developed specifications and guidelines for the use of SCC that covers a number of topics, ranging from materials selection and mixture design to the significance of testing methods. This work becomes an extended part of the new European Concrete Standard EN-206 deployed by The European Committee for Standardization (CEN).

1.4 The ecological component, Concrete Age

Today concrete is one of the most-widely produced products in the world. Looking back into the history it can be seen that since the early ages of mankind, the human race has continuously struggled with the desire to master materials. The gradual progression towards control of workable material is evident in the denotation of periods such as The Stone Age, The Bronze Age, and The Iron Age. The amount of produced concrete that currently exists in our world can justify a spot on this progressive list of human development toward development/control over workable material through history. The Concrete Age seems to be an appropriate title when considering Concrete is the second most widely produced substance on earth, after drinking water. Almost 15 billion tons p.a. of currently produced concrete (Indication of the global annual flows of resources based on the year 2007) (Figure 1-2), generate the largest material flow on earth. Therefore, concrete has a paramount impact on the ecological balance. Even though concrete by itself is a very sustainable and ecologically friendly material, its tremendous application turns it to a serious problem. Hence cement and concrete producers bear heavy social and environmental responsibility when aiming on a competitive product.



	Lime	Gypsum	Plastics	Steel	Cement	Timber	Concrete
■ World production in billion ton/y	0,13	0,2	0,25	1,2	2,4	4	15

Figure 1-2; Indication of the global annual flows of resources, 2007 (Source; CEMBUREAU 2007)

In view of an increased awareness of the environmental impact of mining river sand, depleting supplies, use of manufactured sand, and other alternative fine aggregate has become essential in some parts of the world. In fact, river sand is simply not available in many areas; fortunately, countries like the Netherlands are privilege of having a large amount of resources in regard to river sand among others. Conversely, many studies have been done (Ho et al.,2002) to show that quarry run can also be used as a filler instead of limestone for SCC. However, it is important to note that there has not been sufficient documentation of the use of manufactured sand, either as fine aggregate or as a filler, in SCC.

1.4.1 Mineral additions, substitution of cement

For the sustainability of SCC it is extremely important for the concerns toward the continuation of the SCC product to be addressed, and more importantly the possibility to turn SCC into an even more “green” product is tremendously essential. Effective leverage in concrete is the cement, the main binder, as the production is heavily energy intensive and large amounts of carbon dioxide are released due to this production. The production of one ton of Ordinary Portland Cement (OPC) clinker generates one ton of CO_2 emission according to the Cement&BetonCentrum (2010).The amount and composition of cement in a specific concrete mix can vary greatly and thus gives room for the possibility to improve the overall ecological balance of the final product. The emission of CO_2 and the scarcity of raw materials make’s it desirable to find alternatives to reduce the amount of OPC needed in concrete production. A more efficient use of cement, in conjunction with smart concrete design concepts could greatly improve this ecological balance. The use of waste materials from other industries to increase the powder content of SCC products could put a “greener” stamp to SCC and other concretes. When looking to Figure 1-3 one will see that the world cement production in the CEMbureau countries and the EU 27 (27 EU member countries) is the lowest compared with the upcoming market in Africa and Asia.

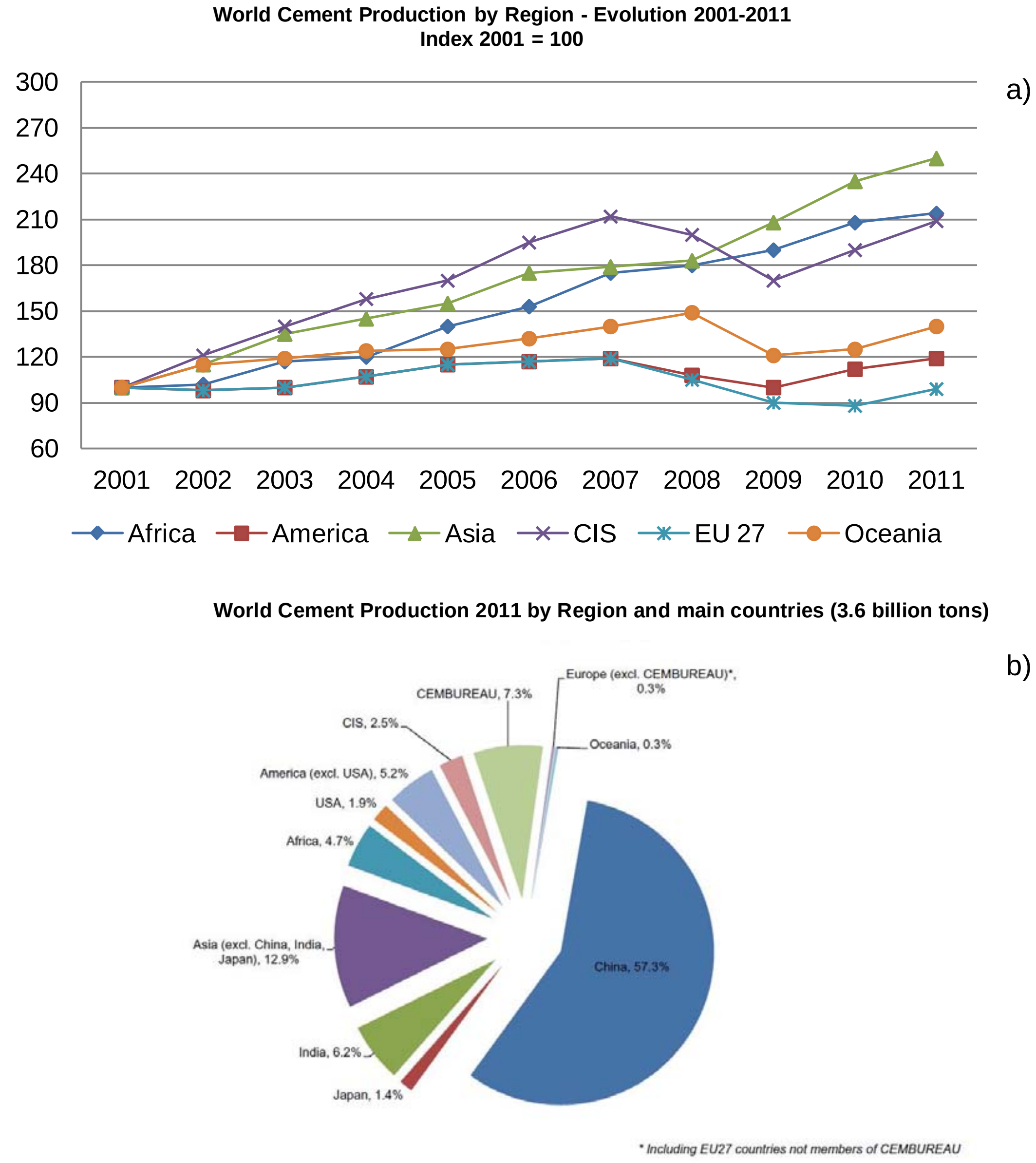


Figure 1-3; a) relative development cementproduction by region 2001-2011 b) World Cement Production by Region (Source; CEMBUREAU 2011)

A benefit can be achieved when the applied powder is a “waste” product. If we look to powder coal fly ash, a more or less reactive powder is also a “waste”, generated upon power coal combustion. For instance in polishing operations and in the photovoltaic industry (e.g. solar cell industry), large amounts of mineral wastes are produced. These waste products do not have any application and are mostly disposed in landfills or open-dumped into waste pits and open areas. The disposal produces major problems, not only for the companies but also in social ecological point of view. The utilization of this waste material, especially in SCC with its typically high powder content, could turn this material into a valuable resource (Calmon et al., 2005; Ho et al., 2002).

1.4.2 Construction issues

Use of SCC has been demonstrated in a number of structures in Japan and Europe. A frequently cited case is the construction of anchorages for the Akashi-Kaikyō bridge in Japan. The Akashi-Kaikyō Bridge also known as the Pearl Bridge, has the longest central span of any suspension bridge, at 1,991 metres (6,532 ft). It is located in Japan and was completed in 1998. The bridge links the city of Kobe on the mainland of Honshū to Iwaya on Awaji Island by crossing the busy Akashi Strait. It carries part of the Honshū-Shikoku Highway. The bridge is one of the key links of the Honshū-Shikoku Bridge Project, which created three routes across the inland sea. This bridge is a typical example of constructing with SCC. The two anchorages of the bridge are formed and filled with Self-compacting concrete. Examples of other applications include: construction of a wall for a large liquefied natural gas tank in Japan, a viaduct in Yokohama City, and a number of bridges in Sweden (Kitamura et al. Kosaka et al Nilsson and Arima et al, 1998).

Another issue is that of lateral pressure of the SCC on the formwork, due to the highly fluid nature of SCC (Billberg). Higher rates of casting with SCC could compound the problem of excess formwork pressure. Prima facie, it may appear that more robust formwork and falsework will be required. However it is interesting to note that available results indicate that SCC exerts about the same pressure as conventional concrete. This can be attributed perhaps to the inherent thixotropy of SCC, or in other words, the significant build up of viscosity following a period of rest. Research from Sweden has shown that the use of SCC actually resulted in pressures less than the design values for conventional concrete, and only slightly more than the conventionally-vibrated concrete.

1.5 Test methods

Many different test methods have been developed in attempts to characterize the properties of SCC (Okamura and Ouchi, 2003; Skarendahl and Petersson ,2000). Thus far no single method or combination of methods has achieved universal approval. Similarly no single method has been found to characterize all the relevant workability aspects. Therefore each mix design should be tested by more than one method for the different workability parameters. Alternative test methods for the different parameters are listed in Tables 1-2 and 1-3. The test methods are described in detail in Appendix A.

	Method	Property
1	Slump-flow by Abrams cone	Filling ability
2	V-funnel	Filling ability
3	J-ring	Passing ability
4	V-funnel at $T_{5minutes}$	Segregation resistance

Table 1-2; List of test methods for workability properties of SCC. (Source; EFNARC guidelines)

For the initial mix design of SCC all four workability parameters described in paragraph 1.2 must to be assessed to ensure that all aspects are fulfilled. A full-scale test should be used to verify the self-compacting characteristics of the chosen design for a particular application. These lab and pilot tests are explained further within this thesis. In the case of site quality control, two test methods are generally sufficient when monitoring production quality. Typical combinations are Slump-flow and V-funnel or Slump-flow and J-ring.

Property	Test methods Lab (mix design)	Field (pilot)	Modification of test according to max aggregate size
Filling ability	1 Slump-flow	1 Slump-flow	None
	2 V-funnel	2 V-funnel	Max 20 mm
Passing ability	-	3 J-ring	Different openings
Segregation resistance	4 V-funnel at $T_{5minutes}$	4 V-funnel at $T_{5minutes}$	None

Table 1-3; Workability properties of SCC and alternative test methods. (Source; EFNARC guidelines)

Changes in workability which occur during transport should be taken into account within production. Typical acceptance criteria for Self-compacting Concrete with a maximum aggregation size of up to 20 mm are shown in Table 1-4.

	Method	Unit	Typical range of values Minimum	Maximum
1	Slump flow by Abrams cone	mm	650	800
2	V-funnel	Sec	6	25
3	J-ring	Mm	0	10
4	Time increase, V-funnel at $T_{5minutes}$	Sec	0	+3

Table 1-4; Acceptance criteria for Self-compacting Concrete. (Source; EFNARC guidelines)

The requirements outlined in the table above and according to each test method are based on current knowledge and practice. Values outside these parameters may be acceptable if the producer can demonstrate satisfactory performance in the specific conditions, eg, large spaces between reinforcement, layer thickness less than 500 mm, short distance of flow from the point of discharge, few obstructions in the formwork and very simple design of formwork etc. Special care should always be taken to ensure no segregation of the mix occurs. At present there is no simple and reliable test which provides information about segregation resistance of SCC in all practical situations.

1.6 Summary

During the 1980s a number of countries including Japan, Sweden and France developed concretes that are self-compacting, known as Self-Consolidating Concrete in the United States. This SCC is characterized by:

- extreme fluidity as measured by flow, typically between 650–750 mm on a flow table, rather than slump (height)
- no need for vibrators to compact the concrete
- placement is easier.
- no bleed water, or aggregate segregation
- Increased Liquid Head Pressure, which can be detrimental to Safety and workmanship

SCC can save up to 50% in labor costs due to 80% faster pouring and reduced wear and tear on formwork. As of 2005, self-consolidating concretes account for 10-15% of concrete sales in some European countries. In the US precast concrete industry, SCC represents over 75% of concrete production. 38 departments of transportation in the US accept the use of SCC for road and bridge projects. This emerging technology is made possible by the use of polycarboxylates plasticizer instead of older naphthalene based polymers. As for adaptations to the Self-compacting concrete with the waste silica, there must be a continued result in the savings of the labor costs, and a significant reduction in the amount of Carbon dioxide emission by the production of CEM I 52,5R that is used in SCC mixtures.

2 Application of Chemical Mechanical Polishing (CMP) waste

2.1 Introduction

Every hour the sun generates enough energy to satisfy global energy needs for an entire year. Photovotalic technology is the technology used to harness the sun's energy and make it usable. Today this technology produces less than one tenth of one percent of global energy demand. Many people are familiar with so-called photovoltaic cells, or solar panels, found on structures such as spacecraft, rooftops, and handheld calculators.

Photovoltaics or PV is the technology which converts sunlight into electricity. With increasing concerns surrounding the global climate and the uncertainty of oil sources and prices among other traditional fuels concerns adding economic pressures, the solar power industry has been growing substantially in recent years. In 2010, the photovoltaic (PV) industry production more than doubled and reached a world-wide production volume of 23.5 gigawatt (GW) of photovoltaic modules. Since 1990, photovoltaic module production has increased more than 500-fold from 46 megawatts (MW) to 23.5 GW in 2010, making it the world’s fastest-growing energy technology (ScienceDaily Sep. 5, 2011). In addition to the growth in output, there has also been substantial investment in pioneering new technologies and manufacturing practices in order to reduce the cost of PV and improve material efficiencies.

Solar cells, photovoltaic modules and photovoltaic arrays are all assembled components, however, a core part of all of these products is the photovoltaic material. Currently, there are several prevailing processes for manufacturing PV material, they are:

- Crystal Growers and Silicon Wafers - One technology uses Silicon wafers and is similar to traditional semiconductor manufacturing processes. This process involves growing the silicon crystal, then slicing it into wafers.
- Thin Film Coating - An alternative technology involves applying a deposition process and thin-film coating process using a manufacturing system that is similar to a printing press.

Looking at the enormous amount of produced solar cells, all those cells need to be polished, to archieve the smooth appearance as we know a solar panel. Chemical Mechanical Polishing (CMP) is a conventionally adopted process in a integrated-circuit (IC) factories by using nano silica for the polishing, this process called “planarization” on silicon wafers. Due to the fact that planarization consumes considerable amounts of water, large quantities of potentially dangerous waste water and sludge are released into the environment. Several studies have attempted to develop treatment processes for this sludge and waste water. The most effective process of removing dangerous material is by abrasive scraping; similar to rubbing sandpaper on wood. Furthermore, the chemicals in the slurry also react with and/or weaken the material to be removed. The abrasive scraping accelerates this weakening process and the polishing pad helps to wipe the reacted materials from the surface. The process has been compared a child eating a gummy candy. If the candy sits on the tongue without being moved around the candy becomes covered with a gel coating yet the majority of the candy is not affected. Only with a vigorous scraping does the candy dissolve away. The CMP process is shown in Figure 2-1.

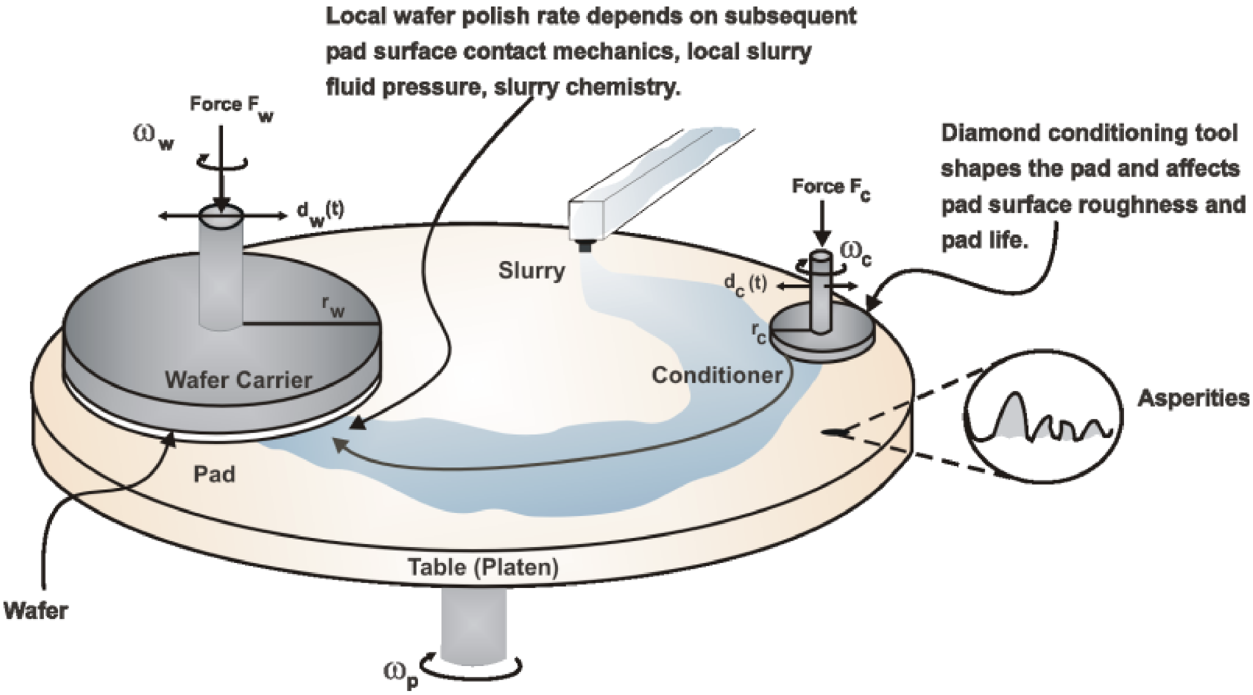


Figure 2-1; Functional principle of CMP; source (De La Paz, 2009)

Before 1990, CMP was considered too "dirty" to be included in high-precision fabrication processes because the abrasives used for polishing are not without impurities. The waste generated by CMP is neutralized with sodium hydroxide (NaOH); water-soluble calcium chloride ($CaCl_2$) is then added to precipitate fluorine ion into insoluble calcium fluorite (CaF_2). Thus, CMP waste contains numerous chemicals. Such waste is called wet waste in the photovoltaic polishing process. Solid CMP waste recovered after water removal is called “sludge”. Photovoltaic sludge contains both organic and inorganic material. The organic materials include: oxidizing agents, additives and dispersing agents, mainly of proprietary compositions made of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulfur (S) and others. The inorganic materials constist of nano-particles, principally silicon dioxide (SiO_2) more commonly known as sand ore quartz, CaF_2 and others which are typically 20-300 nm in size depending on the vendors. When dumping sites are close to reservoirs or underground water sources, these nano-particles (debris of the polishing process) can pollute drinking water. Humans are vulnerable to nano-particles in sludge, they can cause lung complications and other diseases.

2.2 Problem Definition

If the silicon Photovoltaic industry continues to rapidly expand, the environmental impact of its manufacturing processes and products will receive increased attention. In The Netherlands it is important for renewable energy technology to address its environmental impact during manufacturing because the primary benefit of renewable energy generation is its low environmental impact. The CMP sludge is a chemically and physically complex product which makes its combination with cement questionable. Particle size distribution, loss of ignition, density, specific surface area, leaching properties as well as pozzolanic/cementitious properties must be tested in order to confirm CMP suitability; CMP sludge contains contaminants such as: large amounts of chlorides, (SiO_2) silicon dioxide, also known as silica, (Fe_2O_3) Iron(III) oxide or ferric oxide and (Al_2O_3) Aluminum oxide, any of which may have negative influences on the hydration of cement. As an alternative to cement, the pozzolanic activity in CMP effects the normal hydration process: consequently upgrading and lowering the properties of concrete at early ages.

2.3 Background

The replacement of Ordinary Portland Cement (OPC) has been conducted by several studies. Dried and pulverized sludge was used to replace 5–20 wt.% of OPC in the cement mortar, the sludge was recovered from the waste water of semiconductor-industries. In a study done by Lee and Liu (2009), semiconductor sludge was used to replace OPC in the cement mortar. the strength of the mortar after a substitution of 10 wt.% sludge improved by 25–35% after curing for 7–90 days. Thus, the replacement of OPC increases the values and strength of the mortar. With this knowledge the use of industrial photovoltaic waste could potentially replace CEM I 52,5R in cement mortar. The use of this waste nano-silica sludge produces a more economical form of concrete and reduces the carbon dioxide (CO_2) footprint of any produced concrete structures. Furthermore, the environmental impact created by the photovoltaic industry is reduced through the usage of the waste nano-silica. Currently, 15% of the European market uses SCC. With this in mind, an alternative type of SCC which uses the waste nano-silica will result in a huge reduction of the CO_2 emission. The goal is to reach up to 100% of the binder CEM I52,5R in a SCC mixture containing CEM III/B LH/HS 42,5 and fly ash and limestone.

2.4 Objectives and research Questions

This research project aims to combine the nano-silica rich sludge: a waste product of photovoltaic production, with SCC mixtures. In the previous paragraphs, the positive and negative aspects of SCC are explained. Several experiments will be conducted on the replacement of CEM I 52,5R and other common fillers with nano-silica rich sludge for the production of SCC mixes used by Kijlstra Betonmortel B.V. These experiments shall be explained further in this thesis report.

The goal is to develop a more sustainable and cost-efficient concrete that improves concrete products while also reducing the CO_2 emissions of the concrete product. In order to do so, nano-silica waste must be tested for longevity and applicability, before it can be utilized in the concrete industry. The following objectives can be defined in accordance with the problem definition:

- Determine the physical and chemical properties of the different waste nano-silica batches;
- Test the best batches based on contaminants in the PV industry by treatment to increase the reactivity in concrete mixtures on strength, chloride and CO_2 contamination.
- To determine the effects on SCC if cement is replaced by a nano-silica waste for use in construction elements.

Research question;

What are the effects on Self-Compacting Concrete (SCC) if cement (CEM I) is replaced by a waste nano-silica sludge in building construction elements?

2.5 Hypothesis

Using a broad literate study the following hypotheses have been formulated:

1. Using nSS as a replacement binder for CEM I 52,5R, the properties of the SCC mixtures , mentioned in Chapter one and 5 will be improved;
2. After curing the concrete and after the slurry optimization the nSS will fulfill 100% replacement value for CEM I 52,5R in the fly ash system and limestone system for use as a building material in pre-casted concrete.

2.6 General Approach

To address the main research question, as well as the objectives listed above, this study has been structured into two parts. The first part (Chapters 1-3) contains insight in SCC based on literature study to obtain data. This includes insight and information that can be used to set up the practical laboratory test and to better analyze the results. The second part (Chapters 4-7) consists of the practical experiments. This part describes the performed laboratory and field tests. Based on the experimental results, further tests are performed to meet the stated requirements and objectives.

2.7 Report structure

This report covers a broad field containing slightly different yet related topics. All of these topics are connected based on the aim to improve sustainability of construction material such as Self-compacting Concrete (SCC), the most used manmade material. In Figure 2-2 the framework of this thesis is presented. It is composed of 8 chapters with it contents as follows. The first part focuses on the development of SCC, the development and when it is deployed to the construction market. Chapter two of this thesis focuses on the CMP compound and possibilities as a sustainable replacement material.

Chapter 3 analyzes the powder fraction of SCC and CMP material and the essential differences aside from water-reducing admixtures, as compared to CVC. This chapter introduces the first stage of designing a new concrete mixture, the mortar stage.

Chapter 4 shows the characteristics of the waste nano-silica sludge and analyses the obtained slurry from previous tests.

Chapter 5 addresses the practical application of the developed Self Compacting Mortar (SCM) mixture. Based on the theory provided, optimal mortars are generated in several steps to adjust and to reach the desired self-compacting properties. All the laboratory tests are shown and explained.

Chapter 6 demonstrates the practical application of re-designing the SCM to SCC. Based on the results of previous tests the design is finalized and brought into realization. This final part of the laboratory research on SCC is then presented. The developed SCC is applied on a full scale test including aggregates up to 16 mm in particle size. One will see that with comparatively little effort, stable and optimized SCC can be produced. The obtained results from the full scale tests are also shown in this chapter.

Chapter 7 demonstrates the usage of the CMP material in SCC. It is the translation of this concrete recipe into a more “green” sustainable recipe, The reduction of the cement content and the application of suitable waste CMP material.

Chapter 8 summarizes the achievements of the work presented and obtained from this study. As well as proposing recommendations and ideas for further research in continuation of this work.

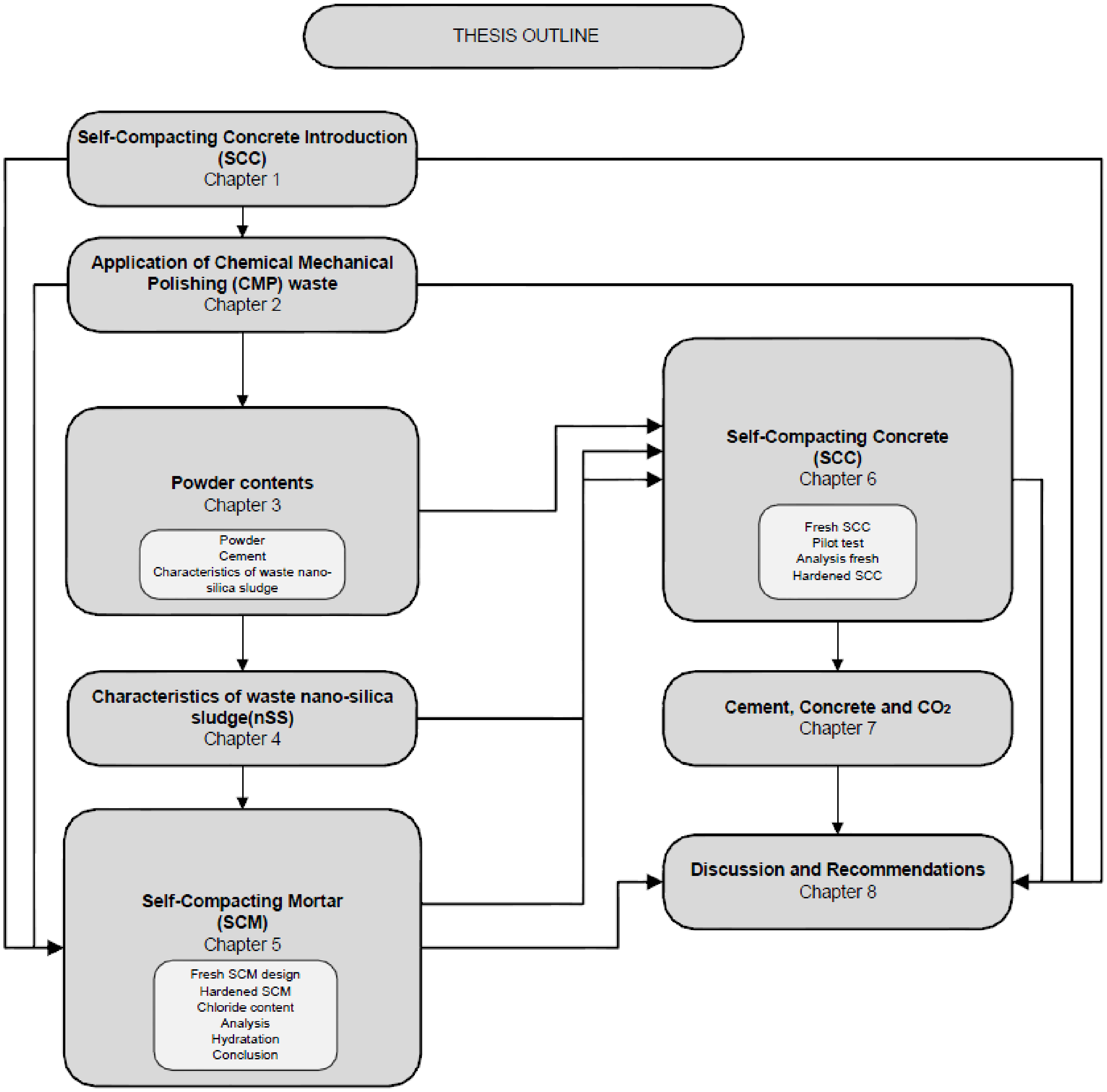


Figure 2-2; Thesis outline

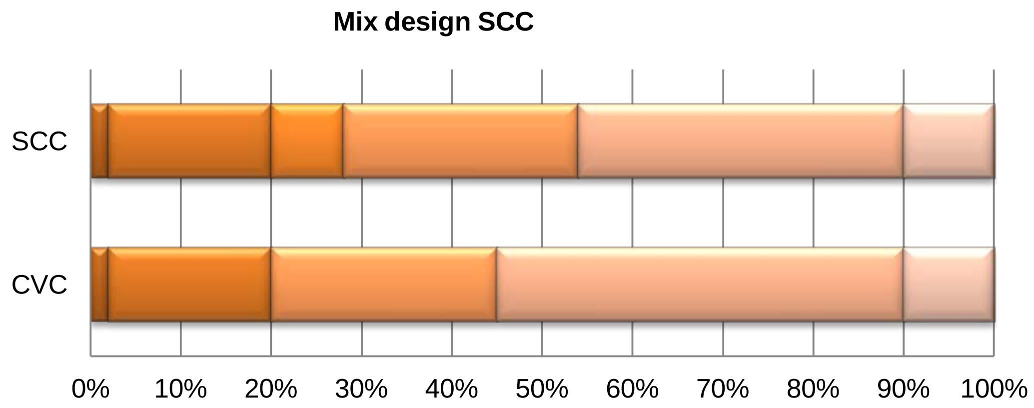
3 Powder contents

3.1 Cement

This chapter describes various power products which are used throughout this thesis. It is intended to gain further insight before the design stage of the Self-Compacting Mortar (SCM). Pursuant to the European Standard the total variety of inorganic additive materials for concrete is classified into two categories according to their reactive capacity with water;

- Type I; inert or semi-inert, nearly inactive additions. (mineral fillers such as; limestone, dolomite, etc.)
- Type II; reactive additions , pozzolanic or hydraulic (fly ash, silica fume and ground granulated blast furnace slag (GGBFS)

Compared to regular concrete, in the case of SCC a finer material is used in order to fill all the voids between the aggregates in the mortar and to ensure the smooth flow of the concrete. Figure 3-1 shows the difference between Conventional Vibrated Concrete (CVC) and the composition of SCC. The fine parts of aggregates are counted amongst the inert or semi-inert additive materials mentioned above in Type I. The effect of these fillings is the decrease in void volume. Depending on the granular size the voids between coarser particles are filled with fine particles. By filling these voids the initial hydration process of the cement is accelerated, which often results in a decreased dormant period.



	CVC	SCC
■ Air	2	2
■ Water	18	18
■ Powder/fines	0	8
■ Fine Aggregate	25	26
■ Coarse Aggregate	45	36
■ cement	10	10

Figure 3-1; Comparization between CVC and SCC

Examples of reactive additive materials (Type II) are fly ash (EN 450) and silica fume (EN 13263). These fillers create a strengthening and structure forming reaction product in addition to its physical filling effects. By adding these fillers to the research further classification arise; the physical filler effects of these additions.; (i) physical filler effect, and (ii) a chemical and mineralogical reactivity to concrete mixtures.

3.2 Powder

Due to the chemical and mineralogical composition of powders they have the ability to react. This means that in the presence of water or cement they form on their own or with the help of accelerators like cement clinker, crystalline reaction products. These reaction products contribute to the development of strength (Taylor, 1997). There are different reaction mechanisms, it can be summarized as (i) hydraulic, (ii) latent-hydraulic and (iii) pozzolanic. Hydratation (i) is the dominant reaction type for the curing of OPC. In the presence of water the siliceous cement clinker phases react to achieve hydration. For the development of strength, the fibrous (C-S-H) are of the outmost importance. Other clinker components such as ferrite ore aluminates react slower yet it influences the stiffening of concrete significantly. Furthermore, influencing the durability at later ages (Taylor ,1997). Latent-hydraulic materials (ii) will react with the cement clinker along with the influence of calcium hydroxide of sulfate to accelerate the hydration process. The most common of these materials is GBFS (granulated blastfurnace slag). The third reaction mechanism is pozzolanic (iii), this mechanism requires the influence of calcium hydroxide to achieve a reaction. Dissolved silicates along with the puzzolan react with calcium hydroxide and form C-S-H phases, which have less calcium compared to OPC or GBFS. Representatives of this mechanism are fly ash, microsilica and trass (Taylor, 1997).

According to the European standard EN 206-1 reactive powder materials, refer to type II listed above, can be partially considered as cement by means of the k-value. For the k-value the amount of reactive powder $m_{p,rea}$ is reduced by the factor k and added to the cement content m_{cem} to form a new equivalent water/cement ratio w/c_{eq}, which reads as;

$$\mathrm{w/c_{eq}} = \frac{\mathrm{m_w}}{\mathrm{m_{cem}} + k \cdot \mathrm{m_{p,rea}}} \tag{3.1}$$

Minimum cement content and maximum w/c ratio (3.1) are important design parameters when using the exposure classes following EN 206-1. This way the k-value can be used to achieve certain w/c ratio limits. This is achieved by using less cement and in turn adding type II (reactive powders) to the cement content. There are slight differences in the application of k-values according to national and international standards of the EN 206-1.

When using silica fume instead of fly ash these k-value application must also be used (only by using CEM I). The maximum amount of silica fume to meet the water/cement ratio (3.2) is shown in Table 3-2, and must achieve the following requirements: silica fume/cement ≤ 0.11 by mass.

$$w/c_{eq} = \frac{\mathrm{m_w}}{\mathrm{m_{cem}} + (k \cdot m_{p,rea,fly}) + (k \cdot \mathrm{m_{p,rea,sf}})} \tag{3.2}$$

Cement type	EN 206-1 (2000)	NEN 5008 (2004)
CEM I 32,5	0.2	n.s.
CEM I 42,5 and higher	0.4	n.s.
CEM III A and/or B	n.s.	0.2
Silica fume	2.0	n.s.
Fly ash	0.2	0.2
Waste silica (estimation this thesis)	*0.3*	*0.3*

Table 3-1; *k*-values for fly ash taken from standards. For not specified (n.s.) cement types the equivalent concrete performance concept has to be applied.

Cement type	EN 206-1 (2000)	Exposure class XC - XF
Specified water/cement ratio ≤ 0.45	2.0	n.s.
Specified water/cement ratio > 0.45	2.0	1.0
Specified water/cement ratio ≤ 0.45	0.3	n.s.

Table 3-2; Specified water/cement ratio SCM mixture

3.2.1 Admixtures

Admixtures are chemicals which are added to the mix to meet certain construction conditions or for other special purposes.. There are four main types: (i) air-entraining agents, (ii) workability agents, (iii) retarding agents and (iv) accelerating agents.

In climates where the concrete will be exposed to freeze-thaw cycles air is deliberately mixed into the concrete in the form of billions of tiny air bubbles about 0.004 mm in diameter. The bubbles provide interconnected pathways so that water near the surface can escape as it expands due to freezing temperatures. Without air-entraining, the surface of the concrete will almost always chip off when subjected to repeated freezing and thawing. Furthermore, the act of air-entraining also increases workability without increasing the water content. Entrained air is not to be confused with entrapped air, which creates much larger voids and is caused by improper placement and consolidation of the concrete. Entrapped air, unlike entrained air, is never beneficial.

Workability agents, including water-reducing agents and plasticizers, are meant to reduce the likelihood of cement particles binding together which causes them to be insufficiently hydrated. Fly ash, a by-product of burning coal, is often used to achieve a similar result. Superplasticizers (SP) are relatively new admixtures, which when added to a cement mixture serve to increase the slump greatly. The mixture becomes very soupy for a short time and enabling a low-water-content or otherwise very stiff concrete to be easily placed. Superplasticizers are responsible for the recent development of very high strength concretes, some in excess of 100 MPa because they greatly reduce the need for excess water for workability (Nagataki, 1998).

Retarders are used to slow the setting period of concrete when large masses are placed the concrete must remain malleable for a long period of time to prevent the formation of "cold joints" between one batch of concrete to the next. Accelerators serve to increase the rate of strengthening and to decrease the initial setting time. This can be beneficial when concrete must be placed on a steep slope with a single form or to protect concrete from freezing. The best known accelerator is calcium chloride, which acts to increase the heat of hydration, tin turn causing the concrete to set faster. Other types of chemical additives are available for a wide range of purposes. Some of these can have deleterious side effects on strength gain, shrinkage being one concer. Test batches are strongly advised if there is any doubt concerning the use of a particular admixture.

As shown chemical admixtures can be effective in increasing the workability of concrete. The use of air-entraining agents produce air bubbles which acts as ball bearing between the particles and increases mobility and workability, while decreasing bleeding and segregation. The use of fine pozzolanic materials also have better lubricating effects and increasing workability. In Germany 90% of the produced concrete contains at least on type of admixture. Together, these additives can be divided into eleven different classes with respect to their effect, with the main emphasis on plasticizers. Nearly 70% of all commonly used admixtures are plasticizers. However this being said, the effect admixtures have on the hydration of cement is still an issue and controversially discussed (VDZ, 2005).

3.2.2 Selected admixtures

Concrete superplasticizers (SPs) are expected to disperse cement and other particles in a fresh mortar/concrete mixture. The dosage of these SPs is based solely on the cement content, not on the other powder materials that are involved in the mixture. This could cause problems for certain types of concrete. SPs are added to perform two functions: (i) to reduce the water amount in the mixture and (ii) to maintain and obtain a specified workability in the mixtures fresh state. Within this thesis the SP CUGLA R11 from CUGLA BV is the most used SP. Pantarhit® RC 100, RC 176 and PC 150 from Ha-Be Betonchemie GmbH & CO. KG are also used. A summary of their properties are shown in Table 3-3. The usage of the last mentioned SPs are explained in chapter 4.

Material	Chemical description	Density (g/cm^3)	Solid particle content (%)	Maximum Na$_2$0 equivalent (%)	Maximum Chloride content (%)	Dosage (kg per 100 kg of cement)
CUGLA R11	Naphthalenesulfonate/ Lignoulfonate	1.17 ± 0.03 g/cm^3	35.0 ± 5.0	4.2	0.1	>0.8
PANTARHIT® RC 100 (FM)	Modified polycarboxylates	1.07 ± 0.02 g/cm^3	30.0 ± 1.5	4.0	0.1	0.2 – 2.65
PANTARHIT® RC 176 (FM)	Modified polycarboxylates	1.05 ± 0.02 g/cm^3	24.5 ± 1.5	8.5	0.1	0.2 – 2.65
PANTARHIT® PC150	Modified polycarboxylates	1.05 ± 0.02 g/cm^3	21.5 ± 1.1	4.0	0.1	0.2 – 2.1

Table 3-3; Properties of the used plasticizers (Source; www.Ha-Be.com, www.cugla.nl)

The volume of the admixtures used is not counted in the total volume of concrete. Due to the low dosage they are not considered within the volumetric calculations of concrete, maintaining they do not exceed a volume of 3 L/m^3 fresh concrete (EN 206-1, 2000). The amount of admixture in the reference mixture given by Kijlstra Betonmortel is 3.03 L/m^3. Therefore, this amount of admixture must be included into the total amount of water.

3.2.3 Selected powders and cements

Following to the given values by Kijlstra Betonmortel the choice of cement powder is not negotiable. The used powders are CEM I 52.5 R and CEM III/B 42,5 LH/HS. The composition of these cements are shown in Table 3-4. Furthermore Table 3-5 shows the characterization of the basic cement based on EN 196-1.

Cement type	Portland Cement clinker %	Blast furnace slag %	Na_20 equivalent % (m/m)	Chloride content Cl^-	Minor constituents
CEM I 52,5 R – micro cement	≥ 95	-	≤ 0.60	0.08 ≤ 0.10	0 - 5
CEM III/B 42,5 N LH/HS	20-34	66-80	≤ 1.30	-	0 - 5

Table 3-4; Cement composition (Source; ENCI (the Netherlands), H.C.M Hollandse cement Maatschappij (the Netherlands), GMBH Hüttenzement readymix (Germany))

Cement type	Initial set min	Water demand % (m/m)	Specific density (g/cm^3)	Compressive strength (N/mm^2) 2 days	7 days	28 days
CEM I 52,5 R – micro cement	≥ 45	54.9	3.150	≥ 30	-	≥ 52,5
CEM III/B 42,5 N LH/HS	≥ 45	37.9	2.962	≥ 10	33.0 ± 4.0	≥ 42,5 ≤ 62,5
Limestone powder	-	0	0.43 to 0.98	-	-	-
Silica fume	-	-	2.451	-	-	-

Table 3-5; Characterization of cement (EN 196-1) (Source; EN 196-1, ENCI (the Netherlands), H.C.M Hollandse cement Maatschappij (the Netherlands), GMBH Hüttenzement readymix (Germany) www.bnminerals.com; Quercia et al., 2011)

3.2.4 Limestone

Powders of regular fineness should not influence the strength development of concrete. It is known that fine limestone powders can exhibit a limited hydraulic reactivity (Reschke, 2000). Limestone powder mainly consist of the mineral calcium carbonate ($CaCO_3$). Natural limestone contains silica in different proportions and is largely composed of calcite mineral. The powder contains calcite mineral based on the marine organism. There are a few points of interests when used in the cement industry;

- Limestone containing about 45% CaO and above is usually preferred for the manufacturing of cement.
- Magnesia content in the stone should ideally be less than 3%, although as high as 5% MgO is used by the industry.
- The proportion of $Al_2O_3 + Fe_2O_3$: SiO_2 should be 1:2:5. Magnesia sulphur and phosphorus are regarded as most undesirable impurities.

The use of limestone powder can enhance many aspects of cement-based systems through physical or chemical effects. Some physical effects are associated with the small size of limestone particles, which can enhance the packing density of powder and reduce the interstitial void, thus decreasing entrapped water in the system. For example, the use of a continuously graded skeleton of powder is reported to reduce the required powder volume to ensuring adequate formability for concrete (Fujiwara et al., 1996). Chemical factors include the effect of limestone filler in supplying ions into the phase solution. In Table 3-6 the chemical composition is shown, thus modifying the kinetics of hydration and the morphology of hydration products (Daimon and Sakai, 1998). Partial replacement of cement with an equal volume of limestone powder with a specific surface area ranging between 500 and 1000 m^2/kg resulted in an enhancement in fluidity and a reduction of the yield stress of highly flowing mortar (Yahia et al., 1999). Other investigations have shown that partial replacement of cement with an equal volume of limestone powder varying from 5% to 20% resulted in an enhancement of the fluidity of high-performance concrete having a w/c ratio ranging between 0,35 and 0,41 (Nehdi et al., 1998). This improvement may be due to the increase in w/c or in paste volume. As proven earlier, for a given water content, partial replacement of cement by equal volume of filler results in an increase in w/c. On the other hand, partial replacement of cement by an equal mass of limestone powder results in an increase of powder content, i.e. an increase in paste volume.

3.2.5 Fly ash

Fly ash, is a waste product from the energy production process. It remains following the combustion of hard coal. European countries produce 18 million tons of hard coal yearly. A major proportion is consumed by the building material industry, where it is used as a ingredient for the cement production or as an additive material for concrete production (Euroment, 2005). In the case of fly ash, the k-value is applied in order to deem part of the fly ash as cementious material. This value is explained in paragraph 3.2. The development of strength with the usage of fly ash in mortar and concrete mixtures is due in large part to its fineness. Increased fineness will result in the rise of strength development. The chemical composition of fly ash is shown in Table 3-6.

Elements Oxides	Limestone powder % (m/m)	Fly ash % (m/m)	Waste silica fume % (m/m)
SiO_2	-	47 - 53	41.411
SO_3	0.05	0.2 - 2.0	0.225
Na_2O	0.01	0.6 - 1.1	2.120
Al_2O_3	-	26 - 30	1.615
Fe_2O_3	-	5.0 - 15	0.435
CaO	-	2.4 - 3.9	51.517
Cl	<0.01	0.01	2.351
$CaCO_3$	97.84	-	-
$CaCO_3 + M_gCO_3$	99.27	-	-
K_2O	0.02	3.0 - 4.6	0.154
MgO	-	1.9 - 2.5	-
P_2O_5	-	-	0.021
TiO_2	-	-	0.058
MnO	-	-	0.043
PbO	-	-	0.014
SrO	-	-	0.036

Table 3-6; Composition of used powders (Source; Hemweg Euroment, www.bnminerals.com, international innoveren report 1 Quercia et al., 2011)

3.2.6 Density

Densities are explained in fourteen different ways according to the British Standards Institute (Webb, 2001). Similarly, the variety of test methods is also immense. This thesis only uses the standart tests according to the European Standard; as well as one automated method for the determination of volume and specific density which is used for the cement replacement tests. Table 3-8 represents the density of the included powders. Materials for concrete production according to EN 206-1 are separated into three different classes using their particle density:

- Particle density (oven-dry) in light weight aggregates of mineral origin $P_s < 2.0$ g/cm^3 ore a loose bulk density (oven-dry) $P_{loose} \leq 1.2$ g/cm^3,
- Particle density (oven-dry) in ordinary aggregates $P_s > 2.0$ g/cm^3 and < 3.0 g/cm^3,
- Particle density (oven-dry) in heavy weight aggregates $P_s \geq 3.0$ g/cm^3.

Material	Specific density (g/cm^3)	Density class
CEM I 52,5 R	3.150	Heavy weight aggregates
CEM III/B 42,5 LH/HS	2.962	Ordinary aggregate
Limestone	2.600 – 2.700	Ordinary aggregate
Fly ash	2.211	Ordinary aggregate
Waste Silica fume	2.451	Ordinary aggregate
Gravel 4-16	2.605	Ordinary aggregate
Sand 0-4	2.642	Ordinary aggregate

Table 3-7; Density properties used powders-fillers (Source; ENCI)

4 Characteristics of waste nano-silica sludge (nSS)

4.1 Introduction

Coal fly ash, ground granulated blast furnace (GGBF) slag, cenospheres, and silica fumes are recovered materials that are readily available in certain areas for use as ingredients in cement or concrete. Coal fly ash is a byproduct of coal burning at electric utility plants. Slag is a byproduct of iron blast furnaces. The slag is ground into granules finer than Portland cement and can be used as an ingredient in concrete. Cenospheres are small, inert, lightweight, hollow glass spheres that are components of coal fly ash. These spheres be added to cement to produce a specialty, high performance concrete. Silica fume is a waste material recovered from alloyed metal production. It can also be added to cement to produce a high performance concrete. The construction sector calls for concrete with a lower environmental impact. Based on this knowledge the International Innovation Project, has been established between Kijlstra Betonmortel B.V. and The Eindhoven University of Technology (TU/e). This study makes use of the findings and characteristic values of nano-silica rich sludge waste from the South Korean PV industry (Quercia et al., 2011).

4.2 Characterisation waste nano-silica (nSS)

Quercia et al. (2011) characterizes the nSS used in this study both physically and chemically. To get more insight of the used product in this chapter only a summary has been given, the full characterization is explained in the International Innoveren Report 1 (Quercia et al., 2011). A short explanation of the employed techniques is also provided in this thesis in order to gain insight on the method of extracting values. The characterization techniques that included are:

- Scanning electron microscopy (SEM)*.
- X-ray energy dispersive spectroscopy (EDS)*.
- X-ray powder diffraction (XRD).
- Nitrogen physical adsorption isotherm (BET, t-plot and BJH methods).
- Density by helium pycnometry*.
- Particle size distribution determined by laser light scattering (LLS).
- Dynamic light scattering (DLS).

*described in this thesis

4.2.1 SEM analysis of waste nano-silica

A Scanning Electron Microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. These electrons interact with the electrons found in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The morphology of nano-silica sludge was analyzed with a high-resolution Scanning Electron Microscope (FEI Quanta 600 FEG-SEM) using a Schottky field emitter gun. Furthermore, a general chemical analysis was performed using EDAX, X-ray energy dispersive spectroscopy (EDS).

The analysis of the silica sludge shows a low content of larger angular particles. It does however show a highly agglomerated state (Figure 4-1f) small angular (Figure 4-1c) and spherical particles (Figure 4-1b) as identified by the FEG-SEM. The spherical particles (Figure 4-1b) are composed of SiO_2 (silica fume) commonly used in the preparation of CMP slurries (Min and Kwan, 2004). In addition to the spherical particles, small angular particles with a high content of Ca (detected by EDS) were also identified. The calcium rich particles are most likey composed of $CaCO_3$, which is used for CMP slurries as well (Min and Kwan, 2004; Yamamoto et al., 2002; Morioka et al., 2002)

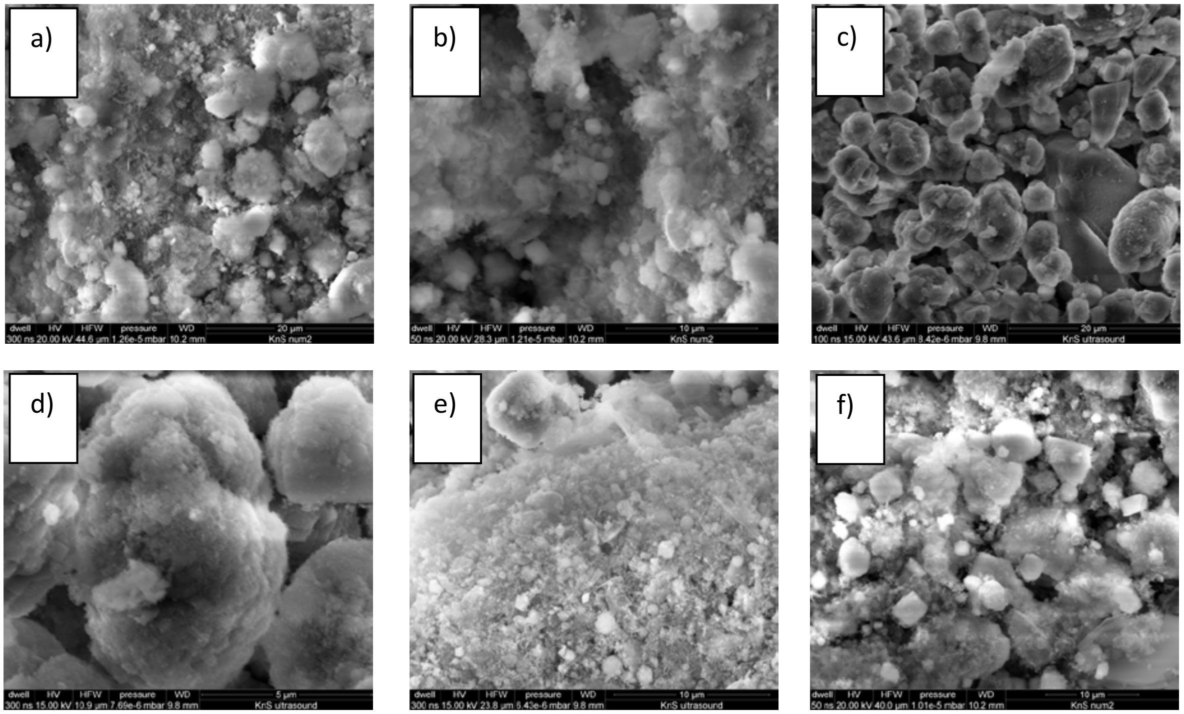
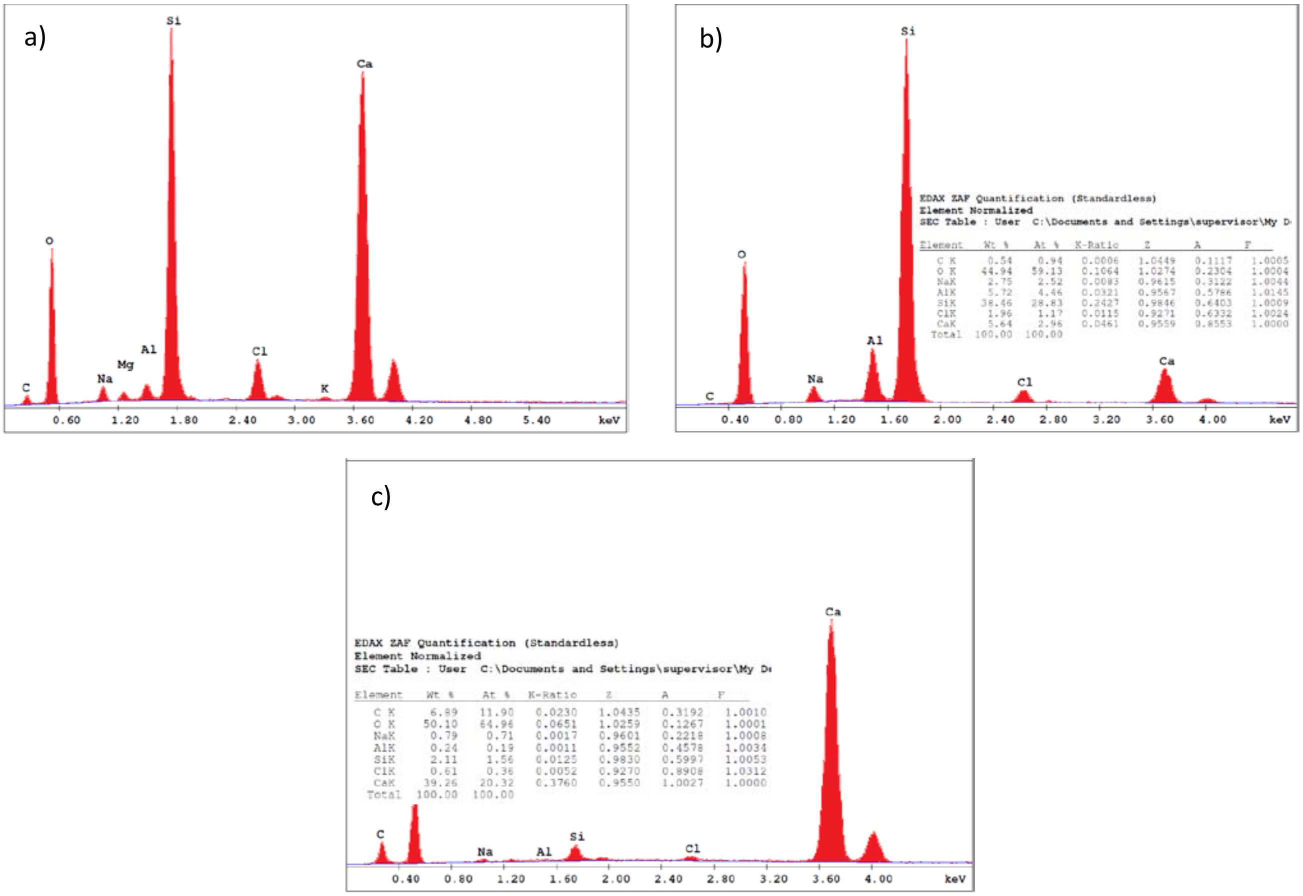


Figure 4-1; FEG-SEM photomicrograph of nano-silica sludge (Source; Quercia et al., 2011)

4.2.2 EDS analysis waste nano-silica

Energy-dispersive X-ray spectroscopy (EDS) is an technique used to analyze the elemental factors of chemical characterization of this waste nano-silica ore other materials. It relies on the investigation of X-ray stimulation on specified samples. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles is focused into the sample. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell thus creating an electron hole where it had previously been. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The energy levels and number of X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays represent the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured (Goldstein, 2003).

Through the analysis with EDS (Quercia et al., 2011), the amount of silica (Si) or silicon dioxide (SiO_2) is determined at 46.79%. Other chemical elements that are identified in the nano-silica sludge (Figure 4-2) are; Carbon (C), Sodium (Na), Chloride (Cl), Calcium (Ca), Magnesium (Mg), Potassium (K) and Aluminum (Al). Within the angular particles a high concentration of C and Ca is detected, these products probably compose to Calcium carbonate ($CaCO_3$). Other observations shown that the chloride content in the sample is high, reaching values of 2.64 wt %. This chloride concentration is above the maximum concentration (0.3% by mass) documented for silica fume in NEN EN 13263-1 A1 (Netherlands Standardization Institute, 2005). In chapter 5 the chloride content in mortar mixtures is analyzed and explained.



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EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : User  C:\Documents and Settings\supervisor\My D

Element   Wt %    At %   K-Ratio     Z        A        F
   C K     0.54    0.94   0.0006   1.0449   0.1117   1.0005
   O K    44.94   59.13   0.1064   1.0274   0.2304   1.0004
   NaK     2.75    2.52   0.0083   0.9615   0.3122   1.0044
   AlK     5.72    4.46   0.0321   0.9567   0.5786   1.0145
   SiK    38.46   28.83   0.2427   0.9846   0.6403   1.0009
   ClK     1.96    1.17   0.0115   0.9271   0.6332   1.0024
   CaK     5.64    2.96   0.0461   0.9559   0.8553   1.0000
  Total  100.00  100.00
```

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EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : User  C:\Documents and Settings\supervisor\My D

Element   Wt %    At %   K-Ratio     Z        A        F
   C K     6.89   11.90   0.0230   1.0435   0.3192   1.0010
   O K    50.10   64.96   0.0651   1.0259   0.1267   1.0001
   NaK     0.79    0.71   0.0017   0.9601   0.2218   1.0008
   AlK     0.24    0.19   0.0011   0.9552   0.4578   1.0034
   SiK     2.11    1.56   0.0125   0.9830   0.5997   1.0053
   ClK     0.61    0.36   0.0052   0.9270   0.8908   1.0312
   CaK    39.26   20.32   0.3760   0.9550   1.0027   1.0000
  Total  100.00  100.00
```

Figure 4-2; EDS spectrum of waste nano-silica sludge a) EDS spectrum from the area show in Figure4-2a, b) typical spectrum found for agglomerated particles shown in Figure 4-2d and c) spectrum found for angular particles shown in Figure 4-2f. (Source; International innoveren report 1, Quercia et al., 2011)

4.2.3 Waste nano-silica Sludge

Silica fume consists of amorphous (non-crystalline) silicon dioxide (SiO_2) described in paragraph 4.2.2. The individual particles are extremely small, because of its fine particles, large surface area, and the high SiO_2 content. Silica fume, also referred to as microsilica or condensed silica fume, is a byproduct material that is used as a pozzolan. To determine the particle density of filler material a test is carried out according to EN 1097-7, which shows the particle size of the NSS waste used. The specific density of the silica sludge was measured by Quercia et al. (2011) using a helium pycnometer AccuPyc® II 1340 from Mircromeretics. The relative density of silica fume is generally in the range of 2.20 g/cm^3 - 2.5 g/cm^3. Portland cement has a relative density of about 3.15. In this context can be concluded that the value given in Table 3-5, the average values obtained were 2.451 g/cm^3. The reason of the high density values is the content of $CaCO_3$, the value is 52 % by mass, which has a density of 2.73 g/cm^3 (Quercia et al., 2011).

4.3 Slurry design

4.3.1 Slurry design of waste nano-silica sludge (nSS)

Based on the results of the International Innoveren Report (Quercia et al., 2011), a stabilized slurry was designed and used for testing. The majority of the tests in the mortar stage were performed with this slurry, having a solid content of 16.72%. Table 4-1 shows the different components that where used to obtain the slurry. The slurry with the solid content of 16.72% was obtained through pre-dispersed the waste nano-silica powder for 1 hour at 7000 rpm in water, using a glass stirred vessel (2L beaker) coupled to a high energy shear mixer (Silverson L5M with an Ultramix® mixing shaft, see Figure 4-3a). Prior to the pre-dispersion step, KOH and a polycarboxylate type SP (Viscocrete® 2610 from Sika®) were added to stabilize the slurry, and to modify the final pH value between 9.1 to 9.6. After this, the dispersions were transferred to the high shear mixer, but using a size reduction stator head for additional 30 min (Figure 4-3b). The obtained slurry was stable in time (no gelling observed), but sedimentation was observed after 2 hours of static condition without any dispersion (Figure 4-3c). Despite the sedimentation, the slurries were easy to re-disperse by hand agitation (Figure 4-3d) inclusive at longer time of static conditions (ex. 3 weeks) as shown in Figure 4-3d. With these obtained slurry the replacement levels up to 30% were made in the SCM tests.

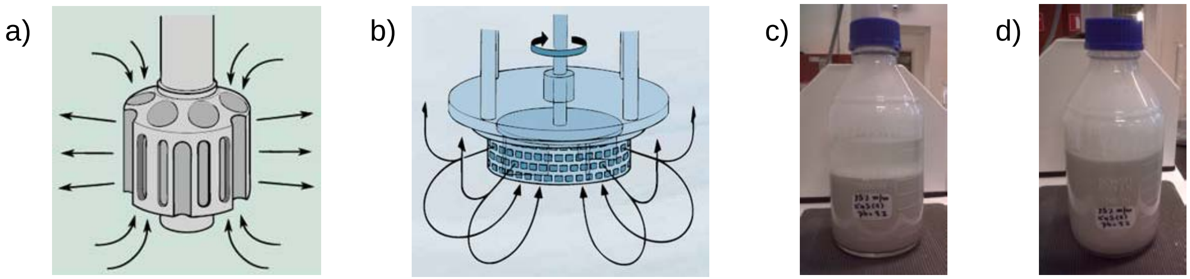


Figure 4-3; a) Ultramix® dispersion mixing shaft , b) high shear reduction size stator head, c) sedimentation example of one prepared slurry mix after 2 h of static conditions, d) same slurry of Figure 4-3c after hand agitation.

Batch number	**2b**	**$2b^2$**
Water (g)	600	600
Powder waste nano-silica sludge (g)$^{+}$	200	376
NH_4OH (cm^3)	-	-
KOH (g)	1.13	3.6
SP (g)	4.4	5.9
Final pH	9.30	9.29 + 0.4
Slurry density (g/cm^3)	1.109	1.19 ± 0.02
Solid content (% m/m)*	16.72	26.50 ± 2.0

Table 4-1; Slurry dimension of used materials. (+): 30 to 35% content of H2O, (*): Obtained by drying 5 g of slurry at 100°C for 72 h.(Source; Quercia et al. 2011)

4.3.2 Re-design slurry

After the first results carried out by Quercia et al. (2011), subsequent tests with these slurry has resulted into a more stable slurry with a solid content of almost 10% higher than the previous slurry design. The new slurry design has an solid content of 26.5% (Table 4-1 $2b^2$). After increasing the nano-silica waste powder used, a higher amount of KOH and SP is necessary. The final pH value must to be 9.2 or higher. The increased solid content results in a decreased mixing time. The nano-silica waste powder was dispersed for 15 minutes at 7000 rpm in water, a 2L glass beaker was used coupled with a high energy shear mixer (Silverson L5M) with an Ultramix® mixing shaft, similar to that used in the mixture of 16% slurry design. After this 15 min the dispersions were transferred to the high shear mixer, but using a size reduction stator head for additional 30 min. The obtained slurry of 26.5% didn't have sedimentation for 3 days (Figure 4-4 a), also this slurry was easy to re-disperse by means of hand agitation (Figure 4-4b). In the preparation of large amounts of slurry for the SCC with only 30 minutes of mixing with the high shear size reduction stator head the same results are found. Further attempts to increase the solid content of the slurry were impossible. Slurries with a solid content of 50% result in a clay-like consistency with an increase in gelling.

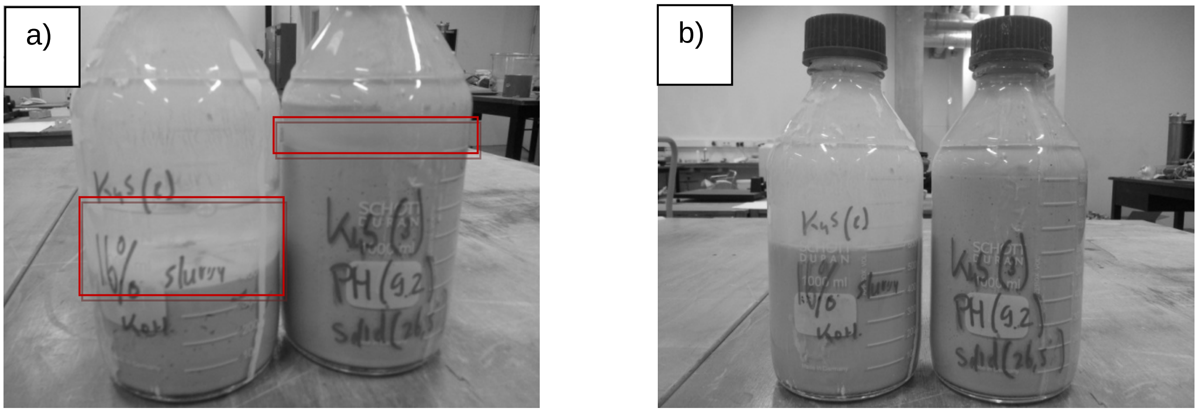


Figure 4-4; Slurries 16.72% and 26.5% sedimentation(a) and re-dispensed(b) (Source; Putten 2012)

5 Self-Compacting Mortar (SCM)

5.1 Introduction

This chapter continues the design of a new SCM with waste silica as cement replacement. Chapter 2 discussed the application of waste nSS into the construction process and, Chapter 3 gave more insight about the powder materials to be used and chapter 4 explained the waste nano-silica slurry that is used. In this chapter it is needed to explain two more ingredients for a new mortar, this will be sand and gravel. In Europe a particle size of 4 mm is used as a separation criteria between coarse and fine aggregate. Table 5-1 classifies the aggregates into fractions. From the packing point of view, as well as taking into account other fresh properties such as water demand and flow behavior; there is no major difference between mortar and concrete. However, when designing a concrete, the mortar is of great importance because of the little effort and smaller quantities required to adjust the desired properties. The mortar mixture can be easily adapted into a full-scale concrete mixture. This chapter will explain the design and test procedures in order to adjust the water and plasticizer amounts in the desired fresh mortar composition.

Material	Sieve size (Upper)	Sieve size (Lower)	Fraction distribution
Powder materials (filler)	0.063 (70%)	-	0
Sand (Fine aggregates)	≤ 4 mm	0	0-1, 0-4
Gravel (Coarse aggregates)	≥ 4 mm	≥ 2 mm	2-8, 4-16, 16-32

Table 5-1; Aggregates classification into fractions (Source; EN 12620 maximum particle size)

Another aggregate classification pertaining to specific gravity is presented in paragraph 3.2.7, it displays the specific density of the final mortar and concrete.

5.2 Reference design Fresh SCM

At this point all the materials used have been explained and introduced. The design steps in creating this mortar must now be tested. As such there will be a number of trial and error mixtures before the desired properties are reached. Kijlstra Betonmortel B.V. has provided a reference mixture for this stage of development – using concrete with waste silica as a cement replacement. Given these ingredients and their classification, the proportions are already delivered therefore there is no need to change the powder or aggregate fraction for the reference mix design. The w/c is fixed and given to the amount of cement. This has been done in order to ensure the strength development in a later stage, which relies on the w/c (or w/p). The amount of the w/c is determined on 0.427.

The following factors have been calculated by equation (3.1) in paragraph 3.2 with the receipt documented in Table 5-2 and 5-3 for the fly-ash system and limestone system respectively.

Materials (g)	Ref.	10%	20%	30%	100%
Silica sludge (16 or 26,5$^{(+)}$ wt.% solid)	0	89.1	178.1	267.2	305.7$^{(+)}$
CEM I 52.5 R	142.5	128.3	114.0	99.8	0
CEM III/B 42.5 LH/HS	382.5	382.5	382.5	382.5	534.7
Fly-Ash Hemweg	240.0	240.0	240.0	240.0	190.8
Fine gravel 0-8 Smal	1267.7	1267.7	1267.7	1267.7	1195.3
Water	244.5	166.0	87.0	8.0	30.5
SP (Cugla® PCE type)	5.2	5.8	5.8	5.8	7.1
w/b	0.427	0.428	0.428	0.428	0.427

Table 5-2; Material amount SCM Fly-ash system

Materials (g)	Ref.	10%	20%	25%	100%
Silica sludge (16 or 26,5$^{(+)}$ wt.% solid)	0	117.2	234.4	293.0	176.9 $^{(+)}$
CEM I 52.5 R	187.5	168.8	150.0	131.3	0
CEM III/B 42.5 LH/HS	360.0	360.0	360.0	360.0	540.0
Limestone powder (Betofill®)	277.5	277.5	277.5	277.5	277.5
Fine gravel 0-8 Smal	1290.8	1290.8	1290.8	1290.8	1290.8
Water	257.5	153.5	49.5	0.0	107.0
SP (Cugla® PCE type)	5.4	5.4	6.0	6.3	8.1
w/b	0.427	0.427	0.427	0.439	0.427

Table 5-3; Material amount SCM limestone system

5.2.1 Test results for self-compact-ability (slump flow)

Flow-ability is mainly measured using a slump flow test or mini slump flow in the mortar stage, which is simple and reliable. Apendix A describes the slump flow for SCC. There is little difference between these tests on the mortar scale. The slump flow of the mortar mixture is investigated using the Hägermann cone as shown in Figure 5-1. The slump flow test is a classical method in determining the slump flow of a mixture. For the production of the paste an ordinary mortar mixer is used. To obtain the best results a mix procedure is predetermined (Hunger, 2010). The recommended working surface to obtain the most reliable data is a dry, clean, horizontal and non-sticking surface. A glass plate was used for the slump flow test in this thesis.

5.2.2 Mixing procedure

After appropriate mixing following a defined mix procedure, the paste is filled in a special conical mold in the form of a frustrum, better known as the Hägermann cone (EN 1015-3) (Figure 5-1) which is lifted straight upwards in order to allow free flow for the paste without any jolting. A mixing procedure is described in EN 196-1, and adjusted to the supplemental of the waste nSS. The test procedure is described below

- Add the weighed amount of water into the moisturized mixing bowl.
- Continue with adding the complete amount of powder mixture (CEM I,CEM III, Fly ash, Limestone).
- Add the weighed amount of Slurry into the moisturized mixing bowl.
- Start mixing for 30 seconds on speed level 1.
- Add in 30 seconds the weighed amount of additives (fine gravel 0-8 mm).
- Stop the mixing activity for 60 seconds, where the first 15 seconds are used to scratch splashed material from the wall of the mixing bowl and the paddle.

- Add the amount of Super plasticizer that is weighed into the mixture.
- Continue mixing for further 90 seconds on speed level 2.

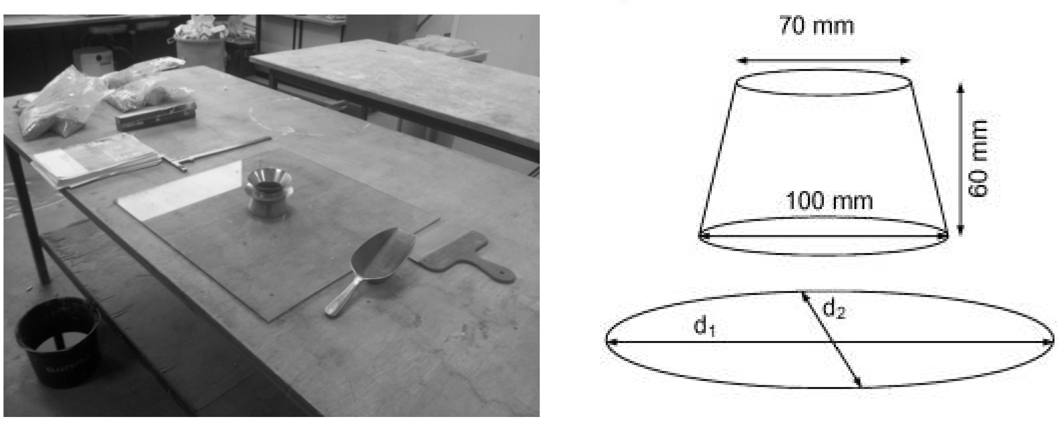


Figure 5-1; Hägermann cone test setup (Source; picture J van der Putten)

The reached paste, prepared in this way needs to be filled into a light moisturized Hägermann cone using a filing hopper. The hopper needs to be removed and surplus material needs to be wiped off, to get the same material volume every time. The test needs to be done twice to get at least four different values to obtain a statistically reliable average of the tested mortar (d). From the spread flow of the paste, two diameters perpendicular to each other (d_1 and d_2) can be determined following:

$$d = \frac{d_1 + d_2}{2} \tag{5.1}$$

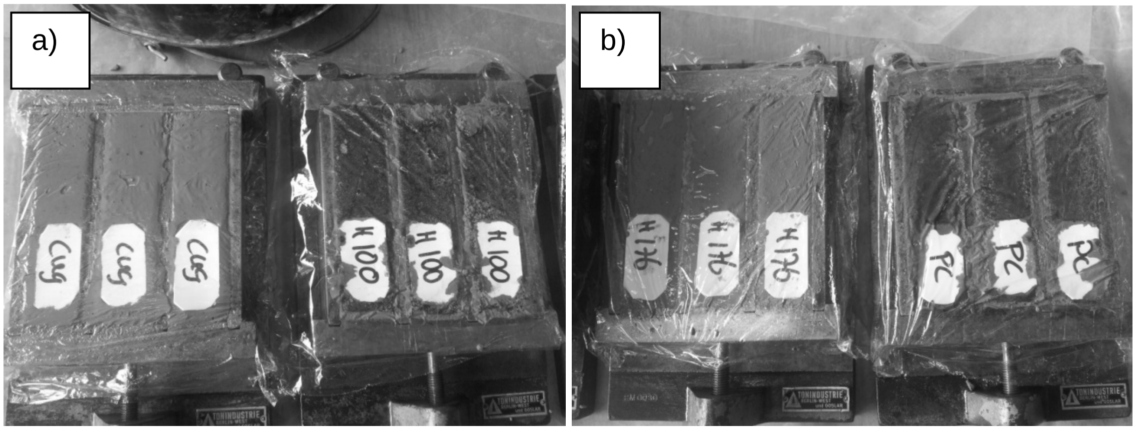
The achieved mortar values are shown in Table 5-4. The formula above, when paired with the spread flow test measures the control criteria to assess the limit of flow and the slump flow. When the measured spread was smaller than the reference (required slump flow diameter given by the reference mixture by Kijlstra Betonmortel B.V.), plasticizer was added in respectively small amounts until the measurement corresponded with the desired values. Similarly, in the case of a high slump flow measurement, the super plasticizer must be decreased until the desired value is reached. The reference mixture has a spread flow of 259 ± 25 mm in the first trials. The spread flow increased up to 311 ± 2 mm in the 7-28 day mixture, according to the target range of Kijlstra Betonmortel B.V. This closely corresponds to the target flow of 650 to 900 mm for the fully scaled concrete mixture.

Property measured	Test method	Material (mortar) Fly ash (additive)	Reached values (mm) *Serie 1*$^+$	Reached values (mm) *Serie 2**	Material (mortar) Limestone (additive)	Reached values (mm) *Serie 1*$^+$	Reached values (mm) *Serie 2**
Flowability	Slump flow	Reference	259 ± 25.0	311 ± 2.0	Reference	333 ± 9.0	328 ± 22.0
		10 %	277 ± 14.0	312 ± 2.0	10 %	318 ± 4.0	317 ± 4.0
		20 %	278 ± 30.0	309 ± 19.0	20 %	306 ± 5.0	310 ± 9.0
		30 %	257 ± 22.0	312 ± 34.0	25 %	306 ± 4.0	306 ± 8.0
		100 %	277 ± 11.0	259.5 ± 11.0	100 %	304 ± 5.0	274 ± 11.0

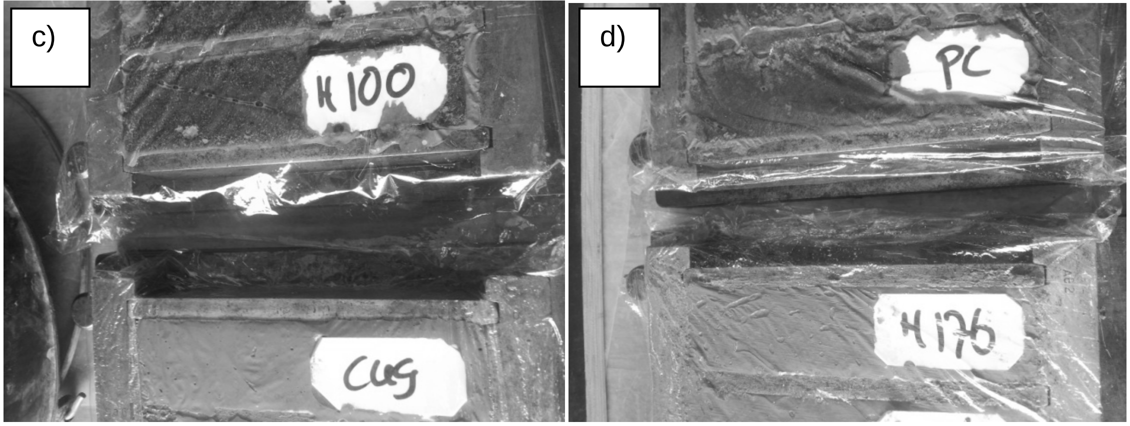
Table 5-4; SCM mini slump flow results $^+$ Values for 16 hour mixtures, * values on 7 – 28 day mixtures

5.2.3 Influence of Superplacticizer on mortar

Another interesting element of designing the mixture in its fresh state is the influence of different superplacticizers. The required compression strength values (further explained in paragraph 5.4) for the 100% replacement in the fly ash system do not meet the requested values of Kijlstra Betonmortel. Therefore other plasticizers must be tested. The SPs CUGLA R11 from CUGLA BV, Also the SPs Pantarhit ® RC100 and Pantarhit ® RC176 and Pantarhit® PC 150 from Ha-Be Betonchemie GmbH & CO. KG are used. Figure 5-2 displays the different influences of the SP on mortar once it has been casted. The casting of the mixture with CUGLA and RC 176 as additives show no remarkable differences compared to plain mortar after casting. When comparing the usage of RC 100 and PC 150, a separation of the fly-ash particles (black top layer) exists in the self-compacting stage, immediately after pouring. The reason for the separation of the fly-ash particles is unclear, this phenomenon has not occurred in the replacement of 10%-20%-30%. It may be due to the inclusion of too much H_2O or SP in the systems.



(a) Cugla R11 – TB 100 (b) RC 176 – PC 150



(c) Cugla R11 – RC 100 (d) RC 176 – PC 150

(e) Cugla R11– RC 100 – RC 176 – PC 150

Figure 5-2; Segregation of fly ash in different mortar mixtures (Source; Putten, 2012)

5.3 Hardened mortar

5.3.1 Introduction

For this study extensive fresh mortar tests have been carried out to investigate the effect of CEM I 52,5 R substitution with nSS. In total 138 test samples (69 for the fly ash system and 69 for the limestone system) were made and measured based on the desired values given by Kijlstra Betonmortel. For the most part the fresh mortar experiments are only intended to provide groundwork for the final full–scaled concrete mixtures. The tests conducted on the 138 specimens show that they do not have the same properties as a concrete. The additives influence small-scale production. All poured elements are tested for their developed compressive and flexural strength at 16 hour, 7 and 28 days.

5.3.2 Fly-ash

The most important value to be measured is the 16 hour compressive strength, strength value. It must be fixed in the range of the industrial point of view. This strength value is the most important, because it is related to the productivity of precast concrete units. Two different systems have two different required values. In this case, the minimum compressive strengths required are 8 and 14 MPa for the fly-ash and limestone systems, respectively.

Figure 5-3a, shows a clear decrease in the 16-hr strength value compared to the SCM reference for substitution levels higher than 10%. This suggests that the optimum replacement ratio depends on the amount of nSS in the system and the decrease in CEM I 52,5R. This ratio would be between 10 and 30 % bwoc. Despite the reduction in the compressive strength values, the fly ash SCM with 30% bwoc of the silica sludge resulted in a higher compressive strength than the required limit of 8 MPa. There was little increase in the amount of SP when compared to the reference mixture (Figure 5-3b). It is important to notice that the 16-hr compressive strength is influenced by the amount of SP added to the SCM. Thus, the higher the replacement level the more SP is required for the same flow class. As a result, the early strength drops significantly due to the increased amount of SP.

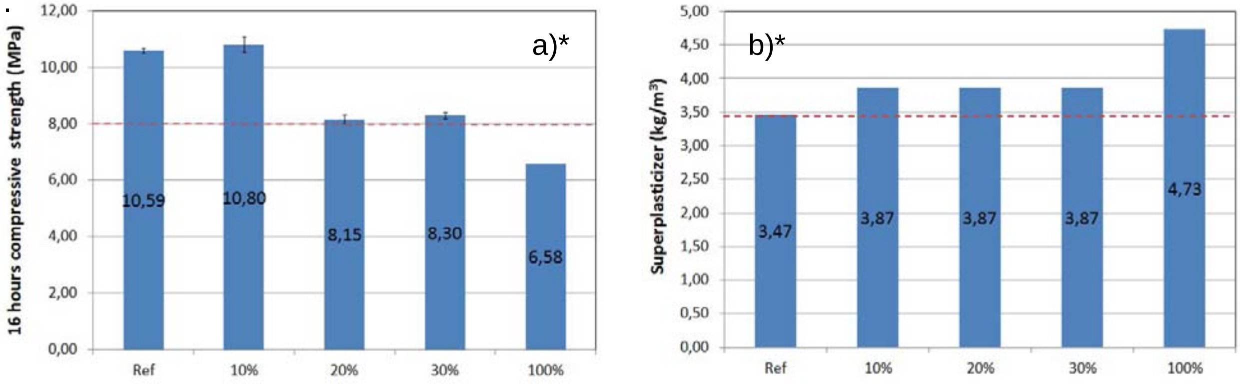


Figure 5-3; Compressive strength of the tested SCM-fly ash system with different replacement levels of CEM I **a)** 16-hr, **b)** SP amount *replacement levels 10-20-30% with 16 wt.% solid, 100% replacement 26,5 wt.%)

The reference mixture has a amount of SP of 1.49% bwob or 3.47 kg/m^3, all the tested mixtures with replacement levels had an increased usage of SP of 1.66% bwob or 3.87 kg/m^3. It is a slight increase of usage of SP but it results in the desired values of spread flow and compression strength. Due to the influence of the SP content in the first hours, further experiments were carried out with other different SP types to determine the correct dosage and type of the SP that, allows an increase in the replacement level of cement with nSS. A 100% replacement of CEM I 52,5R by nSS needs a SP dosage of 2.03% bwob or 4.73 kg/m^3. On the contrary to the 16 hour results, the 7 and 28-days compressive strength of almost all SCM was improved by the replacement of CEM I by the nSS in the range of 10 to 100% bwoc. In Figure 5-4c and 5-4d the 7 and 28-days compressive strength is displayed. Similar to the compressive strength results, the flexural strength was improved. The flexural strength was slightly affected showing the lowest value for 30% of substitution as it is shown in Figure 5-5 a and 5-5 b

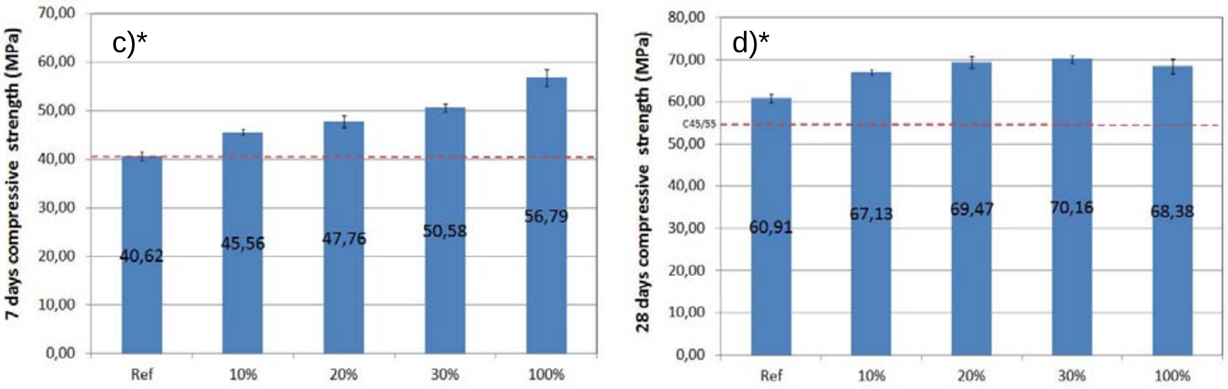


Figure 5-4; Compressive strength of the tested SCM-fly ash system with different replacement levels of CEM I **a)** 16-hr, **b)** 7 days, **c)** 28 days, **d)** SP amount *replacement levels 10-20-30% with 16 wt.% solid, 100% replacement 26,5 wt.%)

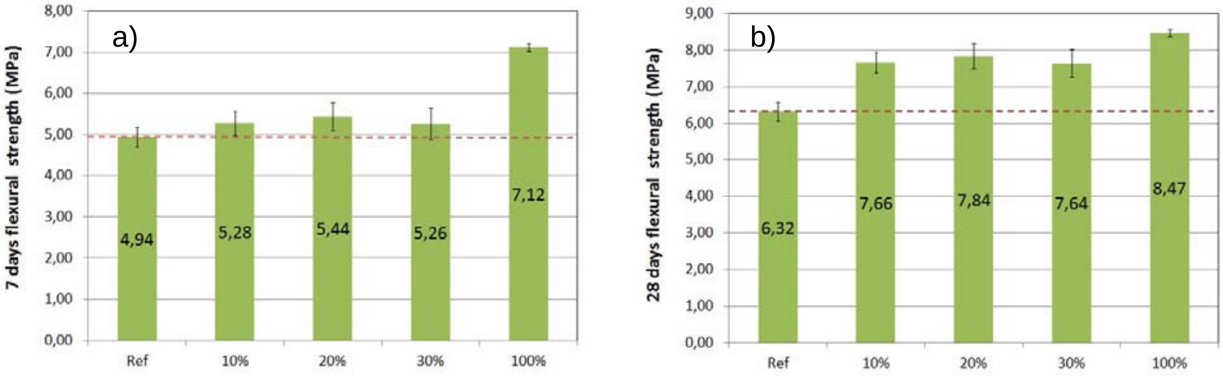


Figure 5-5; Flexural strength of the tested SCM-fly ash system. **a)** 7 days, **b)** 28 days

The flexural strength values are determined using a 3-point flexural test (Figure 5-6a). As a result of the compression test, lateral shearing stresses are effective in the concrete specimen. Effects of the shearing are less evident towards the centre of cube as shown in (Figure 5-6b) therefore the core is relatively undamaged.

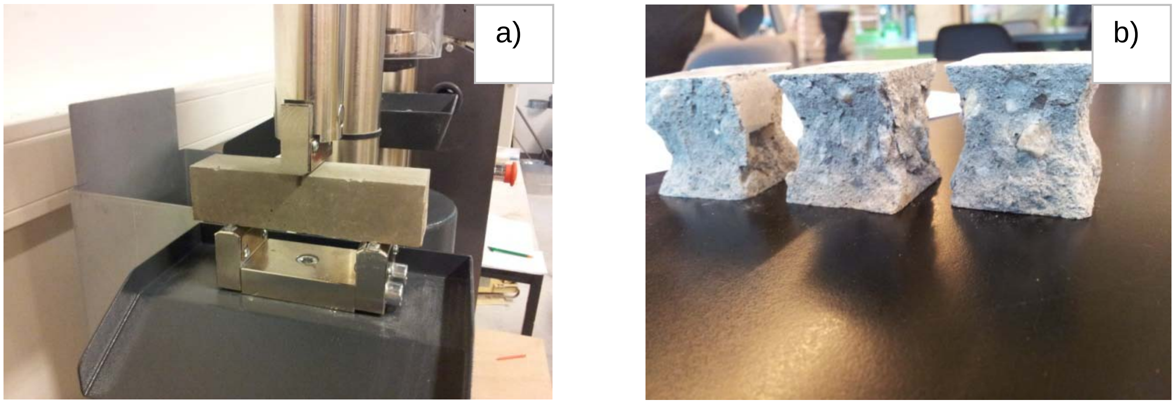


Figure 5-6; a) Determination Flexural strength **b)** Compressive strength result (Source; Putten 2012)

Paragraph 4.3.2 explains the SPs used throughout this study. When looking at the system it seems that the 16 hours strength can be improved for higher substitution levels of CEM I 52.5R up to 100% using nSS. It has been determined that not every SP can reach the requested value, and the amount of SP can be reduced to obtain the minimum required strength at 16 hours for the fly-ash system. Figure 5-7 shows the different SPs at the 100% replacement mixture. As previously stated the minimal value reached is 8 MPa. Of the SPs tested only one reached this value. It becomes evident that the best SP is the PC 150 because it results in higher compressive strength with a lower amount of SP. Along with the high compressive strength the amount of chloride content in the mixture is also a parameter that should be taken into account. These tests will be explained in paragraph 5.5.

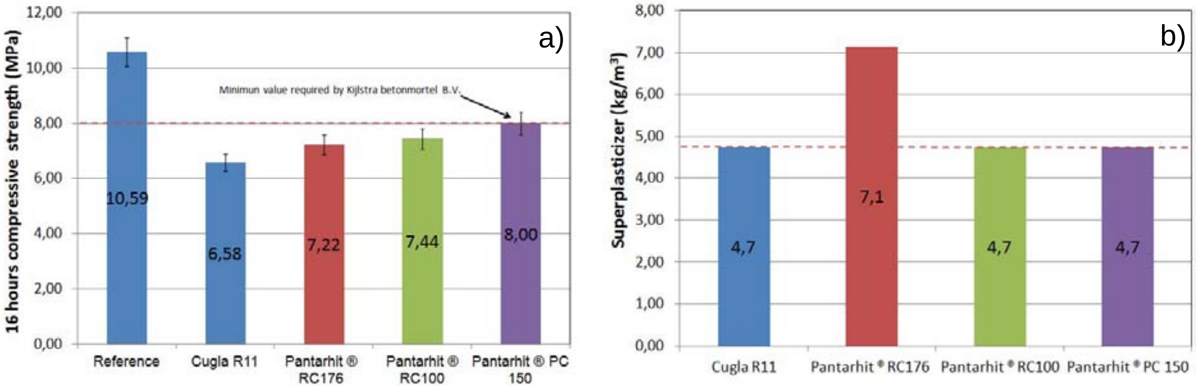


Figure 5-7; SCM with 100% replacement of CEM I by nSS **a)** 16 hourcompressive strength of the tested SCM with different types of superplasticizer, **b)** concentration and type of superplasticizer used. (Silica sludge 26,5 wt.% solid)

5.3.3 Limestone

Similarly to the previous paragraph the limestone system was also tested. For this system the requested value is 14 MPa. Figure 5-8a shows a clear decrease in the 16 hour strength compared to the reference SCM for substitution levels higher than 25% for the limestone system. This suggests that the optimum replacement ratio depends on the system (type of filler). This ratio would be between 20 and 25% bwoc for the limestone powder system. Despite the reduction in the compressive strength only the mortars with 10 and 20% replacement meet the required minimum (14 MPa). The influences of SP on the system, as shown in paragraph 4.4.2, also apply to the limestone SCM.

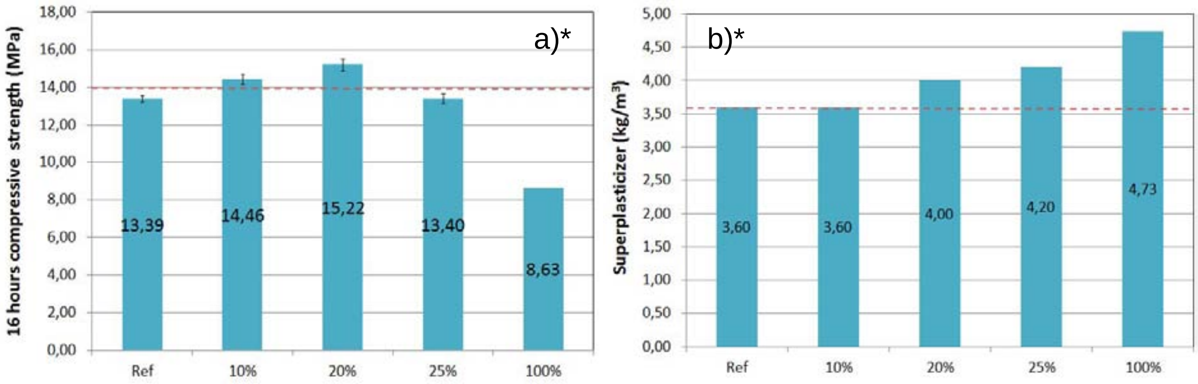


Figure 5-8; Compressive strength of the tested SCM-Limestone with different replacement levels of CEM I **a)** 16-hr, **b)** SP amount *replacement levels 10-20-25% with 16 wt.% solid, 100% replacement 26,5 wt.%)

The reference mixture has an SP amount of 1.54% bwob or 3.60 kg/m^3, which is the same for the 10% replacement mixture. The following two systems of 20 and 25% both have an increased SP usage of 1.71% bwob or 4.00 kg/m^3 and 1.80% bwob or 4.20 kg/m^3 respectively. The slight increase in SP provides the desired values of spread flow and compression strength. Due to the influence of the SP content in the first hours, further experiments were carried out with different SP types. This was done in order to determine the correct dosage and type of the SP that allows an increase in the replacement level of cement with nSS. For 100% replacement, an SP dosage of 2.03% bwob or 4.73 kg/m^3 is required – which is the same for the fly ash system. Contrary to the 16 hour results, the 7 and 28-day compressive strength values of most SCMs were improved by replacing the CEM I with nSS in the range of 10 to 100% bwoc. One exception in the strength development exists within the 7 and 28 day tests. The 25% replacement level, which showed a slight drop in strength, is still higher than the minimum strength class specified as C45/55 MPa. In Figure 5-9a and 5-9b the 7 and 28-days compressive strength is displayed. Similar to the compressive strength results, the flexural strength was improved. The flexural strength was slightly affected with 25% of substitution displaying the lowest value. It is shown in Figure 5-10a and 5-10b.

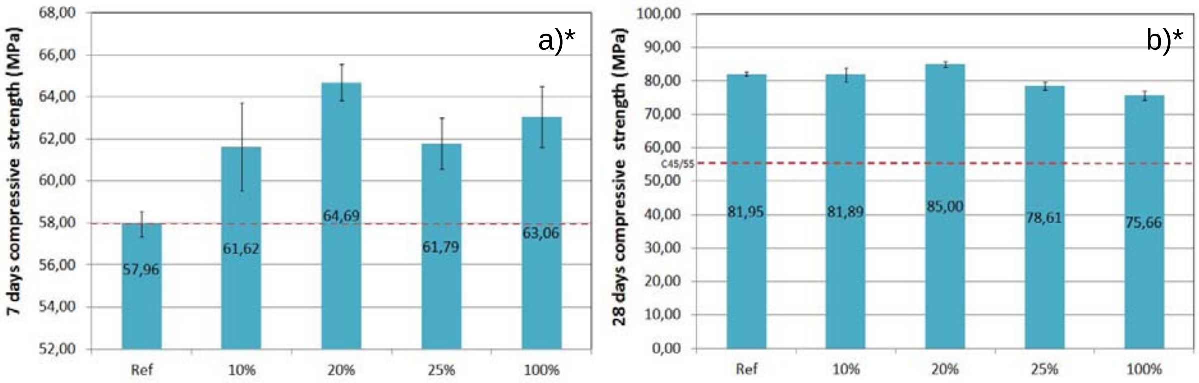


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Figure 5-9; Compressive strength of the tested SCM-limestone with different replacement levels of CEM I **a)** 7 days **b)** 28 days, *replacement levels 10-20-25% with 16 wt.% solid, 100% replacement 26,5 wt.%)

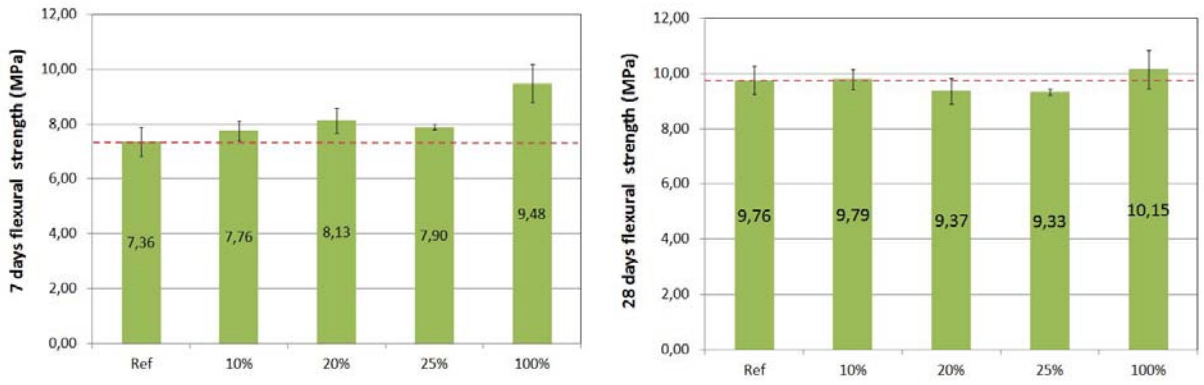


Figure 5-10; Flexural strength of the tested SCM-limestone. **a)** 7 days, **b)** 28 days

Following the observation of the fly ash system, the limestone system has also been analyzed. When looked at this system it seems that the 16 hours strength can be improved for higher substitution levels of CEM I 52.5R up to probably 100% by the nSS. The influence of SP shows that not every SP can reach the requested value of 14 MPa after 16 hour. None of the tested SPs reaches this value. It is evident from Figure 5-11a that the best SP is the PC 150 because it results in the highest value after the 16 hour, but still not enough to get to the 14 MPa. It can be concluded that a 100% replacement is not possible for the limestone system. The values that are nearest to 14 MPa are the 20 and 25%. Further test are needed to determine the maximum replacement value.

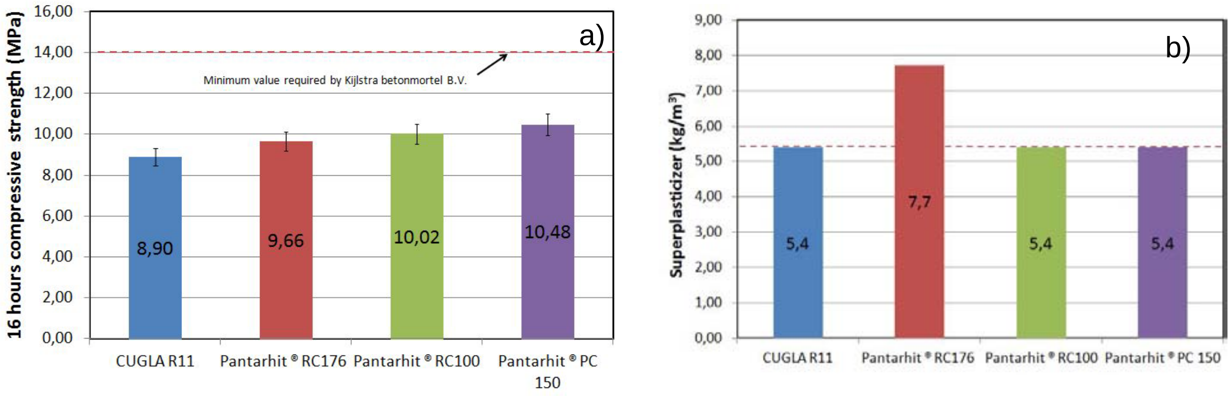


Figure 5-11; SCM with 100% replacement of CEM I by nSS **a)** 16 hourcompressive strength of the tested SCM with different types of superplasticizer, **b)** concentration and type of superplasticizer used. (Silica sludge 26,5 wt.% solid)

Compressive strength is the only controlling factor at play. The amount of chloride content in the mixtures is a critical value. These tests will be explained further in the next paragraph.

5.4 Chloride content of SCM

5.4.1 Introduction

It is well recognized that the presence of chloride in reinforced concrete can lead to corrosion of the reinforcement by destroying the passive layer on the steel surface (Page & Treadaway 1982). While modern standards impose restrictions on the amount of chloride that may be introduced to the fresh concrete mix, penetration of chloride into hardened concrete is currently the major cause for pitting corrosion in concrete structures. The concept of critical chloride content in reinforced concrete is based on the general agreement that corrosion in non-carbonated, alkaline concrete can only start once the chloride content at the steel surface has reached a certain threshold value. This value is normally referred to as critical chloride content or chloride threshold value (Angst & Vennesland, 2009).

5.4.2 The critical chloride content

The critical chloride content is most commonly expressed as total chloride content relative to cement weight. The main reason for this is the fact that the determination of total chloride content is relatively simple and well documented in standards (BS EN 206-1, 2007). Since the binder content is not always known, it is sometimes preferred to relate the total chloride content to the weight of concrete. Since free chlorides are generally considered to be of most importance for corrosion initiation, the critical chloride content is generally expressed by use of free chloride contents, either related to the binder or concrete weight or as a concentration in mol/l in the pore solution. Glass & Buenfeld (1997) suggested that presenting critical chloride contents is best done in the form of total chloride by weight of binder. The various forms to express critical chloride contents reflect both the destructive species and the inhibitive properties of the concrete in different ways. Table 5-5 summarize the available expression forms.

Aggressive species	Inhibitive property	Expressed as
Total chloride	By binder weight	% by weight
	By concrete weight	% by weight
Free chloride	By binder weight	% by weight
	By concrete weight	% by weight
Free Cl^- concentration	-	mol/l

Table 5-5; Different forms to express critical chloride (Source; U. Angst & Ø. Vennesland, 2009)

The European standards (BS EN 206-1, 2007), requires that concrete should have a maximum chloride ion content by mass of cement depending on certain criteria. This is expressed as a chloride class e.g. Cl^- 0.40. Prestressed concrete or concrete containing reinforcement of other embedded metal that is to be heat cured, should normally be specified as chloride class Cl^- 0.10. In prestressed post-tensioned and unbounded prestressed concrete, no particular guidance is given as the appropriate class will depend on the construction and exposure conditions. For internal post-tensioned office construction, Cl^- 0.40 is considered appropriate. Reinforced concrete with ordinary carbon steel or other embedded metal it should be specified as chloride class Cl^- 0.40, or Cl^- 0.30 where significant external chloride exists. However, for concrete made with cement conforming to BS 4027 (SRPC), the chloride class should be Cl^- 0.20. All the mentioned values above are shown on Table 4-7.

Concrete use	Chloride content class[a]	Maximum Cl^- content by mass of cement[b]
Not containing steel reinforcement or other embedded metal with the exception of corrosion-resisting lifting devices	Cl^- 1.00	1.0 %
Containing steel reinforcement or other embedded metal	Cl^- 0.20	0.20 %
	Cl^- 0.40	0.40 %
Containing prestressing steel reinforcement	Cl^- 0.10	0.10 %
	Cl^- 0.20	0.20 %

[a] For a specific concrete use, the class to be applied depends upon the provisions valid in the place of use of the concrete.

[b] Where type II additions are used and are taken into account for the cement content, the chloride content is expressed as the percentage chloride ion by mass of cement plus total mass of additions that are taken into account.

Table 5-6; Maximum chloride ion content by mass of cement (Source; BS EN 206-1, 2007)

5.4.3 Test procedure

The total chloride content of the mixtures systems is determined following different procedures. The first tested procedure was by following the procedure using a potentiometric titration technique (Spiesz & Brouwers, 2012). The obtained values of these tests were transformed in equivalent chloride concentration based on the binder content of the mixture, and compared to the limits given in EN 206-1 (Table 5-6). The procedure used to analyze the total chloride content is described as follows:

- Dry the powder of the systems in an oven of 105 degrees for 24 hour.
- Take a 2 gram sample and place it in a 150ml beaker.
- Add 35ml distilled water and 5ml nitric acid into the 150ml beaker.
- Shake the solution manually for about 1 min.
- The beaker needs to be set on a preheated hot plate and brought to a boil.
- Cool the solution in cold water, then gently pour the solution into the filter paper, rinse the beaker into the filter paper with distilled water.
- The total solution is adjusted to 100ml, and then 10 ml solution is pipette for the determination of the concentration of chloride.

An automatic technique titrator shown in Figure 5-12a (a Metrohm MET 702) is used to analyze the chloride concentration of the system sample. A silver nitrate solution of 0.01 mol/l was used as a titration solution. A magnetic stirrer was used for dispensing solution during titration. The chloride concentration is calculated automatically by the mv-volume curve (Figure 5-12b).

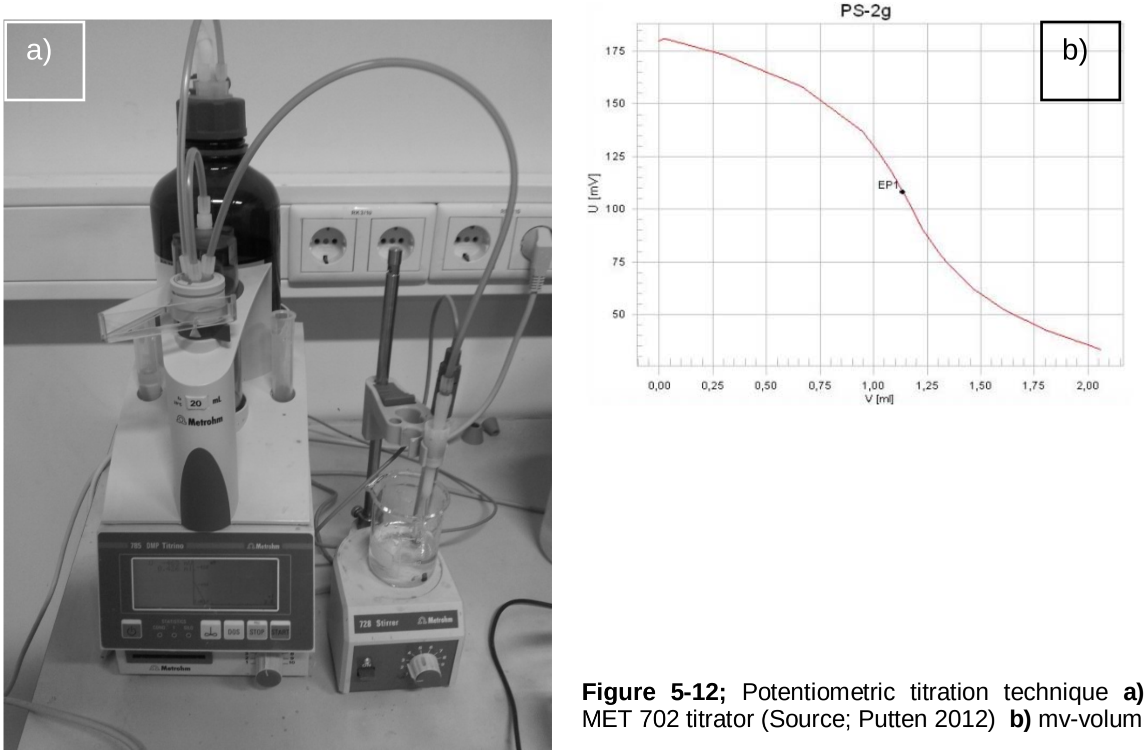


Figure 5-12; Potentiometric titration technique **a)** metrohm MET 702 titrator (Source; Putten 2012) **b)** mv-volume curve

To determine the critical chloride content, another procedure has been conducted to test all of the systems, which does not follow the procedure of Speiz & Brouwers but instead, follows the standard EN 14629 (2007). The procedure to analyze the total chloride is is approximately equal to the procedure as from Spiesz. This procedure is different after the fist step of Spiesz:

- Place 2 gram of concrete powder in a 250ml beaker.
- Add 50ml distilled water to the powder.
- 50ml of hot water needs to be added in the beaker.
- Add 10ml of 5 mol/l nitic acid.
- The mixture needs to be heated at a boil for at least 3 min, with a magnetic stirrer to stirring continuously.
- Lastly for this procedure, it is not necessary to filter the solution for potentiometric titration.

The results of the titration technique by Spiesz & Brouwers (2012), are given in Figure 5-13a. The results were unexpected as the standard SCM in the fly ash system (without nSS) is out of the specified area for the chloride content for pre-stressed steel reinforced concrete, given by kijlstra as 0.079% chloride content. It means that this type of system can only be used in concretes with steel reinforcement and with a maximum replacement level of 18%. For the limestone system the results are more reliable, it is possible to infer that it would be possible to replace CEM I by the nSS in concrete with steel or other metal embedded reinforcement up to 30% replacement level. Due to the unexpected results especially in the fly ash system, all chlorides measurements where repeated. The second set of results below was successful and the values are more reliable than the first test. (Figure 5-13b)

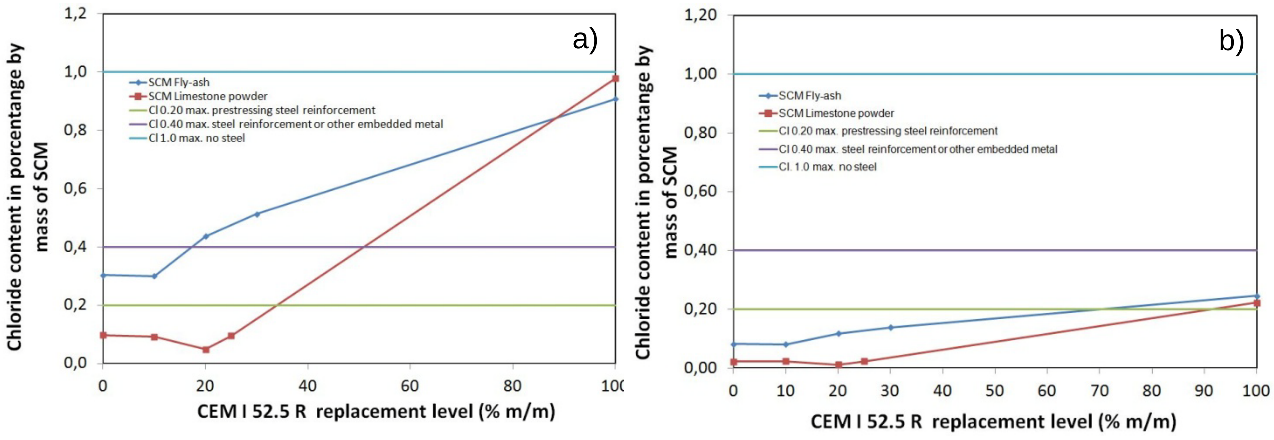


Figure 5-13; a) Potentiometric titration technique out of specified area (Spiesz & Brouwers, 2012). **b)** re-done test (Spiesz & Brouwers, 2012)

Following the procedure of the British standard, it can be seen from Figure 5-14 that the total chloride content of the limestone powder system increases slowly for replacement ratios between 0 and 10% bwoc, after 10% a rapid increasing can be seen.. The aforementioned mixes can be used for pre-stressed concrete. Following the trends presented for the limestone system, it is possible to infer that it would be possible to replace CEM I for 100% by the nSS in concrete with steel or other metal embedded reinforcement based on the critical chloride content.

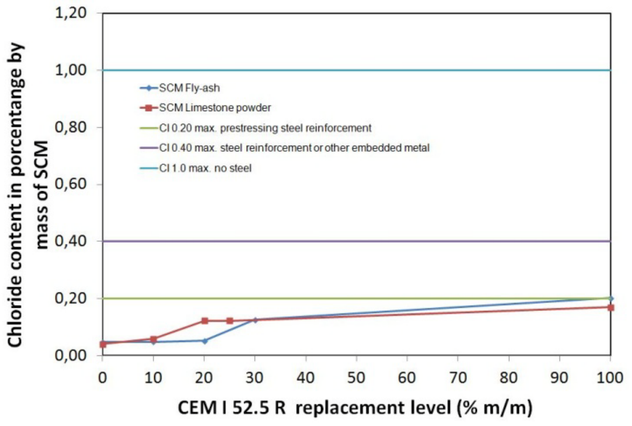


Figure 5-14; Potentiometric titration technique (EN 14629, 2007).

Similar analysis can be done for the fly-ash system. In this case, the results show that the limestone system chloride content increased slightly between 0 and 20% bwoc, after 20% there was a notable and rapid increase of chloride content. These test procedure show that all the mixtures except the 100% fly ash system are in the requirements of the EN 206-1 for a maximum chloride content of 0.20 for prestressing steel reinforcement concrete.

Due to standards given by Kijlstra it shows that the calculation of the chloride content is based on the mass balance of all components in the SCM. Considering the specified chloride content in each compound (ex. fly-ash, CEM III/B, etc.) and the measured chloride content in the silica sludge (1.35% by mass). The chloride content by mass of binder was estimated. The results are shown in Figure 5-15. For these cases, all the SCM could be used in steel reinforced concrete, but not in pre-stressed steel concretes. The calculated chloride content and measured chloride content in the sludge (1.35% by mass) is higher than the maximum specified range limit for micro-silica of 0.1 to 0.3% by mass given in EN 14629 (2007).

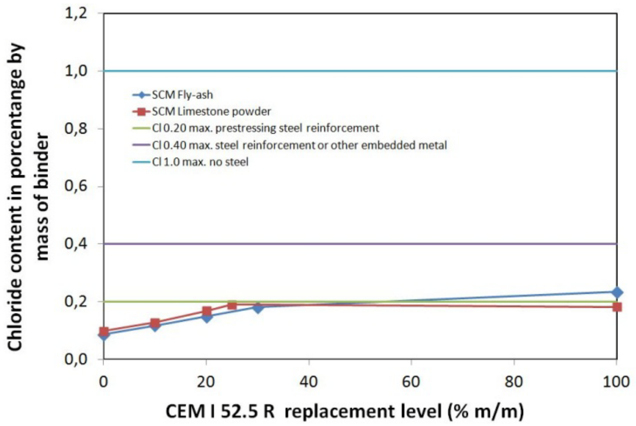


Figure 5-15; Estimated percentages of chloride content (mass of binder for SCM systems)

Based upon the results presented above from the tested systems (10-20-25*-30-100%) it can be concluded that the cement content of the SCM can be decreased up to 30% by mass using the nano-silica sludge and the correct type of SP in the fly ash system. These values obtained from the lab tests were successful in this early stage; however, nest steps will include further research to determine the long-term effects on the durability of concrete containing this type of waste material.

5.5 Conclusion; Analysis of the SCM systems

In paragraphs 5.3 and 5.4 are the systems compared based on the compressive strength, the flexural strength and the critical chloride content that occurs when using the nano-silica waste. Also the evaluation of Kijlstra Betonmortel B.V. results in the following recommendation and continuation for further research in this thesis. Table 5-7 shows an overview for the approved or denied systems.

System replacement % nSS	Compressive strength (MPa)	Critical Chloride Content (CCC)			Approved/ denied strength	Approved/ denied C_1-C_2-C_3
		EN 14629 (C_1)	Speisz (C_2)	Estimated by binder (C_3)		
Fly-ash 10%	10.80	0.049	0.082	0.25	√	√ - √ -X
Fly-ash 20%	8.15	0.052	0.081	0.28	√	√ - √ - X
Fly-ash 30%	8.30	0.126	0.139	0.31	√	√ - √ -X
Fly-ash 100%	6.58 (8*)	0.202	0.246	0.35	X (√*)	X - X - X
Limestone 10%	14.46	0.059	0.023	0.26	√	√ - √ - X
Limestone 20%	15.22	0.123	0.012	0.30	√	√ - √ -X
Limestone 25%	13.40	0.123	0.024	0.32	X	√ - √ - X
Limestone 100%	8.63 (10.48*)	0.170	0.223	0.31	X (x*)	√ - X - X

Table 5-7; Analysis Fly ash and Limestone system, *different SP used

The influence of the SP for the 100% replacement on the chloride content is negligible, a difference of ± 0.002 chloride content is observed by testing these systems. In the case of early age strength development they have a major influence. The system that is developed further is the 30% replacement level on the fly ash system. The Limestone system is put on a hold, the values that need to reached is only possible with the 20% system. This system could developed further in the future but not in this thesis.

Based on the obtained results and conclusions, all the previous tests (paragraph 5.3) need to be repeated for the 30% replacement value of CEM I by nSS. Due to these repeated tests it is possible by monitoring the results to determine the best SP, based on strength development.

5.5.1 30% Fly ash system

After all the results given about the systems in paragraph 5.3 about strength development in the SCM al the tests are repeated for the 30% system. According to paragraph 5.4 critical chloride content also this is the system that should be take into further investigation. All the results for the repeated tests are given in figure 5-17 and 5-18.

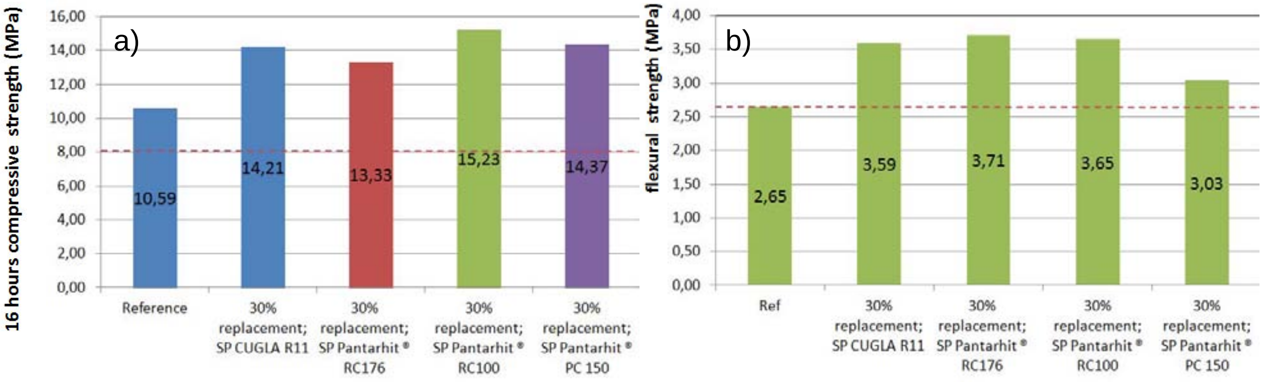


Figure 5-16; 16 hour test results 30% replacement fly ash system **a)** Compressive strength (MPa) **b)** Flexural strength (MPa) (Silica sludge 26,5 wt.% solid)

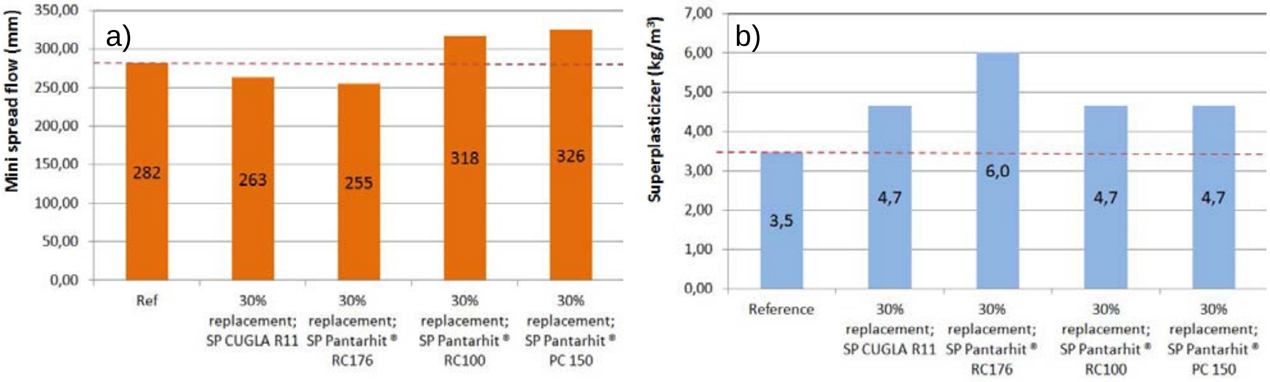


Figure 5-17; 16 hour test results 30% replacement fly ash system **a)** Spread flow (mm) **b)** Superplasticizer (kg/m^3)

Looking at the results of the test, it could been seen that the SPs RC 100 and PC 150 are the SP with the highest influence on the total workability and development of strength. All the SPs reaches the value of 8 MPa after 16 hour. At the spread flow test it is possible to see that the amount of SP that is needed to get a high workability concrete is depending of the SP that is chosen. RC 176 is the SP with the highest amount of SP content per m^3 and still the lowest spread flow. All the other systems have an slight increase of SP usage of 1.2 kg/m^3. The amount of SP usage in the systems with the RC 100 and the PC 150 could be decreased with 0.5 to 1.0 kg/m^3. This is an estimated value, in the concrete tests the real amount of SP is tested by starting lower and slightly increase till the desired workability has been reached.

5.6 Hydratation studies

The American Society for Testing and Materials ASTM defines portland cement as "hydraulic cement” (cement that not only hardens by reacting with water but also forms a water-resistant product) produced by pulverizing clinkers consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate as an inter ground addition". Clinkers are nodules (diameters, 5–25 mm) of a sintered material that is produced when a raw mixture of predetermined composition is heated to high temperature. The low cost and widespread availability of the limestone, shales, and other naturally occurring materials make Portland cement one of the lowest-cost materials widely used over the last century throughout the world.

Portland cement clinker is made by heating, in a kiln that consists of an rotating steel cylinder Ø 6 m and 180 m in length on an angle. (Figure 5-18), a homogeneous mixture of raw materials to a calcining temperature, which is about 1450 °C for modern cements. The aluminium oxide and iron oxide are present as a flux and contribute little to the strength. For special cements, such as Low Heat (LH) and Sulfate Resistant (SR) types, it is necessary to limit the amount of tricalcium aluminate ($3\,CaO{\cdot}Al_2O_3$) formed. The major raw material for the clinker-making is usually limestone ($CaCO_3$) mixed with a second material containing clay as source of alumino-silicate. Normally, an impure limestone which contains clay or SiO_2 is used. The $CaCO_3$ content of these limestones can be as low as 80%. Secondary raw materials (materials in the raw mix other than limestone) depend on the purity of the limestone. Some of the materials used are clay, shale, sand, iron ore, bauxite, fly ash and slag. When a cement kiln is fired by coal, the ash of the coal acts as a secondary raw material.

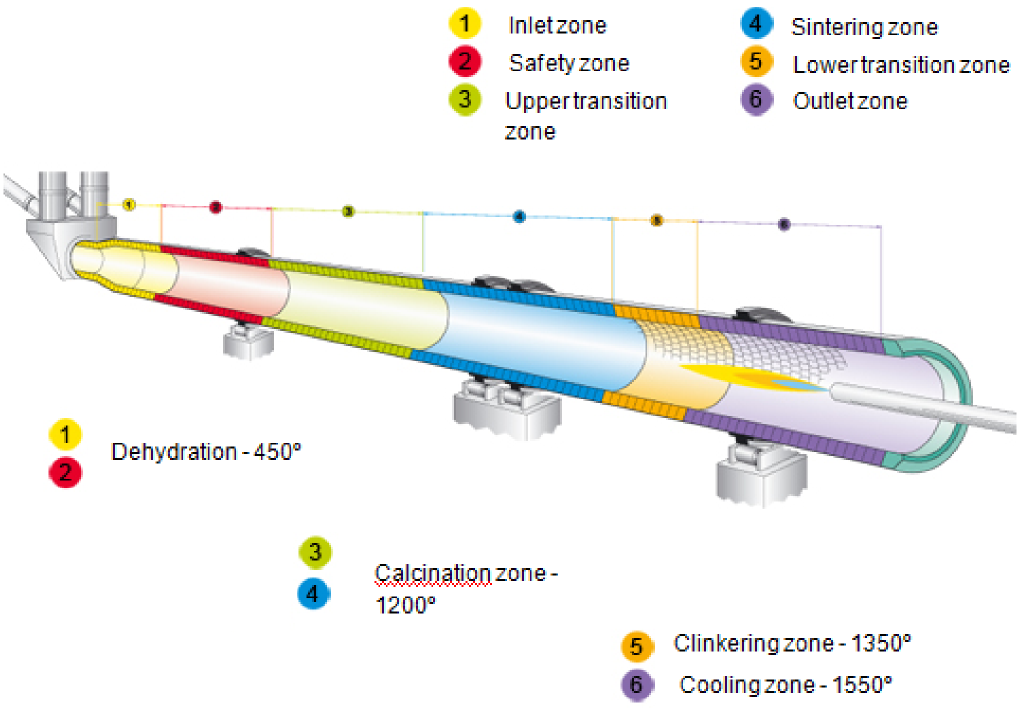


Figure 5-18; Schematic diagram of rotary kiln (Source; berita-iptek.blogspot.com)

Clinker is anhydrous (without water) having come from a hot kiln. Cement powder is also anhydrous if we ignore the small amount of water in any gypsum added at the clinker grinding stage.

The reaction with water is termed "hydration". This involves many different reactions, often occurring at the same time. As the reactions proceed, the products of the hydration process gradually bond together the individual sand and gravel particles, and other components of the concrete, to form a solid mass.

Portland cement consists of five major compounds and a few minor compounds: tricalcium silicate (Ca_3SiO_5 or $3CaO\cdot SiO_2$), dicalcium silicate (Ca_2SiO_4 or $2CaO\cdot SiO_2$), tricalcium aluminate ($Ca_3Al_2O_6$ or $3CaO\cdot Al_2O_3$), tetra-calcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$ or $4CaO\cdot Al_2O_3\cdot Fe_2O_3$) and Gypsum ($CaSO_4\cdot 2H_2O$). In an abbreviated notation differing from the normal atomic symbols, these compounds are designated as C_3S, C_2S, C_3A, and C_4AF, where C stands for calcium oxide (lime), S for silica, A for alumina, and F for iron oxide. Small amounts of uncombined lime and magnesia also are present, along with alkalies and minor amounts of other elements. Table 5-8 describes oxides that are found in Portland cement, together with their chemistry notation. Table 5-9 shows the typical constituens of Portland clinker and gypsum. Figure 5-19 shows the clinker phases during the process described above.

Cement	**Oxide**	**CCN**	**Mass %**
Calcium oxide,	CaO	C	61-67%
Silicon dioxide,	SiO_2	S	19-23%
Aluminum oxide,	Al_2O_3	A	2.5-6%
Ferric oxide,	Fe_2O_3	F	0-6%
Sulfate	SO_2	$\bar{S}$	1.5-4.5%
Water	H_2O	H	0-18%
Carbon Oxide	CO_2	C	-
Magnesium oxide	MgO	M	0 – 3%

Table 5-8; Portland cement chemists notation (Source; Heidelberg cement; Neville, 2004)

CCN	Cement Compound	Weight Percentage	Chemical Formula
C_3S	Tricalcium silicate	45-75 %	Ca_3SiO_5 or $3CaO\cdot SiO_2$
C_2S	Dicalcium silicate	7-32 %	Ca_2SiO_4 or $2CaO\cdot SiO_2$
C_3A	Tricalcium aluminate	0-13 %	$Ca_3Al_2O_6$ or $3CaO\cdot Al_2O_3$
C_4AF	Tetracalcium aluminoferrite	0-18 %	$Ca_4Al_2Fe_2O_{10}$ or $4CaO\cdot Al_2O_3\cdot Fe_2O_3$
	Gypsum	2-10 %	$CaSO_4\cdot 2H_2O$

Table 5-9; Typical constituents of Portland clinker and gypsum. (Source; Neville, 2004)

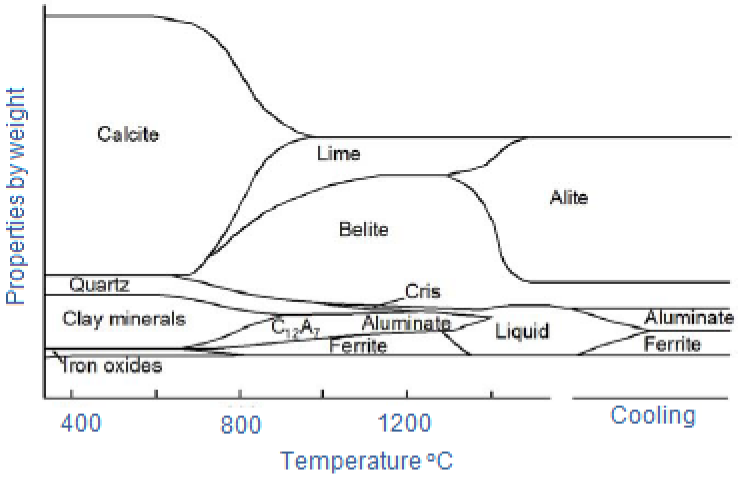


Figure 5-19 schematic diagram showing the variations in type contents of phases during the formation of Portland cement clinker (Source; Taylor, 1997)

5.6.1 Tricalcium silicate (C_3S)

Tricalcium silicate is the most important as it controls the setting and hardening of cement especially in the early stages of strength development. When water is added to cement, each of the compounds undergoes hydration and contributes to the final concrete product. In combination with water, C_3S hydrates into two products, Calcium Silicate Hydroxide (C-S-H) and calcium hydroxide (known as CH or $Ca(OH)_2$). On this stage the development of heat increases rapidly to the max. The hydration of C_3S can be accelerated by the addition of anhydrite, gypsum or fine inert calcium carbonate. In equation (5.2) the hydration of tricalcium silicate is given:

Tricalcium silicate + Water--->Calcium silicate hydrate + Calcium hydroxide + heat

$$2\ Ca_3SiO_5 + 7\ H_2O \text{--->} 3\ CaO\cdot 2SiO_2\cdot 4H_2O + 3\ Ca(OH)_2 + \Delta H\ kJ \qquad (5.2)$$

5.6.2 Dicalcium silicate (C_2S)

Dicalcium silicate also affects the strength of concrete through its hydration. Dicalcium silicate reacts with water in a similar manner compared to tricalcium silicate, but much more slowly. The heat released is less than that by the hydration of tricalcium silicate because the dicalcium silicate is much less reactive. The products from the hydration of dicalcium silicate are the same as those for tricalcium silicate (5.3):

Dicalcium silicate + Water--->Calcium silicate hydrate + Calcium hydroxide +heat

$$2\ Ca_2SiO_4 + 5\ H_2O\text{--->} 3\ CaO\cdot 2SiO_2\cdot 4H_2O + Ca(OH)_2 + \Delta H\ kJ \qquad (5.3)$$

5.6.3 Tricalcium aluminate- Tetracalcium aluminoferrite (C_3A- C_4AF)

The other major components of portland cement are aluminates, tricalcium aluminate and tetracalcium aluminoferrite also react with water. Despite their little amount these products are crucial for cement because the reactions with them are affecting the hydration of the calcium silicates phases. Comparing to C_3S, the hydration of C_3A is very fast. Their hydration chemistry is more complicated as they involve reactions with the gypsum as well. Therefore gypsum in the form of calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$) is added to slow down the hydration sped of C_3A. The rate of hydration of a compound may be affected by varying the concentration of another. In general, the rates of hydration during the first few days ranked from fastest to slowest (Barron 2010):

tricalcium aluminate > *tricalcium silicate* > *tetracalcium aluminoferrite* > *dicalcium silicate.*

5.6.4 The hydration process: reactions

The hydration of cement is obviously far more complex than the sum of the hydration reactions of the individual minerals, especially in this form of SCM mixture. Aside from the usual reactions occurring there is also the influence of the nSS that needs to be taken into account for this research. The typical depiction of a cement grain involves larger silicate particles surrounded by the much smaller C_3A and C_4AF particles. The setting (hydration) of cement can be broken down into several distinct periods (Figure 5-20).

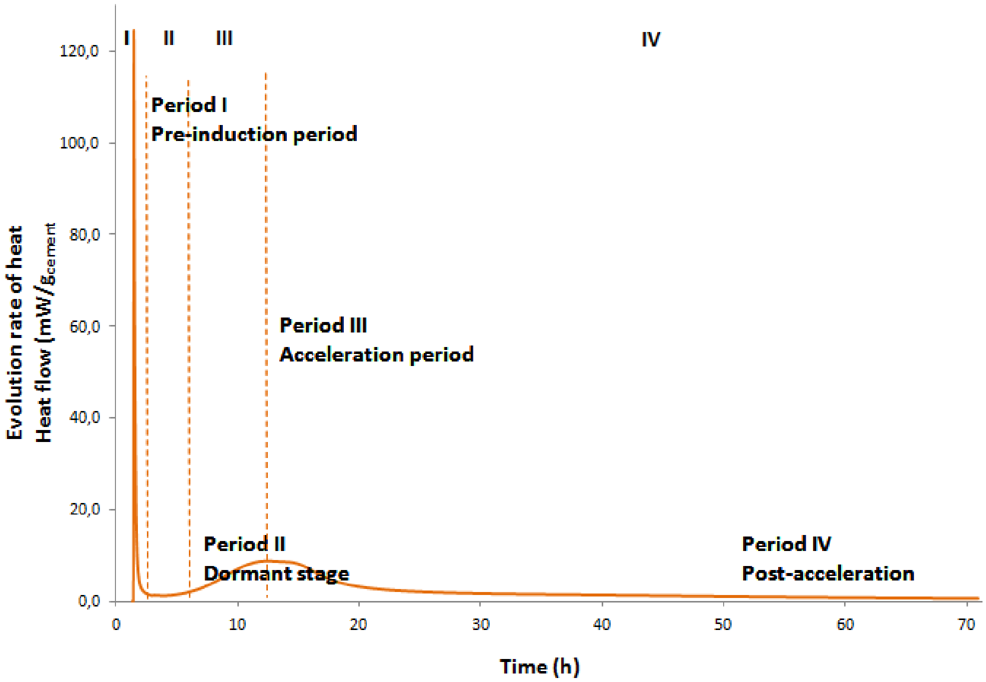


Figure 5-20; Schematic illustration of the different stages of hydration Stages II to IV (Source; Putten 2012)

The more reactive aluminate and ferrite phases react first, and these reactions dramatically affect the hydration of the silicate phase. A widely accepted model is developed (Scrivener and Pratt , 1984) this model is depicted in Figure 5-21. Almost immediately on adding water some of the clinker sulphates and gypsum dissolve producing an alkaline, sulfate-rich, solution. This solution is formed in the pre-induction period (stage I) it only lasts for a few minutes (Figure 5-21a/b). Soon after mixing, the C_3A reacts with the water to form an aluminate-rich gel. The gel reacts with sulfate in solution to form small rod-like crystals of ettringite (Hewlett, 2004). The early fast hydration reaction appears to be slowed down due to the deposition of a layer of hydration products at the cement grain surface. In this way a barrier is formed between the non-hydrated material and the bulk solution (Figure 5-22a).

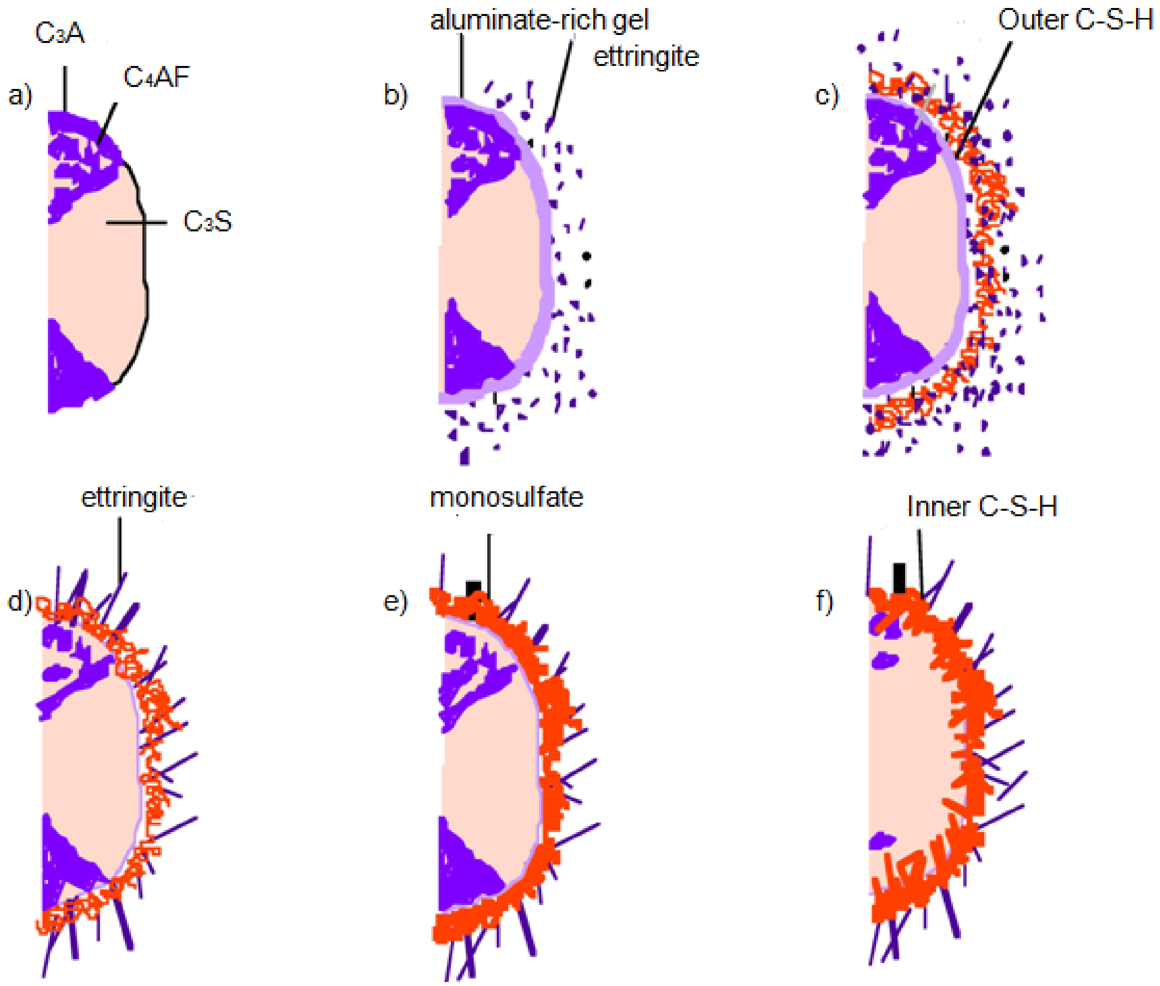


Figure 5-21; Schematic representation of anhydrous cement **a)** and the effect of hydration after **b)** 10 minutes, **c)** 10 hours, **d)** 18 hours **e)** 1–3 days, and **f)** 2 weeks (Source; Bishop, 2001, Rice University; Barron, 2010)

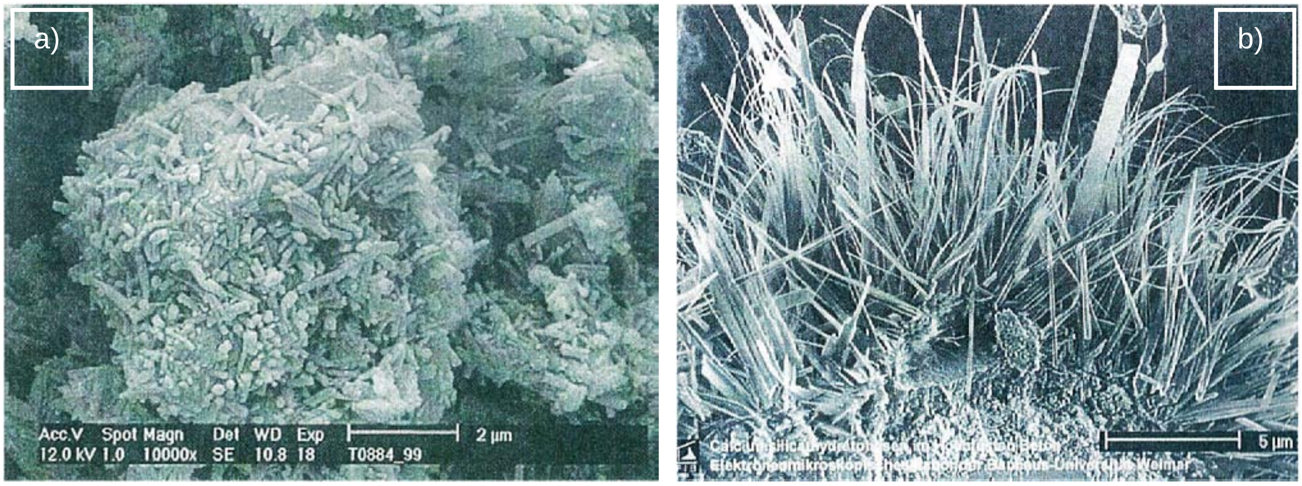


Figure 5-22; Fibers were observed with an electron microscope **a)** cement grain enveloped by sulfate **b)** fibers of C-S-H (Source; Bauhous-Universitat Weimar; Betonvereniging 2006)

After this initial period of reactivity, cement hydration slows down and the induction period or dormant stage begins. In this period the hydration of all clinker minerals progress very slowly. As the dormant period progresses, the paste becomes too stiff to be workable. In general the “Impermeable hydrate layer theory” assumes the creation of a barrier layer that prevents the non reacted cement from reacting due to the lack of water penetration to the inorganic oxide in the cement grains. This is also tipped in the pre-induction period above. After about 3 hours of hydration, the induction period ends and the acceleration period begins.

During the acceleration period (stage II) from 3 to 24 hours, about 30% of cement reacts to form calcium hydroxide and C–S–H. The development of C–S–H in this period occurs in 2 phases. After ca. 10 hours hydration (Figure 5-21c), C_3S has produced “outer C–S–H,” which grows out from the ettringite rods rather than directly out from the surface of the C_3S particles (Figure 5-21b). Therefore, in the initial phase of the reaction, the silicate ions must migrate through the aluminum and iron rich phase to form the C–S–H. In the later part of the acceleratory period, after 18 hours of hydration, C_3A continues to react with gypsum, forming longer ettringite rods (Figure 5-21d). This network of ettringite and C–S–H appears to form a “hydrating shell” about 1 µm from the surface of anhydrous C_3S. A small amount of “inner C–S–H” forms inside this shell. The period of maximum heat evolution occurs typically between about 10 and 20 hours after mixing and then gradually tails off. In a mix containing OPC only, most of the strength gain has occurred within about a month. Where OPC has been partly-replaced by other materials, such as fly ash, strength growth may occur more slowly and continue for several months or even a year. The results of replacing CEM I 52,5R and the development of heat and strength as it is applicable to this for thesis will be further explained later on in this.

After 1–3 days of hydration, reactions slow down and the decelerator period (stage III and IV) is initiated (Figure 5-21e). C_3A reacts with ettringite to form some monosulfate. “Inner C–S–H” continues to grow near the C_3S surface, narrowing the 1 µm gap between the “hydrating shell” and anhydrous C_3S. The rate of hydration is likely to depend on the diffusion rate of water or ions to the anhydrous surface. After 2 weeks hydration (Figure 5-21f), the gap between the “hydrating shell” and the grain is completely filled with C–S–H. The original, “outer C–S–H” thus becomes more fibrous.

5.6.5 Hydratiation process SCM: Pozzolanic reaction

The chemical reaction that occurs in portland cement containing pozzolans is called the pozzolanic reaction. This reaction can be schematically represented on the following way: $Ca(OH)_2 + H_4SiO_4 \rightarrow Ca^{2+} + H_2SiO_4^{2-} + 2\ H_2O \rightarrow CaH_2SiO_4 \cdot 2\ H_2O$ ore in a abbreviated notation CH + SH → C-S-H. The product formed is a calcium silicate hydrate (C-S-H).

From a few hours to one day, the formation of hydration products accelerates. AFm and AFt phases occur in cement, one of the most common AFm phases in hydrated cement is monosulfate. By far the most common AFt phase in hydrated cement is ettringite. The formation of ettringite ($[Ca_3Al(OH)_6.12H_2O]_2.2H_2O$] or, mixing notations, $C_3A.3CaSO_4.32H_2O$.) by C_3A in the presence of calcium sulphate $CaSO_4$ slows down because of the consumption of Ca^{2+} and SO_4^{2-} ($CaSO_4$). Because of this, C_3A will react with ettringite resulting in monosulfate ($C_3A.CaSO_4.12H_2O$). While monosulfate formation is increased, the ettringite content declines. At the same time CH products are formed by the C_3S and C_2S hydration. Though the whole process the porosity (empty spaces) is decreasing because the hydration products are filling the voids in the concrete. The reactions in the system with nano-Silica sludge are very complex due to the presence of SiO_2, $CaCO_3$ and some contaminants like CaO, $CaCl_2$, Na, K. The addition of nano-particles are promoting the precipitation of AFt or AFm phases, explained further on in this thesis.

5.6.6 Hydratiation process SCM: CEM I replacement

The two most essential properties of SCC are a high flow ability and a high segregation resistance. The use of admixtures in combination with a high concentration of fine particles makes it possible to combine these apparently incompatible properties. However, the high concentration of cement and fillers with puzzolanic properties, can lead to the development of a high heat of hydratation. This might induce rather high thermal stresses in the hardening concrete element, possibly causing early age thermal cracking. In SCM research hydratation tests are carried out in order to evaluate the heat of hydratation of the SCM. However, the usage of nSS in these mixtures may result in unexpected test results. The results are documented further on in this chapter.

The evolution of heat of hydratation of the SCM mixtures is determined using a an 8-channel TAM® Air isothermal micro calorimeter from TA Instruments (U.S.A.), at a constant temperature of 20ºC. The tested mortar samples are conducted with the mixture recipe mentioned in pragraph 4.3. A sample of 5 gram is dealed in a designated 20 ml flask and placed in the calorimeter, after which the test is started. The experiment is continued for 3 days and the results are presented as the rate of heat production in regards to function of time (hr), per unit of cement (J/g).

5.6.6.1 SCM CEM I vs. SCM 5-10-15% nSS

When observing the curves (Figure 5-24a-b-c-d) obtained from the TAM® Air it is evident that the replacement of the cement with different concentration of silica sludge, have a high effect on the hydration kinetics. A higher heat flow was found due to the nucleation effects produced in the cement paste and due to the pozzolanic activity promoted by the presence of amorphous nano-silica and $CaCO_3$ particles. The usage of SP in the silica sludge may have a small influence on the dormant period (possible extension), but the period is shortened (accelerated), see Table 5-10. Based on the graphs in Figure 5-24c, the dormant period is shortened due to the presence of nano-particles in the nSS. In addition, the shortening of the relative setting time, as well the time to rich the maximum hydration peaks of the cement paste were affected (Figure 5-24a and 5-24d). It is postulated that at the end of the induction period a renewed acceleration of the hydration process is controlled by the nucleation and growth of a second-stage C-S-H which is different from the first-stage product (C_3S) formed initially. The second-stage C-S-H starts to form after the thermodynamic barrier (Figure 5-21) has been overcome (Taylor, 1997). It assumes that the first-stage product, precipitated at the C_3S surface, does not act as a barrier layer and is not involved in the slowing down of the hydration reaction. A faster hydration, associated with a second heat release gets under way. The higher amounts of nSS replacement are promoting the forming of secondary precipitated ettringite from the C_3A phases (Hewlett, 2004).

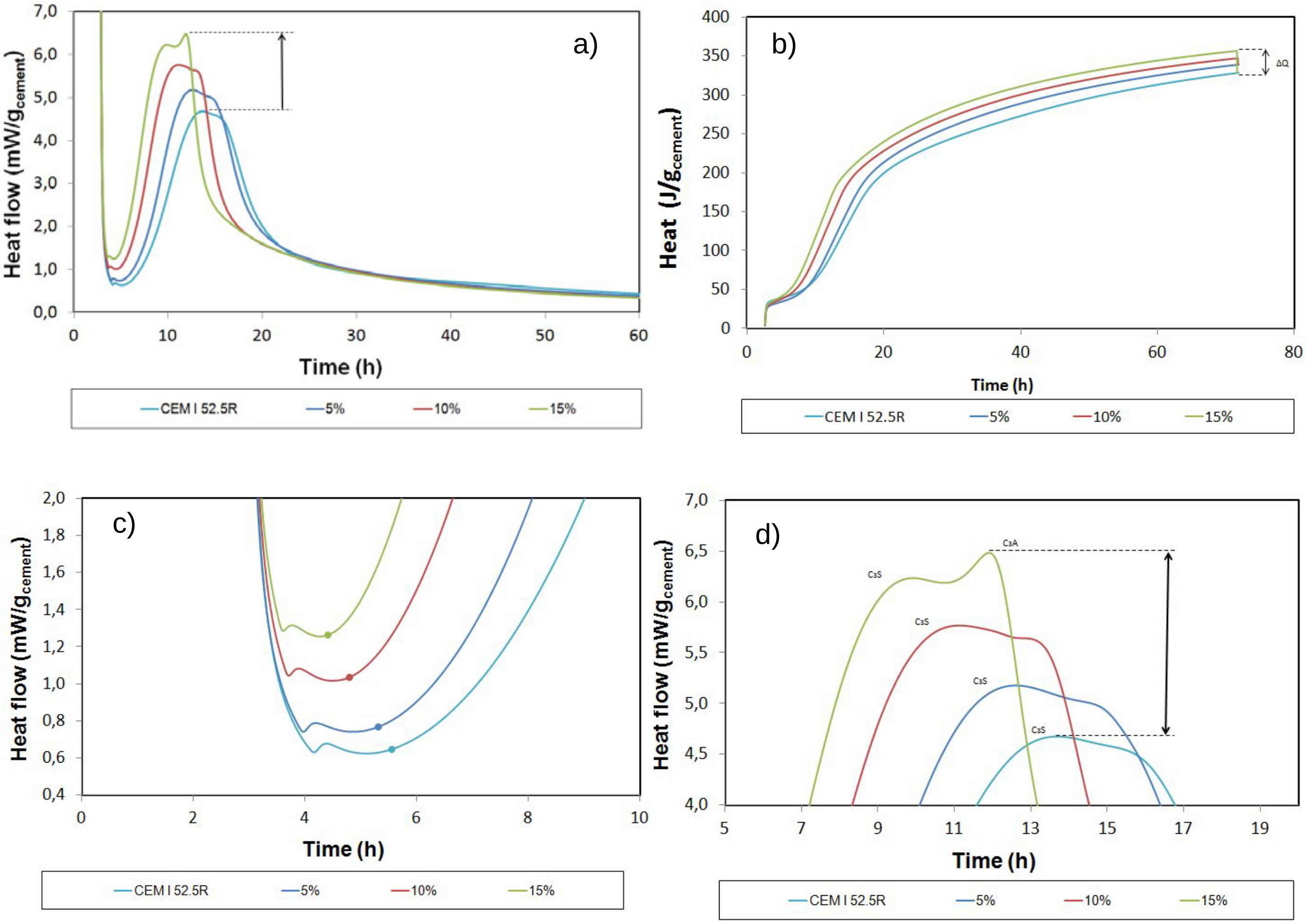


Figure 5-23;Heat flow rates(mW/g$_{cement}$) and Cumulated heat (J/gcement) for CEM I 52,5R **a)** reference – 5-10-15% nSS, **b)** Normalized total heat evolution of cement pastes **c)** different dormant period **d)** maximum heat peak

Paste type	Dormant period (h: min)	Setting time (h: min)	Peak time (h: min)	Max. heat J/g
CEM I 52,5R	1:27	3:25	13:22	328
5 % nSS	1:21	3:52	12:36	338
10% nSS	1:15	2:44	11:08	348
15% nSS	1:06	2:43	11:54	356

Table 5-10; Hydration kinetics of CEM I with silica sludge

When Figure 5-23 is compared with Figure 5-24, both figures give the same results. The correlations between the amount of nSS and SCM are given by: the maximum peak time in Figure 5-24a follows the graph in Figure 5-23a, when increasing the amount of nSS the peak time shortens. Also Figure 5-24b shows similar outcomes as Figure 5-23b, increasing the amount of nSS shows an higher max heat. The slope acceleration period (Figure 5-24c) is shortened due to the amount of nano particles in the nSS. So the forming of C-S-H products results that C_3S forming starts faster.

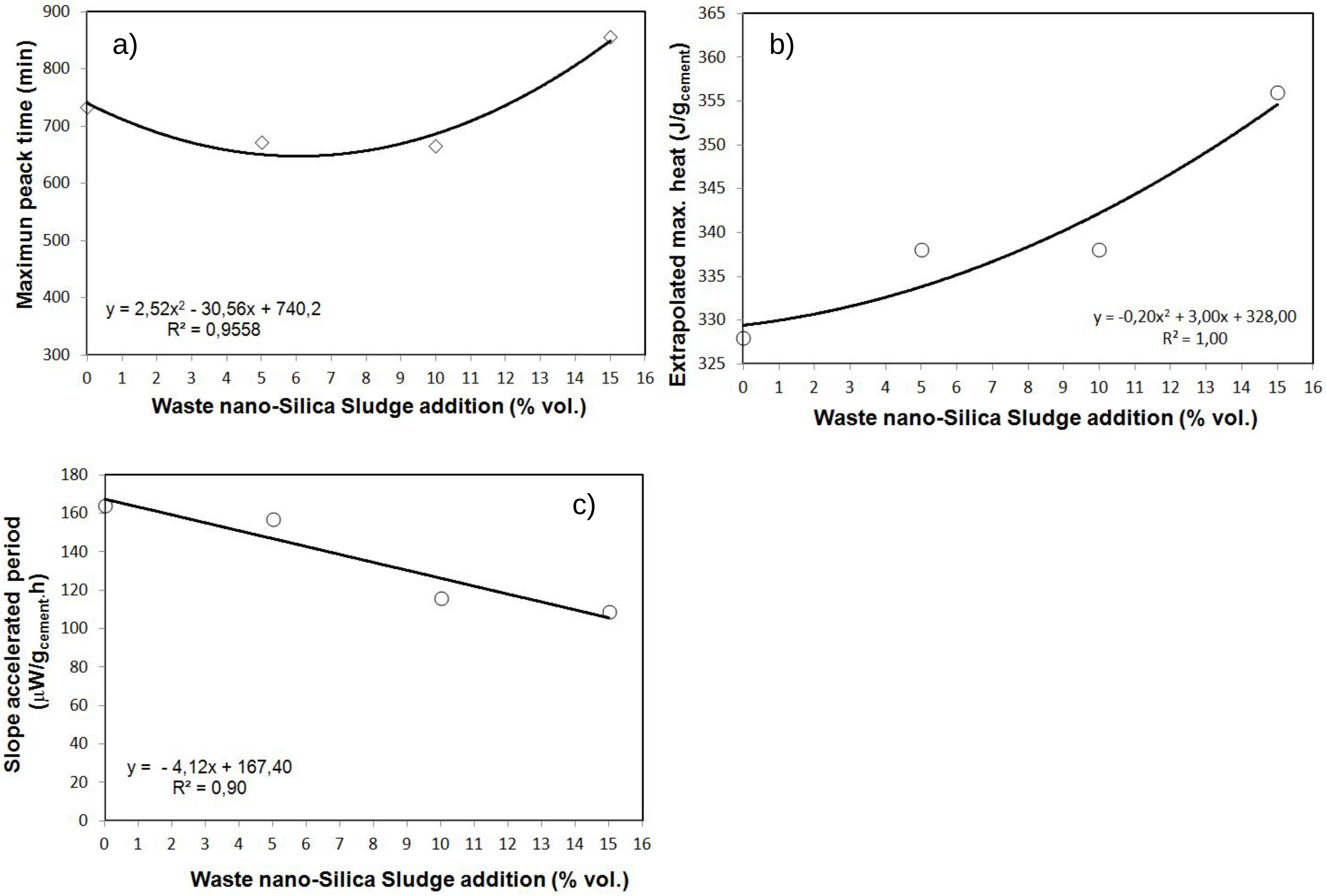


Figure 5-24; Correlations SCM vs addition Waste nano-Silica a) maximum peak time vs nSS addition b) Extrapolated heat vs nSS addition c) Slope accelerated period.

5.6.6.2 SCM CEM III/B vs. SCM 5-10-15% nSS

The curves of Figure 5-25a obtained from the TAM® Air, shows different levels of replacement with silica sludge that affect the hydration kinetics of the mixture referring to the reference specimen. Looked to the heat flow it shows that there is a difference. This is possible due the nucleation effects produced in the cement paste and the pozzolanic activity promoted by the presence of amorphous nano-silica and $CaCO_3$ particles. The dormant period (Figure 5-25b) is extended in time by ca. 30 min (Table 5-11), but the heat flow stays higher to start a faster acceleration period.

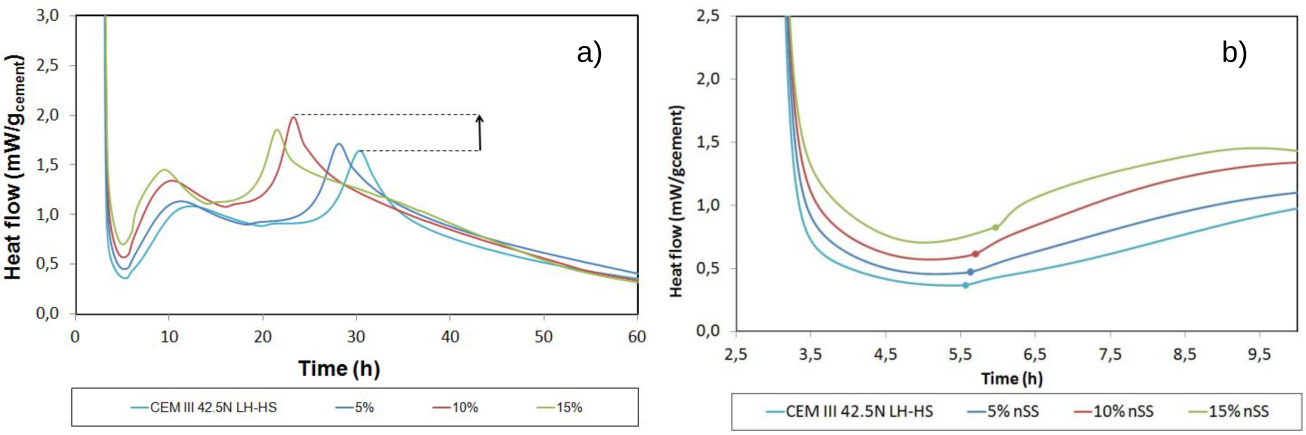


Figure 5-25;Heat flow rates(mW/g_{cement}) and Cumulated heat (J/gcement) for CEM III/B 42,5n LH-HS **a)** reference – 5-10-15% nSS, **b)** different dormant period

Paste type	Dormant period (h: min)	Setting time (h: min)	Peak time (h: min)	Max. heat J/g
CEM III/B 42,5	0: 44	22:49	30:21	179
5 % nSS	0:48	20:40	28:06	197
10% nSS	0:51	15:55	23:14	212
15% nSS	1:13	14:50	21:29	217

Table 5-11; Hydration kinetics CEM III with silica sludge

The presence of SP in the silica sludge may contribute to the rapid heat development in a shorter period of time (Figure 5-26a). The pozzolanic activity of the silica sludge is confirmed due to the presence of a positive change in the total heat curve shown Figure 5-26b. The total heat is the contribution of heat produced by the cement particles themselves and the heat contribution of the pozzolanic reaction between the nano-silica particles and the precipitated $Ca(OH)_2$.

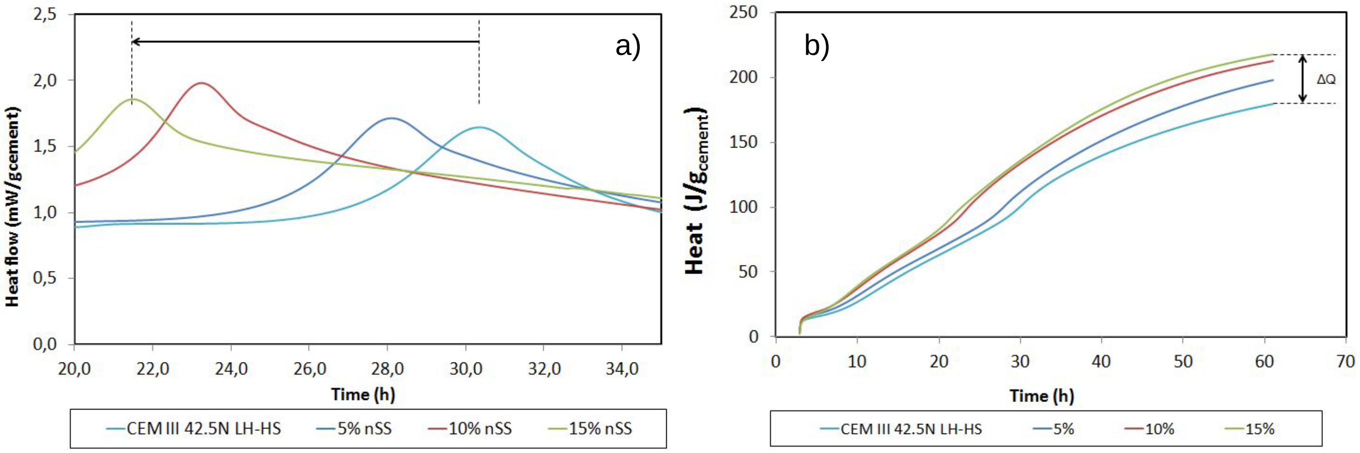


Figure 5-26; c) maximum heat peak d) Normalized total heat evolution of cement pastes

When the Figure 5-26a and 5-26b are compared with Figure 5-27, all figures give the same results. The correlations between the amount of nSS and SCM are given by: the maximum peak time in Figure 5-25a follows the graph in Figure 5-27a, when increasing the amount of nSS the peak time shortens. Also Figure 5-26b shows similar outcomes as Figure 5-27b, increasing the amount of nSS shows an higher max heat. The slope acceleration period (Figure 5-27c) is shortened due to the amount of nano particles in the nSS.

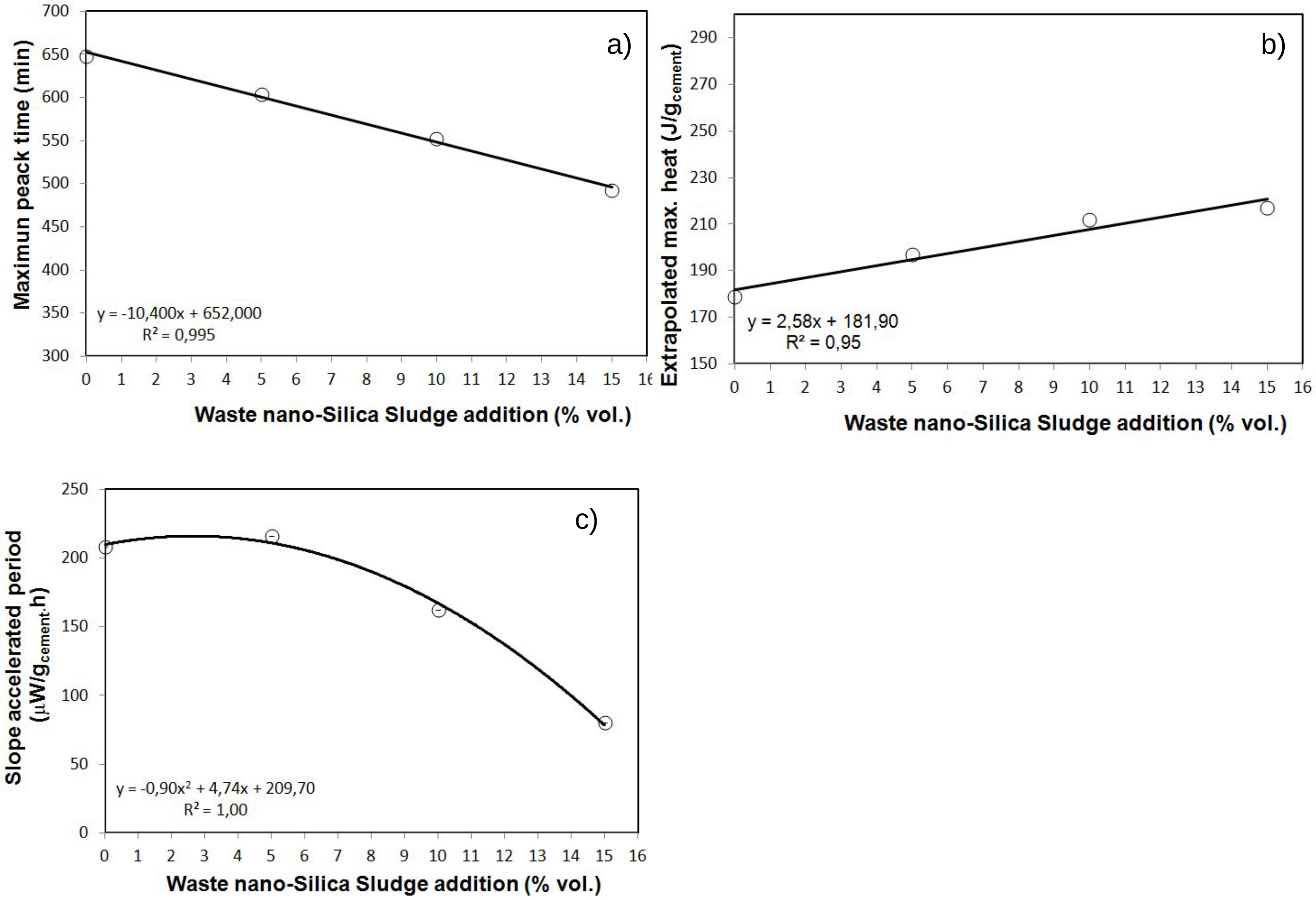


Figure 5-26; Correlations SCM vs addition Waste nano-Silica a) maximum peak time vs nSS addition b) Extrapolated heat vs nSS addition c) Slope accelerated period.

5.6.6.3 SCM CEM III/B + FA vs. SCM 5%-30% nSS

For the systems CEM III/B 42,5n LH-HS the reference mixture, to which all the other mixtures are compared is shown in Figure 5-28a. The first peak of hydratation after 2hours might be related to the strong reaction of alite during the first hours (more than 70%) (de Weerdt, 2010), in the second peak after ca. 10 hours hydration,C_3S has produced monosulfate or “inner C–S–H”. Fly ash (FA) is also accelerate the polymerization of hydrated silicates, when the reaction of gypsum continuous, the hydratation speed decreases. This occurs between 12-15 hours. The pozzolanic reaction of FA starts later, because the particles need to be dissolved, depending on the alkali amount (pH-value). When the creation of C-S-H around FA is less than around the cement grain, FA can start reaction and consuming CH, after these reaction the hydratation increases rapidly to the peak of the maximum heat evolution (Figure 5-28d). After these developments it tails off. The reactivity of nSS is generally larger than the reactivity of slag or FA due their small particle size, causes a accelerated hydration, a higher heat flow and a reduced induction period. The decrease of heat hydratation which is observed can be attributed to the fast reaction of the nSS to form C-S-H. The results of the higher amounts (10-20-30%) of nSS are quite similar to the 5% replacement level (Figure 5-28b), only in these amounts of replacement are all the values increased in which more heat occurs. Most likely when these tests are going to be preformed for concrete batches the amount of SP also changes the dormant period (Table 5-12) (Figure 5-28c). The SP changes the hydration kinetics and the adsorption of the SP molecules at the surface of the cement grains, which has an adverse effect on the diffusion of water and calcium ions.

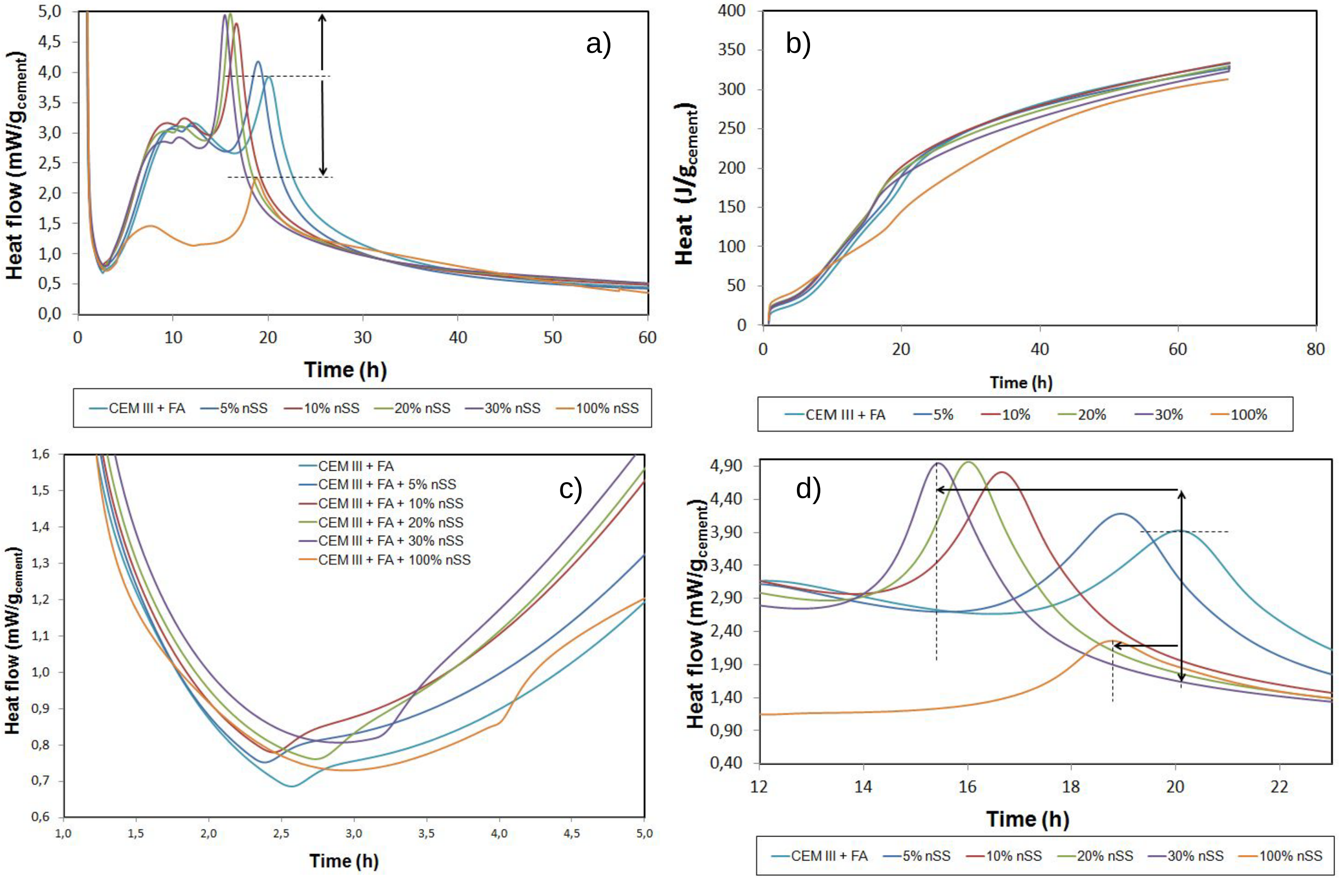


Figure 5-27;Heat flow rates(mW/g_{cement}) and Cumulated heat (J/g_{cement}) for differrent mixture groups fly-ash system a) reference -– 5 -10 -20 -30 - 100% nSS b) Normalized total heat evolution of cement pastes c) dormant stage d) acceleration period

Paste type	Dormant period (h: min)	Setting time (h: min)	Peak time (h: min)	Max. heat J/g
CEM III/B 42,5 + FA	0:12	16:00	20:03	333
5 % nSS	0:17	15:09	19:36	327
10% nSS	0:17	13:10	16:39	334
20% nSS	0:13	12:33	16:00	329
30% nSS	0:13	11:45	15:25	320
100% nSS	1:03	14:50	19:22	313

Table 5-12; Hydration kinetics CEM III - fly ash - with silica sludge

SCM CEM III/B + FA vs. SCM 100% nSS

When CEM I 52,5 R is replaced by nSS and an slight increase of CEM III 42,5 LH-HS (Chapter 5 paragraph 2), the effects on the development of the heat of hydratation are important. The rate as well as the total heat of hydratation is much lower (Figure 5-29a), The dormant period increase in time, on the contrary a decrease in time of maximum heat development and hydratation of heat are visual in Figure 5-29b.

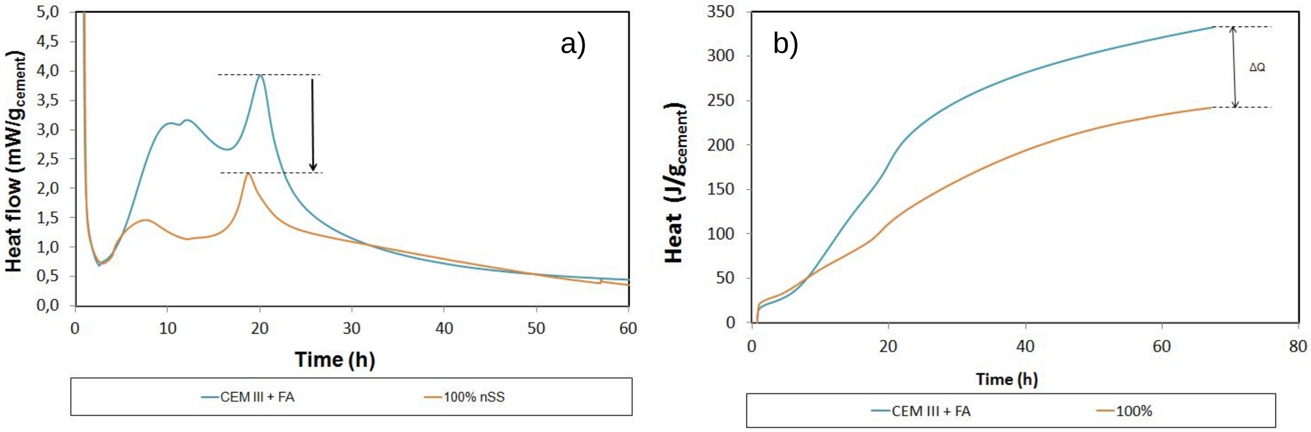


Figure 5-28;Heat flow rates(mW/gc$_{ement}$) and Cumulated heat (J/g$_{cement}$) for differrent mixture groups Fly-ash system a) reference - 100% nSS b) reference-100% nSS

When the results are translated into a new graph, this graph shows values that are similar as the graphs contained from the TAM® Air. The correlations between the amount of nSS and SCM are given by: the maximum peak time in Figure 5-30a follows the graph in Figure 5-28a, when increasing the amount of nSS the peak time shortens. Also Figure 5-30b shows similar outcomes as Figure 5-28b, increasing the amount of nSS shows lower max heat.

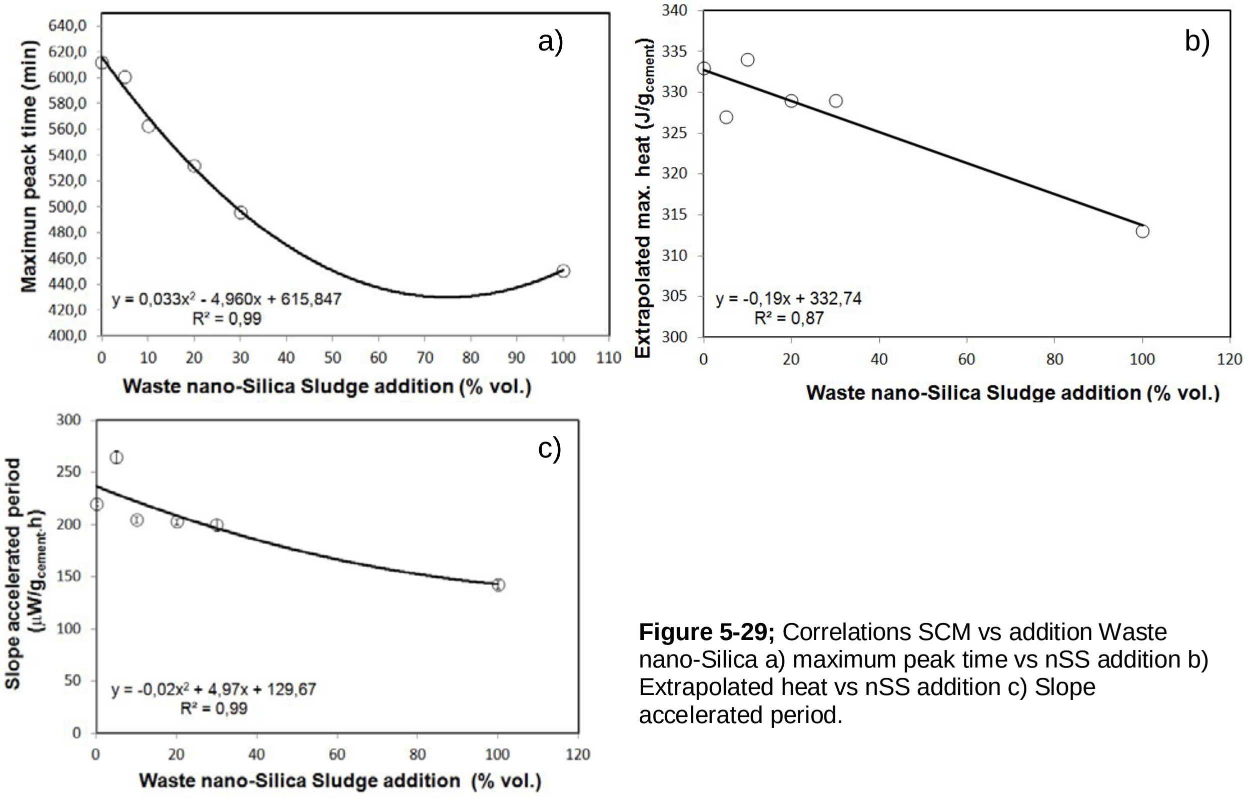
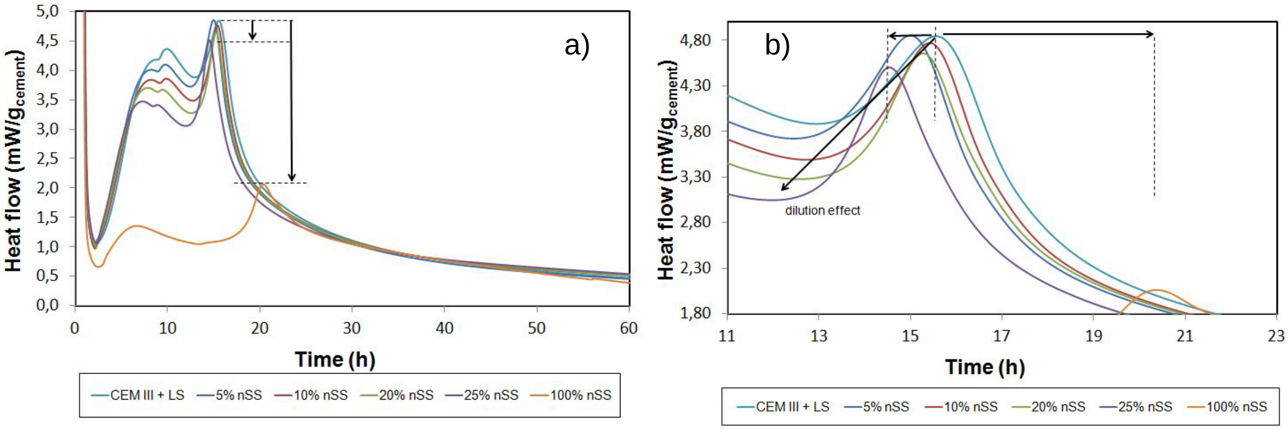


Figure 5-29; Correlations SCM vs addition Waste nano-Silica a) maximum peak time vs nSS addition b) Extrapolated heat vs nSS addition c) Slope accelerated period.

5.6.6.4 SCM CEM III/B + LS vs. SCM 5%-25% nSS

In order to investigate whether the observed effect of the limestone powder in combination with CEM I 52,5R, CEM III/B and nSS (Figure 5-31a). The first peak of hydration after 2 hours might be related to the strong reaction of alite. The dormant period of all the systems changes due to the amount of nSS that is added (Table 5-13). In the second peak after ca. 10 hours hydration C_3S is formed, It assumes that the first-stage product, precipitated at the C_3S surface, does not act as a barrier layer (Hewlett, 2004) and is not involved in the slowing down of the hydration reaction. A faster hydration, associated with a second heat release gets under way and forms the hydration product C_3A. After this stage the hydration rate slows down gradually, as the amount of still non-reacted material declines. The C-S-H phase continues to be formed due to the continuing hydration of both C_3S and C_2S. The contribution of C_2S to this process increases time and, as a consequence, the rate of forming calcium hydroxide decline. When the supply of calcium sulfate is exhauste, the Aft phase that has been formed in the early stage of hydration starts to react in a reaction with additional C_3A and $C_2(A,F)$, until all the original cement becomes consumed, limestone affects the chemical process of C_3A and contributes to the third peak, better known as slag hydration. So the third peak can be related to the reaction of unconsumed cement. After this it tails off. The reactivity of nSS is generally larger due their small particle size, causes a slightly accelerated hydration. It is shown that the nSS results in enhancements in the degrees of hydration of the cement grains in the system. In order to quantify the relative effects of dilution (reduction in cement content, and thus of the hydration products). An increased heat of hydration is observed in the 5% system, however after this content of nSS, the heat of hydration decreases due to the dominance of the dilution effect (Figure 5-31b). The results of the higher amount of replacement levels are following the trendline of the 5% replacement.



5-30; Heat flow rates(mW/gcement) and Cumulated heat (J/gcement) for differrent mixture groups limestone system a) reference - 100% nSS b) reference-100% nSS dilution effect

Paste type	Dormant period (h: min)	Setting time (h: min)	Peak time (h: min)	Max. heat J/g
CEM III/B 42,5 + LS	0:13	12:15	15:34	381
5 % nSS	0:15	11:49	15:00	371
10% nSS	0:15	12:25	15:25	378
20% nSS	0:16	12:10	15:16	364
25% nSS	0:17	11:22	14:33	356
100% nSS	0:32	16:25	20:23	222

Table 5-13; Hydration kinetics CEM III - limestone - with silica sludge

SCM CEM III/B + LS vs. SCM 100% nSS

When CEM I 52,5 R is replaced by nSS and an increase of CEM III 42,5 LH-HS and limestone, the effects on the development of the heat of hydration are highly visually (Figure 5-32a). The rate as well as the total heat of hydration is 8-10 times lower, the induction period and the dormant period are extended (Figure 5-32b), the peak C_3A is gone, an increase in time of maximum heat development and hydration of heat are visual in Figure 5-32c-d. Most likely the effect of this amount of nSS and the absence of CEM I is the result of these phenomenon, this mixture shows a significant variation in the composition, while in other mixtures CEM I 52,5R is still present in a small amount to start the reaction of C-S-H.

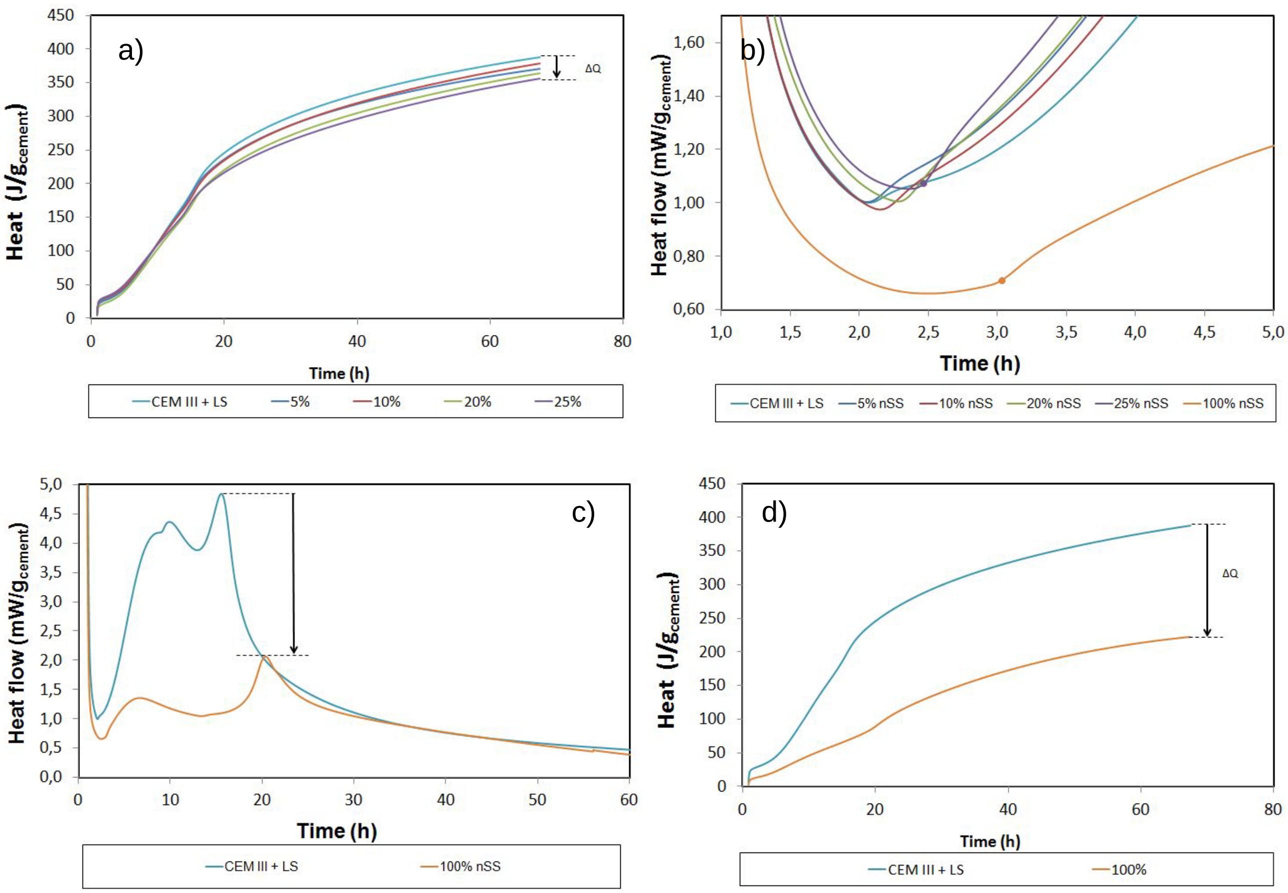


Figure 5-31; Cumulated heat (J/g_{cement}) and Heat flow rates(mW/gc_{ement}) for diferrent mixture groups limestone system a) reference - 25% nSS b) dormant period reference – 100% nSS c) reference vs. 100%nSS d) reference vs. 100% nSS

When the results are translated into new graphs, this graphs shows values that are similar as the graphs contained from the TAM AIR, The correlations between the amount of nSS and SCM are given by: the maximum peak time in Figure 5-33a follows the graph in Figure 5-31a, when increasing the amount of nSS the peak time shortens and decrease. Also Figure 5-33b shows similar outcomes as Figure 5-32a, an decrease in heat in all the systems beyond 5%..

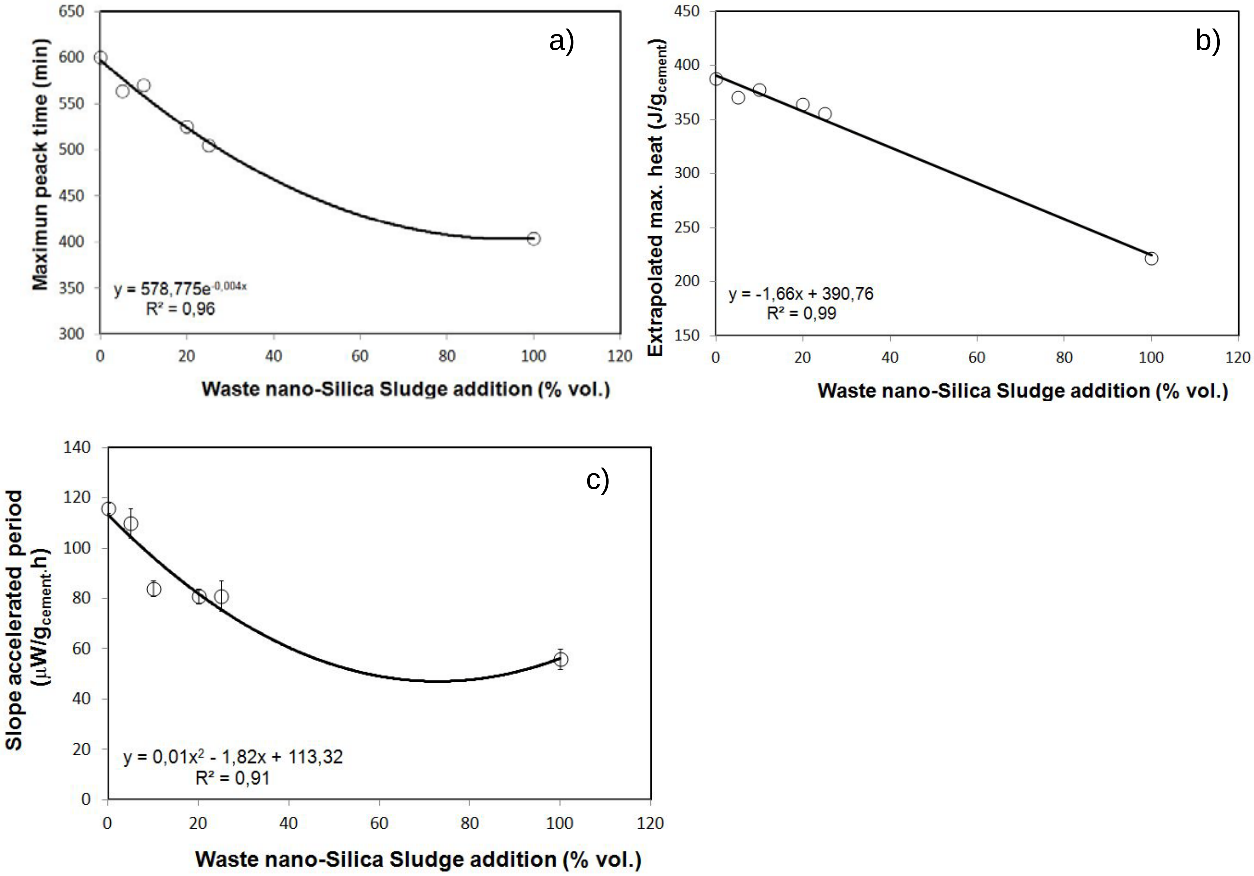


Figure 5-32; Correlations SCM vs addition Waste nano-Silica a) maximum peak time vs nSS addition b) Extrapolated heat vs nSS addition c) Slope accelerated period.

5.7 Conclusion

The previous chapters provide the knowledge and tools that can be used to design and adjust the self-compacting mortars. It has been shown that the determination of the critical choloride content linked with the hardened mortars and the hydration behavour of all the tested mortars. Potentiometric titration techniques are used to determine the critical chloride content, a TAM® Air isothermal micro calorimeter is used for the hydration studies that have been conducted. With regard to this chapter the following can be summarized:

- Aggregates, which are necessary to adjust the reference design of Kijlstra Betonmortel B.V are introduced.
- There is a range of superplasticizers that could be used, these are tested and discussed in the different SCM systems.
- The effect of nSS on the SCM in hydration kinetics and compressive strength is high. Thrue these observations the hydration kinectics are combined with the strength results and can be say from both ways how the systems should be react.

The core of this chapter surrounds the explanation of the self-compacting mortar design and production, which follows after the previous chapter the determination of the maximun amount of replacement is possible. In regards to this the following can be concluded:

- A stable waste nano-silica slurry is designed with 26.5%, higher values (test up to 50%) solid content results into a clayey consistency with an increasing of viscosity and gelling.
- On the contrary to the 16 hourresults, the 7 and 28-days compressive strength of almost all SCM FA was improved by the replacement of CEM I by the nSS in the range of 10 to 100% bwoc
- The dosage of SPs is based on the cement content, and not based on the other powder materials that are involved in the mixture. Pantarhit® PC 150 from Ha-Be Betonchemie GmbH & CO. KG. is the SP with best features, it is the only SP that reached the minimum value of 8 MPa after 16 hour in all the fly-ash systems. The influence of Pantarhit® PC 150 on the limestone system to reach the minimum value of 14 MPa is neglected; with these superplastisizer it is not possible to reach the value in 16 hour.
- Following the procedure of potentiometric titration technique of the British standard and following the technique of Spiesz & Brouwers (2012), it is possible to replace CEM I 52,5R for 100% by the nSS in concrete with steel or other metal embedded reinforcement on the critical chloride content. All the mixtures except the 100% replacement fly ash system are in the requirements of the EN 206-1 for a maximum chloride content of 0,20 for prestressing steel reinforcement concrete.
- Due to standards given by Kijlstra Betonmortel B.V. it shows that the calculation of the chloride content is based on the mass balance of all components in the SCM. Considering the specified chloride content in each compound (ex. fly-ash, CEM III/B, etc.) and the measured chloride content in the silica sludge (1.35% by mass). The chloride content by mass of binder was estimated. For these calculations, all the SCM could be used in steel reinforced concrete, but not in pre-stressed steel concretes. The calculated chloride content and measured chloride content in the sludge (1.35% by

mass) is higher than the maximum specified range limit for micro-silica of 0.1 to 0.3% by mass given in EN 206-1

- The cement content of the SCM can be decreased up to 30% by mass using the nano-silica sludge and the correct type of SP in the fly ash system and stay in the range of the critical chloride content.
- The replacement of the cement CEM I with different concentration of silica sludge has a high effect on the hydration kinetics.
- The hydration kinetics of all systems where affected by the replacement of CEM I 52,5R by the nSS. In the fly ash system strong reaction of alite during the first hours results in an high hydration peak. In the second peak after ca. 10 hours hydration,C_3S has produced monosulfate or “inner C–S–H” . Fly ash is accelerating the polymerization of hydrated silicates, when the reaction of gypsum continuous, the hydration speed decreases. When the creation of C-S-H around fly-ash is less than around the cement grain, fly-ash start reaction and consuming CH, after this reaction the hydratation increases rapidly to maximum heat. The reactivity of nSS is generally larger than the reactivity of slag or fly-ash due their small particle size; this causes an accelerated hydration, a higher heat flow and a reduced induction period. The decrease of heat hydratation which is observed can be attributed to the fast reaction of the nSS to form C-S-H. All the obtained figures could be compared with the strength results and these results are fully consistent.
- The presence of the fly ash filler and nSS in the mortar determines significant decreasing of the compressive strengths, in comparison with the reference, especially in early age. After 7 days all the systems achieved a higher compressive strength.
- If fine limestone is present, carbonate ions become available as some of the limestone reacts. The carbonate displaces sulfate or hydroxyl in AFm; the proportion of monosulfate or hydroxy-AFm therefore decreases as the proportion of monocarbonate increases. The displaced sulfate typically combines with remaining monosulfate to form ettringite, but if any hydroxy-AFm is present, the sulfate will displace the hydroxyl ions to form more monosulfate. The key here is the balance between available alumina on the one hand, and carbonate and sulfate on the other.
- The presence of the limestone filler and nSS in the mortar determines significant decreases of the compressive strengths, in comparison with the reference, especially in early age, consequence of the dilution effect of the active component (CEM I 52,5R) in the binder. After a longer period of time such as 28 days, the compressive strength has become higher as the reference.
- Cement content of the SCM can be decreased up to 30% by mass using the nano-silica sludge for hydration kinetics.
- The limestone system is divested for further development. Further tests will be done following the results of the 30% replacement fly-ash system.

6 Self-Compacting Concrete (SCC)

6.1 Introduction

This chapter concludes the analysis of the application of waste nano-silica sludge into SCM and SCC. The influences of this material on the workability, strength, chloride and hydratation kinetics are tested. The present chapter adresses a deeper analysis of the SCC mixes produced within the framework of this thesis, the fundamentals of SCC are outlined in the previous chapters. In particular this chapter will discuss the increase in size of aggregates from 4 mm to 16 mm. Due to the increased size of aggregates at this stage, additional consideration will be given to addressing questions of stability, passing ability, and the influence of the aggregate size. In additional to the previous stage slump flow, V-funnel and J-ring tests are used, which are described in appendix A, and these results are presented and analyzed in the current section of this thesis as well.. The hardened concrete properties will be compared with Kijlstra Betonmortel's results of the last year to see if the adapted SCC could be take into production, this focus is mainly on the compressive strength after the 16 hour demolding time. With this concrete batch a real size element is made to see the inner influence and difference of the use of nSS.

6.2 Laboratory test

Laboratory trials should always be used to verify properties of the initial mix composition with respect to the specified characteristics and classes. If necessary, adjustments to the mix composition should then be made. Due to the results in the SCM, lab tests are conducted by the 30% fly-ash system and with the best SP according to the SCM test Pantarhit® PC 150. The steps leading from mortar to concrete will be explained in more detail further on within this thesis. The change of aggregates and the amount of SP could change the results comparing the mortar results monitoring production; the system quality could be adjusted. All the standard test described in chapter one where conducted for the lab concrete fly-ash system, except the J-ring.

6.2.1 Order of addition

To conduct a 20 l test for SCC a pan mixer is used for producing this batch. According to the findings of Hunger (2010) an mix procedure has been developed. This mix procedure is given below with the addition of nSS:

- All fractions such as sand, gravel and all the powders are mixed for 20 sec in dry state.
- Disperse the nSS by hand agglomeration.
- 80-90% of the total amount of water is added while further mixing for another 120 seconds. The remaining 10 - 20% is added on a later moment in order to prevent unintentional over dosage. All the amount of nSS is added while mixing.
- After these 120 seconds the mixture need to be scraped of the walls of the mixer
- A specific amount of SP is added while continuing to mix for 60 seconds.

6.2.2 Fresh SCC

After mixing, the concrete can be used for tests based on the EFNARC guidelines, EN12350 (Table 6-1), and to the preferred values of Kijlstra Betonmortel B.V (Table 6-2). In Okamura and Ouchi's study (2003) the filling ability, passing ability and stability of mixtures can be considered as the distinguishing properties of fresh SCC.

indication	**Compaction (C)**		**Slump (S)**		**Flow (F)**		**Flow (SF)**		**viscossity**	
	class		class	mm	class	mm	class	mm	class	s
Dry	C0	>1,46								
Nature moist	C1	1,45-1,26	S1	10-40	F1	<340				
Half plastic	C2	1,25-1,11	S2	50-90	F2	350-410				
Plastic	C3	1,10-1,04	S3	100-150	F3	420-480				
Very plastic			S4	160-210	F4	490-550				
Liquid			S5	>220	F5	560-620				
Very liquid					F6	>630	SF1	550-650	VS1/VF1	<8
							SF2	660-750	VS2/VF2	9-25
Very liquid (Self-Compacting Concrete)					**F7**	**650-900**	**SF3**	**760-900**	VS1/VF1	<8
									VS2/VF2	**9-25**

Table 6-1; Viscosity classes SCC (Source; EN 12350)

Property measured	Test method	Material	Recommended values EN 206-1	Recommended values Kijlstra
Flow ability / Filling ability	Slump flow	Concrete mortar	650 – 800 mm Average flow diameter	700 mm
	V – funnel	Concrete / mortar	6 – 30 sec Time for emptying of funnel	12 – 13 sec Time for emptying of funnel
Stability ability (t_{5min}-t_0) [s]	V-funnel	concrete	<3 sec	<3 sec
Passing ability	J - ring	Concrete	0 – 10 mm Difference in heights at the beginning and end of flow	0 – 6 mm Difference in heights at the beginning and end of flow

Table 6-2 Summary of common testing methods and limiting test values for SCC

6.2.3 Laboratory test results

The fresh concrete produced through the mixture design has been tested. All the observed values are given in Table 6-3. When looking at results of the slump flow test Figure 6-1a concludes that the required value is passed by the reference mixture as well as by the 30% replacement mixture. A slight decrease in slump flow occurred in the nSS mixture, based on visual observation bleeding within in the mixture also occurred (Figure 6-1b). The V-funnel (Figure 6-2a) values are collected following the test procedure described in appendix A. The requested viscossity of Kijlstra is 12-13 seconds, both mixtures are below this requisted time, the nSS mixture closest to this specified time. The stability time may not exceed the V-funnel time with more than 3 seconds, due to the fact that the nSS has an smaller size of particles, however the time is increased in comparisation to the reference mixture. Interestingly, in the SCC test with the stability time the phenomenen of segregation of fly-ash particles aprears, which is seen in Figure 6-2b. Through a misstake only the density of the reference mixture is measured, it couldn't be repeated because the blocks are curred on the time of notice. The laboratiorium test is aimed to reach the right values for a 16 hour demolding, due to the SCM results the values of the 7 and 28 days are not tested, the values are all higher then the reference mixture. The results of this 16 hourtest are exceed the requisted 8 N/mm^2 with 11.46 N/mm^2 and 11.50 N/mm^2 for the reference mixture and 30% nSS system respectively. Neverthe less, the testing of fresh SCC has been acounted all the test except the J-ring. The obtained results prove that the system could take the next step to the pilot test.

Value	Reference	Silica sludge	Required
Slump flow [mm]	800 - 805	780 - 800	700
V-funnel time [s]	9.68	11.48	12/13
Stability time (t_{5min}-t_0) [s]	+ 1.8	+ 0.73	< 3
Fresh density [g/cm^3]	2.425	-	-
16 hourcompressive strength [N/mm^2]	11.46	11.50	> 8

Table 6-3; Reached values laboratory test SCC

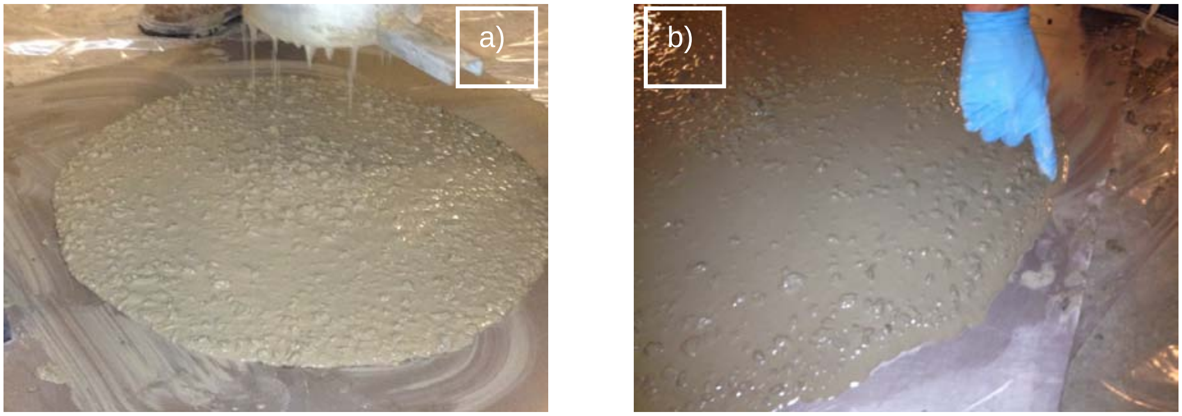


Figure 6-1; a) slump flow SCC with 30% reduction CEM I 52,5R, b) observing bleeding in slump flow test.

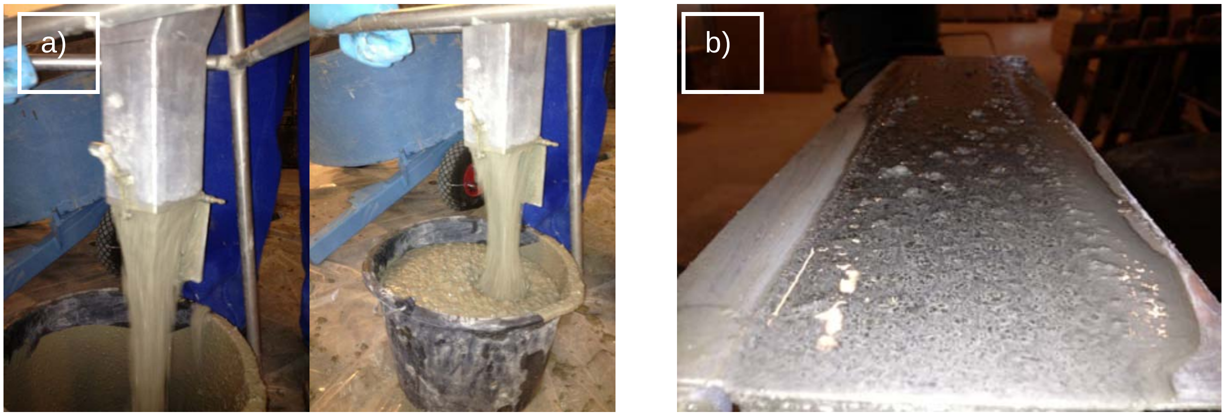


Figure 6-2; a) V-funnel time test, b) phenomenon of segregation in V-funnel stability test

6.3 Pilot test

6.3.1 Introduction

At full scale, self-compacting concrete is less tolerant to changes in constituent characteristics and batching variances than lower workability concrete. Accordingly, it is important that all aspects of the production and placing processes are carefully supervised following the guidance of the EFNARC guidelines (2005). A full description of all the erected tests is given in appendix A. This stage is following the laboratory tests. The production of self-compacting concrete pilot test is carried out at the plant; Vianen Betonmortel. This plant works with equipment, operation and materials that are controlled under a quality assurance scheme which is accredited to ISO 9001. Prior to starting with the pilot test several trial batches are being produced, to adapt the plant to produce smaller amounts and reduce weight differences. All values of the test are referred to the reference compound No. 51 of Kijlstra concrete. This composition has the following properties; recipe 51, strength class C45/55, viscosity class F7, and exposure class XA3 (chemical attack; humic acid, hydrochloric acid, sulfuric acid).

6.3.2 Pilot test

The mix design calculated after the SCM stage and when it is used in the laboratory SCC test the amount of produced SCC is determined on 2 times a ½ m^3. During production of the mixture, there may be a number of factors that individually or collectively contributed to variations in the uniformity. The main factors are changes in the free moisture of the aggregate, aggregate particle size distribution and variations in batching sequence. Changes in properties may also be observed when new batches of other constituents are introduced. Because it is normally not possible to immediately identify the specific cause, due to this deviation the adjustments to the consistence should be achieved by adjusting the level of superplasticiser or amount of water. The amount of the batches is weighed by a fully automatic system (Figure 6-3a), approximately two thirds of the mixing water is added to the mixer. This is followed by the aggregates and cement. After this stage the mixer starts to immediately form an SCC mixture, before adding the nSS this has to be dispersed to avoid the possible sedimentation that has occur due to the high amount of nSS. This dispersion has been done by a hand operated concrete mixer (Figure 6-3b), after dispersion the nSS is added into the already mixed amount of aggregates, cement and water (Figures 6-3c and 6-3d).

Figure 6-3; a) Automatic weight system, b) dispersion by a hand concrete mixer, c) adding nSS into the mixer, d) nSS in the mixer

Visual observation during the mixing procedure, on the same time adding the amount of superplasticizer shown that the time necessary to achieve complete mixing of SCC may be longer due to reduced frictional forces and to fully activate the nSS and superplasticiser (Figures 6-4a and 6-4b).

Figure 6-4; a-b) inside mixer Kijlstra Betonmortel B.V.

All the factors mentioned above result in an increase of water in the mixture (+3 liters in the first batch and +6 liters in batch 2) (Table 6-5), these adjustments result in better SCC based on visual expertise.

Materials	Reference	Silica sludge (30% bwoc) (Laboratory)	Batch 1 (Pilot test)	Batch 2 (Pilot test)
		[kg/m^3]		
CEM I 52.5R	95	66.5	52	66
CEM IIIB LH/HS	255	255	252	255
Fly ash	160	160	156	160
Sand (0-8 mm)	825	825	840^5	825^5
Gravel (4-16 mm)	845	845	840^4	845^4
Silica sludge (26.5 % solids)	0	107.5*	107.5	107.5
Water	163	90.5	105	118
SP	3.5^1	4.7 (5.35)*^{,2}	3.5^3	2.740^3
w/c	0.427	0.427	0.426	0.441

Table 6-4; Mix design CEM I replacement with 30% nSS

(*) Included SP (0.60% based on the slurry weight), 1) Cugla®, 2) PC 150 3) TB 100 4) 2.2% moisture 5) 2.8% moisture.

6.3.3 Test results

The recommended test for characterizing SCC on site is slump-flow in combination with the J-ring test (appendix A). This gives a good indication of the uniformity of concrete supply. A visual assessment for any indication of paste separation at the circumference of the flow and any aggregate separation in the central area also gives some indication of segregation resistance and blocking resistance (Figure 6-5a and 6-5b and Table 6-5). In a parallel test the V-funnel is executed. All the values of these tests are given in Table 6-6.

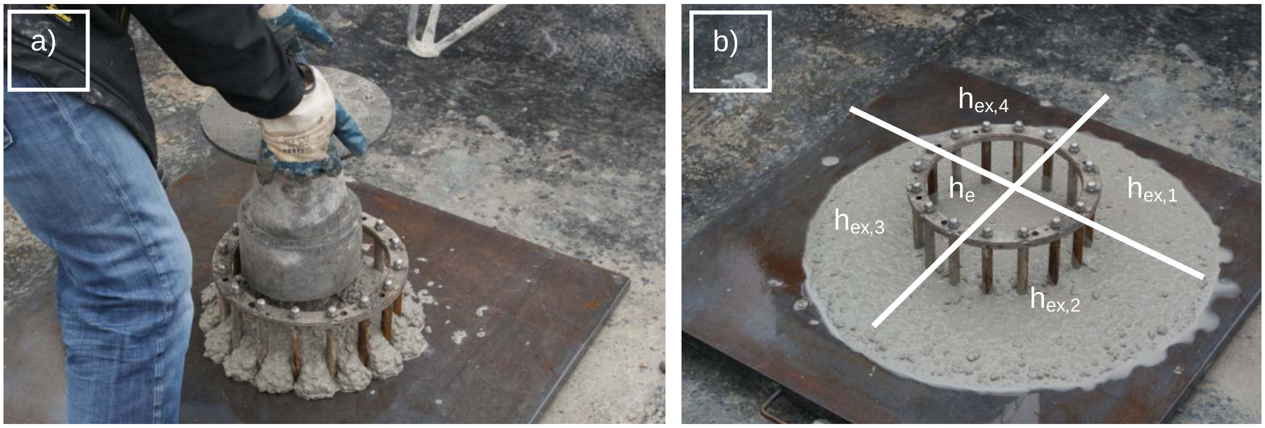


Figure 6-5; a) Automatic weight system, b) dispersion by a hand concrete mixer, c) adding nSS into the mixer, d) nSS in the mixer

test	J-ring	$h_{ex,1}$	$h_{ex,2}$	$h_{ex,3}$	$h_{ex,4}$	h_c	st_j
Batch 1		126	125	124	125	120	5
Batch 2		122	125	122	124	108	9

Table 6-5; Results field test overview *an additional 1,5 liters of water is added to the system

Mix.	Slump flow (SF) SF (mm)	V-funnel time t_v (s)	V-funnel time t_v (s)	V-funnel stability time (5min) $t_{v,stab}$ (s)	Max stability time <3 s (s)	Blocking step EN-206-9 st_j <10 mm (mm)
Batch 1 (0899)	820	16.0	23.4	27.2	3.8	5.0
	810	-	-	-	-	-
Batch 2 (0899)	730	12.45	18.45	23,8	5.35	9.0
	740	10.36*	10.71*	13.6*	2.89*	-

Table 6-6; Results field test overview *an additional 1,5 liters of water is added to the system

In Figure 6-6 the values extracts from Table 6-6 are shown. Batch 1 has an higher spread flow as the median value of 757,7mm. All reference values are taken from the production results of Kijlstra from May 2012 till September 2012. The values of batch 1 and batch 2 are inside the production band of Kijlstra Betonmortel B.V; these also show achievement of the requested slump flow of Kijlstra, reached in both systems.

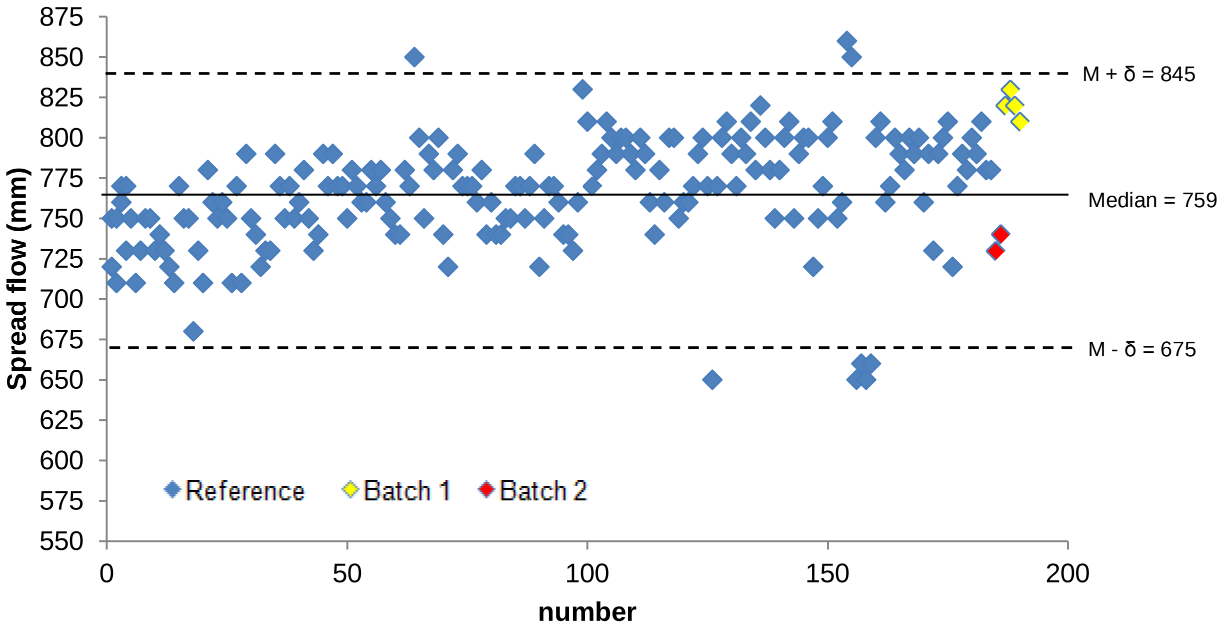


Figure 6-6; Spread flow overview May 2012-September 2012

High V-funnel times can be related to a low deformability or a high paste viscosity, a high interparticle friction or a blockage in the flow (Sonebi and Bartos, 1999). The slump flow values of the batches obtained with the J-ring method where larger than compared to the standard slump flow. Directly linked to this observation long $t_{v,stab}$ values are observed, they are in the range of 6 to 30 sec but the $t_{v,stab}$ criterium of < 3 seconds is largely exceeded. These observations are shown in Table 6-6. The further observations are based on the data given by Kijlstra Betonmortel in the same period as the spread flow values. A conclusion from these values is that batch one needs an higher V-funnel time than batch two. After a small adjustment in batch two by adding 1,5 liters of water, the V-funnel time is reduced by 10 sec in the stability time. This is also shown in Figure 6-7 by looking at the green dots.

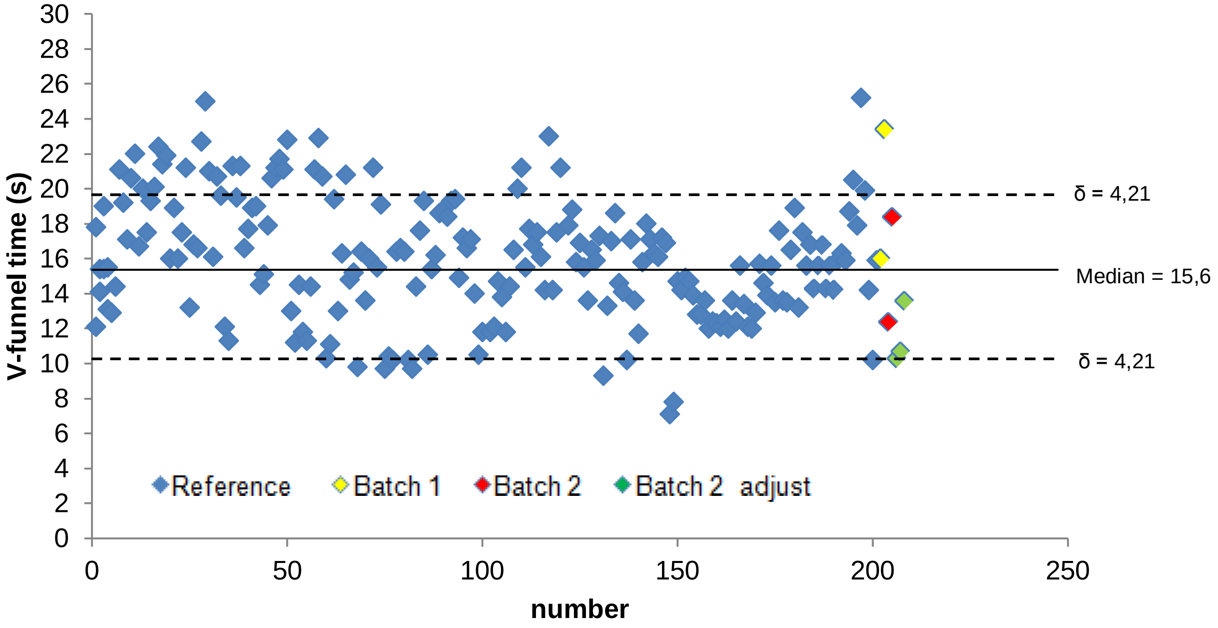


Figure 6-7; V-funnel overview May 2012-September 2012

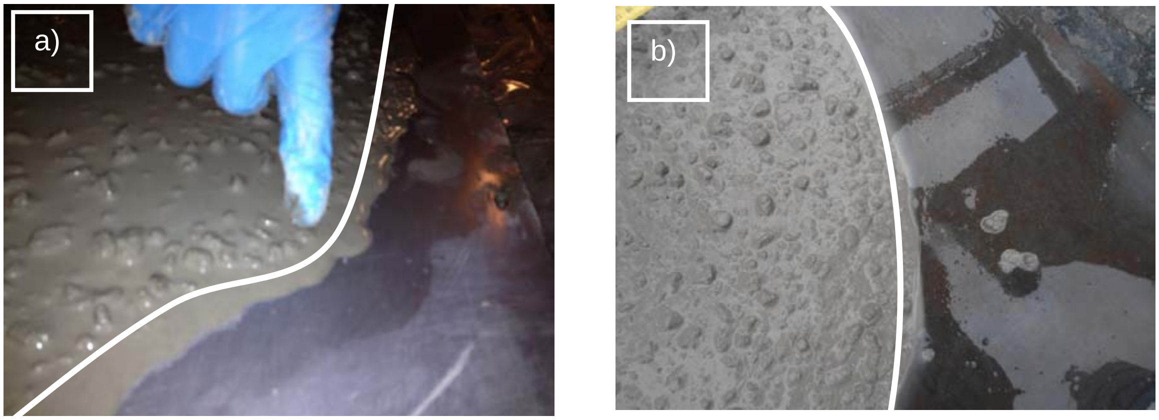
6.4 Conclusion; Analyzing fresh SCC

When aanalyzing results obtained from the two different compositions, in this case it is possible to conclude that the first composition, batch one has a more stabilized mixture in comparison to batch 2. The added nSS has increased the flow dimension in the slump flow test and the J-ring test, the Stability time is in range of the requested values of < 25 seconds. But there are several points of attention to this composition, there arise problems with the V-funnel test at the set time of less than 3 seconds after 5 minutes the $t_{v,stab}$. In the first case of batch 2 the stabilizing time is high, but the re-mix was very stable.

By compairing the slump flow test in the laboratory and the pilot test, a mild form of bleeding is observed in the laboratory. Figure 6-8 shows the bleeding that occurred during testing at the facility site, other than this occurrence there were no other forms of bleeding observed. A cause of this bleeding could be the usage of PANTARHIT® PC150 in the laboratory test;

PANTARHIT® RC 100 is used in the pilot testing it can be concluded that the mixing results with the RC 100 in a stable composition.

The use of superplasticizer in the different configurations were significant in workability. Reduction in amount in batch 2 was possible, which is directly reflected in the flow dimension that are increased by almost 100 mm. The SP that is used in contrast to the tests in the laboratory is the type PANTARHIT® RC 100 instead of PANTARHIT® PC150. This change has a major impact on the composition of the self-compacting concrete, in the lab the PC 150 was the best, but due to this absence it could not be used in the field test. To provide a reliable conclusion it would be advisable to do more tests from this composition, and in larger quantities.



igure 6-8; Bleeding SCC **a)** bleeding occurs in laboratory **b)** no bleeding observed

To improve the V-funnel stability time in batch one, PC 150 is recommended as the super plasticizer that needs to be used instead of the RC100, the lab results prove the operation of the PC 150. Another striking difference is the separation of the fly ash during the settlement time of self-compacting concrete. The black topcoat during the testing at the facility is not observed. Figure 5-6 shows this separation. Whitin both systems there is no visible blocking of the SCC, all differences between normal flow dimension and with the J-ring are in the range of 0 – 25 mm. This means no visible blocking. When these values increase to 25-50 or above 50mm, there is minimal to moderate blocking and significant to extreme blocking in the system (de Schutter, 2005).

6.5 Hardened concrete

6.5.1 Introduction

All the tests that are conducted for determining the strength measurements (compressive) are carried out with standard cubes with the dimensions of 150 x 150 x 150 mm^3, all these cubes comply with the EN 12390-1 (2000). At the moment of casting these cubes no vibrating energy is applied. The storage of these cubes is also handled according to the EN 12390-2 (2000). This norm requires that the poured cubes need to stay one day in the mold, which protects against impact and dehydration. After this day the molds can be taken off and the cubes need to be stored under water until testing. This water temperature needs to be in the range of 20 ± 2ºC. Only the cubes for the 7 and 28 days compressive strength test needs to be put in the water. The other cubes are crushed after 16 hour to determine the early age strength for demolding as described in chapter 5.

6.5.2 Compressive strength

Compressive strength (N/mm^2) is measured on a universal testing machine, these range from very small table top systems to ones with over 53 MN capacity. Measurements of compressive strength are affected by the specific test method and conditions of measurement. The batches are tested until failure takes place. All the results are given in Table 6-7. From the graph in figure 6-11 it becomes clear that the replacement mixture of the fly-ash system in combination with the mixture number 51 it is evident that the compressive strength results are in line with the reached strength values of Kijlstra Betonmortel B.V.

Mixture No.	1 day (N/mm^2)	7 days (N/mm^2)	28 days (N/mm^2)
Lab test	11,5 ± 1	n.a.	n.a.
Batch 1	12 ± 1	53 ± 1	60 ± 1
Batch 2	11,5 ± 1	51,5 ± 1	59 ± 1

Table 6-7; Compressive strength results pilot test

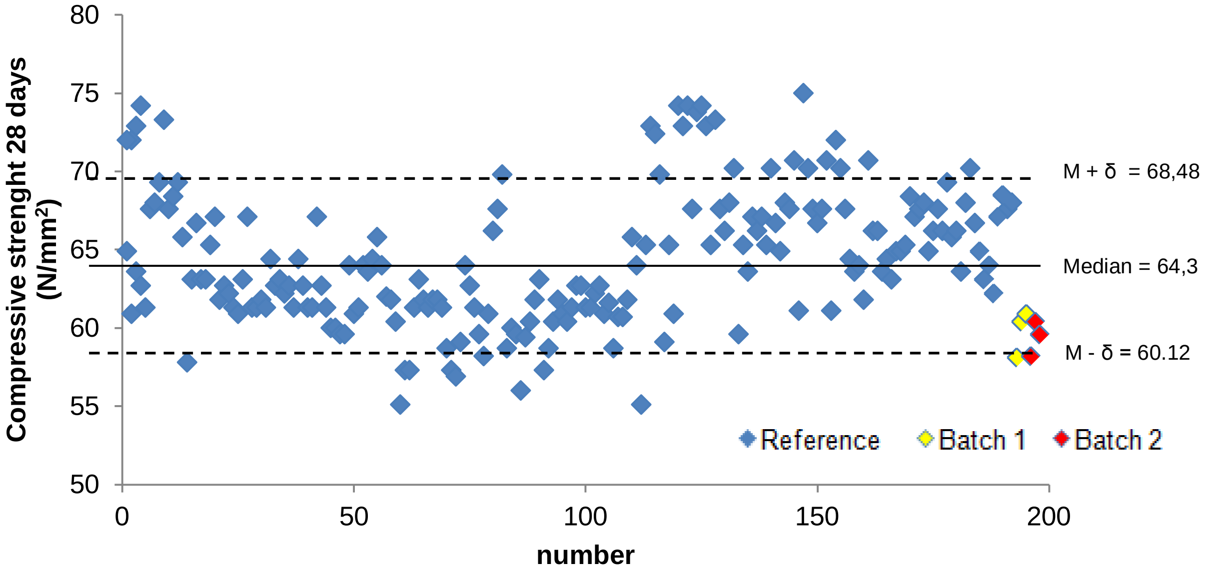


Figure 6-9; Compressive strength 28 days results May 2012-September 2012

6.5.3 The test specimen

After all the tests, Batch 1 was used to cast a real size element slab (Figure 6-12a, and during the concrete pouring several observations were made. The pouring is done from an exocentric point (Figure 6-12b). Taking consideration for the flowing nature of such concrete is essential; care is required to ensure excellent filling ability and adequate stability. This is especially important when concrete can block the flow, as a result of the low yield stress and the influence of gravity it can be excluded that this state will be obtained, the self-compacting concrete flow out through the entire formwork (Figure 6-12c and 6-12d). The coarse aggregate needs to be uniformly spread throughout the entire concrete placement and floating on the surface. Once the concrete placement was complete an examination has been conducted to check the quality of the hardened concrete looking for surface laitance, a non-uniform surface colour, specific areas where air bubbles are being trapped on the formed surfaces and any other unwanted defects (Figure 6-12e – 6-12j).

Figure 6-10; SCC real size element **a)** mold with all reinforcement bars to test blocking in real size **b-d)** casting the element with SCC batch one, c) filling ability at all corners.

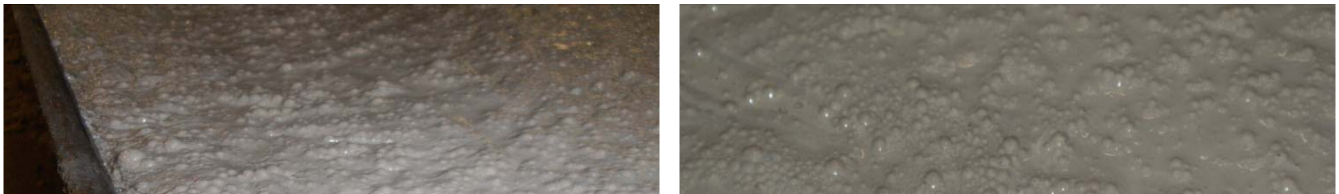


Figure 6-11; e-f) de-airing SCC, the entrapped air comes out of the concrete and forms a top layer of bubbles, **g)** wiping the air bubbles of the concrete to get smooth surface, **h-i)** the casted element must stand for 16 hour, before demolding it, **k)** the element after 16 hours of hardening after demolding

6.5.4 Extracted Section

After the hardened state of 28 days the demolded slab was cut and sectioned with a diamond saw to give an internal check of the slab for defects and verification if Batch 1 produced a homogeneous cast. The extracted piece of the slab is shown in Figure 6-13. Examining the extracted section it is possible to observe the effect that SCC is familiar with, the de-airing of the foam top layer forming during the casting. Due to this de-airing a small section of segregation occurs, this section consists of an higher amount of fine particles. Nevertheless, the total view of the cast, referred to this cut section looks very homogeneous, no defects of blocking in the reinforcement is detected (Figure 6-13b). When adapting the optimized mixture that is used for this test, the segregated layer mentioned above probably disappear. Therefore the use of water and SP must be adapted. Given these results the main conclusion of this test is that the test was a success trial, which needs to be redone on major scale.

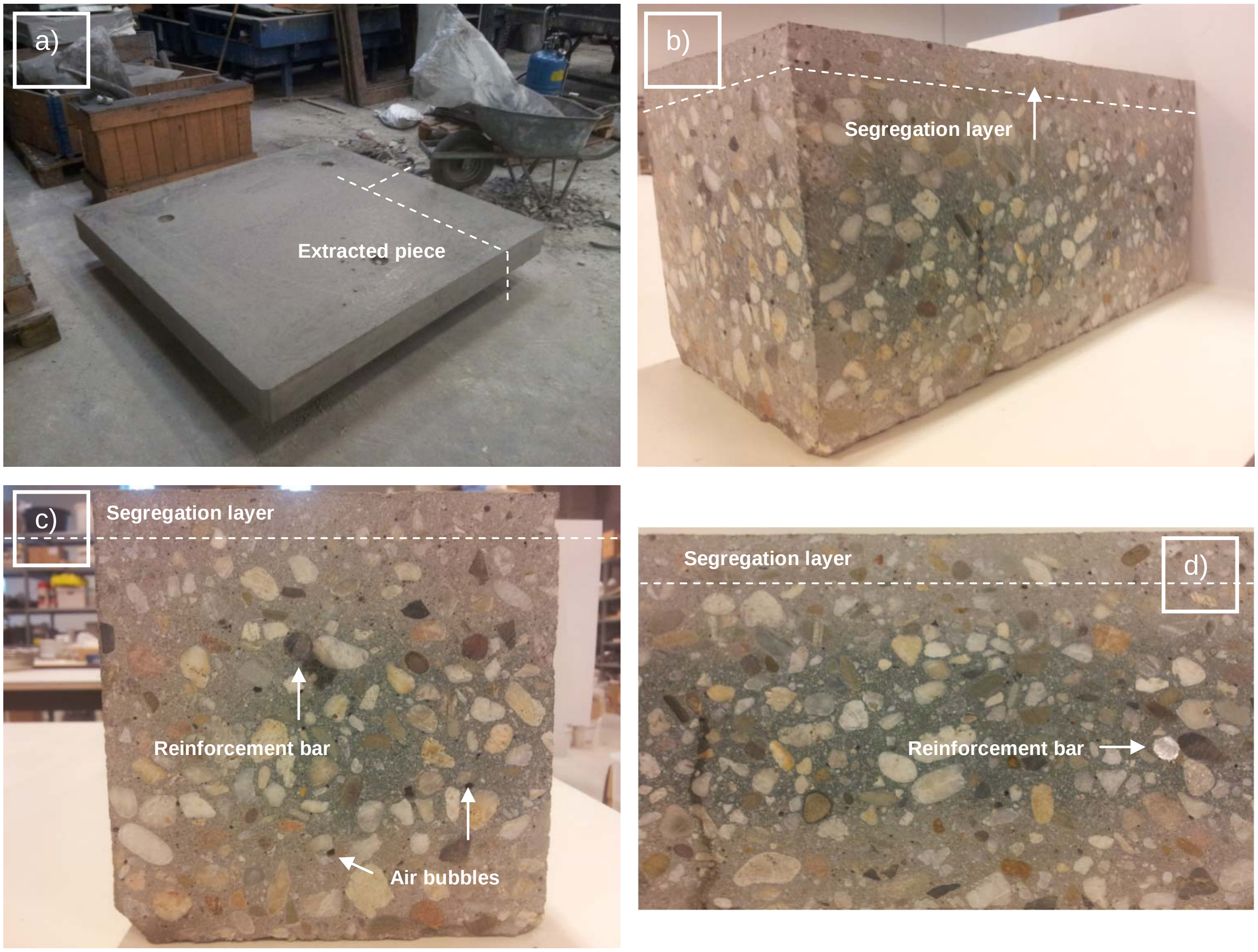


Figure 6-13; Extracted section from Batch 1 the slab casted with the SCC+nSS mixture a) extracted element, b) segregation layer, c-d) reinforcement bar, air bubbles and segregation layer

7 Cement, concrete and carbon dioxide

7.1 Introduction “it is just like a medal”

The greenhouse gas carbon dioxide (CO_2) is one of the most comprehensive policy themes ever. The tax on cars has become dependent on the amount of CO_2 emitted per kilometer driven. Factories are now settled on their annual CO_2 emissions.

Carbon dioxide (CO_2) is also emitted during the production of cement and concrete. This is one side of the coin, the other side is that by intelligent use of the building material concrete a large amount of CO_2 can be saved. In previous chapters the production process of cement clinker was explained, in this chapter the different equivalent sources and the production worldwide on European base, and the reduction of cement clinker usage will be explained.

Ask yourself the question, how much CO_2 emissions belong to a product that you want to buy in the shop? If the product comes of the cold ground from Netherlands there is, for example, only CO_2 emissions from picking and transport in refrigerated lorries. If they come out of the greenhouses then the heating in greenhouses should be taken into account. If the product is from Spain the transport from Spain may also not be forgotten. Generally this shows how difficult it is to quickly get a ruling on the amount of CO_2 emissions.

7.2 Carbon dioxide (CO_2)

CO_2 is the chemical designation of the gas carbon dioxide, also known as carbon dioxide. The gas is composed of one carbon atom and two oxygen atoms. Carbon dioxide is a colorless and odorless gas. Approximately 0.03% of the air around us consists of this gas (Kaufman, 1996).

Carbon dioxide exists in all of nature’s plants, humans, and animals. Plants take water and carbon dioxide into glucose and fixed this into, what is a building block for the production of cellulose in e.g. the leaves. The energy that is needed for this conversion comes from the Sun. This reaction process is known as photosynthesis. It is very important for a human that during this process oxygen (O2) is released. Animals and people do the reverse. They breathe oxygen (O_2) in and carbon dioxide (CO_2) out. This CO_2 comes free from the incineration of energy binding nutrients (fats and carbohydrates) in the body when using energy for example moving muscles. The released CO_2 is available again for the plants. Thus is the natural CO_2 cycle. The last 100 years there is a significant change in the release of CO_2 emission into the atmosphere. Widely it is accepted, that it is caused by mankind, who deploy more CO_2 than plants release. The amount of 3-4% in relation to the release of the natural terrestrial CO_2 emissions is very low. Yet this low percentage is sufficient for the strong increase in CO_2 concentration in the last 100 years, Figure 7-1 shows the diagram of CO_2 in relation with temperature over the last 300.000 years.

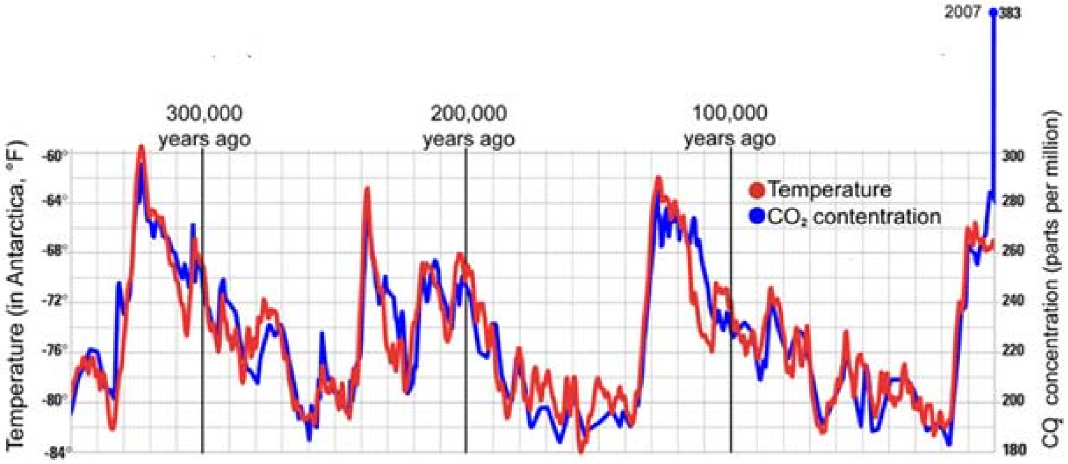
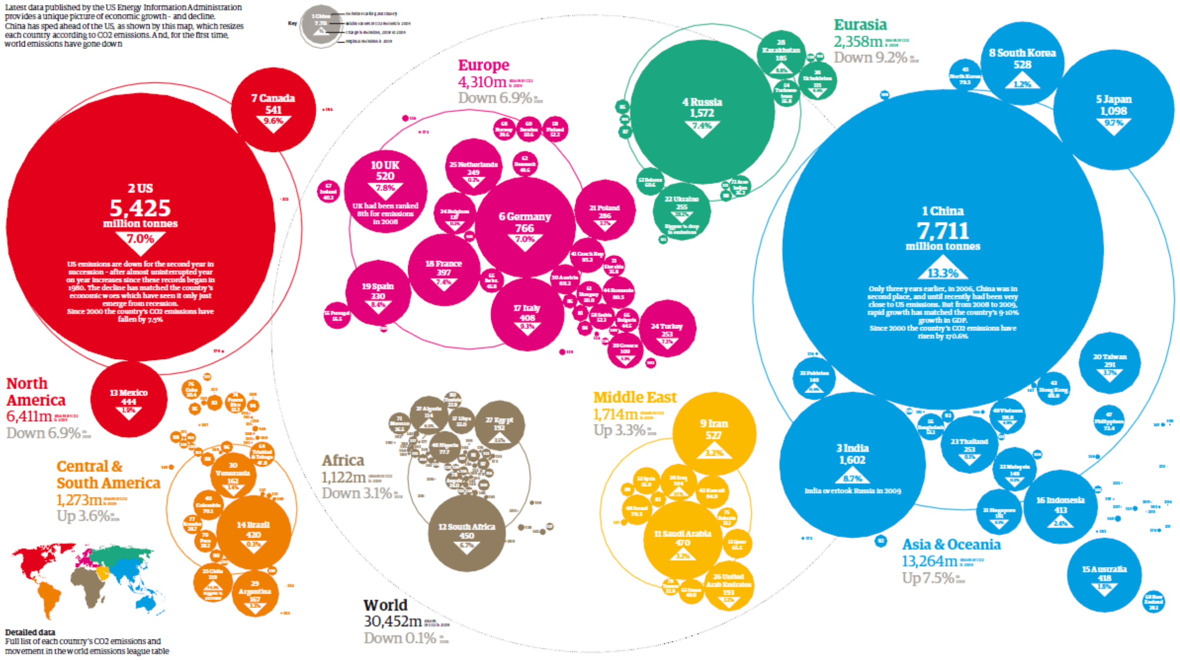


Figure 7-1; CO_2 concentration against temperature over last 300,000 years (Source; www.betternature.wordpress.com)

Global carbon dioxide (CO_2) emissions continue to rise despite best efforts to date to curtail them. CO_2 emissions reached a record-high 31.6 gigatonnes (Gt) in 2011, according to preliminary estimates from the International Energy Agency, a 1 Gt, 3.2% year-over-year increase. As a region, Asia Pacific has added even more cumulative carbon dioxide than developing countries. Rapidly industrializing countries such as China and India are increasing their emissions as they increase standards of living (Figure 7-2). Asia Pacific is the source of 45% of global carbon dioxide emissions, and is on a growth trajectory to reach 50% by the end of the decade. The coal consumption is on the decline because new supplies of natural gas are displacing coal in power plants. Coal accounted for 45% of total energy-related CO_2 emissions worldwide last year, followed by oil at 35% and natural gas accounting for 20%, as the International Energy Agency (IEA) reported in 2012.



Latest data published by the US Energy Information Administration provides a unique picture of economic growth - and decline. China has sped ahead of the US, as shown by this map, which resizes each country according to CO2 emissions. And, for the first time, world emissions have gone down

US emissions are down for the second year in succession - after almost uninterrupted year on year increases since these records began in 1980. The decline has matched the country's economic woes which have seen it only just emerge from recession. Since 2000 the country's CO2 emissions have fallen by 7.5%

Only three years earlier, in 2006, China was in second place, and until recently had been very close to US emissions. But from 2008 to 2009, rapid growth has matched the country's 9-10% growth in GDP. Since 2000 the country's CO2 emissions have risen by 170.6%

UK had been ranked 8th for emissions in 2008

India overtook Russia in 2009

Detailed data
Full list of each country's CO2 emissions and movement in the world emissions league table

Figure 7-2; An atlas of pollution: the world in carbon dioxide (Source; McCormich and Scruton, 2011; Guardian.co 2011)

On pure emissions alone, the key points are:

- China emits more CO_2 than the US and Canada together - up by 171% since the year 2000.
- India is now the world's third biggest emitter of CO_2 - pushing Russia into fourth place.

Analyzing the key points given in Figure 7-2 and described above, a link can be established between the development of a country or continent. The emerging markets in China and India and the use of raw materials for the production of products results in high emissions of CO_2.

7.2.1 Carbon concentration

Carbon concentration in cement spans from approximately 5% in cement structures up to 8% in the case of cement usage in the construction of roads (Scalenghe et al. 2012). Carbon dioxide emissions from a cement plant are divided into two source categories: combustion and calcination. Combustion accounts for approximately 40% and calcination 60% of the total CO_2 emissions from a cement manufacturing facility. The combustion-generated CO_2 emissions are related to fuel use. The CO_2 emissions due to calcination are formed when the raw materials (mostly limestone and clay) are heated to over 1450°C and CO_2 is liberated from the decomposed limestone. The CO_2 emissions are related indirectly through the use of energy. The cement industry produces about 5% of global man-made CO_2 emissions, (Figure 7-3).

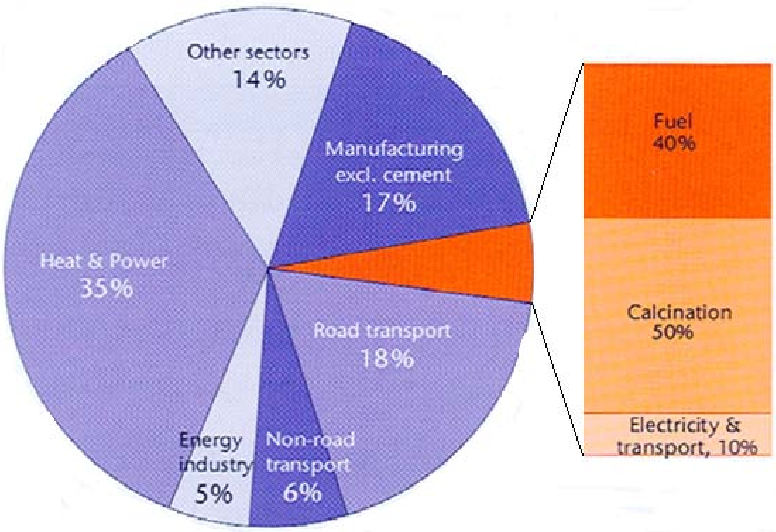


Figure 7-3; Cement industry process (Source: The Cement Sustainability Initiative Progress Report, June 2005)

The high proportion of carbon dioxide produced in the chemical reaction leads to large decrease in mass in the conversion from limestone to cement. So, to reduce the transport of heavier raw materials and to minimize the associated costs, it is more economical for cement plants to be closer to the limestone quarries rather than to the consumer centers. To this observation, the production of cement could directly be linked to the high emissions of China and India. The values of the cement production of the year 2010 are shown in Figure 7-4.

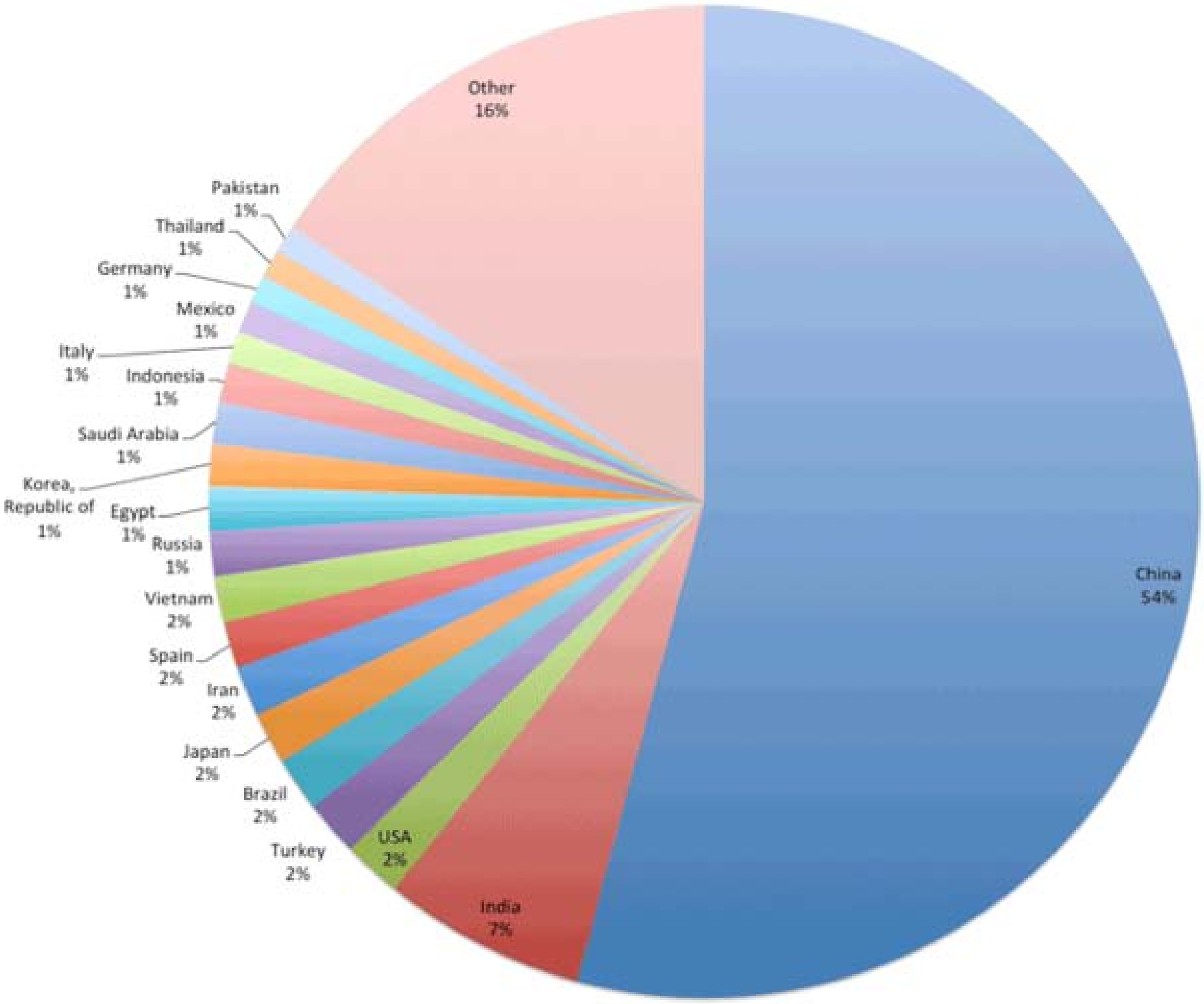


Figure 7-4; Cement production 2010 (Source; CEMBUREAU 2011)

7.2.2 The European cement Industry

After the previous vision on the world usage of cement, the vision in this paragraph is reduced to the European and Dutch cement market. The European cement industry is one of the most concentrated in the world. The 5 largest European companies accounted for 57% of the total cement output in the EU27 in year 2008, and each comprises between 23 - 34 cement plants in the whole EU. According to Öko Institut and Ecofys (2008) the 10 largest producers together accounted for 75% of the total EU27 cement output. Table 7-1 shows the annual production in the period of 2005 till 2008 for cement in the EU27.

Country	No. of instal.	CITL: Volume of CO_2 verified emissions for annual production of cement clinker only (kt CO_2)				Allocation
		2005	2006	2007	2008	Total 2005 - 2008
AT	9	2682	2966	3241	3221	12109
BE	5	4860	5133	5057	4849	19899
BG	5	0	0	3680	3463	7143
CY	2	1481	1471	1460	0	4412
CZ	6	2553	2796	3219	3015	11583
DE	48	20066	20433	22032	20434	82965
DK	1	2566	2695	2765	2236	10262
EE	1	746	802	1177	1179	3903
ES	36	27385	27366	27468	23405	105624
FI	2	921	963	989	1019	3892
FR	30	14005	14367	14651	13789	56813
GB1	16	9781	9827	10080	8259	26476
GR	8	10974	10745	10459	9878	42055
HU	4	2055	2123	2224	2111	8512
IE	4	3812	3793	3820	3391	14815
IT	54	27633	27861	28629	26156	110278
LT	1	783	1064	1092	902	3842
LU	1	732	697	678	641	2748
LV	1	285	358	363	358	1364
NL	**1**	**621**	**563**	**615**	**616**	**2415**
PL	11	8080	9638	11424	10466	39607
PT	6	6610	6505	6713	6376	26203
RO	7	0	0	6516	6594	13110
SE	3	2065	2277	2108	2203	8653
SI	2	776	836	898	968	3478
SK	4	2093	2138	2287	2357	8874
Total EU 27	**268**	**153564**	**157417**	**173641**	**157884**	**631034**

Table 7-1; CO_2 emissions of cement clinker plants 2005 – 2008 (Source; CEMBUREAU, 2009a)

The amount of CO_2 emitted by the cement industry is between 500 kg and 1000 kg of CO_2 for every 1000 kg of cement produced. The Cement & Concrete Centre gives the following approximate figures for the emissions of CO_2 in 2010 attributable to cement used in the Netherlands.

- Portland cement NL, Medium (CEM I) 940 kg / ton of cement.
- Blast furnace cement EN, Medium (CEM III) 330 kg / ton of cement.
- Cement NL, average of 540 kg / ton of cement.
- European Cement, average of 750 kg / ton of cement.
- Cement world, average > 1,000 kg / ton of cement.

The production of cement follows three fundamental stages raw material preparation, clinker production and cement grinding respectively (Öko Institut and Ecofys, 2008). At first the raw mixture of limestone (approx. 90%) and other materials (e.g. clay, iron ore, bauxite) is prepared. For this, blocks of raw materials are extracted from a local quarry or imported from other sites. These consist mostly of limestone but other materials are added to reach the desired chemical composition. After this the raw materials are crushed into smaller particles, homogenized and ground into a thin powder called “raw meal”.

The second stage according to the Öko Institut and Ecofys is the Clinker production. It is the most energy-intensive step in the cement production. Temperatures over 900°C transform the limestone ($CaCO_3$) into lime (CaO), thus releasing CO_2. This is called the calcination process which is mentioned in paragraph 5.6. The calcinated raw meal reaches temperatures of up to 1450°C which allow its sintering to form clinker. This clinker lends the cement its binding properties. Once the clinker is formed, it is then rapidly cooled down to 100-200°C. The clinker that is produced is mixed with different ingredients to produce the cement (third step of Öko). In the case of Ordinary Portland Cement (OPC), around 5% gypsum is added. Not only OPC is used in Europe but so-called blended cements are also widely used. These cements consist of a mixture of clinker and other products with cementitious properties. These are mostly by-products from other industries such as blast furnaces, slags from pig iron production, fly ash from coal power plants or other available pozzolans. Chapter 3 was describing these additives before.

7.3 The Carbon dioxide emission links of the chain

Cement production is responsible for the largest amount of CO_2 released into the atmosphere. It should be noted that the specific CO_2 emissions per ton of cement is influenced by various factors. The most important of these factors is the clinker content in cement, the specific energy consumption (SEC), kiln size and the fuel mix used to provide the required energy, but in general, more than 1 ton of CO_2 is released when 1 ton of cement is produced. If a comparison is made between the European market and the Netherlands, then the emission numbers are almost the same; 0,94 tons for the production of 1 ton of Portland cement (CEM I) and 0,33 tons for the production of Blast Furnace Cement (CEM III) (Cement&BetonCentrum 2010) the share in the concrete production chain of the cement industry is very high, which is also visible in Figure 7-5.

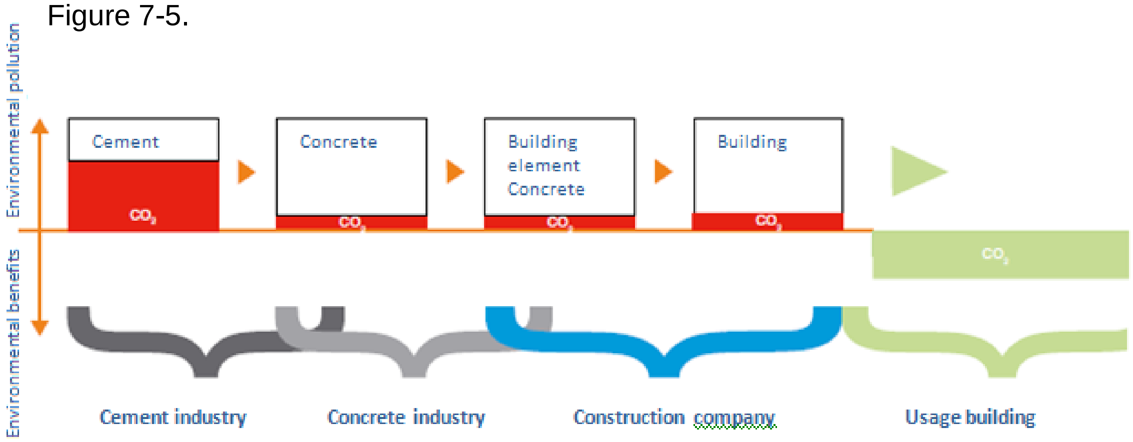


Figure 7-5; CO_2 emission in concrete chain (Source; Cement&BetonCentrum 2010)

7.4 STREAM, Study on TRansport Emissions of All Transport Modes

In recent years there have been plenty of developments in the field of clean and efficient transport. Given the climate aspirations of the European Commission as well as national governments, this is an increasingly urgent issue. Therefore a Study on the Transport Emissions of All transport Modes (STREAM) is conducted by CE Delft. This study gives a comprehensive review of emissions by all forms of transport. The aim of STREAM is to provide a readily understandable and comprehensive review of the emissions of the various transport modes per unit performance for freight carriage. The results yield insight into the fleet-average CO_2, NOx and PM_{10} emissions, in each of the market segments and for several time horizons (2005, 2010, 2020). For this part of this thesis the data of the WLO-study (MNP, 2006) is used, also the Basic data of STREAM (den Boer et al. 2008).

The cleanest modality does not exist. The scale of this transport is very important especially in freight transport, often more important than the modality. Logistical factors also play an important role, such as occupying and load factors. A car with four people is roughly four times more efficient than a car with one person. A full ship is cleaner than an empty freight car or train and vice, versa. The influence of technology on fuel consumption is much smaller than on technological developments. For example, the effect of hybrid technique is not greater than 25%. In the case of longer and heavier trucks, emissions per ton-kilometer can potentially be reduced by the same percentage, this is also for rail and inland shipping.

Reviewing the previous chapters the conclusion is a replacement of 30 % OPC with nSS. Due to this replacement some aspects of Freight transport needs to be observed to calculate if the usage of the nSS not only, as a replacement element lowers the CO_2 footprint but in the entire trajectory, to gain insight into how these emissions from transport are dependent on different parameters;

Freight transport

- Differences in CO_2 emissions per ton kilometer between and within all the transport modes are in most cases of the same order of magnitude, especially on short distances. Therefore, the scale of transport is often as important as the modality of choice.
- On the short distance the energy performance of rail transport and, to a smaller extent inland shipping, is better than that of large trucks. On long distances, large ships and trains generate clearly less CO_2 per ton kilometer.
- With respect to air pollutant emissions, large trucks often outperform inland shipping. This especially counts for PM_{10}, for NOx the modalities are closer together.
- Electrically powered goods trains are relatively clean and efficient.
- The greenhouse gas emissions of aircraft (B-747) are eight times higher than for transport by large truck. Compared with rail and shipping, this factor is even greater.
- Maritime shipping is only more efficient than alternative modes if the vessel is sufficiently large. On average, the smaller vessels typically employed in coastal shipping are no more fuel-efficient than other modes. In terms of air pollutant emissions, on the other hand, maritime shipping performs worse than other modes. The detour factor is of major

influence here. If this is low, maritime shipping scores well, but otherwise smaller vessels, in particular, come off inadequate.

7.4.1 The CO_2 reduction, choice of transportation

Emissions from vehicles can be expressed in different ways:

- Emissions per amount of energy used, expressed in grams of emissions per amount of energy: g/MJ or g/kWh;
- Emissions per vehicle kilometer, expressed in grams of emissions per vehicle kilometer: g/vkm;
- Emissions per amount of transport volume, expressed in grams of emissions per amount of use full cargo moved kilometers (ton-kilometers or travelers kilometer): g/tkm-rzg or g/km;
- Total emissions for a particular trip, expressed in kilograms or tones of emissions per trip.

It performs too far in this study to take all environmental topics, not all themes are equally good to quantify. For this reason, the following demarcation was chosen. The limit will be to environmental effects associated with the use of means of transport. Environmental effects that are almost independent of the use but that is mainly associated with the present infrastructure let's disregard. These are for example space usage and fragmentation by construction of infrastructure.

The above definition means that this study is limited to energy use and emissions of CO_2 and NOx, SO_2 emissions: (relevant) atmospheric and PM_{10} (only combustion). Despite that NO_2 is a relevant atmospheric dust, this also is not included because no sufficient quantitative data is available.

Basic data that is used consists of environmental taxation of vehicles and boats: emission factors (usually in g/v km) and energy use (in MJ per v km)both bottom-up. Emissions from refineries and power stations (in grams per MJ fuel or MJ electricity) and logistic characteristics like load or utilization, percentage productive kilometers, detour percentage, pre-and post-transport:

$$EM_{total} = \frac{(1+ORF)*\left(EM_{vrt}+EM_{raff}+EM_{electr}\right)*\left(1-\%_{v/n\_trans}\right)+(\%_{v/n\_trans}*EM_{v/n\_trans})}{loading} \tag{6.1}$$

EM_{total}: Emissions per ton-travellers or mileage (per tkm or rzg-km).
ORF: Detour percentage compared to road transport.
EM_{vrt}. : Direct emissions of transport (per vkm).
EM_{raff}. : Emissions during fuel refining (per vkm).
EM_{electr}. : Emissions during electricity generation (per vkm).
$EM_{v/n\ trans}$.: Emissions during pre-and post-transport (per vkm).
$\%_{v/n\ trans}$.: Share and post-transport throughout the chain (%).
$(1-\%_{v/n\ trans}.)$: Share transportation by on modality (%).
Loading: Number of tones or persons per vehicle.

Within the freight transport there is a distinction between bulk and nonbulk/container transportation. The main difference between the two modes is the density of the cargo. In the bulk transport is generally to paid-up goods, (e.g. ores, sand and cement products), where the loading capacity for the quantity of goods in tonnes of restrictive which can be loaded, while in the non-bulk transport is much lower the density of the goods and the loading volume restrictive. Furthermore, the load factor and the number of productive kilometers for both modes are different. In this thesis there is chosen for transportation like cement on a dry bulk transport. See Table 7-2 and 7.3. In the bulk transport the calculation is based on the load factor to payload at loaden journeys multiplied by the number of productive kilometers, or nautical miles.

Goods	Bulk transportation	Volume/container
Road		Van[1]
		Truck 3,5-10 tons[1]
		Truck 10-20 tons
	Truck > 20 tons	Truck > 20 tons
	Truck-trailer (> 20 tons) 37m^3	**Truck-trailer (> 20 tons) (46 tons)**
Rail	Train – diesel 1.700 tons	Train – diesel 800 tons
	Train – electric 1.700 tons	Train – electric 800 tons
Inland Shipping	350 tons (spits)	
	550 tons (kempenaar)	32 TEU
	1.350 tons (rhine-heme canal)	96 TEU
	5.500 tons (couple)	200 TEU
	12.000 tons (Four-barges convoy)	470 TEU
Maritime Shipping	coastal shipping 1.300 GT	144 TEU 908 T
	coastal shipping 5.800 GT	580 TEU 3.957 T
	coastal/deepsea shipping 20.000 GT	1.905 TEU **17.262 T (20.923 T)** 4.103 TEU 39.544 T
	deep sea shipping 45.000 GT	6.957 TEU 73.340 T
	deep-sea shipping 80.000 GT	
Aviation		B737-400 (Europe)[1]
		B747-400F (Continental)[1]

Table 7-2; Goods, Bulk transportation, Volume overview (Source; Stream 2008)

[1] non bulk goods, TEU; **T**wenty feet **E**quivalent **U**nit

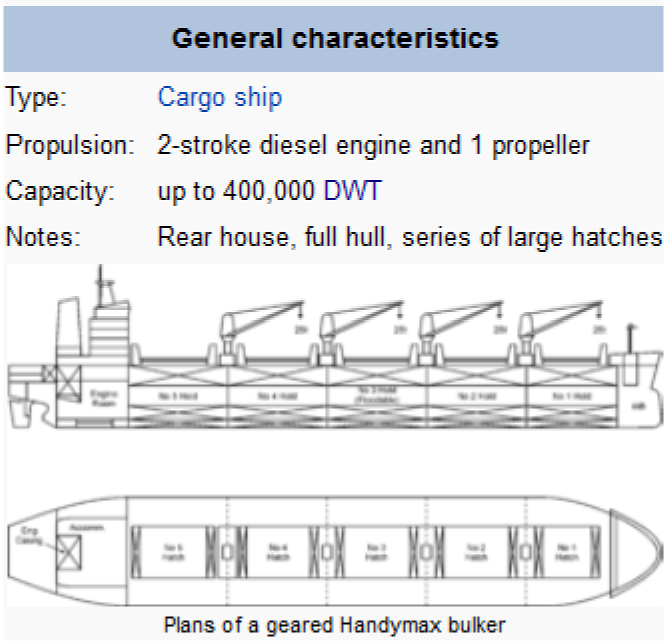
Maritime Shipping		**Energy consumption**		**Emission factor**			
		MJ/km	CO_2 kg/km	CO_2 g/km-ton	NO_x kg/km	PM_{10} kg/km	SO_2 kg/km
dry bulk							
CS GT	1.300	693	54	-	1,2	0,09	0,66
CS GT	5.800	1.113	87	-	2,3	0,20	1,39
CS/ DS GT	**20.000**	**1.886**	**147**	**7.01**	**4,3**	**0,34**	**2,29**
DS GT	45.000	2.381	186	-	5,4	0,39	2,64
DS GT	80.000	3.503	273	-	8,0	0,63	4,27

		capacity	**loading**	**Loading-factor**	**productive kilometers**
		ton/vtg	ton/vtg	% of loading capacity	%
dry bulk					
CS GT	1.300	1.815	908	100	50
CS GT	5.800	7.934	3.957	100	50
CS/ DS GT	**20.000**	**29.830**	**17.262 (20.923)**	**100**	**50**
DS GT	45.000	79.088	39.544	100	50
DS GT	80.000	146.680	73.340	100	50

Table 7-3; Emissions and energy use in the maritime transport & Logistic parameters in the maritime transport CS; Coastal shipping DS; Deep sea shipping (Source: TNO, 2003)

The maritime transport become more efficient in recent decades. It is particularly through the growing of ships that the transport per unit of the product has become more efficient. In addition to the shift to increasingly larger ships, there are also technical measures which have brought increased energy efficiency and an improvement of the hydrodynamics (hull and screw). But because of the long lifetime of ships the impact on the park average emissions is limited. In addition, on the other hand the development is that there is a higher vessel speed, particularly in the dry bulk transport. To take all the collected values into account a choice needs to be made for a vessel. Bulkers are segregated into six major size categories: small, handysize, handymax, panamax, capesize, and very large. Although there is no official definition in terms of exact tonnages, Handysize most usually refers to a dry bulk vessel (or, less commonly, to a product tanker) with deadweight of about 15,000–35,000 tons. Above this size are Handymax bulkers (typically 35,000 - 58,000 tons deadweight); there is no well-defined or widely accepted size sector below 15,000 tons. In this case, a handysize bulk freightener was chosen, for example the SABRINA I as mentioned in Figure 7-6.

Figure 7-6; Handysize bulk Freighter Sabrina I



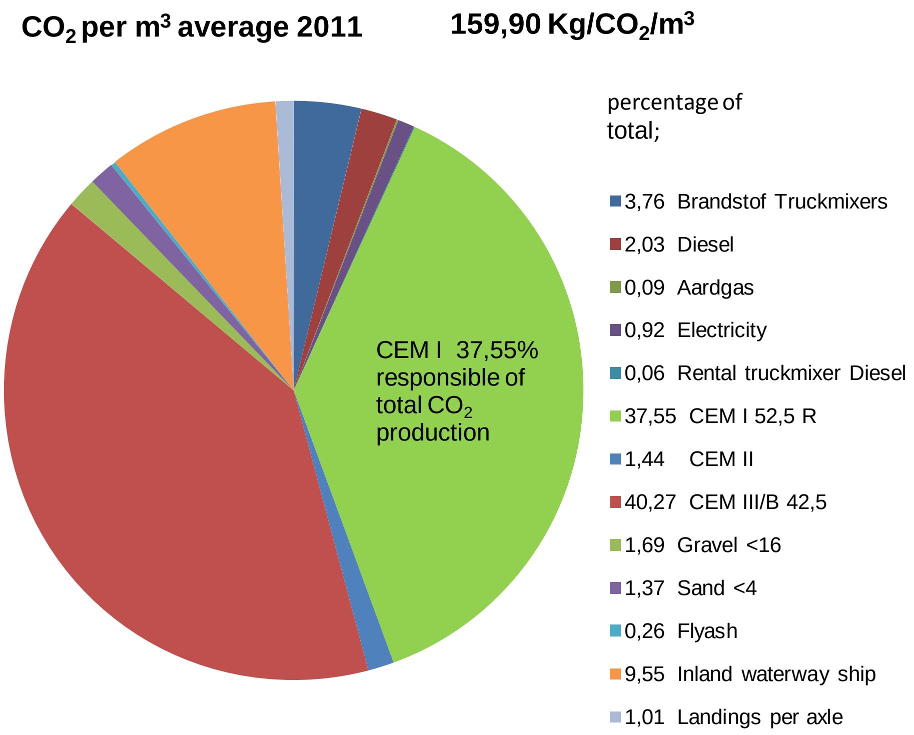
General characteristics	
Type:	Cargo ship
Propulsion:	2-stroke diesel engine and 1 propeller
Capacity:	up to 400,000 DWT
Notes:	Rear house, full hull, series of large hatches

Plans of a geared Handymax bulker

7.4.2 CO_2 reduction: reliable and sustainable solutions

It is important to be aware that climate change and emission of carbon dioxide does not stop at the Dutch border when the vowel production by the Dutch cement industry is terminated in the future: importing cement correctly will lead to higher CO_2 emissions. Foreign cement industries punches per ton of cement is more CO_2 than the Dutch cement industry. In addition, this creates an additional CO_2 emissions resulting from the transport of this cement to Netherlands. CO_2 and climate change therefore could not be regarded as a national problem; it is a global problem that all nations should contribute to reducing.

In the Netherlands annually per capita a 1000 litres concrete either over 360 kg cement. Approximately 40% of the concrete finds its way in housing. Another 40% is used for the construction of offices. The rest of the concrete produced in the Netherlands finds its way into, water and road construction. If there is a possibility to reduce the usage of cement, the way to creating a concrete with an higher green footprint is open. But what are the results of adapting the SCC with the nSS from Korea, this is the fastest to answer in the following: To determine the reduction in the CO_2 the mixtures are analyzed and compared. The reference CO_2 amount of a Kijlstra Betonmortel B.V. mixture is 159.9 $kg/CO_2/m^3$ given by the national knowledge centre and network organisation for corporate social responsibility CSR (2012), shown in Figure 6-7. The most valuable addition to replacing is the element CEM I 52,5 R. due that the emission of this element is the highest. The value of this CO_2 calculation can only be performed on this element due to the replacement in the systems emission value is given. One kg of CEM I is compared with 0.828 kg of nSS. So this replacement results in 30 % reduction in material usage recording the mixture given in Table 7-4. The amount of reduction is 18 $kg/CO_e/m^3$ shown in Table 7-4 and Figure 7-8. The addition of nSS in SCC does not contribute in an increase of CO_2. Due to the fact that nSS is a waste product, CO_2 values obtained in Korea do not have to take into account in this system, only transportation of the nSS needs to be explained further.



CO_2 per m^3 average 2011 **159,90 Kg/CO_2/m^3**

Figure 7-7; Amount of emission, reference mixture (Source; VOBN 2012; Kijlstra Betonmortel 2012)

Materials	Reference Kg/m^3	CO_2 Value Kg/m^3	Silica sludge (30% bwoc)	CO_2 Value Kg/m^3
CEM I 52.5R	95	60.04	66.5	42.03
CEM IIIB LH/HS	255	64.39	255	64.39
Fly ash	160	0.415	160	0.415
Sand (0-8 mm)	825	2.19	825	2.19
Gravel (4-16 mm)	845	2.70	845	2.70
nano-Silica Sludge	0	-	28.48	0.00026
Other		30.15		30.15
total		159,9	0.427	141.9

Table 7-4; Carbon dioxide value per cubic meter of SCC

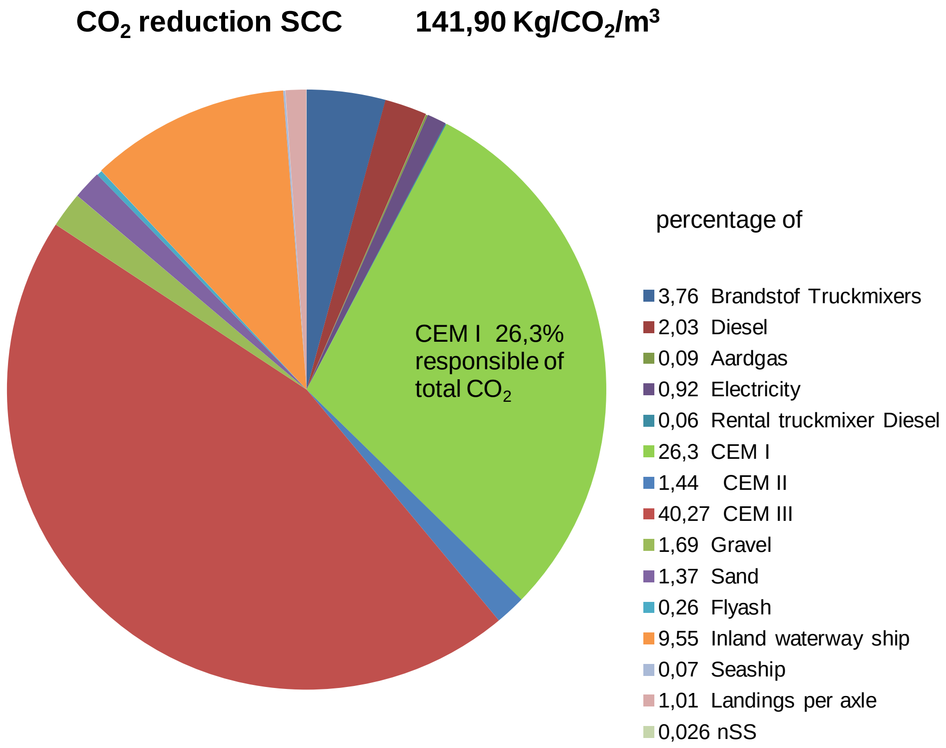


Figure 7-8; Emission amount 30% CEM I replacement (Source; VOBN 2012; Kijlstra Betonmortel 2012)

7.5 "Be the change" Conclusion

To get a good overview of the results in transportation, the total journey from South Korea to Vianen with the amount of bulk load (nSS) that a handysize freightener can transport in one journey has been investigated, the results are given in Table 7-5. On the other hand the same amount of bulk mass (CEMI) is transported from Maastricht (ENCI) to Vianen the trip from Maastricht-Vianen-Maastricht is calculated. Not taking into account is the transport in South Korea from the production plant to the harbor because reliable data is not available. A bulk truck for transportation of dry cement can be transported by road at a maximum of 37 m^3 which results in a max road load of 46 tons. The emissions for road transportation are given in Table 7-5. Inland shipping with a bulk tanker for dry bulk, in this case nSS, will result in a max capacity of 901 tons per shipping.

transportation	Max load (tons)	multisize	CO_2 g/ton-km	distance	Total trip distance (km)	Total emission (tons)
truck	46	365 x	41.2	340	124.100	137.371,75
Inland shipping	901	20 x	43.0	200	4.000	4121,60
Deepsea shipping	17.262	1 x	7.0	20.087	40.174	27.426 (metric tons) (MEA) 21.052,46 (metric tons) (CPV)

Table 7-5; Calculated emission per transportation possibility

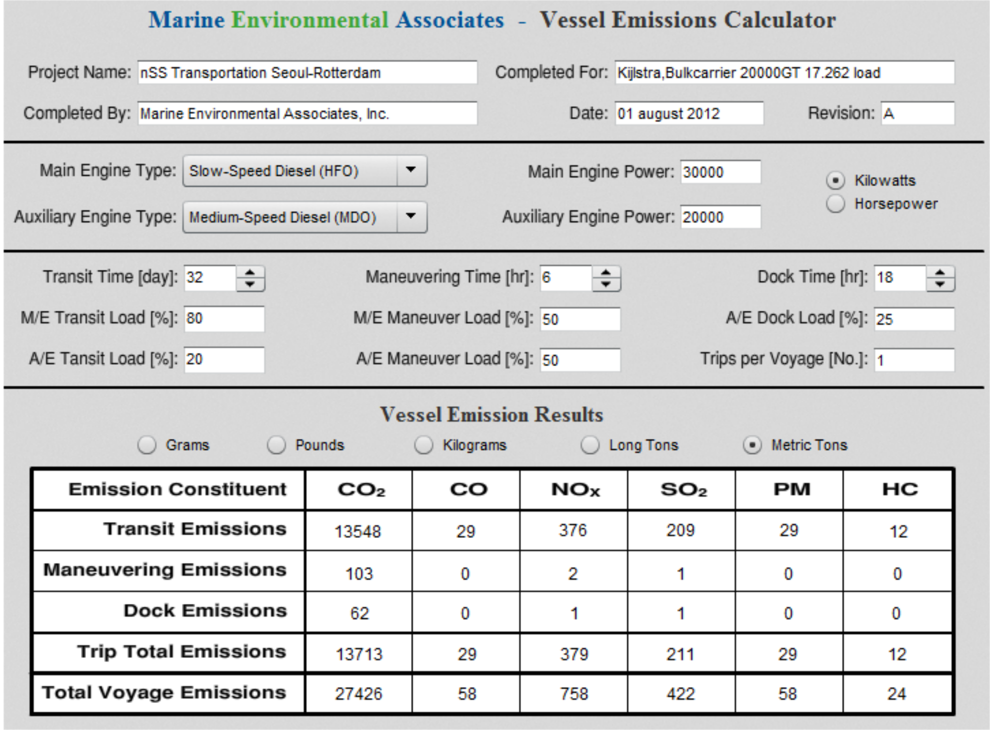
Actual emissions for a voyage will vary from this theoretical calculation due to the fuel consumption and consequent emissions varying with voyage characteristics such as actual speed and weather conditions. With the data extracted from www.searates.com, it is possible to determine the distance between ports; this diagram shows the calculation results of the port to port distance (Figure 7-9).

Calculation results

Port of loading: Seoul, KP
Port of discharge: Rotterdam, NL
Distance: 10846 nautical miles
Vessel speed: 14 knots
Time: 32 days 7 hours

Figure 7-9; Port to Port distance nSS (Source; www.searates.com)

A recalculation of the total trip distance and the chosen handysize frightener into an emission value has been done by the Marine Environmental Associates (Figure 7-10). In this emission calculation the transit, maneuver and dock emissions for the vessel are calculated.



Marine Environmental Associates - Vessel Emissions Calculator

Project Name: nSS Transportation Seoul-Rotterdam
Completed For: Kijlstra,Bulkcarrier 20000GT 17.262 load
Completed By: Marine Environmental Associates, Inc.
Date: 01 august 2012
Revision: A

Main Engine Type: Slow-Speed Diesel (HFO)
Main Engine Power: 30000
Auxiliary Engine Type: Medium-Speed Diesel (MDO)
Auxiliary Engine Power: 20000
● Kilowatts
○ Horsepower

Transit Time [day]: 32
Maneuvering Time [hr]: 6
Dock Time [hr]: 18
M/E Transit Load [%]: 80
M/E Maneuver Load [%]: 50
A/E Dock Load [%]: 25
A/E Tansit Load [%]: 20
A/E Maneuver Load [%]: 50
Trips per Voyage [No.]: 1

Vessel Emission Results

○ Grams ○ Pounds ○ Kilograms ○ Long Tons ● Metric Tons

Emission Constituent	CO_2	CO	NO_x	SO_2	PM	HC
Transit Emissions	13548	29	376	209	29	12
Maneuvering Emissions	103	0	2	1	0	0
Dock Emissions	62	0	1	1	0	0
Trip Total Emissions	13713	29	379	211	29	12
Total Voyage Emissions	27426	58	758	422	58	24

Figure 7-10; Marine environmental Associates vessel emission calculator (Source; http://www.marineenvironmental.com)

To determine the value of transport of the same amount of mass 17.262 tons of CEM I (3150 kg/m^3) has the same value as 20.923 of nSS, the weight of nSS (2451 kg/m^3) is lower than the mass of CEM I 52,5R , this analysis is done in 3.2.7, Table 7-5 shows the emission value of the bulk transportation, here it shows that one shipping of an handy carrier is the same as 365 times a road transportation ore 20 times a inland shipping transport. After reviewing all the documentation (Den Boer et al., 2008), it can be conclude that transportation on road results in a value of 41.2 g/ CO_2/ton-km vs. 43.0 g/ CO_2/ton-km vs 7.01 g/ CO_2/ton-km for the international transportation by deep sea shipping.

After reviewing all the values obtained an assumed CO_2 value for the cement replacement nSS could be made. This value only consists of the transportation from Korea to Vianen, other values of the production of the waste nSS are not available. Due to government regulations the usage of waste material does not influence the CO_2 footprint, the CO_2 emission is already calculated at the production process. A determination of CO_2 for nSS has result in a value of 7.01 g/ CO_2/ton.

7.6 Analyzing the CO_2 footprint

Through sincere consideration of all the results in the previous paragraphs it is possible to conclude that lowering the footprint of the reference mixture of Kijlstra betonmortel B.V.with 18 kg/CO_2/m^3 is possible. Furthermore, emission levels can be reduced with the use of the correct type/choice of freight carriers. Looking to models of road and sea transport that differ in CO_2 emissions per ton between modes and within a mode of transport are in many cases of the same order of magnitude, especially for short distance transport. The scale of the transport is often as important as the transport..

In short distance, the CO_2 emissions from large trucks and tractors with trailers are higher than inland shipping. In long distance the CO_2 emission of inland shipping is significantly less than road transport. Ocean shipping is only efficient when the scale is large. Ships that are typically used in coastal shipping are on average not more efficient than the other modalities, on the contrary deep nautical is typically more efficient. The shipping industry increases air pollutant emissions more than other modes, the detour rate it is of great importance to these emission factors. When these factor rates are low, then shipping scored favorably, while in situations where the distance is longer especially the smaller coastal conduct has less favorable scores. The difference between the road transportation and the Ocean shipping is 34.2 g/ CO_2/ton-km. This quantity is very positive for CO_2 emissions of transportation data for Kijlstra Betonmortel B.V. With this data the green footprint has become higher for the new SCC mixture, and the usage of nSS in the production is recommended.

8 Conclusion, discussion and recommendations

8.1 Summary

In the late 1980s self compacting concrete was developed with the aim to eliminate defects that occur by using Conventional Vibrating Concrete (CVC). In recent years Self Compacting Concrete (SCC) conquered the market with, in particular the prefabricated concrete industry. The benefits include faster construction progress, decreased manpower demand, and the possibilities to create difficult projects. However, the main objective of this research is to use waste nano-silica to replace part of the cement in self- compacting concrete production, which will essentially make the product more environmentally friendly. Concrete is the building material of the present and will be in the future, environmental regulations are taking over and become more important. Cement is the most energy consumption component of concrete, with high CO_2 emission during it manufacturing. Based on the experimental research, the final conclusions on these matters and some discussions will be summarized all together in the following part.

8.2 Conclusions

Self-Compacting Concrete production could not be possible without powders, in the design of SCC it is the most important element. In SCC it is important that finer material is used in comparison to normal concrete, the purpose is to fill all the voids between the aggregates and ensure the workability of the concrete. The obtained waste nano-silica sludge (nSS) was physically and chemically characterized. (Quercia et al. 2011). These features where important to the application and design of concrete mixtures. Several tests with CEM I 52.5 N and the development of a slurry prove that the waste nano silica has a high puzzolanic activity. It was found that the continuity of the provided samples is not stable, and there are doubts of the actual source. Based on the results of Quercia et al. (2011) with CEM I 52.5 N, the design and testing of SCM with nano-silica sludge (nSS) was performed. Several mixes were tested to investigate the effect of substitution of CEM I 52.5 R by nSS at different mass proportions (10 to 100% based on the weight of CEM I). The mix designs were based on commercial concrete recipes of Kijlstra (one mix series with fly-ash and another series with limestone powder as fillers) and adjusted for mortars test. Due to the mortar test stage it can be concluded that the usage of SP has an high influence on the workability of SCM. Parallel on these tests the slurry has been adapted to a slurry with an higher solid content up to 26.5%. This slurry is stable up to 3 weeks of static conditions. The mechanical performance of the nSS test was very encouraging. It was demonstrated in this thesis that nSS can be used in mortar samples up to 30% replacement ratio without causing large effects on the mechanical properties in hardened state. SCC with nSS addition can still be categorized as strength class C45/55 according to the European standard of EN 197-1. Replacing cement with nSS and the presence of the fly ash filler in the mortar will determine a decrease of the compressive strengths in early age but in all cases the achieved replacement result in a higher strength after 7 days. In the hydration study all the cement substitution materials showed significant negative effect in the limestone system at more than 5% replacement ratio and in the fly ash system at more than 30% replacement ration because of the water absorption value and the dilution effect to the cement. Due to the potentiometric titration technique of the British standard and following the technique of Spiesz & Brouwers (2012), it is possible to replace CEM I 52,5R for 100% by the nSS in concrete with steel or other metal embedded reinforcement on the critical chloride content. All the mixtures except the 100% replacement fly ash system are in the requirements of the EN 206-1 for a maximum chloride content of 0,20 for prestressing steel reinforcement concrete. The limestone system is divested after all the results All the tests results on full scale contradict assumptions that are made in the mortar stage. The k-value amount of is determined on 0.3, for micro-silica this k-value is 2.0. So probably the k-value of nSS is in the range of 0.6 to 0.8. Also this reflects to the water/cement ratio, at the calculations the amount of water was to low in the mortar stage.

After all it can be concluded that with the use of nSS the amount of CEM I 52,5R could be reduced and becomes a use full replacement product in SCC. Reduced cement contents, excellent properties in fresh and hardened state, and a large percentage of waste material turn these types of SCC into an ecological alternative with a higher green footprint compared to common SCC.

8.3 Final discussions

Based on the research presented in this thesis, there are several topics that will require more discussion in the future:

1. The laboratory nSS concrete aggregates have a much better quality comparing to the field nSS concrete aggregates which usually have an higher moisture content due to influence of weathering.
2. In this research, the 16-hr strength was used to compare the effect of the nSS influence of the mortar mechanical performance. It will be interesting to test 90 days strength, and especially to see what happens after the 28 days.
3. The source of the collected nSS from Pyung Ceramics Co., Ltd should be investigated, to see if the waste material is really a waste product of the photovotalic industry. Also the amount of nSS that could transported needs to be of a consistent amount.
4. The influence of nSS after being exposed to large amounts of water for a long time when the concrete is fully submerged

8.4 Recommendations

For this thesis the following recommendations can be given and subsequent investigations could lead to further research:

1. Due to a relatively short time frame, the durability of the SCC with nSS could not be investigated. Possible tests are freeze and thaw tests and an exposure to a highly aggressive environment for a long time.
2. nSS is very promising as an replacement material in SCC. The effects in the laboratory and in the pilot test are convincingly demonstrated. But, the transfer to the full scale production could be could be difficult, due to the amount of waste nano-siilca and the plant adaption with a high shear energy mixture and a basin that keeps the produced slurry in constant motion.
3. Also the calculated amount of chloride is only tested in the SCM stage, not in the SCC stage, so a reliable influence on the reinforcement is not available.
4. The influence on the healthy conditions of the environment when nSS is used in construction materials has also need to be investigated, what is the influence of the air quality when nSS in concrete is used.

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APPENDIX A

Slump flow
Introduction

Filling ability, passing ability and stability of mixtures can be considered the distinguishing properties of fresh SCC (Okamura and Ouchi, 1999). These requirements are not common to conventional concrete and, therefore, are handled through special tests. These tests should be done carefully to ensure that the ability of SCC to be placed remains acceptable. The flow properties of SCC have been further characterized (Sonebi and Bartos, 2002 and Geiker et al., 2002). Based on their experience with SCC, researchers have suggested limits on test values. The methods presented here, are descriptions rather than fully detailed procedures following the EFNARC guidelines.

When considering these tests, there are a number of points which should be taken into account:

- One being that the principal difficulty in devising such tests is that they have to assess three distinct, though related, properties of fresh SCC – its filling ability (flow ability), its passing ability (free from blocking at reinforcement), and its resistance to segregation (stability). Thus for no single test can measure all three properties.
- A lack of clear relation between test results and performance on site.
- A lack of precise data, therefore no clear guidance on compliance limits.
- Duplicate tests are advised.
- Test methods and values are stated for a maximum aggregate size of up to 20 mm; different test
  values and/or different equipment dimensions may be appropriate for other aggregate sizes;
- Different test values may be appropriate for concrete being placed in vertical and horizontal elements and similarly, different test values may be appropriate for different reinforcement densities;
- When performing the tests, concrete should be sampled in accordance with EN 12350-1.
- Finally, it is wise to re-mix the concrete with a scoop first unless the procedure indicates otherwise.

The slump flow test aims to investigate the filling ability of SCC. It assess the horizontal free flow of SCC in the absence of obstructions.

Equipment

The apparatus is shown in figure A-1

- The mould resembles a truncated cone with the internal dimensions of 200 mm diameter at the base, 100 mm diameter at the top and a height of 300 mm conforming to EN 12350-2
- The base plate is a stiff non absorbing material, at least 700mm square, marked with a circle indicating the central location for the slump cone, and a further concentric circle of 500mm diameter. Other equipment includes; a trowel, scoop ruler and timer

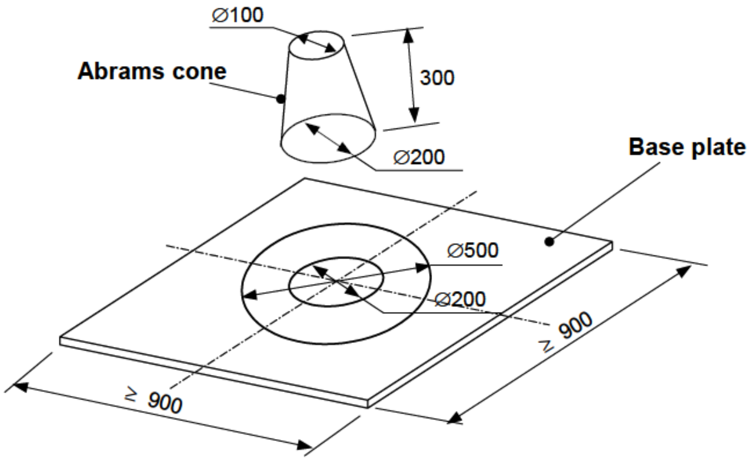

Figure A-1; Dimensions of the Slump flow test (Source; Gridic,2010)

Procedure

About 6 litres of normally sampled concrete is needed to perform the test, sampled normally. Moisten the base plate and inside of slump cone, Place base plate on level stable ground and the slump cone centrally on the base plate and hold down firmly. Fill the cone with the scoop. Do not tamp, off the concrete level at the top of the cone with the trowel. Remove any surplus concrete from around the base of the cone. Raise the cone vertically and allow the concrete to flow out freely. Measure the final diameter of the concrete in two perpendicular directions. Calculate the average of the two measured diameters. (This is the slump flow in mm). Note any border of mortar or cement paste without coarse aggregate at the edge of the pool of concrete.

The higher the slump flow (SF) value, the greater its ability to fill formwork under its own weight. A value of at least 650mm is required for SCC. There is no general acceptance level of tolerance pertaining to a specified value, though ± 50mm, as with the related flow table test, might be appropriate.

V-funnel

Introduction

The V-funnel flow time is the period in which a defined volume of SCC needs to pass through a narrow opening and indicates the filling ability of SCC, provided that blocking and/or segregation do not take place. The flow time of the V-funnel test is to some degree related to the plastic viscosity. The described V-funnel test is used to determine the filling ability (flow ability) of the concrete with a maximum aggregate size of 20 mm. The funnel is filled with about 12 litres of concrete and its flow time through the apparatus is measured. Following this test, the funnel can be re-filled with concrete and left for 5 minutes to settle. If the concrete shows segregation then the flow time will increase significantly.

Equipment

The apparatus is shown in figure A-2

- V-funnel
- bucket (±12 litre)
- trowel
- scoop
- stopwatch

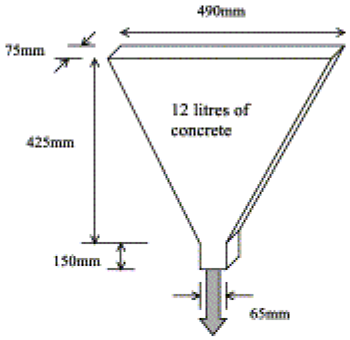

Figure A-2; Dimensions of the V-funnel (Source; Safawi,2004)

Procedure

About 12 litres of normally sampled concrete is needed to perform the test. Set the V-funnel on firm ground. Moisten the inside surfaces of the funnel. Keep the trap door open to allow any surplus water to drain. Close the trap door and place a bucket underneath. Fill the apparatus completely with concrete without compacting or tamping, simply swipe off the concrete with the top of the trowel. Open within 10 sec after filling the trap door and allow the concrete to flow out under gravity. Start the stopwatch when the trap door is opened, and record the time for the discharge to complete (the flow time). The flow is complete when light is visible from above through the funnel. The whole test must be performed within 5 minutes.

Procedure flow time at T 5 minutes

Do NOT clean or moisten the inside surfaces of the funnel again. Close the trap door and refill the V-funnel immediately after measuring the flow time. Place a bucket underneath. Fill the apparatus completely with concrete without compacting or tapping, simply swipe off the concrete with the top of the trowel. Open the trap door 5 minutes after the funnel is fulled a second time and allow the concrete to flow out under gravity. Simultaneously start the stopwatch when the trap door is opened, and record the time for the discharge to complete (the flow time at T 5 minutes). The flow is complete when light is visible from above through the funnel.

J-ring method

Introduction

The Japanese ring test, or shortened J-ring test appeared for the first time in 1999 (Petersson; Sonebi and Bartos)in the final report of the Brite EuRam on the workability of SCC. This test evaluates the passing ability of SCC. The J-ring test is performed along with or as an extension of the slump flow test. A steel ring standing on rods is placed around the Abraham cone in such a way the spreading concrete must pass the obstacles. The J-ring test aims to investigate both the filling ability and the passing ability of SCC. The equipment consists of a rectangular (30mm x 25mm) open steel ring with holes drilled into it vertically in order to accept threaded sections of reinforcement bars. These sections of bar can be of different diameters and spaced at different intervals; in accordance with normal reinforcement considerations, 3x the maximum aggregate size will be appropriate. The diameter of the ring of vertical bars is 300mm, and the height is 100 mm. The J-ring flow spread indicates the restricted deformability of SCC due to the blocking effect of reinforcement bars. The blocking step measures the effect of blocking. After the test, the difference in height between the concrete inside and that just outside the J-ring is measured. This is an indication of passing ability, or the degree to which the passage of concrete through the bars is restricted.

Equipment

The apparatus is shown in figure A-3

- It constists of a mould, WITHOUT foot pieces, in the shape of a truncated cone with the internal dimensions 200 mm diameter at the base, 100 mm diameter at the top and a height of 300 mm.
- A base plate of stiff non absorbing material, at least 700mm square, marked with a circle indicating the central location for the slump cone, and a further concentric circle of 500mm diameter Other equipement includes: a trowel, scoop,ruler and the J-ring. The J-ring is a rectangular section (30mm x 25mm) open steel ring, drilled vertically with holes. Reinforcement bars are then threaded into the J ring (length 100mm, diameter 18mm)

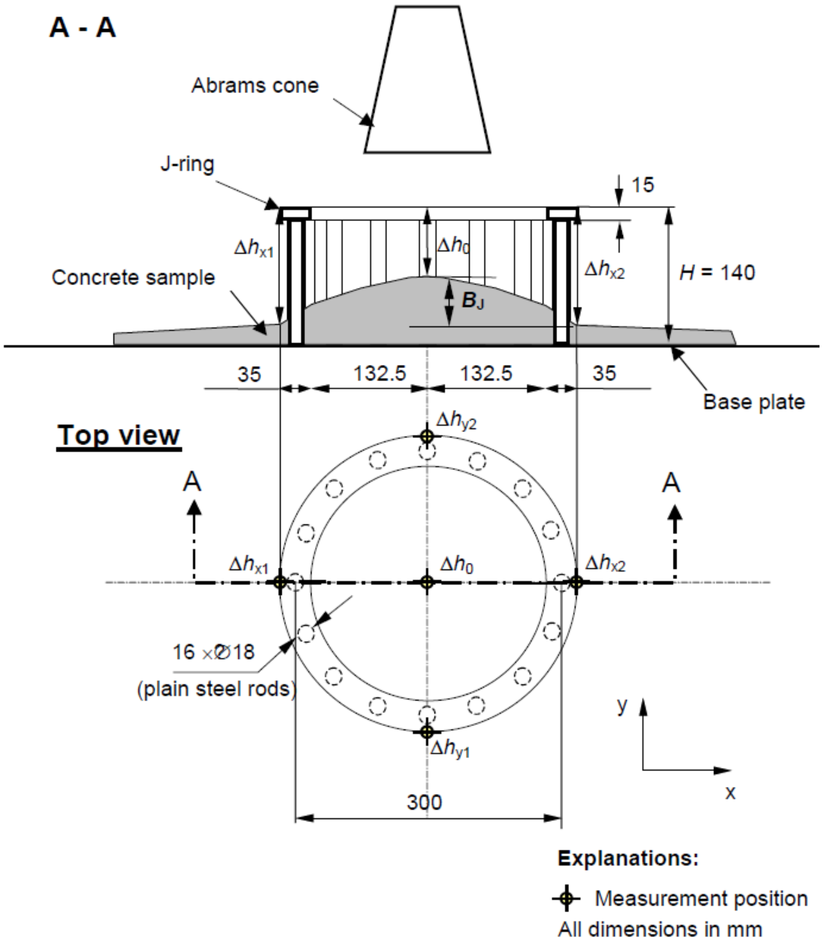

Figure A-3; Dimensions of the J-ring and positions for measurement of height differences (Source; de Schutter,2005)

Procedure

About 6 litres of concrete of normally sampled concrete is needed to perform the test, sampled normally. Moisten the base plate and inside of slump cone. Place the base-plate on level stable ground. Place the J-ring centrally on the base-plate with the slump-cone centrally inside the J-ring and hold down firmly. Fill the cone with the scoop. Do not tamp, simply strike off the concrete level with the top of the cone with the trowel. Remove any surplus concrete from around the base of the cone. Raise the cone vertically and allow the concrete to flow out freely. Measure the final diameter of the concrete in two perpendicular directions. Calculate the average of the two measured diameters. (in mm). Measure the difference in height between the concrete just inside the bars and that just outside the bars. Calculate the average of the difference in height at four locations (in mm). Note any border of mortar or cement paste without coarse aggregate at the edge of the pool of concrete.

APPENDIX B

The smart use of waste silica as a sustainable cement replacement

Self Compacting Concrete adaption for smart and special building constructions

Paper

The smart use of waste silica as a sustainable cement replacement

Self Compacting Concrete adaption for smart and special building constructions

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Department of the Built Environment, Eindhoven University of Technology, December 2011

Abstract
Waste silica, is a waste cake or sludge recovered from the polishing of photovoltaic panels industries. It is composes of agglomerates of nano-particles like SiO2(silica) and debris. This sludge is potentially a cement replacement. It's deflocculates in acidic and alkaline aqueous solutions into nano-particles. The replacement of cement with these particles can cause considerable air-pollution reduction when it is combined in the cement production process of self compacting concrete. A dried and pulverized sludge was used to replace 5-20 wt.% Portland cement in cement mortar. The compressive strength of the modified mortar was higher than that of plain cement mortar after curing for 3 days and more. In particular, the strength of mortar wit 10wt.% substitution improved by 25-35% after curing for 7-90 days [1]. This was done by using sludge, a recovered material out of wastewater of semiconductor-industries. It was proven that the semiconductor sludge can thus be used as a useful resource to replace portion of cement in cement mortar, thereby avoiding their potential environment hazard. The scope will be that the sludge of the photovoltaic polishing process is a usable cement-replacement material. It can replace about 10-30 wt.% Portland cement in mortar The aim will be a replacement of that percentage.

Keywords: Sludge, waste silica, cement mortar, Self-compacting concrete, Chemical mechanical polishing, CO_2

1.0 Introduction

Concrete is the most used artificial construction material in the world. Unfortunately, the production process of Portland cement, an essential constituent of concrete, leads to a significant release of CO_2 a greenhouse gas. The production of one ton of Portland cement clinker generates one ton of CO_2 emission according to the Cement&BetonCentrum (2010). Environmental issues will play a leading role in the sustainable development of the cement and concrete industry in this century. The emission of CO_2 and the scarcity of raw materials make it desirable to find alternatives to reduce the amount of Portland cement needed in concrete production. About 3.3 billion ton was produced in 2010 [2](fig 1-3). Concrete is a solid material made of cement, sand, water, aggregates and often with admixtures. When the concrete is in fresh state, it has a certain workability and takes the form of the mould into which it is put. On het contrary, when the concrete is set and hardened, it is as strong as natural stone and resists time, water, frost, mechanical constraints and fire. Typically, concrete is the essential material used in all types of construction [residential (housing), non-residential (offices) and civil engineering (roads, bridges, etc.)]. The overall grading of the mix, containing particles from 300 nm to 32 mm determines the mix properties of the concrete [3-4].

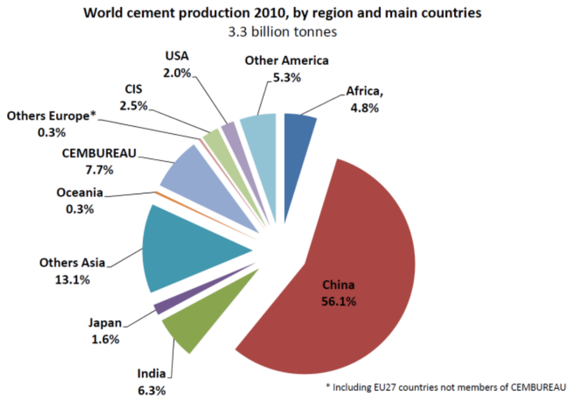
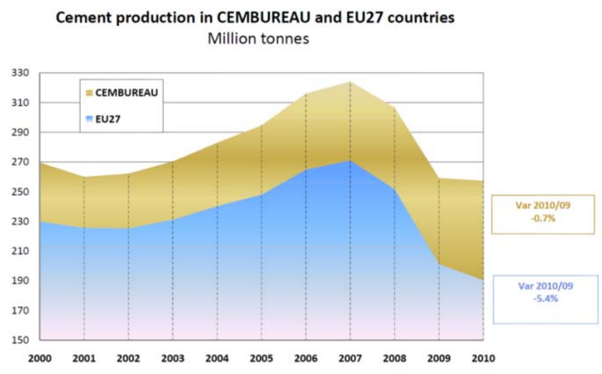


Figure 1 world cement production 2010



Note: Cement production includes cement produced with imported clinker

Figure 2 cement production

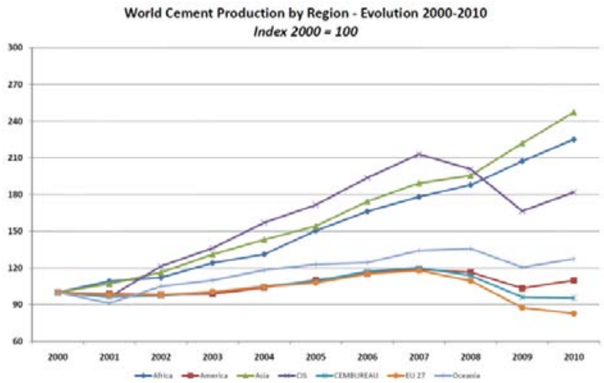


Figure 3 world cement production

In this Graduation project a waste nanosilica produced from the polishing process of photovoltaic panels will be applied and tested in the mix design of SCC [5-7].

The aim of this graduation-research is to create a more sustainable building material witch is desired to reduce the amount of cement in concrete by replacing the cement by waste silica. The balance between economical and ecological costs is optimized. The effects of this replacement material and its interaction with the cement admixtures (super plasticizer) are unknown. Thus the effects of a partial replacement of cement by waste silica on the early age(hydratation kinetics an workability) and long term properties (permeability and chloride migrations) are not fully understood.

1.1 Chemical Mechanical Polishing

The Chemical Mechanical Polishing (CMP) is a conventionally adopted process in a integrated-circuit (IC) factories during the process called “planarization” on silicon wafers. Because planarization consumes considerable amounts of water, large quantities of wastewater and sludge that are potentially dangerous are released into the environment. Several studies have attempted to develop treatment processes for this sludge and wastewater. Before 1990, CMP was looked as too "dirty" to be included in high-precision fabrication processes, the abrasives used for poleisten are not without impurities. [8]. Adoption of this process has made CMP processing much more widespread. In addition to aluminum and copper, CMP processes have been developed for polishing tungsten, silicon dioxide, and (recently) carbon nanotubes [8]. In an IC factory the etching process which uses hydrofluoric acid, usually follows CMP and is used to remove silicon oxide and other unwanted debrees from the wafer. The creation of solar panels typically involves cutting crystalline silicon into tiny disks less than a centimeter thick. These thin, wafer-like disks are then carefully polished and treated to repair and gloss any damage from the slicing process. After polishing, dopants (materials added to alter an electrical charge in a semiconductor or photovoltaic solar cell) and metal conductors are spread across each disk. The conductors are aligned in a thin, grid-like matrix on the top of the solar panel, and are spread in a flat, thin sheet on the side facing the earth. The waste generated by CMP is then neutralized with sodium hydroxide (NaOH); water-soluble calcium chloride ($CaCL_2$) is then added to precipitate fluorine ion into insoluble calcium fluorite (CaF_2). Thus, CMP waste contains numerous chemicals. Such waste is called wet waste in the photovoltaic polishing process. Sometimes simply CMP waste, the solid waste recovered after water removal is called sludge. fig (4)

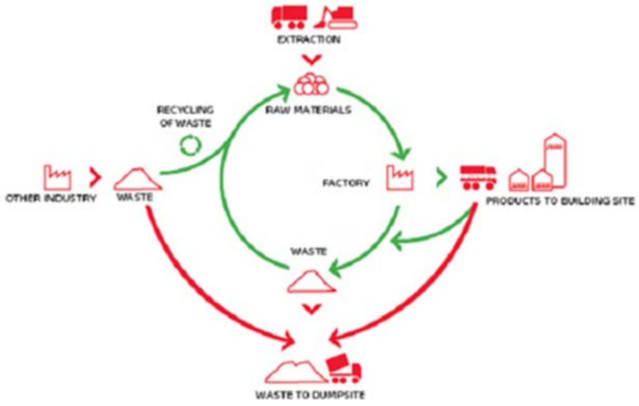


Figure 4 production process green belt

Photovoltaic sludge contains both organic and inorganic material. The organic materials includes oxidizing agents, additives and dispersing agents, mainly of proprietary composistions made of C, H, O, N, S and others. The inorganic materials constists of nanoparticles, principally SiO_2, CaF_2 and others which are typically 20-300 nm in size, depending on the vendors[1]. When dumping sites are close to reservoirs or underground water sources, these nano-particles (debris of the polishing process) can pollute drinking water and cause lung and other diseases[9]. This sludge is utilized as raw material in rotary kilns for cement production. The nano-particles may be released into air due to the strong convection forced of burning hot gases. They will remain in the atmosphere for a very long time, counting by years, due to their fineness. Since human health is vulnerable to nanoparticles in sludge. The disposal of this potentially replacement material to reduce the amount of Portland cement in SCC is the purpose of this study.

2.0 Materials

Considering the complexity and structure of the construction sector, there is no doubt that the development of Self Compacting Concrete – SCC – has been extraordinarily rapid. This is true both in terms of the generation of new knowledge as well as regarding the penetration of the technology on the market. The development of SCC has changed fresh concrete from being a granular material needing vibration for compaction into a fluid.[10] The method for achieving self-compactability involves not only high deformability of paste or mortar, but also resistance to segregation between coarse aggregate and mortar when the concrete flows through the confined zone of reinforcing bars. Self compactability can be largely affected by the characteristics of materials and the mix proportion.

A rational mix-design method for self-compacting concrete using a variety of materials is necessary. fig (5) Okamura and Ozawa (1995) have proposed a simple mix proportioning system assuming general supply from ready-mixed concrete plants. The coarse and fine aggregate contents are fixed so that self-compactability can be achieved easily by adjusting the water-powder ratio and super plasticizer dosage only[11]

(1) The coarse aggregate content in concrete is fixed at 50% of the solid volume.
(2) The fine aggregate content is fixed at 40% of the mortar volume.
(3) The water-powder ratio in volume is assumed as 0.9 to 1.0 depending on the properties of the powder.
(4) The super plasticizer dosage and the final water powder ratio are determined so as to ensure self-compactability.

2.1 characteristics

The characteristics of powder and super plasticizer largely affect the mortar property and so the proper water-powder ratio and super plasticizer dosage with the adaption and supplementary of the waste silica cannot be determined without trial mixings. These will be determined by several tests. The adaption of the SCC mixture with the waste silica and without the waste silica. The U-flow,slump flow and funnel tests wil be tested on the SCC also several other analyses. [1][11] The relationships between the properties of the mortar in self-compacting concrete and the mix proportion need to be investigated in detail. The current status of selfcompacting concrete is “special concrete”rater than “standard concrete” Applications with SCC are fore instance; Bridge’s (Shin-kiba Ohashi bridge, Japan), buildings, tunnels, dams and precast concrete products

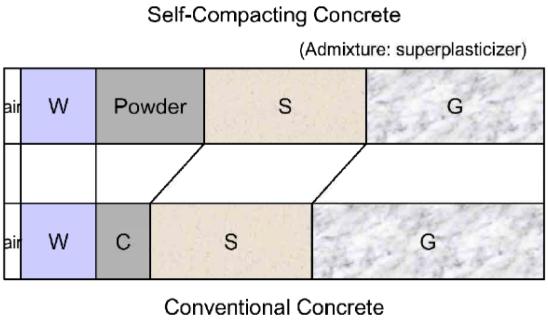


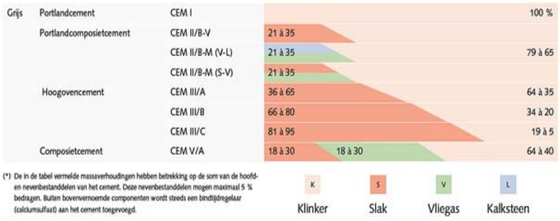
Figure 5 comparison of mix proportioning between SCC and conventional concrete

Regular concrete, which is designed following European standards is the lay term describing concrete that is produced by following the mixing instructions that are commonly published on packets of cement. Typically using sand or other common material as the aggregate, and often mixed in improvised containers. This concrete can be produced to yield a varying strength from about 10 MPa (1450 psi) to about 40 MPa (5800 psi), depending on the purpose, ranging from blinding to structural concrete respectively. Many types of premixed concrete are available which include powdered cement mixed with an aggregate, it needing only sand and water.

2.2 Construction on large scale with SCC

As was previously despised SCC is used in several concrete production processes, several constructions at small and large scale. The shortening of production time is one of the aspects that its usage is increasing rapidly. The Akashi-Kaikyō Bridge (明石海峡大橋 Akashi Kaikyō Ō-hashi), also known as the Pearl Bridge, has the longest central span of any suspension bridge, at 1,991 metres (6,532 ft). It is located in Japan and was completed in 1998. The bridge links the city of Kobe on the mainland of Honshu to Iwaya on Awaji Island by crossing the busy Akashi Strait. It carries part of the Honshu-Shikoku Highway.

The bridge is one of the key links of the Honshū-Shikoku Bridge Project, which created three routes across the Inland Sea. This bridge is a typical example of constructing with SCC. The two anchorages of the bridge are formed and filled with Self-compacting concrete.[12]



Grijs	Portlandcement	CEM I			100 %
	Portlandcomposietcement	CEM II/B-V	21 à 35		
		CEM II/B-M (V-L)	21 à 35		79 à 65
		CEM II/B-M (S-V)	21 à 35		
	Hoogovencement	CEM III/A	36 à 65		64 à 35
		CEM III/B	66 à 80		34 à 20
		CEM III/C	81 à 95		19 à 5
	Composietcement	CEM V/A	18 à 30	18 à 30	64 à 40

(*) De in de tabel vermelde massaverhoudingen hebben betrekking op de som van de hoofd- en nevenbestanddelen van het cement. Deze nevenbestanddelen mogen maximaal 5 % bedragen. Buiten bovenvernoemde componenten wordt steeds een bindtijdregelaar (calciumsulfaat) aan het cement toegevoegd.

K Klinker
S Slak
V Vliegas
L Kalksteen

Figure 6 Portlandcement (OPC)

3.0 Necessity for the future adaption, resume

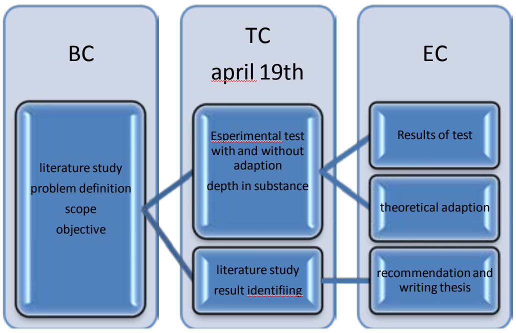
During the 1980s a number of countries including Japan, Sweden and France developed concretes that are *self-compacting*, known as self-consolidating concrete in the United States. This self-consolidating concrete (*SCC*s) is characterized by:

- extreme fluidity as measured by *flow*, typically between 650–750 mm on a flow table, rather than slump(height)
- no need for vibrators to compact the concrete
- placement being easier.
- no bleed water, or aggregate segregation
- Increased Liquid Head Pressure, Can be detrimental to Safety and workmanship

SCC can save up to 50% in labor costs due to 80% faster pouring and reduced wear and tear on formwork. As of 2005, self-consolidating concretes account for 10-15% of concrete sales in European countries according to the American Paving Specialists and CEMBUREAU. In the US precast concrete industry, SCC represents over 75% of concrete production. 38 departments of transportation in the US accept the use of SCC for road and bridge projects. This emerging technology is made possible by the use of polycarboxylates plasticizer instead of older naphthalene based polymers, and viscosity modifiers to address aggregate segregation. So an adaption of the Self-compacting concrete with the waste silica needs to result in a saving of the labor costs, and pouring also in the amount of Carbon dioxide emission by the production of (OPC) that will be used in the SCC mixtures.

4.0 Research question waste silicaproposal

What are the effects in SCC if cement is replaced by a waste silica in building construction elements?



Conclusion

If the silicon Photovoltaic industry continues to rapidly expand, the environmental impact of its manufacturing processes and products will receive increasing attention. It is important for a renewable energy technology to address its environmental impact during manufacturing because one of the primary benefits of renewable energy generation is its low environmental impact. There need to be found an solution for the waste of this production process.

In summary, sludge a nano-silica (nS) from wet and dry waste produced by several industries was analyzed. Semiconductor sludge was used to replace Portland cement in cement mortars. It is proven that 10wt% sludge the compressive strength of the modified cement mortar, becomes 125-135% that of mortar made of ordinary Portland cement after curing for 7-90 days. So the replacement of Portland cement is proven by this waste silica of this industry. Probably it is possible to use the waste of the photovoltaic industries to replace the portlandcement in cement mortars. The use of this nS makes concrete financially more attractive and reduces the CO_2 footprint of the produced concrete structures. Also the environmental impact of the photovoltaic industry is reduced by the usage of this waste nS. In total 15% of the European market uses SCC. Therefore adaption of SCC with the usage of the nS will result in a huge reduction of the CO_2, the aim is a reduction of 20-30% portlandcement in the SCC mixture by use the nS. If it is possible, there can be given a second dimension to the usage off SCC as clean concrete, not only in structural surfaces but also in the production of SCC.

Recommendation

How nano-silica can change the concrete world, though many facets are known, the exact science of the replacement of portlandcement isn't know. Therefore we need to test the SCC mixture with the nS. The adapted mixture needs of the same capacity as the original mixture. So tests with the slump flow, u-box test and V-funnel tests are needed, in several stages of adaption (%).

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