Portlandklinker van bijproducten en gerecycleerde materialen uit de bouw- en constructiesector

Portland Clinker from By-Products and Recycled Materials out of the Building and Construction Sector

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“*Moeilijk gaat ook*!” – Delphine Menschaert

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Abbreviations

AACC: Autoclaved Aerated Cellular Concrete
ADR: Advanced Dry Recovery
Ag: Aggregates
Ant: Antoing
ARM/ADR: ADR fines fraction
ARM/CCC: Cellular Concrete Clean
ARM/CCP: Cellular Concrete Polluted
ARM/CS: Corrugated fibrecement Sheets
ARM/CTP: fines fraction CTP
ARM/DL: Dolomitic Limestone
ARM/DLS: Dolomitic Limestone Sludge
ARM/HD: autoclaved High Density fibrecement boards
ARM/KHD: KHD fines fraction
ARM/MD: autoclaved Medium Density fibrecement boards
ARM/Pp: Porphyry
ARM/PpF: Porphyry Fines
ARM/RS: fibrecement Roofing Slates
ARM: Alternative Raw Material
Bxl: Brussels
CCM: Cold Clinker Meal
Cl: Clinker
CRM: Classic Raw Material
CTP: Centre Terre et Pierre
CSH: Calcium silicate hydrates
De: Dendermonde
Decarb E: Decarbonation Energy
DL: Dolomitic Limestone
DLSl: Dolimitic Limestone Sludge
DoS: Degree of Sulfatisation
FA: Fly Ash (Al_2O_3-source)
FC: FibreCement
Gk: Genk
HCM: Hot Clinker Meal
IB: Inter Beton
IC: Iron Carrier (Fe_2O_3-source)
KHD: KHD Humboldt Wedag AG
LiqSimple: Liquid Simple
Lo: Loam (SiO_2-source)
LOI: Loss on ignition
LSF: Lime Saturation Factor
Lxh: Lixhe
Ma: Marl (CaO-source)
Maa: Maastricht
PL: Poor Limestone (CaO-source)
Pp: Porphyry
PpF: Porphyry Fines
PSD: Particle Size Distribution
Ref: Reference
RL: Rich Limestone (CaO-source)
SC: Sabulous Clay (SiO_2-source)
SCP: Sludge Concrete Plant
SR: Saturation Rate
Tu: Tuffeau (specific type of limestone)
VLB: Villers-Le-Bouillet
VSI: Vertical Shaft Impactor
XRD: X-Ray Diffraction
XRF: X-Ray Fluorescence
Zb: Zeebrugge

Cement chemistry

A: Aluminium oxide (Al_2O_3)

C: Calcium oxide (CaO)

F: Iron oxide (Fe_2O_3)

S: Silicium oxide (SiO_2)

C_3S: Tricalcium silicate (Alite)

C_2S: Dicalcium silicate (Belite)

C_3A: Tricalcium aluminate (Celite)

C_4AF: Tetracalcium aluminoferrite (Ferrite)

Used parameters/factors

ε: Enrichment factor

β: Bypass factor

C%: average of the cumulative percentage under size passing through a screen

MM: Molecular Mass

C_{125}: Limestone ($CaCO_3$) particles with a size superior to 125 µm

Q_{45}: Quartz (SiO_2) particles with a size greater than 45 µm

W_{Tot}: The total amount of water added

WA: Water Absorption of the sand

Cem: The total amount of cement

WD_{cem}: Water demand of the used Cement

Sa_{4mm}: The used sand smaller than 4mm

NCV: Net Calorific Value

Sqrt: squareroot

n: number of samples

Statistical formulae

Sample mean = $\bar{x} = \Sigma x_i / n$

Sample standard deviation (Stdev) = sqrt $[\ \Sigma\ (x_i - x)^2 / (n - 1)\ ]$

Standard Error of the Mean (SEM) = Stdev/sqrt(n)

Other Formulae

Bogue calculation Alite (C_3A) = $(2.650 \cdot Al_2O_3 - 1.692 \cdot Fe_2O_3)$

Bogue calculation Belite (C_2S) = $8.6024 \cdot SiO_2 + 1.0785 \cdot Fe_2O_3 + 5.0683 \cdot Al_2O_3 - 3.0710 \cdot CaO$

Bogue calculation Celite (C_3A) = $2.650 \cdot Al_2O_3 - 1.692 \cdot Fe_2O_3$

Bogue calculation Ferrite (C_4AF) = $3.0432 \cdot Fe_2O_3$

Chemico granulometric expr. (CaO_{free}) = $0.33 \cdot LSF + 0.018 \cdot SR + 0.56 \cdot C_{125} + 0.93 \cdot Q_{45} - 0.349$

(C_{125}= $CaCO_3$ particles with size superior to 125 µm, Q_{45}= SiO_2 particles with size superior to 45 µm)

Degree of Sulphatisation (DoS) factor = $100 \cdot (0.774 \cdot SO_3 / (Na_2O + 0.658 \cdot K_2O))$

Lime Saturation Factor (LSF) = $100 \cdot (CaO - CaO_{free}) / (2.8 \cdot SiO_2 + 1.18 \cdot Al_2O_3 + 0.65 \cdot Fe_2O_3)$

Liquid formation equation (%Liq) = $3.00 \cdot Al_2O_3 + 2.25 \cdot Fe_2O_3 + MgO + K_2O + Na_2O$

Silica Ratio (SR) = $SiO_2/(Al_2O_3 + Fe_2O_3)$

Simplified liquid formation equation (LiqSimple) = $(3 \cdot Al_2O_3 + 2.25 \cdot Fe_2O_3)$

Sodium equivalent (Na_2O_{eq}) = $Na_2O + K_2O \cdot 0.658$

Water Demand sand (WD_{sand}) = $(\ W_{Tot} - (\%\ WA \cdot Sa_{4mm}) - Cem \cdot WD_{cem}) / Sa_{4mm}$

Abstract

Many companies are revising their business operations whilst gearing their pursuit of profitable growth to the assurance of environmental protection and quality of life for present and future generations. Even when this adaption is not desired, they are forced to it by economic necessity, public opinion or by governmental pressure to decrease their ecological impact. Based on this new perspective, some companies are thus beginning to make significant changes in their policies, commitments and business strategies.

The cement manufacturing process consumes large quantities of non-renewable raw materials. This process is also an important source of CO_2 emissions. Many initiatives are already taken to make the cement production processes more sustainable. The cement sustainability initiative is one example that demonstrates the global effort of the cement industry in pursuing sustainable development. This PhD study is elaborated in line with the cement sustainability initiative. It explores how the cement industry could integrate by-products or recovered materials out of the building and construction sector in their Portland clinker process, which is a part of the cement manufacturing process. Indeed, different producers and consumers within this sector could exchange materials or energy to pursue mutual ecological advantage.

To determine the fitness of these by-products or recycled materials as alternative raw material, specific material properties important for Portland clinker production were investigated in a practical and objective way to not lose track with the real manufacturing process itself. To determine this specific fitness, a good evaluation of the physical, chemical and mineralogical composition and variation of these materials is necessary. Furthermore, theoretical simulations of alternative clinker compositions or artificial made Portland clinkers on lab scale have to be used to evaluate the impact of these materials on the Portland clinker process.

It is quite difficult to realistically simulate clinker production on lab scale because of the specific construction of a clinker kiln. The typical properties of a kiln have to be taken into account while imitating the production process to generate an artificial clinker. Therefore, a specific set-up was used to make an objective evaluation of the fitness of an alternative raw material possible. Variations specific for the simulation itself were identified, avoided if possible and included in the evaluation of the final results if necessary.

Three factories located in the Benelux were chosen to act as a reference for the Portland clinker process. By their different technical specifications as well as used Classic Raw Materials (CRM), they will deal in another way with these by-products or recycled materials resulting in specific mathematical simulations and the artificial produced clinkers which will differ from each other.

Five specific material sources were investigated as possible alternative raw materials for Portland clinker production. Their recycling in the Portland clinker process could lower use of natural resources and counter landfill. They were specifically chosen to represent a wide variety of materials having their origin as by-product out of an existing production process or as waste material from demolished building or concrete constructions.

First, the impact of by-products out of porphyry and dolomitic limestone aggregates production on Portland clinker production was investigated. Porphyry and dolomitic limestone aggregates represent a group of raw materials which are used at a daily base in many construction applications. The by-products are generated in the processing steps to improve the quality of the produced aggregates. In most cases, this improved aggregate quality will create an ecological benefit in the related applications such as concrete and asphalt. By avoiding waste disposal by landfill and a redistribution of the energy required for the aggregates production process, the valorisation of these by-products is also ecologically and economically beneficial for the aggregates manufacturing business itself. A recycling of both aggregate types at the end of a life cycle of a derived concrete or building material could also be a valid source for these types of materials.

Neither porphyry nor dolomitic limestone is up until now used at regular base in Portland clinker production. This is partly due to the presence of high levels of MgO. MgO is avoided in Portland clinker production due to the specific limitations within national and international cement standards related to the risk of unsoundness of concrete. This investigation, nevertheless demonstrated that MgO, when cautiously introduced in line with well-defined limitations, should rather be taken into account for its positive mineralogical influence on clinker than avoided because of its possible periclase formation and related unsoundness properties. Valorisation of by-products of porphyry and dolomitic limestone materials in Portland clinker production could therefore be maintained as valuable and realistic solution.

Secondly, materials out of niche markets for cement consumption in the form of non-asbestos fibrecement and cellular concrete were investigated. These materials show a limited chemical variation initiated by their specific production processes. Fibrecement as well as cellular concrete materials could have their origin as by-product out of their own production process or as demolition waste at the end of a life cycle. A small chemical variation of the raw material mix is a very important process parameter for Portland clinker production which substantiates the choice of these materials. Non-asbestos fibrecement is partly composed out of organic fibres as cellulose, polyvinyl alcohol and/or polypropylene which replaced asbestos in earlier versions of fibrecement. Furthermore fibrecement as well as cellular concrete contain organic contaminations in the form of glues, plastics, paint etc. when recycled out of an end of life cycle of a construction. Presence of organic components in the raw material mix could provoke blockage of the cyclone tower as well as generate a crossing of the TOC (Total Organic Carbon) emission limits at the chimney of the Portland clinker process. Nevertheless this investigation demonstrates that the presence of these organic constituents in a raw material, although better avoided, is not insurmountable if introduced at a specific point of the Portland production process. Non-asbestos fibrecement could for this reason be catalogued as a valid raw material for Portland clinker production. On the other hand, research on cellular concrete demonstrated that the presence of high levels of coarse quartz particles makes it a raw material unsuited for Portland clinker production. Fineness and particle size distributions affect the burnability of the raw material mix. A sufficient specific surface area has to be created to facilitate the sintering process and to decrease sintering temperature. Quartz (SiO_2) particles although having a quite high mineral hardness have to be ground the finest to obtain optimal burnability of the raw material mix.

Finally by-products out of common concrete production in the form of concrete sludge and waste materials out of demolished concrete in the form of fines fractions were investigated as raw material for Portland clinker production. Common concrete represents the biggest market as a function of cement consumption and is therefore a logical choice when investigating possible alternative raw materials out of the construction sector. For the evaluation of concrete sludge, eighty-seven samples were collected to have a good overview of its chemical variation. Out of this evaluation, it was concluded that the big chemical variation makes concrete sludge unsuited for Portland clinker production. Also the possible presence of coarse quartz particles was investigated and demonstrated to be a serious bottleneck although preparation phases by screening allowed to successfully decrease the presence of coarse quartz particles and to improve the related burnability of the alternative raw material mix. Nevertheless, these preparation phases turned out to be ineffective to improve the chemical variation. Concrete sludge has therefore to be avoided for Portland clinker production.

Although fines fractions out of recycled concrete and concrete sludge originate both from the same base material, the fines fractions out of recycled concrete demonstrated to be different in terms of physical, chemical as well as mineralogical composition when compared to concrete sludge. A reduction in chemical variation of these fines fractions was obtained by the use of innovative separation techniques. Fines fractions seem to be a valid raw material if generated by these specific separation techniques. Nevertheless, more samples will be necessary to evaluate the chemical composition, the related dosing potential as well as the necessity of a homogenisation phase.

The examination of the suitability of these five alternative raw materials for Portland clinker production is also an effort to determine attention points and thus facilitate future evaluations of other materials than those investigated in this PhD study. These attention points are related to specific properties of a material such as its chemical variation, the presence of organic constituents, its average chemical composition, fluxing effects due to the presence of some minor components, its particle size distribution as a function of its mineralogical composition, and possible material preparations phases. The fitness of a material as alternative raw material for Portland clinker production will be a combination of each of these points and their combined impact on the Portland clinker process and the final Portland clinker quality. At the one hand, using an alternative raw material could improve the environmental impact of its proper production process and decrease waste disposal by landfill. Nevertheless, on the other hand, it could be classified as a non-sustainable solution if it has a negative influence on the Portland clinker process and final clinker quality. Indeed, the environmental impact analysis of the specific valorisation of an alternative raw material in Portland clinker production has to be an objective evaluation of pro’s and con’s, to determine whether it can be classified as a next step in the continuing sustainable development of the cement production process, or better be avoided due to the additional insurmountable energy expenditure for alternative raw material valorisation or/and an adverse impact on the Portland clinker process and quality.

Although no sufficient data were available to perform an objective LCA (Life Cycle Assessment) on the use of each of the five investigated materials in the Portland clinker production or the production processes where they originated from, an evaluation based on the normalised guidelines of the LCA procedure was still possible.

Abstract

Verschillende bedrijven herzien hun bedrijfsvoering om de bescherming van het milieu en het vrijwaren van de levenskwaliteit voor de huidige en toekomstige generaties overeen te laten stemmen met hun streven naar winstgevende groei. Zelfs wanneer ze zich niet vrijwillig zouden aanpassen, worden zij hiertoe verplicht door economische noodzaak, de publieke opinie of de druk van overheidsinstanties om hun ecologische impact te verminderen. Hiervan uitgaande, zijn sommige bedrijven begonnen met het maken van significante beleidsveranderingen en het wijzigen van hun lange termijn verbintenissen en zakelijke strategieën.

Het cementproductieproces verbruikt grote hoeveelheden niet-hernieuwbare grondstoffen. Dit proces is ook een belangrijke bron van CO_2 emissies. Er werden reeds veel initiatieven genomen om het proces te optimaliseren. Het cement-duurzaamheidsinitiatief is hiervan een voorbeeld. Het toont aan op welke wijze de cementindustrie, wereldwijd, duurzaamheid nastreeft.

Dit doctoraatsonderzoek kadert in dit cement–duurzaamheidsinitiatief. Doelstelling ervan is om te onderzoeken hoe de cementindustrie bijproducten of gerecycleerde materialen uit de bouw- en constructiesector in haar Portlandklinkerproces kan integreren. Het opzet is dat verschillende producenten en consumenten binnen deze sector materialen of energie uitwisselen om een wederzijds ecologisch voordeel te bekomen.

Om de geschiktheid van bijproducten of gerecupereerde materialen uit afvalstromen als alternatieve grondstof vast te stellen, werden op een praktische en objectieve manier specifieke materiaaleigenschappen onderzocht. Uitgangspunt hierbij was het reële productieproces van Portlandklinker. Om deze specifieke geschiktheid te bepalen is een goede evaluatie van de fysische, chemische en mineralogische samenstelling en variatie van deze materialen noodzakelijk. Theoretische simulaties van alternatieve klinkersamenstellingen of artificieel gemaakte Portlandklinkers werden gebruikt om de impact van deze materialen op het Portlandklinkerproces te evalueren.

Het is vrij moeilijk om klinkerproductie op een realistische wijze op laboratoriumschaal te simuleren vanwege de specifieke constructie van een echte klinkeroven. De typische eigenschappen van een klinkeroven moeten in rekening worden gebracht bij het imiteren van het productieproces voor het aanmaken van artificiële Portlandklinkers. Om deze reden werd een specifieke set-up gebruikt om een objectieve evaluatie van de geschiktheid van een alternatieve grondstof mogelijk te maken. In de uiteindelijke evaluatie van de eindresultaten werden variaties, specifiek voor de simulatie op zich, geïdentificeerd en meegenomen of indien mogelijk, vermeden. Drie fabrieken binnen de Benelux werden gekozen om op te treden als referentie voor het Portlandklinkerproces. Door hun verschillende technische specificaties, en het verschil in de gebruikte grondstoffen, zullen ze op een andere manier omgaan met bijproducten of gerecycleerde materialen. Dit brengt met zich mee dat specifieke simulaties en artificiële klinkerstalen sterk van elkaar kunnen verschillen.

Vijf specifieke materiaalbronnen werden onderzocht als mogelijke alternatieve grondstof voor Portlandklinkerproductie. Allen kunnen ze het gebruik van natuurlijke grondstoffen beperken en eveneens de mogelijke storting van afval vermijden. Er werd gestreefd naar een grote verscheidenheid van materialen; De materiaalbronnen werden speciaal gekozen als vertegenwoordiger van een bijproduct uit een bestaand productieproces of als afvalmateriaal uit een gesloopt gebouw of betonnen constructie.

Vooreerst werden bijproducten uit de productie van porfier en gedolomitiseerde kalksteengranulaten op hun effect op de Portlandklinkerproductie onderzocht. Porfier en gedolomitiseerde kalksteengranulaten vertegenwoordigen een groep van grondstoffen die op dagdagelijkse basis gebruikt worden in verscheidene bouwtoepassingen. De onderzochte bijproducten komen vrij tijdens verschillende bewerkingsstappen om de kwaliteit van de granulaten te verbeteren.

In de meeste gevallen zal deze verbeterde granulatenkwaliteit, een ecologisch voordeel creëren voor de afgeleide toepassingen zoals beton en asfalt. Voor de granulatenproducenten zelf, is de valorisatie van deze bijproducten ecologisch en economisch voordelig. Het vermijdt stortafval en biedt de mogelijkheid om de energie noodzakelijk voor het productieproces te herverdelen. Recyclage van beide granulaattypes op het einde van de levenscyclus van een afgeleid beton- of bouwmateriaal zou ook een valabele bron voor dit type van materialen kunnen zijn.

Porfier noch gedolomitiseerde kalksteen worden tot op vandaag op regelmatige basis gebruikt in Portlandklinkerproductie. Dit is deels te wijten is aan de aanwezigheid van hoge gehaltes aan MgO. MgO wordt in Portlandklinkerproductie vermeden omwille van de specifieke beperkingen binnen de verschillende nationale en internationale cementnormen. Dit met betrekking tot het risico op betonexpansie. Door dit onderzoek werd echter aangetoond dat indien MgO voorzichtig wordt geïntroduceerd volgens goed gedefinieerde beperkingen, het beter is om kleine MgO-concentraties in de grondstoffenmix te behouden omwille van hun positieve mineralogische invloed op Portlandklinker dan ze te vermijden vanwege mogelijke periclaas-vorming en gerelateerde expansieproblemen op verhard beton. Het gebruik van bijproducten uit porfier en gedolomitiseerde kalksteenmaterialen als alternatieve grondstof in Portlandklinkerproductie kan hierdoor dus beschouwd worden als een waardevolle en realistische oplossing.

Ten tweede werden materialen uit nichemarkten voor cementconsumptie, zoals asbestvrije vezelcement en cellenbeton, onderzocht. Deze materialen bezitten een beperkte chemische variatie dankzij hun specifieke productieprocessen. Een kleine chemische variatie van de grondstoffenmix is een uiterst belangrijke procesparameter voor Portlandklinkerproductie. Vezelcement alsook cellenbeton kunnen als bijproduct van hun eigen productieproces of als sloopafval aan het einde van een levenscyclus worden gerecycleerd. Asbestvrije vezelcement is gedeeltelijk opgebouwd uit organische vezels zoals cellulose, polyvinyl alcohol en/of polypropyleen. Zij vervingen de asbestvezels in eerdere versies van vezelcement. Vezelcement en cellenbeton bevatten eveneens organische verontreinigingen in de vorm van lijmen, kunststoffen, verf enz. wanneer ze gerecycleerd worden op het einde van een levenscyclus van een constructie. De aanwezigheid van organische componenten in de grondstoffenmix kan echter verstopping van de cyclonentoren van een klinkeroven veroorzaken en leiden tot een overschrijding van de TOC (Total Organic Carbon) emissielimieten bij de schoorsteen van het Portlandklinkerproces. Niettemin bleek uit dit onderzoek dat de aanwezigheid van organische componenten in een grondstof, hoewel beter vermeden, niet onoverkomelijk is wanneer de grondstof op een specifieke plaats binnen het Portlandklinker productieproces wordt ingebracht. Asbestvrije vezelcement kan om deze reden worden beschouwd als een valabele grondstof voor Portlandklinkerproductie.

Anderzijds heeft het onderzoek op cellenbeton aangetoond dat de aanwezigheid van hoge concentraties aan grove kwartsdeeltjes, cellenbeton ongeschikt maakt als grondstof voor Portlandklinkerproductie. Fijnheid en deeltjesgrootteverdeling hebben een invloed op de brandbaarheid van de grondstoffenmix. Een voldoende groot specifiek oppervlak moet worden gecreëerd om het sinterproces te vergemakkelijken en de sintertemperatuur te verlagen. Kwarts (SiO_2) deeltjes die een vrij hoge minerale hardheid bezitten, moeten het fijnst worden gemalen om de optimale brandbaarheid van de grondstoffenmix te bekomen.

Tenslotte werden bijproducten van een normale betonproductie zoals betonslib en afvalproducten uit gesloopt beton in de vorm van fijne fracties onderzocht als grondstof voor Portlandklinkerproductie. Beton vertegenwoordigt de grootste markt in functie van de gerelateerde cementconsumptie en was daarom een logische keuze bij het onderzoek naar mogelijke alternatieve grondstoffen uit de bouw- en constructiesector. Voor de evaluatie van betonslib werden zevenentachtig monsters verzameld om een goed beeld te krijgen van de chemische variatie van betonslib. Uit deze evaluatie kon besloten worden dat de grote chemische variatie, betonslib ongeschikt maakt voor Portlandklinkerproductie. Ook de mogelijke aanwezigheid van grove kwartsdeeltjes werd onderzocht. Dit bleek een ernstig knelpunt te zijn. Een voorafzeving om de aanwezigheid van deze grove kwartsdelen te verlagen en hierdoor succesvol de gerelateerde brandbaarheid van de alternatieve grondstoffenmix verbeterde, bleek echter ondoeltreffend te zijn om de chemische variatie te verbeteren. Betonslib zou hierdoor voor Portlandklinkerproductie moeten worden vermeden.

Ondanks dat de fijne fracties uit gerecycleerd beton en betonslib hun oorsprong vinden in hetzelfde basismateriaal, werd toch aangetoond dat de fijne fracties uit gerecycleerd beton, in vergelijking met betonslib, verschillend zijn op grond van hun fysieke, chemische en mineralogische samenstelling. Via het gebruik van innovatieve scheidingstechnieken lijken deze fijne fracties wel een valabele grondstof te zijn. Aanvullende monsters zullen echter nog noodzakelijk zijn om de chemische samenstelling, het gerelateerde doseerpotentieel en de mogelijke noodzaak van een homogenisatie fase verder te evalueren.

Het geschiktheidsonderzoek van deze vijf alternatieve grondstoffen voor Portlandklinkerproductie, liet toe aandachtspunten te bepalen die de evaluatie van toekomstige materialen, anders dan diegene reeds onderzocht voor deze doctoraatstudie, te vergemakkelijken. Deze aandachtspunten zijn gerelateerd aan de specifieke eigenschappen van een materiaal zoals zijn chemische variatie, mogelijke aanwezigheid van organische bestanddelen, hun gemiddelde chemische samenstelling, mogelijke mineralogische effecten door de aanwezigheid van bepaalde fluxen, de deeltjesgrootteverdeling in combinatie met een bepaalde mineralogische samenstelling en mogelijke voorbereidingenstappen tot het verkrijgen van de uiteindelijke alternatieve grondstof. De geschiktheid van een materiaal als alternatieve grondstof voor Portlandklinkerproductie zal telkens een combinatie zijn van elk van deze aandachtspunten alsook hun gecombineerde impact op het Portlandklinkerproces en de uiteindelijke Portlandklinkerkwaliteit.

Het aanwenden van een bijproduct als alternatieve grondstof zou enerzijds de milieu impact van zijn eigen productieproces kunnen verbeteren en tegelijkertijd het te storten afvalvolume kunnen verlagen. Anderzijds zou het ook kunnen bestempeld worden als niet duurzaam, mochten er negatieve invloeden op het Portlandklinkerproces of de uiteindelijke klinkerkwaliteit worden vastgesteld. De analyse van de milieu-impact van de valorisatie van een specifieke alternatieve grondstof in Portlandklinkerproductie moet het resultaat zijn van een objectieve evaluatie zijn van alle pro 's en contra's. Op die manier kan bepaald worden of deze valorisatie beschouwd kan worden als een stap in de duurzame ontwikkeling van het cementproductieproces, of beter vermeden wordt vanwege het additionele energieverbruik en/of de negatieve impact op het Portlandklinkerproces en de finale Portlandklinkerkwaliteit.

Hoewel er nog niet voldoende gegevens beschikbaar waren om een objectieve LCA (Life Cycle Assessment) -berekening uit te voeren op basis van het gebruik van de vijf onderzochte materialen in de Portlandklinkerproductie of op de productieprocessen waar ze vandaan komen, was een beoordeling op basis van de genormaliseerde richtlijnen van de LCA procedure toch mogelijk.

Chapter 1

General introduction

Architecture and civil engineering have always been an important part of human activity. In the course of years, the materials out of which constructions are made have strongly evolved. Originally, constructions were mainly build from natural substances such as clay, rocks, sand, and wood, whereas now they are more and more composed out of man-made products. Concrete made with hydraulic binders is by far the most widely used man-made construction material. It is indispensable for infrastructure, industry and housing. Concrete is produced with inert and reactive raw materials which are easily available. Most of the concrete produced worldwide today, is based on cement as a hydraulic binder. Cement is composed out of raw materials which are present in nature, such as puzzolanic materials, or which are formed artificially by an industrial process, such as fly ash, blast furnace slag and Portland clinker. Early versions of cement were already found in the third millennium B.C. in Mesopotamia but it was only as of the time of the Ancient Macedonians that cement was used as raw material in concrete and later on at larger scale by Roman engineers. Cement in those days was a mix of natural and artificial puzzolans as well as hydrated non-hydraulic lime **[1]**. It was only in 1824 that the manufacture of Portland cement was patented by Aspdin and production of artificial cement based on Portland clinker, a name derived from the isle of Portland in Dorset, England **[2]**, was induced. Based on this long history, it could be remarked that there is not much to learn anymore about cement production. Truth is that cement industry **[3]** currently is confronted with some ecological challenges that will be the central concern of cement manufacturing for the next decades (**Figure 1.1.**).

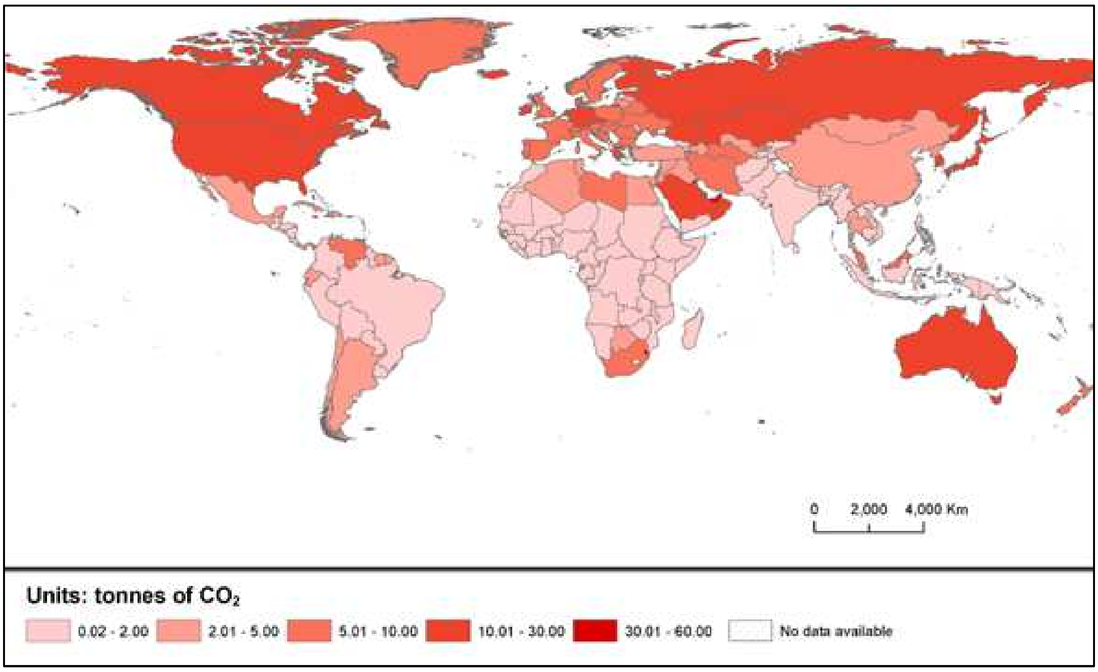

Figure 1.3.: CO_2 emission per capita per year per country in 2007
(Ref. http://unstats.un.org/unsd/environment/air_co2_emissions.htm [cited 2014 May 2])

It has to be recognised that cement production has a significant impact on the environment, which is related to the specific production process as well as the high market demand of derived building products and associated production volumes (**Figure 1.2.**).

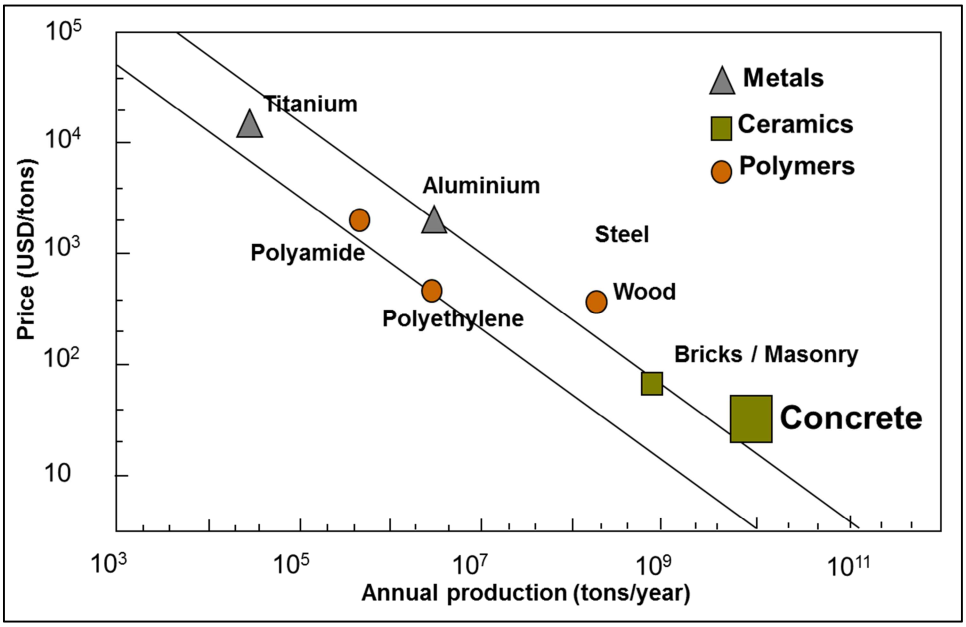

Figure 1.2.: Annual production of concrete compared to other construction materials
(Ref. Introduction à la science des matériaux, Kurz, Mercier, Zambelli, PPUR, 3rd ed 2002)

Much scientific evidence links climate change to greenhouse gas emissions of which carbon dioxide (CO_2) ranks amongst the most important. It is estimated that the cement industry is responsible for approximately 5 v% of the global manmade CO_2 emissions (**Figure 1.3.**) **[3]**. For innovative sustainable development, it will therefore be necessary to cope with these challenges.

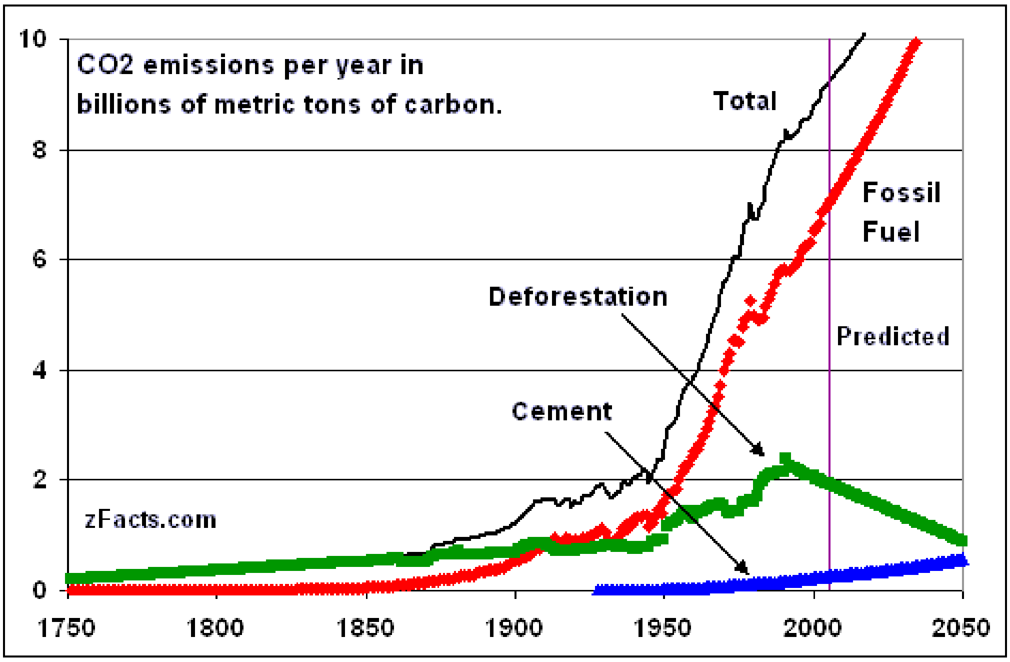

Figure 1.3.: CO_2 emissions per year in billions of metric tons of carbon
(Ref. http://zfacts.com/p/194.html [cited 2014 May 2])

Sustainable development is defined by the World Business Council for Sustainable Development (WBCSD) as forms of progress that meet the needs of the present without compromising the ability of future generations to meet their needs **[4]**. Within this context, adaptations in cement production to improve the ecological impact without degrading the cement quality should have priority on those adaptations that would significantly decrease the cement quality in terms of strength development, temperature sensitivity, durability, etc.

In the scope of this PhD study, measures are investigated to improve the ecological impact of cement production in line with the Cement Sustainability Initiative by adaptations to the production process of Portland clinker, the main constituent of cement. This Cement Sustainability Initiative **[5]** is a progress report to improve the impact of cement production on the environment that was undersigned by sixteen cement companies under the auspices of the WBCSD, which will further be explained in **section 4.2.** By improving the ecological impact of Portland clinker, also Portland clinker based cements as well as their derived construction products could benefit.

The ecological impact of Portland clinker production is mainly related to two important aspects of the production process. Firstly, Portland clinker production needs high kiln temperatures to obtain optimal Portland clinker reactivity, which is highly energy-consuming and greenhouse gas emitting. The burning of both traditional and alternative hydrocarbon fuels is used to attain these temperatures**.** The use of alternative fuels based on recovered materials or non-marketable by-products is already well established in the cement industry **[6]**. In Europe, the total fuel mix consisted already out of 14 wt% alternative fuels in 2003 which increased to 18 wt% in 2009 based on their calorific value. More locally in Belgium, even a replacement of approximately 70 wt% (CBR Antoing) is already attainted **[7]**. The amount of required fuels to burn 1 ton of Portland clinker is also directly related to the used process equipment as will be further explained in **chapter 2**. Secondly, despite the significant CO_2-emissions related to the combustion of these fuel materials, more than half of the CO_2-emissions generated by a Portland clinker process come from the use of limestone as main raw material. Limestone, primarily consisting out of $CaCO_3$, will release CO_2 during decarbonation and will deliver CaO as main constituent of Portland clinker.

By-products of other industries are already used to replace the Classic Raw Materials (CRMs) for the production of Portland cement clinker. In 2009 for example, about 5 wt% of the raw materials used in the production of clinker consisted out of alternative raw materials, totalling about 14.5 Mt/year **[7]**. Examples of alternative raw materials include contaminated soil, waste from road cleaning and other iron-, aluminium-, and silica-containing materials, such as coal fly ash and blast furnace slag. It is expected that this ratio of alternative raw materials will grow in the next decades when other materials than those quoted above will be valorised.

In spite of these replacements, reduction in CO_2 emissions is limited because the foregoing described materials rarely contain enough CaO to replace significant amounts of limestone. Blast furnace slag is an exception but unfortunately this material is too rich in Al_2O_3 *[wt%]* and/or SiO_2 *[wt%]* to be dosed in large quantities to the Cold Clinker Meals (CCMs) which are fed to a clinker kiln. Instead, blast furnace slag as well as fly ash could preferentially be used as raw material in cement production, based on their latent hydraulic or puzzolanic properties, as is already common practice.

Nevertheless, the replacement of limestone could reduce CO_2 emissions, energy related and therefore environmental effects of quarrying, as well as improve the environmental impact by energy reduction on the kiln. Also the replacement of the other primary raw materials could have ecological advantages.

When investigating the fitness of these alternative raw materials for Portland clinker production, it is very important to not lose track with the real manufacturing process itself. Nevertheless, it is not possible to perform all investigations immediately on industrial scale. Therefore, a good theoretical and artificial simulation, imitating the specific environment and properties of a real clinker kiln, is necessary and is defined in **chapter 3**. Furthermore, the possible ecological benefices due to the use of these materials have to be objectively framed. This will be further explained in **chapter 4**. Based on these preceding chapters, the objectives of this PhD study could clearly be defined in **chapter 5**.

Five main Alternative Raw Materials (ARMs) sources were investigated within this PhD study. They all have potential to decrease the use of natural resources and to counter landfill. They were chosen to represent a wide variety of materials that have their origin as by-product of an existing building material production process or as demolition waste of constructions made up out of building materials.

In **chapter 6**, by-products out of the aggregates production were investigated which are normally not used in Portland clinker production because of their specific nature, but which nevertheless originate from a natural source. The related aggregates are used in a wide variety of applications as concrete and asphalt production but also as ballast and armour stones. This means that they could also return at the end of life stage to the Portland clinker process expanding possible sources from which it could be recovered. **Chapter 7** and **chapter 8** deal with materials that represent niche markets for cement consumption. Indeed fibrecement as well as cellular concrete do not represent a big market share in function of cement consumption. Nevertheless, the fact they show a small chemical variation by their specific production process, could render them suitable as raw material for Portland clinker production. The production as well as demolition waste of these materials could be recycled as ARM. The biggest market share for cement consumption is nevertheless found in common concrete. One by-product and one demolition waste material out of concrete were investigated and are presented in **chapter 9** and **chapter 10**: the first, concrete sludge out of ready-mixed concrete plants or at the beginning of the life cycle of common concrete, the second, fines fraction separated out of a recycled concrete aggregates production stream or at the end of the life cycle of common concrete.

The goal of this PhD study is to use these ARMs, without altering the specific characteristics of Portland clinker which could compromise specific cement properties; a goal which is in line with the definition of sustainable development. The focus is primarily set on two key performance indicators of the Cement Sustainability Initiative (**Chapter 4**) specific for Portland clinker production: climate change management as well as fuel and material use. Specifically for climate change management, efforts are made to decrease CO_2-emissions by a lowered $CaCO_3$ *[wt%]* use and to provoke a reduced energy consumption related to a lower required decarbonation energy (MJ/Ton).

Also lower kiln temperatures induced by mineraliser effects coming from alternative sources are investigated which could have a positive impact on the energy consumption of a Portland kiln. On the other hand, some ARMs could also increase clinker reactivity at a fixed kiln temperature, which could decrease clinker/cement ratio in the derived cement production. Some of these alternative raw materials make it also possible to increase biomass related to the presence of some organic fibres such as cellulose.

Still, most of the materials are investigated because a possible valorisation in the Portland clinker process instead of a waste deposition as landfill would already create a big ecological benefit. By investigating these five specific alternative raw materials from different origins, an attempt is also made to determine basic rules and attention points for the use of recycled materials or by-products as alternative raw material for Portland clinker production. Worldwide, different alternative raw materials could be available, but based on this PhD study, their fitness for Portland clinker production could be interpreted faster.

References

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[2] A.J. Francis (1977). The Cement Industry 1796–1914: A History. Newton Abbot; North Pomfret, Vt.: David & Charle; 1977

[3] J.S. Damtoft, J.Lukasik, D. Herfort, D Sorrentino, E.M. Gartner, Sustainable development and climate change initiatives, Cement and concrete research 38 (2008) 115-127.

[4] Definition Sustainable development [cited 2014 Apr 30]
Available from: http://www.wbcsd.org/

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[6] H. Baier, K. Menzel, Proven Experiences with Alternative Fuels in Cement Kilns, 13th International Congress on the Chemistry of Cement (2011) Pages: 1-7.

[7] Sustainable cement production: Co-processing of Alternative Fuels and Raw Materials in the Cement Industry: CEMBUREAU, January 2009

Chapter 2

General literature study

2.1. Outline

Concrete compositions worldwide, in contrast to the Benelux, are based in most cases on Portland cement as hydraulic binder. Portland cement consists almost completely out of Portland clinker ground together with a few percent of calcium sulfate. Also other blends are possible, in which Portland clinker always plays an important role.

Economically, Portland clinker producers are pushed to use raw materials found locally, which differentiates and specifies their production process. To produce Portland clinker, a wide variety of technical equipment is available, which still improves significantly each decade. Because it is impossible to simulate all these different equipment techniques and raw materials, it was decided to use three local clinker factories in the Benelux as a reference for this PhD study.

The chosen factories are CBR Antoing and CBR Lixhe located in Belgium and ENCI Maastricht located in the Netherlands, all belonging to the Heidelbergcement Benelux group. CBR Antoing has the most recent kiln, ENCI Maastricht the oldest one. Both the kilns of CBR Lixhe and ENCI Maastricht were revamped in time to fulfil the present demands and modern standards. By their different technical specifications as well as used Classic Raw Materials (CRMs), these three kilns will deal in another way with the five investigated Alternative Raw Materials (ARMs) by which the specific mathematical simulations and the artificial clinker production will differ from each other.

Clinker production is based on some basic rules and typical restrictions, which will be discussed in the next sections. The literature specifically for each individual ARM will on its turn be discussed in their assigned chapters (**Chapters 6-10)**.

2.2. Portland clinker [1-2]

Portland clinker is produced by heating a mixture of primarily limestone and some additional raw materials as loam, sabulous clay, fly ash, artificially produced Fe_2O_3 sources, etc. in a kiln to a temperature of about 1450 °C. The heating of this raw materials mix changes the characteristics of the mixture turning them into oxides, mainly lime (CaO), silica (SiO_2) and to a lesser extent alumina (Al_2O_3) and iron oxide (Fe_2O_3) as can be noticed in **table 2.1.** and combines them to hydraulic phases. The objective of the kiln operation is to make clinker out of this raw materials mix, further called Cold Clinker Meal (CCM), at the maximum rate that the size of kiln will allow, while meeting environmental standards and hydraulic reactivity, at the lowest possible operating cost.

The most important used raw material is limestone consisting essentially out of $CaCO_3$, which will deliver almost exclusively all of the CaO and a significant amount of SiO_2 to the CCM. It is specifically for this reason that Portland clinker production plants are located near important sources of limestone. The limestone is intimately ground with the other raw materials, which are used to optimise the composition in terms of SiO_2, Al_2O_3 and Fe_2O_3. Based on the chemical analyses of the raw materials, their dosages will be constantly corrected to attain the desired and specific chemical composition of the Portland clinker. A clinkering phase up to 1450°C will deliver the potential reactivity that could be expected out of the chemical composition of the Portland clinker.

Table 2.1.: The average chemical composition of the reference clinker of each clinker factory

Clinker		Antoing	Lixhe	Maastricht
		Average	Average	Average
CaO	(wt%)	65.90	65.87	64.92
SiO_2	(wt%)	21.42	21.42	20.40
Al_2O_3	(wt%)	4.44	4.84	5.01
Fe_2O_3	(wt%)	2.61	3.65	3.52
K_2O	(wt%)	0.74	0.57	0.47
Na_2O	(wt%)	0.21	0.30	0.34
SO_3	(wt%)	1.21	0.51	0.92
MgO	(wt%)	1.70	2.01	2.08
Cl	(wt%)	0.068	0.017	0.020
CaO free	(wt%)	1.46	0.55	2.33
LSF_MgO	(wt%)	98.24	98.19	98.20
C3A	(wt%)	7.35	6.65	7.33
LiqSimple	(wt%)	19.18	22.73	22.97

2.3. Description of a kiln process [1-8]

Portland clinker is already produced on industrial scale as of 1825, after the Englishman Aspdin took a patent on the fabrication of Portland cement. The first Portland cement factories were built in England, France and Germany. Before this date there was already some experience with straight chalk kilns on which the first Portland kilns were based. In 1890, the first wet rotary kilns were constructed, a technique that is still used up to day to produce Portland clinker.

The rotary kiln is constructed out of a tube of steel which is protected with firebrick. The tube slopes slightly and rotates round its axis. CCM is fed, and the rotation of the kiln makes it move downhill to the other end of the kiln over a period of 60 to 90 minutes, undergoing different chemical reactions as the temperature increases. It is very important that the clinker meal moves slowly to allow the different chemical reactions to be completed. At the end of the tube, fuel is blown in through a burner pipe producing a flame in the lower part of the kiln tube. As material moves closer to the end of the kiln tube, temperature rises and is peaking just under the flame before the material is dropped out of the kiln tube into the cooler. Air for the combustion of the fuel is first heated up in the cooler by cooling down the clinker, before it is used for the combustion of the fuel. The primary fuels for Portland clinker production are coal, petroleum coke, heavy fuel oil, natural and refinery gases, etc.

In addition to these primary fuels, various combustible waste materials are used for Portland clinker production. In theory, cement kilns are an attractive way to dispose of hazardous materials, because of the high temperatures in the kiln and the ability of the clinker to absorb heavy metals into its mineralogical structure. In reality, these secondary fuel materials have to be closely monitored to manage their impact on the production process. Typically the general reaction zones in the Portland clinker kiln are as follows:

- 70°C to ~ 450˚C - Dehydration zone: Within this temperature range, free water is removed and evaporated.

- 450 to 900°C - Calcination zone: Different chemical reactions are taking place in this zone. Up to 600˚C, the chemically bound water is evaporated, and ($CaMg(CO_3)_2$) decomposes to $CaCO_3$, MgO and CO_2. Between 800 and 900˚C, the calcium carbonate ($CaCO_3$) is further decomposed to CaO and CO_2. By the end of the calcination zone, the clinker meal consists out of different oxides necessary for the reaction into the different hydraulic phases. The clinker meal is still in solid state.

- 900 to 1300°C - Solid-state reaction zone: Within this zone there is still no melting, but solid-state reactions begin to take place. CaO and SiO_2 already combine to belite ($2CaO \cdot SiO_2$), one of the four main cement minerals. Also some intermediate calcium aluminates and calcium ferrite complexes are formed.

- 1300 to 1450°C - Clinkering zone: This is the hottest zone of the Portland clinker process where the formation of the most important cement mineral, alite ($3CaO \cdot SiO_2$), takes place. The melting of the solid state takes place and $2CaO \cdot SiO_2$ reacts with CaO to form $3CaO \cdot SiO_2$. This zone begins when the intermediate calcium aluminate and ferrite complexes begin to melt. By this action a liquid phase is formed allowing crystals to be formed. The clinkering process is complete when all SiO_2 is present in the $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ crystals and the amount of free lime (CaO_{free}) is reduced to a minimal level (<1 wt%).

- 1450 to 200°C - Cooling zone: If the hot clinker drops out of the end of the kiln, clinker temperature drops rapidly and the liquid phase becomes solid, by which two other important cement minerals celite/aluminate (C_3A) and ferrite (C_4AF) are formed. Also alkali (K_2O, Na_2O) and sulphate, which were dissolved in the liquid phase, combine to form different forms of alkali sulfates as well as $CaSO_4$ (**Section 2.5.**). The resulting product is the final clinker. The speed of cooling is quite important because optimal Portland clinker reactivity benefits from a rapid cooling.

Two different methods of mixture preparation are used up to day to produce Portland clinker. The so called dry kiln process where a CCM is ground to form a fine powder or the so called wet kiln process where the CCM is mixed with water to produce a slurry.

2.3.1. The wet kiln process [1-8]

Typically for a wet kiln process, the CCM preparation is wet-ground to produce a fine slurry with a typical water content of 40-45 wt%**.** This has the big disadvantage that the generated slurry needs a lot of additional energy and therefore a higher fuel consumption to evaporate the added water, which also necessitates a longer kiln compared to a dry process. Typically, the above described dehydration zone (70°C to ~ 450˚C) would require up to half the length of the kiln.

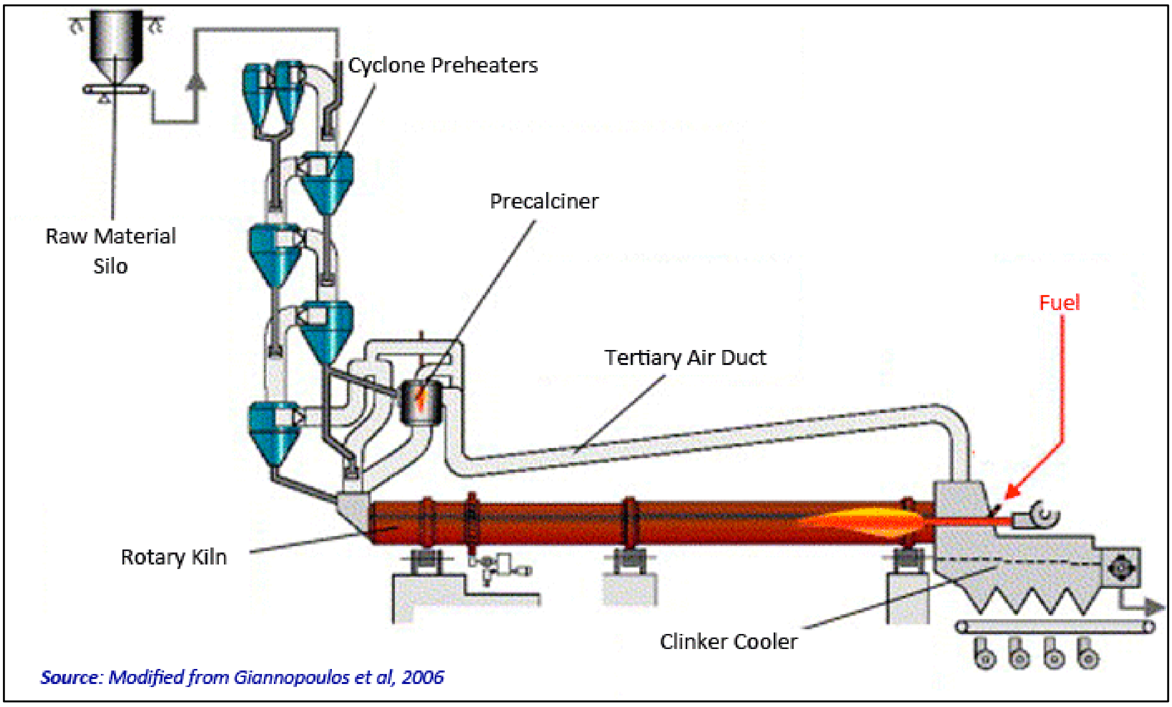
On the other hand, the wet kiln process has a number of advantages. Primarily, wet grinding of hard minerals is usually more efficient than dry grinding. Secondly, when slurry is dried in the kiln, it forms a granular crumble, which is much easier to heat in the kiln than a fine-ground powder. In the dry process, the fast-flowing combustion gases can blow the fine-ground CCM back out again.

Nevertheless, the higher energy consumption of the wet kiln process is the reason why more and more Portland clinker producers re-orientate to dry kiln technology to reduce energy costs and CO_2 emissions. Therefore it was not appropriate to investigate the use of the ARMs in a wet clinker process, because the first step to make a Portland clinker process more environmental friendly, should be the adaption to a dry clinker process.

2.3.2. The dry kiln process [1-8]

In a dry kiln process, the raw materials pass through a series of crushing, milling and blending stages which results in a dry homogenised CCM. With automated computer-controlled procedures, the chemical composition can be maintained stable by altering continuously the raw material dosages *[wt%]*. After the CCM is ground to a fine powder in a ball mill up to sufficient fineness (**Section 2.8**), the CCM is stored into a silo. Out of normally two or more of these silos which make blending possible, the CCM is fed to the kiln and gradually heated up in contact with the hot gases from the combustion of the kiln fuel.

In modern dry kiln processes (**Figure 2.1.**), the raw meal passes through a preheater and in most modern kilns also a precalciner (**Figure 2.2.**) will be present. The preheater is a heat exchanger, which is composed in most cases out of series of cyclones stages in which the moving powder is dispersed in a stream of hot gas coming from the kiln and or the precalciner. A cyclone is a vessel where the solid materials are thrown to the outside by the centrifugal forces and leave the cyclone through a valve. The number of cyclones stages used in practice varies from one to five and are mounted vertically under each other in a tower construction. ENCI Maastricht has two cyclones stages, CBR Antoing and CBR Lixhe both five.



Source: Modified from Giannopoulos et al, 2006

Figure 2.1.: A modern Portland clinker dry kiln
(Ref. Fives: http://www.fivesgroup.com [cited 2014 May 2])

The CCM has a very short residence time (1-2 min) in the preheater system and is heated up to about 900°C. Within a preheater, 90-95% of the $CaCO_3$ present in the clinker meal can already be decomposed. The ashes of the burned fuels are incorporated into the clinker meal. Because almost all $CaCO_3$ can already be decarbonated in a preheater, the clinker meal can pass more rapidly through the kiln. By using a pre-calciner (**Figure 2.2.**), it is possible to introduce heat directly into the cyclones tower.

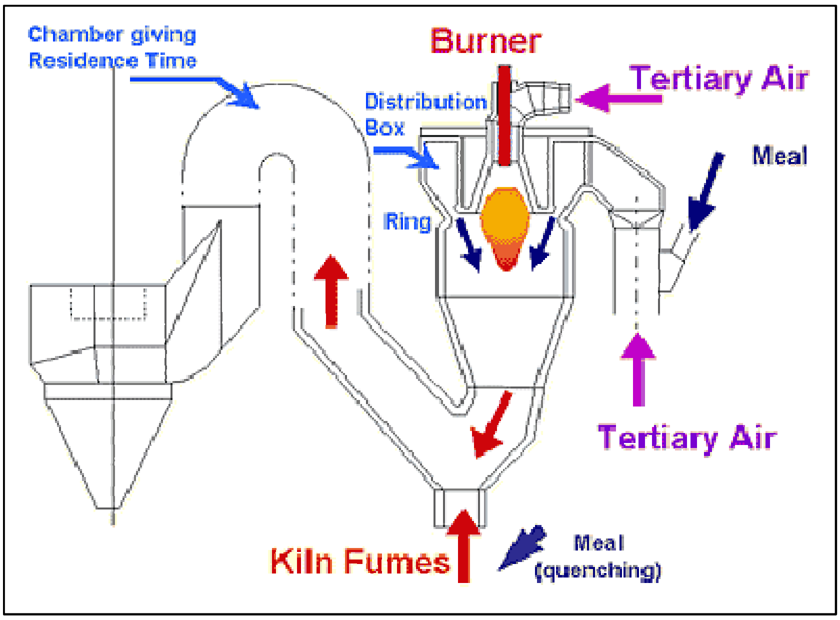


Figure 2.2.: A pre-calciner system
(Ref. Fives: http://www.fivesgroup.com [cited 2014 May 2])

A precalciner is a specially designed combustion chamber at the bottom of the lowest cyclones stage. Within the combustion chamber of a pre-calciner, approximately 50-65% of the total amount of fuel to the kiln can be introduced if gases are not extracted directly from the kiln but bypassed and extracted directly from the clinker cooler. In the case this bypass is not present, the amount of fuel that can be burned in the precalciner will be limited.

A disadvantage of preheaters is their tendency to block up by salts combined out of SO_3, Cl and alkali. These so called volatiles will come into the Portland clinker process through the raw materials and fuels. They tend to evaporate in the burning zone of the kiln and are carried back in the kiln by the gas stream, and re-condense when a sufficiently low temperature is attainted. Because they re-circulate back into the clinker meal and re-enter the burning zone, an accumulation cycle is generated. The condensation usually occurs in the preheater, gluing dusty clinker meal into a hard deposit and is part of a phenomenon that is called the clogging effect, which will be further explained in the next sections. It can block the preheater to the point that air-flow can no longer be maintained in the kiln. Modern installations often have automatic devices installed at vulnerable points to knock out build-up form this clogging effect on a regular base.

A by-pass installation (**Figure 2.3.**) can partly avoid this clogging effect by cleaning the dust out of the gas stream which is coming from the end of the kiln. It is generally placed at the bottom of the cyclones tower.

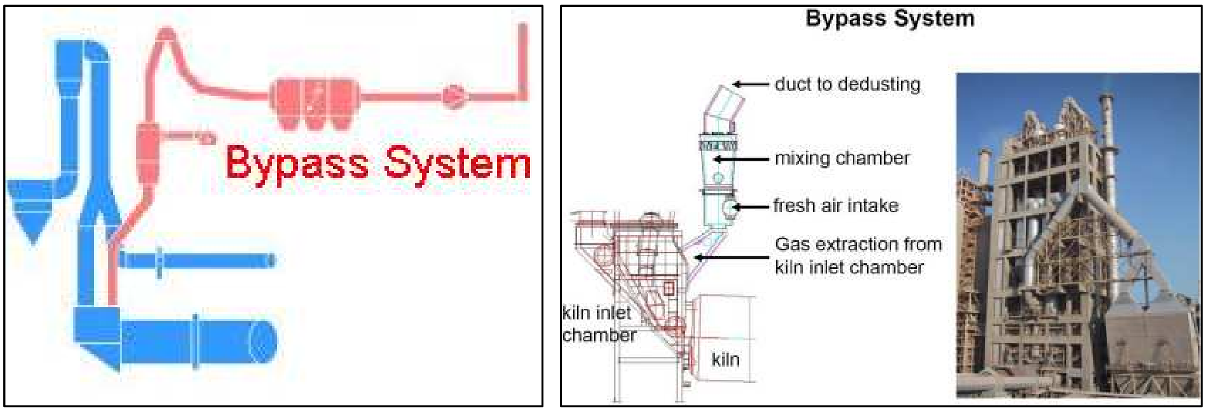


Figure 2.3.: A Bypass-installation at the bottom of the cyclones tower
(Ref. KHD Humboldt Wedag: http://www.khd.com/bypass-systems.html [cited 2014 May 2])

One of the advantages of a bypass installation is that, with the capturing and reducing of the dust content, parts of the volatiles *[v%]* as chloride, SO_3 and alkali can be reduced in the gas stream. This can minimise the clogging phenomena initiated by salts based on these volatiles and/or can allow the use of fuels/raw materials richer in chloride, SO_3 and alkali without compromising the kiln process.

A disadvantage of a by-pass installation is the loss of heat during purging, resulting in higher energy costs. Furthermore, the generated dusty purge material is difficult to recycle in other parts of the process because of the high concentration of these volatiles *[wt%]*. **Figure 2.4.** demonstrates the reduction in volatiles by the use of a bypass installation.

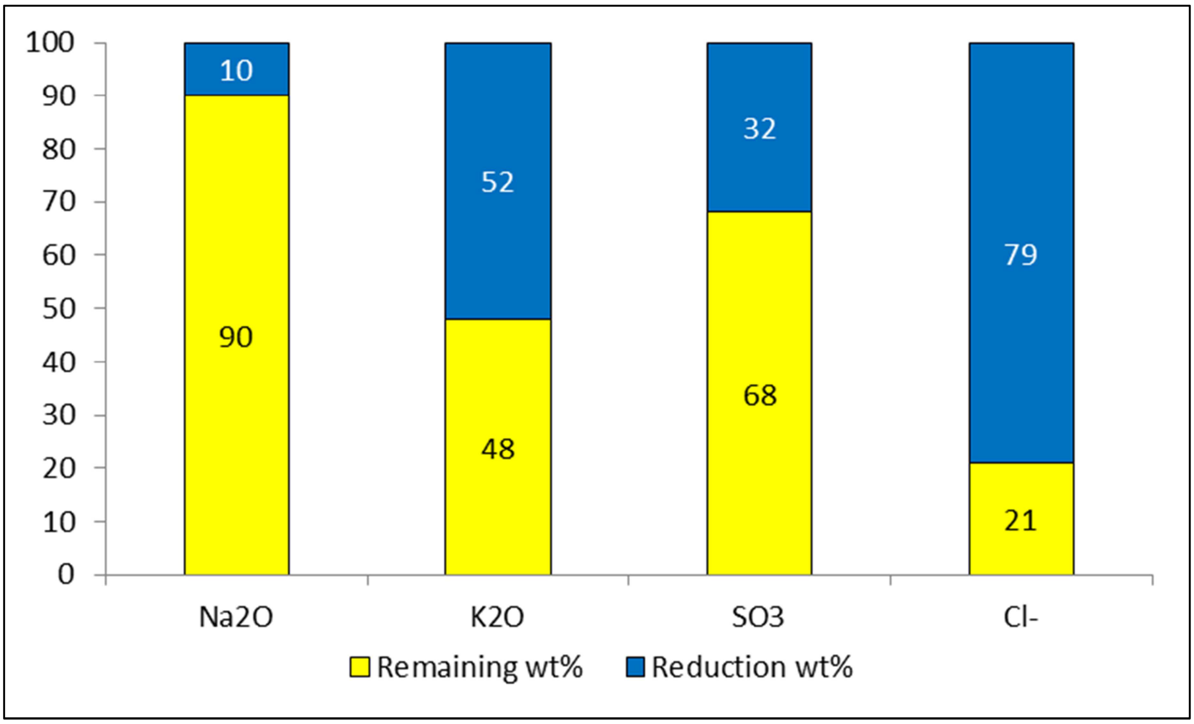


Figure 2.4.: Reduction in volatiles by the use of a bypass installation tower with 8 v% by-pass gas (Ref. KHD Humboldt Wedag: http://www.khd.com/bypass-systems.html [cited 2014 May 2])

2.4. Mineralogical composition of Portland clinker [1-2]

As described, the heat treatment up to 1450°C transforms the specific chemical composition to some typical hydraulic phases. The major hydraulic phases in Portland clinker are alite, belite, celite (aluminate) and ferrite, which are formed during the different stages of the Portland clinker process. Minor secondary phases such as alkali sulfates are also formed and will play an important role in the reactivity of the clinker.

- Alite (C_3S) is the most important hydraulic phase of Portland clinker. Portland clinker consists out of 50-70 wt% of this phase. Chemically, it is a tricalcium silicate ($3CaO \cdot SiO_2$), which is typically abbreviated as C_3S in cement chemistry. It reacts relatively quickly with water and has an important influence on the strength development of a Portland clinker based cement especially within the first 28 days. **[1-2]** C_3S occurs in two monoclinic forms: M_1 and M_3.
  Although the unit cell is quite similar, they differ in space group; M_1 is a Pc, M_3 a Cm space group **[9]**. There is some uncertainty as to the number and nomenclature of these polymorphs; reported M_{1b} and M_{2b} forms appear to be identical with M_3, leaving reported M_{1a} to be called simply M_1 and M_2 **[1]**. Higher MgO *[wt%]* increases the probability of M_3 (**Figure 2.5.**) **[1] [10-11].** The correlation between the monoclinic form and its reactivity is still an open question but it is assumed that M_1 is more reactive than M_3. Contrary to MgO, higher sulfate (SO_3) *[wt%]* increases the probability for M_1 by lowering the viscosity of the melt.

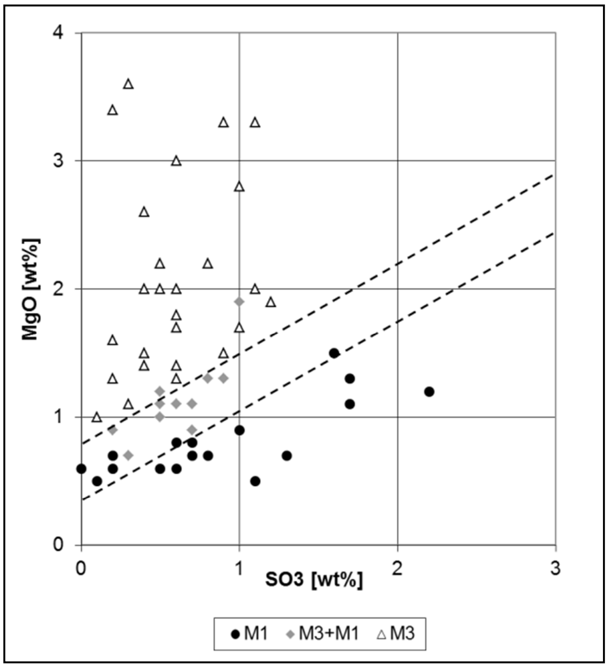


Figure 2.5: M1/M3 alite formation as a function of the SO_3 *[wt%]* and MgO *[wt%]* of different industrial made Portland clinkers **[11]**

- Belite (C_2S) is the second most important cement mineral which is present up to 15-30 wt% in normal Portland clinkers. It is chemically a dicalcium silicate ($2CaO \cdot SiO_2$), which reacts slowly with water and will play an important role in the strength development of cement typically after 28 days. **[1-2]**

- Celite (C_3A) also called aluminate contributes less to the composition of a Portland clinker than alite and belite. It is present up to 5-10 wt% in Portland clinker and is a tricalium aluminate ($3CaO \cdot Al_2O_3$). It reacts very rapidly with water, and is one of the reasons why a binding regulator has to be used to produce cement. It has an influence on the young age strength development. Al_2O_3 also plays a role as fluxing agent to lower the sintering temperature of the Portland clinker and increase liquid formation. **[1-2]**

- Ferrite (C_4AF) or tetracalcium aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) is a constituent that is not present in all Portland cements. In white Portland cement for example, ferrite is absent by the lack of Fe_2O_3 to guarantee the white colour. Ferrite does not play an important role in the strength development of Portland clinker but Fe_2O_3 will lower the sintering temperature significantly, which has a huge advantage towards the energy consumption of the Portland clinker production. It will be present in grey Portland cement up to 5-15 wt%. **[1-2]**

The presence of these major hydraulic phases in Portland clinker will be an important indicator on the suitability of the cold clinker meal and the conditions under which Portland clinker can be produced.

2.5. Chemical composition of Portland clinker [1-2]

Portland clinker has a desired and specific composition of about 67% CaO, 22% SiO_2, 5% Al_2O_3, 3% Fe_2O_3 and 3% other components which allows, after a heat treatment, to generate the different major hydraulic phases. This composition is very important for the formation of the major hydraulic phases in Portland clinker and is therefore closely monitored. In practice, the chemical composition of the produced CCM is measured each 1/2h. As could be noted out of **section 2.2.**, the dosages of the different raw materials have to be balanced to guarantee a fixed chemical composition of the CCM. This chemical composition is maintained by calculating the dosages of the different raw materials of the CCM by a computer program based on their chemical composition. This means that small chemical variations in the CCM can be managed by small adaptations in the raw material dosages. When the chemical variation increases, bigger adaptations are necessary up to the point that these adaptations will increase themselves the chemical variation of the CCM. To counter this cascade effect, clinker factories have defined minor and major limits for the variations of the four major metal oxides: CaO, SiO_2, Al_2O_3 and Fe_2O_3 as well as for the dosages of the raw materials. As an example, the limits of the four metal oxides defined for the kiln of CBR Antoing are presented in **table 2.2.** When the minor limits are attainted, actions have to be taken to lower the chemical variation of the CCM. When the major limits are attainted, the Portland clinker production is no longer guaranteed.

Table 2.2.: The average chemical composition and variations of the four metal oxides for the CCM of CBR Antoing

CCM		Average	Minor	Major
CaO	(wt%)	43.46	0.5	2.3
SiO_2	(wt%)	13.59	0.4	1.9
Al_2O_3	(wt%)	2.84	0.2	0.9
Fe_2O_3	(wt%)	1.59	0.15	0.7

The other components consist out of a wide group of minor metal oxides and some other components as SO_3, Cl and alkali (as K_2O and Na_2O). MgO is an important minor metal oxide that will be built exclusively into the C_3S mineral to about max. 1.5 – 2.0 wt% whereby MgO simply replaces the CaO in the alite ($3CaO \cdot SiO_2$) structure **[20-21]**. The average MgO *[wt%]* in CCM used in European clinker plants is 1.05 wt% **[14]**. MgO has to be monitored because of its limitation within the cement standards **[12-13]** and because of the risk related to the unsoundness of concrete (**Figure 2.6.**) **[14]**.

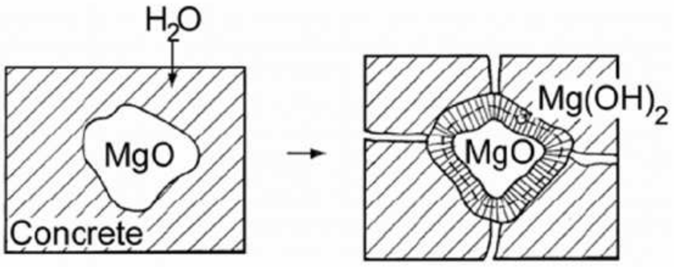


Figure 2.6.: MgO hydration with volume expansion in concrete **[19]**

In general, MgO *[wt%]* is limited in Portland cement and clinker to a maximum between 4.0 – 6.0 wt% depending on the countries standardisation **[12-17]** although some researchers claim that MgO up to 7.5 wt% induces no evidence of deterioration **[23]**. It was clear out of **[23]** that these high levels of MgO only could be achieved without deleterious influences by specific and not always attainable process parameters as specific calcining conditions, kiln temperature, residence time, cooling rate, etc. **[18]**. MgO will crystallise as periclase in clinker when MgO *[wt%]* is higher than 2.5 wt% **[20]**. Periclase tends to hydrate, forming brucite ($Mg(OH)_2$), a condition which causes excessive expansion and possible disruption of concrete (**Figure 2.6.**) which could be measured by standardised methods as EN 196-3 **[22]**. This is the reason why the different national standardisations limit the presence of MgO in Portland cement or clinker. The European Standard EN 197-1 describes a limit value of 5.0 wt% for MgO on the basis of Portland cement **[15]**. The limit for the total MgO *[wt%]* for Portland Cement according to the US Standard ASTM C 150 is 6.0 wt% **[16]**. The National Standards of New Zealand (NZS 3122) and Australia (AS3972) differ from the already mentioned limit values and refer to a total MgO *[wt%]* < 4.5 wt% on the basis of Portland cement clinker **[17]**.

Furthermore, some researchers have found equilibriums between MgO and other constituents, which could influence the expansion probability in concrete but these were only found in some internal work manuals of CBR (HeidelbergCement Benelux) and could not be cited out of other scientific literature.

- MgO/Fe_2O_3 ratio < 1.20: expansion failure due to MgO very unlikely.
- MgO/Fe_2O_3 ratio > 1.40: dangerous with high probability of expansion.

Also SO_3 *[wt%]*, alkali *[wt%]* and Cl^- *[wt%]* have to be limited according to these normalisation standards **[22]** but in reality have to be limited even stricter for the proper functioning of the Portland clinker process as already described in **paragraph 2.3.2.** SO_3 is in cement chemistry the general form to describe all forms of SO_4^{2-} *[wt%]* present in clinker or cement **[1]**. SO_3 will generally be formed after oxidation of S compounds in a clinker kiln. High concentrations of S are often present in pet coke fuel where contents up to 3 wt% are no exceptions **[1]**. Also limestone, clay or blast furnace slag, used as Classic Raw Materials (CRMs), can bring significant levels of S or SO_3 in clinker as can be noticed in **table 2.3**. When an excess of SO_3 towards alkali is present, $CaSO_4$ will be formed. When $CaSO_4$ is present in a poorly soluble form, a durability problem by formation of expansive ettringite in the final hardened concrete could occur. However there is yet no unequivocal evidence found of this assumption and even Taylor **[1]** claims that there is no relationship between them.

The reason for the existence of $CaSO_4$ of varying solubility is explained in different ways in literature.

The first theorem states that anhydrite could occur in three allotropic forms (anhydrite I, II and III), each with their own specific characteristics, including a different solubility. The bigger the unbalance between alkali and SO_3 in favour of the last, the greater the chance is that insoluble $CaSO_4$, known as Anhydrite I and II could be formed. This theorem was only stated in a work-manual within CBR

(Heidelberg Benelux group) and had no references. No other references were found which could substantiate this theorem. Another theorem states that the formed $CaSO_4$ has similar solubility but could be built in the various phases of the clinker (alite, belite) that have a different solubility of their own **[24]**.

Table 2.3.: Average chemical analysis of the limestones of CBR Antoing, CBR Lixhe and ENCI Maastricht (LOI: Loss Of Ignition)

CRM		Poor limestone Antoing	Rich limestone Antoing	Tufa Lixhe	Marl Maastricht
CaO	(wt%)	42.9	50.1	51.8	50.8
SiO_2	(wt%)	15.1	6.4	4.7	7.1
Al_2O_3	(wt%)	2.2	0.9	0.4	0.8
Fe_2O_3	(wt%)	0.9	0.4	0.3	0.4
K_2O	(wt%)	0.68	0.21	0.07	0.13
Na_2O	(wt%)	0.25	0.25	0.02	0.20
SO_3	(wt%)	0.90	0.57	0.09	0.21
MgO	(wt%)	1.1	0.9	0.7	0.8
Cl	(wt%)	-	-	0.011	-
LOI 975°C (O_2)	(wt%)	35.04	40.18	42.03	40.18

Conversely in an alkali-rich environment, sulfates can be found particularly in the form of alkali sulfates as arcanite, aphthitalite, thenardite and calcium langbeinite (**Table 2.4.**) and which will be particularly present in the C_3S and C_2S phases **[24]**.

Table 2.4.: Different compounds of SO_3 in clinker **[1]**

SO_3	Name
Alkali Sulfates	
K_2SO_4	Arcanite
$3K_2SO_4.Na_2SO_4$	Aphthitalite
Na_2SO_4	Thenardite
$K_2SO_4.2CaSO_4$	Calcium Langbeinite
$CaSO_4$	Anhydrite

These alkali sulfates will all have their own specific solubility, which may affect the hydration process of cement in a different way. Alkali sulfates will decrease the viscosity of the melt and therefore increase the formation of alite **[1].**

If no sufficient SO_3 content is available, the majority of the free alkali will be built into the belite phase. The free alkali will also increase viscosity of the melt and decrease the formation of alite **[1]**. Also an excess of alkali emitted to the gas phase of a clinker kiln by his high volatility, will ensure that clogging phenomena will appear faster what could lead to faster wear of the refractory bricks.

Alkali often comes from the limestone (**Table 2.3.**) but will also be present in the other used raw materials. Alkali is often expressed by equation **(2.1)** as sodium equivalent which recalculate stoichiometrically the wt% of K_2O to the wt% of Na_2O by their Molecular Masses (MMs). The ratio between the MM of Na_2O and the MM of K_2O equals 0.658 ($MM_{Na2O}/MM_{K2O} = 0.658$).

$$Na_2O_{eq} = Na_2O + K_2O \bullet 0.658 \qquad \textbf{(2.1)}$$

Chloride (Cl) is especially fed by fuel materials as waste oils, tires, plastics, animal meals, etc. **[25]**. Chloride is problematic because it can initiate corrosion on the iron used in reinforced concrete and is therefore limited in cement by normalisation. Chloride is nevertheless also known as accelerator of several cement hydration processes and was in the past commonly used in the form of $CaCl_2$ as admixture in concrete applications.

2.6. Process parameters and their impact on the Portland clinker production

Process parameters were developed to attain the ideal chemical ratios between the major metal oxides initialising the different already described mineralogical phases. Process parameters are also set on the minor elements to ensure a good functioning of the kiln, optimal reactivity of the final clinker and the absence of negative impacts on Portland clinker based cement and its derivatives **[13]**.

Lime Saturation Factor (LSF), aluminate (C_3A) and Liquid Simple (LiqSimple) **[1]** are used at a daily base in the three selected clinker factories (**Table 2.5.**) to manage the chemical composition of their CCMs. They are merely chemical limitations on equations with the four major metal oxides in the clinker.

Table 2.5: Chemical and mineralogical limitations on the final clinker

Clinker		Antoing	Lixhe	Maastricht
Cl	(wt%)	x < 0.08	x < 0.08	x < 0.08
SO_3	(wt%)	x < 1.4	x < 1.2	x < 1.1
Na_2Oeq	(wt%)	x < 1.2	x < 1.2	x < 1.2
MgO	(wt%)	x < 4.0	x < 4.0	x < 4.0
MgO/Fe_2O_3	(wt%)	x < 1.40	x < 1.40	x < 1.40
DoS-level	(wt%)	80 < x < 120	80 < x < 120	80 < x < 120
LSF_MgO	(wt%)	98.2 ± 0.5	98.19 ± 0.5	98.20 ± 0.5
C_3A	(wt%)	7.35 ± 0.5	6.65 ± 0.5	7.33 ± 0.5
LiqSimple	(wt%)	19.18 ± 0.5	22.73 ± 0.5	22.97 ± 0.5

The LSF **(2.2)** for the Cold Clinker Meal (CCM) governs the ratio between alite and belite.

$$LSF = 100 \bullet (CaO - CaO_{free}) / (2.8 \bullet SiO_2 + 1.18 \bullet Al_2O_3 + 0.65 \bullet Fe_2O_3) \qquad \textbf{(2.2)}$$

A LSF which is too high will give rise to an excessive content of free lime (CaO_{free}) because a higher LSF implies more CaO has to react, which is energetically unfavourable. An increasing LSF can also result in an increasing expansion potential. Additionally, if MgO is significantly present in the CCM, MgO has to be incorporated in the LSF because it will be built in the alite structure up to 2.0 wt%. Therefore an adapted lime saturation factor, LSF_MgO **(3)** is used with a refinement for MgO.

$$LSF\_MgO = 100 \bullet (CaO - CaO_{free} + 0.75 \bullet MgO) /(2.8 \bullet SiO2 + 1.18 \bullet Al_2O_3 + 0.65 \bullet Fe_2O_3) \quad \textbf{(2.3)}$$

This equation **(2.4)** has to be altered if MgO *[wt%]* is bigger than 2 wt% because the surplus will be formed as periclase.

$$LSF\_MgO = 100 \bullet (CaO - CaO_{free} + 1.5) / (2.8 \cdot SiO_2 + 1.18 \bullet Al_2O_3 + 0.65 \bullet Fe_2O_3) \quad \textbf{(2.4)}$$

The remainder of MgO *[wt%]* above 2 wt%, being the part which will form periclase, will percentually be subtracted from the four major metal oxides *[wt%]* and the corresponding process parameters achieved in clinker when MgO *[wt%]* is 2 wt%. In this way, the ratio between these metal oxides *[wt%]* is maintained as well as the ratio between the different major constituent phases. This will further be explained in **paragraph 6.7.2.**

Celite or aluminate is one of the four major hydraulic phases that was already described in **section 2.3.** For the calculation of aluminate, the commonly known Bogue calculation **(5)** is used, which governs the ratio between Al_2O_3 and Fe_2O_3.

$$C_3A = (2.650 \bullet Al_2O_3 - 1.692 \bullet Fe_2O_3) \quad \textbf{(2.5)}$$

The formation of the liquid phase, while heating the cold clinker meal (CCM), is very important to generate the different hydraulic phases of Portland clinker during the sintering process. Formulae **(2.6-2.9)** are used to calculate the percentage of Liquid (%Liq) at various temperatures and Al_2O_3 / Fe_2O_3 ratios:

1450°C $\%Liq = 3.00 \bullet Al_2O_3 + 2.25 \bullet Fe_2O_3 + MgO + K_2O + Na_2O$ **(2.6)**
1400°C $\%Liq = 2.95 \bullet Al_2O_3 + 2.20 \bullet Fe_2O_3 + MgO + K_2O + Na_2O$ **(2.7)**
1338°C ($Al_2O_3 / Fe_2O_3 \geq 1.38$) $\%Liq = 6.10 \bullet Fe_2O_3 + MgO + K_2O + Na_2O$ **(2.8)**
1338°C ($Al_2O_3 / Fe_2O_3 \leq 1.38$) $\%Liq = - 5.22 \bullet Fe_2O_3 + MgO + K_2O + Na_2O$ **(2.9)**

The composition of the liquid is mainly governed at 1450°C by Al_2O_3 and Fe_2O_3. In practice, a simplified equation **(2.10)** is used to describe the liquid formation, namely the liquid simple (LiqSimple), in the three factories.

Together with the aluminate Bogue calculation, it completely fixes the Al_2O_3 *[wt%]* and Fe_2O_3 *[wt%]* within the Cold Clinker Meal and at the end also in the final clinker.

$$\text{LiqSimple} = (3 \bullet Al_2O_3 + 2.25 \bullet Fe_2O_3) \qquad \textbf{(2.10)}$$

The presence of free lime or CaO_{free}, is an important process parameter to evaluate the burning of Portland clinker. Regular measurement of the CaO_{free} *[wt%]* is used as a way to supervise the clinker quality.

As already mentioned, alkali and SO_3 have to be in balance to avoid free alkali and/or the formation of $CaSO_4$. Therefore a stoichiometric balance has to be imposed, expressed as the so called Degree of Sulphatisation (DoS) factor calculated by equation **(2.11)** using the chemical analysis of the final clinker.

$$\text{DoS} = 100 \bullet (0.774 \bullet SO_3 / (Na_2O + K_2O \bullet 0.658)) \qquad \textbf{(2.11)}$$

The factors in the numerator and the denominator of the fraction are based on the ratio in Molecular Masses (MMs) between the Na_2O and SO_3 ($MM_{Na2O}/MM_{SO3}=0.774$) as well as between Na_2O and K_2O ($MM_{Na2O}/MM_{K2O}=0.658$) **(2.11)**. DoS levels between 80 to 120 wt% are recommended and used at present-day in the three clinker factories as process parameter. For this reason these DoS levels will be retained in all kiln simulations presented in this work (**Table 2.5.**).

The SO_3 *[wt%]* and Cl^- *[wt%]* of the simulated clinkers should be monitored and limited (**Table 2.5.**) even stricter than already done to be in line with the cement standards **[12]** because of their high volatility in the Portland clinker process to prevent clogging phenomena in the clinker kiln.

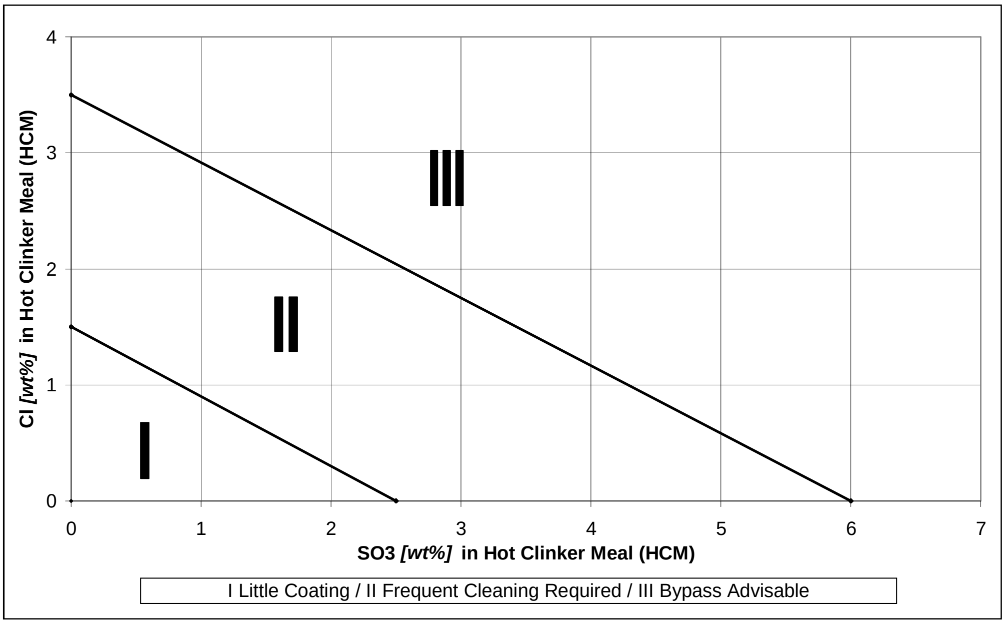


Figure 2.7.: Increasing clogging Levels as a function of SO_3 *[wt%]* and Cl *[wt%]* of Hot Clinker Meal (ref. KHD Humboldt Wedag International AG)

As shown in **figure 2.7.**, the risk for kiln clogging can be evaluated and classified as little coating, frequent cleaning required and bypass advisable (http://www.khd.com/bypass-systems.html) based on the Cl^- *[wt%]* and SO_3 *[wt%]* present in the Hot Clinker Meal (HCM). Each factory is different with regard to their used raw materials and technical installations. How these differences work out on the Cl^- *[wt%]* and SO_3 *[wt%]* and also alkalis *[wt%]* of the Hot Clinker Meal (HCM) and finally on the clinker is described by the so-called enrichment factor (ε) specific for Cl, SO_3 and alkalis, which calculates their return *[wt%]* from the gas phase to the HCM. These enrichment factors (ε) are also specific for each kiln when operating in routine (**Table 2.6.**).

Table 2.6.: Used enrichment factors (ε) and bypass factors (β) specific for each clinker kiln

	Antoing	Lixhe	Maastricht
Enrichment factor ε_{Cl}	96.5	99.2	91.0
Enrichment factor ε_{SO3}	60.0	89.1	20.0
Bypass factor β	2.6	4.9	41.4

Figure 2.8. shows a schematic calculation for these enrichment factors. By using and adjusting the settings of a bypass system, these enrichment factors could be altered. Therefore, bypass factors (β) specific for each clinker kiln are incorporated by which enrichment factors (ε) can be maintained stable independently from the bypass installation.

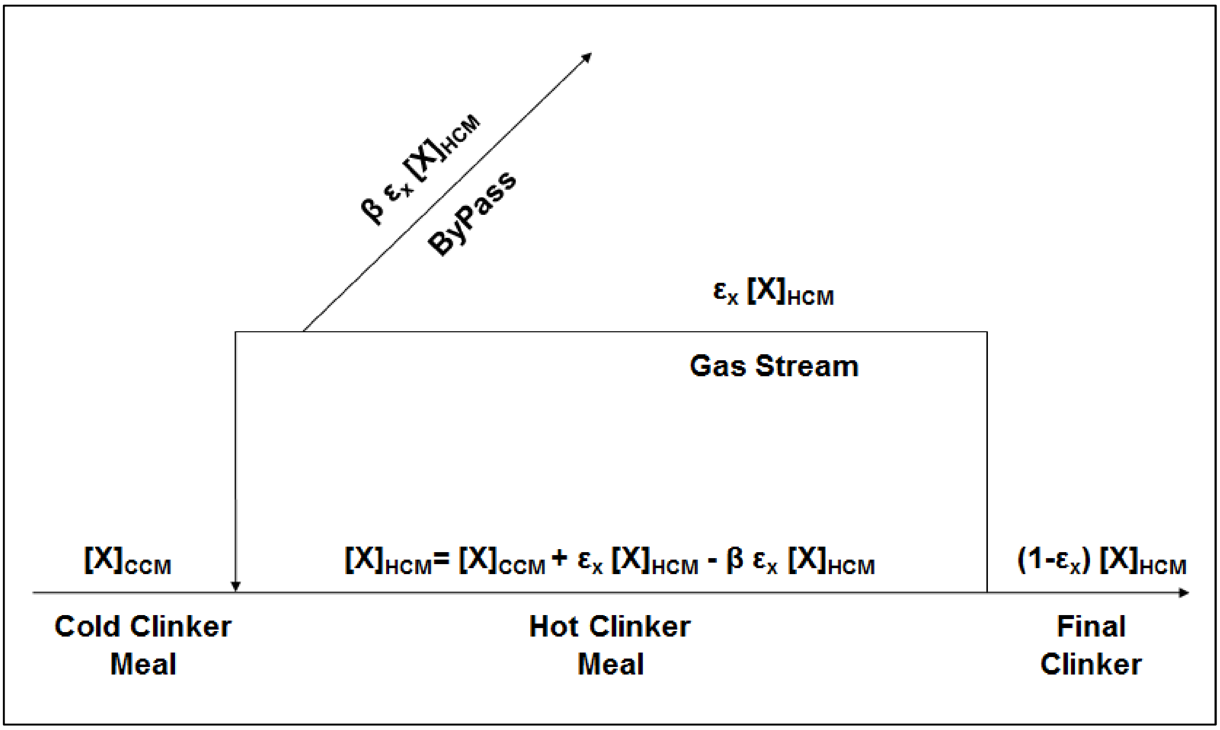


Figure 2.8.: Circulation diagram of volatiles by gas and HCM stream
(X = $[SO_3]$, [Cl], $[Na_2O]$, $[K_2O]$ of the HCM)

The bypass factors (β) calculate the amount of Cl, SO_3 and alkalis that could be captured in the gas phase lowering the amount of Cl, SO_3 and alkalis that normally would return to the HCM. These considerations are described in **figure 2.8.** and by the linear equation **(2.12)**.

$$[X]_{HCM} = [X]_{CCM} + \varepsilon_X \cdot [X]_{HCM} - \beta_X \cdot \varepsilon_X \cdot [X]_{HCM} = [X]_{CCM} / [1 - \varepsilon_X \cdot (1 - \beta)] \qquad \textbf{(2.12)}$$

Because the levels of Cl *[wt%]* and SO_3 *[wt%]* and alkalis *[wt%]* can be lowered by the presence of a bypass installation, higher Cl^- *[wt%]*, SO_3 *[wt%]* and alkalis *[wt%]* in the gas phase can be allowed without compromising the process and the final clinker quality. Based on this assumption, limits on Cl *[wt%]* and SO_3 *[wt%]* can be set for the final clinker.

The investigated Alternative Raw Materials (ARMs) within this PhD study will bring no significant Cl^- *[wt%]* into the clinker meal. Also the specific fuel mix of each Portland clinker kiln individually will not be included in this study so the equilibrium between SO_3 and Cl can be simplified as a SO_3 limitation (max) on the raw meal as listed for each clinker factory in **table 2.5**. These SO_3 limitations were derived out of **Figure 2.7.** by using equation **(12)** for SO_3 and Cl with the specific ε and β factors of each clinker kiln and the average Cl^- *[wt%]* of each reference clinker (**Table 2.1.**).

2.7. Mineralisers / fluxing agents

Mineralisers or fluxing agents are minor components that can be introduced into the clinker meal. They could have a positive effect on the energetic consumption or the mineralogical composition of the final clinker. Two of the major metal oxides, Al_2O_3 and Fe_2O_3 have already an important role in the clinkering process as fluxing agents **[1]**. It is the primary reason that Portland clinker contains Al_2O_3 and Fe_2O_3 in the first place. As already described in **section 2.3.**, these phases melt at the beginning of the clinkering zone at 1300˚C, which significantly increases the liquid formation. Without these two metal oxides, the formation of the calcium silicate minerals would be slow and difficult.

Other mineralisers could lower the temperature even more and/or promote the rate of the liquid formation and additionally increase the C_3S formation **[26] [30-31]**. The reaction of CaO and C_2S to form C_3S (**Section 2.3.**) is strongly controlled by the transport of both reactants through the liquid. This transport depends on the quantity, viscosity and surface tension of the liquid. Mineralisers have an influence on these parameters.

CaF_2 is the best known mineraliser **[27-29]**. In general, it can be stated that ions of strongly electronegative elements as Cl^- and F^- decrease the viscosity of the melt. As already mentioned in **section 2.5.**, strongly electropositive elements as Na^+ and K^+ or the so called free alkali increase the viscosity of the melt **[1]**. Also $CaSO_4$ is a much used and well investigated mineralizer. Also other mineralisers/fluxes whether or not in combination with CaF_2 could have, although minor, mineraliser effects. One of them is MgO **[32]**. The mineralizer effect of MgO will be further be discussed and described in **chapter 6**.

The mineraliser effect can be monitored by the CaO_{free} *[wt%]* **[1]**. An increase in CaO_{free} demonstrates that the clinker was less easy to burn or vice versa, which indicates the efficiency of the mineralizer.

2.8. Grinding Fineness

Fineness and particle size distributions affect the burnability of the Cold Clinker Meal (CCM). As the fineness of the CCM becomes finer, a surface area is created that will facilitate the sinter process which will lower the sintering temperature. This relationship is extensively described in literature **[33-35]**. The raw meal fineness will have its influence particularly on the formation of the liquid phase and the growth rates of silicate crystals **[33]**. Especially, the fineness of quartz is found to have a very strong effect on the CCM burnability **[36-37]**. In fact the maximum permissible particle size of quartz, feldspars and calcite is theoretically recommended to be 45 µm, 63 µm and 125 µm respectively**[35]**, although these values are not used in clinker factories as steering parameters.

Target finenesses of the CCM are described to be maximum 12 wt% residue on a 90 µm sieve and 2.6 wt% on a 211 µm **[36]**. Taking in account that quartz is the most difficult to grind compared to feldspar and calcite judging from the Mohs scale, it is quite uncertain that a particle size below 45 µm will be obtained if the target for CCM fineness is 12 wt% residue at 90 µm. In modern clinker factories such as CBR Antoing, CBR Lixhe and ENCI Maastricht, even coarser CCM finenesses with regard to the residue on 90 µm sieve, are pursued (**Table 2.7.**) as also stated by **[33]**.

Table 2.7.: Target values for particle size distribution of the reference CCMs

CCM		Antoing	Lixhe	Maastricht
		wt%	wt%	wt%
63	µm	< 27.0	-	-
90	µm	< 19.0	< 16.0	< 20.0
200	µm	< 3.5	< 1.0	< 3.5

The relationship between the raw material finenesses and the burnability of the CCM expressed as the CaO free *[wt%]* of the final clinker was investigated and described mathematically by E. Fundal and N.H. Christensen **[35-37]**. Their mathematical expressions by a so called chemico granulometric approach are based on chemical and physical analyses of thirty industrial raw mixtures and some steric assumptions and approximations. A mathematical expression **(2.13)** is used to describe the relationship between the individual raw material finenesses and their burnability **[38-39]**.

$$CaO_{free}\,(1400°C) = 0.33 \cdot LSF + 0.018 \cdot SR + 0.56 \cdot C_{125} + 0.93 \cdot Q_{45} - 0.349 \qquad \textbf{(2.13)}$$

C_{125} = Limestone ($CaCO_3$) particles with a size superior to 125 µm

Q_{45} = Quartz (SiO_2) particles with a size superior to 45 µm

LSF = Lime Saturation factor = (See equation **(2.2)**)

$$SR = \text{Silica Ratio} = SiO_2 / (Al_2O_3 + Fe_2O_3) \qquad \textbf{(2.14)}$$

This explains, although not used in industrial practice, quite nicely the importance of the quartz fineness on the CCM burnability.

2.9. Dust and gas emissions

The exhaust gases from a Portland clinker kiln are composed out of a large amount of dust. To be in line with environmental regulations specific for each country, dust emissions have to be reduced. Therefore, several types of filtration aids have been developed and installed in clinker kilns, varying from bypass installation to electrostatic and bag filters. As mentioned before, also the emission of volatile components has to be monitored closely to be in line with environmental regulations.

Another reason to manage closely the volatiles in the kiln is the clogging phenomena (**Section 2.6.**) which are related to the volatility of some components containing Cl, SO_3 and alkalis but also to other organic volatiles, which can be formed after thermal decomposition of the fuels necessary to heat up the kiln. The volatility or the tendency to vaporise of some typical substances in the Hot Clinker Meal (HCM) during heating (< 1450°C) are presented in **table 2.8.**

Table 2.8.: Melting points and volatility of some substances in the HCM of a Portland clinker kiln (Ref. Wikipedia: http://en.wikipedia.org [cited 2014 May 2])

Components	Melting point (°C)	Volatility (wt%)
KCl	776	60 - 80
K_2SO_4	1069	40 - 60
NaCl	801	50 - 60
Na_2SO_4	884	35 - 50
$CaCl_2$	772	60 - 80
$CaSO_4$	1280	-

Because it is almost impossible to analyse each individual organic compound that the organic fuels could form after thermal degradation, emission analysers measure the so called Total Organic Carbon or TOC emissions. TOC emissions are closely measured and limited by environmental regulation. Also the presence of O_2, CO, NO_x and SO_2 is continually analysed in the exhaust gases because it gives important information on the good functioning of the kiln. The formation of NO out of nitrogen and oxygen for example takes place only at high temperatures, and so the NO level gives an indication of the combined feed and flame temperature. SO_2 is formed by thermal decomposition of calcium sulfate in the clinker, and so also gives an indication of clinker temperature. CO gives information about the reducing conditions of the kiln. For reasons of clinker quality the burning process takes place under oxidising conditions. Modern computer control systems usually make a "calculated" temperature, using analyses of these exhaust gases. The kiln temperature in the sintering zone of a rotary kiln is around 1450°C.

To reach these kiln temperatures, flame temperatures of about 2000 °C are required. The clinker meal and rotary kiln exhaust gases make intimate contact in counter-flow and are therefore mixed thoroughly. By this process, a good temperature distribution and residence time is created which delivers favourable conditions for organic compounds, introduced by fuels or derived from them, to be completely destroyed.

During the clinker burning process CO_2 is emitted and accounts for the main share of the emission gases. CO_2 emissions are both raw material-related especially from limestone and energy-related from organic fuels. Raw material-related CO_2 emissions are produced during limestone decarbonation ($CaCO_3$) and account for about 60 v% of total CO_2 emissions. This explains why the input of CaO by Alternative Raw Materials (ARMs) could be ecologically beneficial.

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Chapter 3

Materials and methods

3.1. Introduction

When investigating the fitness of alternative raw materials for Portland clinker production, it is very important not to lose track with the real manufacturing process itself. Theoretical simulations of clinker compositions or artificial made Portland clinkers on lab scale often deliver specific properties which cannot be generalised for Portland clinker production in practice.

On the other hand, it is not possible to perform all investigations immediately on industrial scale, certainly not if they could have a severe impact on the Portland clinker process. Because this PhD study has as goal to investigate how the five proposed Alternative Raw Materials (ARMs) could be applied for Portland clinker production and which positive or negative influences they could have on the process, this simulation setup is crucial. A good theoretical and artificial simulation, imitating the specific environment and properties of a real clinker kiln, is therefore essential.

A realistic simulation of the clinker production on lab scale is quite difficult because of the specific construction of a clinker kiln as already explained in **section 2.3.** The typical properties of a kiln have to be taken into account while imitating the three reference clinker kilns (**Section 2.1.**). A comparison between specific Classic Raw Materials (CRMs) used in the three reference kilns and the five investigated ARMs can only be done if they are analysed by the same methods. It is very important to have a good reference which could indicate positive and/or negative influences of the five to investigated ARMs when producing clinker. Therefore reference Cold Clinker Meals (CCM) of the three kilns based on their currently used CRMs will be simulated, artificially produced under lab conditions and evaluated in comparison with the alternative CCM partly based on the ARMs to decrease as much as possible external factors in the comparison. These reference CCMs are based on chemical and mineralogical data that were collected in the first six months of 2011 out of the three reference clinker kilns and are described in **table 2.1.**

Several parameters need to be investigated to make an objective evaluation on the fitness of an ARM possible. These measures are summarised in the next steps:

- A good evaluation of the chemical variation of the ARMs:
  This is a crucial step to evaluate whether or not an ARM could directly be used in a Portland clinker kiln or if a preparation phase is necessary to decrease the chemical variation. Because the chemical composition of the CCM (**Section 2.5.**) is very important to deliver optimal Portland clinker reactivity based on the foreseen formations of predefined quantities of mineralogical complexes, a big chemical variation of one or more of the raw materials together with a high dosage in the CCM could disrupt severely the Portland clinker process.

The evaluation will also help to determine which preparation phases could be the most successful to decrease the chemical variation but also to improve chemical composition and/or physical properties of the ARMs.

- Parameters which could severely disturb the clinker kiln process:
  The physical and chemical parameters of an ARM that could disturb the Portland clinker process have to be identified and quantified to determine the ARM's fitness and also its possible maximisation *[wt%]* in the alternative CCM. These parameters were already thoroughly discussed in **chapter 2** and will be further evaluated throughout the complete investigation. The chemical parameters when limited by standard normalisation or as process parameters based on the technical installation of the kiln (**Section 2.6.**) will be included in the simulation of the different CCMs.

- Artificial clinker preparation and characterisation of the physical, chemical and mineralogical properties:
  Based on the simulation, artificial CCMs are prepared which are sintered comparable to what could be expected in a real Portland clinker kiln taken into account as much as possible, the typical environment of a Portland clinker kiln in terms of temperature, atmosphere and treatment time. Also the different physical, chemical and mineralogical properties of the Classic and Alternative Raw Materials (CRMs, ARMs) as well as the Cold Clinker Meals (CCM) before and after sintering have to be analysed and evaluated taken in account as much as possible the typical environment of a real Portland clinker kiln in terms of temperature, atmosphere and treatment time.
  Based on these clinker preparations and characterisation, conclusions can be formulated on the feasibility to use each of the five ARMs as raw material for Portland clinker. In the next sections, they will be described in detail. An important aspect of these characterisation steps is the error that could be made during analysis. Most of the used analysis methods as well as the errors of the outcome of the measurements are described in European standards. Because the equipment of the labs where analyses were performed are certified and controlled based on these European or derived national standards, the limits of the measurements errors described in these standards are also valid for the measurements within this PhD study. The measurement errors will be further discussed in **section 3.10.**

3.2. Evaluation of the chemical variation of an Alternative Raw Material

Attempts were made to collect big batches of samples to investigate the chemical variation of the five ARMs. Samples of porphyry and dolomitic limestone materials out of the quarries of Sagrex Quenast and Sagrex Chanxhe were collected monthly from different aggregate calibres and by-products in time spread over the 12 months of 2011. They were all sampled according to EN 932-1 **[1]**.

Also four sources of fibre cement material were recovered at 24 different points in time spread over the first 6 months of 2011 out of the factories of Eternit Kapelle op den Bos en Eternit Goor. They were all taken out of the stock of fresh made materials.

Cellular concrete materials were selected from two sources, polluted recycled cellular concrete and production waste of clean cellular concrete. The first source was collected spread over a period of two months, the second over a period of twenty-eight weeks in 2011. Both selection points were selected to generate a representative sample for the investigated source.

Finally, a big batch of eighty-seven sludge samples was collected between January 2011 and December 2012. They were sampled according to a specific procedure that will be further described in **chapter 9**.

Only for the fines coming out of recycled concrete, it was not possible to sample an extensive period due to the fact that these fines were created with although existing, innovative techniques for the separation of recycled fines.

This extensive collection of ARM samples made it possible to objectively evaluate the chemical variation of each of the selected ARMs. They will be further discussed in the allocated chapters of each of these ARMs.

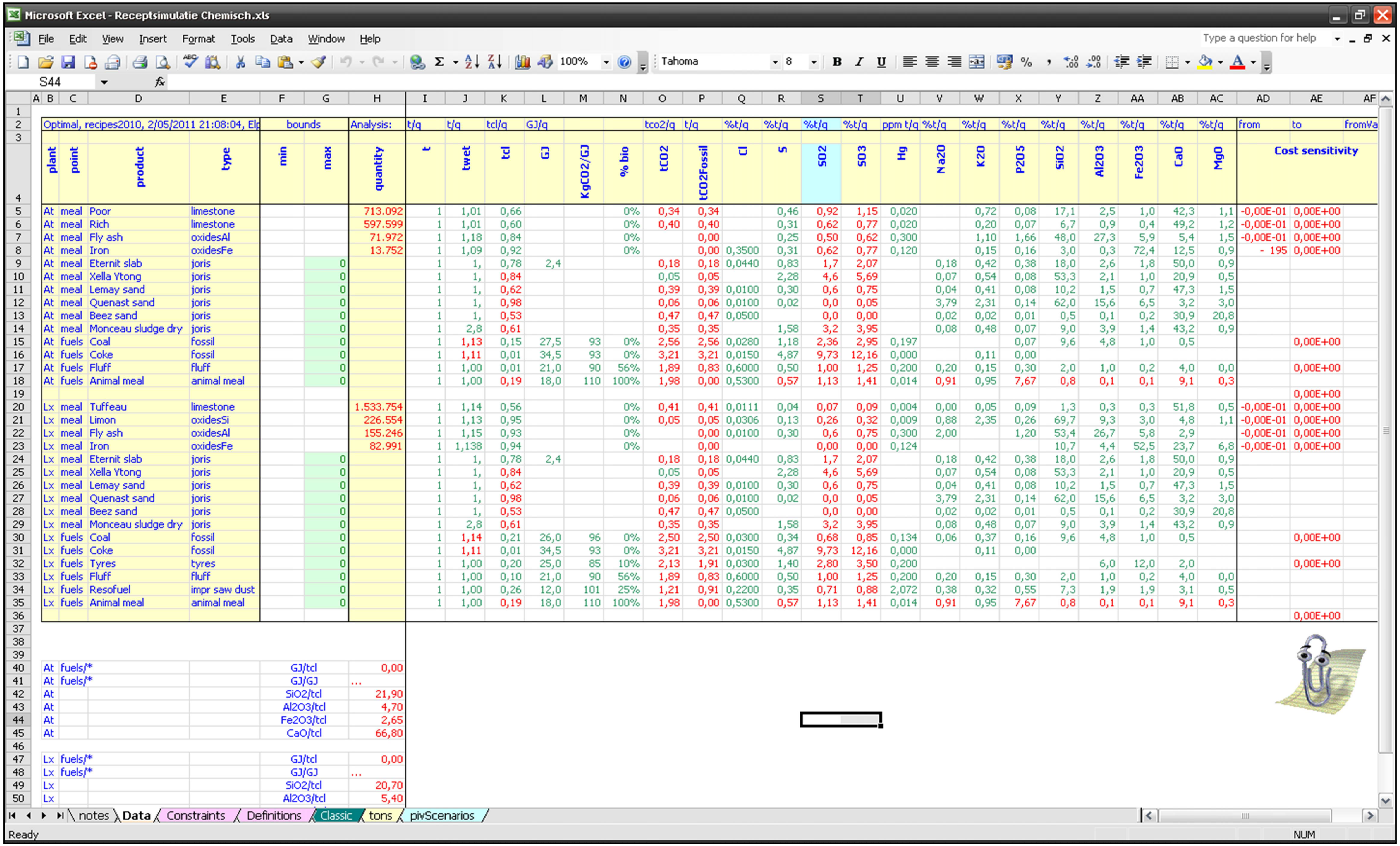
3.3. Mathematical simulations and calculations

A Portland clinker simulation program based on linear equations and integers was used to calculate clinker meal mixtures for each factory individually. The program uses Mixed-Integer Linear Programming (MILP) in which some or all of the variables are restricted to be integers. The remaining constraints are linear. It was originally developed in 2000 for fuel recipe optimisation of cement kilns. It calculates Cold Clinker Meal (CCM) recipes that satisfy the given constraints out of the chemical composition of the different raw materials. It has been designed to be flexible and was developed in Microsoft Excel.

On the Data sheet (**Figure 3.1.**), the different raw materials are defined by providing the following information: the material label, the material analysis, the minimum and maximum quantity allowed for a material and some typical factors that can be used to convert the original data to related analysis when convenient.

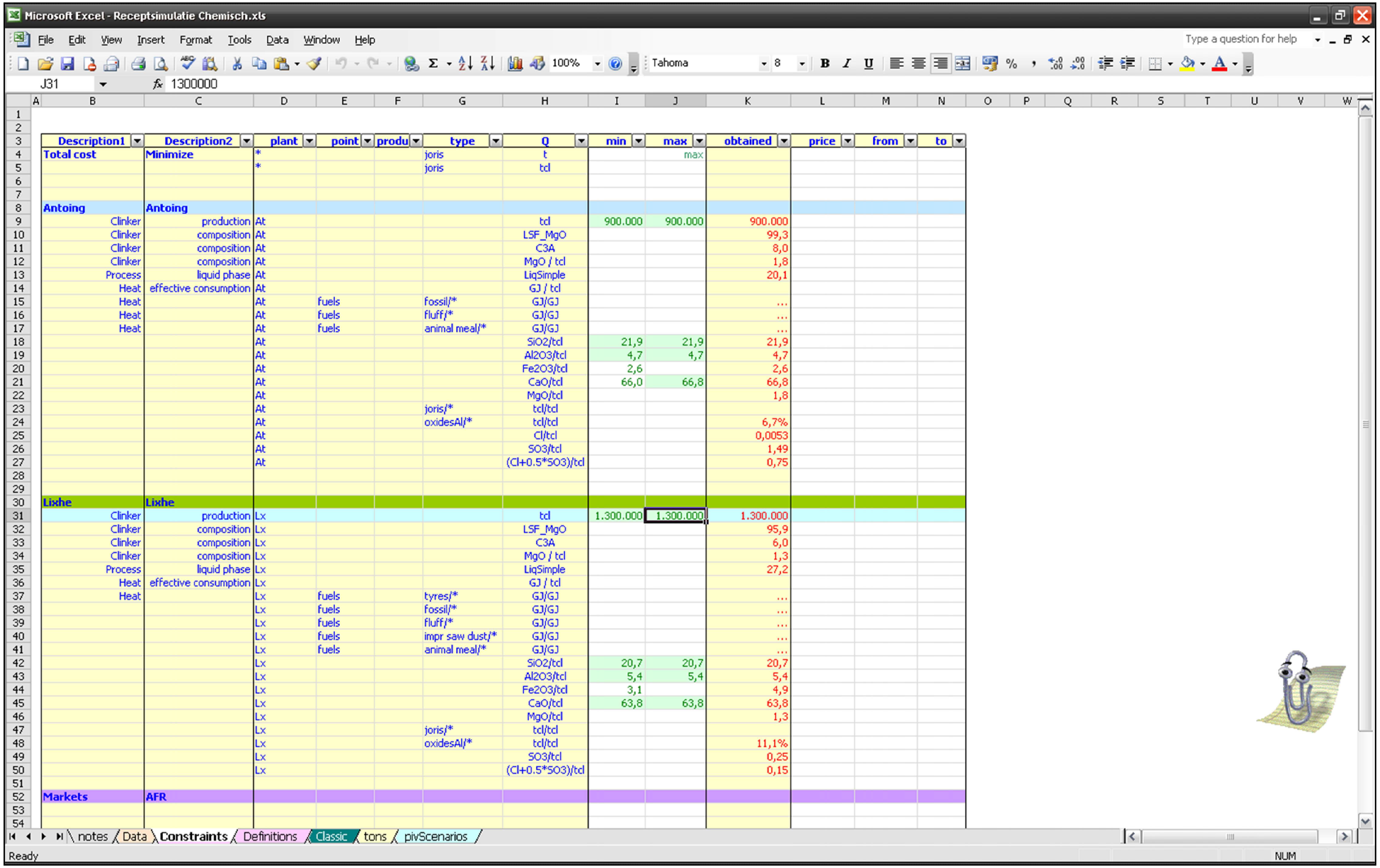
The Constraints sheet (**Figure 3.2.**) collects typically the constraints used to calculate the recipe. Each constraint is defined by a quantity (between a minimum and a maximum) that has to be constrained and a set of recipe components on which this quantity should be calculated. Also some results are already displayed as for example the constraint values or the values actually reached by each constraint for the given recipe.

Finally the Definitions sheet (**Figure 3.3.**) makes it possible to define symbols for complicated quantities. These symbols can then be used on the constraint sheet. For clinker recipes, the definitions sheet is a good place to store the definitions used for the clinker indices like LSF, SM, liquid phase, etc. (**Section 2.6.**). On the same sheet, some factors can also be defined that are used in the data sheet.



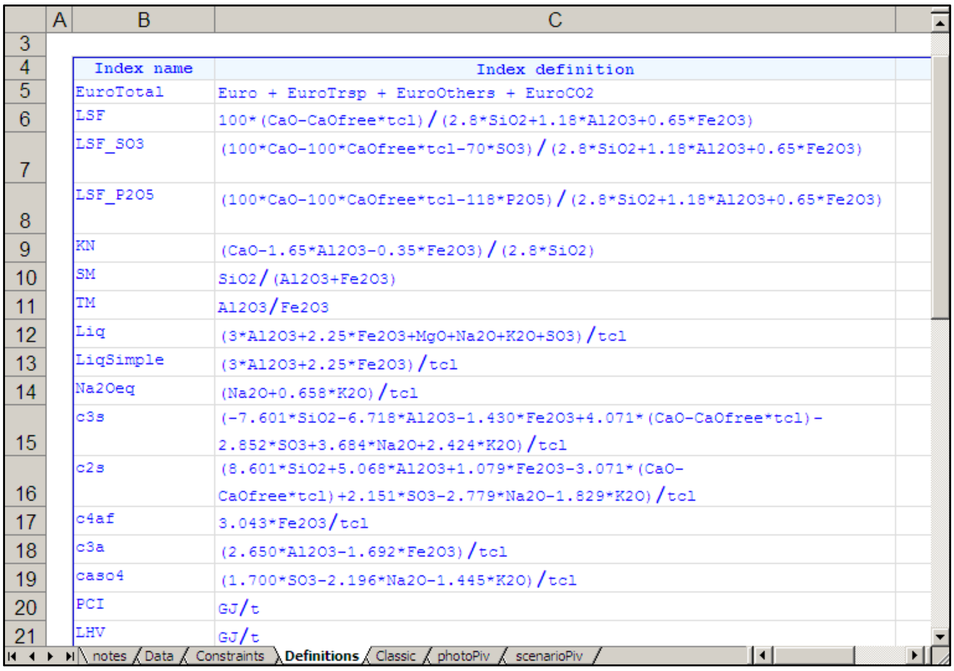
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF
1																																
2		Optimal, recipes2010, 2/05/2011 21:08:04, Elp				bounds		Analysis:	t/q	t/q	tcl/q	GJ/q			tco2/q	t/q	%t/q	%t/q	%t/q	%t/q	ppm t/q	%t/q	%t/q	%t/q	%t/q	%t/q	%t/q	%t/q	%t/q	from	to	fromVa
3																																
4		plant	point	product	type	min	max	quantity	t	twet	tcl	GJ	KgCO2/GJ	% bio	tCO2	tCO2Fossil	Cl	S	SO2	SO3	Hg	Na2O	K2O	P2O5	SiO2	Al2O3	Fe2O3	CaO	MgO	Cost sensitivity		
5		At	meal	Poor	limestone			713.092	1	1,01	0,66			0%	0,34	0,34		0,46	0,92	1,15	0,020		0,72	0,08	17,1	2,5	1,0	42,3	1,1	-0,00E-01	0,00E+00	
6		At	meal	Rich	limestone			597.599	1	1,01	0,60			0%	0,40	0,40		0,31	0,62	0,77	0,020		0,20	0,07	6,7	0,9	0,4	49,2	1,2	-0,00E-01	0,00E+00	
7		At	meal	Fly ash	oxidesAl			71.972	1	1,18	0,84			0%		0,00		0,25	0,50	0,62	0,300		1,10	1,66	48,0	27,3	5,9	5,4	1,5	-0,00E-01	0,00E+00	
8		At	meal	Iron	oxidesFe			13.752	1	1,09	0,92			0%		0,00	0,3500	0,31	0,62	0,77	0,120		0,15	0,16	3,0	0,3	72,4	12,5	0,9	- 195	0,00E+00	
9		At	meal	Eternit slab	joris		0		1	1,	0,78	2,4			0,18	0,18	0,0440	0,83	1,7	2,07		0,18	0,42	0,38	18,0	2,6	1,8	50,0	0,9			
10		At	meal	Xella Ytong	joris		0		1	1,	0,84				0,05	0,05		2,28	4,6	5,69		0,07	0,54	0,08	53,3	2,1	1,0	20,9	0,5			
11		At	meal	Lemay sand	joris		0		1	1,	0,62				0,39	0,39	0,0100	0,30	0,6	0,75		0,04	0,41	0,08	10,2	1,5	0,7	47,3	1,5			
12		At	meal	Quenast sand	joris		0		1	1,	0,98				0,06	0,06	0,0100	0,02	0,0	0,05		3,79	2,31	0,14	62,0	15,6	6,5	3,2	3,0			
13		At	meal	Beez sand	joris		0		1	1,	0,53				0,47	0,47	0,0500		0,0	0,00		0,02	0,02	0,01	0,5	0,1	0,2	30,9	20,8			
14		At	meal	Monceau sludge dry	joris		0		1	2,8	0,61				0,35	0,35		1,58	3,2	3,95		0,08	0,48	0,07	9,0	3,9	1,4	43,2	0,9			
15		At	fuels	Coal	fossil		0		1	1,13	0,15	27,5	93	0%	2,56	2,56	0,0280	1,18	2,36	2,95	0,197			0,07	9,6	4,8	1,0	0,5			0,00E+00	
16		At	fuels	Coke	fossil		0		1	1,11	0,01	34,5	93	0%	3,21	3,21	0,0150	4,87	9,73	12,16	0,000		0,11	0,00								
17		At	fuels	Fluff	fluff		0		1	1,00	0,01	21,0	90	56%	1,89	0,83	0,6000	0,50	1,00	1,25	0,200	0,20	0,15	0,30	2,0	1,0	0,2	4,0	0,0		0,00E+00	
18		At	fuels	Animal meal	animal meal		0		1	1,00	0,19	18,0	110	100%	1,98	0,00	0,5300	0,57	1,13	1,41	0,014	0,91	0,95	7,67	0,8	0,1	0,1	9,1	0,3			
19																															0,00E+00	
20		Lx	meal	Tuffeau	limestone			1.533.754	1	1,14	0,56			0%	0,41	0,41	0,0111	0,04	0,07	0,09	0,004	0,00	0,05	0,09	1,3	0,3	0,3	51,8	0,5	-0,00E-01	0,00E+00	
21		Lx	meal	Limon	oxidesSi			226.554	1	1,13	0,95			0%	0,05	0,05	0,0306	0,13	0,26	0,32	0,009	0,88	2,35	0,26	69,7	9,3	3,0	4,8	1,1	-0,00E-01	0,00E+00	
22		Lx	meal	Fly ash	oxidesAl			155.246	1	1,15	0,93			0%		0,00	0,0100	0,30	0,6	0,75	0,300	2,00		1,20	53,4	26,7	5,8	2,9		-0,00E-01	0,00E+00	
23		Lx	meal	Iron	oxidesFe			82.991	1	1,138	0,94			0%		0,00			0,00	0,00	0,124				10,7	4,4	52,5	23,7	6,8	-0,00E-01	0,00E+00	
24		Lx	meal	Eternit slab	joris		0		1	1,	0,78	2,4			0,18	0,18	0,0440	0,83	1,7	2,07		0,18	0,42	0,38	18,0	2,6	1,8	50,0	0,9			
25		Lx	meal	Xella Ytong	joris		0		1	1,	0,84				0,05	0,05		2,28	4,6	5,69		0,07	0,54	0,08	53,3	2,1	1,0	20,9	0,5			
26		Lx	meal	Lemay sand	joris		0		1	1,	0,62				0,39	0,39	0,0100	0,30	0,6	0,75		0,04	0,41	0,08	10,2	1,5	0,7	47,3	1,5			
27		Lx	meal	Quenast sand	joris		0		1	1,	0,98				0,06	0,06	0,0100	0,02	0,0	0,05		3,79	2,31	0,14	62,0	15,6	6,5	3,2	3,0			
28		Lx	meal	Beez sand	joris		0		1	1,	0,53				0,47	0,47	0,0500		0,0	0,00		0,02	0,02	0,01	0,5	0,1	0,2	30,9	20,8			
29		Lx	meal	Monceau sludge dry	joris		0		1	2,8	0,61				0,35	0,35		1,58	3,2	3,95		0,08	0,48	0,07	9,0	3,9	1,4	43,2	0,9			
30		Lx	fuels	Coal	fossil		0		1	1,14	0,21	26,0	96	0%	2,50	2,50	0,0300	0,34	0,68	0,85	0,134	0,06	0,37	0,16	9,6	4,8	1,0	0,5			0,00E+00	
31		Lx	fuels	Coke	fossil		0		1	1,11	0,01	34,5	93	0%	3,21	3,21	0,0150	4,87	9,73	12,16	0,000		0,11	0,00								
32		Lx	fuels	Tyres	tyres		0		1	1,00	0,20	25,0	85	10%	2,13	1,91	0,0300	1,40	2,80	3,50	0,200					6,0	12,0	2,0			0,00E+00	
33		Lx	fuels	Fluff	fluff		0		1	1,00	0,10	21,0	90	56%	1,89	0,83	0,6000	0,50	1,00	1,25	0,200	0,20	0,15	0,30	2,0	1,0	0,2	4,0	0,0			
34		Lx	fuels	Resofuel	impr saw dust		0		1	1,00	0,26	12,0	101	25%	1,21	0,91	0,2200	0,35	0,71	0,88	2,072	0,38	0,32	0,55	7,3	1,9	1,9	3,1	0,5			
35		Lx	fuels	Animal meal	animal meal		0		1	1,00	0,19	18,0	110	100%	1,98	0,00	0,5300	0,57	1,13	1,41	0,014	0,91	0,95	7,67	0,8	0,1	0,1	9,1	0,3			
36																															0,00E+00	
37																																
38																																
39																																
40		At	fuels/*			GJ/tcl		0,00																								
41		At	fuels/*			GJ/GJ		...																								
42		At				SiO2/tcl		21,90																								
43		At				Al2O3/tcl		4,70																								
44		At				Fe2O3/tcl		2,65																								
45		At				CaO/tcl		66,80																								
46																																
47		Lx	fuels/*			GJ/tcl		0,00																								
48		Lx	fuels/*			GJ/GJ		...																								
49		Lx				SiO2/tcl		20,70																								
50		Lx				Al2O3/tcl		5,40																								

Figure 3.1.: Program screenshot of the data sheet with the chemical composition of the raw materials



	Description1	Description2	plant	point	produ	type	Q	min	max	obtained	price	from	to
4	Total cost	Minimize	*			joris	t		max				
5			*			joris	tcl						
6													
7													
8	Antoing	Antoing											
9	Clinker	production	At				tcl	900.000	900.000	900.000			
10	Clinker	composition	At				LSF_MgO			99,3			
11	Clinker	composition	At				C3A			8,0			
12	Clinker	composition	At				MgO / tcl			1,8			
13	Process	liquid phase	At				LiqSimple			20,1			
14	Heat	effective consumption	At				GJ / tcl						
15	Heat		At	fuels		fossil/*	GJ/GJ			...			
16	Heat		At	fuels		fluff/*	GJ/GJ			...			
17	Heat		At	fuels		animal meal/*	GJ/GJ			...			
18			At				SiO2/tcl	21,9	21,9	21,9			
19			At				Al2O3/tcl	4,7	4,7	4,7			
20			At				Fe2O3/tcl	2,6		2,6			
21			At				CaO/tcl	66,0	66,8	66,8			
22			At				MgO/tcl			1,8			
23			At			joris/*	tcl/tcl						
24			At			oxidesAl/*	tcl/tcl			6,7%			
25			At				Cl/tcl			0,0053			
26			At				SO3/tcl			1,49			
27			At				(Cl+0.5*SO3)/tcl			0,75			
28													
29													
30	Lixhe	Lixhe											
31	Clinker	production	Lx				tcl	1.300.000	1.300.000	1.300.000			
32	Clinker	composition	Lx				LSF_MgO			95,9			
33	Clinker	composition	Lx				C3A			6,0			
34	Clinker	composition	Lx				MgO / tcl			1,3			
35	Process	liquid phase	Lx				LiqSimple			27,2			
36	Heat	effective consumption	Lx				GJ / tcl						
37	Heat		Lx	fuels		tyres/*	GJ/GJ			...			
38			Lx	fuels		fossil/*	GJ/GJ			...			
39			Lx	fuels		fluff/*	GJ/GJ			...			
40			Lx	fuels		impr saw dust/*	GJ/GJ			...			
41			Lx	fuels		animal meal/*	GJ/GJ			...			
42			Lx				SiO2/tcl	20,7	20,7	20,7			
43			Lx				Al2O3/tcl	5,4	5,4	5,4			
44			Lx				Fe2O3/tcl	3,1		4,9			
45			Lx				CaO/tcl	63,8	63,8	63,8			
46			Lx				MgO/tcl			1,3			
47			Lx			joris/*	tcl/tcl						
48			Lx			oxidesAl/*	tcl/tcl			11,1%			
49			Lx				SO3/tcl			0,25			
50			Lx				(Cl+0.5*SO3)/tcl			0,15			
51													
52	Markets	AFR											
53													
54													

Figure 3.2.: Program screenshot of the constraints sheet with the limitations within the CCMof the raw materials



Index name	Index definition
EuroTotal	Euro + EuroTrsp + EuroOthers + EuroCO2
LSF	100*(CaO-CaOfree*tcl)/(2.8*SiO2+1.18*Al2O3+0.65*Fe2O3)
LSF_SO3	(100*CaO-100*CaOfree*tcl-70*SO3)/(2.8*SiO2+1.18*Al2O3+0.65*Fe2O3)
LSF_P2O5	(100*CaO-100*CaOfree*tcl-118*P2O5)/(2.8*SiO2+1.18*Al2O3+0.65*Fe2O3)
KN	(CaO-1.65*Al2O3-0.35*Fe2O3)/(2.8*SiO2)
SM	SiO2/(Al2O3+Fe2O3)
TM	Al2O3/Fe2O3
Liq	(3*Al2O3+2.25*Fe2O3+MgO+Na2O+K2O+SO3)/tcl
LiqSimple	(3*Al2O3+2.25*Fe2O3)/tcl
Na2Oeq	(Na2O+0.658*K2O)/tcl
c3s	(-7.601*SiO2-6.718*Al2O3-1.430*Fe2O3+4.071*(CaO-CaOfree*tcl)-2.852*SO3+3.684*Na2O+2.424*K2O)/tcl
c2s	(8.601*SiO2+5.068*Al2O3+1.079*Fe2O3-3.071*(CaO-CaOfree*tcl)+2.151*SO3-2.779*Na2O-1.829*K2O)/tcl
c4af	3.043*Fe2O3/tcl
c3a	(2.650*Al2O3-1.692*Fe2O3)/tcl
caso4	(1.700*SO3-2.196*Na2O-1.445*K2O)/tcl
PCI	GJ/t
LHV	GJ/t

Figure 3.3.: Program screenshot of the definitions sheet

Specifically for this PhD study, the program was downgraded to avoid too much variables that could interfere with an objective comparison between the reference and the alternative CCMs. By this downgrade, only the process parameters explained in **section 2.6.**, were incorporated in the constraints sheet. The simulated reference CCM mixtures (**Table 3.1.**) of each Portland clinker plant, indicated as classic CCMs (CCM/Ant,Lxh,Maa/Ref) are very close to the mixtures actually used in these factories to attain the chemical composition of the clinkers described in **table 2.1.**

Table 3.1.: Compositions (wt%) of the reference clinkers made to be fed to the static kiln

	Raw Materials	**Origin**	**CRM**	**Quantity**
CCM/Ant/Ref	Poor limestone	CBR Antoing	CRM/Ant/CP	55.25
	Rich limestone	CBR Antoing	CRM/Ant/CR	37.50
	Fly Ash	CBR Antoing	CRM/Ant/FA	6.38
	Iron Carrier	CBR Antoing	CRM/Ant/IC	0.87
	Sum			100.00
CCM/Lixhe/Ref	Tufa	CBR Lixhe	CRM/Lxh/Tu	79.44
	Loam	CBR Lixhe	CRM/Lxh/Lo	6.63
	Fly Ash	CBR Lixhe	CRM/Lxg/FA	12.34
	Iron Carrier	CBR Lixhe	CRM/Lxh/IC	1.59
	Sum			100.00
CCM/Maa/Ref	Marl	ENCI Maastricht	CRM/Maa/Ma	84.38
	Sabulous Clay	ENCI Maastricht	CRM/Maa/SC	2.90
	Fly Ash	ENCI Maastricht	CRM/Maa/FA	11.02
	Iron Carrier	ENCI Maastricht	CRM/Maa/IC	1.70
	Sum			100.00

The mixture of the raw materials resulting in the specific chemical composition of the three reference CCMs was merely adjusted to obtain the mineralogical and chemical limitations without taking into account the ashes of the fuels that would actually be used to heat up the clinker meal. It will also be demonstrated throughout the complete study of the five ARMs that the specific enrichment factors for each volatile and for each real clinker kiln are different than these specific for the high temperature furnace (**Figure 3.4.**) used to produce the artificial clinkers on lab scale. Nevertheless, it was chosen to retain the DoS-factors (**Table 2.5.**) as well as the specific enrichment factors (ε) and bypass factors (β) specific for each clinker kiln (**Table 2.6.**) in the simulation program to not lose track with the real manufacturing process itself.

Figure 3.4.: The electric high temperature static furnace Carbolite BLF1800

3.4. Artificial clinker production under lab conditions

On top of the sampled Alternative Raw Materials (ARMs) described in **section 3.2.**, representative samples have to be taken of the Classic Raw Materials (CRMs) that are used on a daily base in the three reference clinker factories. These CRMs will be used to generate reference and alternative CCMs based on the mathematical simulations, that will be sintered in the high temperature furnace (**Figure 3.4.**), forming the final artificial clinkers. From each of these three reference Portland clinker factories, four of their most important CRMs (**Table 3.1.**) were collected, more specifically those that act as the main sources of the four critical metal oxides in clinker: CaO, SiO_2, Al_2O_3 and Fe_2O_3.

- CBR Antoing uses two kinds of Limestones: Rich (CRM/Ant/RL) and Poor (CRM/Ant/PL). These act as CaO and SiO_2 sources.

- CBR Lixhe uses Tufa (CRM/Lxh/Tu) which was formed geologically by the precipitation of carbonate minerals. It is much softer than, and extremely porous compared to, regular limestone. Loam (CRM/Lxh/Lo) is used as SiO_2 source.

- ENCI Maastricht uses a typical Marl (CRM/Maa/Ma) or Marlstone which is an impure argillaceous limestone and Sabulous Clay (CRM/Maa/SC) as CaO and SiO_2 source respectively.

All three factories use Fly Ash (CRM/Ant,Lxh,Maa/FA) as Al_2O_3 source and an artificially produced Fe_2O_3 source or Iron Carrier (CRM/Ant,Lxh,Maa/IC).

All of these four CRMs from each clinker factory were sampled at three different points in 2011 spread in time according to EN 196-7 **[2]**. Furthermore, they were homogenised to generate representative CRM materials. Their average chemical analyses performed by XRF (**paragraph 3.5.1.**) are presented in **tables 3.2., 3.3.** and **3.4.** All raw materials were first crushed in a Siebtechnic Disc mill.

Table 3.2.: Average chemical analysis of the CRMs of CBR Antoing

CRM		CRM/Ant/PL	CRM/Ant/RL	CRM/Ant/FA	CRM/Ant/IC
CaO	(wt%)	42.9	50.1	4.8	6.2
SiO_2	(wt%)	15.1	6.4	53.1	8.0
Al_2O_3	(wt%)	2.2	0.9	20.7	1.2
Fe_2O_3	(wt%)	0.9	0.4	7.6	63.7
K_2O	(wt%)	0.68	0.21	1.98	0.20
Na_2O	(wt%)	0.25	0.25	0.87	-
SO_3	(wt%)	0.90	0.57	0.34	1.01
MgO	(wt%)	1.1	0.9	1.6	0.3
LOI 975°C (O_2)	(wt%)	35.04	40.18	16.00	7.61

Table 3.3.: Average chemical analysis of the CRMs of CBR Lixhe

CRM		CRM/Lxh/Tu	CRM/Lxh/Lo	CRM/Lxh/FA	CRM/Lxh/IC
CaO	(wt%)	51.8	5.6	13	10.7
SiO_2	(wt%)	4.7	68.9	46.4	2.6
Al_2O_3	(wt%)	0.4	7.4	18.6	1.3
Fe_2O_3	(wt%)	0.3	3.8	7.0	59.0
K_2O	(wt%)	0.07	1.68	1.93	-
Na_2O	(wt%)	0.02	0.71	0.57	-
SO_3	(wt%)	0.09	0.06	0.57	1.14
MgO	(wt%)	0.7	0.8	1.4	1.1
LOI 975°C (O_2)	(wt%)	42.03	10.1	7.00	5.6

Table 3.4.: Average chemical analysis of the CRMs of ENCI Maastricht

CRM		CRM/Maa/Ma	CRM/Maa/SC	CRM/Maa/FA	CRM/Maa/IC
CaO	(wt%)	50.8	2.66	5.3	18.4
SiO_2	(wt%)	7.1	86.83	50.8	7.2
Al_2O_3	(wt%)	0.8	3.73	23.0	1.6
Fe_2O_3	(wt%)	0.4	2.58	7.4	61.2
K_2O	(wt%)	0.13	1.14	2.36	0.11
Na_2O	(wt%)	0.20	0.14	0.97	0.21
SO_3	(wt%)	0.21	0.05	1.07	0.47
MgO	(wt%)	0.8	0.28	1.8	1.4
LOI 975°C (O_2)	(wt%)	40.18	3.43	4.00	9.33

The different raw materials were brought together in dosages *[wt%]* calculated for the different raw meals by the simulation program (**Section 3.3.**). The calculated dosages to achieve 500 g of CCM were brought together in a vessel used for the analysis of the micro-Deval abrasion resistance **[3]**. This procedure was used to homogenise the raw meal as good as possible before it was thermally treated in a kiln and to simulate the grinding by a ball mill. If fineness measured according to EN 196-6 **[4]**, should not be sufficient (<5000 m²/g), the CCM were further ground in a laboratory ball mill. The chemical analyses performed by XRF of the three reference CCMs are presented in **table 3.5.**

Table 3.5.: Chemical analysis of the reference Cold Clinker Meals (CCM) fed to the static kiln

CCM		CCM/Ant/Ref	CCM/Lxh/Ref	CCM/Maa/Ref
CaO	(wt%)	43.48	45.26	44.79
SiO_2	(wt%)	14.00	12.01	12.83
Al_2O_3	(wt%)	2.89	2.90	3.09
Fe_2O_3	(wt%)	1.84	2.72	2.42
K_2O	(wt%)	0.59	0.41	0.39
Na_2O	(wt%)	0.11	0.13	0.13
SO_3	(wt%)	0.48	0.24	0.28
MgO	(wt%)	1.10	0.88	0.97
TiO_2	(wt%)	0.16	0.21	0.20
P_2O_5	(wt%)	0.12	0.15	0.09
Cl	(wt%)	0.02	0.04	-
LOI 975°C(O_2)	(wt%)	34.89	34.75	34.51
C_{total}	(wt%)	8.98	8.82	8.79
S_{total}	(wt%)	0.36	0.09	0.15

Figure 3.5.: Granulation plate for raw meal preparation before sintering

Figure 3.6.: Air-cooling of the sintered hot clinker meal

Before sintering, the different raw meal compositions were granulated on granulation plates with 5 mm holes (**Figure 3.5.**). Artificial clinker production was performed by sintering the raw meal in an electric high temperature static kiln (Carbolite BLF1800) to 1450 °C at a constant heating rate of 10°C/min. The hot clinker meals were maintained for 1h at 1450 °C after which they were immediately air-cooled to room temperature by open air to form the final clinker (**Figure 3.6.**).

Unfortunately, the typical atmosphere of a Portland clinker kiln could not be simulated due to the technical set-up of the electric kiln which will create specific differences between the artificial and the industrial produced Portland clinker which were already extensively discussed in **section 2.6.** On the other hand, by manufacturing the reference Portland clinkers in the same artificial way as the alternative clinkers, objective comparison between the reference and alternative Portland clinkers was still possible.

Table 3.6.: Chemical analysis and Bogue calculations of the final clinkers produced in a static kiln

Clinker		Cl/Ant/Ref	Cl/Lxh/Ref	Cl/Maa/Ref
CaO	(wt%)	65.90	66.28	66.18
SiO_2	(wt%)	22.27	21.93	21.39
Al_2O_3	(wt%)	4.14	4.40	4.54
Fe_2O_3	(wt%)	3.02	4.21	3.98
K_2O	(wt%)	0.59	0.21	0.33
Na_2O	(wt%)	0.17	0.20	0.21
SO_3	(wt%)	0.89	0.12	0.36
MgO	(wt%)	1.73	1.28	1.52
TiO_2	(wt%)	0.25	0.30	0.30
P_2O_5	(wt%)	0.21	0.24	0.17
LOI 975°C (O_2)	(wt%)	0.48	0.39	0.48
DoS-factor		123.42	27.47	65.24
Alite (C_3S)	(wt%)	66.84	67.52	70.61
Belite (C_2S)	(wt%)	13.44	11.95	8.07
Aluminate (C_3A)	(wt%)	5.86	4.54	5.30
Ferrite (C_4AF)	(wt%)	9.19	12.81	12.11

Table 3.7.: Mineralogical analysis by XRD of the reference clinkers produced in a static kiln

Clinker		Cl/Ant/Ref	Cl/Lxh/Ref	Cl/Maa/Ref
Alite (C_3S)	(wt%)	64.52	65.04	71.33
Belite (C_2S)	(wt%)	19.73	14.93	8.56
Aluminate (C_3A)	(wt%)	1.79	3.68	4.64
Ferrite (C_4AF)	(wt%)	12.86	15.87	14.89
Free Lime (CaO)	(wt%)	0.23	0.23	0.35
Periclase (MgO)	(wt%)	0.39	0.18	0.23
Arcanite (K_2SO_4)	(wt%)	0.32	0.07	-

The chemical analysis performed by XRF together with the simple Bogue calculations **[5]** of these artificial reference clinkers of CBR Antoing, CBR Lixhe and ENCI Maastricht are presented in **table 3.6.** The corresponding mineralogical analyses of the three reference clinkers performed by XRD measurement are represented in **table 3.7.** The methods used to perform these chemical and mineralogical analyses will be described in the next sections.

3.5. Methods to determine the chemical composition of the different materials

The materials which have to be chemically characterised within this PhD study are the Classic (CRMs) and Alternative Raw Materials (ARMs) as well as the cold clinker meals (CCMs) and the final clinkers. XRF, IR spectrometer and TGA/DTA are used as analytical methods to characterise as much as possible the chemical composition of the different materials. These methods gave individually some specific information on the chemistry of each of these materials. The specific measurement error of each method will be further discussed in **section 3.10.**

3.5.1. X-Ray Fluorescence analysis

X-Ray Fluorescence (XRF) analysis is a well-known technique to investigate the chemical composition of metals, glass, ceramics and building materials. The term fluorescence is used as the absorption of radiation of a specific energy results in the re-emission of radiation of a different energy.

The underlying principle is that when materials are exposed to short-wavelength X-rays or gamma rays, ionisation of their atoms take place. By the removal of an electron, the electronic structure of the atom becomes unstable resulting in the replacement of the ejected electron into the lower orbital by an electron of a higher orbital by which energy equal to the energy difference of the two orbitals involved, is released. The energy which is emitted as typical radiation as well as the intensity is characteristic for a specific atom present. By calibrating the equipment using samples with known concentrations of the major, the minor metal oxides and some other components, the typical radiations of these components together with their intensities can be recalculated to the concentration *[wt%]* of the specific atoms present in the investigated material. The XRF analyses used within this PhD study were performed on a Philips PW2404 (**Figure 3.7.**) in accordance to EN 197-2 **[6-7]**. The Philips PW2404 is equipped with a sequential WDXRF-spectrometer and a 4kW Rh-tube. UniQuant calculation models were used including the correction for Loss Of Ignition (LOI) and normalisation.

Representative samples out of the material that has to be analysed, were first ground for two minutes in a Siebtechnic rotary disc mill after which the material was pressed into a stainless steel sample holder with an internal diameter of 35 mm and an external diameter of 51 mm. Sample preparation was done by using a Polysius APM Plus automatic grinding & pressing unit. The sample preparation method of some typical materials is presented as example in **table 3.8.**

Table 3.8.: Polysius APM Plus sample preparation for XRF

Material		Clinker	Sand/Concrete	Fly ash
Mill speed for primary grinding	tpm	1070	1070	1070
Quantity grinding aid for primary grinding	g	2	2	2
Grinding time for primary grinding	S	300	330	300
Quantity grinding aid for blind sample	g	0	0	0
Grinding time for blind sample	sec	0	0	0
Quantity grinding aid for main grinding	g	1	1	1
Grinding time for main grinding	sec	150	150	150
Quantity grinding aid for finish grinding	g	1	1	1
Grinding time for finish grinding	sec	30	30	30
Emptying time of fine grinding mill	sec	8	8	8
Pressure holding time	sec	5	5	5
Minimum value of tablet thickness	mm	4	4	4

Chemical analyses of the used CRMs, reference CCMs as well as their final clinkers were already presented in **section 3.4.** They will be used as reference for the evaluation of the ARMs, alternative CCMs and alternative clinkers that will be further discussed in the next chapters.

3.5.2. Thermogravimetric analysis / Differential thermal analysis

Thermogravimetric analysis (TGA) linked to Differential Thermal Analysis (DTA) is used within this PhD study to evaluate how materials react on the heat treatment by a Portland clinker process. It is especially useful to quantify some specific chemical components and to evaluate part of the chemical reactions which will take place during the heating up to 1450°C. An additional Differential Thermal Analysis (DTA) is convenient because this method can detect and quantify either exothermic or endothermic changes in the samples relative to an inert reference which could unveil the presence of some typical chemical compounds. These two techniques are combined in the Netzsch STA 449F3 apparatus (**Figure 3.8.**). To simulate the typical atmosphere of a clinker kiln, a typical gas mixture of 95 v% N_2 and 5 v% O_2 was used during analysis TGA/DTA. Especially for the Fe_2O_3 source CRMs, the gas mixture was adapted to 100 v% inert N_2 atmosphere to identify possible oxidation reactions.

Figure 3.8.: The TGA/DTA apparatus Netzsch STA 449F3

The TGA part of the TGA/DTA instrument is a balance that continuously weighs a sample as it is heated to temperatures of up to 1450°C.

The DTA part on its turn consists out of two thermocouples connected to a voltmeter. One thermocouple is placed underneath a reference which was in this case an empty inert Al_2O_3 crucible, while the other is placed underneath the crucible containing the sample of the material under study. As the temperature is increased, there is a brief deflection of the voltmeter if the sample is undergoing a phase transition.

Approximately, 50 mg of the material under study was weighed after a tare was performed to eliminate the mass of the crucible. The temperature was gradually increased from 25°C to 1450°C at 10°C/min. The analyses were always corrected as a function of the presence of physical bound H_20. The mass losses *[wt%]* were recalculated to the mass at 100°C. No information was extracted out of the TGA/DTA analyses above 1250°C because there was a suspicion of the presence of a buoyancy effect. The buoyancy effect is an increase or decrease in weight, which is not related to chemical or physical changes in the sample and which is observed with all conventional thermo balances to some degree. The term buoyancy, which is generally used, is actually a combination of factors: True buoyancy effects, convection currents, gas flow drag and gas velocity effects, thermo molecular forces, thermal effects on the balance mechanism. The buoyancy effect is as much as possible avoided by the use of the reference. Nevertheless as of 1300°C, the melting of the solid state takes place (**Section 2.3.**) by which the densities of the solid as the liquid phase will have their impact on the mass measurement which can't be corrected by the reference (**Figure 3.9.**). A solid object submerged in the liquid phase will experience greater pressure at the bottom than at the top explaining the presence of a possible buoyancy effect.

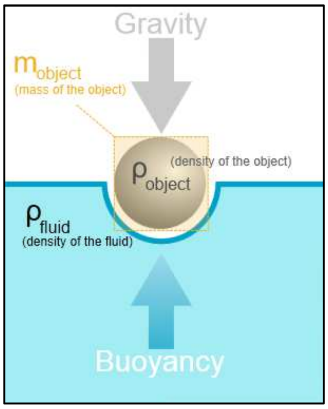


Figure 3.9.: The forces at work in buoyancy (Ref. Wikipedia [cited 2014 September 22])

In **table 3.9.**, some interesting evaluated parameters out of TGA/DTA analysis are enlisted for the Classic Raw Materials (CRMs) of each of the three reference clinker kilns. TGA/DTA measurements were used to determine the CO_2 *[wt%]* coming from the decarbonation of $CaCO_3$, the combined amount *[wt%]* of organic compounds and the chemically bound H_2O which are liberated during heating up of these materials in the specific gas mixture. Based on the measured CO_2 *[wt%]*, a $CaCO_3$ *[wt%]* (TGA Der) can be derived which is logically the biggest in the limestone materials (**Table 3.9.**).

The $CaCO_3$ *[wt%]* is calculated by the molecular masses of both CO_2 and $CaCO_3$, based on the theorem that the measured CO_2 *[wt%]* arises exclusively from the decarbonation of $CaCO_3$. Nevertheless, this calculation can be affected significantly by the decarbonation of dolomite, if present, although this will occur at slightly lower temperatures.

Table 3.9.: TGA/DTA evaluation of all the used Classic Raw Materials (CRMs) of CBR Antoing, CBR Lixhe and ENCI Maastricht.

CRM	Inorg CO_2 700-900°C	Organic + H_2O 200-700°C	$CaCO_3$	$[Ca,Mg]CO_3$*	Decarb E	Decarb E**
	TGA (wt%)	TGA (wt%)	TGA Der (wt%)	XRF Der (wt%)	DTA (µVs/mg)	TGA Der (J/g)
CRM/Ant/RL	39.9	1.0	90.7	91.3	226.2	1618
CRM/Ant/PL	34.9	1.2	79.4	78.8	219.4	1415
CRM/Ant/IC	4.8	4.0	10.9	11.7	28.5	196
CRM/Ant/FA	0.0	4.7	0.0	14.4	0.0	0
CRM/Lxh/Tu	39.5	3.4	89.8	93.8	251.8	1601
CRM/Lxh/Lo	4.2	3.1	9.6	11.7	37.8	171
CRM/Lxh/IC	6.2	3.1	14.1	21.4	31.2	252
CRM/Lxh/FA	0.0	6.0	0.0	21.9	0.0	0
CRM/Maa/Ma	40.0	1.1	91.0	92.3	255.1	1622
CRM/Maa/SC	1.1	1.99	2.5	5.4	12.2	46
CRM/Maa/IC	4.1	1.1	9.3	35.8	6.6	167
CRM/Maa/FA	0.0	4.0	0.0	36.6	0.0	0

* Theoretical calculation of the intrinsic $[Ca,Mg]CO_3$ that could be present in the material based on the present CaO *[wt%]* and MgO *[wt%]*

** Theoretical calculation of the intrinsic decarbonation energy that could be required if all inorganic CO_2 measured in the material would be present as $CaCO_3$ *[wt%]*

The calculation of the $[Ca,Mg]CO_3$ *[wt%]* derived from the XRF analysis $[Ca,Mg]CO_3$ (XRF Der), based on the theorem that all the CaO *[wt%]* and MgO *[wt%]* present in the sample is carbonated, can help to identify this deviation as well as demonstrate the introduction of decarbonated CaO or MgO by classic or alternative raw materials without heating. The bigger, the deviation between $CaCO_3$ (TGA Der) and $[Ca,Mg]CO_3$ (XRF Der), the more decarbonated CaO *[wt%]* and MgO *[wt%]* will be present and the more potential a material has to decrease the inorganic CO_2 emission of the Portland clinker production. Also the decarbonation energy (Decarb E) measured by DTA analysis is visualised in **table 3.9.** Also out of the TGA analysis, the Decarb E can be derived by TGA from the known reaction enthalpy of 1782 kJ/kg for $CaCO_3$ stated by Taylor **[5]** and $CaCO_3$ *[wt%]* derived from TGA analysis $CaCO_3$ (TGA Der). TGA/DTA analyses of the CRM are quite straightforward.

The limestones, tufa and marl have an endothermal decarbonation area between 700 and 900°C which is quantified in **table 3.9.** A good match is found between XRF analysis and the CO_2 loss by TGA/DTA by comparing the $CaCO_3$ *[wt%]* derived from TGA analysis and the intrinsic $[Ca,Mg]CO_3$ *[wt%]* derived from XRF analysis. This indicates that Ca is almost completely present as $CaCO_3$.

The TGA/DTA analyses (**Figure 3.10.**) of loam and sabulous clay also show small but distinct quantifiable decarbonation area between 650 and 800°C (**Table 3.9.**).

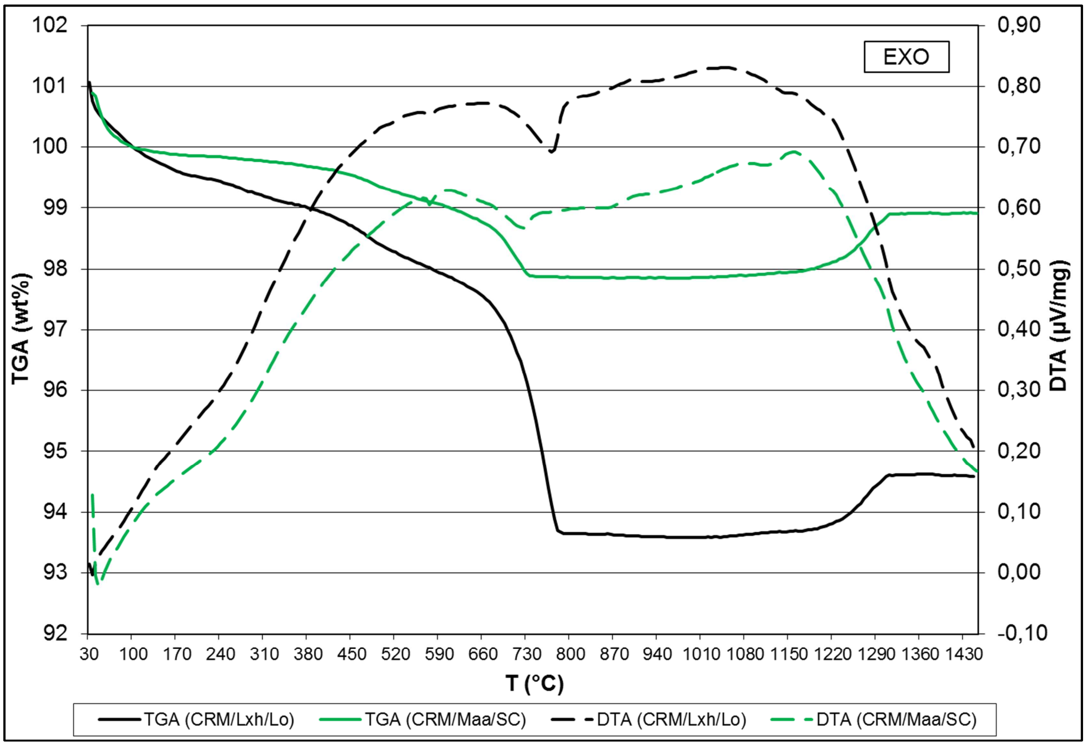


Figure 3.10.: TGA/DTA analysis of the classic raw materials, ARM/Lxh/Lo and ARM/Lxh/SC

A deviation between the $CaCO_3$ *[wt%]* derived from TGA/DTA analysis $CaCO_3$ and $[Ca,Mg]CO_3$ *[wt%]* derived from XRF analysis is noticed, indicating that not all Ca and Mg are present in a carbonated form. The quantification of the loss of H_2O (i.e. the amount of chemically bound water) is quite difficult (**Figure 3.10.**). Because no significant exothermic reactions could be observed in **figure 3.10.**, it could be stated that there is no or only negligible amounts of organic material present in loam or sabulous clay. The changes registered in the TGA/DTA analysis (**Table 3.9.**) which are normally attributed to the combined loss of organics and H_2O may therefore be considered to be mainly due to the evaporation of chemically bound H_2O.

The Fe_2O_3 sources are difficult to evaluate due to the fact that they mostly concern artificially made raw materials, derived from waste. In inert atmosphere, the loss of mass is two times bigger than in the presence of 5 v% O_2 what indicates that the different forms of Fe present in the Fe_2O_3 sources perform oxidation reactions while heating. TGA curves of the CRM/Lxh/IC and CRM/Maa/IC show small decarbonation reactions that can be quantified in the same way as for the other CRMs (**Table 3.9.**).

The fly ashes have an opposite behaviour in the two atmospheres, with a bigger loss of mass in oxidative than in inert atmosphere indicating the presence of organic material. The mass loss in inert atmosphere indicates the formation of organic volatiles in absence of O_2. Because fly ash is a material which has had already a thermal treatment at high temperatures, no decarbonation related mass losses are detected (**Table 3.9.**) which is demonstrated by the big difference between $CaCO_3$ *[wt%]* derived from TGA/DTA analysis and $[Ca,Mg]CO_3$ *[wt%]* derived from XRF analysis. Therefore it can be stated that the CaO and MgO incorporated in the fly ash are present in decarbonated form. Because there is a loss of organic volatiles and CO_2 visible in the whole temperature range between 400°C and 1450°C under inert and oxidative atmosphere, the presence of char is indicated.

In **table 3.10.,** these parameters are also listed for the reference CCM compositions composed out of the primary raw materials (**Table 3.9.**). These will be used as reference to evaluate if inorganic CO_2 decrease could be recorded or other interesting reactions could occur by the use of the Alternative Raw Materials.

Table 3.10.: TGA evaluation of the Reference Cold Clinker Meals of CBR Antoing, CBR Lixhe and ENCI Maastricht

CCM	Inorg CO_2 700-900°C	Organic + H_2O 200-700°C	$CaCO_3$	Inorg CO_2 Raw Meal	$CaCO_3$ Raw Meal
Mat	TGA (wt%)	TGA (wt%)	TGA Der (wt%)	TGA (wt%)	TGA Der (wt%)
CCM/Ant/Ref	34.0	0.6	77.3	34.3	78.0
CCM/Lxh/Ref	32.5	0.5	73.9	31.8	72.2
CCM/Maa/Ref	34.2	0,0	77.7	33.9	77.0

By comparing the TGA/DTA analyses of the raw materials and the Cold Clinker Meals (CCMs), an extra check can be made whether or not the estimation of the inorganic CO_2 emission of the reference CCMs was properly performed. This is done by calculating the $CaCO_3$ out of the TGA/DTA analysis of the CCMs and calculating the $CaCO_3$ out of the TGA/DTA analysis of the Raw Materials (RM) (J/g) taking in account the calculated compositions of the reference CCMs (**Table 3.1.**).

The fact that these two totally separated calculations gave a comparable result, proofs that the interpretation of the TGA/DTA analyses was done in an objective way and could therefore be used to evaluate the inorganic CO_2 reduction by the use of the ARMs.

3.5.3. IR spectrometer

Total Carbon and Sulfur analysis of all materials were performed on an IR spectrometer Leco CS230 (**Figure 3.11.**). It uses high temperature combustion in the presence of some typical catalysts followed by infrared detection to determine the carbon and sulfur *[wt%]* simultaneously. Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies. These resonant frequencies are partly related to the mass of the atoms that are measured. The total carbon *[wt%]* and sulfur *[wt%]* analyses of the reference Cold Clinker Meals (CCMs) of CBR Antoing, CBR Lixhe and ENCI Maastricht are presented in **table 3.5.**

Figure 3.11.: The IR spectrometer apparatus Leco CS230

3.6. Determination of the mineralogical composition of the different materials

Solid matter can be described as amorphous when atoms are arranged in a random way similar to the disorder we find in a liquid or as crystalline when atoms are arranged in a regular pattern. About 95% of all solid materials can be described as crystalline. A crystal structure can be presented as an infinitely repeating box containing one or more atoms arranged in 3-dimensions (x,y,z) by repetition, known as unit cell. There are seven unit cells. The unit cell is calculated from the simplest possible representation of molecules, known as the asymmetric unit. The asymmetric unit is translated to the unit cell through symmetry operations, and the resultant crystal lattice is constructed through repetition of the unit cell infinitely in 3-dimensions. There are fourteen so called Bravais lattices divided over seven lattice systems. The lattice parameters are the lengths of the cell edges (a,b,c) and the angles between them (alpha, beta, gamma). The symmetry properties of the crystal are embodied in its space group. There are 230 distinct space groups based on the fourteen lattice types.

The mineralogical composition of a material describes its build-up out of different crystalline compounds. In Portland clinker, the major hydraulic phases are alite, belite, celite (aluminate) and ferrite as described in **section 2.4.** These hydraulic phases can consist each out of monoclinic, cubic and orthorhombic crystal systems. The mineralogical analysis unveiling the different hydraulic phases present in Portland clinker is very important to determine the effectiveness of the sintering process and reactivity of the final clinker. When investigating the influence of an Alternative Raw Material (ARM) on the Portland clinker production, it is very important to evaluate its impact on the mineralogical composition of the Portland clinker. Nevertheless, quantification of this mineralogical composition is difficult. Two techniques were used to investigate the mineralogical composition of the reference and alternative clinkers: XRD-analysis and simple Bogue calculations.

The most widely used method of estimating the possible phase composition of Portland cement is by Bogue calculations which will be presented later. They are still widely used in practice as steering parameters within the clinker production process. However, it is well known that the calculation by this method may be far from reality. This is mainly due to the fact that the four main clinker phases are solid solutions with compositions significantly different from the stoichiometric composition of the pure phase. Furthermore, small errors in chemical analysis are magnified and lead to large variations in the calculation of phase abundance. Their accuracy can be improved by using the so called refined Bogue calculations **[5]**, which take the actual composition of the phases into account. The specific measurement error of the simple Bogue calculations is related to the chemical measurement method that also will be discussed in **section 3.10.**

XRD analysis allows direct measurement of the crystalline phase content of the Portland clinker itself. It can distinguish the different mineralogical forms of the hydraulic phases **[16]**, although within this PhD study each of the major hydraulic phases will be expressed as the total of its mineralogical forms. On the other hand, XRD measurement is very sensitive to sample preparation (grinding, preferred orientation, etc.) and is operator dependant. Rietveld refinement is mostly performed by fitting and accordingly adjusting. The measured mineralogical composition can therefore significantly derive from the actual mineralogical composition present. XRD analysis is therefore quite successful to follow trends in real clinkers out of the same kiln by comparison and less successful to quantify the actual mineralogical composition of an individual Portland clinker sample. Nevertheless the accuracy and precision (**Section 3.10.**) of an XRD-measurement can strongly be improved by confining it to one XRD-apparatus and one experienced operator. The specific measurement error of the XRD analysis will be further discussed in **section 3.10.** Within the confines of the current study, only the total alite, belite phases as also the free lime will be used to compare the reference and alternative clinkers with each other. The other major and minor phases determined by XRD analysis will only be employed in a qualitative way to describe the mineralogy of the different artificial Portland clinker samples. In view of the evaluation of the possible influence of the ARM on the mineralogy of the clinkers, both methods were used to demonstrate differences in the mineralogical composition of the reference clinkers with the alternative clinkers by comparison. The difference of an alite or belite phase calculated by a simple Bogue calculation with the same phase measured by XRD on an artificial clinker sample was compared to a corresponding difference on a reference clinker indicating a possible mineralogical impact of an ARM.

3.6.1. X-Ray Diffraction analysis

X-Ray Diffraction (XRD) is a tool used to determine the atomic and molecular structure of a crystal. A prepared sample is mounted on a goniometer and is gradually rotated while being bombarded with X-rays. When an electron is placed in an alternating electromagnetic field, the electron will begin to oscillate with the same frequency as the electromagnetic field. By bombarding the electron with X-rays, the electron starts to oscillate with the same frequency as the incoming beam. When the electrons within a prepared sample are bombarded like that, the resulting waves will be out of phase and will interfere with each other in a destructive way which results that no energy will leave the solid sample. However atoms that are arranged in a regular pattern as in a crystal structure will demonstrate constructive interference by which X-ray beams will leave the sample in specific directions. These are the so called reflections. The specific direction of these reflections are determined by Bragg’s law (**3.0**) where d represents the spacing between diffracting planes, θ the x-ray incidence angle, λ the wavelength of the characteristic x-ray beam and n any integer.

$$2d \sin\theta = n \cdot \lambda \text{ (Braggs law)} \qquad \mathbf{(3.0)}$$

By these reflections, the mean positions of the atoms in a crystal can be determined, as well as their chemical bonds, their disorder and various other information.

The XRD analyses performed within this PhD study are performed on a Bruker D8 ADVANCE (**Figure 3.12.**) and handled always by the same experienced operator. The used tube power which produces the X-rays consumes 40kV and 55mA. The sample holder spins at 30 rpm within the magnetic field. The configuration is equipped with the LynxEye Point detector in scanning mode (1D). The X-ray diffraction pattern was measured with a vertical Theta-Theta Goniometer based on the Bragg-Brentano geometry with $-110° < 2\theta < 168°$ goniometer control using a step size of 0.02° with a X-ray Cu-tube (1.5456Å). The divergence and detector slits were set on 4°.

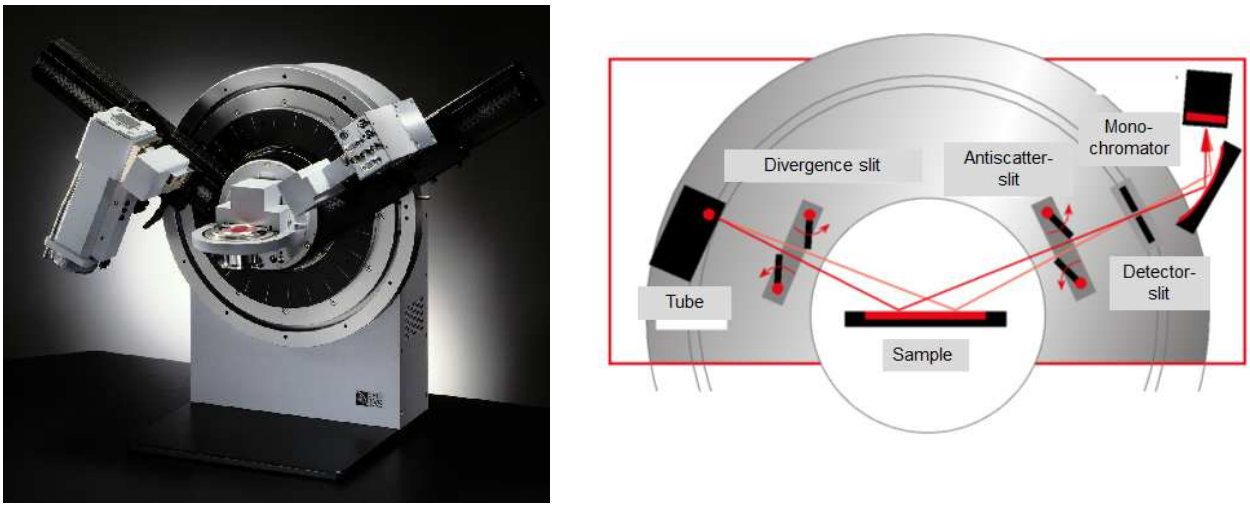


Figure 3.12.: The XRD apparatus Bruker D8 ADVANCE

Rietveld refinement using Topas (DIFFRAC.SUITE) profile and structure analysis software was used to quantify the different mineralogical compounds present in the Portland clinker out of the numerous relections generated by the XRD measurement. Rietveld refinement uses the intensity and the angle of the different produced reflections but also crystal structure models partly presented in **table 3.11.** Background, zero shift, scaling factor, cell parameters and shape parameter were refined. Background was typically refined by a cosine Chebyshev function of 5 polynomial terms.

Table 3.11.: Used crystal structures for Rietveld Refinement of the XRD spectra

Clinker	Formula	Crystal System	ICSD code	PDF code
Alite	Ca_3SiO_5	Monoclinic / M_3	94742	01-070-8632
Belite β	Ca_2SiO_4	Monoclinic / β	79550	01-083-0460
Belite α'_H	Ca_2SiO_4	Orthorombic / α'_H	81097	01-086-0399
Aluminate	$Ca_3Al_2O_6$	Cubic	1841	01-070-0839
Aluminate	$Ca_{8.5}NaAl_6O_{18}$	Orthorombic	1880	00-032-0150
Ferrite	Ca_2AlFeO_5	Orthorombic	51265	01-070-2764
Free Lime	CaO	Cubic	75786	01-082-1691
Periclase	MgO	Cubic	9863	01-071-1176
Arcanite	K_2SO_4	Orthorombic	2827	01-070-1488
Aphthitalite	$K_3Na(SO_4)_2$	Trigonal	26018	01-074-0398

Sample preparation was done by grinding 50 g of the sample for two minutes in a rotary disk mill to pass the 45µm sieve and to load it on a stainless steel sample holder using the back loading technique in order to minimise preferred orientation effects. The mineralogical composition of the artificial clinkers measured by XRD analysis of the three reference CCMs were already presented in **table 3.7.** The complete XRD analysis of some of the reference and alternative clinkers produced artificially in the electric high temperature static furnace are presented in **Appendix A**.

3.6.2. Simple Bogue calculations [5]

The most widely used method of estimating the potential phase composition of a Portland clinker is the Bogue calculation. They are used to calculate the approximate proportions of the four main minerals in Portland cement clinker (**Section 2.4.**) out of the proportions of the four main oxides. Although the result is only approximate, the calculation is extremely useful and widely-used at daily base in the cement industry. Because of their simplicity and their practical use, they were preferred instead of the refined Bogue calculations, to not lose track with the real Portland clinker manufacturing process itself. The simple Bogue calculations assume that the four main clinker minerals are pure minerals with compositions, alite **(1)**, belite **(2)**, aluminate **(3)** and ferrite **(4)** **[5]** as already explained in detail in **section 2.4.** According to the mineral compositions, ferrite is the only mineral which contains iron. The iron *[wt%]* of the clinker therefore fixes the ferrite *[wt%]*. Aluminate is fixed by the total alumina *[wt%]* of the clinker, minus the alumina *[wt%]* in the ferrite phase. Silica is present in belite. The lime *[wt%]* required to form belite out of the total silica *[wt%]* of the clinker is calculated. The surplus *[wt%]* of lime will be allocated to belite, converting some of it to alite.

This theorem is presented in the following equations **(3.1-3.4)** which are known as the simple Bogue calculations.

$$C_3S = 4.0710 \cdot CaO - 7.6024 \cdot SiO_2 - 1.4297 \cdot Fe_2O_3 - 6.7187 \cdot Al_2O_3 \quad \textbf{(3.1)}$$

$$C_2S = 8.6024 \cdot SiO_2 + 1.0785 \cdot Fe_2O_3 + 5.0683 \cdot Al_2O_3 - 3.0710 \cdot CaO \quad \textbf{(3.2)}$$

$$C_3A = 2.650 \cdot Al_2O_3 - 1.692 \cdot Fe_2O_3 \quad \textbf{(3.3)}$$

$$C_4AF = 3.0432 \cdot Fe_2O_3 \quad \textbf{(3.4)}$$

Bogue calculations will not give the real amounts of the four main clinker phases present in the clinker. The real amounts have to be determined by XRD analysis. The deviation between the amounts obtained via these Bogue calculations can differ from the amounts determined by XRD analysis and is caused by different reasons which were already partly described in **chapter 2**. Nevertheless, the differences in mineralogical composition between both methods will provide essential information for the evaluation of the impact of the five ARMs on the mineralogy of the Portland clinker.

The simple Bogue calculations out of the chemical composition of the final reference clinkers of CBR Antoing, CBR Lixhe and ENCI Maastricht presented in **table 3.6.** and their difference towards the mineralogical composition demonstrated in **table 3.7.** will be used as base to perform this evaluation.

3.7. Methods to determine the energy consumption of the different materials

When materials are heated up, they consume energy to increase in temperature. During the increase in temperature, several chemical reactions can occur but also changes between different phases of matter (solid, liquid, gas, and plasma) which both can influence the energy consumption during heating. Some typical reactions take place in well-known temperature ranges. Two analytical methods were used to evaluate the energy consumption of the different materials. By comparing the energy consumption of the CRMs and reference CCMs to the ARMs and alternative CCMs, an evaluation can be made whether or not the use of an alternative material could be beneficial towards energy consumption of a Portland clinker kiln. These two used methods are TGA/DTA analysis and DSC analysis. Their specific measurement errors will be discussed in **section 3.10.**

3.7.1. Thermogravimetric analysis / Differential thermal analysis

This technique was already described in **paragraph 3.5.2.** and was based on the same equipment, the Netzsch STA 449F3 apparatus (**Figure 3.8.**) as well as the determination of the energy consumption was based on the same measurements. One of the energies which could clearly be distinguished out of the TGA/DTA analysis, is the endothermal decarbonation energy of $CaCO_3$ (Decarb E) although the DTA measurement could only be evaluated in a qualitative way because the measurement error of the DTA analysis is too big to be used for quantitative analysis (**Section 3.10.**). On the other hand, the Decarb E can be derived from the known reaction enthalpy of 1782 kJ/kg for $CaCO_3$ stated by Taylor **[5]** together with the $CaCO_3$ *[wt%]* derived out of the TGA analysis.

Table 3.12.: TGA/DTA evaluation of the reference Cold Clinker Meals
of CBR Antoing, CBR Lixhe and ENCI Maastricht (RM=Raw materials)

CCM	Decarb E	Decarb E RM	Decarb E	Decarb E RM
Mat	DTA (μVs/mg)	DTA (μVs/mg)	TGA Der (J/g)	TGA Der (J/g)
CCM/Ant/Ref	213.4	206.3	1378	1390
CCM/Lxh/Ref	189.3	203.0	1318	1287
CCM/Maa/Ref	219.3	215.7	1385	1373

As can be noted in **table 3.12.**, the Decarb E *[J/g]* derived from the TGA analysis relates in the same way as the Decarb E’s *[μVs/mg]* measured by DTA.

By using the TGA/DTA analyses (**Table 3.9.**) of the raw materials and the TGA/DTA analyses of the Cold Clinker Meals (CCMs) (**Table 3.10.**), an extra check can be made whether or not the estimation of the endothermal Decarb E of the reference CCMs was properly estimated. This is done by calculating the Decarb E of $CaCO_3$ out of the TGA/DTA analysis of the CCMs (Decarb E) or calculating them derived out of the TGA/DTA analysis of the Raw Materials (RM) taking in account the calculated compositions out of **table 3.1.** (Decarb E RM). These decarbonation energies are also listed in **table 3.12.** The fact that these two totally separated calculations based on different measurements gave a comparable result, proofs that the interpretation of the TGA/DTA analyses was done in an objective way and could therefore be used to evaluate the Decarb E of the alternative CCMs.

Whereas the Decarb E of $CaCO_3$ can be rather easily derived from the TGA/DTA analysis, this is not the case for the quantification of the energy necessary for the evaporation of chemically bound H_2O (i.e. the amount of chemically bound water). Assuming there is no or only negligible amount of organic material present in loam or sabulous clay, the changes registered in the TGA analysis (**Table 3.9.**) which are normally attributed to the combined loss of organics and H_2O, may be considered to be mainly due to the evaporation of chemically bound H_2O. For other materials which contain organic substances as the fibrecement material, the evaporation of chemically bound H_2O by TGA-analysis is too difficult to be distinguished from the thermal degradation of organic substances and has to be quantified in another way which will be further discussed in **chapter 7**.

Nevertheless, for both types of materials, H_2O will be chemically bound in different ways by which quantification of endothermal dehydration energy out of TGA-analysis is quite difficult. Therefore another method will be used: Differential Scanning Calorimetry (DSC) (**paragraph 3.7.2.**).

For the determination of the exothermal energy coming from the thermal decomposition of organic substances, a bomb calorimeter will be used (**paragraph 3.7.3.**).

3.7.2. Differential scanning calorimetry analysis

Differential scanning calorimetry or DSC is a thermo analytical technique by which the difference in the amount of heat required to increase the temperature of a sample and a reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. The difference in heat consumption between the reference and the sample will demonstrate the energy, specific reactions within the sample will deliver (exothermic) or consume (endothermic) at a certain temperature. A Mettler Toledo Star DSC (**Figure 3.13.**) was used to perform this quantitative measurement in comparison to a reference. To determine the energy required to liberate chemically bound H_2O present in hydrated cement, Differential scanning calorimetry (DSC) analysis will be used. This method was used for the investigation of Fibrecement ARM (**Chapter 7**) by measuring several cement pastes with different W/C ratios as an effort to estimate the total dehydration energy. This will be further discussed in **paragraph 7.6.5.**

Figure 3.13.: The DSC apparatus Mettler Toledo Star DSC

3.7.3. Bomb calorimetry

An IKA Bomb Calorimeter system C7000 (**Figure 3.14.**) was used to measure the gross calorific values of the specific alternative CCMs and some typical ARMs which contain organic compounds.

Figure 3.14.: The DSC apparatus Mettler Toledo Star DSC

A bomb calorimeter is used to measure the heat created by a sample burned under an oxygen rich atmosphere in a closed vessel, which is surrounded by water, under controlled conditions. This technique will be used on materials containing organic substances which is the case for fibrecement materials (**Paragraph 7.6.5.**).

A bomb calorimeter is often used to determine the energy that organic compounds could deliver during the heating up by an exothermal chemical reaction. These gross calorific values or absolute values of the specific energy of combustion are determined according to ISO 1928 **[8]**.

About 1g of solid or liquid matter is weighed into a crucible and placed inside a stainless steel container. The decomposition vessel or bomb is filled with 30 bar of oxygen. The sample is ignited by a cotton thread connected to a solid ignition wire inside the decomposition vessel and burned. During combustion, the core temperature in the crucible can reach 1000 °C. All organic matter is burned and oxidised under these conditions.

To correct this temperature increase, the effective heat capacity of the used calorimeter has to be measured in calibration experiments by combustion of certified benzoic acid under similar conditions. The corrected temperature increase is determined from observation of temperature before, during and after combustion reaction takes place.

3.7.4 Isothermal calorimetry

To determine the reactivity of a Portland clinker sample, a TAM AIR isothermal heat conduction calorimeter (TA instruments) (**Figure 3.15.**) was used. Each channel of this calorimeter is constructed in twin configuration with one side for the test sample and the other side for an inert reference (quartz sand). Beneath each channel, heat flow sensors are installed to measure the heat production rate.

Figure 3.15.: isothermal heat conduction calorimeter TAM AIR (TA instruments)

To have an idea of the reactivity of the clinker, Portland cement was made out of different artificial Portland clinker samples (**Section 3.4.**). The selected artificial clinkers were first ground during 4 minutes in a Siebtechnic Disc mill after which natural anhydrite was added to increase the total SO_3 *[wt%]* of the mix up to 3.0 wt%. Together with the added anhydrite, the clinker was ground for an additional 6 minutes. Out of each of **the** resulting Portland cement samples, 14 g of paste with a W/C ratio of 0.4 was made and filled in a sample ampoule to determine the hydration heat during the first 7 days by an isothermal calorimetric test at 20°C.

3.8. Particle Size Distribution

The particle size distribution (PSD) of a powder or granular materials is a list of values that defines the relative mass of particles present according to size. PSD is also known as grain size distribution. PSD influences the physical and chemical properties of solids. The most common used PSD determination method is sieve analysis, where powder is separated on sieves of different sizes. Also laser diffraction analysis is used especially to characterise materials containing smaller particles.

The PSD is usually determined over a list of size ranges that covers nearly all the sizes present in the sample. Within this PhD study, the PSD is presented in "cumulative" form, in which the total of all sizes "passed" by a single notional "sieve" is given for a range of sizes.

PSD was used for two reasons within research. It was employed to evaluate crushing and separation actions to improve the ARM quality. Furthermore it was also interesting to use this information to understand the influence of the physical properties of an ARM on the burnability of a CCM. Because it is interesting to get information of the coarser particles as well as of the finer particles sieve and laser diffraction analysis were used. Their specific measurement errors will be discussed in **section 3.10.**

3.8.1. Sieve analysis

A sieve analysis (or gradation test) is a method used to determine the PSD of a granular material. A sieve analysis can be performed on any type of non-organic or organic granular matter, down to a minimum size depending on the exact method. The equipment used to perform the sieve analysis within this PhD study was a Haver & Boecker UWL 400 apparatus (**Figure 3.16.**).

Figure 3.16.: The sieve analysis apparatus Haver & Boecker UWL 400

The sieve analysis involves a tower of sieves with wire mesh cloth (screen). A representative weighed sample is poured into the top sieve which has the largest screen openings. Each lower sieve in the column has smaller openings than the one above. At the base is a round pan, called the receiver. The column is placed in a mechanical shaker. The shaker shakes the column, for a standardised fixed amount of time. After the shaking, the material on each sieve is weighed. The weight of each sieve is then divided by the total weight to give a percentage retained on each sieve. The results of this test are mostly provided in graphical form to identify the type of gradation of the aggregate. On the graph, the sieve size scale is normally logarithmic. The complete procedure for this test is outlined in EN 1097 (2013) **[9]**, EN 12620 (2002) **[10]**, EN 13043 (2002) **[11]**.

But as most technics and methods, sieve analysis has also a downside. Primarily, for material finer than 150 µm, dry sieving can significantly be less accurate. The reason for this inaccuracy has its origin in the fact that the mechanical energy required to make particles pass through an opening and the surface attraction effects between the particles themselves and between particles and the screen increase as the particle size decreases.

Secondly, sieve analysis ignores the possibility that particles can be flat or elongated. Particles will pass through the square openings when the smallest particle dimension is less than the size of the square opening in the screen. For elongated and flat particles, a sieve analysis will therefore not yield reliable results, as the particle size reported will assume that the particles are spherical, where in fact an elongated particle might pass through the screen, but would be prevented from doing so if it presented itself side-on. For both problems, laser diffraction analysis could be a useful alternative.

3.8.2. Laser diffraction analysis

Laser diffraction analysis or laser diffraction spectroscopy is a technique which uses the diffraction pattern of a laser beam passed through a powder, to measure the size of its particles. Laser diffraction analysis is based on the theory of Fraunhofer diffraction. Within this theory, the intensity and angle of the light scattered by a particle is directly related to the size of the particle. Although the Fraunhofer model is not suited for the quantification of very small particles (< 5 µm), Laser diffraction analysis will nevertheless provide interesting information of the PSD between 5 and 250 µm.

Figure 3.17.: The laser diffraction analysis apparatus Sympatec Helos Vario

The powder is passed through a laser beam after which the diffracted light is analysed as a function of the angle and the intensity of the scattered light. After these measurements, the results are treated by mathematical algorithms to generate a PSD graphically comparable to that generated by a sieve analysis. Because the intensity of the diffraction pattern is very low and the smallest uncertainties would result in large errors, it is important to get the best possible intensity data before using the algorithms.
Within this research topic, a Sympatec Laser diffraction Helos Vario (**Figure 3.17.**) was used.

3.9. Method to determine the presence of organic volatiles originating out of the heating of some typical materials

For the analysis of the formed volatiles after thermal degradation of some typical materials that contain organic compounds, a specific test setup was designed to heat up these materials as fast as possible to a

specific temperature. The selected specific temperatures that were considered for these tests result from the evaluation of the TGA/DTA analyses described in **paragraph 3.5.2.** and some literature study on the decomposition of the organic compounds known to be present in these materials. In this specific test setup, a quartz reactor was loaded with 400 mg of sample under a gas flow of 95 v% He and 5 v% O_2 which imitates or as already explained in **paragraph 3.5.2.**, the typical atmosphere of a clinker kiln.
A preheated tubular furnace was then quickly raised up around the reactor resulting that the final temperature was reached within 5 minutes. The organic volatiles generated over this period were analysed by Gas Chromatography (GC) by a Varian GC3900 (**Figure 3.18.**) and Mass spectrometry (MS) by a Saturn 2100T (**Figure 3.19.**) while the lower molecular weight gases were monitored by MS by a Balzers Quadstar 422. Gas chromatography is an analytical technique for separating chemicals in a sample using a flow-through narrow tube known as a column. As the chemicals exit the end of the column, they are detected and identified electronically. Mass spectrometry is also an analytical technique by which atoms that are first ionised by knocking one or more electrons off to give a positive ion can be deflected by magnetic fields. The ionised atoms are deflected by their masses and the number of positive charges after which they are detected electrically.

Figure 3.18.: The gas chromatography apparatus Varian GC 3900

Figure 3.19.: The mass spectrometry analysis apparatus Saturn 2100T

The knowledge of the amount as well as the nature of these volatiles and gases measured by GC and MS is important to determine the ideal point of introduction in the clinker kiln of the materials containing these organic compounds. Nevertheless as will be explained in **paragraph 7.6.6.**, this method will not be used for quantitative measurements but only for qualitative comparison.

3.10. Repeatability and reproducibility

The accuracy of a measurement is the degree of closeness to the actual value. By a good calibration of the equipment, the accuracy can be improved. The precision related to reproducibility and repeatability, is the degree to which repeated measurements under unchanged conditions show the same results. The difference between accuracy and precision is schematically described in **figure 3.20.** The overall uncertainty requires consideration of the combined effects of accuracy and precision. As a function of the precision of a measurement, the repeatability is defined as the precision under repeatability conditions where independent test results are obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within short intervals of time.

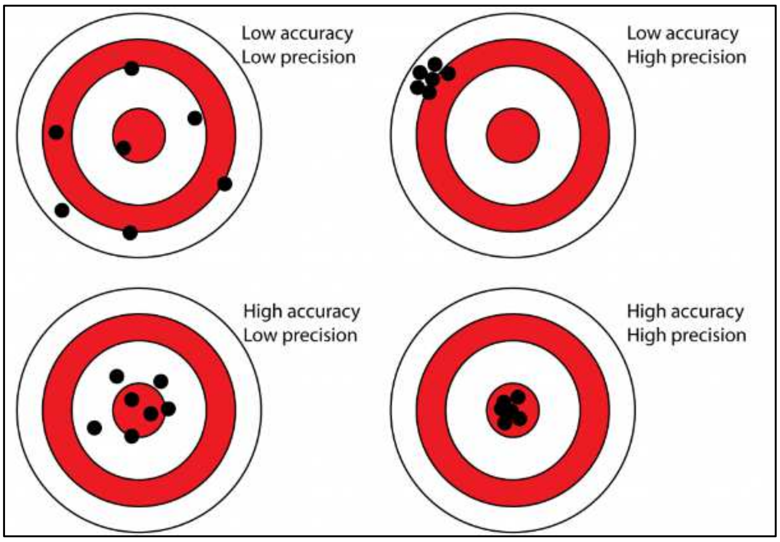


Figure 3.20.: Precision versus accuracy

Reproducibility on his turn is the precision under reproducibility conditions where test results are obtained with the same method on identical materials in different laboratories with different operators using different equipment. The precision related to the repeatability and reproducibility of most analytical methods are described in European standards **[12]** describing the methods for testing cement. Because within this PhD study, analyses were always performed in the same laboratory based on the European standards, using the same equipment and conducted by the same operator, only the precision related to the repeatability has to be taken in account to evaluate the measured results. Repeatability will be expressed as a standard deviation in absolute percent, grams, etc., according to the property tested.

- **XRF**: For the chemical analyses performed by XRF, repeatability limits are defined in **table 3.13.** as a function of the elements mean value *[wt%]* measured according to EN 196-2:2013 **[12]**. Accuracy is optimized by calibrating the XRF equipment with artificial standards. Based on these XRF measurements, Bogue calculations can be made from the chemical analysis of the final clinker samples. New findings **[24]** have now demonstrated that the uncertainty expressed as a Standard deviation (Stdev) can deliver values of about 9.6% for alite and belite, and 2.2% and 1.4% for aluminate and ferrite.

  Fortunately, the simple Bogue calculations within this PhD study are not used to calculate the actual values of alite, belite, celite and ferrite. Otherwise the refined Bogue calculations could deliver higher accuracy as already mentioned in **paragraph 3.6.2.** The simple Bogue calculations are merely used as estimations of the different major phases directly calculated out of the chemical composition of the final clinker with the known fixed calculation factors **(3.1-3.4)**. Therefore they could be used as a good chemical reference for the measured mineralogical composition out of the corresponding XRD analysis of the final clinker.

The mutual comparison of the differences between the major phases calculated by Bogue and measured by XRD will indicate the mineralogical impact of the different ARM out of a stable chemical clinker composition. Therefore the repeatability limits for XRF analysis (**Table 3.13.**) can be used for the simple Bogue calculations within this PhD study.

Table 3.13.: Repeatability limits for XRF analysis validation **[12]**

Element mean value	Repeatability limit (r) for "normal" performance	Repeatability limit (r) for "expert" performance
wt%	wt%	wt%
0 – 0.49	0.057	0.023
0.50 – 0.99	0.080	0.032
1.00 – 1.99	0.110	0.044
2.00 – 3.99	0.135	0.054
4.00 – 4.99	0.155	0.062
5.00 – 6.99	0.172	0.069
7.00 – 9.99	0.202	0.081
10.00 – 14.99	0.240	0.096
15.00 – 19.99	0.290	0.116
20.00 – 24.99	0.335	0.134
25.00 – 29.99	0.372	0.149
30.00 – 34.99	0.405	0.162
35.00 – 39.99	0.437	0.175
40.00 – 44.99	0.465	0.186
45.00 – 49.99	0.492	0.197
50.00 – 54.99	0.517	0.207
55.00 – 59.99	0.542	0.217
60.00 – 64.99	0.565	0.226
65.00 – 69.99	0.587	0.235
70.00 – 74.99	0.610	0.244
75.00 – 79.99	0.630	0.252
80.00 – 100	0.650	0.260

- **IR Spectrometer**: The chemical analyses performed on the IR spectrometer Leco CS230 have to have the same repeatability limits as those described for the reference method in the European normalisation **[12]**. This means that for the total sulfur, a repeatability of 0.07 wt% has to be attaint. Some additional tests were also performed to determine the specific repeatability of the used Leco CS230 for the total C *[wt%]* and additionally also for the total S *[wt%]* related to their concentration in the sample. These tests are visualized in **table 3.14.**

Table 3.14.: Specific repeatability of the total Carbon and Sulfur of the used Leco CS230

Range		Stdev C	Stdev S
		wt%	wt%
0 to 0.49	(wt%)	0.04	0.03
0.50 to 0.99	(wt%)	0.08	0.04
1.00 to 6.99	(wt%)	0.10	0.05
7.00 to 11.99	(wt%)	0.12	-

- **TGA**: The repeatability of the TGA-analysis was determined by measuring five times the sample CCM/Lxh/FC (**Table 3.15.**), an alternative CCM that was specifically prepared for the investigation of fibrecement as ARM for Portland clinker production and which will be further discussed in **chapter 7**. The weight loss *[wt%]* related to the decarbonation of $CaCO_3$ was determined between 725 and 900°C, the combined weight loss *[wt%]* coming from the decomposition of organic components and from the chemically bound H_2O determined between 125 and 725°C.

  The average, the standard deviation (Stdev) as well as the Standard Error of the Mean (SEM) were calculated for both weight losses and are also described in **table 3.15.** The SEM is an estimate of how far the sample mean is likely to be from the population mean, whereas the standard deviation of the sample is the degree to which individuals within the sample differ from the sample mean. Out of **table 3.15.**, it is clear that the TGA-analysis can be used for quantitative measurements. This is not the case for the DTA-analysis. The decarbonation energy that is approximately measured between 725 and 900°C based on the determination of the area under the characteristic peak in the graph can only be used for qualitative measurements and to provide information on the temperature range in which a specific reaction will occur.

Table 3.15.: Specific repeatability of the TGA-analysis based on CCM/Lxh/FC

CCM	Mass 25°C	Inorg CO_2 725-900°C	Organic+H_2O 125-125°C	Decarb E Approx. 725-900°C
	TGA (mg)	TGA (wt%)	TGA (wt%)	DTA (µVs/mg)
CCM/Lxh/FC (1)	54.55	16.96	9.24	96.24
CCM/Lxh/FC (2)	58.73	17.10	9.03	93.53
CCM/Lxh/FC (3)	58.93	17.15	9.16	99.40
CCM/Lxh/FC (4)	54.60	16.97	9.30	95.22
CCM/Lxh/FC (5)	55.52	16.97	8.97	95.34
Average		17.03	9.14	95.95
Stdev		0.09	0.14	2.16
SEM		0.04	0.06	0.97

- **XRD**: Demonstration of accuracy and precision in XRD analysis is typically difficult. Researchers generally must prepare their own standard mixtures to assess accuracy, participate in a round-robin events and/or compare with results of other analyses, such as optical microscopy or chemical calculations. Pattern approaches by Rietveld method have shown already a big improvement in the accuracy and precision of XRD measurement **[16]** and have changed XRD measurement from a qualitative to a semi-quantitative analytical method. This improvement comes from extensive calibration with model mixtures and with materials for which the actual phase composition is known by independent methods. Before the introduction of these pattern fittings, the results of the reproducibility were very poor (**Figure 3.21.**).

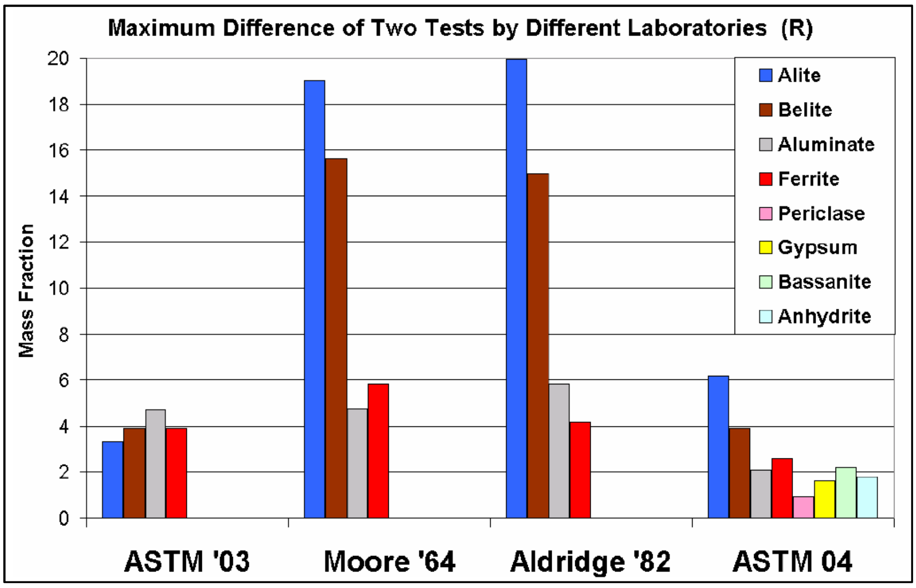


Figure 3.21.: Multi-laboratory standard deviations for alite, belite, aluminate, and ferrite from the round robin of Moore **[17]**, of Aldridge **[18]** and of Stutzman **[22]** shows improvement with the application of Rietveld pattern fitting approach (Ref. Stutzman **[22]**)

Determination of alite *[wt%]* for example by a round robin test of Moore **[17]** and Aldridge **[18]** on a Portland cement batch delivered a standard deviation of about 7.5 wt% and maximum difference of about 20 wt% **[19]**. Pattern fitting by Rietveld method reduced the standard deviation for alite *[wt%]* demonstrated by two ASTM round robin tests to 2.3 wt% and a maximum difference to 6.2 wt% **[20-21]** describing the reproducibility precision by XRD. The difference with the actual value or the accuracy of the XRD analysis (**Figure 3.20.**) may reach 4.7 wt% for alite, 6.3 wt% for belite, 0.9 wt% for aluminate and 2.4 wt% for ferrite **[19]** but this will be less of an issue in the evaluation of the different Portland clinker samples because the analysis will rather be used in comparison with each other and the related Bogue calculations than used as true mineralogical composition.

The repeatability for the XRD measurement within this PhD study is very difficult to determine. Analysing for example the same clinker sample with the same pattern approach on the same Bruker D8 ADVANCE with the same preparation method within short intervals of time, will deliver very small repeatability errors for the major phases but nevertheless will be specific for the clinker sample itself. Because XRD measurement on another clinker sample could require another specific pattern approach, repeatability precision can vary and has to be defined as sample dependent. The repeatability and reproducibility within a Portland cement were nevertheless described in literature by Stutzman **[23]**. Repeatability was calculated out of two tests of the same cement by the same lab, the reproducibility was expressed as two tests on the same cement by two different laboratories.

In **table 3.16.**, he defines although provisional, the repeatability (r) and reproducibility (R) of the major hydraulic phases alite, belite, celite (aluminate) and ferrite as a Standard deviation (Stdev r or Stdev R) and a limit (r or R) by pattern fitting with Rietveld.

Table 3.16.: Repeatability and reproducibility of the major hydraulic phases **[23]**

		Alite	Belite	Celite	Ferrite	Periclase	Gypsum	Anhydrite	Calcite
Repeatability precision									
Stdev r	wt%	0.7	0.6	0.5	0.5	0.2	0.2	0.3	1.0
r	wt%	2.0	1.8	1.3	1.4	0.6	0.6	0.7	2.7
Reproducibility precision									
Stdev R	wt%	2.2	1.4	0.7	1.0	0.3	0.6	0.6	0.5
R	wt%	6.2	3.9	2.1	2.6	0.9	1.6	1.8	1.5

The repeatability limit (r) is the value less than or equal to the absolute difference between two results, obtained under repeatability conditions which may be expected to be within a probability of 95%. As already described in **paragraph 3.6.1.**, it will only be the alite, belite phases and the free lime of the different artificial reference and alternative clinker that will be used for mutual comparing. Based on these results, it can be stated that differences as of 2 wt% for alite and belite could be described as significant although much will be depend on the used equipment and operator.

- **Sieve analysis**: The determination of the particle size distribution (PSD) is performed according EN 933-1 **[13]**. The repeatability limit (r) for the PSD is described as a formula **(3.5)** where C% represents the average of the cumulative percentage under size passing through the current screen.

$$r = 0.042 \text{ x } (C\% \ (100.0 - C\%)) \qquad \textbf{(3.5)}$$

- **Laser diffraction**: The laser diffraction has a big reproducibility but a quite small repeatability error. The repeatability precision specified by Sympatec for their Helos Vario for dry measurement is smaller than 0.3 wt% **[14]** and is therefore suitable for quantitative analysis.

- **Bomb Calorimeter**: The reproducibility of the IKA Bomb Calorimeter system C7000 for the determination of the gross calorific value is defined to be ± 0.2 % of the Relative Standard Deviation described in DIN 51900 **[15]**.

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Chapter 4

Ecological background

4.1. Introduction

Cement industry produces by estimation 5 v% of the global manmade CO_2 emissions **[1]**. As already demonstrated in **section 2.3.**, a big part comes from the raw materials CO_2 emissions, roughly estimated to be 0.53 kg per kg produced clinker **[2]**. Including the CO_2 emissions through the use of fuels, the emission of CO_2 for every kg of produced cement is calculated by Humphreys and Mahasenan to be 0.87 kg on average **[2]** which demonstrates that the decarbonation of $CaCO_3$ generates more than half of the total cement related CO_2 emissions.

Worldwide cement production in 2000 was 1.57 billion tons. In 2004, it had already increased to over 2 billion tons and in 2012, 3.6 billion tons of cement production was attaint (www.Cembureau.be). An analysis carried out by Battelle shows that the demand for cement in industrial nations will increase slowly, but in developing countries will rise exponentially **[2]**. It is therefore critical that CO_2 emissions associated with such growth in cement production are harmonised with international efforts to reduce greenhouse gas emissions **[3]**.

Nevertheless, CO_2 emissions are only part of the manmade influence on ecology although it seems to be quite convenient to define an ecological impact of a production process or product only by its CO_2 emission. Ecology is indeed a study of interactions among organisms and their environment which is far more complex than simply the ecological impact of CO_2 emissions. Also acidification of soil and water, eutrophication, ozone depletion, depletion of raw materials, etc. are important parameters to evaluate the ecological impact of a production process **[4-6]**.

Preservation of ecological balance on the one hand is important for all natural life on earth. Ecological economics including social, cultural, health-related and monetary/financial aspects on the other hand are also vital for mankind **[7]**. The World Business Council for Sustainable Development (WBCSD) defined sustainable development as follows: “Forms of progress that meet the needs of the present without compromising the ability of future generations to meet their needs” **[8]**. Ecological economics deals with living conditions, revalorising of economic sectors or work practices, using science to develop new green technologies, to make adjustments in individual lifestyles that conserve natural resources, etc.

The concept of sustainability has become a major component of the general management policy of most companies, especially for those that operate in the construction industry. With respect to the manufacturing of building materials, this is clearly illustrated by the growing attention that is given to the use of the limited natural resources, the reduction of the non-recyclable waste that is generated by the production process and finally, the recycling of the products in valuable applications at the end of their service lifetime.

With this in mind, a progress report undersigned by sixteen cement companies under the supervision of the World Business Council for Sustainable Development (WBCSD), was published in June 2005, which is called the Cement Sustainability Initiative **[9]**.

4.2. The Cement Sustainability Initiative [9]

The sixteen cement companies, undersigning the Cement Sustainability Initiative were: Ash Grove Cement Company, Cemex, Cimpor, Corporacion Uniland, CRH plc, Gujarat Ambuja Cements, Heidelberg Cement, Holcim, Italcementi, Lafarge, Secil-Companhia Geral de Cal e Cimento, Shree Cement, Siam Cement Industry, Taiheiyo Cement, Titan Cement and Votorantim.

This Cement Sustainability Initiative **[9]** listed five Key Performance Indicators:

- Climate change management
  - Number of facilities and percentage using WBCSD CO_2 protocol
  - Company-wide total CO_2 emissions, tons/year
  - Company-wide gross and net CO_2 emissions per ton of cementitious product

- Fuels and materials use
  - Energy use
    - Specific heat consumption of clinker production in MJ/t of clinker
    - Alternative fossil fuel rate: Alternative Fuel consumption as % of thermal consumption
    - Biomass fuel rate: consumption of biomass as % of thermal consumption
  - Raw materials use
    - Alternative Raw Materials (ARMs) rate: use of ARM as a % of total RM for cement and clinker production
    - Clinker/cement factor

- Health and safety
  - Fatalities
    - Number of fatalities and fatality rate of industry employees
    - Number of fatalities amongst indirectly employed personnel (e.g. contractors)
    - Number of fatalities involving 3rd parties (not employed)
  - Lost-time injuries (LTI)
    - LTI and injury frequency rate (per 1,000,000 man-hours directly employed)
    - Number of LTI for indirectly employed (e.g. contractors)

- Emission monitoring and reporting
  - % of clinker produced by kilns covered by a monitoring system, either continuous or discontinuous, for main and other pollutants
  - % of clinker produced by kilns which have installed continuous measurements for main pollutants
  - Company-wide specific (g/t of clinker), and total (t/year) releases for:
    - NOx
    - SOx
    - Dust

- Local impacts
  - % of sites with community engagement plans in place
  - % of active sites with quarry rehabilitation plans in place
  - Number of active sites where biodiversity issues are addressed.

This PhD study is focusing on two of the five Key Performance Indicators namely climate change management and fuels and materials use and more precisely on the next topics:

- Company-wide total CO_2 emissions, tons/year
- Company-wide gross and net CO_2 emissions per ton of cementitious product
- Energy use
- Raw materials use

Although the cement sustainability initiative is a worthy concept, it has to be supported by an objective evaluation method to demonstrate its influence on the ecological impact of cement production.

4.3. Ecological impact evaluation

Claiming an improved ecological impact of a product or a production process is quite difficult if it has to be based on objective parameters and calculations. As already mentioned, setting the focus only on CO_2-emission to evaluate an ecological impact is too simplistic.

Looking to literature, different ways are defined to evaluate and communicate the ecological impact of a production process or a product itself. Concepts as CO_2-footprint **[10]**, LCA **[11]**, Breeam **[12]**, the Dutch “prestatieladder” **[13]** and different labels as Cradle 2 Cradle **[14]** and Ecolabel **[15]**, etc, all have their proper advantages and disadvantages towards ecological impact evaluation and are individually chosen for the ease by which they can be used and/or calculated, their usefulness/efficiency for a particular industry business (branch) and/or marketing value.

To this moment, the LCA concept is commonly accepted as the most complete method to calculate the ecological impact of a product or production process although it provides to the researcher still a lot of room for interpretation as a function of aspects as variable system boundaries, different statistical information, different product uses, etc. **[4-6]**. This can lead to different and potentially contradictory conclusions. Nevertheless LCA stays a powerful tool that, when based on standardised guidelines, could reduce such conflicts to the minimum.

Within this PhD research, the clinker results are originating from a simulation program and an artificial lab furnace. Although, as explained in **section 3.3.** and **3.4.**, efforts are made to imitate the real clinker production as good as possible, artificial attaint parameters will not give the required data to serve as base for a sensible LCA calculation. Industrial tests as well as objective recycling and transportation process evaluations for each of the five ARMs would be necessary to deliver objective data to make these calculations. A proper LCA calculation of the Portland clinker process as a function of each of the five ARMs falls for this reason out of the scope of this PhD study.

Nevertheless, because the LCA concept is the most complete method up to day to demonstrate the different aspects influencing the ecological impact of a production process or product, the LCA concept will be briefly explained in **section 4.4.** This will make it possible to objectively frame the different aspects of the ecological impact within the Portland clinker process and/or the own production process on which each of the five proposed Alternative Raw Materials (ARMs) will have their influence.

4.4. Life-Cycle Assessment [4-6], [16-17], [24]

Life-cycle assessment is a way to evaluate environmental impacts by using the different stages of a product's life cycle. It is a process of comparing the environmental performance of products or services. The term 'life cycle' refers to the fact that a fair assessment must consider all the stages from cradle to grave. Cradle-to-grave describes the full Life Cycle Assessment (LCA) from the resource extraction ('cradle') to the use phase and disposal phase ('grave') **[4-6]**. All inputs and outputs are considered for all the phases of the life cycle. Cradle-to-cradle (**Figure 4.1.**) is a specific kind of cradle-to-grave assessment, where the end-of-life disposal step for the product is a recycling process. Especially for building materials **[16]**, the life cycle is based on four consecutive steps (**Figure 4.2.**).

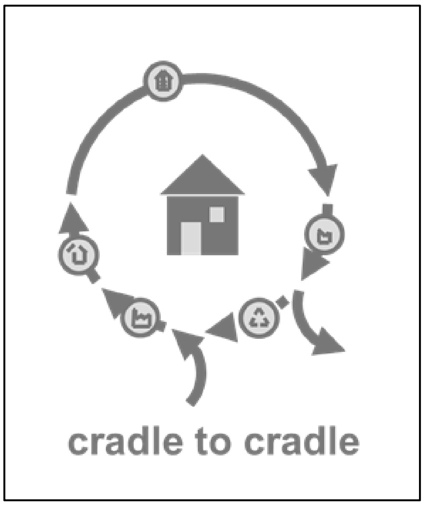

Figure 4.1.: Cradle to cradle principle
(Source: HeidelbergCement AG)

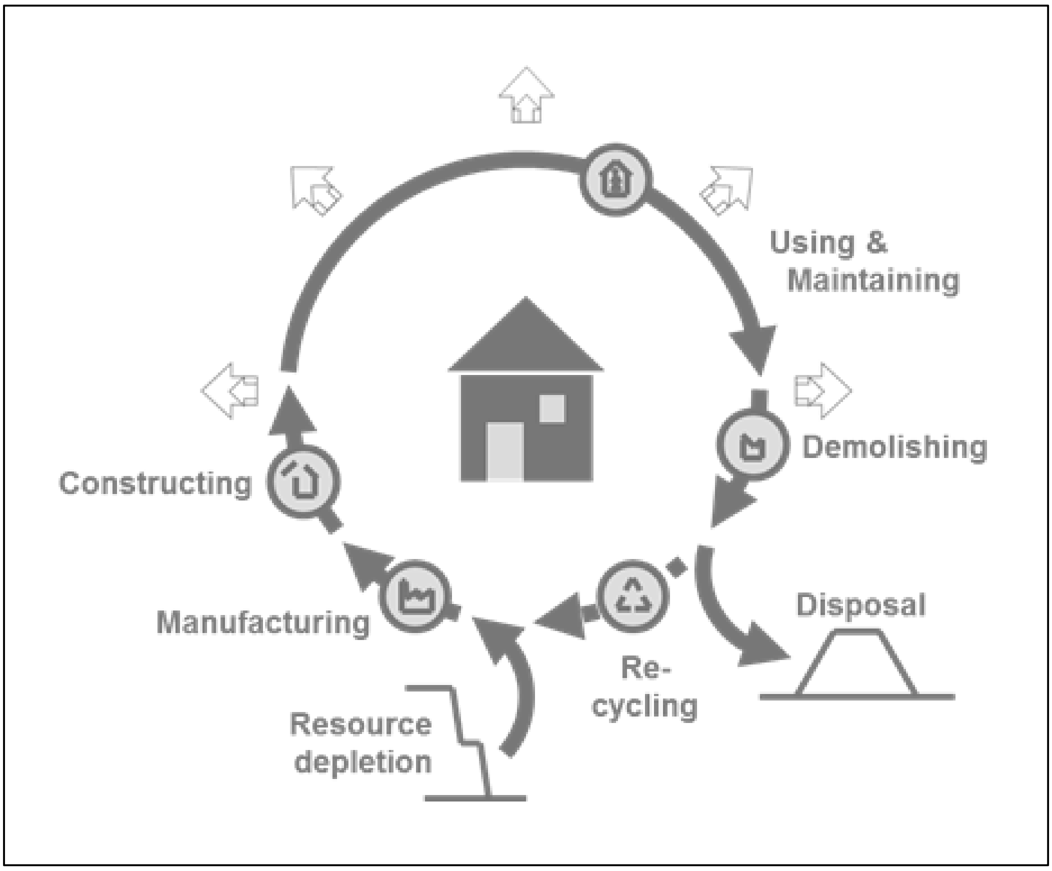

Figure 4.2.: Simplified flow chart with the four consecutive life cycle stages
(Source: HeidelbergCement AG)

- **Manufacturing**: the extraction, processing and transportation of the raw materials and required energy.
- **Constructing**: building or construction phase. Also the transport from factory to yard is included in this stage.
- **Using and maintaining**: energy and water, cleaning, maintenance, repairs and replacements.
- **Demolishing or end of life phase**: demolition and dismantling and final disposal by landfilling or incineration. Also a possible recycling step can be taken in account. This phase includes transportation from the yard, the preparation for final disposal or recycling.

The guidelines for Life cycle assessment (LCA) are described in ISO 14040 (2006) **[4]** and ISO 14044 (2006) **[5]**, both part of the ISO 14000 environmental management standards. In addition, specific European standards are developed for the environmental assessment of construction and buildings materials (NBN EN 15804 **[19]**, DIN EN 15978 **[20]**).

These ISO standards state that four steps should be taken in account to conduct a Life Cycle Analysis. The steps are often interdependent in that the results of one phase will inform how other phases are completed.

- **Target definition and scope [4-6]**:
  The target definition includes the question and the purpose for the life cycle analysis, as well as a description of the target audience and the intended use of the LCA results. The range (width and depth of the LCA) should be compatible with the expressed purpose of the analysis. It should consist out of a description of the (product) process and the determination of the process limits on the one hand and the definition of the requirements (level of detail) on the other.

- **Inventory [4-6]**, **[17]**, **[24]**:
  A second step in an LCA study includes the inventory phase or Life Cycle Inventory (LCI). A LCI provides information about all inputs and outputs in the form of elementary flow to and from the environment of all the unit processes involved in the study. It consists out of a collection of data, which are necessary for carrying out the LCA study. This data of unit processes can be delivered by the so called Environmental Product Declarations or EPDs.

  In a first step the product system under consideration is divided into a series of successive phases and processes. For each of the processes, the corresponding inflows (primary raw materials, energy, etc.) and outflows (emissions to air, soil and water, waste, by-products, etc.) are collected as well as their environmental impact. In case of the use of recycled materials and/or products, the environmental impacts taken in account and/or avoided, are also important. This concerns the saving of energy or raw materials through recycling or reuse of products at the end of their life. Inventory flows can number in the hundreds depending on the system boundary.

  The data to construct these flows in detail are typically collected through survey questionnaires. These questionnaires cover the full range of inputs and outputs, typically aiming to account for 99% of the mass of a product, to make an inventory of all the energy used in the production process and to identify the environmentally sensitive flows. Care has to be taken to ensure that questionnaires are completed by a representative group of producers to guarantee the objectivity of the data.

  The inventory analysis is always followed by an impact analysis.

- **Impact analysis [4-6]**:
  This phase of LCA is aimed at evaluating the significance of potential environmental impacts based on the LCI flow results. Based on the inventory, a Life Cycle Impact Analysis (LCIA) aims to quantify potential environmental impacts of the product during its lifecycle.

  First, a selection of the environmental impact categories is made according to their potential impact on the environment. They could cover effects as acidification of soil and water, eutrophication, ozone depletion, depletion of raw materials, photochemical smog and human toxicity etc., all important for today's society. These effects are usually the result of emissions of certain substances into the soil, air and water, as well as the extraction of natural resources and the use of land for agriculture. Each environmental impact category is quantified by an environmental impact indicator.

The selection of categories and indicators depends on the objectives of the LCA.

In a second step, the data coming from the LCI is classified and attributed to the above-described environmental impact categories. The contribution of the various incoming and outgoing flows to the overall environmental impact of the product is characterised, calculated and expressed in terms of a specific reference unit, usually the most dominant factor of the impact category. Energy consumption and CO_2 emission are often regarded as “practical indicators”.

When expressing the results to a common reference, the results for the various environmental effects can be compared with each other. This allows that some conclusions can be made regarding the most significant impact(s).

Finally, the normalized results out of the different environmental impact categories are expressed together as a number score. The normalized results of the different environmental impact categories can be multiplied by different weighting factors based on the target definition and scope to calculate the number score. Consequently, different sets of weighting factors give rise to different final results which provides the researcher still a lot of room for interpretation.

- **Interpretation [4-6]**:
  Finally, the results are discussed and interpreted. This is done basically in three steps, namely the identification of significant points, the verification of the completeness, sensitivity and consistency of the results and finally the conclusions, limitations and recommendations.

Additionally, literature describes two types of LCA **[21]**. Attributional LCA (ALCA) which seeks to calculate the LCA at a point in time (typically the recent past) and consequential LCA (CLCA) which seeks to identify the environmental consequences of a decision or a proposed change in a system under study (oriented to the future).

When comparing different LCAs with one another, it is crucial that equivalent data are available for either products or processes in question. If one product has a much higher availability of data, it cannot always be compared to another product which has less detailed data. Because none of the selected Alternative Raw Materials (ARMs) have already a history as Alternative Raw Material, it is quite difficult to evaluate their use in Portland clinker production. If more of the required data could be available in the future by industrial practice, consequential LCA calculation will be the obvious choice for each of the five proposed ARMs.

As already described, the life cycle of building materials usually consists out of a number of stages including: manufacturing, constructing, using and maintaining and demolishing or end of life phase. If the most environmentally harmful of these stages can be determined, the impact on the environment can be efficiently reduced by focusing on making changes for that particular phase. A possible alternative for the complete LCA calculation could therefore be to make an LCA calculation according to the cradle-to-gate principle **[22-23]** (**Figure 4.3.**).

Figure 4.3.: Cradle to gate principle
(Source: HeidelbergCement AG)

Cradle-to-gate is an assessment of a partial product life cycle from resource extraction (cradle) to the factory gate (before it is transported to the consumer). Within the cradle-to-grate principle, only the manufacturing stage is taken in account.

The “Cradle to Gate” principle is used to make the Environmental Product Declaration (EPD) **[24]**.

By collecting all of the EPDs of resources being used by the facility, a producer only has to add up the steps involved in their transport to the plant and the manufacturing process to more easily produce his own cradle-to-gate values for their products.

4.5. Environmental Product Declaration [25]

Type III environmental declarations or Environmental Product Declarations or EPDs are based on the ISO14025 (2006) standard **[25]**. They contain detailed, quantitative and certified information on the environmental and health products. The required information is provided voluntarily by the producer or distributor of the product and is entirely based on life cycle analysis and may contain some additional environmental information. Verification of the information delivered by the producer is provided by an independent third party **[25]**.

The main advantages of EPD are the fact that they only inform and do not judge. They are comparable, transparent, credible and flexible. The main disadvantages are again the extensive environmental and health information which should be based on a full LCA which requires a lot of work for the manufacturer or distributor.

EPD’s of building materials are based on LCA calculated by the Cradle to Gate principle (**Figure 4.3.**). EN 15804 **[19]** describes EPD calculation for building materials. The EPDs for CEM I, CEM II and CEM III cements as published by the “Federatie van de Belgische Cementnijverheid” or Febelcem are added in appendix B (Source Febelcem).

4.6. Practical use within this PhD study

Numerous objective data to perform LCA calculations such as EPDs and others are up to day not all available which makes it impossible to make an objective LCA calculation as a function of each of the five ARMs. Nevertheless, by defining the different aspects of the ecological evaluation, it is possible to objectively frame the different parts within the Portland clinker process which will have their influence on the final EPD and/or within the own production process of each of the five proposed

Alternative Raw Materials (ARMs) possibly resulting in a own improved EPD. Improved EPDs will positively influence an LCA calculation of associated processes.

This chapter will be used as background to objectively frame the ecological discussions in the next chapters.

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Chapter 5

Objectives

When speaking about sustainability, it is immediately assumed that the valorisation in the Portland clinker process of by-products or recycled materials out of the building and construction sector is always ecologically beneficial which is also insinuated by the Key Performance Indicator “Fuels and materials use” in the cement Sustainability Initiative (**Section 4.2.**). Indeed their use as an Alternative Raw Material (ARM) could induce the saving of natural resources and/or decrease landfill by production or demolition waste as big ecological advantage. When they are composed partly out of decarbonated CaO, an ecological advantage compared to classic CaO sources as limestone, tufa or marl (**Section 3.4.**) could be induced in the Portland clinker process.

Nevertheless these materials have also to be handled, transported and prepared which is also the case for the current Classic Raw Materials (CRMs). However, the CRMs that they could replace are specifically chosen for their fitness as raw material and ease by which they can be handled, transported and prepared to be used in the Portland clinker process. Limestone, tufa and marl or the CaO sources of CBR Antoing, CBR Lixhe and ENCI Maastricht (**Table 3.2.**) which occupy between 79 and 93 wt% of the classic Cold Clinker Meal, are for this reason quarried in the immediate vicinity of the factory. This is also true but to a lesser extent for the other CRMs which are specifically selected for their fitness as raw material for Portland clinker production. The required energy that an ARM will consume before it could be used as ARM, will therefore represent in most cases an additional energetic and therefore ecological cost compared to the CRMs.

It is therefore crucial that the impact of the ARM on the Portland clinker process, is objectively determined taking into account the Portland clinker quality and its impact on the cement production. Indeed, no energy should be lost to the valorisation of an ARM which is already unsuited for Portland clinker production in the first place and/or to a preparation phase which would not improve the fitness of the ARM significantly. Specifically for the Portland clinker production, it will be the nature and stability of the ARM as a function of its physical structure and chemical and mineralogical composition that will determine its impact and fitness for the production process.

Five materials sources having their origin as by-product of an existing building material production process or in demolished construction waste were therefore specifically chosen to represent materials throughout the complete building and construction sector. They all have potential to decrease the use of natural resources and counter landfill.

The main objective of this PhD study is the estimation of the impact of five selected by-products and recycled materials on the Portland clinker production process to judge their fitness as Alternative Raw Material with or without a specific preparation phase.

The wide range of materials demonstrates the possibilities, different producers and consumers within the building and construction sector could have, to work together to improve the ecological impact of their directly concerned products as well as minimise their waste disposal by landfill of production as well as end-of-life demolition waste. Furthermore it makes it possible to set basic rules and attention points to facilitate the determination of the fitness of other materials as ARM for Portland clinker production than those that were already investigated for this PhD study.

The determination of basic rules and attention points for the use of by-products and recycled materials out of the building and construction sector is a general objective of this PhD study.

To determine the individual fitness of an ARM for Portland clinker production, specific properties of the five selected materials were investigated in a practical and objective way. An objective evaluation as was described in **chapter 3**, makes it possible to have a realistic idea how much of each ARM individually could be maximised in the Cold Clinker Meal (CCM), replacing CRMs in a Portland clinker process by taking in account the influence on the clinker process as well as the final clinker quality. If the maximisation of an ARM in a CCM decreases the $CaCO_3$ *[wt%]* in the alternative CCM compared to the reference CCM, a reduction of inorganic CO_2 emission per ton of Portland clinker could occur. This will have also an impact on the corresponding decarbonation energy of the alternative CCM. Also other parts of the energy consumption of the Portland clinker process as grinding energy and fluxing effects could be influenced by the maximisation of an ARM.

Based on the specific properties of each of the five materials, an estimation will be made whether or not the use of each of the five selected materials could have advantages in terms of energy consumption or inorganic CO_2 emission for the Portland clinker process.

Furthermore the guidelines of the Life Cycle Assessment (LCA) procedure (**Section 4.4.**) will be used to unveil if the use of each of these five selected materials individually could be classified as steps in the continuing sustainable development of the cement production process or better be avoided due to the additional insurmountable energy expenditure for ARM valorisation or/and an adverse impact on the Portland clinker process and quality. Due to some unknown data on the handling, transportation and preparation, specific for each of the five materials individually, as well as on specific industrial practices, an objective LCA calculation is not yet possible. The ecological evaluation will therefore rather be qualitative than quantitative.

The last objective of this PhD study will be the definition of preliminary conclusions on the possible ecological benefits of each of the five selected materials as ARM for Portland clinker production.

Chapter 6

Porphyry and dolomitic limestone by-products as raw material for Portland clinker production

6.1. Introduction

Limestone is the primary used raw material in Portland clinker production. It consists essentially out of $CaCO_3$ and will deliver almost all of the CaO and a significant amount of SiO_2 to the Cold Clinker Meal (CCM). For this reason, clinker kilns are located near quarries which can deliver pure limestone. In some cases, these quarries also produce aggregates or are located near aggregates producing quarries. One of these aggregates producers is Sagrex. Sagrex is a producer and supplier of aggregates on the Benelux market for the construction industry mainly as a raw material for concrete and/or large infrastructures as railway ballast, surfacing, dikes to protect river banks, etc. Sagrex produces aggregates out of porphyry, limestone and sandstone as also sea and river gravel and is part of the global HeidelbergCement Group.

The production of aggregates generates by-products as for example fines or sludge which logically can be valorised in clinker production replacing the original limestone raw material when there is a chemical similarity by the fact that both quarries use the same limestone deposition or the materials come from the same quarry. It is less obvious when these by-products do not have a chemical similarity with the original limestone raw material as in the case of porphyry and dolomitic limestone.

Within this study these materials are recovered from two quarries; Sagrex Quenast for porphyry and Sagrex Chanxhe for dolomitic limestone materials. Basically fines and sludge are the same material but separated in different ways from the aggregates production. When used for concrete or asphalt application being the biggest part of the aggregates market, aggregates will have a big influence on the water demand of concrete or on the optimum use of bitumen in asphalt.

Asphalt producers aim to obtain a perfect ratio between bitumen and fines. For energetic and technical reasons, they rather have insufficient fines in there aggregates and add them than be obliged to extract them. Also regional standardisation **[1]** for aggregates limits the 63 µm fraction (fines) content in normalised aggregates. This explains why aggregates producers extract fines by wet or dry screening, generating respectively sludge and fines as by-product, if the level of fines is too high.

This chapter deals with a method for the valorisation of these by-products as Alternative Raw Material for Portland clinker production. It will be shown that although both materials do not have good chemical similarities with the limestone raw materials currently used in the three reference Portland clinker kilns, their use in Portland clinker production has some additional advantages which could be ecologically beneficial.

6.2. Porphyry [2-4]

Porphyry is a magmatic rock consisting out of large-grained crystals, such as feldspar or quartz, dispersed in a fine-grained Feld spathic matrix or groundmass. It is known for its hardness and durability. Porphyry comes from the Greek word Πορφύριος, porphyrios, and means "purple" named after a deep purple magmatic rock known as imperial porphyry. The name porphyry is further given to describe the texture of magmatic rocks with large crystals. Most types of magmatic rocks have some degree of porphyritic texture.

The porphyry found in Belgium is located in the province of Hainaut, more precisely in the region of Quenast, Bierghes and Lessines. The exploitation of porphyry in this region goes back to the 16th century. Since the 18th century, there is industrial exploitation locally in Quenast. The quarries of Quenast are now regrouped to form the current quarry which is one of the largest open-air quarries.

The porphyry in Belgium was formed during the Upper Ordovician period (about 450 million years ago) when the southern edge of the Brabant Massif was an active volcanic belt. Porphyry in this region is a micro-diorite and was formed when a column of rising magma was cooled in two stages. In the first stage, the magma was cooled slowly deep in the crust, creating large crystal grains consisting out of feldspar, corroded quartz, some magnesium rich silicates and hornblende, with a diameter of about 2 mm or more. In the final stage, the magma was cooled rapidly at relatively shallow depth or as it erupted from a volcano by which it created a fine-grained groundmass (10-40 microns) of quartz-feldspar that is usually invisible for the eye. Up to 80 wt% of the rock consists of various feldspar group minerals. Feldspar and/or the Feld spathic matrix consist mineralogically out of $KAlSi_3O_8$, $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$. Also the so called hornblende is found which is an isomorphous mixture of three compounds; calcium-iron-magnesium silicate, iron-magnesium silicate and aluminium-iron-magnesium silicate or in general $(Ca,Na)_{2-3}(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH,F)_2$. Interesting to know is that the minerals feldspar and quartz have higher hardnesses measured on the Mohs scale than the mineral hornblende which will be of importance for the results of this study.

Porphyry is an extremely durable rock, very resistant to both mechanical as well as chemical influences. Originally, because of its durability, the porphyry of Quenast was used for the production of cobble stones for roads. Today it is mainly used as gravel where hardness, durability and resistance are of great importance. Porphyry of the region of Quenast can be found in the Delta Works in the Netherlands, the tunnel under the channel linking France to the United Kingdom and was used for the high-speed TGV tracks. Even in the USA porphyry cobble stones of Quenast can be found **[2]**.

Because of its magmatic history, the porphyry aggregates out of the quarry of Quenast have similar chemical composition as visualised in **figure 6.1.**

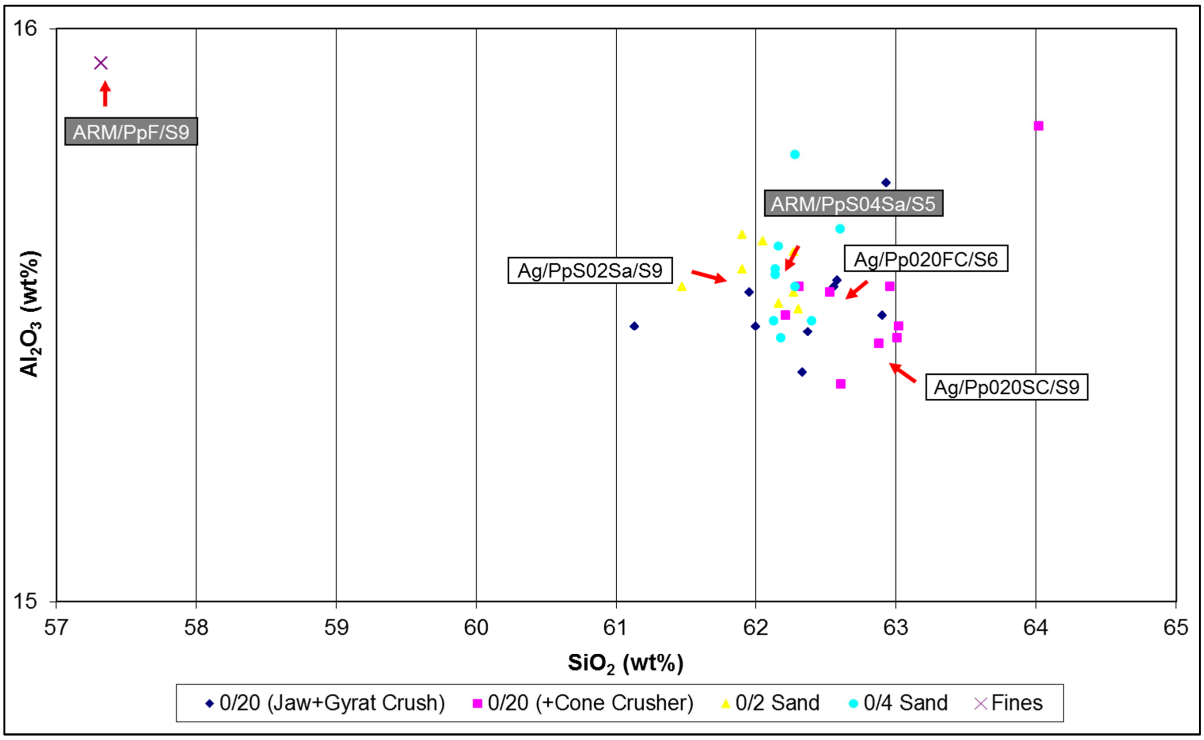

Figure 6.1: SiO_2 *[wt%]* as a function of Al_2O_3 *[wt%]* without Loss of Ignition (950°C) of Porphyry aggregates. The arrow marks the selected Porphyry materials. (White and grey label: Samples for TGA/DTA analyses; Grey label: Samples used for clinker simulation and preparation – **section 3.3.**)

6.3. Dolomitic limestone [3-4]

Limestone is a sedimentary rock which is composed out of calcite and aragonite minerals. Both minerals have a different crystal form of calcium carbonate ($CaCO_3$), more specifically calcite which is trigonal-rhombohedral and aragonite which is orthorhombic. Many limestones are composed out of skeletal fragments of marine organisms. They are used as building material, as aggregate for road construction, but also as white pigment and filler in food and non-food materials. This is for example added to toothpaste, paper, plastics, paint and in a purified form to bread, cereals, livestock feed, medicines and cosmetics.

Limestone is also very common in architecture. It is readily available, relatively easy to cut into blocks and is long-lasting and stands up well to exposure. Limestone was most popular in the late 19th and early 20th centuries. Train stations, banks and other structures from that era are often made out of limestone. Limestone was also a very popular building block in the Middle Ages in the areas where it occurred, since it is hard, durable and commonly occurs in easily accessible surface exposures. Many medieval churches and castles in Europe are therefore made out of limestone. Limestone often contains variable amounts of silica and/or minor amounts of clay, silt and sand. Because of these impurities, limestone can have different colours. Crystals of calcite, quartz, dolomite or barite may be present in small cavities of the limestone rock.

Dolomite is a carbonate mineral composed of calcium magnesium carbonate $CaMg(CO_3)_2$. Dolomite is double carbonated and crystallises in a trigonal-rhombohedral system. Small amounts of iron in the structure give the crystals a yellow to brown tint, manganese substituted up to about 3 wt% in the structure gives the crystals a rosy pink colour. Also lead and zinc can substitute the structure for magnesium. The formation of this mineral is still not fully understood, although geologists are aware of large deposits of primary formed dolomite from the past 600 million years. It was demonstrated that bacteria can facilitate the formation of dolomite. Marine bacteria which use S compounds instead of oxygen for energy production could form primary dolomite crystals down on the ocean floor. Nevertheless large scale deposits from primary dolomite were also formed above the ocean floor which places scientists for a mystery. One possibility is that massive primary dolomite was formed during times when large quantities of organic matter in the seabed are degraded by sulfate-respiring bacteria. Such conditions exist when the sea water above the seafloor is free of oxygen. In Earth's history, several such oxygen-free periods have occurred, partly consistent with time periods of intensified dolomite deposition.

Dolomitic limestone is a type of limestone composed out of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Because limestone is a sedimentary rock, the ratio between dolomite and calcite can vary widely as can be noticed in **figure 6.2.**, whereby the content of dolomite can go up to 50 wt%. Nevertheless the average chemical composition is influenced by the calibre of the aggregates (**Figure 6.2.**) which could reduce the chemical variation. Dolomitic limestone is used as aggregate in all kinds of concrete applications. Tests to determine the mechanical and physical properties of aggregates **[6]** show that dolomitic limestone becomes easier to grind by increasing $CaMg(CO_3)_2$ *[wt%]* compared to pure limestone.

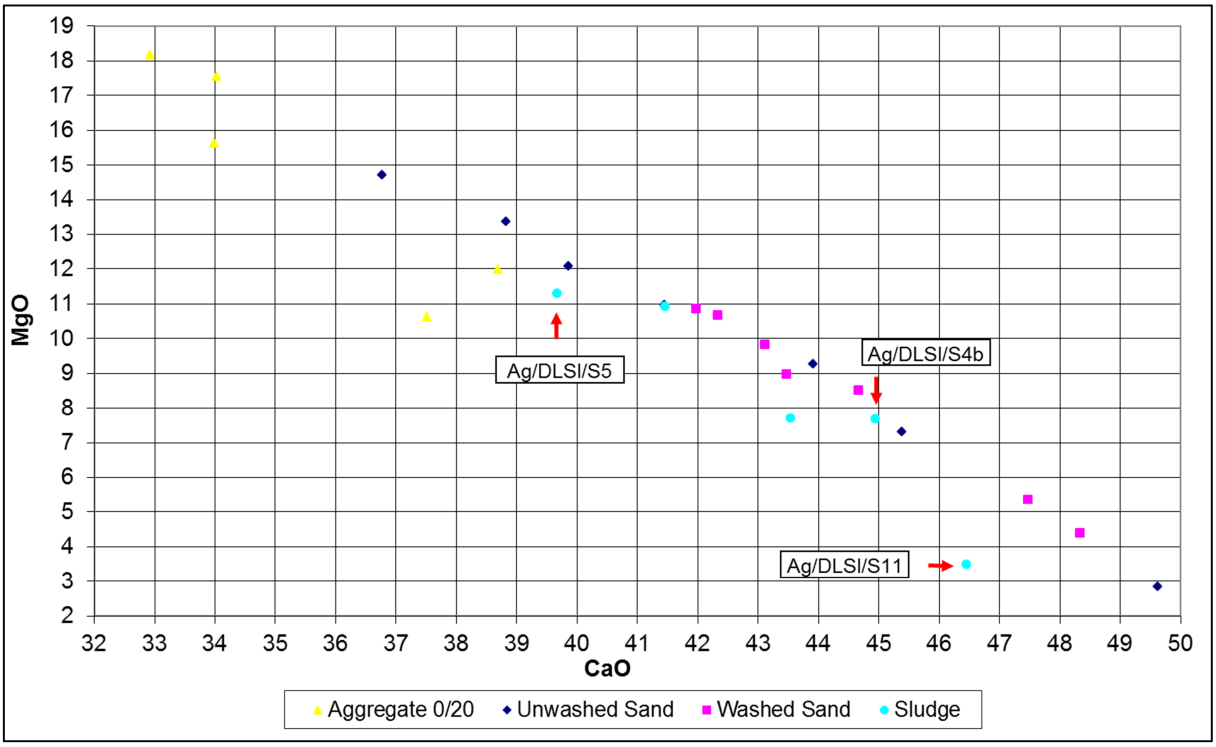

Figure 6.2.: CaO *[wt%]* as a function of MgO *[wt%]* without Loss of Ignition (950°C) of Dolomitic limestone aggregates.

Dolomite is used in architecture, as concrete aggregates and as source for magnesium oxide and magnesium. It also often serves as the host rock for base metals such as lead, zinc, and copper. In agriculture, dolomite and dolomitic limestone are added to soils as a pH buffer and as a magnesium source.

6.4. The production of porphyry and dolomitic limestone aggregates

6.4.1. Porphyry

The quarry of Quenast is located roughly twenty kilometres south-west of Brussels (**Figure 6.3.**).

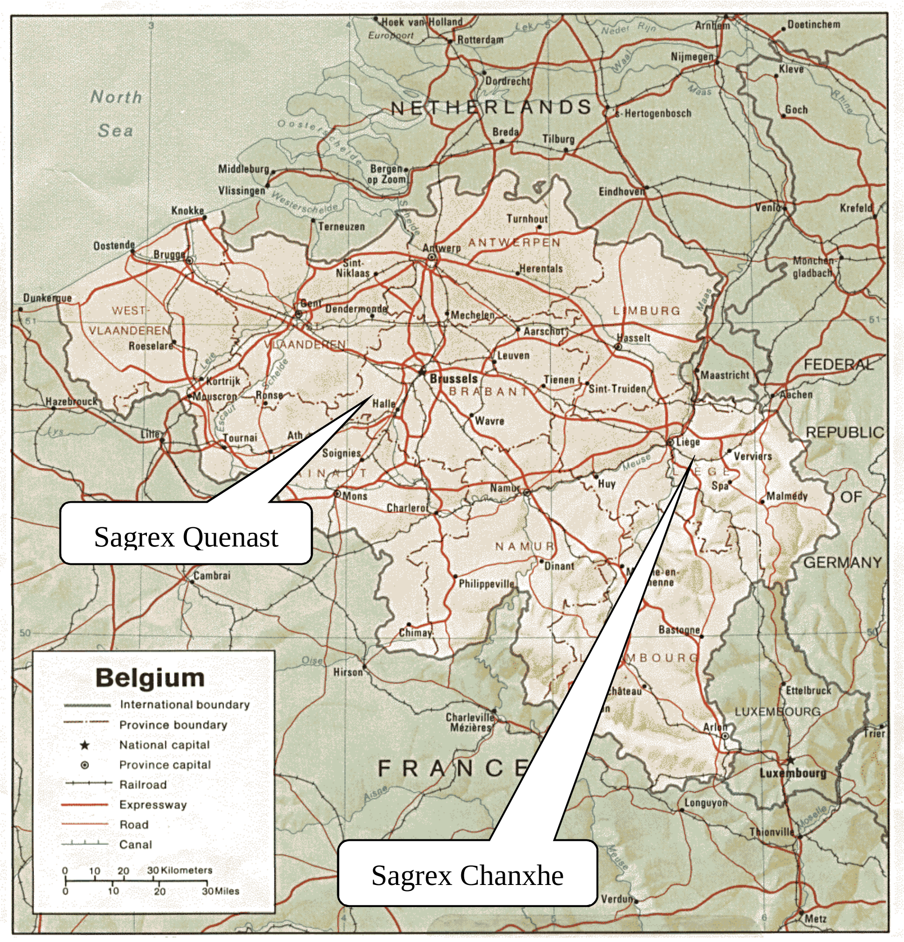

Figure 6.3.: Geographical location of the quarry of Sagrex Quenast and of Sagrex Chanxhe

The quarry extracts aggregates out of magmatic the rock. The current excavation has a maximum depth of 145 m and is divided into six levels. The lowest point of the quarry is located approximately 40 m below sea level.

Sagrex Quenast has a crushed stone production of approximately 1,900,000 tons/year. The production of Quenast is a so called "dry" process because water is only used in small quantities to prevent dust emissions. It can be divided in two parts. The first part of the production delivers a 0/250 mm calibre. The primary crushing after the blasting of the rock by explosives is performed on a jaw and gyrator crusher after which the 0/250 mm calibre is collected on a so called stock pile.

The second part of the production starts when the stock pile 0/250 mm is transported by transport belt out of the quarry to the plant at the surface. A first screening separates the fraction 20/250 mm from the fraction 0/20 mm aggregates (Ag/PpFC) which is also the first place that has been sampled. The 20/250 mm calibre is derived to a cone crusher (Metso HP800), starting point for the secondary crushing. The crushed rock is then passed over a second screen that separates the fraction 20/56 from the fraction 0/20 mm (Ag/PpSC) which delivers the second place for sample collection. The fraction 20/56 mm is derived to two screening lines (in parallel), which sort the different calibres from the largest to the smallest. The ballast 31.5/50 mm of each screening line is put on stock by a conveyor belt. The other screened calibres are stored in specially assigned aggregates silos and if necessary, emptied and transported by wheel loader and articulated truck to separated stocks (**Figure 6.4.**).

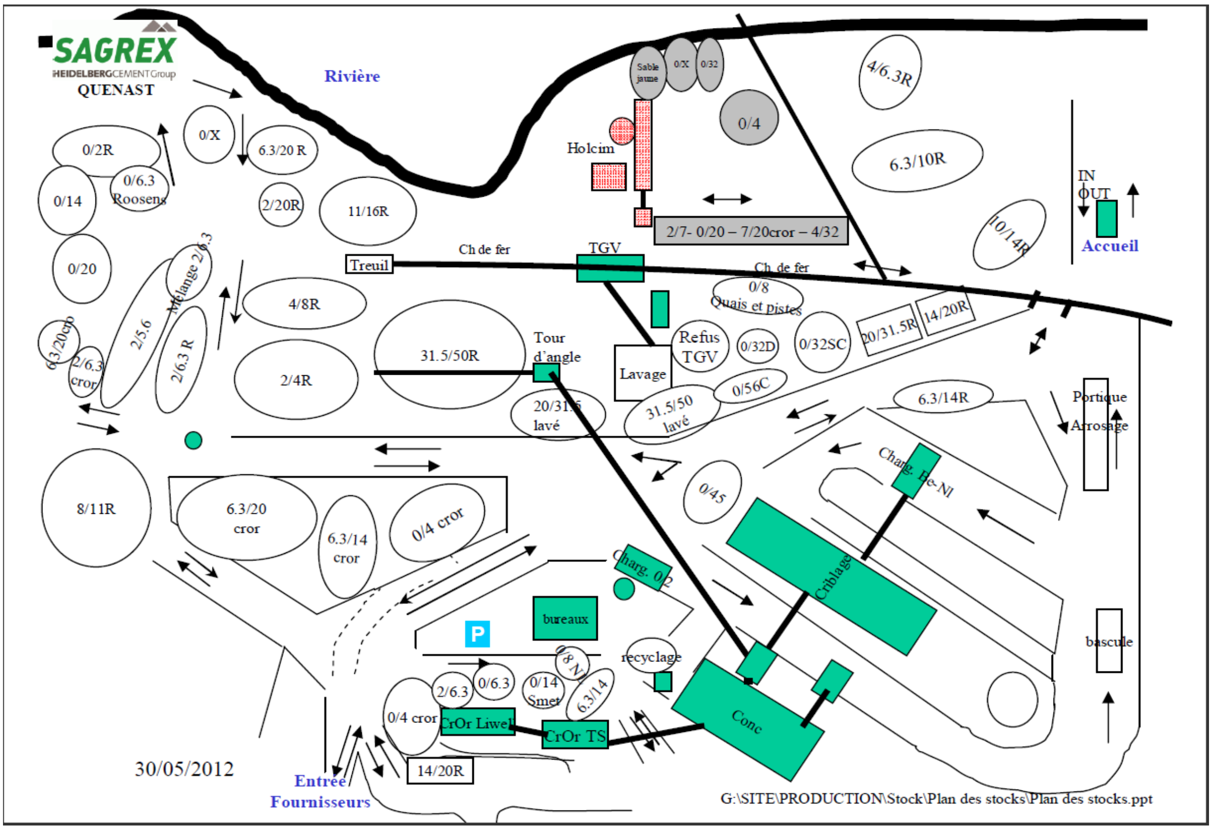

Figure 6.4.: The different aggregates and their stock location in the quarry of Sagrex Quenast

Two of these stocks are the 0/4 mm (Ag/Pp04Sa) and 0/2 (Ag/Pp02Sa) sands which designates the two last sampling places. Calibres can also be redirected to tertiary and quaternary crushing for further manipulation on smaller cone crushers (Metso HP300, HP4 and H4000) after which the generated calibres are redirected to their assigned silo and or stock. Interesting to mention is that materials after tertiary and quaternary crushing contain less fines than the materials collected after primary and secondary crushing.

Figure 6.5. The quarry of Sagrex Quenast

6.4.2. Dolomitic limestone

The operation in the quarry of Sagrex Chanxhe is much smaller than in the quarry of Sagrex Quenast. Sagrex Chanxhe has a crushed stone production of approximately 300,000 tons/year and is located on the right bank of the Ourthe in Chanxhe-Poulseur part of the village Sprimont.

From a geological perspective, the deposit on the Ourthe valley is characterised by a succession of synclines originating from the Carboniferous geologic period (Tournaisian and Visean) and anticlines originating from the Late Devonian geologic period (Famennian). The extracted material from the quarry of Sagrex Chanxhe consists for this reason out of limestone and dolomitised limestone.

The quarry of Sagrex Chanxhe consists out of three levels to extract the dolomitic limestone material for aggregates production. After blasting with explosives, primary crushing is performed on a jaw crusher Bergeaud VB 1311 VB. The crushed material is then collected on a stock pile. By transport belt, material is derived to a Metso NP13-15 percussion crusher for secondary crushing to a 0/31.5mm calibre after which a first screening is performed on a CMB Niagara screen CR26 in to three calibres, a 0/20 mm, a 20/31.5 mm which is collected in an aggregate silo and a fraction bigger than 32 mm that is redirected to the Metso NP13-15 percussion crusher. The 0/20 mm calibre delivered the first place that has been sampled. The 0/20 mm is further screened on a CMB Niagara screen CR30, to separate the 0/20 mm in three fractions; 0/4 mm, 4/8 mm, 8/20 mm. After screening, these calibres are collected in separate aggregate silos and if necessary in designated stocks. The sand 0/4 mm is further treated by directing it to the washing installation where the sludge containing the fine fraction of the sand is separated from the rest of the sand. The unwashed sand, the washed sand and the sludge (ARM/DLSl) were sampled with a frequency described in **section 6.5.**

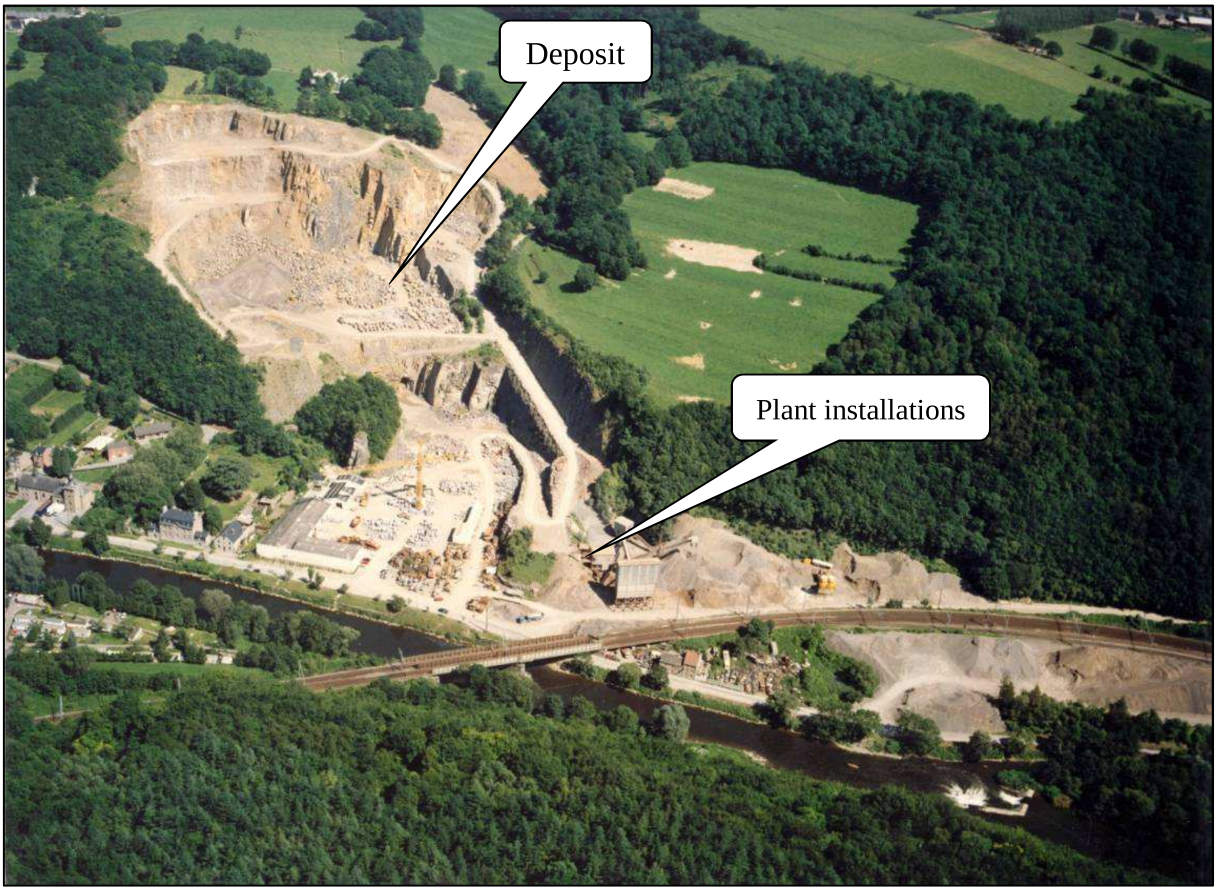

Figure 6.6. The quarry of Sagrex Chanxhe

6.5. Sampling

Porphyry materials selected for analysis were sampled at four different places as described in **paragraph 6.4.1.** Two stocks of 0/20 aggregates, the first formed after the primary crushing (Ag/PpFC) and the second after a secondary crushing (Ag/PpSC) as well as a sand 0/4 mm (Ag/PpS04) and sand 0/2 mm (Ag/PpS02).

By taking these samples at different times spread over 2011 out of the production process, the influence of the Particle Size Distribution (PSD) on the chemical composition can be investigated. The chemical variation of the porphyry materials are graphically presented in **figure 6.1.**

A sample from each stock was randomly selected to be further investigated according to tests described in **section 2.3.**: Ag/PpS04/S5, Ag/PpS02/S9, Ag/PpFC/S6 and Ag/PpSC/S9 (**Figure 6.1.**). Furthermore out of these four samples, the sample with the highest content of fines, logically the 0/2 sand (Ag/PpS02/S9) was wet screened on a sieve of 63 µm to separate the fines fraction (ARM/PpF/S9) from the sand fraction bigger than 63 µm. In practice, this fines fraction can be dry screened with a static separator. The chemical analyses performed by XRF (**Paragraph 3.5.1.**), of both fractions together with the original 0/2 sand (Ag/PpS02/S9) are presented in **table 6.1.**

Table 6.1.: Chemical composition of TM/PpS02/S9 and its fractions bigger and smaller than 63µm

ARM		Porphyry 0/2	Porphyry 0/2 (>63µm)	Porphyry Fines (<63µm)
		Ag/Pp02Sa/S9		**ARM/PpF/S9**
CaO	(wt%)	3.37	3.50	3.06
SiO_2	(wt%)	61.90	62.34	57.32
Al_2O_3	(wt%)	15.58	15.45	15.94
Fe_2O_3	(wt%)	6.70	6.23	9.36
K_2O	(wt%)	2.39	2.41	2.14
Na_2O	(wt%)	3.58	3.77	3.28
SO_3	(wt%)	0.07	0.10	-
S	(wt%)	-	-	0.06
MgO	(wt%)	2.90	2.80	4.24
TiO_2	(wt%)	0.79	0.73	1.03
P_2O_5	(wt%)	0.14	0.13	0.24
Cl	(wt%)	-	0.01	0.01
LOI 975°C (O_2)	(wt%)	2.29	2.20	2.94
C_{total}	(wt%)	0.05	0.04	0.07
S_{total}	(wt%)	0.03	0.03	0.33

As described in **paragraph 6.4.2.**, the dolomitic limestone materials were also recovered at four different times spread over 2011, namely one coming from a stock 0/20 aggregates, two coming from two stocks of 0/2 sand, where one stock was washed, the other stock was unwashed and finally a stock of sludge (Ag/DLSl) coming from the washing of the above described sands or the further to be investigated ARMs. As can be seen from **figure 6.2.**, the chemical variation is quite large.

Table 6.2.: Chemical composition of the three selected dolomitic limestone sludges and their mix

ARM		Ag/DLSl/S11	Ag/DLSl/S4b	Ag/DLSl/S5	ARM/DLSl/Mix
CaO	(wt%)	46.45	44.94	39.67	43.69
SiO_2	(wt%)	4.22	1.91	2.97	3.03
Al_2O_3	(wt%)	1.89	0.63	0.85	1.12
Fe_2O_3	(wt%)	1.39	0.63	1.20	1.07
K_2O	(wt%)	0.42	0.17	0.15	0.25
Na_2O	(wt%)	0.05	0.01	0.01	0.02
SO_3	(wt%)	-	-	-	-
S	(wt%)	0.37	0.20	0.06	0.21
MgO	(wt%)	3.50	7.68	11.30	7.49
TiO_2	(wt%)	0.09	0.03	0.05	0.06
P_2O_5	(wt%)	0.04	0.04	0.02	0.03
Cl	(wt%)	-		-	
LOI 975°C (O_2)	(wt%)	41.27	43.62	43.52	42.80
C_{total}	(wt%)	10.49	12.41	11.95	11.62
S_{total}	(wt%)	0.42	0.12	0.06	0.20

Three samples of sludge, Ag/DLSl/S4b, Ag/DLSl/S5, Ag/DLSl/S11 (**Figure 6.2.**) were selected to be analysed according the tests described in **chapter 3**. These samples were also mixed in equal proportions after which the chemistry of the mix (ARM/DLSl/Mix) was calculated and presented in **table 6.2.**

6.6. Research description

Porphyry neither dolomitic limestone is to our knowledge used up today in Portland clinker production. On the other hand, the use of natural and thermally activated porphyrite by Hojamberdiev **[8]** as also the use of dolomitic limestone by Tsivilis **[9]** was already investigated as raw material for Portland cement production.

The primary objective of this study is to investigate how much of the porphyry and dolomitic limestone fines and/or sludge could be maximised in a Portland clinker process by replacing Classic Raw Materials (CRMs) as a function of each of the three kilns with enumeration of possible limitations. Numerical simulations will be carried out to maximise the use of these materials in clinker kilns taking into account the compositional variation of the fines and sludge, its behaviour within a clinker kiln and the impact on the energy consumption.

Although CaF_2 is the best known mineraliser (**Section 2.7.**) **[10-12],** MgO has also significant fluxing activities. It could lower the temperature of the liquid formation and decrease the viscosity of the liquid phase by which the residual free lime tend to reduce **[12][14-15]**.

Within this investigation, MgO will especially be supplied by the dolomitic limestone sludge but will also be present in significant levels *[wt%]* in porphyry fines.

Furthermore, experimental clinkers will be produced corresponding to ARM dosages that were esteemed as realistic by the numerical simulations. These clinkers will be fully analysed and evaluated according to the evaluation concept described in **chapter 3**. They will be evaluated on the possible presence of fluxing effect of the MgO.

6.7. Results and discussion

Based on the articles “Fines extracted from porphyry and dolomitic limestone aggregates production: MgO as fluxing agent for a sustainable Portland clinker production” published in Construction and Building Materials **[17]** and the congress article “MgO as fluxing agent for a sustainable Portland clinker production” for the First International Conference on the Chemistry of Construction Materials in Berlin in 2013 **[18]**, the results of the investigation on the use of fines and sludge of Porphyry and dolomitic limestone as ARM for Portland clinker production are described below.

As mentioned in the research description, one of the goals is to demonstrate a fluxing effect by the present MgO *[wt%]* in both the porphyry fines as the dolomitic limestone sludge. Without addition of CaF_2, a combined effect of R_2O (R=Li, Na, K), MgO and SO_3 seems to have the most promising fluxing effect **[19]** which could lower the temperature of the liquid formation and significantly increases the rate of C_3S formation at 1350°C **[14]**.

It is important to emphasise that C_3S is not formed at temperatures below approximately 1200°C **[20]**. Formulae for the calculation of the percentage of liquid (%Liq) were already described in **section 2.6.** These formulae indicate why MgO and alkali work together in a combined fluxing effect whereby the %Liq is increased. As stated in **section 2.5.**, alkali sulfates decrease the viscosity of the melt, increasing the alite formation which explains the presence of SO_3 in the combined fluxing effect. When there is not sufficient SO_3, free alkali will be formed, increasing the viscosity of the melt which will lower alite formation **[14-16]** explaining the recommendation and use of the DoS factor (**Section 2.6.**). Furthermore, it was stated by Taylor **[7]** that the burnability of the CCM or the ease by which free lime can be reduced in the kiln to an acceptable value, decreases with increasing LSF or Saturation Rate (SR). Increase in LSF implies more CaO has to react, increase in SR implies less liquid at a given temperature which are both energetically unfavourable. Increase of MgO could therefore have a positive influence on the burnability by lowering the CaO *[wt%]* without an increase in SR and an increase of the liquid phase. Based on this knowledge, the use of porphyry fines and dolomitic limestone sludge will be investigated as ARM for Portland clinker production.

6.7.1. Influence of fines extraction on aggregate application and chemistry

As mentioned in **section 6.5.**, the sample Ag/Pp02Sa/S9 was wet screened on a sieve of 63µm. As can be noticed in **table 6.3**, the extraction of fines (< 63µm) has a positive influence on the water demand of the sand when used in concrete. The concrete mixes described in **table 6.3.** were composed to have a comparable consistency S3 **[21]**.

Compared with the water demand of a concrete based on round river sand 0/2 (ref), broken porphyry sand 0/2 (Ag/Pp02Sa/S9) increases the water demand with 42 wt%, porphyry sand 0/2 (Ag/Pp02Sa/S9) where fines are extracted has only a 25 wt% higher water demand. As already stated, asphalt producers need the perfect ratio between bitumen and fines **[22]** whereby for energetic and technical reasons, they rather like to add than extract fines to attain the perfect ratio.

Table 6.3.: Influence of fines on concrete composition and characteristics

Materials		Reference	Ag/Pp02Sa/S9 (<63µm included)	Ag/Pp02Sa/S9 (<63µm not included)
CEM III/B 42,5 N LH	kg/m³	320	320	320
Water	kg/m³	160	160	160
River sand 0/2	kg/m³	705	0	0
Porphyry 0/2	kg/m³	0	705	0
Porphyry 0/2 > 63 µm	kg/m³	0	0	705
Gravel 2/8	kg/m³	604	604	604
Gravel 8/16	kg/m³	578	578	578
Additional water	**kg/m³**	**0**	**66**	**40**
Slump	mm	105	110	100
Flow	mm	420	440	440

Also regional standardisation demands **[23]** limit the wt% of the fraction smaller than 63 µm (fines) in normalised aggregates. This explains why aggregates producers extract fines by wet or dry screening if the level of fines is too high by which alternative raw materials as ARM/PpF/S9 or ARM/DLSl/Mix could be generated.

6.7.2. Clinker feed calculations and preparations

As already described in **section 3.3.**, a simulation program based on linear equations, was used to calculate Cold Clinker Meals (CCMs) for each factory (CCM/Ant,Lxh,Maa) out of the CRMs, in the case of the reference CCMs as well as partly out of the ARMs, in the case of the alternative CCMs. The increasing levels of MgO entered by the ARMs have to be mastered if higher than 2 wt%.

As explained in **section 2.4.**, MgO will be built in the alite structure up to 2.0 wt% from which the remainder will form periclase. The LSF_MgO governs the ratio of alite and belite. It holds a correction for the incorporation of MgO in C_3S and has to be altered if MgO *[wt%]* is bigger than 2 wt% (**Section 2.6.**). The remainder of MgO *[wt%]* above 2 wt% or the part which will form periclase was percentually subtracted from the four critical metal oxides *[wt%]* achieved in clinker when MgO *[wt%]* is 2 wt% and the mineralogical limitations are in line with those described in **table 6.4.** In this way, the ratio between these metal oxides *[wt%]* is maintained as well as the ratio between the different major constituent phases.

Table 6.4.: Chemical and mineralogical limitations on the final clinker

Clinker		Antoing	Lixhe	Maastricht
Cl	(wt%)	$x < 0.08$	$x < 0.08$	$x < 0.08$
SO_3	(wt%)	$x < 1.4$	$x < 1.2$	$x < 1.1$
Na_2Oeq	(wt%)	$x < 1.2$	$x < 1.2$	$x < 1.2$
MgO	(wt%)	$x < 4.0$	$x < 4.0$	$x < 4.0$
MgO/Fe_2O_3	(wt%)	$x < 1.40$	$x < 1.40$	$x < 1.40$
DoS-level	(wt%)	$80 < x < 120$	$80 < x < 120$	$80 < x < 120$
If [MgO] < 2 wt%				
LSF_MgO	(wt%)	98.24	98.19	98.20
C_3A	(wt%)	7.35	6.65	7.33
LiqSimple	(wt%)	19.18	22.73	22.97
If [MgO] > 2 wt%, the remainder is compensated percentually (X - %MgO)				
CaO	(wt%)	65.92 – 1.51	66.56 – 0.78	-
SiO_2	(wt%)	21.87 – 0.49	21.76 – 0.31	-
Al_2O_3	(wt%)	4.45 – 0.10	4.85 – 0.12	-
Fe_2O_3	(wt%)	2.60 – 0.06	3.63 – 0.09	-

The CCMs for this investigation were calculated with the simulation program (**Section 3.3.**) in line with the chemical and mineralogical requirements described in **table 6.4.** which incorporates some additional information compared to **table 2.5.** The alternative CCMs were calculated to maximise the use of the porphyry and dolomitic limestone ARMs. The compositions of the reference CCMs are presented in **table 3.1.**, these of the alternative CCMs presented in **table 6.5.**

- Porphyry:

  Because of the high Al_2O_3 *[wt%]* in porphyry materials (**Table 6.1.**), it was expected that they could function as Al_2O_3-source in CCM replacing fly ash as classic source. From the four selected samples, the ARM closest to the average SiO_2 *[wt%]* of all sampled porphyry materials, the porphyry sand 0/4 (ARM/Pp04Sa/S5) was used in the simulation program as well as the porphyry fines (ARM/PpF/S9). By maximisation of these materials in the different CCMs, the fly ash dosage *[wt%]* is lowered and even replaced completely in the case of CBR Antoing and CBR Lixhe (**Table 6.5.**). For the alternative CCMs of CBR Lixhe also the SiO_2-source was completely replaced which is not really realistic from a production point of view because three raw materials are not sufficient to manage four metal oxides. As can be noticed in **table 6.1.**, the chemical analysis of the fines (ARM/PpF/S9) was significantly different from the material where it was originated from as well as the other porphyry materials that are presented in **figure 6.1.** This chemical shift could be explained by the fact that hornblende is easier to grind by its lower hardness compared to quartz and feldspar (**Section 6.2**.) which results in a doubled MgO *[wt%]* content as well as an increased Fe_2O_3 *[wt%]* content in the porphyry fines (ARM/PpF/S9) compared to the porphyry sand 0/2 (Ag/Pp02Sa/S9). However, it is the lowered SiO_2 *[wt%]* (**Table 6.1.**) that results in higher porphyry fines ARM (ARM/PpF/S9) dosages in the alternative clinker meal compositions of CBR Lixhe (CCM/Lxh/PpF). Furthermore, the porphyry materials contain higher levels of alkali which will increase the total alkali *[wt%]* of the final clinker interesting from the point of view of the combined fluxing effect described in the beginning of this section.

- Dolomitic limestone:

  The preparation of the CCMs based on the dolomitic limestone ARM (Ag/DLSl/Mix) had as limiting factors the MgO *[wt%]* and the ratio between MgO and Fe_2O_3 described in **section 2.5.** CBR Antoing was ideal to evaluate the influence of high levels of SO_3 *[wt%]* and alkalis *[wt%]* (**Table 3.5.**, **Table 3.6.** and **Table 6.8.**) together with MgO *[wt%]* approaching the maximum limit of 4.0 wt% and an MgO/Fe_2O_3 ratio of 1.4. The alternative clinkers calculated out of the factory of CBR Lixhe will give lower levels of SO_3 *[wt%]* and alkalis *[wt%]* (**Table 3.5.**, **Table 3.6.** and **Table 6.8.**). Comparing these clinkers with those produced for CBR Antoing will demonstrate their influence on the combined fluxing effect to lower the sintering temperature.

  Alternative clinkers of ENCI Maastricht with dolomitic limestone ARM would not result in extra information and were therefore after simulation not further investigated (**Table 6.5.**).

Table 6.5.: Compositions of the different alternative clinker meals made to be fed to the static kiln

	CRM+ARM	Quantity (wt%)		**CRM+ARM**	Quantity (wt%)		**CRM+ARM**	Quantity (wt%)
CCM/Ant/Pp	CRM/Ant/CP	2.81	CCM/Ant/PpD	CRM/Ant/CP	23.30	CCM/Ant/DL	CRM/Ant/CP	64.67
	CRM/Ant/CR	83.37		CRM/Ant/CR	64.93		CRM/Ant/CR	11.82
	CRM/Ant/FA	0.00		CRM/Ant/FA	0.09		CRM/Ant/FA	5.10
	CRM/Ant/IC	0.76		CRM/Ant/IC	0.26		CRM/Ant/IC	0.67
	ARM/Pp04Sa/S5	13.86		ARM/PpF/S9	11.42		ARM/DLSl/Mix	17.75
	Sum	100.00		Sum	100.00		Sum	100.00
CCM/Lxh/Pp	CRM/Lxh/Tu	81.27	CCM/Lxh/PpD	CRM/Lxh/Tu	81.55	CCM/Lxh/DL	CRM/Lxh/Tu	62.53
	CRM/Lxh/Lo	0.00		CRM/Lxh/Lo	0.54		CRM/Lxh/Lo	7.26
	CRM/Lxh/FA	3.07		CRM/Lxh/FA	0.00		CRM/Lxh/FA	10.33
	CRM/Lxh/IC	1.57		CRM/Lxh/IC	0.71		CRM/Lxh/IC	1.31
	ARM/Pp04Sa/S5	14.08		ARM/PpF/S9	17.20		ARM/DLSl/Mix	18.57
	Sum	100.00		Sum	100.00		Sum	100.00
CCM/Maa/Pp	CRM/Maa/Ma	81.09	CCM/Maa/PpD	CRM/Maa/Ma	81.11	CCM/Maa/DL	CRM/Maa/Ma	77.16
	CRM/Maa/SC	1.95		CRM/Maa/SC	3.13		CRM/Maa/SC	5.91
	CRM/Maa/FA	4.10		CRM/Maa/FA	4.53		CRM/Maa/FA	10.94
	CRM/Maa/IC	1.43		CRM/Maa/IC	0.95		CRM/Maa/IC	1.55
	ARM/Pp04Sa/S5	11.42		ARM/PpF/S9	10.29		ARM/DLSl/Mix	4.44
	Sum	100.00		Sum	100.00		Sum	100.00

6.7.3. Chemical and TGA analysis

The chemical variation of the porphyry materials was evaluated by plotting them in **figure 6.1.** by their respective SiO_2 and Al_2O_3 *[wt%]* without L.O.I. since that is the way how the ARM will be fed in reality to the Hot Clinker Meal (HCM). By excluding the LOI, the metal oxides, alkali and sulfate are recalculated to 100 wt%. It is clear that the porphyry materials are chemically very stable regardless of their particle size distribution.

- Porphyry:

  TGA analyses of the selected porphyry materials as well as the porphyry fines presented in **figure 6.5.** show two small but distinct mass losses, the first between 450°C and 600°C and a second between 950°C and 1050°C.

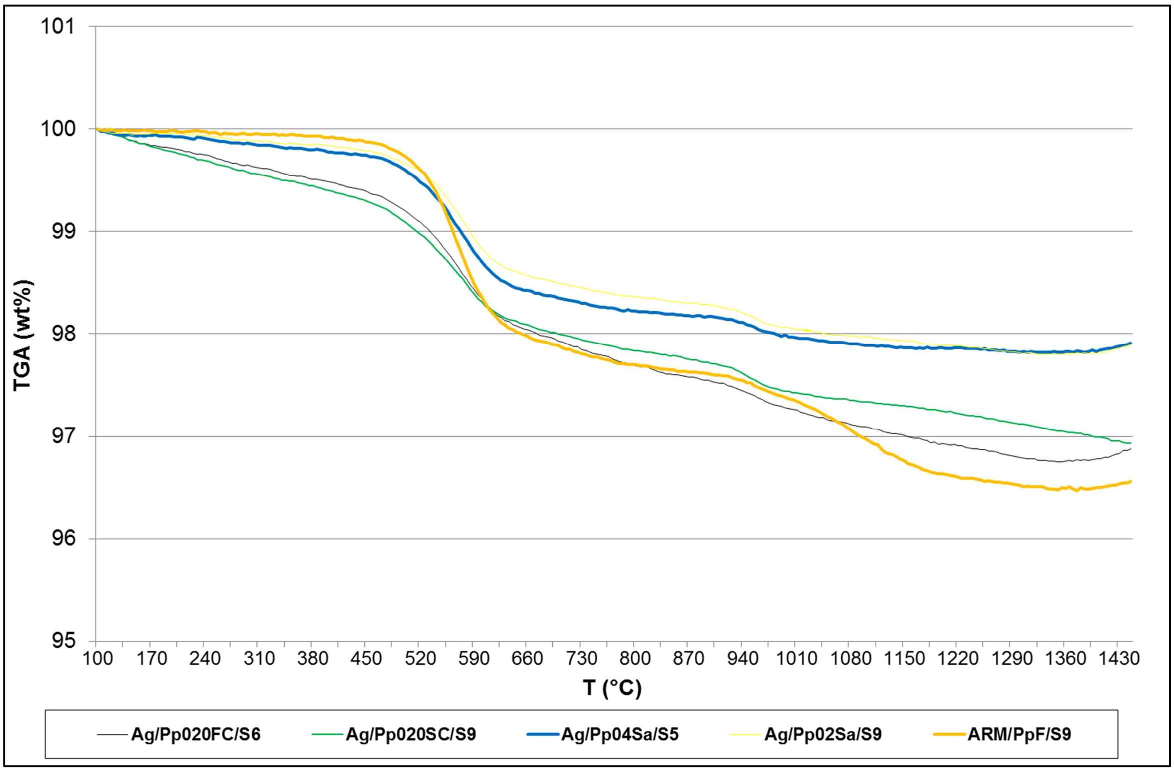

Figure 6.5.: TGA analysis of the four selected porphyry materials as well as the porphyry fines ARMs

Quite remarkable is the fact that the mass losses in both temperature regions are bigger for the fines fraction ARM/PpF/S9, indicating that the mass loss comes most likely from the hornblende which consists partly out of hydroxyl and fluorine. Evaluation of the TGA analysis of the selected porphyry materials and their chemical analyses (**Table 6.1.**) show clearly that CaO as well as MgO are not in carbonated form and will not, in contrast with dolomitic limestone, emit CO_2 when thermally degraded up to 1450°C.

- Dolomitic limestone:

  The chemical instability of the dolomitic limestone materials is quite clear out of **figure 6.2.** This could significantly be ameliorated by selecting them by their particle size. It can also be noticed that CaO is more present in the sand than in coarse aggregates. TGA analyses of the selected dolomitic limestone samples (**Figure 6.6.**), show that all CaO *[wt%]* and MgO *[wt%]* (**Table 6.2.**) are present in carbonated form as $CaCO_3$ and $[Ca,Mg](CO_3)_2$ which will emit CO_2 when sintered in a clinker kiln. The known decarbonation energies found in literature, 1782 kJ/kg for $CaCO_3$ and 1400 kJ/kg for $MgCO_3$, make it possible to calculate the total decarbonation energy out of the chemical analysis.

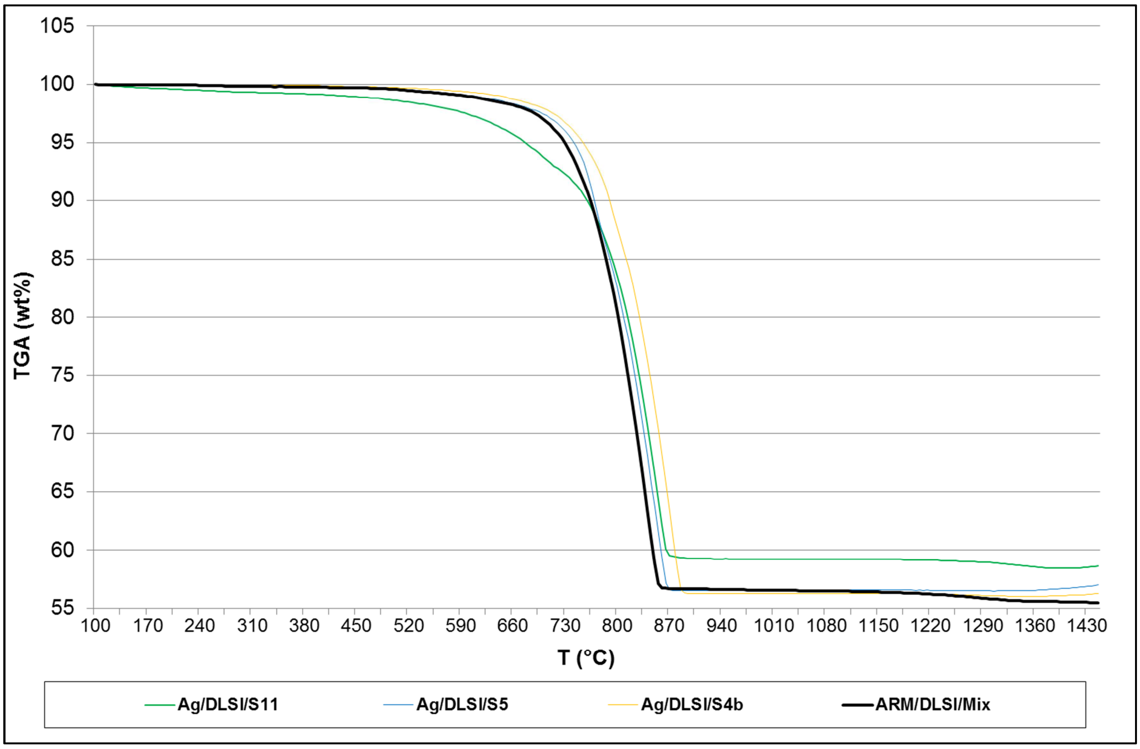

Figure 6.6.: TGA analysis of the three selected dolomitic limestone as well as the dolomitic limestone mix ARM

By its lower decarbonation energy, it is logical that increasing levels of $[Ca,Mg](CO_3)_2$ in the alternative CCMs could lower the energy consumption of Portland clinker production if the increased MgO *[wt%]* could replace CaO *[wt%]* in the mineralogical constituent phases (**Table 6.6.**). However, the decarbonation energies (**Table 6.7.**) out of DTA analysis (µVs/mg) as well as these calculated out of the chemical analysis of CRMs and ARMs (**Table 3.4.** and **Table 6.2.**), the composition of the CCMs (**Table 3.2.** and **Table 6.5.**) and the known decarbonation energies (J/g) for $CaCO_3$ and $MgCO_3$ show no big differences. The increase of MgO added by the ARM which partly replaces CaO coming from the classic limestone source is not sufficient to measure a difference in decarbonation energy. If the limestone CRMs could be lowered even more (**Table 6.5.**) by positive mineralogical influences of the ARM (**Section 4.4**), a decrease of decarbonation energy could possibly be measured.

Table 6.6.: TGA/DTA evaluation of the Reference Cold Clinker Meals of CBR Antoing, CBR Lixhe and ENCI Maastricht

CCM	Inorg CO_2	Total CaO	Total MgO	Inorg CO_2	$CaCO_3$	$MgCO_3$
Mat	TGA (wt%)	XRF (wt%)	XRF (wt%)	XRF Der (wt%)	XRF Der (wt%)	XRF Der (wt%)
CCM/Ant/Ref	34.0	43.48	1.10	35.32	77.60	2.30
CCM/Ant/Pp	34.8	43.97	1.18	35.80	78.48	2.48
CCM/Ant/PpF	34.3	43.68	1.41	35.82	77.96	2.95
CCM/Ant/DL	35.0	42.66	2.31	36.00	76.14	4.83
CCM/Lxh/Ref	32.5	45.26	0.88	36.48	80.78	1.84
CCM/Lxh/Pp	34.0	44.68	1.15	36.32	79.74	2.41
CCM/Lxh/PpF	34.8	44.45	1.44	36.46	79.33	3.01
CCM/Lxh/DL	33.8	43.34	2.27	36.49	77.35	4.75
CCM/Maa/Ref	34.2	44.79	0.97	36.21	79.94	2.03
CCM/Maa/Pp	33.8	44.62	1.09	36.21	79.64	2.28
CCM/Maa/PpF	34.0	44.84	1.19	36.49	80.03	2.49

Table 6.7.: TGA/DTA evaluation of the Reference Cold Clinker Meals of CBR Antoing, CBR Lixhe and ENCI Maastricht

CCM	Decarb E	Decarb E
Mat	DTA (µVs/mg)	XRF Der (J/g)
CCM/Ant/Ref	182.3	1390
CCM/Ant/Pp	166.2	1390
CCM/Ant/PpF	166.1	1381
CCM/Ant/DL	162.3	1393
CCM/Lxh/Ref	161.8	1287
CCM/Lxh/Pp	169.7	1305
CCM/Lxh/PpF	154.4	1308
CCM/Lxh/DL	227.7	1316
CCM/Maa/Ref	228.0	1373
CCM/Maa/Pp	219.0	1319
CCM/Maa/PpF	195.2	1319

Furthermore, the chemical analysis of the final clinkers presented in **tables 6.8.**, **6.9.** and **6.10.** shows that the CCM out of the used ARMs and CRMs were properly assessed by the simulation program.

The increase of MgO in the alternative CCMs with porphyry materials is moderate but significant contrary to the dolomitic limestone materials where it is quite impressive.

Based on **figure 2.5.** and the MgO/SO_3 level, the reference and alternative clinkers will have an alite formation in the monoclinic form M3 as explained in **section 2.4.**, making the influence of the monoclinic form on the reactivity of alite not relevant for this investigation.

Table 6.8.: Chemical analysis and Bogue calculations of the final clinkers with porphyry and porphyry fines produced in a static kiln

Clinker		Cl/Ant/Pp	Cl/Ant/PpF	Cl/Lxh/Pp	Cl/Lxh/PpF	Cl/Maa/Pp	Cl/Maa/PpF
Temp.		1450°C	1450°C	1450°C	1450°C	1450°C	1450°C
CaO	(wt%)	66.56	66.03	66.49	66.64	65.87	66.79
SiO_2	(wt%)	22.30	22.65	21.60	21.70	22.60	22.45
Al_2O_3	(wt%)	4.03	4.02	4.32	4.26	4.46	4.47
Fe_2O_3	(wt%)	2.79	2.62	3.93	3.68	3.55	2.75
K_2O	(wt%)	0.33	0.45	0.20	0.14	0.24	0.14
Na_2O	(wt%)	0.63	0.51	0.64	0.58	0.59	0.47
SO_3	(wt%)	0.50	0.63	0.10	0.06	0.04	0.05
MgO	(wt%)	1.80	2.14	1.60	1.90	1.59	1.76
TiO_2	(wt%)	0.23	0.28	0.27	0.33	0.28	0.31
P_2O_5	(wt%)	0.10	0.04	0.18	0.16	0.14	0.15
Cl	(wt%)	-	0.12	-	-	-	-
LOI 975°C	(wt%)	0.43	0.28	0.31	0.22	0.31	0.33
DoS-factor	(wt%)	45.69	60.50	10.03	6.91	4.14	6.89
Alite (C_3S)	(wt%)	70.37	65.86	71.83	72.44	61.30	67.26
Belite (C_2S)	(wt%)	10.86	15.27	7.75	7.58	18.56	13.63
Celite (C_3A)	(wt%)	5.96	6.22	4.80	5.06	5.81	7.19
Ferrite (C_4AF)	(wt%)	8.49	7.97	11.96	11.20	10.80	8.37

Table 6.9.: Chemical analysis and Bogue calculations of the Final Clinkers of CBR Antoing with dolomitic limestone made in a static kiln (Ref=Cl/Ant/Ref; DL= Cl/Ant/ DL)

Clinker		Ref	DL	Ref	DL	Ref	DL	Ref	DL
Temp.		1450°C	1450°C	1400°C	1400°C	1350°C	1350°C	1300°C	1300°C
CaO	(wt%)	65.90	64.15	65.94	64.50	65.98	64.26	65.19	64.42
SiO_2	(wt%)	22.27	21.66	22.35	21.84	22.43	21.77	22.35	21.95
Al_2O_3	(wt%)	4.14	4.50	4.14	4.14	4.13	4.18	4.14	4.12
Fe_2O_3	(wt%)	3.02	2.88	2.97	2.76	2.92	2.77	2.96	2.76
K_2O	(wt%)	0.59	0.77	0.58	0.83	0.57	0.90	0.76	0.84
Na_2O	(wt%)	0.17	0.16	0.18	0.17	0.18	0.15	0.23	0.16
SO_3	(wt%)	0.89	0.86	0.86	0.84	0.83	0.89	1.08	0.81
MgO	(wt%)	1.73	3.96	1.75	3.93	1.77	3.93	1.78	3.86
TiO_2	(wt%)	0.25	0.23	0.25	0.22	0.25	0.23	0.25	0.23
P_2O_5	(wt%)	0.21	0.17	0.2	0.17	0.19	0.17	0.19	0.17
Cl	(wt%)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
LOI 975°C	(wt%)	0.48	0.30	0.46	0.30	0.44	0.45	0.73	0.38
DoS-factor		123.42	99.86	119.60	90.80	115.75	92.83	114.51	87.98
Alite (C_3S)	(wt%)	66.84	62.13	66.50	64.78	66.16	64.05	63.43	63.75
Belite (C_2S)	(wt%)	13.44	15.24	13.92	13.76	14.41	14.10	16.24	14.85
Celite (C_3A)	(wt%)	5.86	7.05	5.93	6.30	6.01	6.39	5.96	6.25
Ferrite (C_4AF)	(wt%)	9.19	8.76	9.04	8.40.	8.89	8.43	9.01	8.40

Table 6.10.: Chemical analysis and Bogue calculations of the Final Clinkers of CBR Lixhe with dolomitic limestone made in a static kiln (Ref=Cl/Lxh/Ref; DL= Cl/Lxh/ DL)

Clinker		Ref	DL	Ref	DL	Ref	DL	Ref	DL
Temp.		1450°C	1450°C	1400°C	1400°C	1350°C	1350°C	1300°C	1300°C
CaO	(wt%)	66.28	64.79	66.00	64.26	65.93	64.39	65.89	63.97
SiO_2	(wt%)	21.93	22.12	22.02	22.02	21.89	21.91	21.77	22.23
Al_2O_3	(wt%)	4.40	4.26	4.35	4.38	4.42	4.41	4.48	4.18
Fe_2O_3	(wt%)	4.21	3.84	4.26	3.80	4.23	3.86	4.20	3.79
K_2O	(wt%)	0.21	0.11	0.17	0.19	0.20	0.28	0.26	0.36
Na_2O	(wt%)	0.20	0.16	0.18	0.18	0.18	0.20	0.20	0.21
SO_3	(wt%)	0.12	0.15	0.08	0.23	0.19	0.30	0.27	0.42
MgO	(wt%)	1.28	3.38	1.30	3.44	1.29	3.45	1.35	3.26
TiO_2	(wt%)	0.30	0.31	0.30	0.31	0.31	0.30	0.31	0.31
P_2O_5	(wt%)	0.24	0.22	0.24	0.23	0.24	0.22	0.24	0.23
Cl	(wt%)	n.a.	-	-	-	-	-	-	-
LOI 975°C (O_2)	(wt%)	0.39	0.22	0.69	0.56	0.71	0.29	0.63	0.65
DoS-factor		27.47	49.97	21.22	58.37	47.20	60.44	56.32	72.75
Alite (C_3S)		67.52	61.48	65.96	59.34	66.24	60.41	66.63	57.92
Belite (C_2S)		11.95	17.05	13.38	18.38	12.80	17.52	12.16	20.05
Celite (C_3A)		4.54	4.79	4.32	5.18	4.56	5.16	4.77	4.67
Ferrite (C_4AF)		12.81	11.69	12.96	11.56	12.87	11.75	12.78	11.53

Also nicely visualised in **table 6.9.** for the alternative clinkers substituted with dolomitic limestone, the reference as well as the alternative clinkers of CBR Antoing have a ratio of Al_2O_3 / Fe_2O_3 ≥ 1.38. As explained in **section 2.6.**, this should result in sufficient liquid formation at 1338°C. These of CBR Lixhe (**Table 6.10.**) are lower than 1.38. Also the limits described in **section 2.5.**, MgO *[wt%]* ≤ 4.0 wt% and MgO / Fe_2O_3 ≤ 1.4 were reached on the final clinkers minimising possible unsoundness problems related to the elevated MgO *[wt%]*.

6.7.4. XRD Analysis

The XRD analyses with Rietveld refinement of the final clinkers presented in **table 6.11.** (Pp), **table 6.12.** (DL) and **table 6.13.** (DL) , show different mineralogical weight percentages than those calculated by Bogue equations out of the chemical analysis of the final clinkers presented in **table 6.8.** (Pp), **table 6.9.** (DL) and **table 6.10.** (DL). Evaluation between the different clinkers could objectively be done by comparing the differences between these theoretical mineralogical Bogue compositions and the real mineralogical XRD compositions. Nevertheless, the repeatability precision of the XRD measurement explained in **section 3.10.** has to be taken in account during this evaluation.

A possible fluxing effect could be demonstrated, if a significant increase of the real measured alite *[wt%]* occurs in comparison with the theoretical calculated alite *[wt%]*.

Table 6.11.: Mineralogical analysis by XRD of the Final Clinkers with Porphyry and Porphyry fines

Clinker		Cl/Ant/ Pp	Cl/Ant/ PpF	Cl/Lxh/ Pp	Cl/Lxh/ PpF	Cl/Maa/ Pp	Cl/Maa/ PpD
Temp.		1450°C	1450°C	1450°C	1450°C	1450°C	1450°C
Alite (C_3S)	(wt%)	73.54	71.04	60.56	69.91	61.72	66.92
Belite (C_2S)	(wt%)	8.71	12.85	16.56	6.70	16.77	13.84
Celite (C_3A)	(wt%)	9.59	4.75	8.91	11.15	9.21	10.45
Ferrite (C_4AF)	(wt%)	7.07	10.43	11.21	8.57	10.22	7.09
Free Lime (CaO)	(wt%)	0.22	0.02	2.08	2.84	0.36	0.43
Periclase (MgO)	(wt%)	0.55	0.68	0.46	0.77	0.62	0.61
Arcanite (K_2SO_4)	(wt%)	0.10	-	0.02	0.27	0.17	0.17
Aphthitalite	(wt%)	0.16	0.23	0.22	-	0.34	0.17

(Full XRD analysis of Cl/Lxh/PpF in Figure A.2. (Appendix A))

Table 6.12.: Mineralogical analysis by XRD of the reference Final Clinkers and the clinkers with dolomitic limestone of CBR Antoing produced in a static kiln (Ref=Cl/Ant/Ref; DL= Cl/Ant/ DL)

Clinker		Ref	DL	Ref	DL	Ref	DL	Ref	DL
Temp.		1450°C	1450°C	1400°C	1400°C	1350°C	1350°C	1300°C	1300°C
Alite (C_3S)	(wt%)	64.52	66.08	64.66	67.93	64.80	65.69	60.86	59.35
Belite (C_2S)	(wt%)	19.73	15.01	19.59	14.90	19.44	17.38	23.35	21.23
Celite (C_3A)	(wt%)	1.79	5.06	2.73	4.64	3.67	5.13	5.79	5.69
Ferrite (C_4AF)	(wt%)	12.86	10.43	11.81	8.91	10.76	8.00	6.88	6.76
Free Lime (CaO)	(wt%)	0.23	0.02	0.45	0.07	0.66	0.25	1.34	1.94
Periclase (MgO)	(wt%)	0.39	3.05	0.35	3.14	0.31	3.18	0.74	3.16
Arcanite (K_2SO_4)	(wt%)	0.32	0.23	0.27	0.25	0.21	0.23	0.67	0.66
Aphthitalite	(wt%)	-	0.12	0.02	0.15	0.02	0.14	0.14	0.30

(Full XRD analysis of Cl/Ant/DL in Figure A.3. (Appendix A))

Table 6.13.: Mineralogical analysis by XRD of the reference Final Clinkers and the clinkers with dolomitic limestone of CBR Lixhe produced in a static kiln (Ref=Cl/Lxh/Ref; DL= Cl/Lxh/ DL)

Clinker		Ref	DL	Ref	DL	Ref	DL	Ref	DL
Temp.		1450°C	1450°C	1400°C	1400°C	1350°C	1350°C	1300°C	1300°C
Alite (C_3S)	(wt%)	65.04	59.50	64.81	54.82	62.78	50.74	60.13	29.02
Belite (C_2S)	(wt%)	14.93	18.52	15.41	23.58	17.83	27.65	19.16	43.97
Celite (C_3A)	(wt%)	3.68	3.16	3.99	3.60	3.63	2.48	6.43	5.37
Ferrite (C_4AF)	(wt%)	15.87	16.31	14.82	15.55	14.73	13.60	11.91	12.60
Free Lime (CaO)	(wt%)	0.23	0.09	0.20	0.15	0.63	0.60	1.89	5.76
Periclase (MgO)	(wt%)	0.18	2.16	0.16	2.09	0.11	2.30	0.11	3.02
Arcanite (K_2SO_4)	(wt%)	0.07	0.02	0.05	0.12	0.01	-	0.36	-
Aphthitalite	(wt%)	-	0.16	0.44	0.08	0.17	-	-	-

The goal is to demonstrate if there is a fluxing effect by an increasing MgO *[wt%]* and if this fluxing effect is related to a combined fluxing effect together with R_2O (R=Li, Na, K) and SO_3 as described in **section 3.2.** and **section 3.3.** The mineralogical analyses performed on the alternative clinkers made at 1450°C are presented in **table 6.11.** (Pp), **table 6.12.**(DL) and **table 6.13.**(DL).

A significant increase in alite *[wt%]* of ± 2.0 to 3.0 wt% is distinguishable in the alternative clinkers of CBR Antoing in comparison with their reference, which cannot be explained by an increased MgO *[wt%]* in the alite phase because the increase in periclase is bigger than the increase of MgO *[wt%]*.

Table 6.12.: Mineralogical analysis by XRD of the reference Final Clinkers and the clinkers with dolomitic limestone of CBR Antoing produced in a static kiln (Ref=Cl/Ant/Ref; DL= Cl/Ant/ DL)

Figure 6.7. demonstrates that the increase of alite *[wt%]* is due to a combined fluxing effect of MgO, alkali and SO_3. From left to right, clinkers showing the biggest gain up to the biggest decrease in alite formation are plotted. The percentages of MgO, Naeq and SO_3 *[wt%]* (**Table 6.8.**, **Table 6.9.** and **Table 6.10.**) are also included in **figure 6.7.**

It is clear that on the left of **figure 6.7.**, the clinkers are high in MgO, Na_2O_{eq} and SO_3 *[wt%]* but even more important a balance is present between alkali and SO_3 *[wt%]*. The clinkers with lower MgO, Na_2O_{eq} or SO_3 *[wt%]* and where no fluxing effect can be distinguished, are positioned in the middle. The small differences between the XRD and Bogue alite *[wt%]* are for these clinkers within the error margin of the XRD measurement (**Section 3.10.**) and can therefore not be allocated to a possible positive or negative mineralogical effect.

At the right, clinkers with high levels *[wt%]* of alkali but almost no SO_3 [wt%], result in a decrease of alite *[wt%]* due to the increased viscosity of the melt by the presence of free alkali.

The presence of free alkali is demonstrated by the small quantities *[wt%]* of arcanite and aphthitalite in comparison with the high levels *[wt%]* of alkali.

Although all the CCMs were designed to have DoS-factors between 80 and 120, many of the final clinkers didn’t achieve this goal. The reason of this unbalance between alkali and SO_3 *[wt%]* is due to the different volatility of the Cl, SO_3 and alkali in a static lab furnace compared to a real clinker kiln. As described in **section 2.5.**, an excess of alkali will decrease the viscosity of the melt by which the alite formation is increased. Because the alkali have a higher volatility at 1450°C than SO_3, they will be much lower in content in a static kiln and also SO_3 *[wt%]* will be lowered significantly.

On the other hand, it makes it possible to demonstrate the importance of each part of the combined fluxing effect. Based on **figure 6.7.**, it can be concluded that a combined fluxing effect **[19]** exists which can be provoked by the use of the porphyry and dolomitic limestone ARMs.

The combined fluxing effect is also noticeable when sintering temperature is lowered to 1400°C and 1350°C. Both the reference CCMs as well as the alternative CCMs made with dolomitic limestone ARM of CBR Antoing and CBR Lixhe were sintered at 1450°C, 1400°C, 1350°C and 1300°C. The resulting alite contents *[wt%]* measured by XRD are plotted in **figure 6.8**.

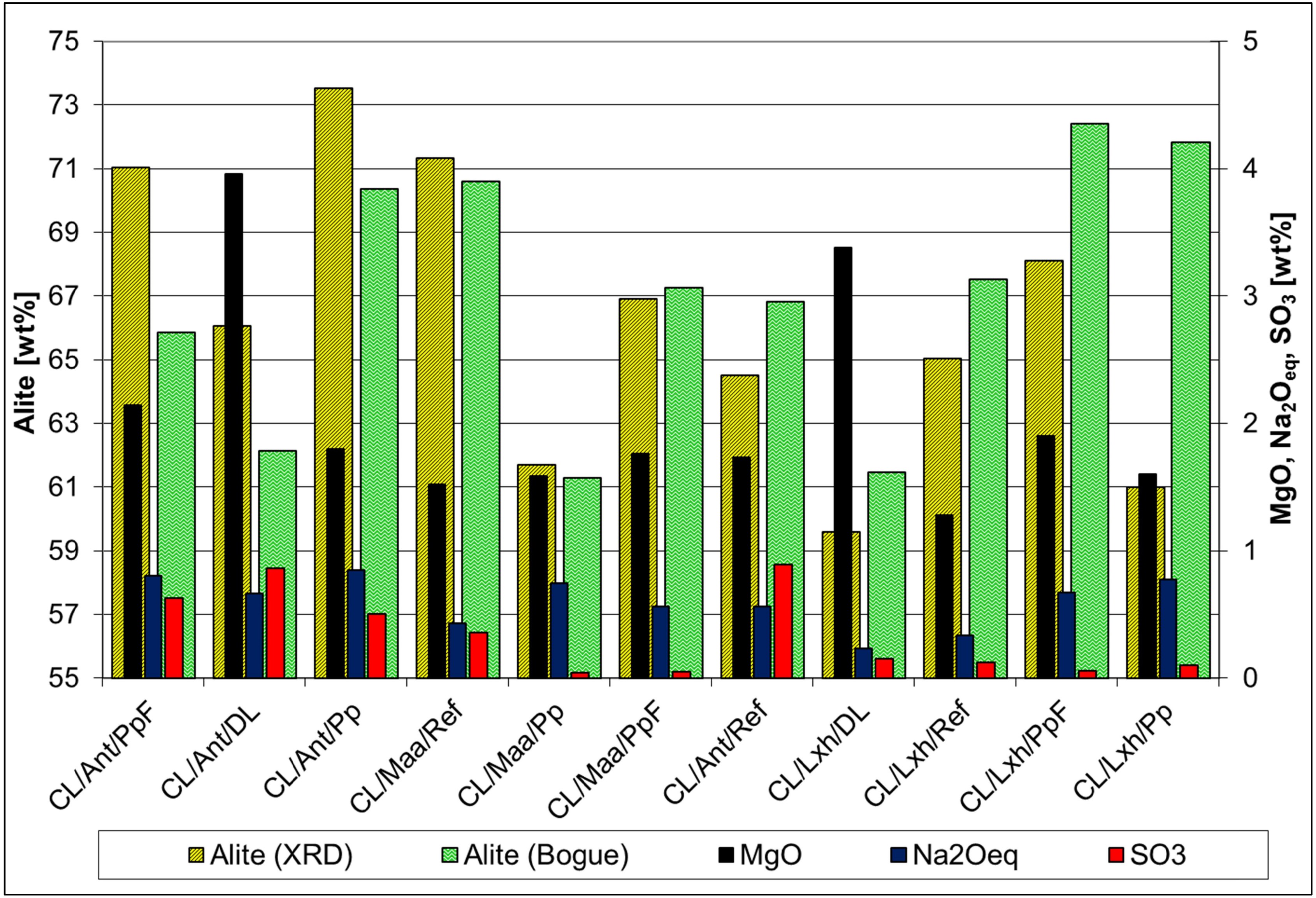

Figure 6.7.: Alite formation sorted from left to right by decreasing mineraliser capacity coming from the combined fluxing effect

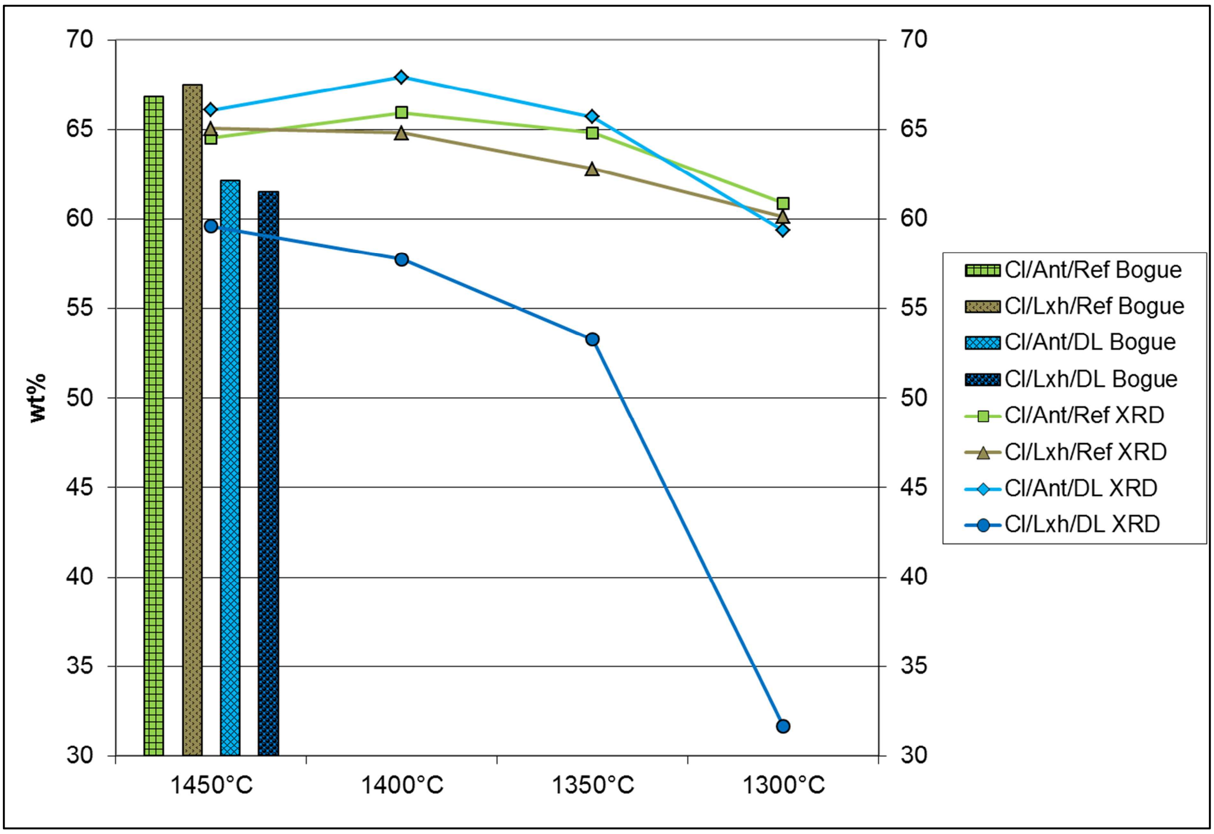

Figure 6.8.: Alite *[wt%]* determined by Bogue and XRD of the classic and alternative clinkers made with dolomitic limestone sludge

The alternative clinker made with dolomitic limestone ARM of CBR Lixhe decreases very rapidly in alite *[wt%]* as of 1400°C. This trend is not so visible though present in the reference clinker of CBR Lixhe (**Figure 6.8.**). In contrary with the clinkers of CBR Lixhe, both clinkers of CBR Antoing maintain the same alite *[wt%]* up to 1350°C. As of 1300°C, all four clinkers decrease in alite *[wt%]*. The difference between the clinkers of CBR Antoing and these of CBR Lixhe, is the presence of alkali and SO_3 *[wt%]*. Although, in the case of the reference clinker of Antoing, an increase in alite *[wt%]* at 1450°C was not measured (**Figure 6.7.**), there is apparently sufficient MgO, alkali and SO_3 *[wt%]* available to generate the combined fluxing effect resulting in the decrease of the sintering temperature to 1350°C. This is also the case for the alternative clinker made with dolomitic limestone ARM of CBR Antoing which already showed a combined fluxing effect at 1450°C. Compared to tests performed by Kacimi **[23]**, both the reference as well as the alternative clinkers of CBR Antoing are quite low in free CaO at the different temperatures but it can be remarked that free CaO *[wt%]* was significantly lower at 1450, 1400 and 1350°C when the combined fluxing effect took place. As can be noted out of **table 6.6.**, the increase in alite *[wt%]* formation in the alternative clinkers has been obtained without an increase in inorganic CO_2. This means that a more reactive alternative clinker, in the case of CBR Antoing, can be made without an increase of inorganic CO_2; or a clinker with the same reactivity but with less CaO and therefore less CO_2 can be made with these higher levels of MgO. Decreasing the CaO by replacing it with SiO_2 will also increase the burnability of the clinker as described in **section 2.6.** This should be further investigated by evaluating the energy consumption up to different temperatures of the reference and alternative clinkers which are composed out of the same final mineralogy (equal alite *[wt%]*).

6.8. Ecological benefit

The use of fines or sludge coming out of aggregates production as ARM for Portland clinker production could have different ecological advantages which could be quantified in a LCA-study and which are in line with Cement Sustainability Initiative. Based on the guidelines of the LCA process (**Section 4.4.**), different principles as cradle to grave, cradle to cradle or cradle to gate, can be used to demonstrate the possible ecological benefit by using recycled fines or sludge out of aggregates production as ARM in Portland clinker production. As demonstrated in **section 6.7.**, porphyry and dolomitic limestone materials will influence differently the raw materials composition of the CCMs. Also the dry or wet separation phase of fines out of aggregates production will have different energy consumption as well as their mode of transport and their impact on Portland clinker production.

- EPD of Portland clinker (cradle to gate):

  Porphyry fines will reduce by their chemical composition, the required volume of fly ash. Dolomitic limestone will decrease the required limestone. This means that the influence of the EPD of the fly ash on the one hand and the limestone on the other will be smaller on the LCA of the Portland clinker production.

  As a result, the influence of the EPD of the porphyry fines or the dolomitic limestone sludge will have to be taken in account. Whether or not this shift in raw material use is an ecological benefit depends on the EPD of both raw materials.

  The transport mode will also have a big influence on the ecological impact of the ARMs. The transport for the dolomitic limestone will induce an increased environmental impact because most Portland clinker kilns are located near their limestone source whereas the dolomite quarry is further away. Also the transport of the wet sludge will be less beneficial than the dry fines by the partial transport of water. The transport of the porphyry fines could be comparable with fly ash because both sources are not located near the Portland clinker factory as in the case of the limestone source.

  Furthermore, the input of MgO by both ARMs could have an influence on the reactivity or the burnability of the Portland clinker by an improved alite formation, but also on its sintering temperature by a mineraliser effect. If the required CaO *[wt%]* could be decreased by the increased reactivity of the Portland clinker, not only the energy consumption will be lowered by an improved burnability (CaO_{free}) but also by a decreased decarbonation energy ($CaCO_3$). Indeed if CaO *[wt%]* could be decreased in the CCM, less $CaCO_3$ will have to be decarbonated and less CaO will have to be built in the different mineralogical phases to decrease CaO_{free} to an acceptable level. A decreased energy consumption and related assigned CO_2 indicator will have as result that the LCA of the

Portland clinker will improve. When the cradle to gate principle is used for the Portland clinker production, this will result in an improved EPD for Portland clinker.

Nevertheless, the use of both ARMs will not purely be beneficial. The introduction of physically bound H_2O by sludge will necessitate extra evaporation energy. Furthermore without taking in account the mineraliser effect of the MgO, the input of MgO by dolomitic limestone will not lead to a decrease in inorganic CO_2 because MgO is present in carbonated form in dolomitic limestone as in the case of porphyry. The decarbonation energy of dolomite is nevertheless lower than calcite as described in **paragraph 6.7.3.** However, a realistic EPD of the Portland clinker including the use of both ARMs can only be calculated based on actual industrial practice.

- EPD's of the other related processes (cradle to gate):

  An improved EPD of Portland clinker will have also a positive impact on the EPD of Portland cement. Nevertheless, industrial practice will be necessary to fine-tune the EPD calculation of Portland cement as a function of the increased alkali in the Portland clinker, grinding energy and required fineness of the final Portland cement as also the other cement types which EPD's will be less but still considerably influenced by the EPD of Portland clinker. Furthermore looking at the EPD of porphyry and dolomitic limestone aggregates itself, the big ecological benefit will be the valorisation of a by-product in the form of dry fines or wet sludge which otherwise would be identified as waste product in a LCA calculation. This means that the total energy necessary to produce these aggregates could be divided over a bigger part of the quarried material. Furthermore no landfill has to be taken in account in the final EPD calculation of the aggregates.

  Aggregates that have a lowered fines fraction (< 63 µm) could have advantages in concrete applications due to lowered water and cement demand as a function of their specific properties. Combined with improved EPDs of Portland cement and other cement types, this will result in an improved concrete EPD. An improved EPD of concrete will make concrete more competitive towards comparable building materials when considering ecological construction of a building.

- Cradle to grave / Cradle to cradle:

  There will be no additional beneficial influences by using fines or sludge of porphyry or dolomitic limestone as ARM in Portland clinker than those already described here above. The LCA of aggregates will consider the different stages of the life cycle of the aggregates. The valorisation of fines or sludge will only influence the resource depletion and manufacturing stage which deal with the extraction, processing and transportation of the aggregates or the part already discussed in cradle to gate assessment (**Figure 4.3.**). Nevertheless, these fines fractions of porphyry or dolomitic limestone could also be generated by an additional process step in the production of recycled aggregates out of waste material and could in this case have their influence on the LCA during the end of life stage of the primary aggregates. This will be further discussed in **chapter 10**.

Based on the results of this study and the cited influences on the LCA calculation, it can be expected that the use of porphyry fines as ARM for Portland clinker production will have ecological benefits. In the case of dolomitic limestone sludge, whether or not an ecological benefit can be observed, will depend on the transport mode and evaporation energy for physical bound water in the sludge.

Nevertheless, the use of both materials is in line with the Cement Sustainability Initiative explained in **section 4.2.** Both ARMs, if used for Portland clinker production, will have their influence on two of the five Key Performance Indicators of the Cement Sustainability Initiative: Climate change management as well as fuels and materials use. The climate change management will be influenced by decreased company-wide total CO_2 emissions (tons/year) as well as the company’s gross and net CO_2 emissions per ton of cementitious product especially in the case of porphyry fines.

The use of fuels will be influenced as a function of the specific heat consumption of clinker production in (MJ/t of clinker). The raw materials use will be on his turn positively influenced by an increased alternative raw materials rate for clinker production and the possible increased use of fly ash as raw material for cement production by its replacement in the CCMs for Portland clinker production by the use of porphyry fines.

6.9. Conclusions

As could be deduced from the performed analyses, porphyry fines and dolomitic limestone sludge could be an interesting Alternative Raw Material (ARM) for Portland clinker production. They could, in both cases, have a positive influence on the ecological effects of aggregates production and application as well as for the excavation of limestone Classic Raw Materials (CRMs) in the case of dolomitic limestone sludge.

In contrast with porphyry fines, dolomitic limestone sludge will need a homogenisation phase to decrease its chemical variation. As could be noted in the different sections, porphyry fines could also replace a CRM with pozzolanic capacity as fly ash. On the contrary, dolomitic limestone sludge ARM will not replace completely the limestone CRMs by its high levels of MgO which will generate an undesired fifth raw material within the Portland clinker production. The MgO out of dolomitic limestone fines will also be presented to the clinker kiln in carbonated form, resulting in an increase of CO_2 emission with increasing inert periclase formation in spite of the lower decarbonation energy of $MgCO_3$.

Furthermore it was demonstrated that MgO when cautiously introduced by the investigated ARM in line with well-defined limitations, should rather be regarded for its positive mineralogical influence on clinker than avoided because of its possible periclase formation and related unsoundness properties. MgO combined with alkali and SO_3 has fluxing activities whereby the alite formation is promoted which could improve the burnability of the alternative clinkers.

Furthermore, it was also demonstrated that in combination with alkali and SO_3, a decrease of the liquid formation temperature is noticeable by which equal mineralogical composition can be attained at

1350°C than without the fluxing effect at 1450°C. Lowering the sintering temperature to 1350°C could safely be considered in combination with the increased alite formation at 1450°C. The combined fluxing effect is not as distinct as this of CaF_2 but at the other hand easier and cheaper to introduce in a clinker kiln by the ARMs. It is also a fact that it is harder for clinker producers to attain too low than sufficient SO_3 *[wt%]* and alkali *[wt%]* to profit from a combined fluxing effect. Therefore the fine-tuning of MgO *[wt%]* up to 2.0 - 2.5 wt% in Portland clinker could be recommended to fully benefit the mineralogical advantages.

Further investigation should be performed to evaluate physical properties of cement based on these ARMs. Additional to materials with decarbonated CaO, ARMs who consist partly out of decarbonated MgO could act as valuable raw materials for Portland clinker production.

Porphyry and to a lower extent dolomitic limestone fines or sludge should therefore, together with the already available alternative fuels and raw materials **[30]**, be considered as a way to get in line with the Cement Sustainability Initiative.

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Chapter 7

Fibrecement recycling as raw material for Portland clinker production

7.1. Introduction [1-9]

The demand for roofing and façade products out of cementious materials still increases year by year, especially in developing countries. For these types of application, asbestos cement materials have been used widely for well over a century and are still used up today.

Principally asbestos cement materials are a mix of 90 wt% cement and 10 wt% asbestos with water. However, the hazard of asbestos to human health has led to a ban of using asbestos in construction material industry in many countries, although asbestos cementious materials are still used up to day in several countries as roofing material. In 2009 for example, import of asbestos in Vietnam was still around 64,000 tons which made it one of the largest asbestos consuming countries in the world **[7]**.

The investigation on new fibers for asbestos substitution, including a new manufacturing process and equipment for non-asbestos cement sheets, has been of great interest for researchers and engineers. In the early 1980's FibreCement out of non-asbestos materials (FC) gradually replaced asbestos cement for roofing material as well as façade products in Australia and Europe.

The manufacturing of roofing and façade products out of cementious materials was not so widespread in the USA because asbestos cement could not compete with the readily available natural and manufactured wood products. However, by the late 1980's the reduction in the amount of available wood and the worldwide environmental movement changed the economics and FC was introduced in the USA with imports from Australia and Europe, which demonstrates the current worldwide use of FC building materials.

A typical FC board is made of approximately 40-60 wt% of cement, 20-30 wt% of fillers, 8-10 wt% of cellulose, 10-15 wt% of mica. Other additives like PolyVinyl Alcohol (PVA) and Polypropylene (PP) are normally used in quantities less than 1%. The actual recipe depends on available raw materials and other local factors. Also the specific used production process will have its influence on the raw material composition as can be remarked in **figures 7.1.** and **7.2.** for Eternit Kapelle o/d Bos, Belgium where the composition evolution of aircured FC Roofing Slates is demonstrated for the years 1996 to 2011.

Buildings materials may remain in service for centuries but studies have demonstrated that the combined volumes of FC demolition waste will start to increase in Europe as of 2020 to measurable volumes. Once a steady supply of FC demolition waste will have come on stream, some millions of tons per year could be expected in Europe which requires a valuable recycling method.

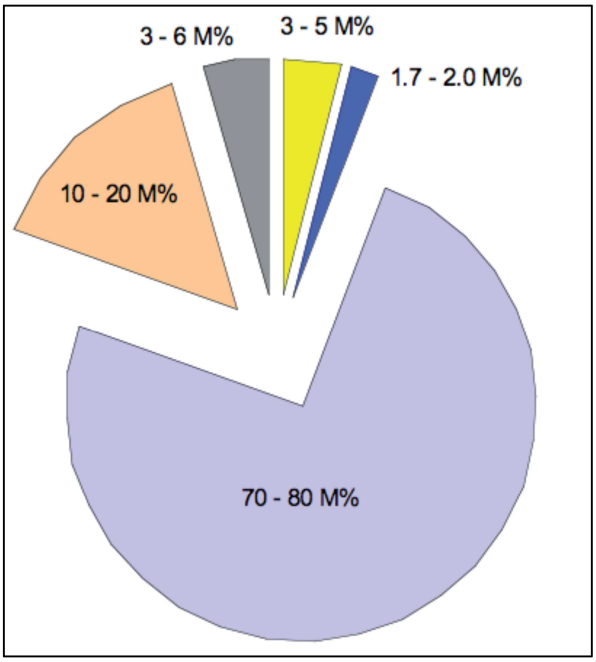

Figure 7.1.: Typical initial dry composition of common air-cured fibrecement products

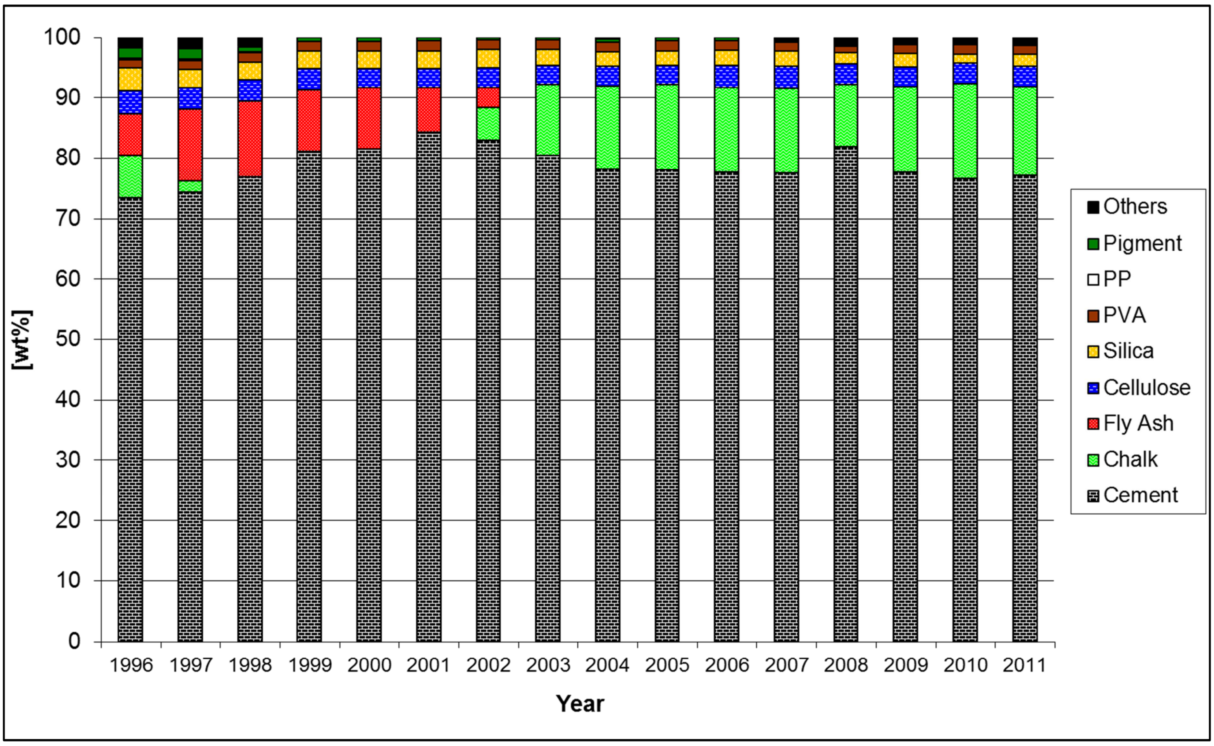

Figure 7.2.: Evaluation of the Composition of Air-cured Fibrecement Roofing Slates produced in Eternit Kapelle o/d Bos

Near InfraRed (NIR) spectroscopy could potentially be used as a simple and reliable method to distinguish asbestos cement from FC during recycling. It appears that NIR diffuse reflectance spectroscopy can remotely analyse asbestos due to the relatively simple spectra in the wavenumber range 7400-6900 cm^{-1} and the high signal-to-noise ratio.

Already some extensive scientific studies have been performed using crushed FC waste in road construction, by internal recycling in the air-cured respectively autoclaved FC production **[1]**. This chapter deals with a recycling method for FC which is applicable whether it concerns production, construction or demolition waste namely as Alternative Raw Material for Portland clinker production.

7.2. Fibrecement / fiber cement (FC)

Fibrecement products out of non-asbestos materials (FC) is the generic term given to a wide variety of composite materials consisting out of Portland cement, inert and/or reactive mineral fillers and a mixture of several types of organic fibres **[2-3]**. FC is used for roofing, wall sidings or claddings and internal linings in both domestic and commercial buildings. Most commonly, it is used in the form of corrugated sheets, slades/shingles, boards and planks. Where used externally, FC is often painted or otherwise coated.

Within the context of the present manuscript, only FC products produced by Hatschek technology will be considered. This technology will be briefly explained in **section 7.3.** The products made by the Hatschek technology harden by normal hydration of Portland cement at ambient pressure, hereafter indicated by "air-curing" or by means of hydrothermal reactions, further indicated by "autoclaving".

Except for crystalline portlandite and ettringite **[4]**, the products formed by normal hydration mainly concern calcium silicate hydrates with predominantly amorphous or cryptocrystalline nature. However, in the case of autoclaving, the chemical reactions occurring in an atmosphere of saturated steam at 7 to 10 bar mainly lead to the formation of crystalline phases next to some less crystalline and even some amorphous materials **[5-6]**. Most commonly used CaO sources are Portland cement and chalk. Quartz is the preferred SiO_2 source, but the silica present in the Portland cement also participates in these reactions.

The FC materials that were used for this investigation came from two FC factories of Eternit in the Benelux, Eternit Kapelle o/d Bos and Eternit Goor. The materials were taken from four different production lines, corresponding with two roofing products, Corrugated FC Sheets (ARM/CS) and FC Roofing Slates (ARM/RS), and two façade products, Medium Density FC boards (ARM/MD) and High Density FC boards (ARM/HD).

The roofing products concern air-cured products (**Figure 7.3.**) whereas the façade products are autoclaved (**Figure 7.4.**). This makes it possible to recycle both FC groups, air-cured and autoclaved, separately based on their application.

The air-cured products (**Figure 7.3.**) have very similar formulations and contain synthetic reinforcement fibres (Polyvinyl Alcohol and Polypropylene), process fibres (cellulose), Portland cement, puzzolanic and inert filler as can be noticed in **figure 7.2.**

The corrugated sheets (ARM/CS) contain twice as much puzzolanic filler as the slates (ARM/RS). The final corrugated sheet density varies between 1.45 and 1.50 g/cm^3. In the case of slates, the density is about 1.85 g/cm^3.

Figure 7.3.: Example of an aircured FC roofing product (source: www.eternit.be [cited 2014 Apr 30])

The autoclaved products (**Figure 7.4.**) mainly contain cellulose reinforcement and cellulose process fibres, Portland cement, quartz and some stabilising agent. Autoclaving has the advantage that the product may be cured and ready for shipping within 48 hours of manufacture as opposed to an air-cured product that may need the traditional 28 days of curing time before use. Autoclaving, however, results in a crystal structure in the hydrated cement products that is different from that produced at ambient temperature. This structure is more susceptible to chemical attack by atmospheric CO_2 and it responds differently to this attack than the air-cured product.

Figure 7.4.: Example of a autoclaved FC façade product (source: www.eternit.be [cited 2014 Apr 30])

Air-cured and autoclaved products each contain some product-specific additional functional mineral filler(s).

7.3. The production of fibrecement: the Hatschek process

The Hatschek process **[7-9]**, invented by Ludwig Hatschek in 1900, results in a strong and durable laminate composite material, which has been widely used as roofing material in many countries around the world. The sheet formation principle in the so-called Hatschek machine resembles the principle of an old wet paper making-machine. By means of a rotating sieve, thin layers of FC (ca. 0.3 mm) are picked up from an aqueous suspension of cement, fibres, fillers and water (ca. 80 to 120 g solids/ l of slurry). Usually, a Hatschek machine contains 3 to 4 sieves mounted in series.

FC composites with varying thicknesses can be made by winding of several layers of these 3 to 4 monolayers holding composites on a so-called forming drum. The fresh sheet (green product) is optionally post-compressed to densify or is optionally passed through a moulding station in order to make corrugated sheets or accessory FC products. The Hatschek machine is illustrated in **figure 7.5**.

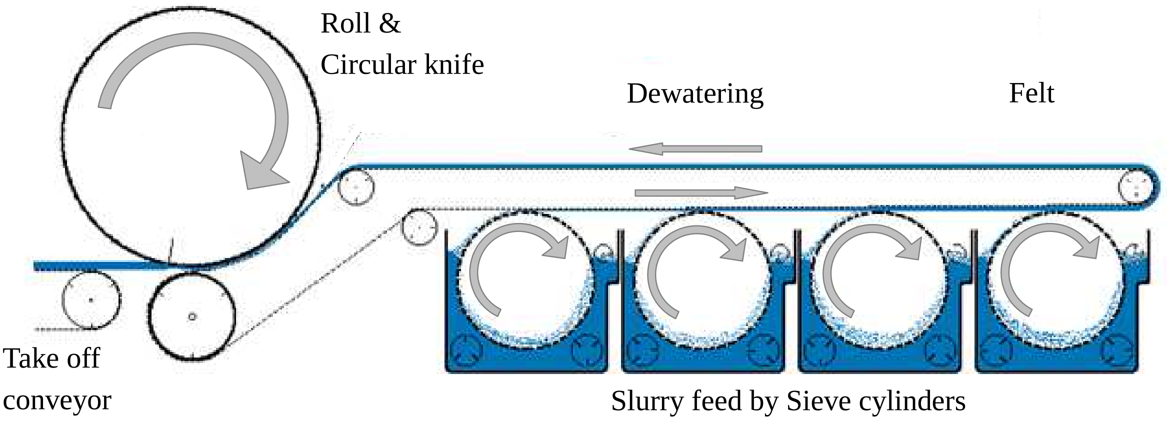

Figure 7.5.: The sheet formation principle used within the Hatscheck Machine (Ref. Eternit NV)

Because the process is very sensible to the smallest changes in the raw material composition, the raw meal composition as well as the quality of the individual raw materials is closely monitored. This is demonstrated in **figure 7.2.** which illustrates how the raw meal composition of FC Roofing Slates (ARM/RS) of Eternit Kapelle o/d Bos, has evolved through the years since the change-over to non-asbestos products. Based on this figure, we can already partially conclude that FC product-selective recycling will generate an alternative raw material with a low chemical variation. **Table 7.1.** lists some of the raw materials that are commonly used in production of FC cement sheets worldwide as well as their respective function and performance (effectiveness).

Table 7.1: Common raw materials used in production of PVA cement sheets

	Material	**Function**	**Performance**
1	Portland cement	Binding agent	Strength of matrix, binding composite
2	PVA fibers	Reinforcement	High bending strength & impact strength
3	Wollastonite, Mica	Stabilizer	Dimensional stability, preventing crack formation
4	Silica Fume	Filler	Densification of matrix, control gravity, better bonding between fibres and matrix, better appearance
5	Attapulgite, Bentonite	Improvement of Forming	Improvement of productivity, layer adhesion
6	Polyacrylamide	Agglutinate Agent	Improvement of productivity

Air-cured and autoclaved products have some specific process specifications which will be described in the next paragraphs.

7.3.1. Air-cured products

The two air-cured products used for this investigation are Corrugated FC Sheets (ARM/CS) and FC Roofing Slates (ARM/RS).

In case of corrugated sheets, the fresh flat FC sheets leaving the Hatschek machine are immediately corrugated and stacked between steel templates. For the slate product, the fresh sheets leaving the Hatschek machine are, partially or fully dimensioned, and stacked between flat steel templates after which these stacks are pressed in order to raise the FC product's density (**Figure 7.6.**).

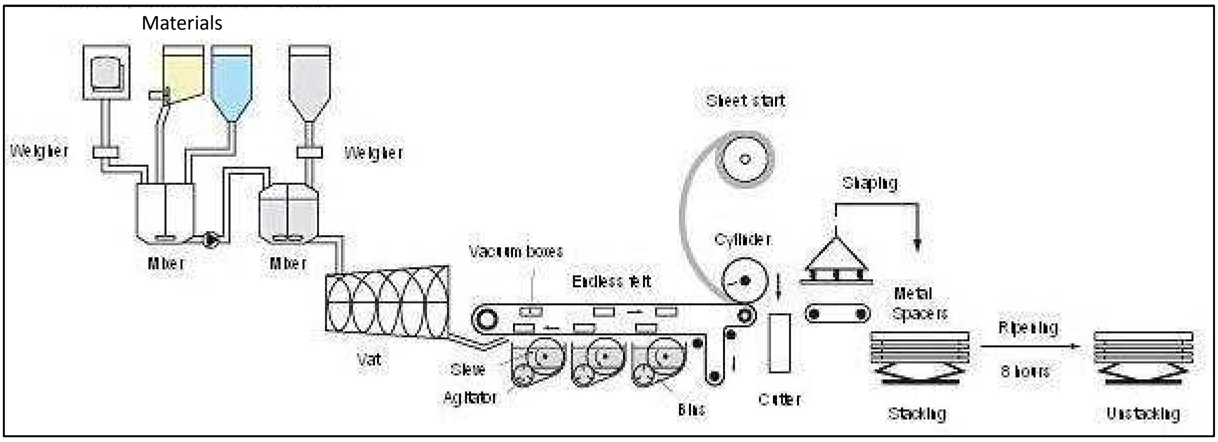

Figure 7.6.: Schematic plant lay-out of aircured FC production plant using a Hatschek machine (Ref. Eternit NV)

Both product types are demoulded after ca. 8 à 10 hours of curing in chambers with air at 60 °C and relative humidity of minimum 90 %.

After the demoulding the uncoated corrugated sheets are immediately wrapped up and stored until dispatch to the client, minimum 7 days after production. Sheets intended to be coated however are stored for some time in the factory hall, until the moment of coating.

In case of the slates, they are re-stacked and stored in the factory hall after demoulding until coating. Once coated (if still required, preceded by cutting into their final dimensions) they are stacked and wrapped up after which they are ready for sale.

7.3.2. Autoclaved products

Within this investigation two autoclaved products both for façade applications were used: Medium Density FC boards (ARM/MD) and High Density FC boards (ARM/HD).

After the production of the ARM/MD on the Hatschek machine, the planks are stacked and cured at ambient temperature for about 24 hours, after which they are autoclaved (**Figure 7.7.**). An important part of the production is coated in the factory before being put into the market.

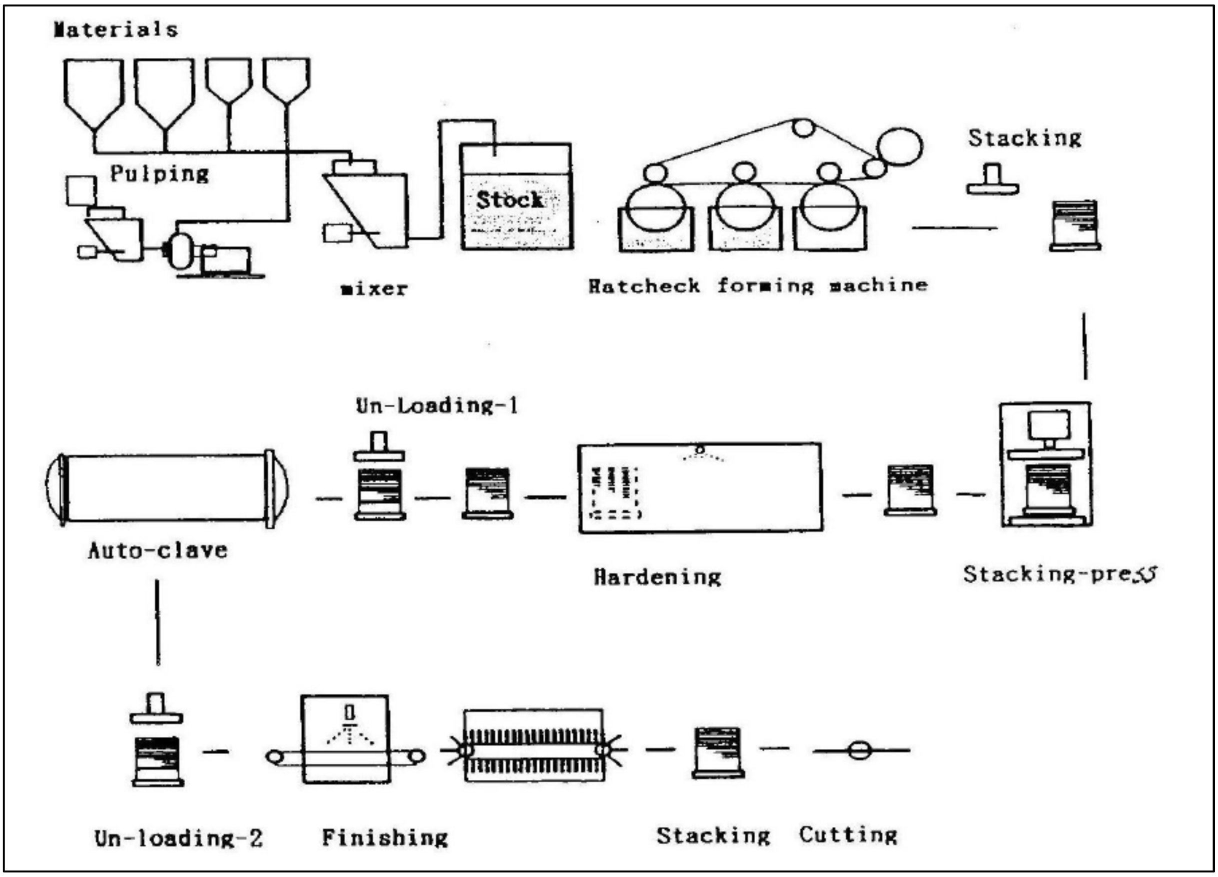

Figure 7.7.: Schematic plant lay-out of autoclaved FC production plant using a Hatschek machine **[9]**

ARM/HD differ from the ARM/MD products by the fact that they are coloured in the mass, and exhibit a higher density which follows from a post-compression step of the fresh boards, stacked between steel templates.

The final step concerns a hydrophobation treatment. The product's final density amounts ca. 1.30 and 1.85 g/cm³ for Medium Density (MD) and High Density (HD) FC boards respectively.

7.4. Sampling

From the four FC products, material was recovered at twenty-four different points in time spread over six months after which they were two by two homogenised. The twelve samples obtained from each type of FC product gave a total of forty-eight samples. After crushing in a Retsch cutting mill those samples were ground for 1 minute in a Siebtechnic disc mill to obtain sufficient fineness.

For each of the four types of FC product, the average chemical analysis, as described in **section 3.5.**, of the twelve samples including their standard deviation is presented in **table 7.2**.

The mutual relationship between the CaO *[wt%]* and the SiO_2 *[wt%]* for the air-cured and autoclaved products respectively is graphically illustrated in **figures 7.8.** and **7.9.**

Table 7.2.: Average chemical analysis of the fibrecement materials

ARM		Corrugated Sheets	Roofing Slates	Autoclaved High Density Boards	Autoclaved Medium Density Boards
		ARM/CS	ARM/RS	ARM/HD	ARM/MD
CaO	(wt%)	51.24 ± 0.83	52.14 ± 0.66	28.55 ± 1.08	25.01 ± 0.43
SiO_2	(wt%)	18.85 ± 0.86	18.42 ± 0.44	44.2 ± 1.07	51.06 ± 0.54
Al_2O_3	(wt%)	2.80 ± 0.10	3.55 ± 0.31	5.95 ± 0.17	4.95 ± 0.25
Fe_2O_3	(wt%)	2.52 ± 0.17	3.15 ± 0.16	2.37 ± 1.25	1.74 ± 0.14
K_2O	(wt%)	0.37 ± 0.04	0.28 ± 0.02	0.22 ± 0.01	0.15 ± 0.01
Na_2O	(wt%)	0.20 ± 0.03	0.17 ± 0.01	0.06 ± 0.02	0.12 ± 0.01
SO_3	(wt%)	1.87 ± 0.15	1.35 ± 0.05	0.69 ± 0.10	0.61 ± 0.04
MgO	(wt%)	1.38 ± 0.12	1.57 ± 0.19	0.59 ± 0.17	0.71 ± 0.07
TiO_2	(wt%)	0.25 ± 0.05	0.43 ± 0.04	0.34 ± 0.40	0.38 ± 0.09
P_2O_5	(wt%)	0.44 ± 0.07	0.31 ± 0.03	0.16 ± 0.02	0.18 ± 0.01
Cl	(wt%)	0.03 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
LOI 975°C (O_2)	(wt%)	19.65 ± 1.38	18.11 ± 0.68	16.13 ± 0.70	14.83 ± 0.31
C_{total}	(wt%)	3.94 ± 0.28	4.10 ± 0.20	3.66 ± 0.12	3.44 ± 0.13
S_{total}	(wt%)	0.86 ± 0.08	0.66 ± 0.03	0.33 ± 0.04	0.31 ± 0.02

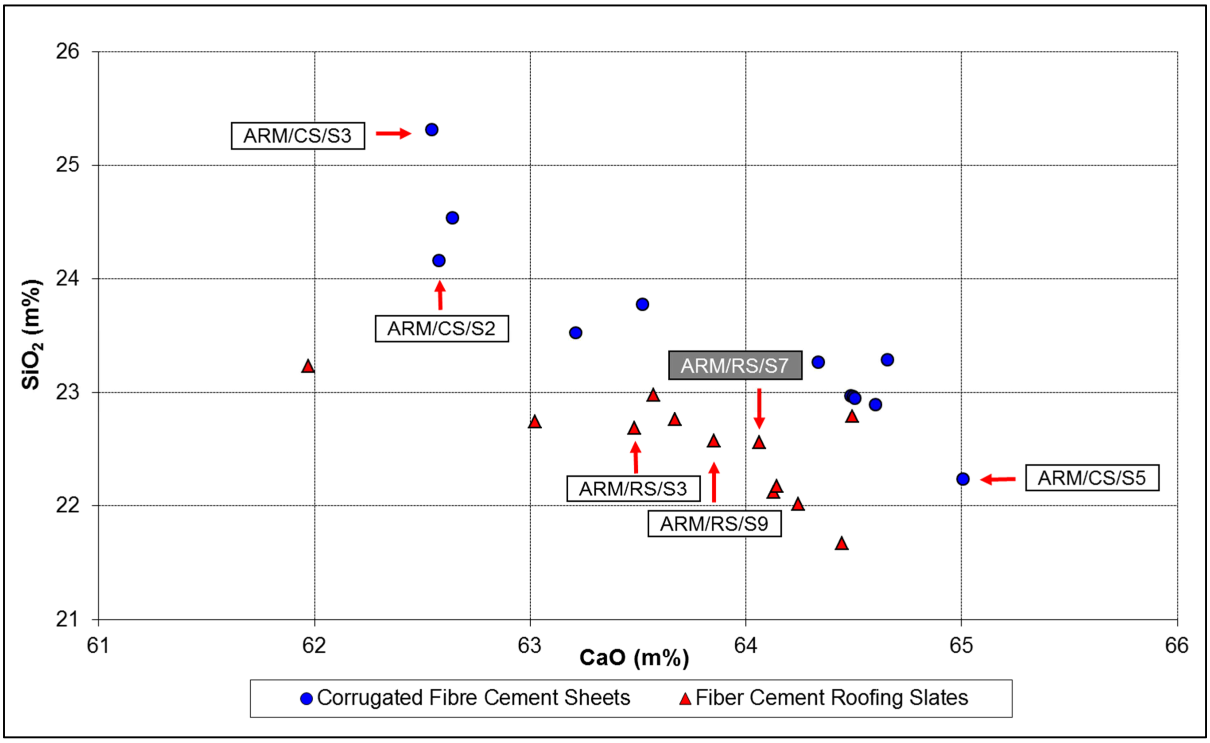

Figure 7.8.: CaO *[wt%]* as a function of SiO_2 *[wt%]* without L.O.I. of Air Cured FC materials
(White and grey label: Samples for TGA/DTA analyses)
(Grey label: Samples used for clinker simulation and preparation)

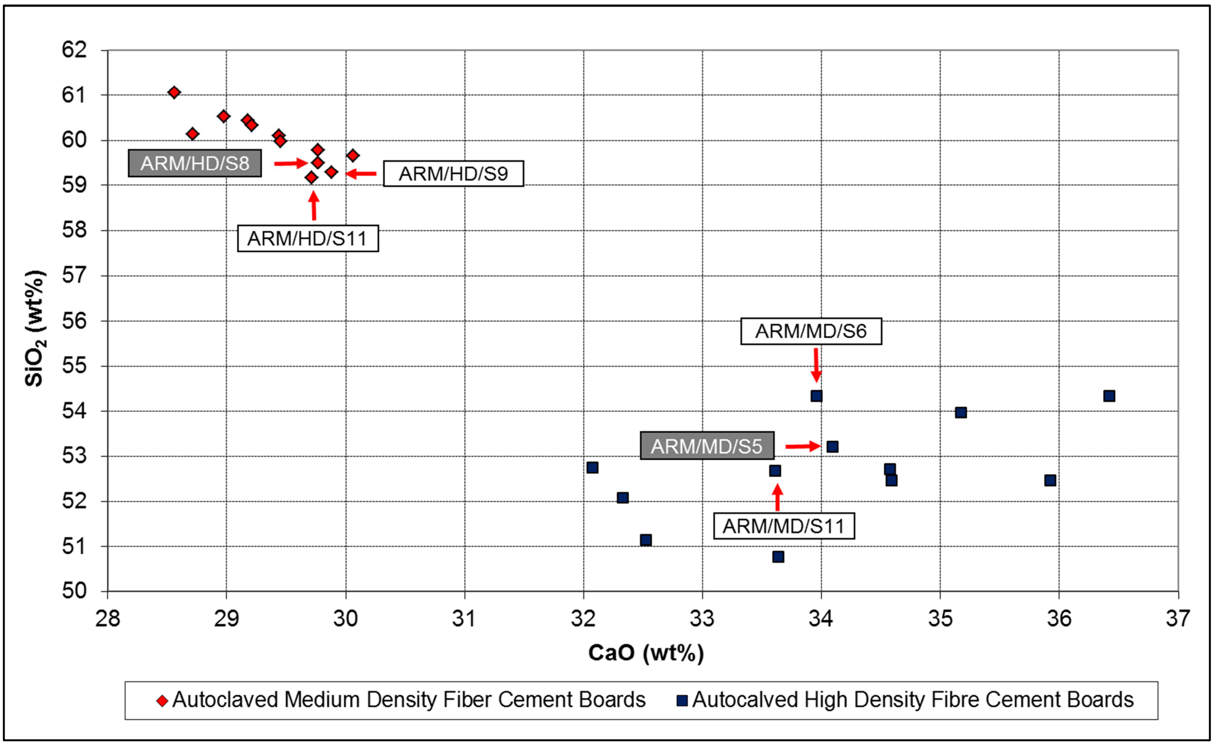

Figure 7.9.: CaO *[wt%]* as a function of SiO_2 *[wt%]* without L.O.I. of Hydro Thermal FC materials
(White and grey label: Samples for TGA/DTA analyses)
(Grey label: Samples used for clinker simulation and preparation)

7.5. Research description

The primary objective is to investigate how much of each of the two described FC groups, air-cured and autoclaved, could be applied in a Portland clinker process to replace the Classic Raw Materials (CRMs). This will be determined as a function of each of the three kilns, CBR Antoing, CBR Lixhe and ENCI Maastricht, with enumeration of possible limitations.

Numerical simulations will be carried out to maximise the use of FC waste in clinker kilns taking into account the compositional variation of the waste, its behaviour within a clinker kiln, the impact on the energy consumption and finally the influence on the carbon footprint calculated from the decarbonation.

Furthermore, experimental clinkers will be produced corresponding with waste dosages that were esteemed as realistic by the numerical simulations. These clinkers will be fully analysed and evaluated according to the evaluation concept described in **chapter 3**.

7.6. Results

Based on the articles “Waste fibrecement: An interesting alternative raw material for a sustainable Portland clinker production” published in Construction and Building Materials **[10]** and the congress article “Fibrecement recycling as raw material for Portland clinker production” for the third International Symposium on Life-Cycle Civil Engineering in Vienna in 2012 **[11]**, the results of the research on the use of FC as ARM for Portland clinker production is described below. Additionally some industrial tests, based on this investigation, were performed, but are not published in this PhD thesis, due to their confidentiality.

7.6.1. Clinker feed calculations and preparations.

A simulation program based on linear equations as described in **section 3.3.**, calculated raw meal compositions for each factory (CCM/Ant,Lxh,Maa/Ref). These raw meal compositions were in line with the chemical and mineralogical requirements listed in **table 2.5.** These compositions indicated as classic Cold Clinker Meals (CCMs) are very close to the compositions actually used in these factories.

The composition of the raw materials was merely adjusted to obtain the mineralogical settings, but without taking into account the ashes of the fuels that will actually be used to heat up the clinker meal. The compositions of these classic Cold Clinker Meals are presented in **table 7.3.**

Furthermore, alternative compositions were calculated with the same program and limits, aiming at the maximisation of the use of the FC ARMs. These alternative Cold Clinker Meals (CCMs) are also presented in **table 7.3.**

The chemical analyses of the limestones in **table 2.3.**, show that the limestones of Antoing have a high SO_3 content, by which that kiln already operates close to its SO_3-limit (**Table 2.5.**) in the routine condition. After simulation, it is clear that the introduction of air-cured ARMs increases the SO_3-content of the Hot Clinker Meal (HCM) because of their higher level of SO_3 compared with that of the CRMs of CBR Antoing. Unlike Air-cured FC ARMs, the use of autoclaved FC ARMs lowers the SO_3 in the HCM since its SO_3 *[wt%]* is lower than that of the two limestones used by CBR Antoing. Clogging phenomena should logically decrease by the lower SO_3 content of the HCM. Therefore, it was chosen to maximise the autoclaved ARM with the highest CaO *[wt%]* (**Table 7.2.**) namely autoclaved High Density FC Boards (ARM/HD) in the CCM/Ant/FC as presented in **table 7.3.** The sample closest to the average Loss Of Ignition at 975°C (L.O.I. (975°C)) of the autoclaved High Density FC Boards (**Table 7.4.** and **Figure 7.9.**) or ARM/HD/S8 was chosen as reference for the FC maximisation in the alternative CCM of CBR Antoing.

The limestone or tufa used by CBR Lixhe has an S content that is much lower than the limestones of Antoing. Also the S feed by the fuel mix is limited. Therefore the SO_3-content of the HCM is not as critical as the one of CBR Antoing. An increase of the SO_3 *[wt%]* could therefore be accepted. By maximisation of the air-cured ARMs in the CCM/Lxh/FC (**Table 7.3.**), the SO_3 *[wt%]* of the simulated final clinker was increased to 0.73 wt% which was still below the maximum of 1.2 wt% (**Table 2.5.)** that is allowed for and in line with the limits set for the DoS factor (**Table 2.5.**). Even with the typical fuel mix of CBR Lixhe, the SO_3 *[wt%]* would be 0.98 wt%. The sample closest to the average L.O.I. (975°C) of the air-cured Roofing Slates (**Table 7.4.** and **Figure 7.8.**) or ARM/RS/S7 was chosen as reference for the FC maximisation in the alternative CCM of CBR Lixhe.

The limestone or marl used by ENCI Maastricht contains a higher S content than the limestone or tufa used by CBR Lixhe. Also the used fuel mix brings more S to the HCM compared to the fuel mix of

CBR Lixhe. Also the maximum allowed SO_3 *[wt%]* is lower than that of CBR Antoing. The SO_3 *[wt%]* could therefore not be changed significantly what automatically suggests the use of autoclaved ARMs. In the case of ENCI Maastricht, the autoclaved ARMs are still quite high in SO_3 *[wt%]* compared to the used limestone or marl. This differentiates the use of autoclaved ARM in this plant from that in CBR Antoing. Because the ARMs from autoclaved Medium Density FC Boards (ARM/MD) were the lowest in SO_3 *[wt%]*, they were maximised in the CCM/Maa/FC as presented in **table 7.3.** The sample closest to the average L.O.I. (975°C) of the autoclaved Medium Density FC Boards (**Table 7.4.** and **Figure 7.9.**) or ARM/MD/S5 was chosen as reference for the FC maximisation in the alternative CCM of ENCI Maastricht.

Table 7.3.: Compositions of the different clinkers made to be fed to the static kiln

CCM	CRM	Quantity (wt%)	**CCM**	CRM+ARM	Quantity (wt%)
CCM/Ant/Ref	CRM/Ant/CP	55.25	CCM/Ant/FC	CRM/Ant/CP	0.00
	CRM/Ant/CR	37.50		CRM/Ant/CR	79.08
	CRM/Ant/FA	6.38		CRM/Ant/FA	7.03
	CRM/Ant/IC	0.87		CRM/Ant/IC	0.61
	ARM/HD/S8	0.00		ARM/HD/S8	13.28
	Sum	100.00		Sum	100.00
CCM/Lxh/Ref	CRM/Lxh/Tu	79.44	CCM/Lxh/FC	CRM/Lxh/Tu	38.52
	CRM/Lxh/Lo	6.63		CRM/Lxh/Lo	0.00
	CRM/Lxg/FA	12.34		CRM/Lxh/FA	9.32
	CRM/Lxh/IC	1.59		CRM/Lxh/IC	0.53
	ARM/RS/S7	0.00		ARM/RS/S7	51.63
	Sum	100.00		Sum	100.00
CCM/Maa/Ref	CRM/Maa/Ma	84.38	CCM/Maa/FC	CRM/Maa/Ma	81.89
	CRM/Maa/SC	2.90		CRM/Maa/SC	0.00
	CRM/Maa/FA	11.02		CRM/Maa/FA	10.33
	CRM/Maa/IC	1.70		CRM/Maa/IC	1.77
	ARM/MD/S5	0.00		ARM/MD/S5	6.01
	Sum	100.00		Sum	100.00

7.6.2. Chemical analysis

The chemical analyses of the Classic Raw Materials (CRMs) are presented in **section 3.4.** and these of the ARMs and CCMs in **tables 7.2.** and **7.4.** The average analyses of the CRMs were as expected and were directly used in the simulation program. The analyses of the ARMs were evaluated by sorting them by source and plotting them in **figures 7.8.** and **7.9.** by their respective CaO and SiO_2 without L.O.I. since that is the way how the ARM will be fed to the HCM. Out of **figures 7.8.** and **7.9.**, it is clear that air-cured ARMs are very similar regardless of their source whereas the different autoclaved ARMs were chemically totally different.

Table 7.4.: Chemical analysis of the Cold Clinker Meals (CCM) fed to the static kiln

CCM		CCM/ Ant/Ref	CCM/ Ant/FC	CCM/ Lxh/Ref	CCM/ Lxh/FC	CCM/ Maa/Ref	CCM/ Maa/FC
CaO	(wt%)	43.48	44.63	45.26	47.92	44.79	44.85
SiO_2	(wt%)	14.00	13.56	12.01	14.03	12.83	12.71
Al_2O_3	(wt%)	*2.89*	2.72	2.90	3.35	3.09	3.05
Fe_2O_3	(wt%)	1.84	1.80	2.72	2.65	2.42	2.40
K_2O	(wt%)	0.59	0.33	0.41	0.32	0.39	0.34
Na_2O	(wt%)	0.11	0.10	0.13	0.12	0.13	0.13
SO_3	(wt%)	0.48	0.41	0.24	0.81	0.28	0.29
MgO	(wt%)	1.10	0.94	0.88	1.18	0.97	0.96
TiO_2	(wt%)	0.16	0.26	0.21	0.29	0.20	0.21
P_2O_5	(wt%)	0.12	0.12	0.15	0.23	0.09	0.10
Cl	(wt%)	0.02	0.02	0.04	0.04	-	-
LOI 975°C(O_2)	(wt%)	34.89	34.79	34.75	28.61	34.51	34.68
C_{total}	(wt%)	8.98	8.89	8.82	6.66	8.79	8.76
S_{total}	(wt%)	0.36	0.25	0.09	0.36	0.15	0.16

From each source, three samples were selected based on their L.O.I. namely the one with the lowest and highest L.O.I. and the one closest to the average L.O.I. of the specific source. For each source, the chemical analysis of the ARM closest to the average L.O.I. was used in the simulation program (**Paragraph 7.6.1.**) as also they were used as source for the experimental production of the different alternative clinker feeds (**Table 7.3.**). Furthermore the GC-MS and MS analysis were performed on these samples. TGA/DTA analysis was performed on all selected samples.

The chemical analysis of the CCMs in **table 7.4.** and that of the final clinkers in **table 7.9.** shows that the mass percentages of the used ARMs and CRMs were properly assessed by the simulation program. The calculated CCMs which are presented in **table 7.3.**, generate specific mass percentages for the four critical metal oxides that after decarbonation and sintering at 1450°C, give a chemical analysis similar to that of the targeted reference clinker as presented in **table 2.1.**. The chemical influence on possible mineralogical differences between the clinker based on the CRMs and the clinker partly produced with the ARMs should therefore be minimal.

7.6.3. TGA/DTA analysis

TGA/DTA analyses of the FC materials (**Tables 7.5.** and **7.6.**) give a lot of information on their raw materials and how they will behave when thermally degraded up to 1450°C. The meaning of each column was already explained in **paragraph 3.5.2.** The TGA peaks of the autoclaved ARMs show the absence of limestone filler which is present for maximum 15 wt% in the air-cured materials. This makes it possible to quantify the CO_2 part coming from the limestone filler of the air-cured products (**Figure 7.10.**).

Table 7.5.: TGA/DTA evaluation of all the used Alternative Raw Materials (ARMs) coming from FC

ARM	Inorg CO_2	Organic+H_2O	$CaCO_3$	CaO	MgO	[Ca,Mg]CO_3
	TGA (wt%)	TGA (wt%)	TGA Der (wt%)	XRF (wt%)	XRF (wt%)	XRF Der (wt%)
ARM/CS/S2	7.1	11.1	16.1	52.09	1.54	70.99
ARM/CS/S3	9.6	12.7	21.9	49.99	1.36	70.22
ARM/CS/S5	10.0	13.5	22.7	50.86	1.64	71.53
ARM/RS/S3	7.7	9.8	17.5	52.55	1.62	71.81
ARM/RS/S7	8.2	11.0	18.7	51.89	1.52	71.41
ARM/RS/S9	7.9	11.6	17.9	52.20	1.56	71.53
ARM/HDB/S8	0.6	16.1	1.4	28.20	0.67	42.32
ARM/HDB/S9	0.5	16.8	1.1	28.62	0.59	42.67
ARM/HDB/S11	0.5	15.8	1.2	28.53	0.67	42.68
ARM/MDB/S5	0.3	14.3	0.6	24.83	0.79	38.28
ARM/MDB/S6	0.3	14.5	0.6	25.24	0.75	38.73
ARM/MDB/S11	0.2	16.6	0.6	25.12	0.59	38.35

Table 7.6.: TGA/DTA evaluation of all the used Alternative Raw Materials (ARMs) coming from FC

ARM	Decarb E $CaCO_3$	Decarb E $CaCO_3$
	DTA (µVs/mg)	TGA Der (J/g)
ARM/CS/S2	14.6	287
ARM/CS/S3	22.5	389
ARM/CS/S5	41.5	405
ARM/RS/S3	26.9	312
ARM/RS/S7	33.6	334
ARM/RS/S9	32.9	319
ARM/HDB/S8	5.3	25
ARM/HDB/S9	9.7	20
ARM/HDB/S11	8.6	21
ARM/MDB/S5	4.8	11
ARM/MDB/S6	5.2	10
ARM/MDB/S11	4.2	10

The TGA peaks of the autoclaved ARMs show the absence of limestone filler which is present for maximum 15 wt% in the air-cured materials. This makes it possible to quantify the CO_2 part coming from the limestone filler of the air-cured products (**Figure 7.10.**).

Nicely visible is also the two-step degradation starting at 480°C of PVA, present at about 1.7-1.9 wt% in the air-cured materials in **figure 7.10.** and the absence of PVA in the hydro-thermally hardened materials like plotted in **figure 7.11.** This indicates that the reaction products of PVA suggested by Zheng Peng **[12]** will be formed when heated.

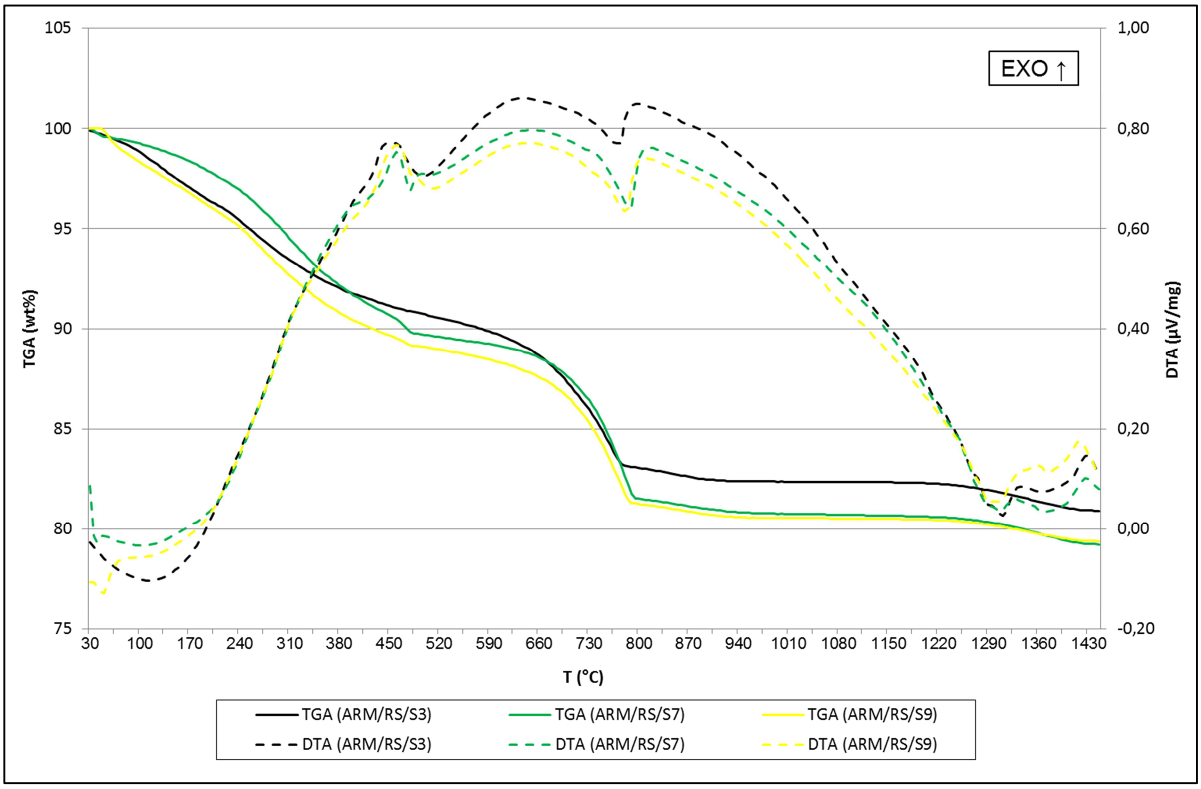

Figure 7.10..: TGA/DTA analysis of the three selected Air-cured FC Roofing Slates (RS)

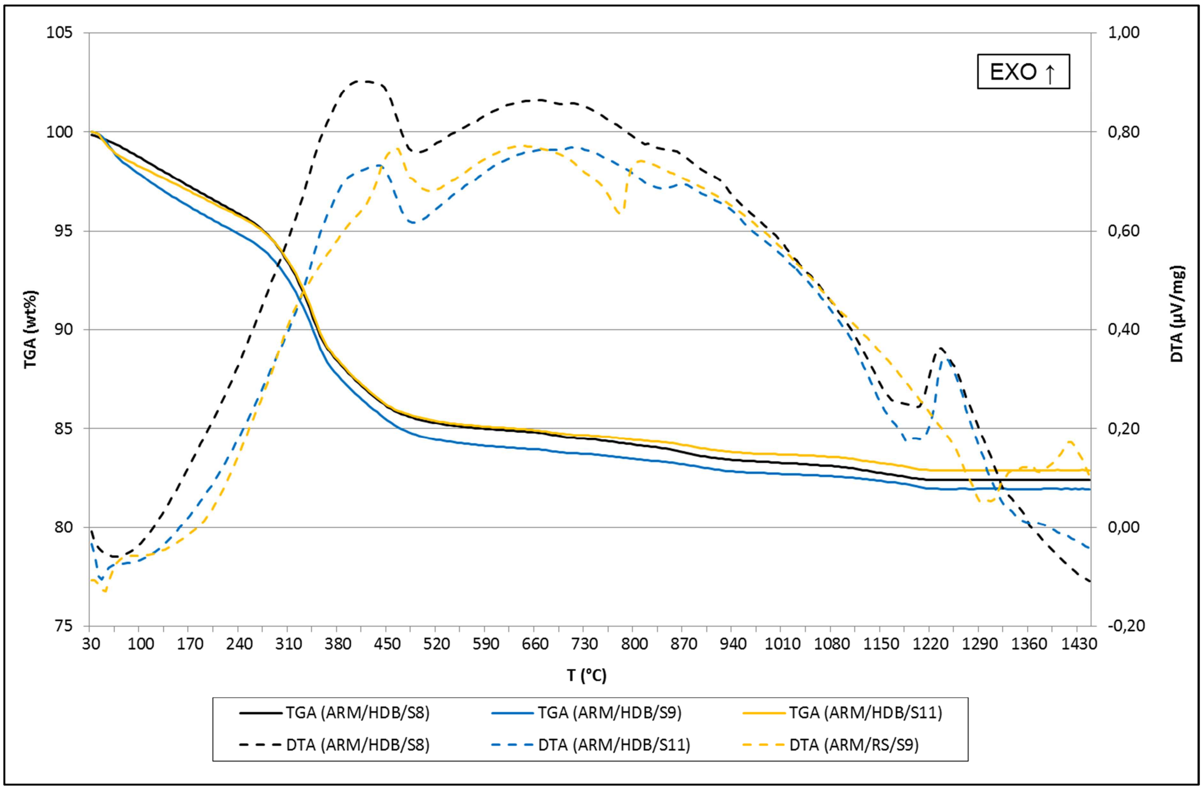

Figure 7.11.: TGA/DTA analysis of the three selected autoclaved High Density FC materials (HD)

Also perfectly quantifiable is the mass loss of the char that is generated by the thermal degradation of cellulose between 800°C and 1000°C.

The presence of char in the TGA/DTA analysis of the ARMs, confirms the Broido-Shafizadeh reaction mechanism (**Figure 7.12.)** and therefore indirectly, the presence of levoglucosan.

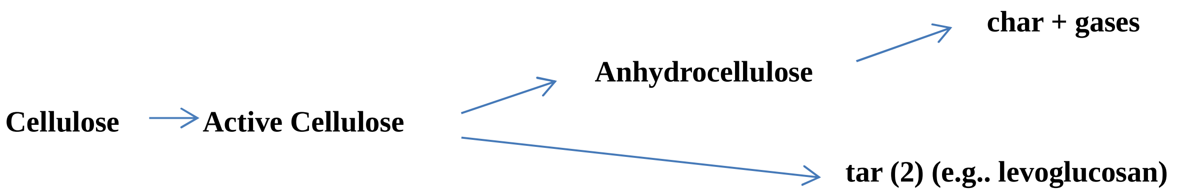

Figure 7.12.: Reaction mechanism of Broido-Shafizadeh

Furthermore, TGA/DTA coupled with XRF analysis makes it possible to calculate the CO_2 fraction originating from $[Ca,Mg](CO_3)_2$ and the associated energy consumption of each raw material presented in **tables 7.5.** and **7.6.** as already explained in **paragraph 3.5.2.** Unfortunately the gain in energy by the decomposition of organic components and the loss of energy coming from the decomposition of chemically bound H_2O is not quantifiable by the performed analysis by TGA/DTA.

By comparing the TGA/DTA analyses of the raw materials and the Cold Clinker Meals (CCMs), the reduction of CO_2 emission as well as the associated energy gain by the lowered endothermal decarbonation can be quantified as presented in **tables 7.7.** and **7.8.**

Table 7.7.: TGA evaluation of the reference and alternative Cold Clinker Meals of CBR Antoing, CBR Lixhe and ENCI Maastricht (RM=Raw Materials)

CCM	Inorg CO_2	Organic+H_2O	$CaCO_3$	Inorg CO_2 RM	$CaCO_3$ RM
	TGA (wt%)	TGA (wt%)	TGA Der (wt%)	TGA (wt%)	TGA Der (wt%)
CCM/Ant/Ref	34.0	0.6	77.3	34.3	78.0
CCM/Ant/FC	29.7	4.8	67.6	31.7	72.1
CCM/Lxh/Ref	32.5	0.5	73.9	31.8	72.2
CCM/Lxh/FC	16.9	9.3	38.4	19.5	44.3
CCM/Maa/Ref	34.2	0,0	77.7	33.9	77.0
CCM/Maa/FC	33.3	1.2	75.8	32.9	74.7

Table 7.8.: TGA/DTA evaluation of the reference and alternative Cold Clinker Meals of CBR Antoing, CBR Lixhe and ENCI Maastricht (RM=Raw materials)

CCM	Decarb E	Decarb E RM	Decarb E	Decarb E RM
	DTA (µVs/mg)	DTA (µVs/mg)	TGA Der (J/g)	TGA Der (J/g)
CCM/Ant/Ref	213.4	206.3	1378	1390
CCM/Ant/FC	190.5	179.7	1205	1284
CCM/Lxh/Ref	189.3	203.0	1318	1287
CCM/Lxh/FC	105.9	115.3	685	800
CCM/Maa/Ref	219.3	215.7	1385	1373
CCM/Maa/FC	199.7	209.3	1350	1332

This is done by calculating the decarbonation energies of $CaCO_3$ (**Table 7.8.**) out of the TGA/DTA analysis of the CCMs (**Table 7.7.**) and calculating the decarbonation energies out of the TGA/DTA analysis (**Table 7.6.**) of the Raw Materials (RMs) taking in account the calculated compositions of **table 7.3.** (**Paragraph 3.5.2.**). The fact that these two totally separated calculations gave a comparable result, proofs that the interpretation of the TGA/DTA analyses were objective as well as correct and could therefore be used to evaluate the CO_2 reduction as well as the gain in Decarb E by the use of the ARMs.

7.6.4. XRD Analysis

The XRD analyses of the final clinkers presented in **table 7.10.**, show different weight percentages than those calculated by Bogue equations out of the chemical analysis of the final clinker presented in **table 7.9.** As stated in **paragraph 7.6.2.**, the chemical analyses were as expected and in line with the average values of the clinkers produced in the first 6 months of 2011 on the 3 factory sites as presented in **table 2.1.** The difference between the C_3A and the C_4AF measured with XRD and the corresponding values calculated with the Bogue equations stems from the method itself.

For the kilns of CBR Antoing and ENCI Maastricht, it can be noted that the 13.28 wt% dosed autoclaved High Density FC Boards ARM (Antoing) or the 6.01 wt% dosed autoclaved Medium Density FC Boards ARM (Maastricht) had no significant influence on the mineralogy of the clinker (**Tables 7.9.** and **7.10.**).

Table 7.9.: Chemical analysis and Bogue calculations of the final clinkers produced in a static kiln

Clinker		Cl/Ant/Ref	Cl/Ant/FC	Cl/Lxh/Ref	Cl/Lxh/FC	Cl/Maa/Ref	Cl/Maa/FC
CaO	(wt%)	65.90	66.71	66.28	65.61	66.18	66.44
SiO_2	(wt%)	22.27	22.72	21.93	21.53	21.39	21.56
Al_2O_3	(wt%)	4.14	3.97	4.40	4.77	4.54	4.45
Fe_2O_3	(wt%)	3.02	2.79	4.21	3.81	3.98	3.99
K_2O	(wt%)	0.59	0.24	0.21	0.25	0.33	0.29
Na_2O	(wt%)	0.17	0.14	0.20	0.20	0.21	0.19
SO_3	(wt%)	0.89	0.44	0.12	0.58	0.36	0.29
MgO	(wt%)	1.73	1.48	1.28	1.7	1.52	1.44
TiO_2	(wt%)	0.25	0.39	0.30	0.40	0.30	0.3
P_2O_5	(wt%)	0.21	0.20	0.24	0.33	0.17	0.16
Cl	(wt%)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
LOI 975°C (O_2)	(wt%)	0.48	0.39	0.39	0.33	0.48	0.45
DoS-factor	(wt%)	123.42	114.33	27.47	123.18	65.24	58.95
Alite	(wt%)	66.84	68.19	67.52	65.92	70.61	70.97
Belite	(wt%)	13.44	13.71	11.95	12.01	8.07	8.29
Celite	(wt%)	5.86	5.80	4.54	6.20	5.30	5.04
Ferrite	(wt%)	9.19	8.49	12.81	11.59	12.11	12.14

Table 7.10.: Mineralogical analysis by XRD of the Final Clinkers produced in a static kiln

Clinker		Cl/Ant/Ref	Cl/Ant/FC	Cl/Lxh/Ref	Cl/Lxh/FC	Cl/Maa/Ref	Cl/Maa/FC
Alite	(wt%)	64.52	64.50	65.04	62.72	71.33	70.58
Belite	(wt%)	19.73	20.61	14.93	17.61	8.56	9.79
Celite	(wt%)	1.79	2.58	3.68	1.56	4.64	4.22
Ferrite	(wt%)	12.86	11.23	15.87	17.61	14.89	14.53
Free Lime	(wt%)	0.23	0.51	0.23	0.28	0.35	0.75
Periclase	(wt%)	0.39	0.19	0.18	0.22	0.23	0.13
Arcanite	(wt%)	0.32	0.20	0.07	-	-	-

(Full XRD analysis of Cl/Lxh/FC in Figure A.4. (Appendix A))

Although a difference of 1-2 wt% could be interpreted to be within the error range as explained in **section 3.10.**, it can be noted that in case of the CBR Lixhe kiln, the alite *[wt%]* of the alternative clinker (Cl/Lxh/FC) is lower compared to the classic clinker (Cl/Lxh/Ref) for XRD analyses and Bogue calculations. Because the difference in alite *[wt%]* between Cl/Lxh/Ref and Cl/Lxh/FC is bigger by XRD analysis (-2.32 wt%) than by Bogue calculation (-1.6 wt%), it may be concluded that the difference in alite *[wt%]* does not only originate from a small difference in the chemical composition of both clinkers. In fact, this difference indicates that most probably, for equal chemistry, there still would be an influence of the air-cured ARM on the mineralogy of the alternative clinker.

Out of **table 7.9.**, it can be noted that the alternative clinkers of CBR Lixhe were quite high in SO_3 compared to the reference clinker, but lower than calculated with the simulation program (**Table 2.5.**). The same can be remarked for the clinkers of CBR Antoing where both the reference as well as the alternative clinkers was high in SO_3 but lower than calculated.

Also the alkali contents of all clinkers were lower than simulated. It can be noted that some of the DoS-factors (**Section 2.6.**) were out of equilibrium: both clinkers of CBR Antoing were still between the limits as also the alternative clinkers of CBR Lixhe but all clinkers of ENCI Maastricht and especially the classic clinker of CBR Lixhe had a DoS-factor that was too low. As described in **section 2.5.**, an excess of alkali will increase the viscosity of the melt by which the alite formation is decreased. The reason for these deviations lies in the fact that the static kiln has other enrichment factors **(Section 2.6.)** than the real clinker kilns that were simulated by the simulation program as described in **section 3.3**. In fact, the enrichment factors of a static kiln will be much lower than those of the real clinker kilns. There is no gas stream flowing in the opposite direction of the hot clinker meal (HCM) stream towards colder regions in the clinker kiln allowing alkali and SO_3 to return to the HCM flow like described in **figure 2.8.** Because the alkali have a higher volatility at 1450°C than SO_3, they will be much lower in content in a static kiln. SO_3 *[wt%]* will also be lowered significantly. The decreased alite formation of the alternative clinker of Lixhe by the use of air-cured ARM, could therefore be explained by a difference in DoS-factor influence by the higher SO_3 *[wt%]*, brought in by the air-cured ARM and the influence of the static kiln on the volatility of SO_3 and alkali.

The conclusion after the evaluation of the XRD analysis is therefore that the use of FC ARMs does not influence greatly the chemical and mineralogical quality of the produced alternative clinker if compared with the use of Classic Raw Materials. The differences, if not already originating from the XRD measurement error, were induced by a deviated DoS-factor due to the use of a static lab kiln.

7.6.5. ARM influence on energy consumption: Calorimetric evaluation

Because organic compounds are present in the FC ARMs and an additional energetic benefit is expected from the reduced endothermic decarbonation part, it is interesting to comparatively evaluate the energy necessary to heat the classic cold clinker meal up to 1450 °C, with that necessary for doing the same but with the alternative cold clinker meal. TGA/DTA and calorimetric measurements were performed to give an idea of this possible energetic gain.

Furthermore, the presence of chemically bound H_2O in the FC ARMs also implies loss of energy while heating. The energy required to perform dehydration reactions is not so easy to quantify because of a variety of hydration products that are generated upon the hydration of cement.

As indicated in **paragraph 7.6.3.**, the decarbonation energies were calculated and presented in **tables 7.6.** and **7.9.** These decarbonation energies together with the Gross Calorific Values (GCV) of the different CCMs (**Paragraph 3.7.3.**) and the selected FC ARMs determined by calorimetric analysis, were plotted in **figures 7.13.** and **7.14.** Nicely visible is the significant energy gain coming from the lowered endothermal decarbonation energy.

The average dry starting compositions of the four types of ARMs give us the ratio between the three types of organic fibres **[7-9]** in the air-cured ARMs: cellulose, PVA and PP. In the autoclaved ARMs, only cellulose is used as organic fibre. Unfortunately, these dry starting compositions cannot be revealed here.

The TGA/DTA analysis of the selected ARM, made it possible to divide the loss of ignition between 100°C and 1000°C in a decarbonation part and an organic / chemically bound H_2O part. Because the decarbonation part concerns CO_2, the part of the total C (**Table 7.4.**) related to CO_2 can be calculated, revealing the C *[wt%]* related to the organic fibre(s). By the molecular mass of each organic fibre and the average ratio between the three types of organic fibres in the air-cured ARM, the wt% of the organic fibres in the ARM can be calculated.

The total wt% of these organic fibres reveals, by using the organic / chemically bound H_2O part measured by TGA/DTA, the chemically bound H_2O. The wt% of the chemically bound H_2O in the alternative CCMs can be deduced from the used wt% of ARM (**Table 7.3.**) and was also plotted in **figures 7.13.** and **7.14.**

Cellulose has a Net Calorific Value (NCV) of about 17520 J/g, PolyVinylAlcohol (PVA) of about 21310 J/g, and PolyPropyleen (PP) of about 42660 J/g **[13]**. The specific NCV of the organic fibres present in the CCMs and the selected ARM were generated out of the calculated wt% and the individual NCV of the organic fibres. They were also plotted in **figures 7.13.** and **7.14.**

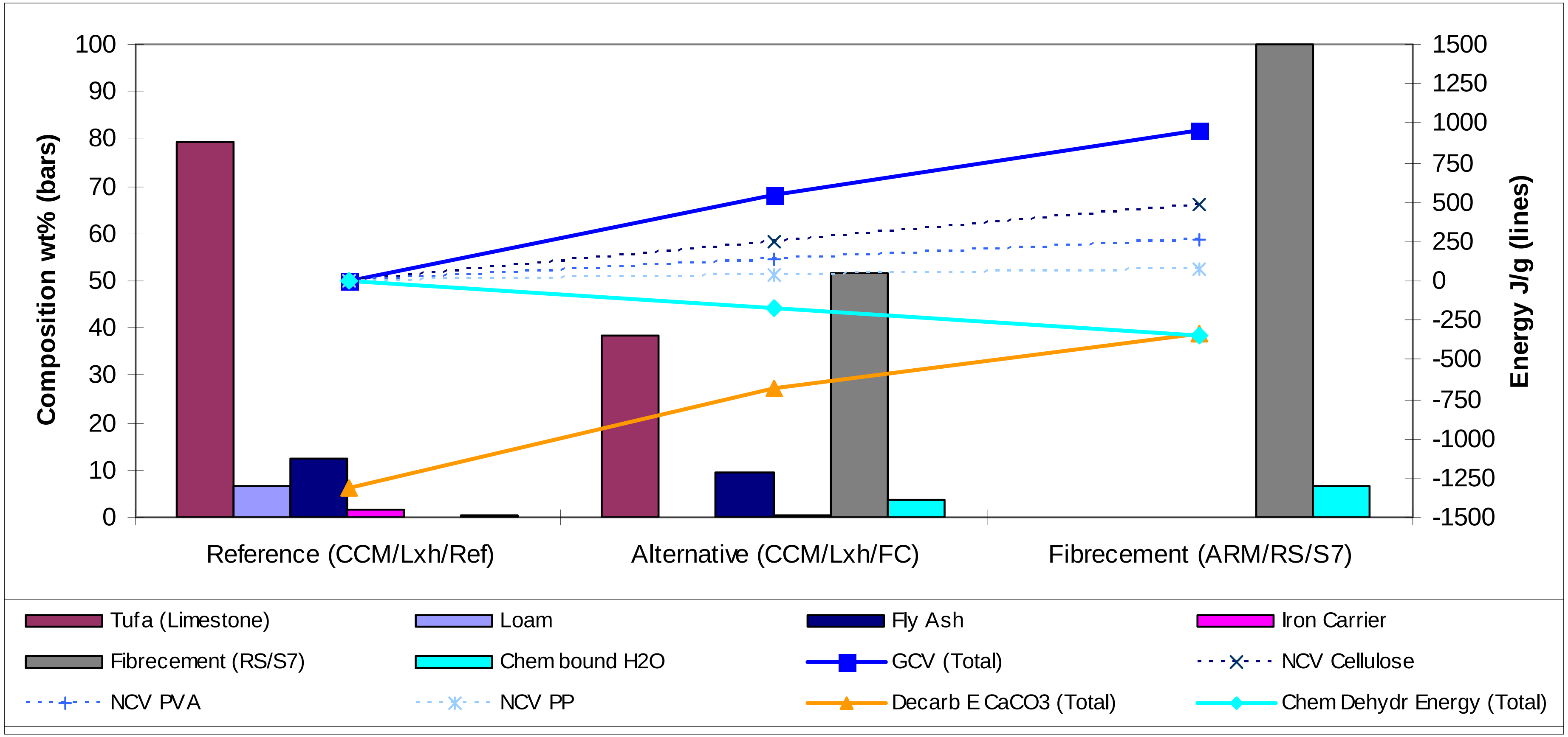

Figure 7.13.: Intrinsic energetic benefit for the alternative CCM of CBR Lixhe (Bars: Composition + total chemical bound H_2O wt%), (Full lines: Gross Calorific Values (GCV) + Decarbonation Energy + Chemical dehydration Energy), (Dotted lines: individual net calorific values (NCV) of the organic fibres)

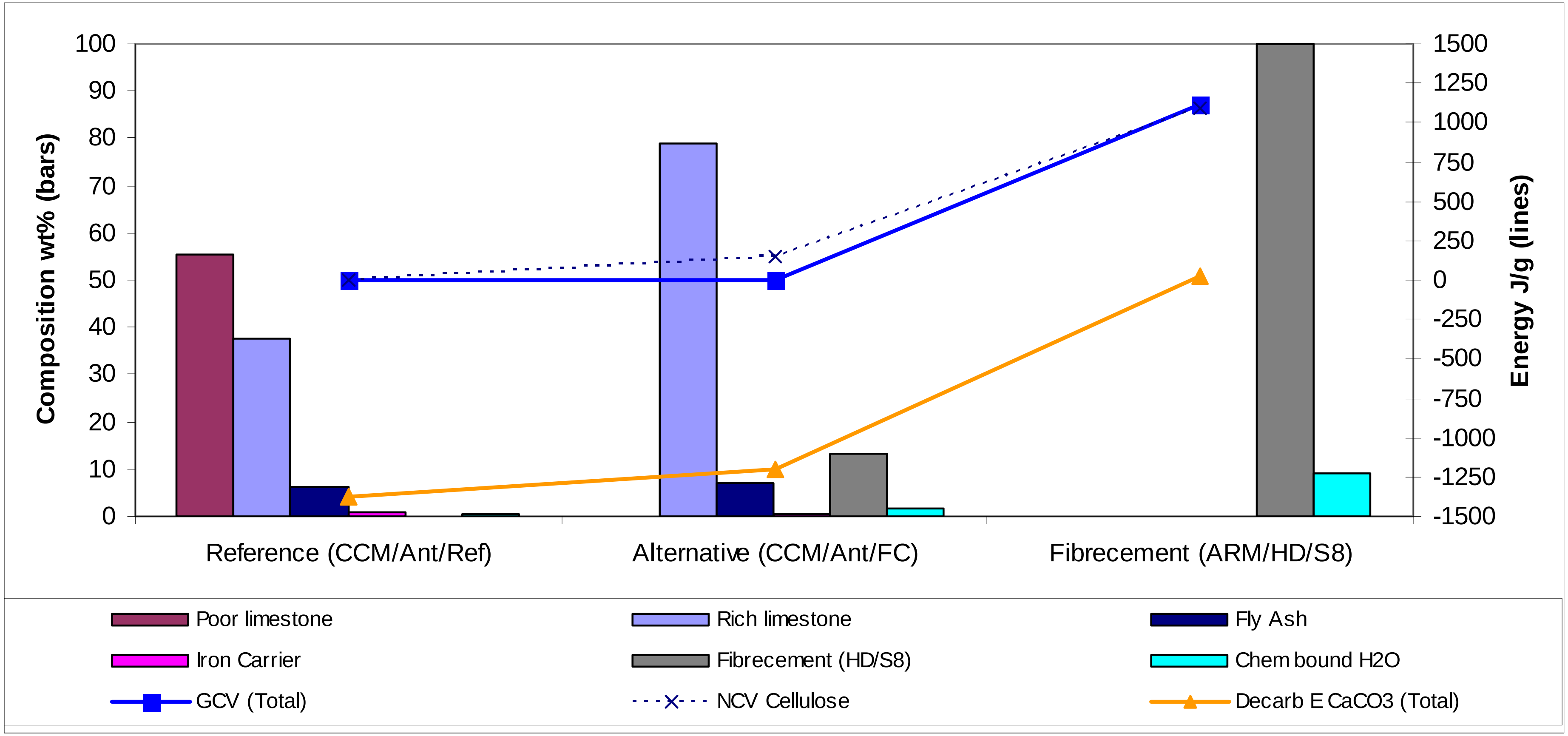

Figure 7.14.: Intrinsic energetic benefit for the alternative CCM of CBR Antoing (Bars: Composition + total chemical bound H_2O wt%), (Full lines: Gross Calorific Values (GCV) + Decarbonation Energy + Chemical dehydration Energy), (Dotted lines: individual net calorific values (NCV) of cellulose)

It could be noted that the GCV of the CCMs and the used FC samples are similar to the sum of the specific NCV of the organic fibres as plotted in **figures 7.13.** and **7.14.** This proofs that the calculations that were performed to determine the wt% of the organic fibres and therefore also the chemically bound H_2O in the ARMs and CCMs, are representative for their compositions.

It could be estimated that the corrugated FC sheets on average contain 7.8 wt% chemically bound H_2O, the FC roofing slates 6.5 wt%, the medium density FC boards 8.4 wt% and the high density FC board 9.5 wt%. The Portland cement *[wt%]* in the ARM could be calculated by using the average dry starting compositions and the chemically bound H_2O *[wt%]* of the ARM which revealed the total paste *[wt%]* present in the ARM. The ratio chemically bound H_2O / paste *[wt%]* present in the selected ARMs are 8.7 wt% for the roofing slate sample (ARM/RS/S7), 23.8 wt% for the high density FC plate sample (ARM/HD/S8) and 20.4 wt% for the medium density FC plate sample (ARM/MD/S5).

As presented in **section 7.2.**, the autoclaving production process will generate other calcium silicate hydrates explaining the high chemically bound H_2O *[wt%]*. These circumstances are not present in the air-cured production process where only cement will hydrate which results in much lower chemically bound H_2O *[wt%]*.

Like stated by Alarcon-Ruiz **[14]**, the chemically bound H_2O of cement hydrates will be liberated between 100°C and 550°C. Three major decomposition reactions will take place liberating H_2O: the decomposition of gypsum, ettringite and a part of the calciumaluminate hydrates between 110°C and 170°C, the loss of chemically bound H_2O from the decomposition of the C-S-H and the other part of calciumaluminate hydrates between 180°C and 300°C and finally the dehydroxylation of portlandite between 450°C and 550°C. Two distinct endothermal energies could be distinguished out of the TGA/DTA analysis measured between 30°C and 600°C on cement pastes, as described in **paragraph 7.6.3.** The first between 150°C and 250°C and the second between 400°C and 500°C.

By performing DSC analyses on cement pastes with different W/C ratios, an effort is made to estimate the total dehydration energy. The pastes are made with the CEM I cement presently used at the FC plant from which the FC production waste for this study was taken. Four pastes were made out of 450 g CEM I type cement and W/C ratios of 0.25, 0.30, and 0.35. To obtain the paste with the lowest W/C ratio (0.18), a paste with a W/C ratio of 0.21 was made, which was subsequently filtered off in view of obtaining a still lower W/C ratio. The pastes were stored for 28 days at 20 ± 1°C hermetically wrapped in plastic and were afterwards dried at 105 °C for the respective curing times that had been selected. By TGA/DTA, the cement *[wt%]* and the chemically bound H_2O *[wt%]* could be determined for each cement paste. A Mettler Toledo Star DSC was used to determine the endothermal energies required to perform the dehydration reactions for the liberation of chemically bound H_2O on the cement pastes.

These energies were subtracted with the calculated heat capacities of the available Portland cement *[wt%]* in the cement pastes and were plotted in **figure 7.15.** as a function of the ratios chemically bound H_2O / paste. The specific heat constant for Portland cement was defined as 0.84 kJ/(kg*K) **[15]**. A good linearity was found what endorses the findings of Abdelrazig **[16]**.

By using the ratio chemically bound H_2O / paste *[wt%]* and the paste *[wt%]* determined for the selected air cured ARM, the energies necessary to perform these decomposition reactions in the selected air cured ARM and alternative CCM were calculated by regression out of **figure 7.15.** and visualised in **figure 7.13.** This was not possible for the autoclaved ARMs (**Figure 7.14.**) because of the presence of calcium silicate hydrates which are not formed by classic cement hydration.

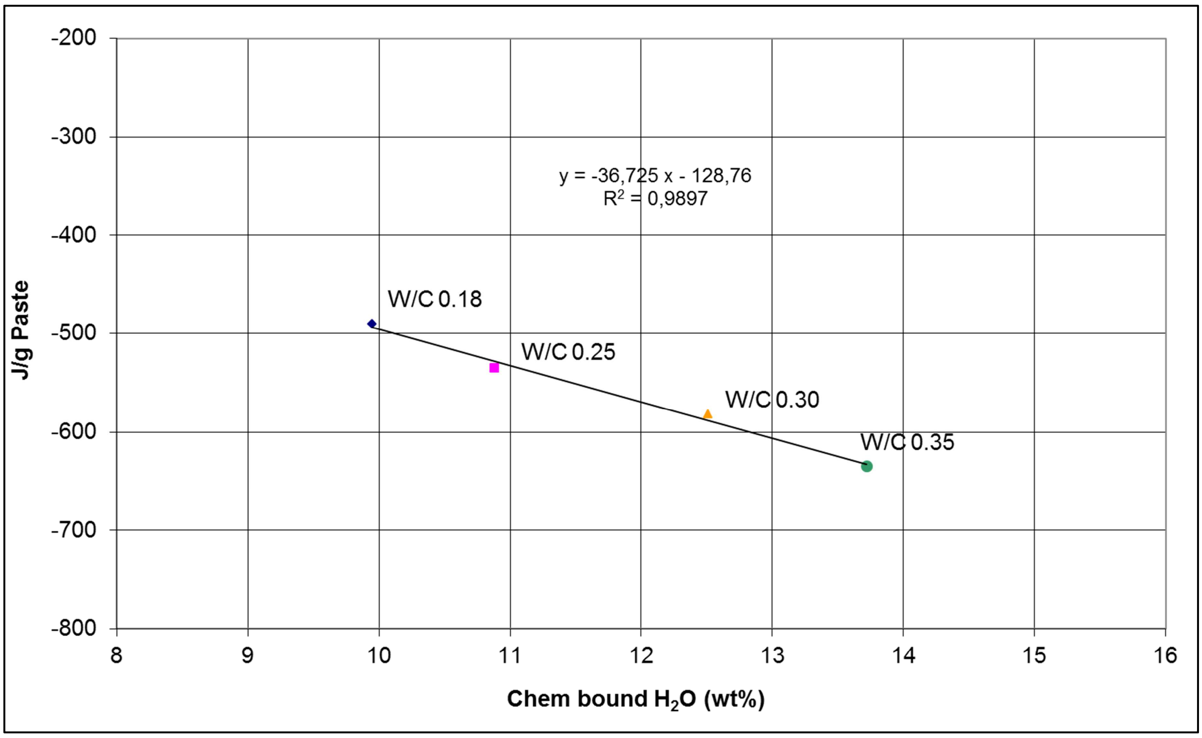

Figure 7.15.: Endothermal dehydration energies for Portland based cement pastes after 28 days

To summarise, it can be stated that for the air cured ARMs, there will also be a balance, between the energy coming from the exothermal decomposition energies of the organic fibres and the energy loss coming from the dehydration of the cement in favour of the first. Relying on the measured chemically bound H_2O of the autoclaved ARMs, a partial recovery of the exothermal decomposition energy of the organic fibres is certainly realistic. Furthermore it can safely be stated that the energy gain by the decreased required decarbonation energy will be fully recuperated.

7.6.6. GC-MS and MS analyses

A variety of organic materials are commonly used in the clinker process to generate energy **[17-21]**. They are brought in the clinker process at specific places where a complete thermal decomposition is made possible. Raw materials are usually introduced at the cold side of the kiln. Therefore thermal decomposition products from cellulose, PVA and PP might not be completely degraded when they reach volatility at low temperature and will be picked up by the gas stream coming from the opposite end of the cement kiln. This could cause blockage of the cyclone tower and generate an excess of the Total Organic Carbon emission limits at the chimney. A solution to this problem could be to introduce the raw material through a pre-calciner **[22]** or through a pre-heater system that feeds the cyclone tower with heat, leading to a complete thermal degradation as described in **paragraph 2.3.2.**

The decomposition reaction mechanism of Broido-Shafizadeh for cellulose (**Figure 7.12.**) is generally accepted as the most likely mechanism **[17]**. The formation of each of the four components is influenced by the decomposition atmosphere, the heating rate, presence of alkali, etc. **[17-21]**. Under inert atmosphere, Polyvinyl Alcohol (PVA) is characterized by two distinctly different temperatures, 380°C and 420°C at which thermal decomposition occurs during heating **[12]**. The decomposition mechanism of PolyPropylene (PP) is very complex and varies greatly depending on the degree of polymerization, the decomposition atmosphere, the heating rate, the polymer structure (isotactic, syndiotactic, atactic), etc. Various volatile degradation products can already be formed below a temperature of 150°C **[23-24]**. The diversity of compounds that the organic materials of FC can liberate by heating them up to 1450°C makes it almost impossible to quantify these compounds completely.

With thermogravimetric analysis (TGA) / differential thermal analysis (DTA), gas chromatography-mass spectrometry (GC-MS) and mass spectrometry (MS) measurements, an effort is made to analyse the organic compounds formed after thermal degradation at specific temperatures (**Section 3.9.**). Two of the selected FC ARMs, ARM/RS/S7 and ARM/HD/S8 were therefore heated up in three separate tests from room temperature to 390°C, 500°C and 800°C.

By comparing the integral calculation of the CO and CO_2 measurement graphs coming from the MS presented in **figure 7.16.** it is clear that the formation of the low molecular CO and CO_2 gases by thermal degradation of the air-cured and autoclaved ARMs increases by higher maximum degradation temperatures as also stated for thermal decomposition of cellulose by D.K. Shen **[19]**.

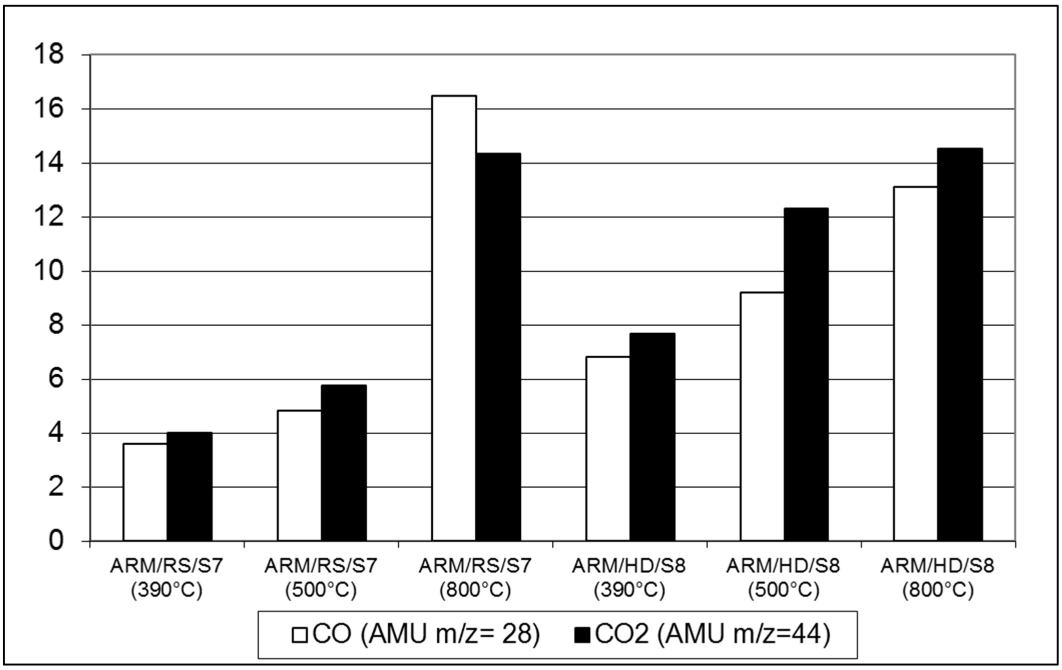

Figure 7.16.: Integral calculation of the CO and CO_2 measurement graphs of air-cured and autoclaved samples measured by MS

Although these calculations could be seen as arbitrary, they can objectively be used to compare the formation of CO and CO_2 gases of the three separated tests (390°C, 500°C and 800°C).

Also the formation as well as the variety of the high molecular volatiles, measured by GC-MS, will increase when the maximum degradation temperature of autoclaved ARM is increased to 800°C as demonstrated in **figures 7.17.** and **7.18.** Only the total ion current chromatograms are presented due to the impossibility at this state of identifying so much different compounds.

Similar to what was found in literature on the thermal decomposition of cellulose (**[17-21]**), the total formation of high molecular volatiles increases when the maximum degradation temperature was increased from 390°C to 500°C. According to the Broido-Shafizadeh mechanism (**Figure 7.12.**), levoglucosan should be generated in high quantities. Unfortunately, the spectrum of levoglucosan was not clearly detected in any of the six GC-MS measurements. Although the glass piping was isolated, there was a brown deposition at the exit of the reactor. We suspect that this deposition descends from the levoglucosan **[25]**. As stated by Hosoya **[26]**, the pyrolytic behaviour of levoglucosan at 400 °C results in a vapour phase and a liquid/solid phase. In the vapour phase, levoglucosan will be converted to non-condensable gases (mainly CO and CO_2), while char and other condensable low molecular weight products were formed in the liquid/solid phase.

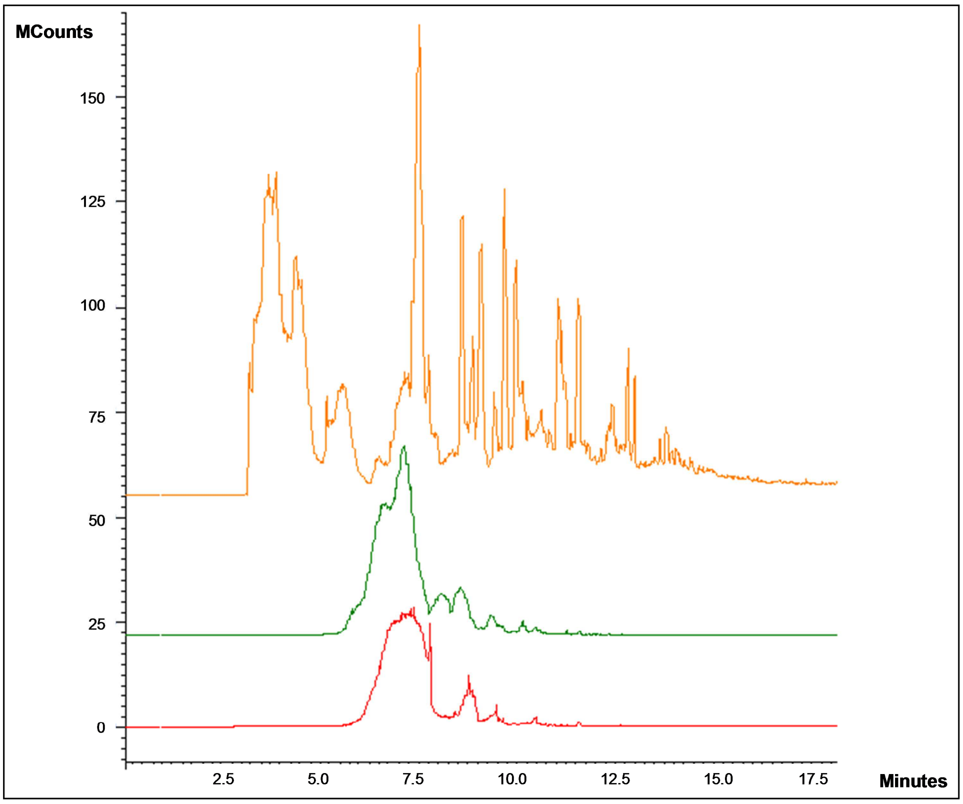

Figure 7.17.: GC-MS measurement of air cured ARM from bottom to top
at 390°C, 500°C and 800°C

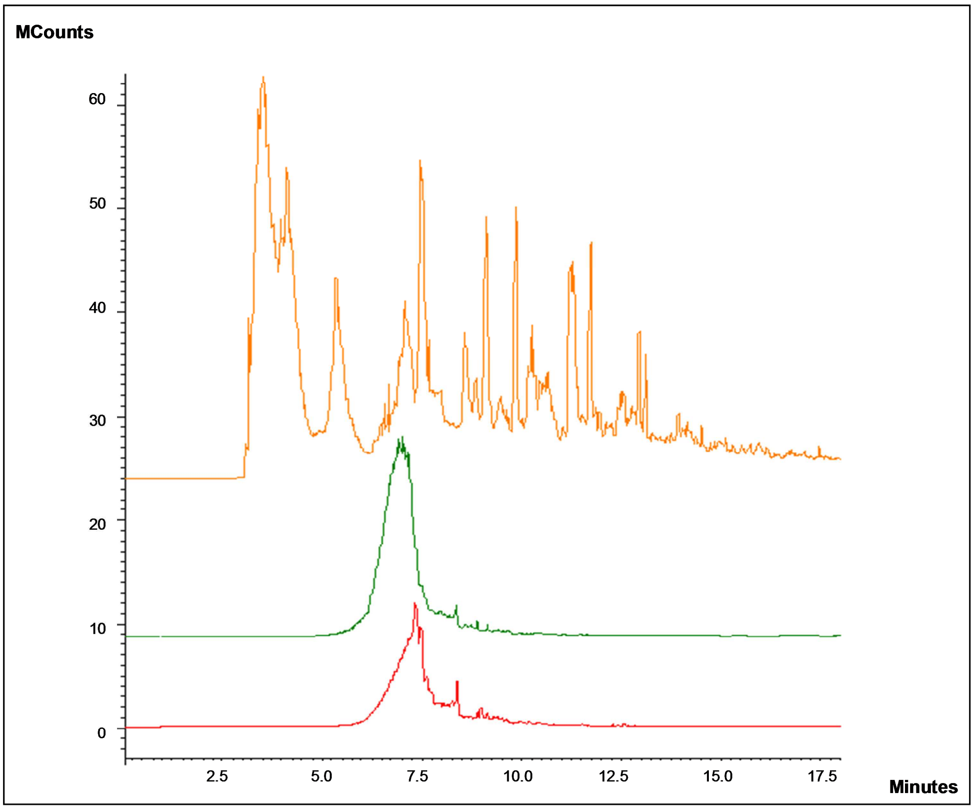

Figure 7.18.: GC-MS measurement of autoclaved ARM from bottom to top at 390°C, 500°C and 800°C

This could explain the absence of levoglucosan in the GC-MS analysis. The GC-MS measurements of the air-cured ARM samples differ from those of the autoclaved ARM samples due to the presence of PVA and PP and the lower wt% of cellulose.

As described by Zheng Peng **[12]**, acetaldehyde should be generated above 420°C by thermal degradation of PVA but the big variety of generated volatiles prevents its identification in the GC-MS measurements of the air-cured ARM.

Although it was not possible to distinguish in a qualitative and quantitative way the different high molecular volatiles by GC-MS, this specific test proofs that introducing the FC ARMs in large quantities by the cold side of the clinker kiln is a bad idea. Even when the clinker kiln is quite modern and has a cyclone tower to heat up the CCM within minutes to 800°C, a lot of generated volatiles will return by the gas stream to colder regions of the cyclone tower causing clogging if returned to their solid state or worse be emitted by the chimney causing an exceeding of the emission limits. The deposition in the glass tubing is a perfect example to endorse this statement. Therefore large quantities of FC ARMs should be introduced at a hot point like a pre-calciner or pre-heater where it will be heated up in seconds to 900°C which will ensure a complete thermal degradation of the organic fibres.

Further research has to be performed to distinguish the different high molecular volatiles by GC-MS and to heat up FC ARM samples on lab scale in seconds to 900°C for example by pyrolysis chromatography.

7.7. Ecological benefit

The use of FC could have different positive ecological advantages. Based on the guidelines of the LCA evaluation (**Section 4.4.**), the possible ecological benefit by using recycled FC as ARM in Portland clinker production can be indicated.

- The EPD of Portland clinker (cradle to gate):

  The use of FC as ARM will reduce the required volume of limestone to produce 1 ton of clinker. This means that the influence of the EPD of the limestone will be smaller on the LCA of the Portland clinker production. On the other hand, the influence of the EPD of the recycled FC will have to be taken in account. Whether or not this shift in raw material use is an ecological benefit depends on the EPD of both raw materials.

  Less limestone means also less $CaCO_3$ that has to be decarbonated as demonstrated in both articles (**Section 7.6.**). Furthermore, the input of cellulose by the FC waste will have a positive influence on the EPD of Portland clinker. Cellulose can be catalogued as biomass and will have a positive impact on CO_2 emissions related to the energy consumption. Reduction of the inorganic CO_2, the required decarbonation energy and the CO_2 assigned to the total energy consumption will have as result that the LCA of the Portland clinker will improve. When the cradle to gate principle is used for the Portland clinker production, this will result in an improved EPD for Portland clinker.

  As described in **section 7.6.**, the negative impact on the energy consumption of the Portland clinker kiln by skipping the cyclone tower for introduction of the ARM (**Paragraph 2.3.2**.) and the introduction of chemical bound H_2O will be smaller than the positive impact by the use of FC.

  However, a realistic EPD of the Portland clinker including the use of FC as ARM can only be calculated with industrial practice due to the fact that impact of FC on the energy consumption of the Portland clinker process cannot be completely numerically simulated. Also the impact of real recycling FC on the Portland clinker process has to be evaluated. One of the factors that will play a role is the impact of the aging of the FC as a function of its carbonation.

- EPD’s of the other related processes (cradle to gate):

  An improved EPD of Portland clinker will have also a positive impact on the EPD of Portland cement. Nevertheless, industrial practice will be necessary to fine-tune the EPD calculation of Portland cement as a function of gypsum/anhydrite dosage due to an increased SO_3 concentration in the Portland clinker, grinding energy and required fineness of the final Portland cement as also of other cement types which EPD’s will be less but still considerably influenced by the EPD of Portland clinker. Furthermore looking to the EPD of FibreCement (FC) itself, the EPD of Portland cement will have a big impact with dosages up to 80 wt% (**Figure 7.2.**) in air-cured FC. An improved EPD of FC will make it more compatible towards comparable building materials when considering ecological construction of a building.

- Cradle to grave / Cradle to cradle:

  When looking to Life-Cycle Assessment (LCA) of Fibre Cement (FC) by using the different stages of its life cycle in the cradle-to-grave assessment, the end-of-life disposal step will be influenced by the recycling of FC as ARM for Portland clinker production. This means that when landfilling can be avoided resulting in a shift of cradle to grave principle towards cradle to cradle principle for LCA calculation, the LCA of FC as well as this of Portland clinker can be improved when the recycling step has a smaller impact than final disposal by landfilling or incineration. This is not so obvious because recycling includes transportation from the yard as well as ARM preparation which has to be compared to the transportation and preparation required for landfilling and/or incineration.

  Nevertheless, the avoidance of the impact of the landfilling or incineration itself on the LCA calculation will be a pure gain towards the use of FC as ARM for Portland clinker production.

Based on the results of this study and the cited influences on the LCA calculation, it can be expected that the use of FC as ARM for Portland clinker production will have ecological benefits which are additionally in line with the Cement Sustainability Initiative (**Section 4.2.**).

FC as ARM for Portland clinker production will have his influence on two of the five Key Performance Indicators of the Cement Sustainability Initiative: Climate change management as well as fuels and materials use.

The climate change management will be influenced by decreased company-wide total CO_2 emissions (tons/year) as well as the company’s gross and net CO_2 emissions per ton of cementitious product.

The use of fuels will be influenced as a function of the specific heat consumption of clinker production in (MJ/t of clinker) as well as by the alternative fossil and biomass fuel rate. The raw materials use will be in its turn positively influenced by an increased alternative raw materials rate.

7.8. Conclusions

FibreCement out of non-asbestos materials (FC) could be an interesting alternative raw material for Portland clinker production. It was shown that compared to a situation where pure limestone is used in the cold clinker meal, an inorganic CO_2 emission reduction as well as a decarbonation energy gain is possible.

Furthermore, it was demonstrated that the chemistry and mineralogy of the final clinkers were not influenced significantly by the use of the FC materials. Due to the ability to recycle FC separately from asbestos cement materials based on Near InfraRed (NIR) spectroscopy, the use of FC as ARM, is realistic.

Because FC can be divided over two FC groups during recycling based on their application (roof or sidings), a recycled FC material could be generated with a compositional constancy and chemical stability.

However, when used in practice, these materials should be introduced at a hot point in the process, e.g. a pre-calciner or a pre-heater, to ensure full thermal degradation of the organic fibres for physical and chemical reasons, as to avoid clogging of the filter system and exceeding organic volatile emissions levels. Therefore the use of FC for clinker production should be investigated further at an industrial scale.

The potential energy loss by skipping the cyclone tower as energetically most profitable way of heating should be minimal because the biggest energy consuming reaction in these cyclones, the decarbonation of $CaCO_3$, will barely be present in FC ARMs.

The possible energy gain for use of FC versus limestone, coming from the exothermal degradation of organic compounds, as also from the lowered decarbonation energy, was quantified. Together with the estimated energy consumption needed for the liberation of chemically bound H_2O, it was shown that using FC as raw material for clinker production lowers the total required energy compared to the use of classic raw materials, without compromising neither on physical, chemical nor mineralogical properties.

It should, together with the already available alternative fuels and raw materials, be considered as a way to get in line with the Cement Sustainability Initiative.

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Chapter 8

Cellular concrete as alternative raw material for Portland clinker production

8.1. Introduction

Cellular or aerated concrete is a type of lightweight concrete with a high concentration of air voids. It is made by introducing air or other gas into a slurry composed of Portland cement and/or and a siliceous filler, mostly a fine sand (**Table 8.1.**). Cellular concrete is used for construction and is produced by over more than 200 plants in 35 countries **[1]**. China, Central Asia, India, and the Middle-East are the biggest markets for cellular concrete in terms of manufacturing and consumption. Nowadays, the production and use of cellular concrete has stabilised in Europe but is still growing rapidly in Asia due to the strong demand in housing and commercial space.

Table 8.1: Composition of autoclaved cellular concrete blocks of Xella Burcht

Raw Materials of autoclaved cellular concrete		Quantity
Ground quartz sand (90 wt% SiO_2)	(wt%)	43.6
Autoclaved Cellular Concrete (ARM/CCC)	(wt%)	14.0
Cement	(wt%)	12.6
Lime	(wt%)	12.4
Non autoclaved Cellular Concrete	(wt%)	11.4
Fine quartz (99.5 wt% SiO_2)	(wt%)	3.3
Anhydrite	(wt%)	2.6
Aluminium (fine)	(wt%)	0.09
Aluminium (coarse)	(wt%)	0.02

Cellular concrete is used for internal and external construction as blocks and panels but can also be applied before hardening as foam or slurry. Cellular concrete has a much better workability than regular hardened concrete due to the fact that it can be cut to size on site by standard hand and power tools. It was first developed in the early 1900’s after which it was further upgraded in 1924. Cellular concrete can be produced according to various production processes. Two big groups can be distinguished: one at ambient temperature, the other autoclaved at temperatures higher than 100°C.

Within this investigation, only the second group is treated focussing on the precast masonry products namely the cellular concrete blocks. The production process of these blocks will be further discussed in **section 8.3.** Due to its long history, numerous applications and its extensive use as building material, it is quite logical that big parts of demolition waste consists out of cellular concrete.

A possible use of cellular concrete as Alternative Raw Material (ARM) for Portland clinker production could therefore be a valid solution to decrease demolition waste. Because the cements and sands used in cellular concrete can also be found in standard concrete compositions, some of the final conclusions of this study will also apply for regular concrete. Rejected autoclaved and non-autoclaved cellular concrete materials are nowadays already reused in the production process of autoclaved cellular concrete itself as can be noted out of **table 8.1.** An effort will be made to demonstrate the possibility to use cellular concrete as ARM but also its impact on the Cold Clinker Meal (CCM) fineness and on the fitness of the used process parameters within the Portland clinker process.

8.2. Cellular concrete

Cellular Concrete was first developed in Stockholm, Sweden in the early 1900's. The original material was known as "gas concrete" and was used in producing heat-insulated building materials. Cellular concrete was optimised in 1924 by a Swedish architect dr. Johan Axel Eriksson. He was looking for a building material that had the same qualities as wood as a function of insulation, strength and workability but without the disadvantages as flammability and impermanence.

The improved cellular concrete concept went into production in 1929 in a factory in Hällabrottet, Sweden. It was found that a mixture of lime (CaO) and finely divided quartz (SiO_2) could be foamed with aluminium powder after which it was autoclaved at 180°C to produce a lightweight, insulating, sound absorbing building material. The air-entraining agent was used to create the cellular structure of air voids by which the density of the concrete is drastically lowered. Air contents from 30 to 80 percent are not uncommon **[2]**. In this way, a wide range of densities could be achieved varying between 500 to 1600 kg/m³ **[3]**. In the 1940s, the well-known trademark Ytong was introduced which is still a popular name up today to describe cellular concrete blocks. After the Second World War, this technology quickly spread to different parts of the world, mostly Europe and the Soviet Union. Cellular concrete is composed out of cementitious mortar surrounding disconnected random air bubbles. The air bubbles are a result of gas formed within the mortar or foam introduced into the mortar mixture **[4]**. Based on the method of curing, cellular concrete can be classified as non-autoclaved or autoclaved **[5]**. When the binder consists of other than just Portland cement, autoclave curing usually is employed **[2]**. As presented in **table 8.1.**, the investigated materials are made out of very fine quartz, ground sand **[6-9]**, lime, cement sometimes combined with fly ashes **[3]** and as air-entraining agent, aluminium powder **[6]** in combination with a foaming agent. The aluminium powder will react with the lime or alkaline substances which will bring hydrogen into the cementious mortar **[6]**, **[9]**. The foaming agent is used to attract the cement particles into the aerosol foam network by which hydrated Portland cement paste is formed around each entrapped air bubble **[4]**. XRD powder studies have already shown that the main reaction products belong to the tobermorite group of calcium silicate hydrates **[7-10]** using the calcium from the lime and cement and the silicates from the quartz, the fine sand and cement (**Table 8.1.**). The reaction products are a mixture of crystalline, semi-crystalline and near amorphous materials with varying degree of crystallinity **[7-8]**, **[10]**. The autoclaved cellular concrete has many applications in building engineering, mainly in the housing, industrial and public utility building **[11]**.

8.3. The production of autoclaved cellular concrete [11-17]

Because the used samples came from the factory of Xella/Ytong Burcht, its process for the production (**Figure 8.1.**) of the autoclaved cellular concrete blocks is described. Nevertheless, the production processes of other plants will only vary slightly from the one described below. The production starts when all the ingredients which are sand, cement, lime, gypsum, water and aluminium as expansion agent are fed to the mixer to form a slurry. The slurry is then transferred to the moulds which are brought to the mixer for filling. The moulds are kept about 1/3 empty because the reaction between expansion agent and other components of cellular concrete causes the slurry to expand. From here the mould is transferred to the riser section where rising of the mix takes place to fill the mould to overflow. After a period of 3-6 hours the casting will have set enough to withstand cutting.

After this the mould is removed and the ‘green’ cellular concrete cake is transferred to the cutting machine. First trimming is done and then parallel cuts are made usually in two directions at right angles, by tensioned wires so as to produce the required blocks. Now the green cellular concrete is ready for autoclaving.

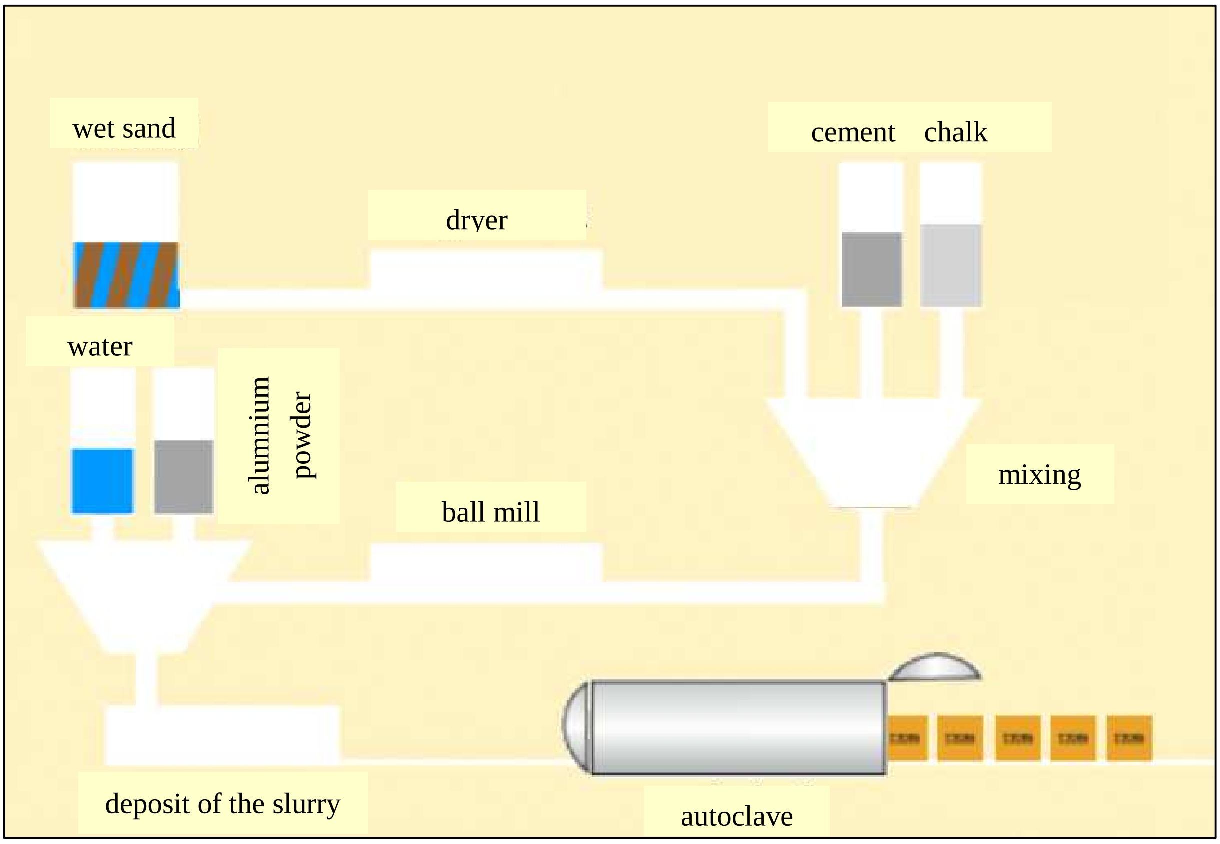

Figure 8.1: Schematical view of the production process of autoclaved cellular concrete (Ref. www.xella.be [cited 2014 Apr 30])

Autoclaving is curing with the help of steam under high pressure. The aerated concrete within the moulds remains in the autoclaves for around 14-18 hours during which the pressure achieved is 11 bars corresponding to a temp of 180 degrees. After the cooling period, the product is taken out.

High pressure steam curing is practically unavoidable in making aerated concrete of first quality when cement is used as a binder and absolutely essential when lime is used. With Portland cement, the initial development of strength in the product depends primarily on the normal setting of the cement, and autoclaving is used to improve the characteristics.

8.4. Sampling

The cellular concrete materials used within this study were selected from two sources, polluted recycled cellular concrete (ARM/CCP) and production waste of clean cellular concrete (ARM/CCC). The ARM/CCP came from a demolition plant KOK in the Netherlands. Six samples spread over a period of two months were delivered and chemically analysed (**Table 8.2.**).

To better interpret the chemical variation of these polluted recycled cellular concrete, the CaO *[wt%]* and SiO_2 *[wt%]* of each of the six samples are plotted in **figure 8.2.**

Table 8.2.: Chemical composition of the recycled cellular concrete samples and the average of these samples

ARM		ARM/ CCP/S1	ARM/ CCP/S2	ARM/ CCP/S3	ARM/ CCP/S4	ARM/ CCP/S5	ARM/ CCP/S6	Average All
CaO	(wt%)	21.73	19.57	16.87	23.75	21.39	21.93	20.87
SiO_2	(wt%)	52.75	56.31	53	45.77	55.49	56.29	53.27
Al_2O_3	(wt%)	2.07	2.25	2.09	1.89	2.06	2.17	2.09
Fe_2O_3	(wt%)	0.72	0.99	0.57	1.23	1.31	1.17	1.00
K_2O	(wt%)	0.63	0.46	0.7	0.44	0.5	0.5	0.54
Na_2O	(wt%)	0.05	0.07	0.17	0.05	0.05	0.05	0.07
SO_3	(wt%)	7.37	2.35	1.7	11.18	6.28	5.27	5.69
MgO	(wt%)	0.6	0.48	0.26	0.47	0.44	0.45	0.45
TiO_2	(wt%)	0.13	0.2	0.18	0.18	0.12	0.22	0.17
P_2O_5	(wt%)	0.05	0.08	0.05	0.1	0.11	0.1	0.08
Cl	(wt%)	-	-	-	-	-	-	-
LOI 975°C (O_2)	(wt%)	13.62	17.15	24.47	14.95	12.21	11.84	15.71
C_{total}	(wt%)	1.68	1.39	0.32	1.68	1.29	1.32	1.28
S_{total}	(wt%)	2.95	0.94	0.68	4.48	2.51	2.11	2.28

The ARM/CCC samples were recovered from the factory of Xella/Ytong Burcht in Belgium during twenty-two weeks. Each week, samples were taken out of the crushed material flow of rejected cellular concrete blocks which were re-entered in the cellular concrete production of Xella Burcht as described in **table 8.1.** These rejected cellular concrete blocks were withheld because of their unsuitable dimensions. These samples were afterwards 2 by 2 homogenised which delivered a total of eleven samples that were further analysed and investigated (**Figure 8.3.**).

Because the process is quite sensitive, it was foreseen that the chemical variation was quite small. Small changes could influence the rising, dimensioning and curing of the cellular concrete blocks.

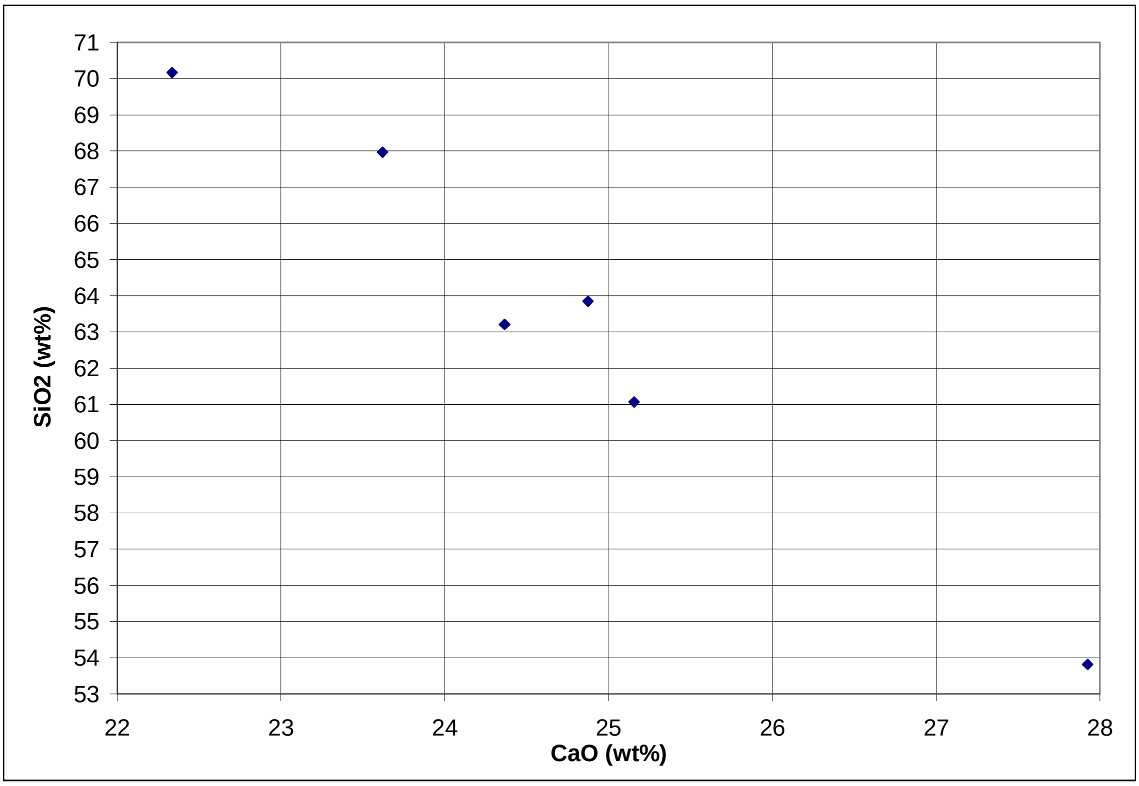

Figure 8.2.: CaO *[wt%]* as a function of SiO_2 *[wt%]* without Loss of Ignition (950°C) of polluted cellular concrete

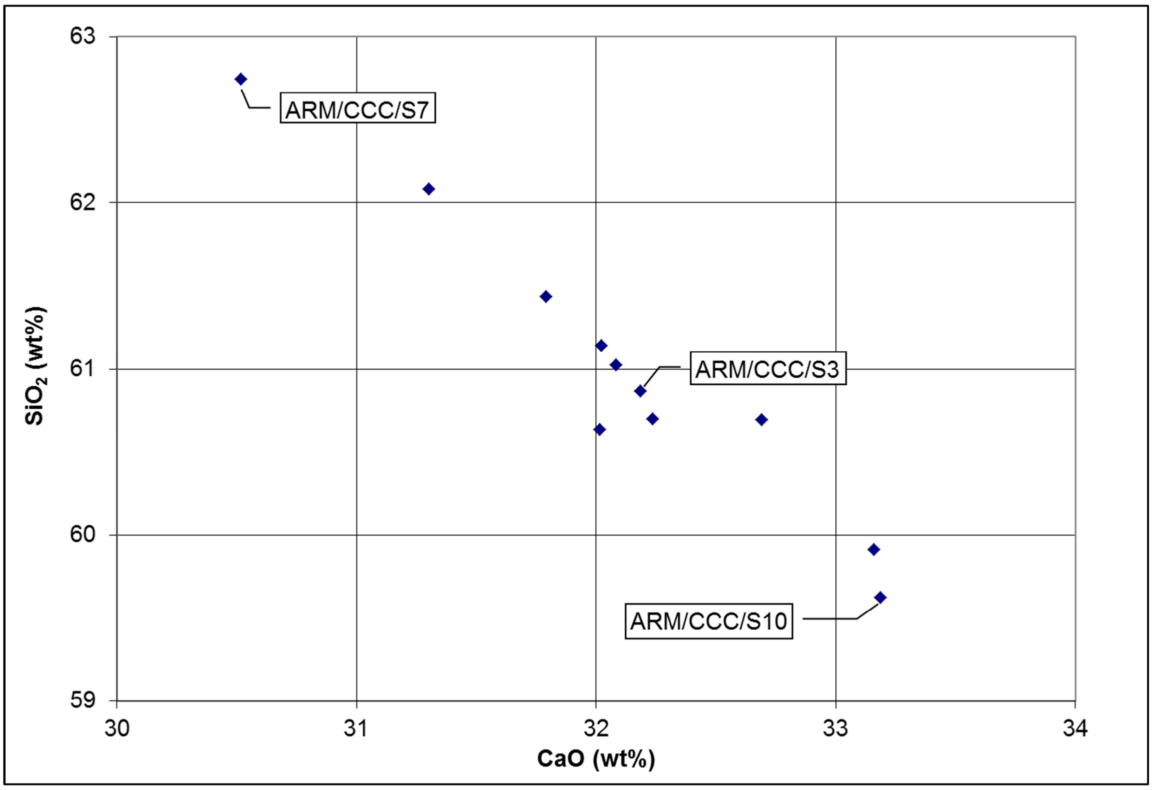

Figure 8.3.: CaO *[wt%]* as a function of SiO_2 *[wt%]* without Loss of Ignition (950°C) of clean cellular concrete. The labels mark the selected Clean Cellular Concrete materials

The ARM/CCP has some inorganic and organic contaminants which will be further explained in **paragraph 8.6.2.** It was decided to investigate the influence and the restrictions of cellular concrete on Portland clinker production with the ARM/CCC materials to avoid too many influencing variables that could make an objective evaluation impossible. The ARM/CCP will give, based on their chemical analysis, additional information about the expected chemical variation and the possible contaminations if real recycled cellular concrete should be used as ARM for Portland clinker production.

8.5. Research description

This investigation aims to evaluate the use of cellular concrete as an Alternative Raw Material (ARM) for Portland clinker kilns. The possibility to generate a raw material with a stable compositional variation was investigated as well as simulations were carried out to maximise their use in clinker kilns. Furthermore, experimental clinkers were produced corresponding with waste dosages that were esteemed as realistic by the numerical simulations.

These clinkers were fully analysed and evaluated according to the evaluation concept described in **chapter 3**.

Because of the presence of important levels of quartz sand in the cellular concrete materials, the energy necessary to grind the alternative raw material in comparison with comparable classic raw materials was investigated as well as the influence of the final particle size distribution of the Cold Clinker Meal (CCM) on the mineralogical composition of the final clinkers.

This investigation will also provide some interesting knowledge on the use of other recycled concrete materials as alternative raw material for Portland clinker production.

8.6. Results and discussion

Based on the articles “Feasibility study on the use of Cellular Concrete as alternative raw material for Portland clinker production” published in Construction and Building Materials **[19]** , the results of the research on the use of cellular concrete as ARM for Portland clinker production is described here below.

8.6.1. Clinker feed calculations and preparations

The CCMs were calculated with a simulation program (**Section 3.3**) in line with the chemical and mineralogical requirements listed in **table 2.5.** The compositions of these CCMs after simulation are presented in **table 8.4.**

The alternative CCMs were calculated to maximise the use of the cellular concrete ARM. Because of the high SiO_2 *[wt%]* in the cellular concrete materials, it was expected that they could function as SiO_2-source in CCM replacing loam or sabulous clay as classic raw materials (**Table 3.4** and **Table 3.5.**).

Table 8.4.: Compositions of the different clinker meals made to be fed to the static kiln

CCM	CRM	Quantity (wt%)	**CCM**	CRM + ARM	Quantity (wt%)
CCM/Ant/Ref	CRM/Ant/CP	55.25	CCM/Ant/CC	CRM/Ant/CP	55.40
	CRM/Ant/CR	37.50		CRM/Ant/CR	36.27
	CRM/Ant/FA	6.38		CRM/Ant/FA	7.41
	CRM/Ant/IC	0.87		CRM/Ant/IC	0.86
	ARM/CCC/S3	0.00		ARM/CCC/S3	0.06
	Sum	100.00		Sum	100.00
CCM/Lxh/Ref	CRM/Lxh/Tu	79.44	CCM/Lxh/CC	CRM/Lxh/Tu	76.54
	CRM/Lxh/Lo	6.63		CRM/Lxh/Lo	0.00
	CRM/Lxg/FA	12.34		CRM/Lxh/FA	14.50
	CRM/Lxh/IC	1.59		CRM/Lxh/IC	1.75
	ARM/CCC/S3	0.00		ARM/CCC/S3	7.21
	Sum	100.00		Sum	100.00
CCM/Maa/Ref	CRM/Maa/Ma	84.38	CCM/Maa/CC	CRM/Maa/Ma	76.71
	CRM/Maa/SC	2.90		CRM/Maa/SC	0.00
	CRM/Maa/FA	11.02		CRM/Maa/FA	11.45
	CRM/Maa/IC	1.70		CRM/Maa/IC	1.78
	ARM/CCC/S3	0.00		ARM/CCC/S3	10.06
	Sum	100.00		Sum	100.00

From the three selected clean cellular concrete samples, the ARM closest to the average SiO_2 *[wt%]* (**Figure 8.3.**) or ARM/CCC/S3 was used in the simulation program and the corresponding alternative Cold Clinker Meal (CCM) preparation. By maximisation of these materials in the different Cold Clinker Meals (CCMs), the loam and sabulous clay dosages *[wt%]* were completely replaced in the case of CBR Lixhe and ENCI Maastricht (**Table 8.4.**).

The only limiting factor was the SiO_2 *[wt%]* of the CCM itself. The dosage of ARM/CCC/S3 in the alternative CCM of CBR Lixhe (CCM/Lxh/CC) was comparable with the dosage of CRM/Lxh/Lo in the reference CCM (CCM/Lxh/Ref) and also the CaO-source CRM/Lxh/Tu was marginally lowered.

This is in contradiction with the alternative CCM of ENCI Maastricht (CCM/Maa/CC) where the dosage of ARM/CCC/S3 almost quadrupled compared to the sabulous clay (CRM/Maa/SC) dosage in the reference CCM (CCM/Maa/Ref) and the CaO-source CRM/Maa/Ma was significantly lowered.

Maximisation of ARM/CCC/S3 in the CCM of CBR Antoing showed little or no possibilities to use cellular concrete. This is due to the fact that CBR Antoing does not use a real SiO_2-source as the necessary SiO_2 is delivered by the two limestone sources, especially the poor limestone (CRM/Ant/CP) (**Table 3.3.**). Decreasing the CRM/Ant/CP dosage would nevertheless result in a too low level of CaO *[wt%]*. Therefore no artificial CCM for CBR Antoing was made because it would differ marginally from the reference.

The CCMs were prepared and sintered as described in **paragraph 2.3.** Additionally, all CCM materials were grinded for 5, 10, 20, 30 minutes at 300 rpm in a laboratory ball mill to obtain different degrees of fineness. These were determined and evaluated by Sympatec laser diffraction. After this evaluation, it was decided to sinter the alternative CCMs with a grinding time of 20 and 30 minutes to investigate the influence on the clinker mineralogy. The physical and chemical analysis of these CCMs as well as the chemical and mineralogical analysis of the final clinkers will be discussed in the following paragraphs.

8.6.2. Chemical and TGA analysis

Three clean cellular samples selected to represent the batch of cellular concrete samples recovered for this investigation (**Figure 8.3.**) are presented in **table 8.5.**

Table 8.5.: Chemical composition of the three selected pure cellular concrete samples and the average of all samples

ARM		ARM/CCC/S3	ARM/CCC/S6	ARM/CCC/S10	Average all
CaO	(wt%)	28.49	28.01	29.63	28.47
SiO_2	(wt%)	53.88	53.05	53.23	53.90
Al_2O_3	(wt%)	1.89	2.23	2.00	1.93
Fe_2O_3	(wt%)	0.69	0.74	0.66	0.68
K_2O	(wt%)	0.47	0.50	0.48	0.48
Na_2O	(wt%)	0.20	0.21	0.18	0.20
SO_3	(wt%)	2.23	2.08	2.42	2.10
MgO	(wt%)	0.33	0.33	0.36	0.36
TiO_2	(wt%)	0.08	0.09	0.07	0.08
P_2O_5	(wt%)	0.10	0.10	0.11	0.10
Cl	(wt%)	0.01	0.01	0.02	0.01
LOI 975°C (O_2)	(wt%)	11.48	12.51	10.72	11.49
C_{total}	(wt%)	0.97	1.14	0.92	1.00
S_{total}	(wt%)	0.91	0.85	0.92	0.86

As can be noticed out of **table 8.5.**, the chemical analyses of the clean cellular concrete materials (ARM/CCC) were significantly different from those originating from polluted cellular concrete (ARM/CCP) as presented in **table 8.2.** Even when comparing **figure 8.2.** with **figure 8.3.**, where both cellular material sources are expressed without L.O.I., being the way the ARM will be incorporated in the final clinker, the difference is quite clear.

Xella Burcht uses white Portland cement which is quite unique in the production process of cellular concrete. The cellular concrete blocks demolished in the Netherlands by Kok, have probably a composition based on grey Portland cement or even high blast furnace slag cement which is demonstrated by the higher level of Fe_2O_3 for grey Portland cement or the lower level of CaO (**Figures 8.2.** and **8.3.**) in the case of blast furnace slag cement compared to these of the clean cellular concrete of Xella Burcht.

Furthermore, it is quite noticeable that the ARM/CCP samples of Kok have on average, higher levels of L.O.I., SO_3 and C than the ARM/CCC samples of Xella Burcht indicating that there are some inorganic and organic contaminants of another origin than the cellular concrete itself. Mainly the high levels of SO_3, probably originating from inorganic contaminants as plaster which could cover the recycled cellular concrete blocks, will be a serious bottleneck when using real recycled or polluted cellular concrete (ARM/CCP) in Portland clinker production as already explained in **Chapter 7**. The organic contaminants as adhesives to glue cellular blocks together which are demonstrated by the increased C *[wt%]* could be critical when cellular concrete ARMs are dosed in significant amounts.

The chemical variation of the cellular concrete materials can be visualised by comparing **figures 8.2.** and **8.3**. It is clear that the ARM/CCC are chemically more stable than the ARM/CCP which is quite logic due to the fact that the ARM/CCC is generated out of production waste and ARM/CCP comes from real recycled waste. When generated out of recycling, cellular concrete could also originate from different production factories with other raw materials. The cellular concrete could also be contaminated by other construction materials when used in construction projects. The chemical instability of ARM/CCP will require a homogenisation phase before it could be used in Portland clinker production. This will consume energy and generate an extra cost. When comparing the ARM/CCC materials with CRM/Lxh/Lo and CRM/Maa/SC being the classic SiO_2-sources of CBR Lixhe (**Table 3.4.**) and ENCI Maastricht **(Table 3.5.**), it is clear that the ARM/CCC (**Table 8.5.**) are significantly lower in SiO_2 *[wt%]* and higher in CaO *[wt%]* taking in account the L.O.I. *[wt%]* of the CRMs. This explains the different alternative CCM compositions mentioned in **paragraph 8.6.1.**

TGA-analyses of the selected ARM/CCC (**Figure 8.3.**), show high levels of physically as well as chemically bound H_2O. The physically bound H_2O, which is released between 25°C and 100°C, originates from the porous structure of the cellular concrete itself generated by the high concentration of air voids. The water absorption of air-cured cellular concrete materials is visualised in **figure 8.4.**

When recycled in practice, these air voids will be filled partly with unreacted and external absorption H_2O which will need energy to evaporate. The mass loss of approximately 10 wt% between 100°C and 500°C out of the TGA-analyses of the ARM/CCC (**Figure 8.5.**), comes from the thermal decomposition of the calcium silicate hydrates **[5], [8-10]**. The TGA-analyses were corrected for the present physical bound H_2O as explained in **paragraph 3.5.2.** Furthermore a small but distinct decarbonation peak between 650 and 850°C of approximately 3 wt% was measured. Both CRM/Lxh/Lo as CRM/Maa/SC, used as classic SiO_2-source in CBR Lixhe and ENCI Maastricht, show small but quantifiable (between 1wt% and 4wt%) decarbonation mass losses between 650 and 850°C (**Figure 3.9.**). The big difference with cellular concrete materials is that the chemically bound H_2O is only marginally present for 2-3 wt% in both CRM/Lxh/Lo and CRM/Maa/SC.

The use of cellular concrete as ARM can have an influence on the decarbonation *[wt%]* of the CCM and hence CO_2 emissions of the clinker kilns when it influences the $CaCO_3$ source, which is tufa for CBR Lixhe and marl for ENCI Maastricht.

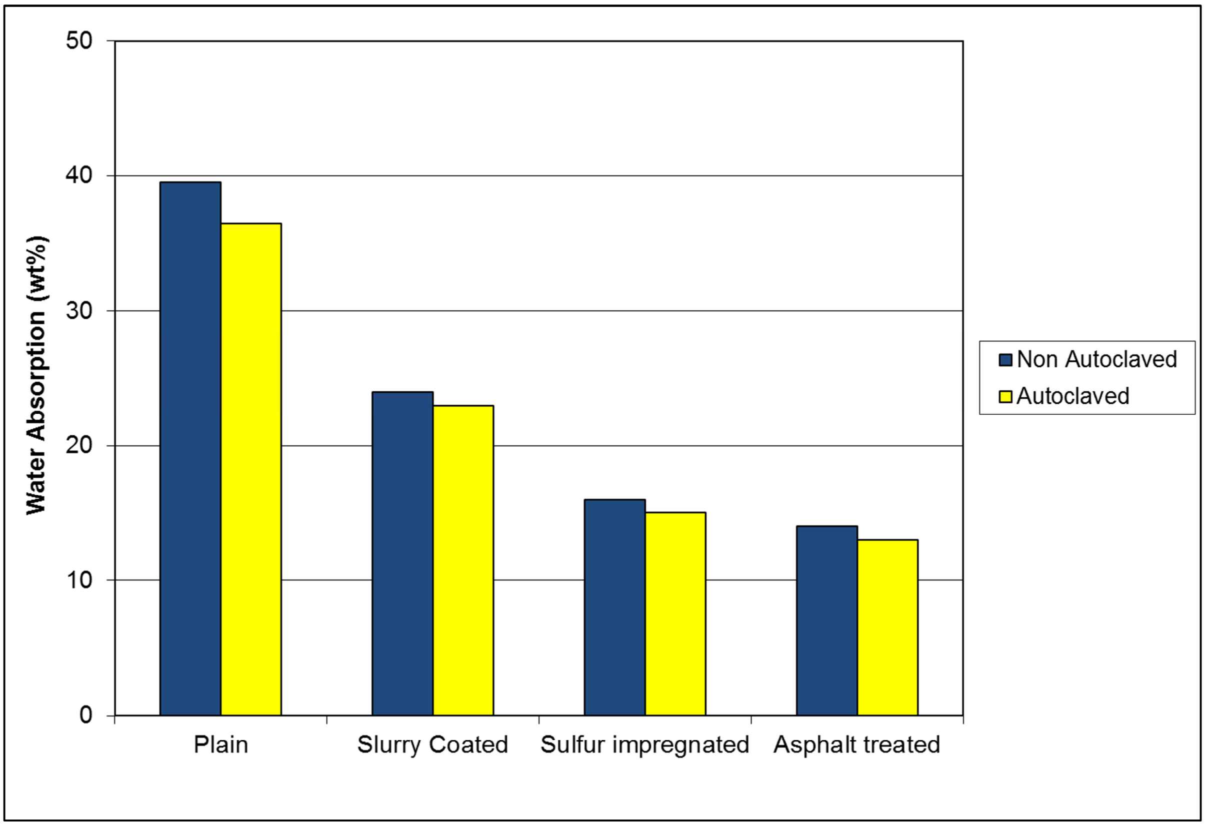

Figure 8.4.. Water absorption characteristics of lightweight concrete **[6]**

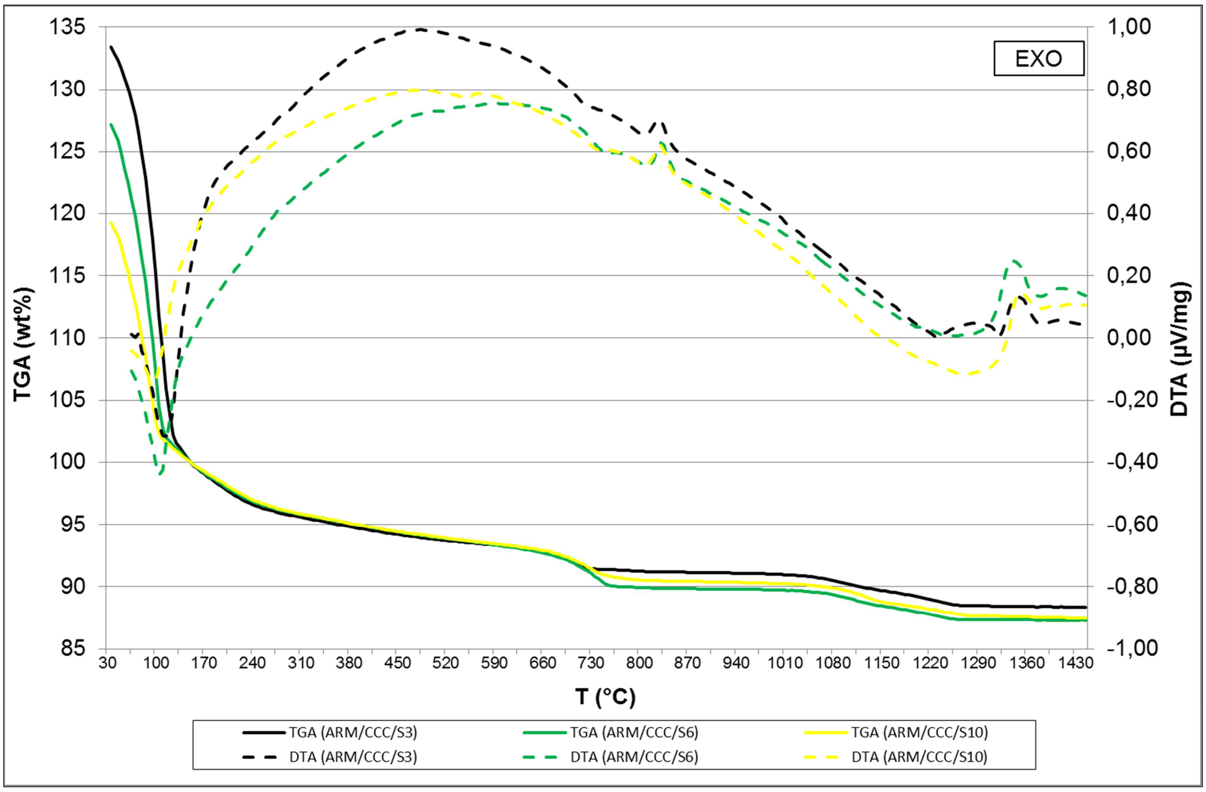

Figure 8.5.: TGA/DTA analysis of the three selected clean cellular concrete materials (ARM/CCC/S3;S6;S10)

In the case of ENCI Maastricht, the marl dosage *[wt%]* is lowered by the use of ARM/CCC/S3 in the alternative CCM (**Table 8.4**). Out of **table 8.6.**, it is clear that the decrease of marl results in a slight decrease in decarbonation.

An additional mass loss of approximately 2 wt% can be measured by the dehydration of the calcium silica hydrates as presented in **table 8.6.** which lowers by increasing grinding time (**Paragraph 8.6.1.**).

Table 8.6.: TGA/DTA evaluation of the reference and alternative Cold Clinker Meals of CBR Lixhe and ENCI Maastricht as a function of the grinding time

CCM (Grinding time)	100 – 500 °C	Inorg CO_2
	TGA Meas (wt%)	TGA Meas (wt%)
CCM/Lxh/Ref (10 min)	0.0	32.5
CCM/Lxh/CC (10 min)	2.9	32.3
CCM/Lxh/CC (20 min)	1.0	31.7
CCM/Lxh/CC (30 min)	1.2	31.6
CCM/Maa/Ref (10 min)	0.0	34.2
CCM/Maa/CC (10 min)	1.5	32.1
CCM/Maa/CC (20 min)	1.2	31.9
CCM/Maa/CC (30 min)	1.0	31.6

This means that the calcium silicate hydrates are affected by grinding and will liberate their components by grinding. The longer the alternative CCMs are ground, the lower the amount of chemically bound H_2O *[wt%]* and therefore the lower the calcium silicate hydrates content *[wt%]* will be. The endothermal dehydration of the cellular concrete ARMs will energetically be disfavoured compared to the use of the classic SiO_2-sources (CRMs) used up to day in the factories of CBR Lixhe and ENCI Maastricht. Together with the high levels of organic and inorganic contaminants measured in the ARM/CCP, cellular concrete will have some restrictions to be used as alternative raw material in Portland clinker production.

These restrictions will also be valid for most recycled concrete materials if used as ARM for Portland clinker production.

8.6.3. XRD analysis and the mineralogical influence of cold clinker meal fineness

The XRD analyses coupled with Rietveld refinement presented in **table 8.7.**, show different total mineralogical weight percentages of each mineral out of its different mineralogical structures than those calculated by simple Bogue equations based on the chemical analysis presented in **table 8.8.** of the final reference and alternative clinkers.

Although all the CCMs were designed to have DoS-factors between 80 and 120 (**Table 2.5.**), many of the final clinkers did not achieve this goal. The reason of this unbalance between alkali and SO_3 *[wt%]* is due to the different volatility of the Cl, SO_3 and alkali in the static lab furnace compared to a real clinker kiln as described in **chapter 2** and **chapter 3**.

Table 8.7.: Mineralogical analysis by XRD of the alternative final clinkers produced in a static kiln

Clinker		Cl/Lxh/CC			Cl/Maa/CC		
Grinding time		10 min	20 min	30 min	10 min	20 min	30 min
Alite (C_3S)	(wt%)	62.39	64.64	65.89	65.83	68.19	68.81
Belite (C_2S)	(wt%)	17.47	16.22	15.20	13.79	13.13	12.05
Aluminate (C_3A)	(wt%)	3.98	2.81	2.60	4.98	4.53	4.68
Ferrite (C_4AF)	(wt%)	13.59	13.85	14.12	13.24	12.97	13.21
Free Lime (CaO)	(wt%)	2.08	0.96	0.67	1.53	0.76	0.74
Periclase (MgO)	(wt%)	0.15	0.11	0.05	0.31	0.24	0.36
Arcanite (K_2SO_4)	(wt%)	-	-	-	-	-	0.05
Aphthitalite	(wt%)	0.09	-	-	0.12	0.09	0.02

(Full XRD analysis of Cl/Maa/CC in Figure A.5. (Appendix A))

Table 8.8.: Chemical analysis and Bogue calculations of the Final Clinkers
of CBR Lixhe and ENCI Maastricht made in a static kiln

Clinker		Cl/Lxh/Ref	Cl/Lxh/CC	Cl/Maa/Ref	Cl/Maa/CC
Grinding time		10 min	10 min	10 min	10 min
CaO	(wt%)	66.28	67.09	66.18	67.10
SiO_2	(wt%)	21.93	21.59	21.39	21.68
Al_2O_3	(wt%)	4.40	4.29	4.54	4.38
Fe_2O_3	(wt%)	4.21	4.00	3.98	3.87
K_2O	(wt%)	0.21	0.20	0.33	0.22
Na_2O	(wt%)	0.20	0.20	0.21	0.21
SO_3	(wt%)	0.12	0.25	0.36	0.18
MgO	(wt%)	1.28	1.28	1.52	1.32
TiO_2	(wt%)	0.30	0.28	0.30	0.26
P_2O_5	(wt%)	0.24	0.25	0.17	0.17
Cl	(wt%)	n.a.	n.a.	-	n.a.
LOI 975°C (O_2)	(wt%)	0.39	0.17	0.48	0.20
DoS-factor		27.47	58.36	65.24	39.28
Alite (C_3S)		67.52	74.45	70.61	73.38
Belite (C_2S)		11.95	5.75	8.07	6.81
Aluminate (C_3A)		4.54	4.60	5.30	5.06
Ferrite (C_4AF)		12.81	12.17	12.11	11.78

This could generate a small difference between the simple Bogue calculation and the XRD analyses although a difference of 1-2 wt% could be interpreted to be within the error range (**Section 3.10.**). Nevertheless, evaluation between XRD analyses of the clinkers made out of the same alternative CCM with different grinding times could still objectively be done by comparing them to the corresponding Bogue equation.

At first sight, as presented in **figure 8.6** to **figure 8.8.** for the residue on 90 µm, 63 µm and 45 µm sieves, the grindability of CCM/Lxh/CC and CCM/Maa/CC is clearly worse than that of

CCM/Lxh/Ref and CCM/Maa/Ref. The residue on the 200 µm sieve was unnecessary to present because 0 wt% was retained after a grinding time of only 5 min.

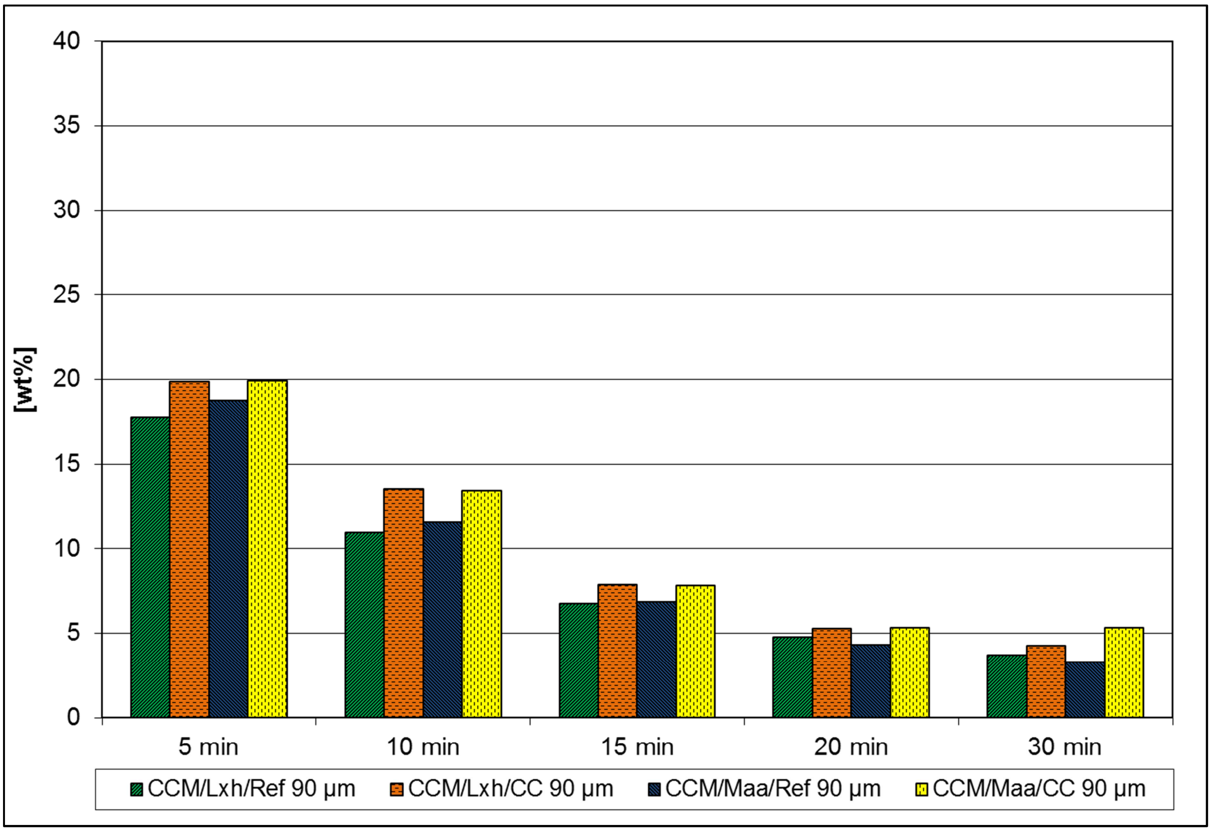

Figure 8.6.: Residue on the sieve of 90 µm for all CCMs after 5, 10, 15, 20 minutes grinding time

Out of **table 8.7.**, it is clear that the burnability of these two alternative CCMs after 10 minutes grinding, is quite insufficient demonstrated by the free CaO *[wt%]* of 2.08 wt% for Cl/Lxh/CC and 1.53 wt% for Cl/Maa/CC compared to 0.23 wt% and 0.35 wt% for the reference clinkers. This results in too low alite *[wt%]* for the alternative clinkers. On the other hand, if the residue on the 90 µm sieve has to be less than 12 wt% as stated by N.S. Gosh **[21]**, both alternative CCMs do not achieve this goal. If the grinding time for the alternative CCMs is increased to 20 minutes, the burnability becomes acceptable with free CaO *[wt%]* of 0.96 wt% for Cl/Lxh/CC and 0.76 wt% for Cl/Maa/CC, which is however still higher than for the reference clinkers. This was not improved after 30 minutes of grinding time although residues on the 90 µm sieve (**Figure 8.6.**) and on the 63 µm sieve (**Figure 8.7.**) were further lowered.

Based on **table 2.7.**, sufficient fineness should be attaint after 10 minutes grinding for all CCMs. However, this is not supported by the measured mineralogy of the alternative clinkers generated out of CCM/Lxh/CC and CCM/Maa/CC. The reason for this deviation can be explained by comparing the residue on the 90 µm sieve and the 45 µm sieve of the two individual Classic Raw Materials (CRMs) that are used as SiO_2-source, CRM/Lxh/Lo (CBR Lixhe) and CRM/Maa/SC (ENCI Maastricht) and the alternative raw material (ARM) or cellular concrete material ARM/CCC/S3 (**Figures 8.9.** and **8.10.**). Both figures have a comparable trend. As explained in **paragraph 4.1.** and presented in **table**

8.4., both CRMs are replaced by the ARM in the alternative CCMs. As already discussed in **paragraph 2.8.**, the fineness of the SiO_2-source is directly related to the burnability of the CCM.

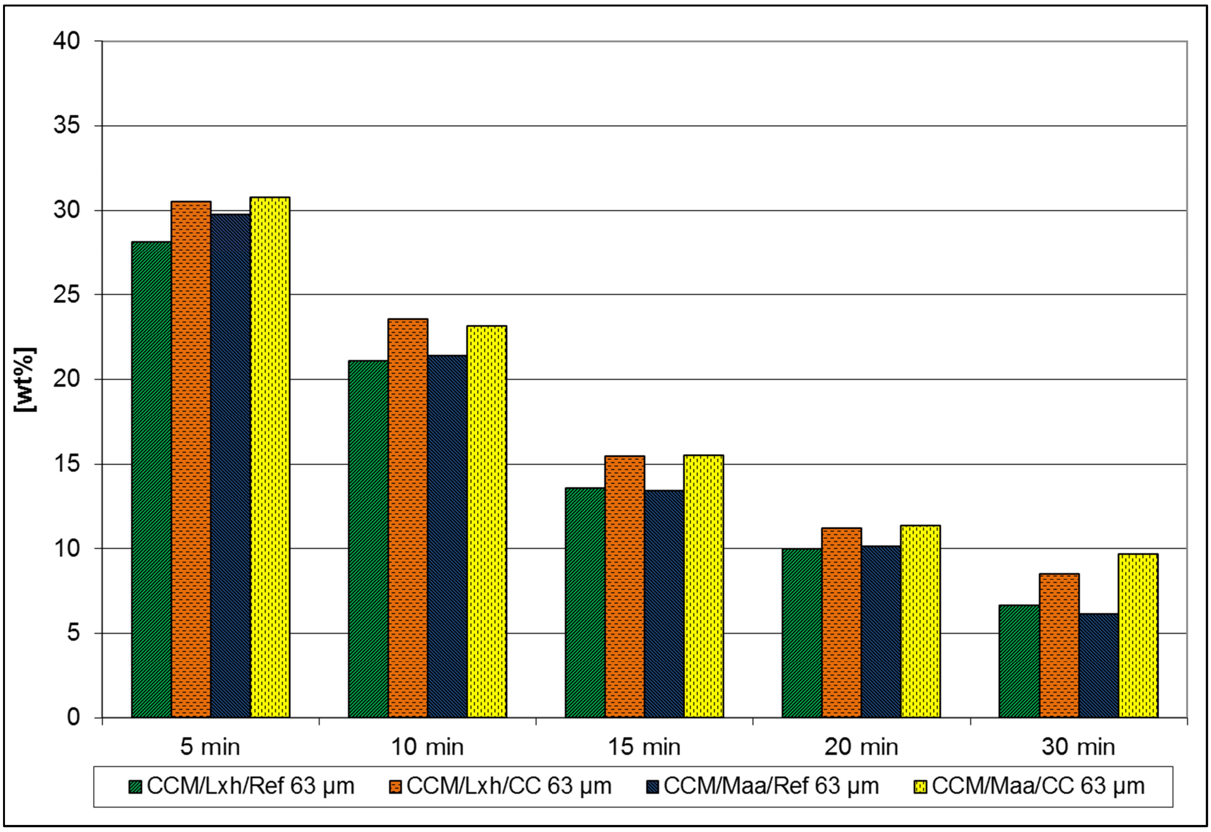

Figure 8.7.: Residue on the sieve of 63 µm for all CCMs after 5, 10, 15, 20 minutes grinding time

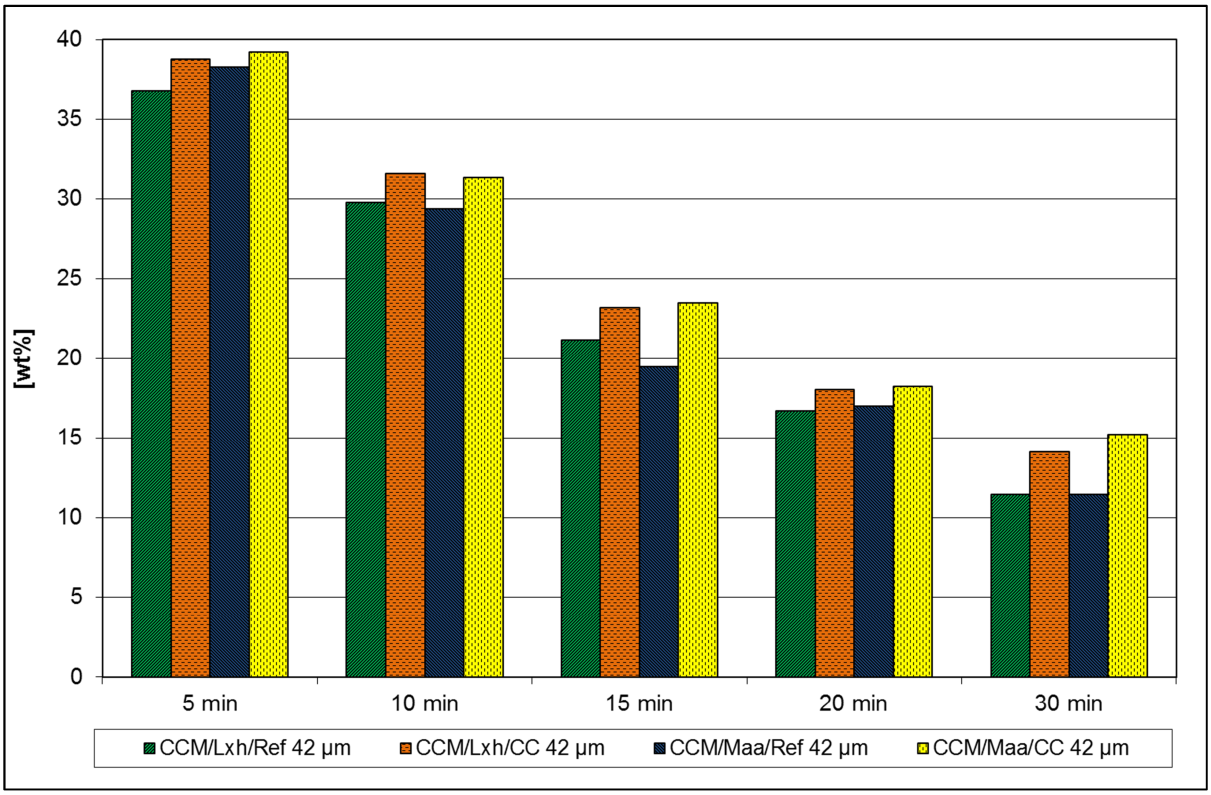

Figure 8.8.: Residue on the sieve of 45 µm for all CCMs after 5, 10, 15, 20 minutes grinding time

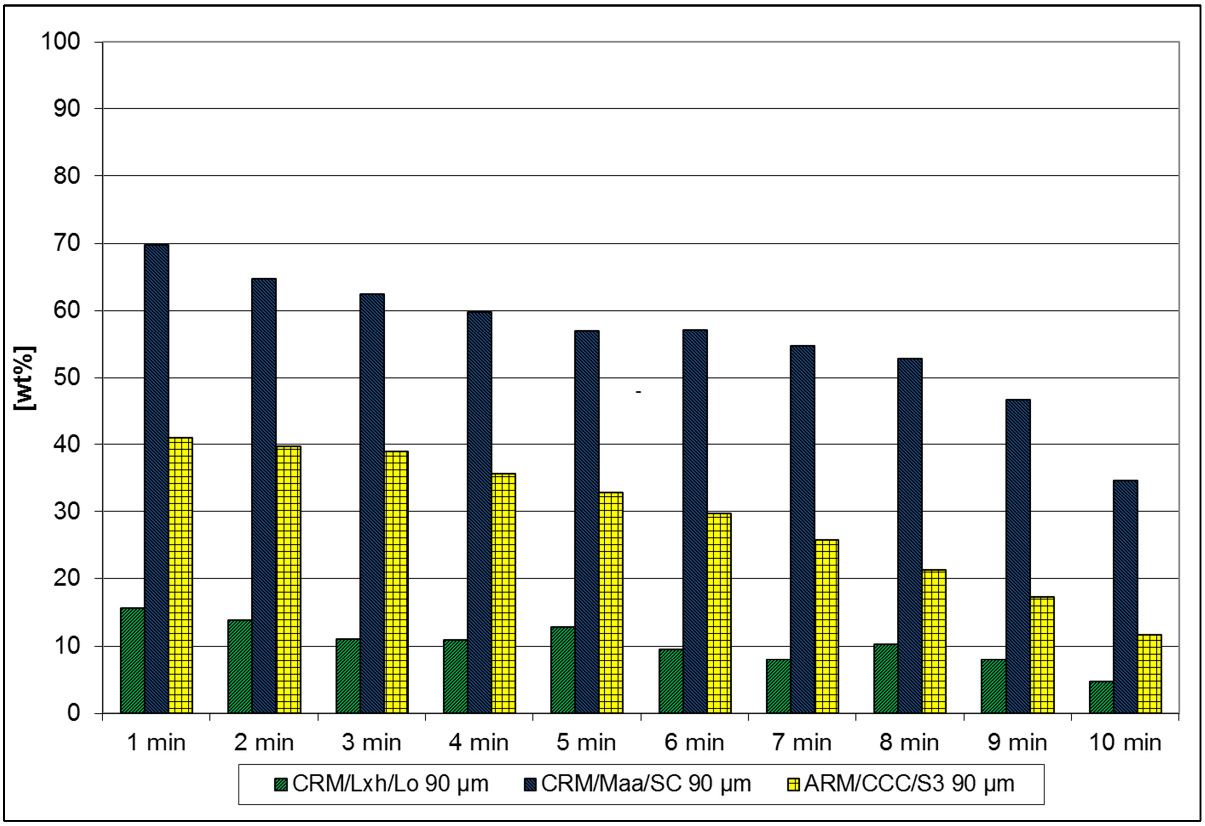

Figure 8.9.: Residue on the sieve of 90 µm for classic SiO_2-sources and cellular concrete material after 1-10 minutes grinding time

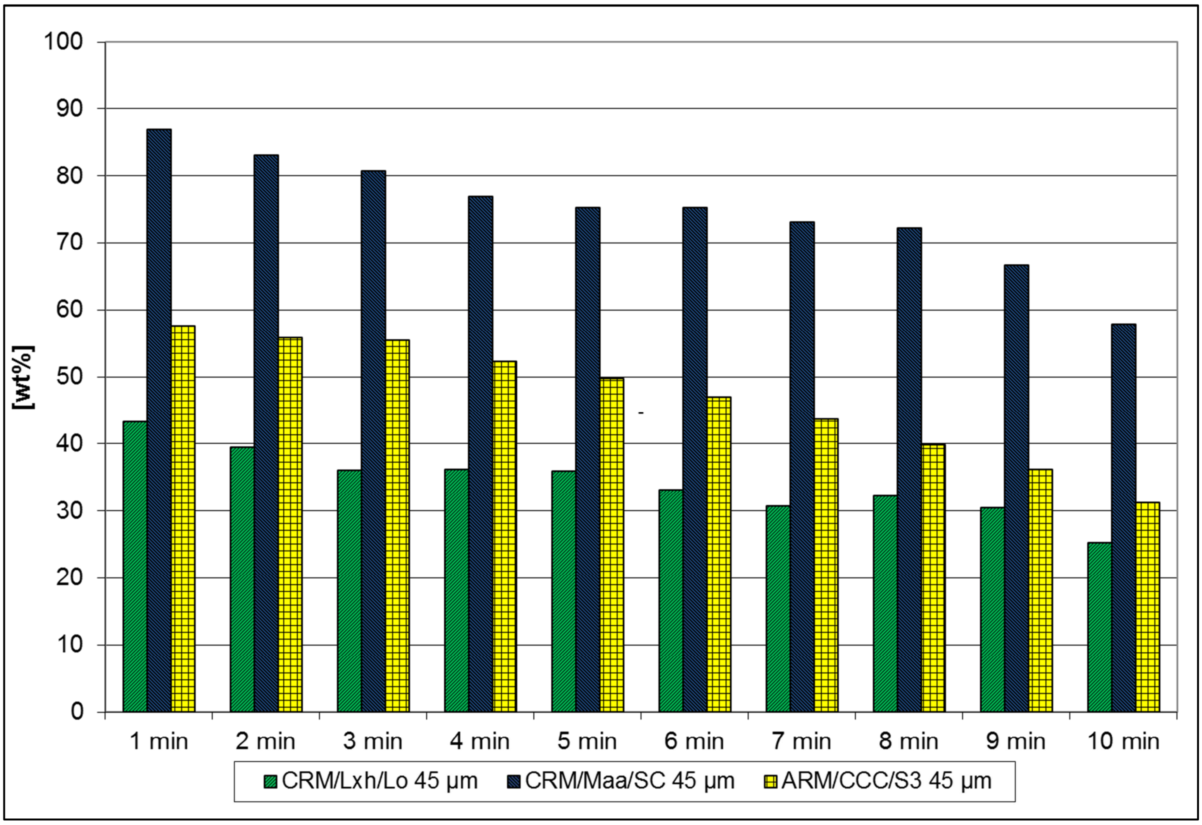

Figure 8.10.: Residue on the sieve of 45 µm for classic SiO_2-sources and cellular concrete material after 1-10 minutes grinding time

CRM/Lxh/Lo is quite easy to grind compared to ARM/CCC/S3 and CRM/Maa/SC which explains the better grindability of CCM/Lxh/Ref compared to CCM/Lxh/CC. The grindability of CRM/Maa/SC is worse than this of ARM/CCC/S3 but on the other hand delivers more SiO_2 to the CCM. This results in the fact that ARM/CCC/S3 has to be dosed almost four times as much in CCM/Maa/CC than CRM/Maa/SC in CCM/Maa/Ref. Therefore the poor grindability of CRM/Maa/SC does not result in a reduced grindability of the CCM/Maa/Ref compared to CCM/Maa/CC, even at the contrary due to the lower dosage *[wt%]*.

The poor grindability of ARM/CCC/S3 as a function of its SiO_2 *[wt%]* can be explained out of **table 8.1.** The ground sand and the very fine quartz form together with the cement and the lime after autoclaving, tobermorite compounds of calcium silicate hydrates. Tobermorite compounds are quite easy to grind (Mohs 2,5) but on the other hand, quartz particles are more difficult to grind (Mohs 7).

The quartz particles coming from the fine quartz have a very high fineness of 6500 cm²/g, more than sufficient for ideal sintering conditions for Portland clinker production. The ground sand has a much lower fineness with a 15-25 wt% residue on 90 µm. Unground residues *[wt%]* bigger than 90 µm (**Figure 8.9.**) will be delivered by the tobermorite compounds, coming from the autoclaving process and the re-entered autoclaved and non-autoclaved recovered cellular concrete materials (**Table 8.1.**). Also non combined quartz sand particles will deliver partly residues bigger than 90 µm. During grinding, the calcium silicate hydrates will increasingly disconnect their components by increasing grinding time as explained in **paragraph 8.6.2.**, liberating part of the fine and coarse quartz particles. The coarse quartz particles coming from the ground sand (**Table 8.1.**), have to be further ground to attain the necessary fineness. It can be concluded, that the grindability of ARM/CCC/S3 will be a combination of the grindability of the tobermorite compounds and the grindability of the coarser quartz particles. As already mentioned, tobermorite is much easier to grind compared to quartz. The fact that tobermorite compounds are still present even after 30 min of grinding (**Table 8.6.**), is related to cushioning and agglomeration effects.

As explained by E. Fundal and N.H. Christensen **[20]**, **[22-23]**, quartz particles bigger than 45 µm will have a major influence on the burnability of the CCM which explains why the alternative CCMs even after 20 and 30 minutes grinding time have an improved but relatively high free CaO *[wt%]*. Nevertheless, no quartz crystals were found in the XRD spectra of the alternative final clinkers.

It can be stated that monitoring CCM fineness by residues only on 90 µm and 211 µm (**Table 2.7.**) is not sufficient to guarantee good burnability when using ARMs with poor grindability as a function of their SiO_2 *[wt%]* which replaces CRMs as SiO_2-source in Portland clinker production. In the case of other ARMs in which also calcium silicate hydrates are present as for example fibrecement materials **(Chapter 7)**, the reduced grindability was not seen because the quartz particles originated from cementitious materials which have already sufficient fineness (4000 cm²/g). Nevertheless, the demonstrated bottleneck with the quartz grindability will be valid for all ARMs composed out of high levels of coarse quartz sand as most recycled concrete materials.

8.7. Ecological benefit

The use of cellular concrete as ARM for Portland clinker production could have minor ecological advantages. These could be quantified in a LCA-study if sufficient data could be collected about the collection and preparation phase, transport and the evaluation of the impact on a real Portland clinker process based on the findings of this study. In this context, the preparation of the CCM by a ball mill (**Section 2.3.2.**) has to be investigated as well as the fitness of the fineness process parameters.

As could be noticed in the earlier sections, the target values for particle size distribution of the three reference kilns for their CCM presented in **table 2.6.**, are not sufficient to guarantee optimal burnability and therefore also optimal clinker reactivity when coarse quartz particles are introduced in the CCM. Therefore the impact of the cellular concrete on the final quality of the Portland clinker has to be evaluated on industrial scale before a realistic LCA calculation can be performed. Nevertheless, based on the guidelines of the LCA process (**Section 4.3.**), different principles as cradle to grave, cradle to cradle, or cradle to gate, can be used to demonstrate the possible ecological benefit by using recycled cellular concrete as ARM in Portland clinker production.

- The EPD of Portland clinker (cradle to gate):

  The use of cellular concrete as ARM will reduce the required volume of limestone slightly to produce 1 ton of clinker. It will lower in bigger extend the used SiO_2-source due to its high SiO_2 *[wt%]*. This means that the influence of the EPD of both the limestone and the SiO_2-source will be smaller on the LCA of the Portland clinker production. On the other hand, the influence of the EPD of the recycled cellular concrete will have to be taken in account. Whether or not this shift in raw material use is an ecological benefit depends on the EPD of both raw materials and this of the recycled cellular concrete.

  The selective demolition, the homogenisation phase as well as the transportation of the recycled cellular concrete to the Portland clinker factory will have to be taken in account and will have an impact on its EPD. On the other hand, avoiding landfilling by demolition waste, will improve greatly the EPD of the cellular concrete ARM.

  A decrease in the limestone dosage although small, means that less $CaCO_3$ has to be decarbonated. Reduction of the inorganic CO_2, the required decarbonation energy and the CO_2 assigned to the total energy consumption will have as result that the LCA of the Portland clinker will improve. On the other hand as could be noted out of the foregoing sections, cellular concrete has some negative impacts on the Portland clinker process as well in terms of grindability of the CCM and/or burnability of the Portland clinker and the extra energy consumption compared to the replaced classic SiO_2-sources due to the endothermal liberation of the chemically bound H_2O. This means that more grinding and heating energy will be needed to produce a Portland clinker comparable to the reference. Whether or not this energy and allocated CO_2 will be bigger, smaller or comparable with the gain in decarbonation energy can only be proven by industrial practice.

Therefore it is still undecided if the use of cellular concrete as ARM for Portland clinker production will result in an improved EPD for Portland clinker.

- EPD's of the other related processes (cradle to gate):
  If the EPD of Portland clinker could be improved by the use of cellular concrete, it could also have a positive impact on the EPD of Portland cement. It could then also have a small impact on the EPD of cellular concrete itself although small, with only dosages of approximately 12 wt% (**Table 8.1.**).

- Cradle to grave / Cradle to cradle:
  When looking to Life-cycle assessment (LCA) of cellular concrete by using the different stages of its life cycle in the cradle-to-grave assessment, the end-of-life disposal step will be influenced by the recycling of cellular concrete as ARM for Portland clinker production. This means that when landfilling can be avoided resulting in a shift of cradle to grave principle towards cradle to cradle principle for LCA calculation, the LCA of cellular concrete as well as this of Portland clinker can be improved when the recycling step has a smaller impact than final disposal by landfilling or incineration. This is not so obvious because as already mentioned recycling includes transportation from the yard as well as ARM preparation which has to be compared to the transportation and preparation required for landfilling. Nevertheless, the avoidance of the impact of the landfilling on the LCA calculation will be a pure gain towards the use of cellular concrete as ARM for Portland clinker production.

Based on the results of this study and the cited influences on the LCA calculation, it is still doubtful that the use of cellular concrete as ARM for Portland clinker production will have ecological benefits. Nevertheless the use of cellular concrete is in line with the Cement Sustainability Initiative (**Section 4.2.**). Cellular concrete as ARM for Portland clinker production will have his influence on one of the five Key Performance Indicators of the Cement Sustainability Initiative: Fuels and materials use.

The raw materials use will be positively influenced by an increased alternative raw materials rate. On the other hand, the use of fuels will be influenced as a function of the specific heat consumption of clinker production (MJ/t of clinker) and it was, as already mentioned, unclear if a positive effect could be noted.

This is also the case for another Key Performance Indicator: climate change management. The climate change management will be influenced by decreased company-wide total CO_2 emissions (tons/year) and the company's gross and net CO_2 emissions per ton of cementitious product. It is very doubtful that big improvements on CO_2 emissions can be obtained based on the energy consumption and reduction in limestone as could be noted in the preceding sections.

8.8. Conclusions

As could be noted in the forgoing paragraphs, cellular concrete material could be used as an alternative first material for Portland clinker production. It was proven that it could replace inert Classic Raw Materials (CRMs) as sabulous clay or loam which are used as SiO_2-source.

On the other hand, the replacement of the CRMs by the cellular concrete ARM will not have major advantages. The physical and chemical bound H_2O, which is present at a larger extent in the cellular concrete ARM than in the CRMs, will consume more energy during evaporation. Also the presence of the quartz sand and their incorporation in calcium silicate hydrates, could act as a serious restriction by the increased required grinding efforts, compared to classic raw materials.

Although not insurmountable, the energy necessary to grind this fraction as a function of the delivered SiO_2, limits the use of recycled cellular concrete as ARM in an energetic and ecological way. Also possible contaminants as plaster, gluing mortars or organic glues and the quite big chemical variety of real recycled cellular concrete renders its use as ARM, although possible, unpractical. A positive effect on the ecological impact of Portland clinker production is that a primary natural material could be replaced by a secondary recycled material which is in line with the Cement Sustainability Initiative. Although the possible use of cellular concrete in Portland clinker production is not a success story overall, this feasibility study reveals nevertheless some of the restrictions which could be generated when using recycled concrete materials as alternative raw material for Portland clinker production.

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Chapter 9

Concrete sludge as alternative raw material for Portland clinker production

9.1. Introduction

The production and transport of ready-mixed concrete necessitates the recuperation of sludge water which is too contaminated with concrete residuals to be discharged into the sewerage. This sludge water is generated by washing of the ready-mixed concrete and the transport equipment during daily maintenance. Prior to the disposal of sludge water from the ready-mixed concrete plants, a pre-treatment in two sedimentation basins is required. The first basin receives the sludge water after which the water fraction with some limited sediment fraction is transferred to a second basin. After sedimentation, water from both basins is recycled and the sludge in the first and the second basin is removed. The water fraction according to NBN EN 1008 **[1]** can be reused in the ready-mix concrete production process, where a fraction of small sediments in the water is allowed.

Globally, the sludge is disposed as landfill which has an ecological impact as well as a financial disadvantage in terms of disposal costs as a function of its Eural-code (101314) **[2]**. The valorisation of this Sludge of Concrete Plant (SCP) is therefore a key issue in the production of ready-mixed concrete and the reason for this feasibility study. Several studies have already been performed on the recuperation of different types of sludge and sludge water in fresh concrete which demonstrated its negative impact on compressive strength and the setting time, workability and water demand **[3-8]**. This paper investigates the valorisation of the sludge fraction as alternative raw material for Portland clinker production, based on an extensive and representative collection of concrete sludge samples data. The study indeed includes a batch of eighty-seven sludge samples from the first basin that were collected over a period of two years in order to ensure a realistic evaluation. The collected samples of the dried sludge were analysed for their chemical composition and variations, and for their physical properties. These parameters are important since they influence the feasibility of using the dry sludge as Alternative Raw Material (ARM) **[9-12]**. The chemical and mineralogical composition of sludge will mainly be influenced by the used raw materials for the production of ready-mixed concrete.

9.2. Sampling

Between January and February 2011, a first batch of Sludge samples out of Concrete Plants (SCP) was collected from twenty ready-mixed concrete plants of Inter Beton (IB) (**Figure 9.1.**) belonging to the Heidelberg Benelux group. This collection was necessary to have a first idea of the chemical variation of the sludge. Out of this first batch, five ready-mixed concrete plants were selected (**Figure 9.1.)** according to their geographic position, a mutual variation in aggregates origin and the widest possible chemical variation based on the chemical analyses of the first batch of sludge samples (**Figure 9.2.**).

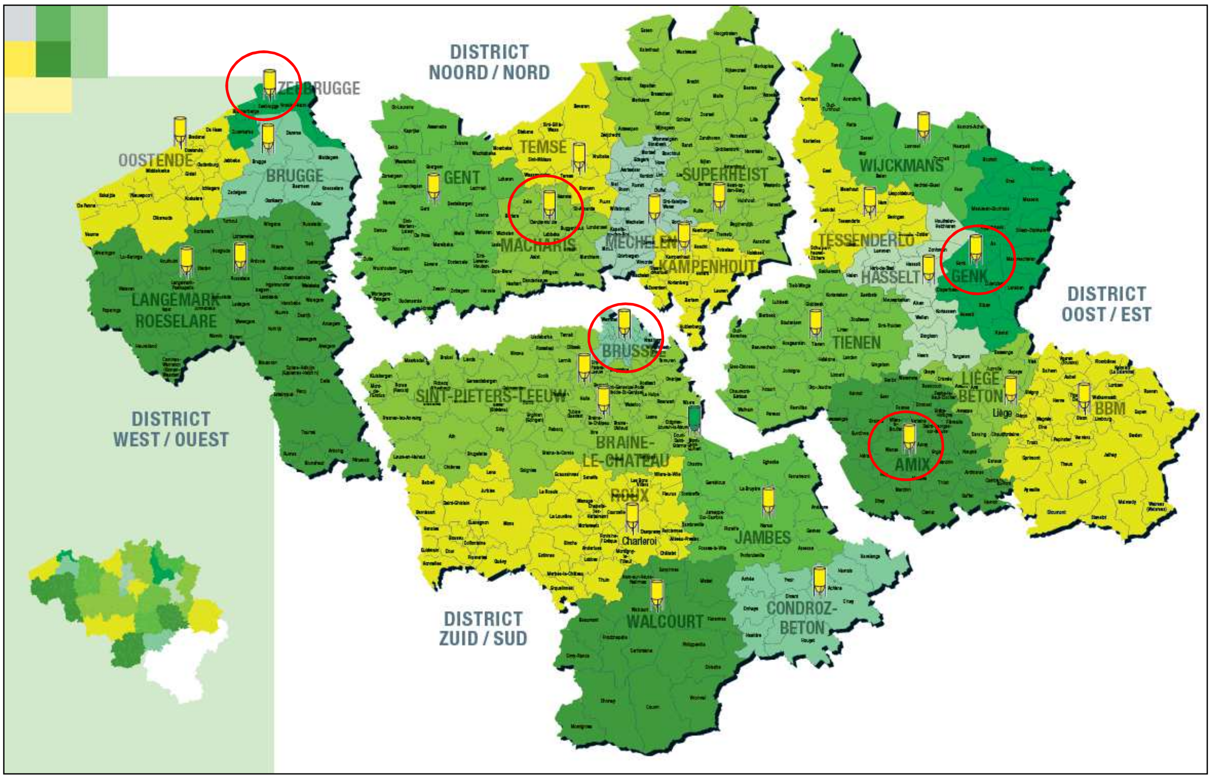

Figure 9.1. Geographical dispersion of the different concrete plants within the Inter Beton group (Ref. Heidelbergcement Benelux). Circled in red, the five selected ready-mixed concrete plants.

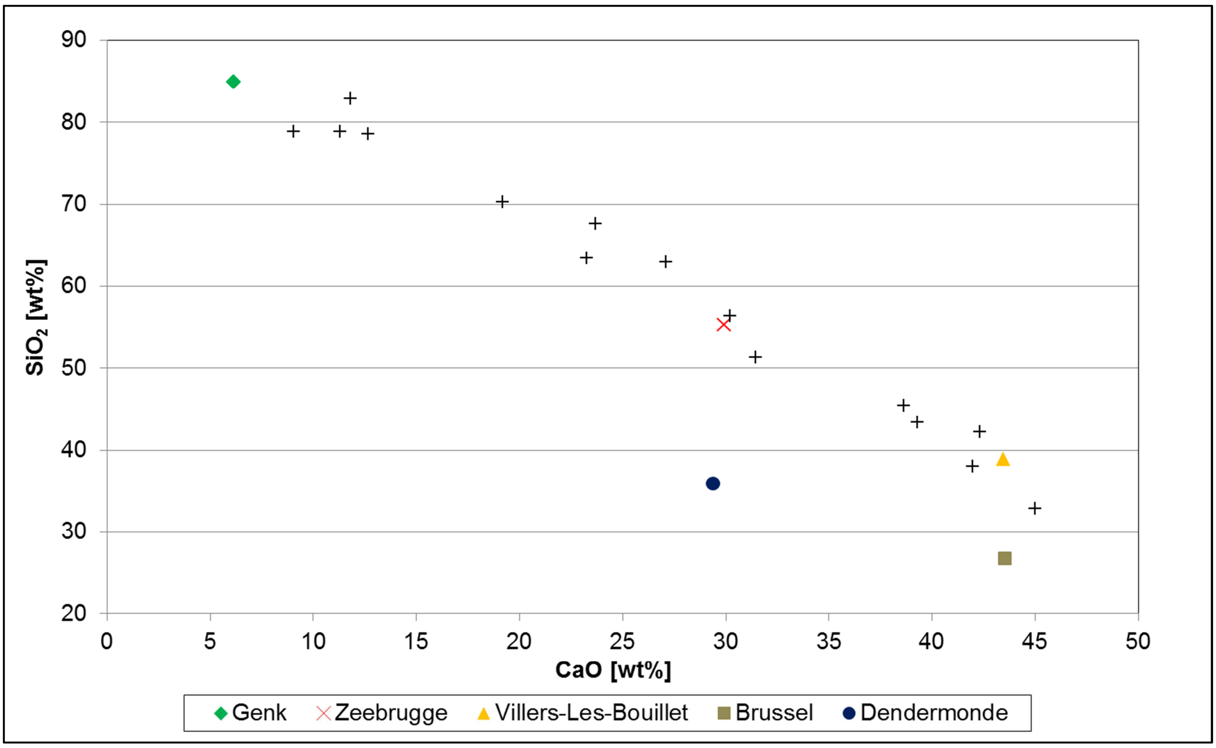

Figure 9.2. Twenty first batch sludge (SCP) samples
presented CaO *[wt%]* as a function of SiO_2 *[wt%]* without L.O.I.

IB Genk (SCP/Gk) was selected from the first batch since the sample had the lowest CaO *[wt%]* and the highest SiO_2 *[wt%]*. Additionally, its geographical position in the North-East of Belgium allows IB Genk to use partially river gravel.

IB Brussel (SCP/Bxl) was chosen because its sample out of the first batch, had the lowest SiO_2 *[wt%]* and is located in the centre of Belgium. Furthermore, IB Brussel works on a regular base with porphyry material **(Section 6.2.)**.

IB Villers-Le-Bouillet (SCP/VLB) was used as back-up for IB Brussel, because it was communicated that adaptions on the water treatment installation were planned by which sampling during a certain time was not possible. Another reason was that this plant is located in the East of Belgium and works with dolomitic limestone which is found locally in the region of Namur **(Section 6.3.)**.

IB Zeebrugge (SCP/Zb) was chosen because it was the closest to the average SiO_2 *[wt%]* in the first batch. This plant uses sea gravel for concrete production, since it is located in the west of Belgium, close to the sea.

IB Dendermonde (SCP/De) was selected because it was the newest and most modern water treatment installation within the Inter Beton group. As IB Brussel, IB Dendermonde is also located in the centre of Belgium and works with a wide variety of aggregates as porphyry, limestone and sea dredged material. It should be remarked (**Figure 9.2.)** that the sludge sample (SCP/De/S1) of IB Dendermonde was out of the linear trend constructed between CaO *[wt%]* and SiO_2 *[wt%]* by the other sludge samples.

From **figure 9.1.**, it is clear that geographically the selected ready-mixed concrete plants are nicely spread over Belgium. To create a representative batch of sludge samples, it was chosen to take a sample each month from the plants of IB Zeebrugge and IB Dendermonde. This makes it possible to investigate, if present, the influence of the seasons on the chemical composition of the sludge. The chemical composition could be altered during winter, by the increased use of Portland cement and during summer by the increased use of slag cement, which is often used in Belgium and the Netherlands. From the plants of IB Genk and IB Villers-le-Bouillet, each 3 months samples were collected. Samples from IB Brussel were collected until March 2011. Later on the water treatment installation was renewed to an installation comparable to the one in IB Dendermonde. After the installation, samples from IB Brussel were collected each month in 2012. This made a total of eighty-seven sludge samples after 2 years of sampling.

The procedure to recover the sludge material out of the basin was to shovel the concrete sludge with the bucket of a wheel loader, deposit the material on a flat floor and leave it drain. After 1h, the sample was collected in the middle of the heap and transferred to a bucket of 5L. Each month, the different sludge samples of the concrete plants were collected and shipped to the lab after which they were dried for two days at 120°C ± 1 and crushed up to ± 4mm sized particles in a jaw crusher (Retsch) to simulate a realistic crushing action. 500g were taken out of the homogenised sludge sample and further prepared for chemical analysis. The rest of the crushed material was collected to determine the particle size distribution (PSD) by a sieve tower from 63 µm up to 16 mm according to **[10]**.

Out of the eighty-seven collected concrete sludge samples, fifteen samples were selected for PSD determination. The particle size distribution of the fines fraction collected after the passing on the sieve of 250 µm was further determined by Sympatec laser diffraction. These fifteen samples were chosen by selecting objectively three sludge samples of each of the five concrete plants assuring a good representation for the whole batch of sludge samples by pursuing a good dispersion in the chemical variation (**Figure 9.3.**).

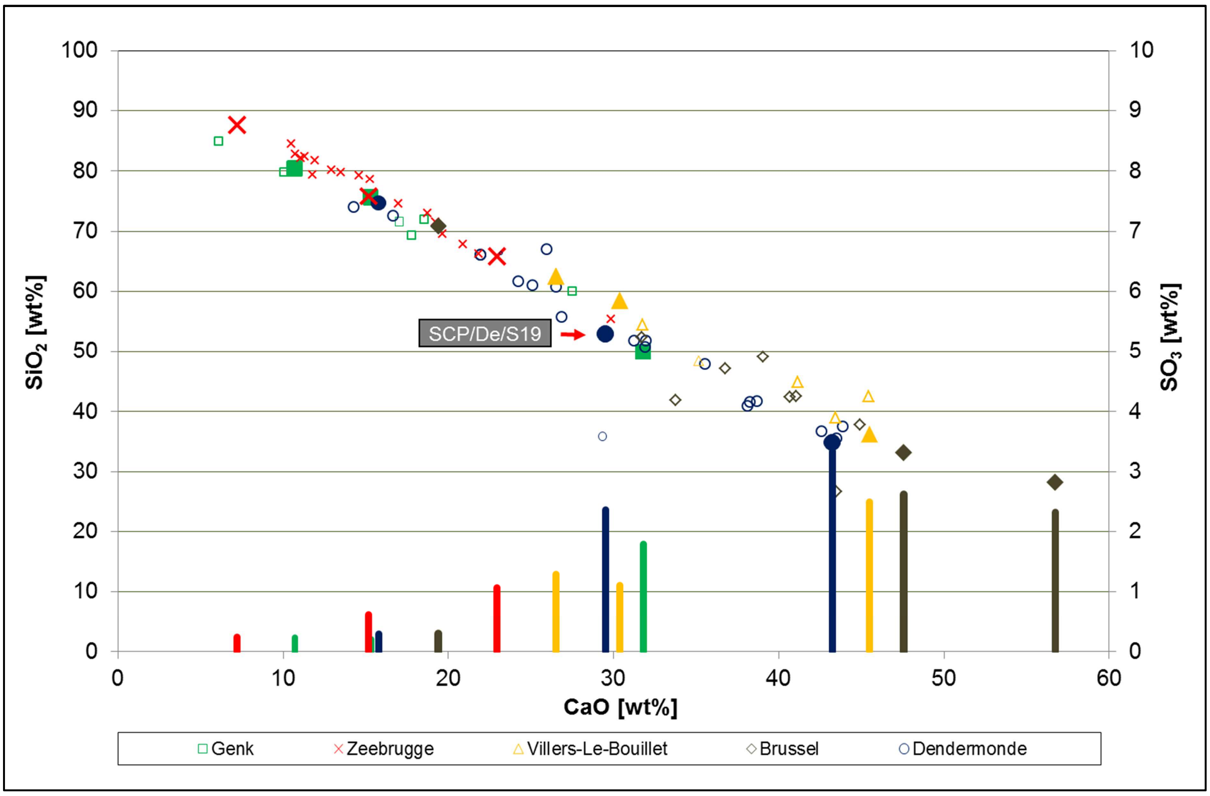

Figure 9.3: Presentation of SiO_2 *[wt%]* as a function of CaO *[wt%]* without L.O.I. for eighty-seven first and second batch sludge samples (The fifteen selected sludge samples with their corresponding SO_3 *[wt%]* are presented in bold. The selected sludge sample for numerical simulation is grey labeled)

To investigate what a separation phase could do to the sludge samples as a function of their intrinsic properties as ARM, these fifteen samples were recovered after PSD measurement in three fractions: a fines fraction smaller than 250 µm, a fraction between 250 µm and 500 µm and a fraction bigger than 500 µm. Finally, out of these fifteen selected samples, the sludge sample SLB/De/S19 was chosen as being the closest to the average SiO_2 *[wt%]* and CaO *[wt%]* (**Figure 9.3.**). SLB/De/S19 as well as its fines fraction (Fines/De/S19) was individually used to make numerical simulations as well as artificial clinkers for each clinker factory as described in **chapter 3**.

9.3. Research description

The primary objective is to investigate if concrete sludge coming from water treatment installations of ready-mixed concrete plants, is a feasible Alternative Raw Material (ARM) for Portland clinker production. This will be determined based on an objective evaluation as described in **section 3.1.**

By its extensive and representative collection of concrete sludge samples data, the big batch of concrete sludge data could also be used for other investigations. Numerical simulations are carried out based on the chemistry of a representative concrete sludge sample, before and after a specific treatment phase, together with classic raw materials of the three reference clinker factories, CBR Antoing, CBR Lixhe and ENCI Maastricht, to investigate the influence of the sludge on the clinker meal composition. Based on these simulations, experimental clinkers were produced which were fully analysed and evaluated for possible mineralogical influences.

9.4. Results and discussion

Based on the article “Feasibility study on the use of concrete sludge as alternative raw material for Portland clinker production” submitted to and already reviewed by the Journal of Materials in Civil Engineering **[13]**, the results of the research on the use of concrete sludge as ARM for Portland clinker production is described below.

9.4.1. Evaluation of the concrete sludge samples before treatment

As can be noticed out of **figure 9.2.**, the first batch of concrete sludge samples collected in the beginning of 2011 already showed a large chemical variation. The second batch of concrete sludge samples of the five selected concrete plants collected over a time period (2011-2012) of two years (**Figure 9.3.**) which gave a total of eighty-seven samples, had a chemical variation quite comparable to the first batch. This proofs that the 20 samples collected in the beginning of 2011 already gave a representative image of the chemical variation of concrete sludge samples in Belgium.

Secondly, the chemical variation, although still pronounced, improves visually out of **figure 9.3.**, if the sludge is collected for each concrete plant individually. Nevertheless, out of the calculated average, Standard deviation (Stdev) and Standard Error of the Mean (SEM) for both the CaO *[wt%]* and the SiO_2 *[wt%]*, the improvement of the chemical variation if collected by concrete plant individually is demonstrated to be rather marginal. **(Table 9.1.)**.

Table 9.1.: Statistical interpretation of the chemical variation of the concrete sludge samples

Concrete Sludge		Total	IB Brussel	IB Dendermonde	IB Genk	IB Villers-Le-Bouillet	IB Zeebrugge
Amount		72	11	23	9	8	21
Average CaO	(wt%)	26.74	39.55	30.29	17.21	37.41	16.16
Stdev CaO	(wt%)	12.13	9.57	9.06	8.22	7.42	5.55
SEM CaO	(wt%)	1.26	2.89	1.89	2.74	2.63	1.21
Average SiO_2	(wt%)	59.81	42.93	53.03	71.49	48.31	75.45
Stdev SiO_2	(wt%)	16.74	12.36	13.32	10.89	9.44	7.98
SEM SiO_2	(wt%)	1.74	3.73	2.78	3.63	3.34	1.74

There was no influence of the seasons noticed in the sludge samples of the two concrete plants where samples were collected each month: IB Dendermonde (**Figure 9.4.**) and IB Zeebrugge (**Figure 9.5.**).

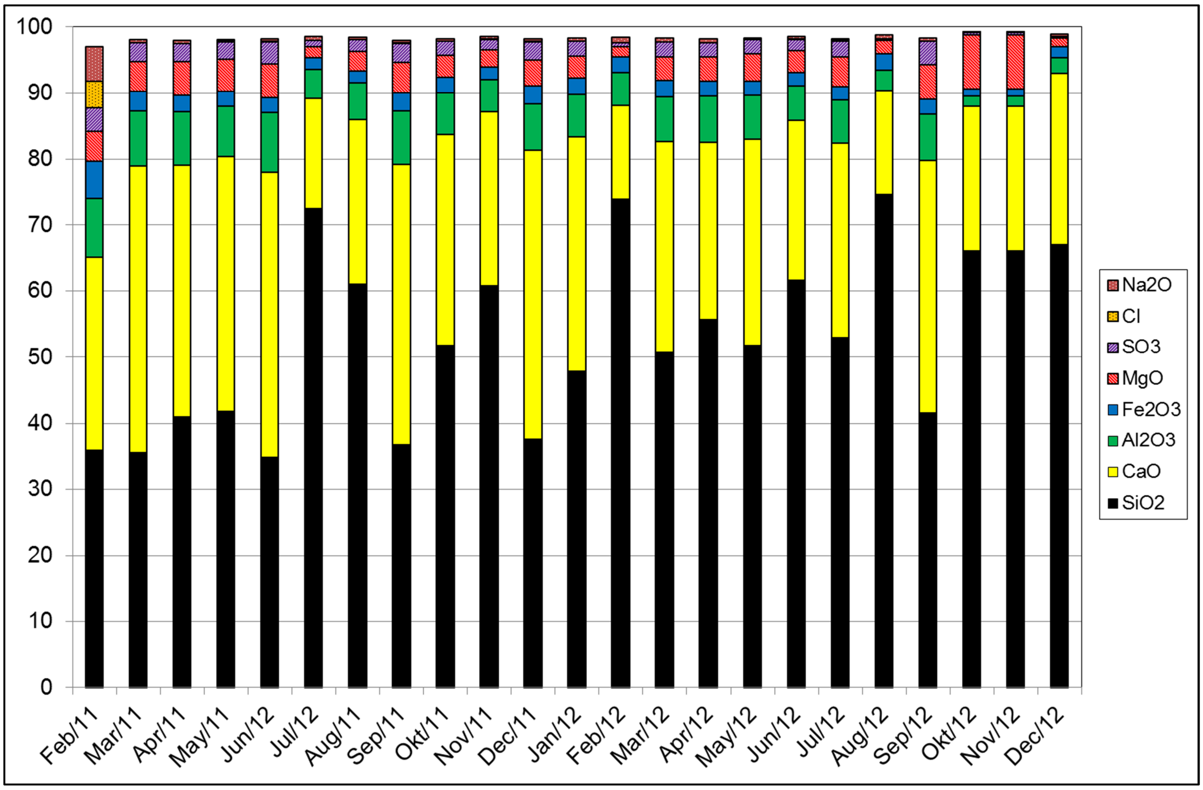

Figure 9.4.: Chemical composition without L.O.I. of the sludge samples of IB Dendermonde

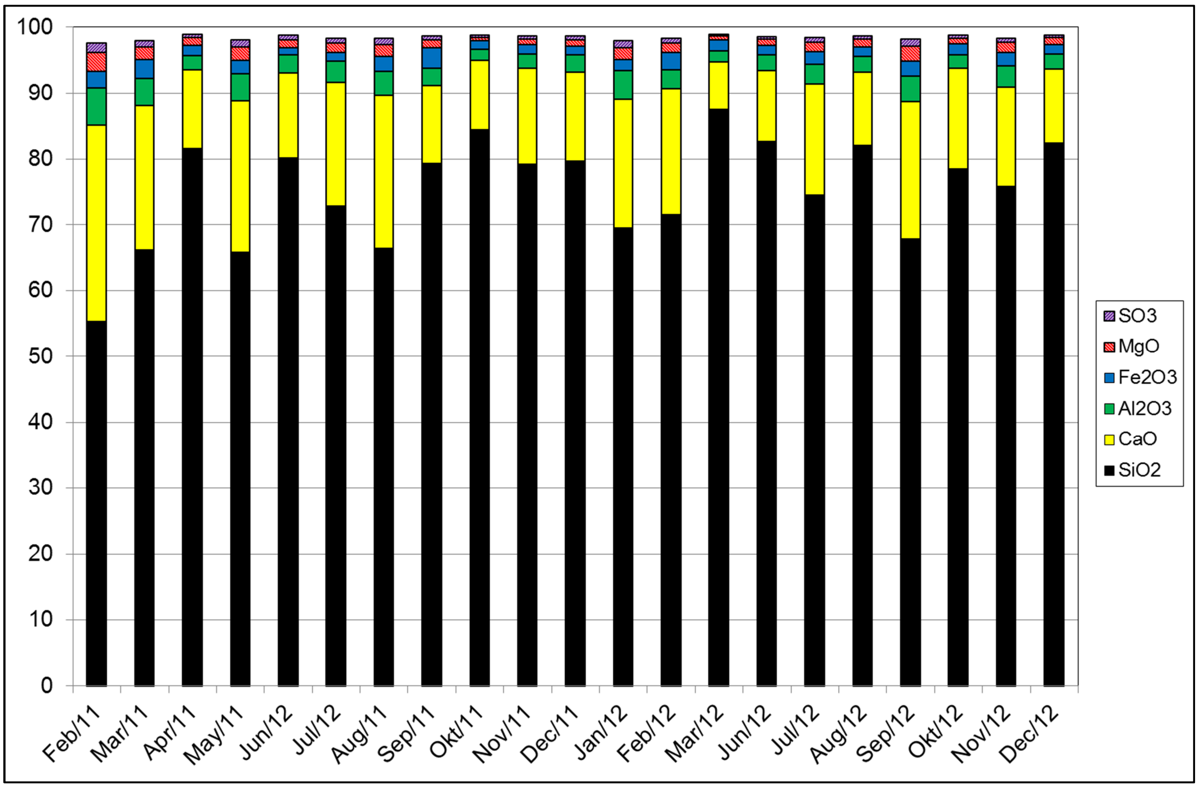

Figure 9.5.: Chemical composition without L.O.I. of the sludge samples of IB Zeebrugge

Furthermore, a strong relationship was noticed between the chemical composition of the sludge and its SO_3 *[wt%]*. The higher CaO *[wt%]* and the lower SiO_2 *[wt%]* without L.O.I. is present in the sludge, the higher the SO_3 *[wt%]* becomes as it is shown in **figure 9.3.** where the SO_3 *[wt%]* of the fifteen selected concrete samples (**Section 2.2.**) is plotted.

This relationship is also demonstrated in **figure 9.6.** where CaO *[wt%]* of all eighty-seven samples is plotted as a function of their SO_3 *[wt%]*. Although SO_3 *[wt%]* can also be present in the aggregate fraction, especially when sea gravel and sea sand is involved, the biggest part of the SO_3 in the sludge will be delivered by the cement fraction. As can be noted out of **figure 9.6.**, the SO_3 *[wt%]* in concrete sludge can go up to 3.5 wt% which indicates a high cement content and perhaps a cumulation of the water soluble SO_3.

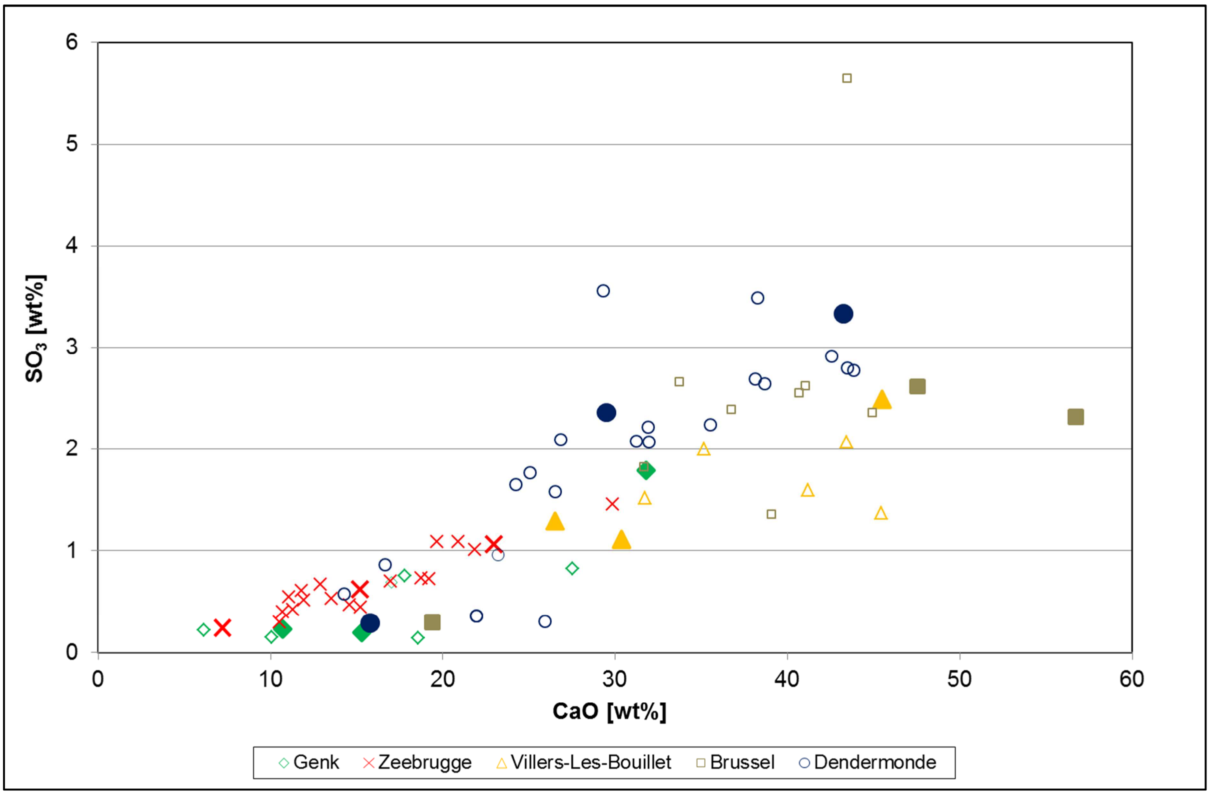

Figure 9.6.: The relationship between CaO *[wt%]* and SO_3 *[wt%]*
for the eighty-seven concrete sludge samples

Particle Size Distribution (PSD) analysis of the fifteen selected sludge samples showed also some interesting findings. The fifteen selected sludge samples have a D (upper limiting sieve size) **[10]** between 4 mm (SCP/ZB/S4) and 16 mm (SCP/Gk/S7) and have sand fractions (0/4 mm) varying from 61 wt% (SCP/Gk/S7) to 100 wt% (SCP/Gk/S2). Also the fines fraction (< 250 µm) has a big variation in this pool of fifteen samples, going from 8 (SCP/Gk/S7) to 58 wt% (SCP/Gk/S2). When focusing on the fraction smaller than 63 µm, a variation between 0 (SCP/Gk/S7) to 20 wt% (SCP/Gk/S2) is found in the fifteen sludge samples. The PSD of the three above mentioned sludge samples are visualised in **figure 9.7.**

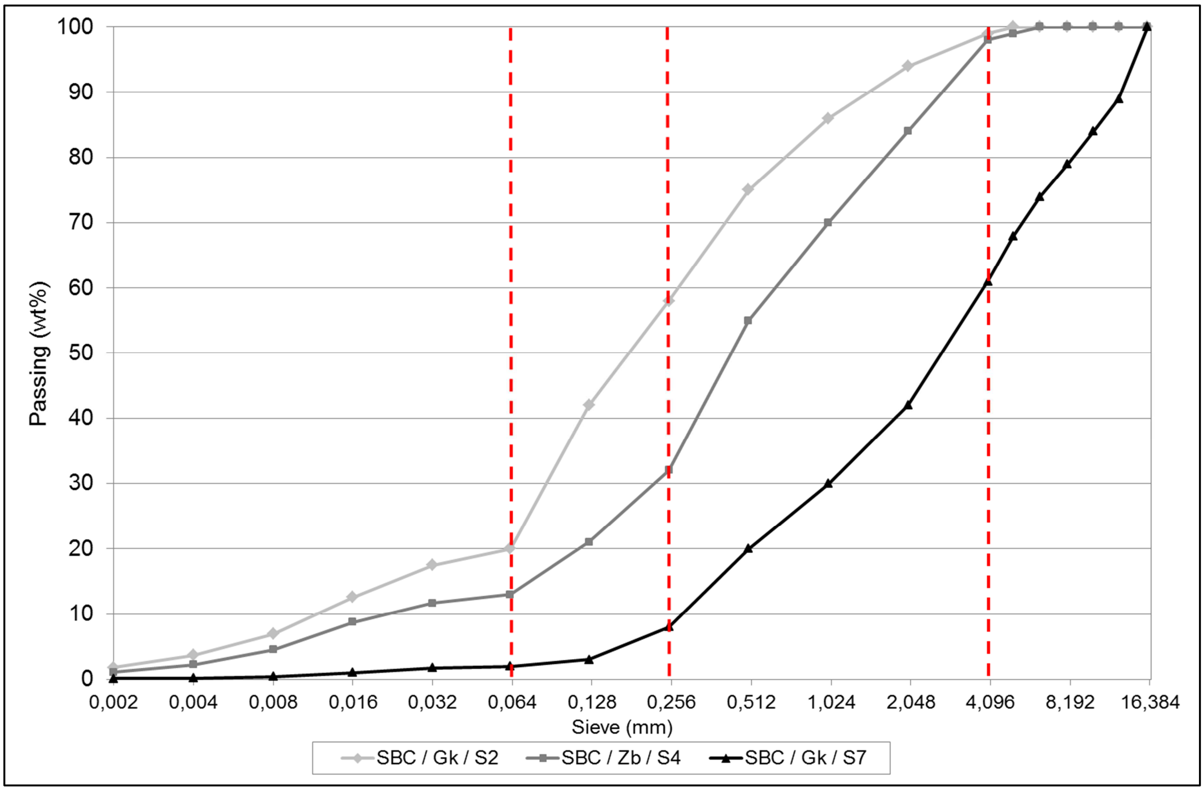

Figure 9.7.: Passings (wt%) for SCP/Gk/S2, SCP/Gk/S7, SCP/Zb/S4

TGA analyses were performed on the separation fractions (**Section 2.3.**) of five concrete sludge samples. They were selected to be closest to the average chemical composition of their proper concrete plant (**Figure 9.3.**) and already present in the collection of the fifteen selected concrete sludge samples. TGA analyses clearly show that these five concrete sludge samples (SCP/Bxl/S10, SCP/De/S19, SCP/Gk/S7, SCP/VLB/S7, SCP/Zb/S14) have mass losses by dehydration of hydration products between 125°C and 650°C and decarbonation peaks between 650°C and 900°C when heated up (**Table 9.2.**). The hydration products result from the reacted cement whereas the carbonated products probably come from limestone originating from the used cement or aggregates present in the sludge. The results of this TGA/DTA evaluation are presented in **table 9.2.**

9.4.2. Evaluation of the concrete sludge samples after a separation phase

The big chemical variation as well as the high SiO_2 *[wt%]* indicates that concrete sludge will not have a high potential as ARM for Portland clinker production if the concrete sludge cannot be altered. To investigate what the influence of a separation phase on 250 µm, shown prosperous for the fitness of fines fraction out of recycled concrete aggregates production **[14]** as ARM for Portland clinker production (**Chapter 10**)**,** could be to the fitness of concrete sludge as Alternative Raw Material (ARM), the fifteen sludge samples (**Section 2.2.**) were recovered in three fractions after the PSD determination: 0/250 µm, 250/500 µm, 0.5/8 mm.

Table 9.2.: Distribution between the different crushing and screening actions

Fractions	Distribution	SiO_2	CaO	SO_3	LOI 975°C (O_2)	125 - 900°C	125 - 650°C	650 - 900°C
μm	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
SCP/Bxl/S10	**100**	**22.14**	**44.49**	**1.82**	**21.56**	**-22.12**	**-9.15**	**-12.97**
> 500	66	15.89	46.17	1.27	*28.93*	*-24.41*	-7.46	-16.95
250 < x < 500	9	37.80	37.45	1.24	*16.55*	*-16.30*	-10.91	-5.39
< 250	25	22.41	41.34	2.40	21.91	*-18.15*	-12.96	-5.19
SCP/De/S19	**100**	**45.53**	**25.37**	**2.03**	**14.00**	**-14.34**	**-10.83**	**-3.52**
> 500	43	46.74	24.53	2.30	14.22	-11.91	-8.89	-3.02
250 < x < 500	6	73.09	11.64	1.01	7.34	-6.25	-4.55	*-1.70*
< 250	51	40.51	26.55	2.21	17.43	-17.35	-13.20	*-4.15*
SCP/Gk/S7	**100**	**67.04**	**13.57**	**0.17**	**11.27**	**-11.21**	**-2.69**	**-8.52**
> 500	80	65.73	14.55	0.13	11.82	-11.71	-1.82	-9.89
250 < x < 500	12	80.34	6.27	0.21	4.99	-3.54	-1.35	-2.19
< 250	8	53.08	17.90	1.17	13.51	-17.71	-13.37	-4.34
SCP/VLB/S7	**100**	**48.04**	**24.94**	**0.91**	**17.87**	**-17.79**	**-8.72**	**-9.07**
> 500	40	37.39	30.52	0.92	22.94	-18.37	-5.72	-12.65
250 < x < 500	16	82.77	6.59	0.21	4.88	-4.83	-1.43	-3.39
< 250	44	30.90	31.53	1.77	23.02	-21.98	-14.10	-7.89
SCP/Zb/S14	**100**	**83.12**	**6.84**	**0.23**	**5.11**	**-5.67**	**-2.85**	**-6.68**
> 500	49	71.27	13.27	0.37	9.86	-6.64	-3.94	-10.57
250 < x < 500	31	88.20	4.53	0.10	3.37	-2.28	-0.10	-2.18
< 250	20	74.25	10.62	0.53	6.49	-8.57	-4.46	-4.11

Although it was foreseen that a crushing action combined with a separation phase on 250 μm would separate the hydrated cement from the aggregate fraction as will be demonstrated in **chapter 10**, the chemical composition and chemical variation did not significantly improve for the recovered fines fraction (< 250 μm) (**Figure 9.8.**) compared to the total concrete sludge sample (**Figure 9.3.**) where the fines fraction originated from.

The fines fraction (< 250 μm) had similar chemical compositions and chemical variation and there was also a clear relationship between the chemistry (CaO and SiO_2) and SO_3 *[wt%]* (**Table 9.3.** and **Table 9.4.**) as was also demonstrated for the concrete sludge samples.

TGA analyses of the three separation fractions for the sludge samples close to the average chemical composition of their concrete plant (**Table 9.2.**) give a clear view on the composition of the three separated fractions and the sludge sample itself.

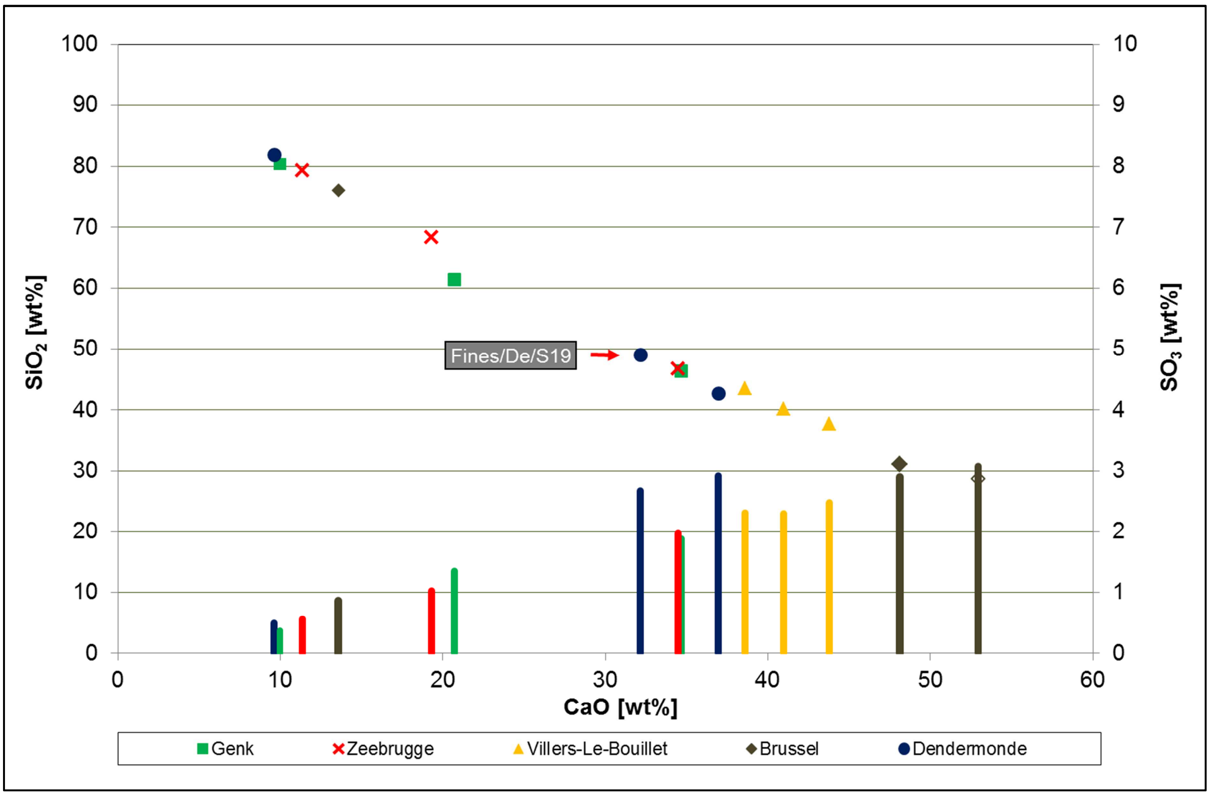

Figure 9.8.: Fines (< 250 µm) out of the fifteen sludge samples from the five selected concrete plants (The selected fines fraction for numerical simulation and artificial Portland production is grey labeled)

Table 9.3.: The average chemical composition of the three selected sludge samples of each concrete plant

ARM		**SCP/Bxl**	**SCP/De**	**SCP/Gk**	**SCP/VLB**	**SCP/Zb**
		Average	**Average**	**Average**	**Average**	**Average**
CaO	(wt%)	33.08	24.53	17.01	27.76	13.54
SiO_2	(wt%)	36.78	46.60	61.67	43.14	69.75
Al_2O_3	(wt%)	4.54	5.14	3.98	4.26	2.71
Fe_2O_3	(wt%)	1.80	1.89	2.62	1.55	1.72
K_2O	(wt%)	0.53	0.52	0.53	0.50	0.47
Na_2O	(wt%)	0.37	0.34	0.22	0.14	0.37
SO_3	(wt%)	1.39	1.64	0.65	1.32	0.57
MgO	(wt%)	2.44	3.23	2.06	2.40	1.23
TiO_2	(wt%)	0.32	0.32	0.27	0.32	0.15
P_2O_5	(wt%)	0.15	0.15	0.14	0.12	0.13
Cl	(wt%)	0.04	0.06	0.02	0.05	0.07
LOI 975°C (O_2)	(wt%)	18.25	15.24	10.59	18.15	9.10

Table 9.4.: The average chemical composition of the three selected sludge fines of each concrete plant

ARM		Fines/Bxl	Fines/De	Fines/Gk	Fines/VLB	Fines/Zb
		Average	**Average**	**Average**	**Average**	**Average**
CaO	(wt%)	30.02	21.85	18.74	31.56	18.86
SiO_2	(wt%)	38.23	50.78	55.85	31.08	58.10
Al_2O_3	(wt%)	4.91	5.12	5.13	5.48	4.70
Fe_2O_3	(wt%)	2.03	1.61	2.71	1.79	1.84
K_2O	(wt%)	0.54	0.66	0.69	0.47	0.73
Na_2O	(wt%)	0.28	0.31	0.27	0.16	0.52
SO_3	(wt%)	1.80	1.68	1.03	1.81	1.03
MgO	(wt%)	2.67	3.10	2.79	3.46	2.20
TiO_2	(wt%)	0.36	0.32	0.37	0.45	0.26
P_2O_5	(wt%)	0.20	0.16	0.17	0.15	0.17
Cl	(wt%)	0.04	0.07	0.02	0.07	0.13
LOI 975°C (O_2)	(wt%)	18.60	14.08	11.96	23.19	11.24

As expected, the fraction < 250 µm contains a lot of cement hydration products visible between 125°C and 650°C as will also be observed for recycled concrete fines (**Figure 9.9.**). More interesting was the fact that the fraction > 500 µm in each of the fifteen analysed sludge samples contained comparable Loss Of Ignition (L.O.I.) values at 975°C but that the fraction > 500 µm contains on average more $CaCO_3$ than the fraction < 250 µm which contains more cement hydration products (**Table 9.1.**). The fraction between 250 µm and 500 µm contained a low Loss Of Ignition (L.O.I.) values at 975°C.

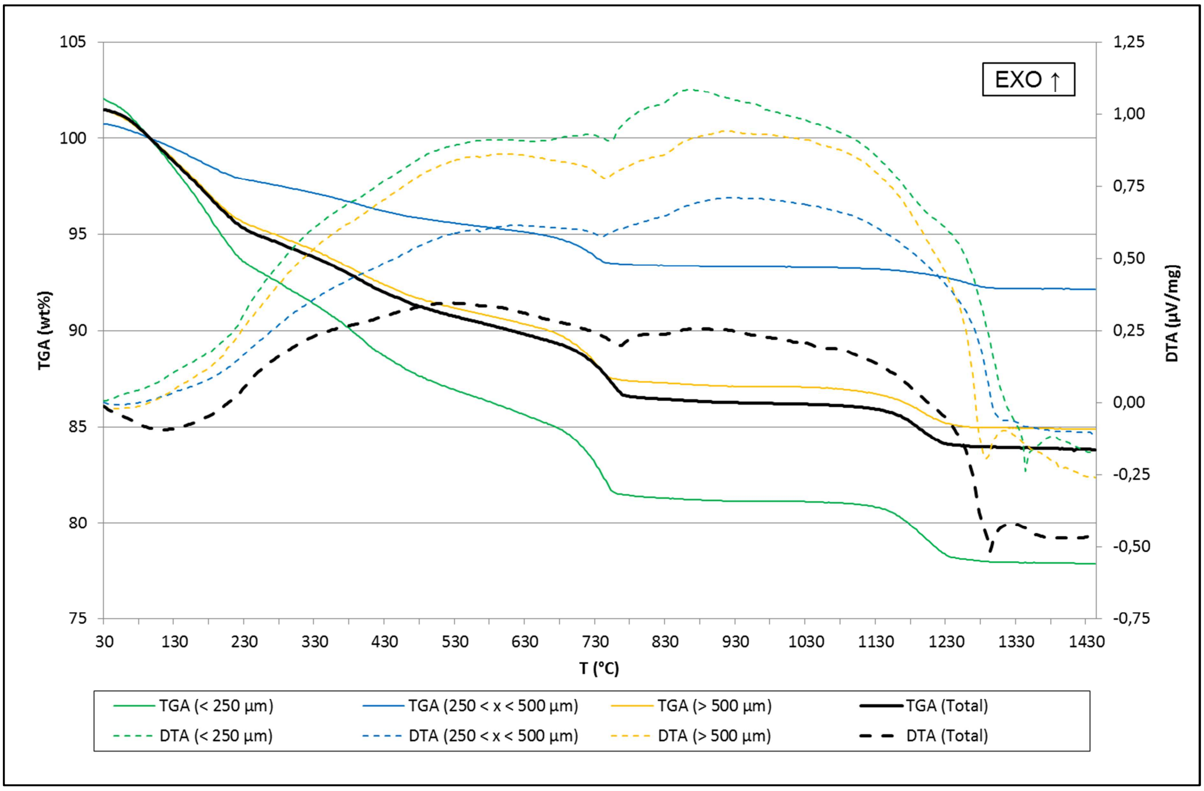

Figure 9.9.: TGA/DTA analysis of SCP/De/S19 and its three fractions after a separation phase

The same conclusions could be drawn from the chemical analysis by XRF of the three separated fractions. As demonstrated in **table 9.2.**, the fraction > 500µm and the fraction < 250 µm have comparable CaO *[wt%]* and SiO_2 *[wt%]*. The fraction between 250 and 500 µm consists out of an excess of SiO_2 *[wt%]* demonstrating the presence of quartz particles and a much lower CaO *[wt%]* and SO_3 *[wt%]* which indicates that a smaller cement fraction is present compared to the fractions > 500 µm and < 250 µm. These quartz particles have their origin out of the aggregates fraction of the concrete sludge. The slightly higher SiO_2 *[wt%]* in the fraction > 500 µm originates out of the fact that part of quartz particles present in the fraction between 250 µm and 500 µm will also be present in the fraction > 500 µm.

To demonstrate this trend in more detail, a full chemical analysis of the three fractions of the sludge sample SCP/De/S19, which was selected to make numerical simulations as well as artificial clinkers for each clinker factory (**Section 2.2.**), are presented in **table 9.5.**

Table 9.5.: The chemical composition of the three separation fractions of SCP / DE / S19

Fractions		**Fraction**	**Fraction**	**Fines / DE / S19**	**SCP / DE / S19**
µm		**> 500**	**250< x < 500**	**< 250**	**Total**
wt%		**43**	**6**	**51**	**100**
CaO	(wt%)	24.53	11.64	26.55	25.37
SiO_2	(wt%)	46.74	73.09	40.51	45.53
Al_2O_3	(wt%)	5.55	3.04	5.81	5.66
Fe_2O_3	(wt%)	1.51	0.87	1.60	1.65
K_2O	(wt%)	0.53	0.49	0.59	0.54
Na_2O	(wt%)	0.30	0.21	0.24	0.26
SO_3	(wt%)	1.97	1.01	2.21	2.03
MgO	(wt%)	3.76	1.87	4.08	3.93
TiO_2	(wt%)	0.37	0.19	0.42	0.41
P_2O_5	(wt%)	0.18	0.09	0.18	0.17
Cl	(wt%)	0.05	0.03	0.07	0.06
LOI 975°C (O_2)	(wt%)	14.22	7.34	17.43	14.00

From TGA/DTA (**Figure 9.9.**) results and XRF analyses (**Table 9.5.**), it can be concluded that the fractions < 250 µm and > 500 µm are similar in chemical composition but also in origin. Based on the TGA analysis (**Table 9.2.**), it is clear that they both consist out of comparable cement hydrates and based on the SO_3 *[wt%]* measured by the XRF analysis, they have a similar cement content. This indicates that a crushing action on 4 mm and a separation phase on a sieve of 250 µm is not sufficient to recover all the hydrated cement in the fraction < 250µm as was expected and which was demonstrated successfully to recycle fines as ARM out of recycled concrete aggregates (**Chapter 10**). An explanation can be found in the fact that the composition of sludge is not comparable with that of recycled concrete. It is composed out of the fine particles of the different raw materials (cement, sand, raw aggregates, fly ash, etc.) used to produce concrete. This explains why hydrated cement is much more present in the sludge than in the recycled concrete (**Chapter 10**).

The increased presence of hydrated cement and the lack of an aggregate structure have a negative influence on the crushing action. The fact that the cement present in the concrete sludge has reacted with an excess of water in the concrete sludge basin before it is collected, makes the cement stone in the sludge sample, when hardened, to be very weak. In that way it rather crumbles instead of breaking apart, still leaving a lot of cement stone particles in the fraction bigger than 500 µm. A smaller or a more intensive crushing action should therefore be necessary to separate the hydrated cement stone fraction from the aggregates fraction, although questions could be raised about the economic feasibility and the necessity of this intensified crushing action. One reason to strongly consider this intensified crushing action could be the grindability of the coarse quartz particles **[15-18]** present in fractions 250 µm < x < 500 µm and > 500 µm and their influence on the burnability of the clinker which was also described in **chapter 8**. This was further investigated in **sections 9.4.3.** and **9.4.4.**

9.4.3. Clinker feed calculations and preparations

Although the chemical compositions of the SCP/De/S19 and Fines/De/S19 are comparable, the possible influence on the burnability could be investigated when sintering alternative CCMs with both materials. Therefore, they were both used as ARM for clinker feed calculation and preparation. The CCMs were calculated with a simulation program (**Section 3.2.**) in line with the chemical and mineralogical requirements listed in **table 2.5.** The compositions of these alternative CCMs after simulation are presented in **table 9.6.**, the compositions of the reference CCMs in **table 3.2.**

The alternative CCMs were calculated to maximise the use of the two ARMs, SCP/De/S19 and Fines/De/S19. Because of the high SiO_2 *[wt%]* in both ARMs, it was expected that they would act as SiO_2-source in the CCM replacing loam or sabulous clay as classic raw materials in the case of CBR Lixhe and ENCI Maastricht (**Tables 3.4.** and **3.5.**). Fines/De/S19 completely replaced the classic SiO_2-source in CCM/Lxh/Fines and CCM/Maa/Fines. The maximisation of SCP/De/S19 was limited by the required CaO *[wt%]* defined by the LSF and LiqSimple of both kilns and therefore only partly replaced the complete SiO_2-source. Because the SiO_2 *[wt%]* of the ARM is lower than those present in the classic SiO_2 sources (**Table 3.4.** and **Table 3.5.**), higher volumes of the ARMs have to be dosed to attain the required SiO_2 *[wt%]*. To compensate these higher volumes, limestone dosages will be decreased. Because less limestone is dosed, CaO *[wt%]* in the CCMs have to be compensated by the CaO *[wt%]* present in the ARMs.

In the case of SCP/De/S19, the available CaO *[wt%]* was not sufficient to allow the complete replacement of the SiO_2-source of CBR Lixhe and ENCI Maastricht. In the case of CBR Antoing, the influence on CaO *[wt%]* acted as limitation in both alternative CCMs (ARM/Ant/SCP and ARM/Ant/Fines).

Table 9.6.: Compositions of the different clinker meals made to be fed to the static kiln

	CRM+ARM	Quantity (wt%)		CRM+ARM	Quantity (wt%)
CCM/Ant/SCP	CRM/Ant/CP	32.76	CCM/Ant/Fines	CRM/Ant/CP	5.91
	CRM/Ant/CR	54.71		CRM/Ant/CR	70.46
	CRM/Ant/FA	6.74		CRM/Ant/FA	6.36
	CRM/Ant/IC	0.91		CRM/Ant/IC	0.97
	SCP/De/S19	4.87		SCP/De/S19	0.00
	Fines/De/S19	0.00		Fines/De/S19	16.30
	Sum	100.00		Sum	100.00
CCM/Lxh/SCP	CRM/Lxh/Tu	75.20	CCM/Lxh/Fines	CRM/Lxh/Tu	75.31
	CRM/Lxh/Lo	2.01		CRM/Lxh/Lo	0.00
	CRM/Lxh/FA	11.36		CRM/Lxh/FA	12.78
	CRM/Lxh/IC	1.80		CRM/Lxh/IC	1.54
	SCP/De/S19	9.64		SCP/De/S19	0.00
	Fines/De/S19	0.00		Fines/De/S19	10.37
	Sum	100.00		Sum	100.00
CCM/Maa/SCP	CRM/Maa/Ma	77.14	CCM/Maa/Fines	CRM/Maa/Ma	76.32
	CRM/Maa/SC	1.62		CRM/Maa/SC	0.00
	CRM/Maa/FA	8.61		CRM/Maa/FA	10.31
	CRM/Maa/IC	1.68		CRM/Maa/IC	1.56
	SCP/De/S19	10.94		SCP/De/S19	0.00
	Fines/De/S19	0.00		Fines/De/S19	11.80
	Sum	100.00		Sum	100.00

Maximisation of the two different ARM materials is different than for the two foregoing factories due to the fact that CBR Antoing does not use a real SiO_2-source. The necessary SiO_2 is delivered by its two limestone sources especially the poor limestone (CRM/Ant/CP) (**Table 3.3.**). Fines/De/S19, due to their higher CaO *[wt%]* and lower SiO_2 *[wt%]*, can be dosed in higher quantities compared to SCP/De/S19.

Summarised, the sludge sample or its corresponding fines fraction with the highest SiO_2 *[wt%]* will be dosed the least. The CCMs were prepared and sintered as described in **section 2.3.** The physical and chemical analysis of these CCMs as well as the chemical and mineralogical analysis of the final clinkers will be discussed in the **section 4.4.**

9.4.4. Evaluation of the artificial produced Portland clinkers

As already remarked in **section 4.3.** and presented in **table 9.6.**, limestone CRM dosages were decreased by maximising the two ARMs, SCP/De/S19 and Fines/De/S19 in the alternative CCMs of Antoing, Lixhe and Maastricht. Therefore, a decrease in decarbonation of $CaCO_3$ was expected, although the different ARMs also bring carbonated material into the alternative CCMs.

Evaluation of the TGA analysis of the alternative CCMs are presented in **table 9.7.** and visualised in

figures 9.10. and **9.11.** They show small but quantifiable decreases in decarbonation mass loss between the reference and alternative CCMs. This is quite logical because, although the different ARMs by their aggregates fraction also bring carbonated material into the alternative CCMs, the decreased limestone CRM dosages have a much bigger impact on the decarbonation mass loss of the final alternative CCM.

Table 9.7.: TGA/DTA evaluation of the Reference and alternative Cold Clinker Meals of CBR Antoing, CBR Lixhe and ENCI Maastricht

CCM	Inorg CO_2	$CaCO_3$	Decarb E $CaCO_3$	Decarb E $CaCO_3$ Der
Mat	TGA Meas (wt%)	TGA Der (wt%)	µVs/mg Mat DTA	J/g Mat TGA
CCM/Ant/Ref	34.0	77.3	213.4	1378
CCM/Ant/SCP	33.0	75.0	172.2	1337
CCM/Ant/Fines	30.4	69.1	140.3	1232
CCM/Lxh/Ref	32.5	73.9	189.3	1318
CCM/Lxh/SCP	31.7	72.1	176.4	1285
CCM/Lxh/Fines	31.6	71.8	161.9	1281
CCM/Maa/Ref	34.2	77.7	219.3	1385
CCM/Maa/SCP	32.6	74.1	181.6	1321
CCM/Maa/Fines	31.8	72.3	171.1	1289

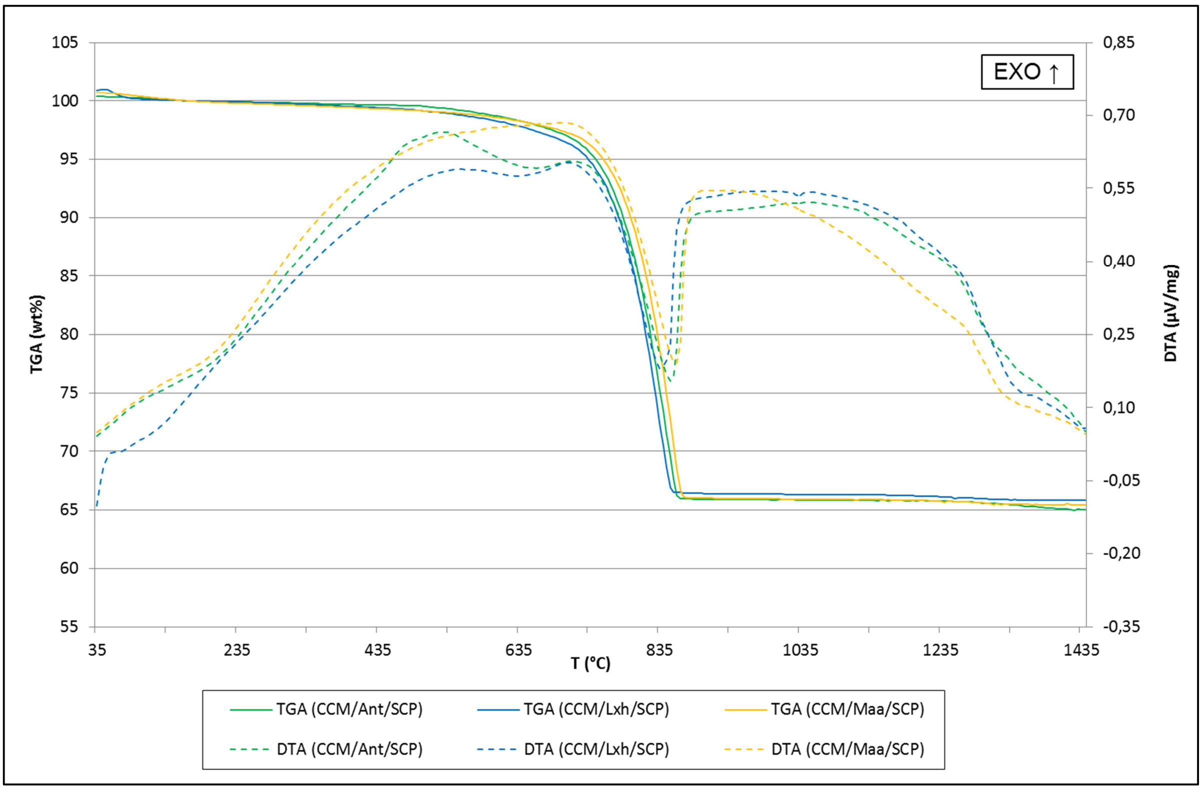

Figure 9.10.: TGA/DTA analysis of the three alternative CCMs partly made with SCP/De/S19

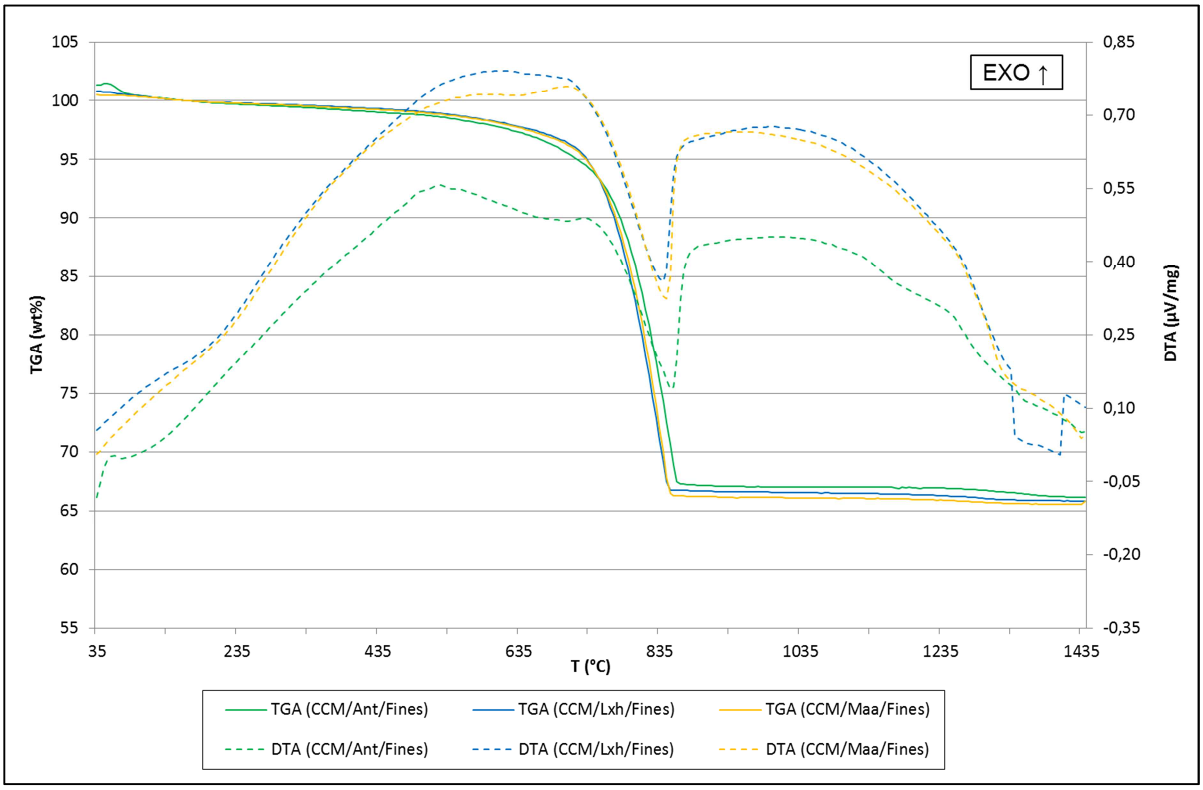

Figure 9.11.: TGA/DTA analysis of the three alternative CCMs partly made with the fines fraction (< 250 µm) of SCP/De/S19

The XRD analysis with Rietveld refinement of the final reference and alternative clinkers, presented in **tables 3.8.** and **9.8.**, shows mineralogical weight percentages that are in the same order of magnitude but nevertheless different than those calculated by the Bogue equations based on the chemical analysis of the final clinkers presented in **tables 3.7.** and **9.9.**

Table 9.8.: Mineralogical analysis by XRD of the final alternative clinkers produced in a static kiln

Clinker		Cl/Ant/ SCP	Cl/Ant/ Fines	Cl/Lxh/ SCP	Cl/Lxh/ Fines	Cl/Maa/ SCP	Cl/Maa/ Fines
Alite	(wt%)	65.37	56.88	61.54	51.99	61.86	60.86
Belite	(wt%)	20.32	27.56	20.69	29.06	19.53	19.36
Aluminate	(wt%)	1.84	3.78	2.30	2.03	2.61	3.15
Ferrite	(wt%)	12.00	10.42	14.59	16.03	14.18	15.66
Free Lime	(wt%)	0.06	0.04	0.25	0.09	0.85	0.09
Periclase	(wt%)	0.36	1.08	0.48	0.40	0.50	0.50
Arcanite	(wt%)	-	-	-	0.02	-	0.05
Aphthitalite	(wt%)	-	0.09	-	0.13	0.05	0.08
Anhydrite	(wt%)	-	-	-	-	0.12	0.02
Portlandite	(wt%)	0.06	0.12	0.03	0.24	0.31	0.22

(Full XRD analysis of Cl/Maa/SCP in Figure A.6. (Appendix A))

Table 9.9.: Chemical analysis and Bogue calculations of the final alternative clinkers produced in a static kiln

Clinker		Cl/Ant/ SCP	Cl/Ant/ Fines	Cl/Lxh/ SCP	Cl/Lxh/ Fines	Cl/Maa/ SCP	Cl/Maa/ Fines
CaO	(wt%)	66.30	65.33	66.08	65.58	66.64	65.98
SiO_2	(wt%)	22.60	22.58	22.29	22.82	22.12	22.20
Al_2O_3	(wt%)	4.04	4.40	4.13	4.45	4.11	4.50
Fe_2O_3	(wt%)	2.92	2.86	3.87	3.70	3.53	3.66
K_2O	(wt%)	0.36	0.30	0.21	0.12	0.22	0.23
Na_2O	(wt%)	0.17	0.20	0.18	0.15	0.19	0.21
SO_3	(wt%)	0.57	0.70	0.24	0.17	0.21	0.20
MgO	(wt%)	1.79	2.41	1.65	1.71	1.77	1.81
TiO_2	(wt%)	0.26	0.29	0.29	0.29	0.26	0.29
P_2O_5	(wt%)	0.20	0.21	0.23	0.23	0.19	0.17
Cl	(wt%)	n.a.	0.03	n.a.	n.a.	n.a.	n.a.
LOI 975°C (O_2)	(wt%)	0.34	0.33	0.40	0.38	0.35	0.31
DoS-factor		108.44	136.35	58.39	57.48	48.56	42.85
Alite (C_3S)	(wt%)	66.77	60.65	66.27	58.30	70.47	64.36
Belite (C_2S)	(wt%)	14.43	18.00	13.92	21.45	10.27	15.10
Aluminate (C_3A)	(wt%)	5.77	6.82	4.40	5.53	4.92	5.73
Ferrite (C_4AF)	(wt%)	8.89	8.70	11.78	11.26	10.74	11.14

The first reason for this deviation is the fact that the DoS-factors although calculated between 80 and 120, were not attaint for the final clinkers of CBR Lixhe and ENCI Maastricht. The reason of this unbalance between alkali and SO_3 *[wt%]* is due to the different volatility of the SO_3 and alkali in a static lab furnace compared to a real clinker kiln which was already explained in **section 3.3.** For both the alternative clinkers of CBR Lixhe and ENCI Maastricht, DoS-factors were too low and resulted in alite fractions *[wt%]* measured by XRD lower than these calculated by Bogue. The alternative clinker (Cl/Ant/SCP Fines) partly produced with the fines fraction (Fines/De/S19) has a DoS-factor slightly higher (136.35) than the DoS-limits and had a difference of approximately 4 wt%. This is due to the fact that by high maximisation of the fines fraction (Fines/De/S19), which was about 16 wt%, high SO_3 *[wt%]* was introduced into the alternative CCM which induces the unbalance in the DoS-factor.

Secondly, by the increased presence of MgO (2.41 wt%) (**Table 9.8.**) introduced by Fines/De/S19 (**Table 9.5.**), an increased periclase *[wt%]* was measured compared to Cl/Ant/Ref (**Table 3.8.**) and Cl/Ant/SCP (**Table 9.8.**) which will partly replace alite **(Section 2.6.)**. Together with the unbalanced DoS-factor, it explains the deviation measured in Cl/Ant/Fines. Furthermore, the deviation for the alternative clinkers increases with an increasing dosage *[wt%]* of SCP/De/S19.

As can be noted from **table 9.8.**, higher levels *[wt%]* of SCP/De/S19 also increase the presence of free lime *[wt%]*, indicating a reduced burnability of the clinker which was already described in **section 2.8.**

It can therefore be concluded that the presence of quartz in the fraction > 250 µm has a negative effect on the burnability of the clinker. This is also demonstrated by the fact that, although Cl/Lxh/SCP and Cl/Maa/SCP had comparable ARM dosages *[wt%]* compared to Cl/Lxh/Fines and Cl/Maa/Fines, the free lime *[wt%]* was much higher which proved once again that the fraction > 250 µm induces a reduced burnability in the alternative clinkers. It can therefore be concluded that if sludge out of a concrete plants should be used as ARM for Portland clinker production, low dosages have to be maintained due to the presence of quartz. A separation phase on 250 µm could counter this problem and allow possibly an increased ARM dosage. Nevertheless the presence of minor constituents as alkali, SO_3 and MgO has to be closely monitored to minimise their negative influences on the Portland clinker process.

9.4.5. Hypothesis to improve the feasibility of concrete sludge as ARM for Portland clinker production

As was demonstrated in **figures 9.2**, **9.3** and **9.6**, a clear relationship was demonstrated between CaO *[wt%]* and SO_3 *[wt%]*. This means that if concrete sludge materials could be recovered with the same SO_3 *[wt%]*, they could have comparable chemical compositions. An investigation will be started to evaluate whether or not the SO_3 *[wt%]* of concrete sludge can be measured in a feasible way and if the SO_3 *[wt%]* of concrete sludge follows a trend in time by which it increases, decreases or is randomly dispersed.

When a clear trend is noticeable, the recovery of the concrete sludge could be managed for each concrete plant individually based on the SO_3 *[wt%]* by which a decrease of the chemical variation of the concrete sludge could be possible. Further investigation should demonstrate whether or not this decrease in chemical variation should be sufficient low, together with the findings in this chapter, to be acceptable to catalogue concrete sludge as a valid Alternative Raw Material (ARM) for Portland clinker production.

9.5. Ecological benefit

The use of concrete sludge as ARM for Portland clinker production could have different positive ecological advantages. As a by-product of ready-mixed concrete production it can be handled accordingly within the guidelines of the LCA process (**Section 4.4.**). It could also have beneficial aspects in line with Cement Sustainability Initiative. Whether or not, the valorisation of the concrete sludge in Portland clinker production will be ecological beneficial, should objectively be evaluated based on different principles as cradle to grave, cradle to cradle or cradle to gate.

- EPD of Portland clinker (cradle to gate):

  As demonstrated, concrete sludge could reduce the required volumes of limestone or SiO_2-source based on their chemical composition. However, by the big chemical variation which was demonstrated during this investigation, maximisation of the sludge in the CCM will be limited. If this chemical variation cannot be improved, dosages of more than 2 wt% of the total CCM will be quite unlikely as described in **section 2.5.**

If higher dosages would be possible, a decrease of inorganic CO_2 emission could be possible due to the partially presence of decarbonated CaO. Nevertheless the high amount of chemical bound H_2O (**Table 9.2.**) will limit the energetic advantage due to the required endothermic dehydration energy.

If the concrete sludge is not screened at 250 µm, the presence of coarse quartz particles will worsen the burnability of the Portland clinker as demonstrated by the conducted tests in **paragraph 9.9.4.**

A small ecological advantage could be noted if the EPD of the concrete sludge would be ecologically beneficial compared to the EPDs of the limestone and/or the SiO_2-sources which it could replace. Nevertheless this effect will be quite small due to the limited replacement capacity.

If the screening of the concrete sludge will be necessary as a function of the burnability of the Portland clinker, the EPD of the concrete sludge will be negatively influenced due to the increase of the required treatment energy.

- EPD’s of the other related processes (cradle to gate):

  Because it is very doubtful that the EPD of Portland clinker will be influenced in a positive way by the use of concrete sludge as ARM, no improvement of the EPD of Portland cement and other cement types will be expected. In fact, if clinker burnability is negatively influenced by the use of the concrete sludge, the decreased clinker quality will require higher grinding energies and/or induce durability issues on the related cement derivatives due to the presence of free lime. Also the influence of minor components as SO_3, alkali, MgO, ZnO, etc. on the sintering of the clinker and the hydration reactions of the Portland cement have to be monitored.

- Cradle to grave / Cradle to cradle:

  The valorisation of the concrete sludge could improve the EPD of the ready-mix concrete. Concrete sludge that otherwise has to be handled as waste, will be reused as an ARM. The gain on the EPD of ready-mix concrete will be related to the energy that will be spent during collection, transport and treatment of the concrete sludge to the Portland clinker factory, compared to the impact of landfill and its related handling energy. Industrial practice will unveil the possible improvement this switch could represent for the ecological footprint of ready-mix concrete.

Based on the results of this study and the cited influences on the LCA calculation, it is quite unlikely that using concrete sludge as ARM for Portland clinker production will be ecologically beneficial if the chemical variation of the concrete sludge cannot be improved, although its use is in line with the Cement Sustainability Initiative (**Section 4.2.**). The concrete sludge will have its influence on one of the five Key Performance Indicators of the Cement Sustainability Initiative: fuels and materials use.

Nevertheless valorisation of the concrete sludge could be ecologically beneficial for ready-mix concrete production process. Further investigations should therefore be performed on other possible valorisation routes of the concrete sludge or/and the improvement of the chemical variation of the concrete sludge.

9.6. Conclusions

The long sampling period, the geographical dispersion and the amount of collected concrete sludge samples, make it possible to make a good interpretation of the chemical and mineralogical variation of the sludge samples in an objective way. A big chemical variation between the different concrete sludge samples was noted which could only be marginally decreased when the concrete sludge samples were collected for each concrete plant individually. Nevertheless the chemical variation was still too large to be used as a valid Alternative Raw Material (ARM) in Portland clinker production.

A hypothesis was set which states that when the SO_3 *[wt%]* of concrete sludge could be closely monitored, the collection out of the sludge basin could be performed in a way which would lower the chemical variation of the concrete sludge to an acceptable level suited for use as ARM for Portland clinker production.

It was also shown that the sludge from the water treatment system of concrete plants specifically collects the finer fractions of the various raw materials of the concrete by which the cement content in the sludge samples is much higher than in normal recycled concrete. Because of this difference, techniques demonstrated prosperous to create an ARM out of recycled concrete (**Chapter 10**), were not successful for concrete sludge. When a separation technique was used on 250 µm, it was demonstrated that a separated fines fraction on 250 µm does not have an improved chemical composition and variation, but nevertheless had an improved burnability within the alternative Portland clinker.

The presence of coarse quartz particles in the sludge has a negative impact on the burnability of the Portland clinker which limits its maximisation as ARM. The presence and variation in concentration of minor constituents as alkali, SO_3 and MgO, coming from the high cement content, will act as a second limit on the maximization of both sludge samples and their specific fines fractions. Furthermore, the fraction bigger than 250 µm that has an improved suitability after a crushing and separation phase on 250 µm for concrete applications in the case of recycled concrete does not show this improvement in the case of recycled concrete sludge by the presence of high levels of cement derivatives.

As could be noted out of the different sections, sludge samples as well as their specific fines fractions could replace Classic Raw Materials (CRMs), primarily the classic SiO_2-sources as sabulous clay or loam, but also in small amount, limestone CRMs by an increasing CaO *[wt%]*.

The possible energy gain coming from the lowered decarbonation energy due to a decreased limestone dosage will nevertheless be negligible because of the required energy for the liberation of the chemically bound water.

The only positive effect on the ecological impact of Portland clinker production will be that a primary natural material could be replaced by a secondary recycled material.
After this study, it can be concluded that sludge out of concrete plants cannot be classified as a feasible alternative raw material for Portland clinker production due to the cited restrictions.

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Chapter 10

Fines out of recycled concrete aggregates as alternative raw material for Portland clinker production

10.1. Introduction

When structures made of concrete are demolished, the use of the demolished construction debris as aggregates is an increasingly common recycling method. Recycling of construction debris into new construction offers a way to reduce waste disposal sent to area landfills and to extend the life of natural resources.

The production of recycled aggregates is already well studied and is especially used in practice in Belgium, Denmark and the Netherlands where recycling rates of more than 80 wt% are attained **[1]**. The use of recycled aggregates is less common in the Southern European countries, where landfill is widely practiced to get rid of demolition waste **[1-2]**. It is estimated that the annual generation of construction and demolition waste in the EU could be as much as 450 million tons, which is the largest single waste stream, apart from farm waste **[1]**, **[3]**. Even if the earth and some other wastes were excluded, the construction and demolition waste generated is estimated to be 180 million tons per year **[1]**, **[3]**.

An EU study calculated that an average of 28 wt% of all Construction and Demolition waste was already recycled in the late 1990s. Most EU member countries have established goals for recycling that range from 50 wt% to 90 wt% of their construction and demolition waste, in order to substitute natural resources. Nevertheless according to the official statistics in 2008 [4], the use of landfill in for example Italy was still used for 80 wt% as disposal method for demolition waste **[1]**.

To produce recycled concrete aggregates, construction debris is normally put through a crushing machine. Crushing facilities accept only uncontaminated concrete, which must be free of trash, wood, paper and other such materials. The resulting recycled concrete aggregates are sorted by size in the same way as primary aggregates are handled. Larger chunks may go through the crusher again. Based on the quality of the recycled concrete aggregates, it can be used as sub-base and base gravel for pavements but also as dry aggregate for brand new concrete if it is free of contaminants. When evaluating recycled concrete aggregate characteristics, it should always be kept in mind that each recycled aggregate particle is still a piece of concrete composed of the original primary aggregate and the adhered mortar.

The most frequently asked question is what the impact of the recycled aggregates on the durability and strength development **[5]** of the final concrete will be. The overall quality of recycled concrete aggregates is generally lower than that of natural aggregate, due to the mortar that remains attached to the natural aggregate **[6]**. Studies on the use of recycled concrete aggregates in concrete show that the compressive strength **[5-6]**, drying shrinkage **[5]**, creep **[7]**, shear resistance **[7]**, freeze and thaw resistance **[8-9]**, abrasion resistance **[6]**, sulfate content [6] etc. can be improved, if the attached mortar can be separated better from the recycled aggregates. It was proven that the performance regarding durability and strength development is related to the attached mortar content in the recycled aggregate. Some researchers even came to the conclusion that only recycled aggregates with an attached mortar content lower than 44 wt% can be used for structural concrete **[6]**. Different researchers have investigated ways to separate as much of this cement stone from the recycled aggregates as possible **[10]**.

Within this PhD study, a classic recycling process was used supplemented with some additional treatment phases to upgrade the recycled aggregates even more and to obtain a higher valorisation ratio for the derivatives of the recycling process. This will be further explained in **section 10.2.**

10.2. The recycled aggregates production process

When using a classic recycling process, exhibiting only one crushing action by a jaw or impact crusher, approximately 50 wt% of recycled aggregates and 50 wt% of recycled sand extremely high in filler *[wt%]* (< 63 µm), can be obtained (**Table 10.1.**).

When incorporating a second crushing action by a Vertical Shaft Impactor (VSI) to clean the recycled aggregates, the sand fraction is increased and the amount of recycled but improved aggregates is decreased **[10]**. Improving recycled aggregates by decreasing the attached mortar content, will therefore generate more low grade sand which is unsuitable for high end concrete production. To improve this sand quality, the filler content (<63 µm) has to be lowered to have an acceptable water demand for high end concrete production **[1]**, improved mechanical properties **[1]** and better durability performances **[11-12]**.

Within this PhD study, different separation techniques were applied, generating fines fractions which could be used as possible Alternative Raw Material (ARM) for Portland clinker production. Encouraging the increased use of alternative raw material in Portland clinker production is in line with the Cement Sustainability Initiative as key action in the sustainable development of the cement industry (**Section 4.2.**). Other applications for these fines were already investigated, for example as filler in asphalt production **[13]**.

Three specific separation installations were incorporated: Advanced Dry Recovery (ADR) installation **[14]**, the CTP (Centre Terre et Pierre) concept installation **[15]** and a static KHD separator **[16]**. The treated sands coming out of these three separation installations separated from their fines fractions were tested on their water demand to determine whether or not they were suitable for the production of high end concrete.

To have a practical starting point, 0/200 recycled concrete material was recovered from an old concrete construction for this study. The treatment of this material generated different recycled materials as shown schematically in **table 10.1.**

Table 10.1.: Percentual distribution between the different crushing and screening actions

Grading (d/D)	Impact Crusher	Power Screen 1	VSI Crusher	ADR Screen	Power Screen 2	CTP Screen	KHD Screen
	wt%	wt%	wt%	wt%	wt%	wt%	wt%
0/200	**100**						
0/50	*100*						
0/50		**100**					
0/63		*53*					
0/8 (7.3 wt%<63µm)		*47*					
0/63			**53**				
0/14			*53*				
0/14				**53**			
0/8 (7.3 wt%<63µm)				**47**			
0/12.5				*33.6*			
Ag/Sa04/ADR (0/4)				*34.1*			
ARM/ADR (0/2)				*32.3*			
0/14					**53**		
0/8 (7.3 wt%<63µm)					**47**		
0/20					*9*		
0/6.3 (7.8 wt%<63µm)					*91*		
0/6.3 (7.8 wt%<63µm)						**91**	
Ag/Sa06/CTP (0/6.3)						*84*	
ARM/CTP (0/250µm)						*7*	
0/6.3 (7.8 wt%<63µm)							**91**
Ag/Sa06/KHD (0/6.3)							*86.2*
ARM/KHD (0/250µm)							*4.8*

The recycled concrete was first crushed on an impact crusher Nordberg LT 1213 (**Figure 10.1.**) before it was crushed for a second time on a VSI crusher Magottaux 2400 (**Figure 10.2.**) to remove the attached mortar from the recycled aggregates even more as described in **[5]**. After this crushing action the resulting material was further treated separately on the three separation installations which will further be explained in the next sections.

Figure 10.1.: The impact crusher Nordberg LT 1213

Figure 10.2.: The VSI crusher Magottaux 2400

10.3. The Advanced Dry Recovery installation [14]

The Advanced Dry Recovery (ADR) installation is a new type of classification method to upgrade recycled aggregates. The primary goal of the ADR is to reduce the amount of fines within the recycled concrete materials. It allows classification of the moist material down to 2 mm without drying or washing the recycled aggregates. Two pilot plants are currently in use (**Figure 10.3.**). In order to study the effects of this new separation technique, a unit was built on lab-scale at the faculty of civil engineering of the TU Delft (**Figure 10.4.**). For this PhD study, experiments were done on this installation.

Figure 10.3.: Pilot ADR plant Theo Pouw group (Utrecht)

The ADR installation is a sort of wind sifter that by the use of kinetic energy and air knifes, can separate crushed recycled concrete in coarse aggregates, sand and fine fractions (ARM/ADR). It uses kinetic energy to break the forces of cohesion that are present by the moisture associated with the fine particles. By this action, the fitness of the coarse recycled aggregates should be improved for high end concrete applications. During the process, the recycled concrete aggregates are split into various products.

The cut-off point determines the quality of the classification. Using this cut-point the input is separated into a fine product (target: 0-1mm) and a coarse product (target: 1-12mm). The coarse product can further be processed by using an air-knife.

Figure 10.4.: ADR installation on lab-scale (TuDelft)

10.4. The CTP concept installation [15]

This installation is located in Tournai (Belgium) in the research department of the Centre Terre et Pierre (Tournai/Belgium) **[15]**. It can only be used to separate sand from fines fractions because of its technical specifications. It consists out of a ball mill (5) which is connected to two separators connected in series: a static (10) and dynamic separator (9). The separator can be heated by a hot air stream (**Figure 10.5.**).

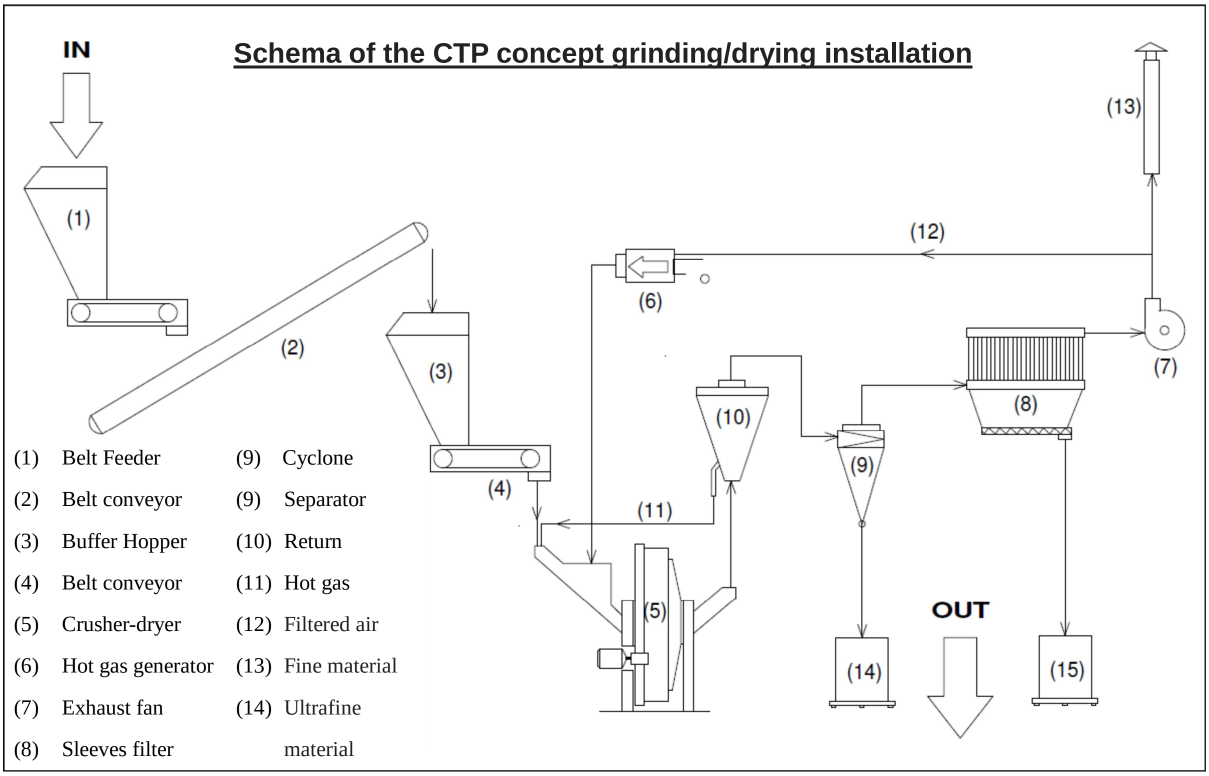

Figure 10.5.: Schematical view of the CTP concept installation (Ref. CTP)

The ball mill wasn't filled with balls for this test, but was only used to throw the sand in the hot air stream which fed the dynamic separator with the entrained fine sand fraction. After the separation phase set at 250 µm, the fine sand fraction returned to the ball mill and the fines fraction (ARM/CTP) was recovered. The upgraded CTP sand fraction was recovered in the ball mill. Comparable installations can already be purchased for industrial practice.

10.5. The KHD separator [16]

The so called KHD separator is in fact a V-separator. As for the CTP-concept, it can only be used to separate sand from fines fractions. Material is fed from above to the built in step grate. From here, the fine material is carried upwards with the air through the separating channels; the coarse material falls down over the step grate and is discharged at the bottom of the housing (**Figure 10.6.**).

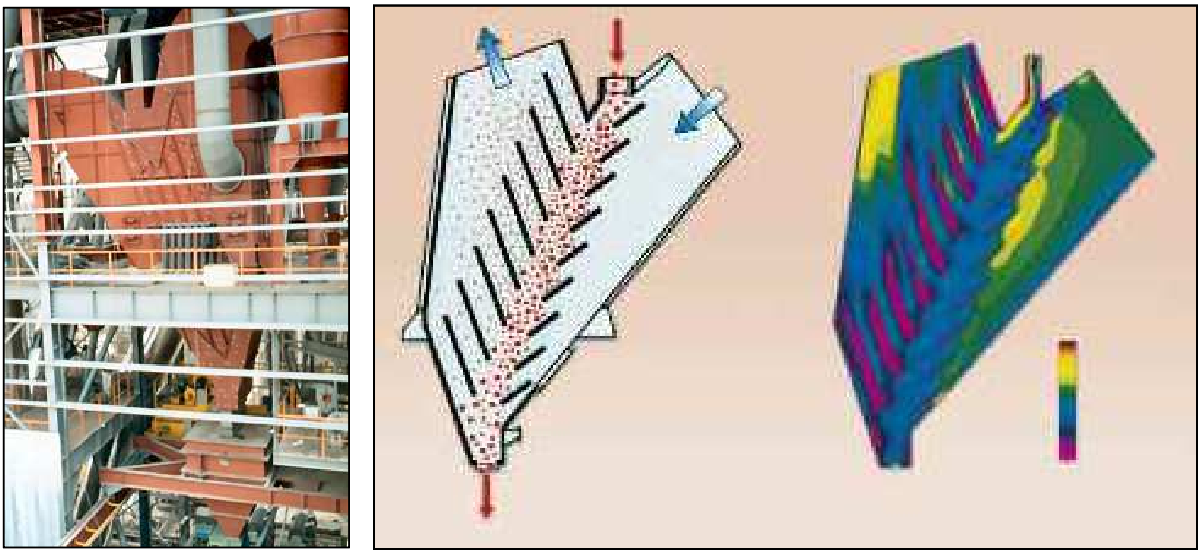

Figure 10.6.: The V-separator of KHD (left) and the working principle (right)

The required product fineness is achieved by adjusting the air speed in the separating channels. Cut-off point range is approximately from 80 µm to 1.5 mm. The V-separator is an uncomplicated static separator without any moving parts.

The experiments done as a function of this PhD-study were performed on lab-scale at the research department of the KHD Group Support Center in Cologne (Germany) (**Figure 10.7.**). The sand was first dried to a maximum humidity of 4 wt% at open air before it was completely fed to the static separator which was also set at 250 µm. The separation generated the third fines fraction (ARM/KHD).

Figure 10.7.: V-separator on lab-scale (KHD Cologne)

10.6. Sampling

About 282 tons 0/200 concrete material was recovered from a demolished concrete construction, an old plant of Inter Beton (Heidelberg Benelux group) (**Figure 10.8.**). Only the concrete of the pylons and the slabs were selected for this investigation.

Figure 10.8.: The old concrete plant of Inter Beton Sint-Pieters-Leeuw (Belgium)

Figure 10.9.: The 0/200 recovered concrete debris

The selected concrete debris (**Figure 10.9.**) was crushed according to the recycled aggregates production process described in **section 10.2.** which generated different recycled materials (**Table 10.1.**). The recycled concrete (0/200) was first crushed on an impact crusher Nordberg LT 1213 (**Figure 10.1.**) to 0/50 aggregates by which 53 wt% recycled 0/63 aggregates and 47 wt% recycled 0/8 sand out of the 0/50 was generated by separation on a power screen Chieftain 400. The recycled 0/63 aggregates were then crushed for a second time on a VSI crusher Magottaux 2400 (**Figure 10.2.**) to remove the attached mortar from the recycled aggregates even more as described in **[5]**. This action made the recycled aggregates smaller (0/14).

The crushed material (0/14) delivered by the VSI crusher was homogenised with the recycled 0/8 sand which recompleted the recycled material to 100 wt%. A batch of 1.5 tons was sampled to serve as feed material for the ADR installation without drying, being the way the installation works in practice.

The separation by the ADR installation generated three fractions: a coarse fraction (0/12.5), a 0/4 sand fraction (Ag/Sa04/ADR) and a fine fraction (ARM/ADR) which in fact is a sand 0/2. Furthermore, the same homogenised crushed material as fed to the ADR installation was inserted to a power screen Chieftain 400 which separated the recycled 0/20 aggregates fraction (9 wt%) from the sand fraction (91 wt%) which was a recycled 0/6.3. It may seem bizarre that by a separation action the coarse fraction has a higher D_{max} (20 mm) than its starting material (14 mm). In fact, the nomination of D_{max} implies a statistical determination based on the particle size distribution **[17-18]**. It may therefore happen that the D_{max} of the coarse fraction increases compared to the starting material when the generated finer fraction after separation is high, in this case 91 wt% of 0/6.3 aggregates.

Two batches of 1.5 tons were sampled to serve as feed for the CTP and the KHD installations.

The reason that the batch for the ADR installation **[14]** was taken before the power screen in contrast to the two other installations, is that the ADR installation should, by specification, be capable to separate also the coarse recycled 0/20 aggregates fraction from the sand and fine (ARM/ADR) fractions. After being processed by the separation installations, three sand fractions were generated with a decreasing fines fraction *[wt%]*: Ag/Sa04/ADR (6.9 wt%), Ag/Sa06/CTP (0.1 wt%) and Ag/Sa06/KHD (2.2 wt%), as described in **table 10.1.** The separation processes also generated three so called fines fractions: ARM/ADR, ARM/CTP and ARM/KHD.

As can be noticed out of **figure 10.10.**, the sand coming out the ADR installation, is a 0/4 sand (Ag/Sa04/ADR) in contrast to the CTP and KHD installations which generated both a 0/6.3 sand. This is due to the fact that the ADR 0/4 sand is cut above 4 mm which should generate recycled 4/20 aggregates. Nevertheless this separation left too much sand in the coarse aggregates fraction to be called 4/20 aggregates and can therefore only be catalogued as 0/20 aggregates.
Furthermore, it is clear out of **table 10.1.** that although the ADR separation generates a lot more ARM *[wt%]*, it also leaves more fines (<63µm) *[wt%]* in the sand fraction (**Figure 10.10.**).

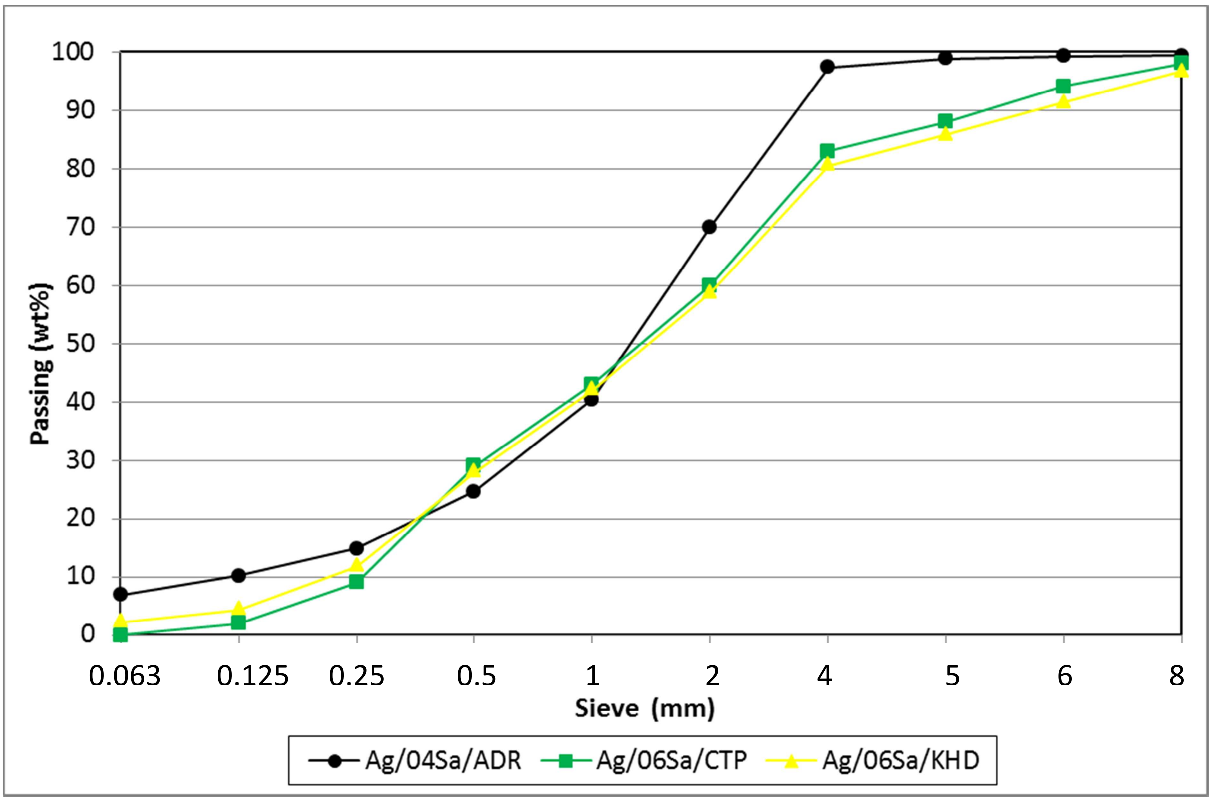

Figure 10.10. Passings (wt%) for Ag/04Sa/ADR, Ag/06Sa/CTP and Ag/06Sa/KHD on different sieves (mm)

A method was developed by Sagrex Benelux to evaluate the water demand of different sands for concrete applications. In this method, 10 kg of sand is dried at a temperature of 110 ± 5 °C for 24 ± 1h after which the sand is cooled to room temperature in open air. All sand fractions are sieved on a normalised sieve of 4 mm after which 3857 ± 1 g of sieved sand is weighed into a mixer bowl with a capacity of 10 L and a fixed mixing speed setting of 100 rpm. 500 ± 1 g water is added to the sand after which this mixture is mixed for 10 minutes. 1285 ± 1 g of a homogenised batch of CEM III/A 42.5 N LA cement is dosed to the sand/water mixture after which the paste is mixed for another 10 minutes at the same constant speed. After 5 minutes, extra water is added until a slump consistency between 50 and 75 mm is obtained. This consistency can be situated in the first half of the consistency class S2 **[17]**. The final Water Demand (WD_{sand}) (g) is calculated by **(10.1)**:

$$WD_{sand} = (W_{Tot} - (WA\% * Sa_{4mm}) - Cem * WD_{cem}) / Sa_{4mm} \quad \textbf{(10.1)}$$

W_{Tot} = The total amount of water added (g)

WA% = Percentage of Water absorption of the sand **[18]**

Cem = The total amount of cement added = 1285 g

WD_{cem} = Water demand of the used CEM III/A 42.5 N LA= 28.2 wt% **[19]**

Sa_{4mm} = The used sand after sieving smaller than 4mm = 3857 g

The water absorption and the absolute density of the recycled sand were determined according to NBN EN 1097-6 **[18]**.

10.7. Research description

The primary objective is to investigate how much of each of the three described fines (ARM/ADR, ARM/CTP and ARM/KHD), could be applied in a Portland clinker process to replace Classic Raw Materials (CRM). This will be determined as a function of each of the three kilns, CBR Antoing, CBR Lixhe and ENCI Maastricht, with enumeration of possible limitations. Numerical simulations will be carried out to maximise the use of these materials in clinker kilns taking into account the compositional variation of the fines as a function of the used separation technique, its behaviour within a clinker kiln and the impact on the energy consumption. Furthermore, experimental clinkers will be produced corresponding with ARM dosages that were esteemed as realistic by the numerical simulations. These clinkers will be fully analysed and evaluated according to the evaluation concept described in **chapter 3**.

Secondly, the water demand of the treated sand after each of the three separation techniques will be investigated to determine whether or not the fitness for concrete applications is improved.

10.8. Results and discussion

Based on the articles “Fines extracted from recycled concrete as alternative raw material for Portland clinker production: Fineness as determinant factor” submitted to Cement and Concrete Composites **[20]** and the congress article “Fines extracted from recycled concrete as alternative raw material for Portland clinker production” for the Concrete Innovation Conference in Oslo in 2014 **[21]**, the results of the research on the use of recycled concrete as ARM for Portland clinker production are described below. Additionally, some lab tests on concrete were performed based on the recycled aggregates out of this investigation, but these weren’t published in this PhD thesis, due to their confidentially.

10.8.1. Influence of the filler content on the water demand of the recycled sands

The filler content which is defined as the amount of particles passing *[wt%]* through a sieve of 63 µm is an important parameter for aggregate producers. A higher filler (<63 µm) content *[wt%]* could increase the water adsorption which explains its limitations by regional standardisation **[22]**. Dry and wet screening is applied to decrease as much as possible the filler content *[wt%]* in coarse aggregates and sand **(Paragraph 6.7.1.)**. The filler (<63 µm) content in recycled aggregates often originates from cement stone which explains the increase in water absorption in comparison with natural sand. Water absorption in recycled aggregates can vary from 3 to 12 wt% **[5]**. Concrete producers avoid high filler (<63 µm) content *[wt%]* in their aggregates because of the increased water demand it generates in the concrete mixtures. Asphalt producers on the other hand desire a perfect ratio between bitumen and filler **[23]**. For energetic and technical reasons, they rather like to add than to extract filler to attain the perfect ratio.

The sands coming out of the three different fines separation installations were evaluated on their intrinsic water demand (**Table 10.2.**). As reference, the sand 0/6.3 after Power Screen 2 will be taken which is the recycled sand before treatment on the CTP and KHD installation (**Table 10.1.**). There will be no influence of the fact that the ADR 0/4 sand is finer than the reference, CTP and KHD 0/6.3 sand because for this measurement all four sand samples were cut off at 4 mm as described in **section 10.6**. Nevertheless the particle size distribution of these four sands will stay different.

Table 10.2.: Influence of fines [wt%] on the water demand of the recycled sand

Sand		Reference	Ag/Sa06/ADR	Ag/Sa06/CTP	Ag/Sa06/KHD
Filler content (< 63 µm)	wt%	7.8	6.9	0.1	2.2
Absorption Water (EN 1097-6)	wt%	4.70	3.50	5.50	6.40
Absolute Density (EN 1097-6)	kg/m³	2365	2374	2356	2360
Water Demand	kg/kg	0.167	0.129	0.070	0.088

The water that has to be added to a sand, is influenced by the absorption water **[18]** introduced into the porous structure of the sand and the adsorption water needed to wet the specific surface of the sand. Nevertheless, it will only be the adsorption water regardless of the absorption water which will have an impact on the effective W/C ratio of concrete and therefore on the water demand of the sand as described in formula **(10.1)** in **section 10.6.** The sand with the highest water adsorption will therefore have the highest water demand *[kg water/kg sand]*.The finer the sand, the bigger its specific surface will be. An increasing filler (<63 µm) content *[wt%]* will therefore increase the water demand. This relationship demonstrates the dislike the concrete industry has against fines in aggregates. It is also valid for recycled sands by which the treatment to lower the filler (<63 µm) content *[wt%]* is a must to upgrade recycled sands for utilisation in common concrete applications. Without this treatment, producing durable concrete with recycled sands based on their W/C ratio **[17]**, would be very expensive and in some cases even impossible. The water absorption **[18]** for the recycled ADR sand, although still higher than in natural sands, is lower than for both CTP and KHD sands. This is due to the fact that the ADR sand is cut below 2 mm demonstrated by the fineness of the ARM/ADR presented in **figure 10.11.** ARM/ADR is composed out of less cement stone fraction *[wt%]* than the two other recycled sands which are cut below 250 µm. The water absorption of sands will be an important parameter for the production of concrete because it could requisite the pre-wetting of the sand fraction to maintain the stability of the concrete consistency **[17]**.

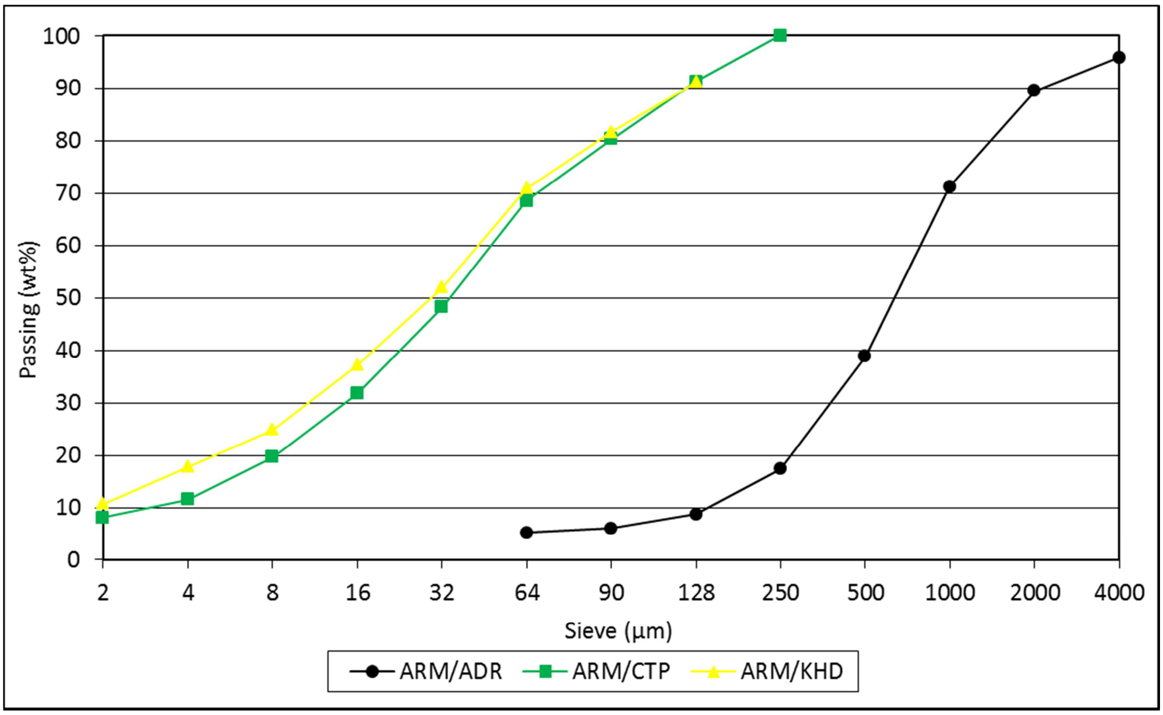

Figure 10.11.: Passings (wt%) for ARM/ADR, ARM/CTP and ARM/KHD measured by laser diffraction (µm)

Based on the water demand, sands out of the CTP and/or KHD installation are more suitable to produce high end concrete than the sand coming out of the ADR installation.

10.8.2. Influence of fines particle size distribution on the chemistry of the generated fines

As described in **section 10.6.**, three different separation installations were used to generate ARM/ADR, ARM/CTP and ARM/KHD. As can be noticed out of **table 10.3.**, these three samples have different chemical compositions.

Table 10.3.: Chemical composition of the starting material ARM/ADR, ARM/CTP and ARM/KHD

ARM		Starting material	ARM/ADR	ARM/CTP	ARM/KHD
CaO	(wt%)	13.03	15.14	24.38	22.99
SiO_2	(wt%)	67.52	64.07	44.78	44.61
Al_2O_3	(wt%)	5.27	4.80	6.02	5.86
Fe_2O_3	(wt%)	2.60	2.74	3.22	4.06
K_2O	(wt%)	0.92	0.87	0.89	0.97
Na_2O	(wt%)	0.61	0.49	0.39	0.48
SO_3	(wt%)	0.63	0.76	1.23	1.24
MgO	(wt%)	0.96	1.02	1.38	1.44
TiO_2	(wt%)	0.27	0.24	0.33	0.32
P_2O_5	(wt%)	0.14	0.14	0.20	0.20
Cl	(wt%)	0.12	0.11	0.18	0.13
LOI 975°C (O_2)	(wt%)	7.69	9.39	16.68	17.40
C_{total}	(wt%)	1.39	1.75	3.31	3.93
S_{total}	(wt%)	0.23	0.29	0.50	0.53

Compared to the 0/50 starting material (**Table 10.1.**) recovered after the first crushing action, it is clear that the amount of CaO *[wt%]* is increased and SiO_2 *[wt%]* is decreased in the three samples. The lower the SiO_2 *[wt%]*, the more ARM can be dosed if no other restrictions are present as described in **chapter 2.**

It is clear that ARM/CTP and ARM/KHD have very similar chemical compositions and also have comparable dosages in the alternative CCMs (**Table 10.4.**). This is the reason why only alternative lab clinkers with ARM/CTP where produced to be representative for both ARMs. This is quite logical because the separator for the CTP as well as for the KHD concept, have cut the ARM and the sand fractions at 250 µm. ARM/ADR is much coarser and is in fact a sand 0/2 (**Figure 10.11.**).

By comparing the chemical compositions (**Table 10.3.**) and the particle size distribution of the three ARMs, it can be concluded that the fraction between 250 µm and 2 mm consists primarily out of coarse quartz particles. In **chapter 8**, it was demonstrated that the presence of coarse quartz particles in ARM could act as a serious restriction **[24-28]** when used in big quantities in Portland clinker production. Therefore the grindability of ARM/ADR which has the highest SiO_2 *[wt%]* of the three ARMs, will impose the most severe restrictions regarding the grindability of the ARMs. The grindability of ARM/ADR compared with these of the CRMs, will be evaluated in **paragraph 10.8.5.**

10.8.3. Clinker feed calculations and preparations

The CCMs were calculated with the simulation program (**Section 3.3.**) in line with the chemical and mineralogical requirements listed in **table 2.5.** The compositions of the reference CCMs after simulation are presented in **table 3.1.**, these of the alternative CCMs in **table 10.4.** The alternative CCMs were calculated to maximise the use of the different ARMs. Because of the high SiO_2 *[wt%]* in the different ARM materials (ARM/ADR,CTP,KHD), it was expected that they would function as SiO_2-source in CCM replacing loam or sabulous clay as classic raw materials (**Tables 3.4.** and **3.5.**) for CBR Lixhe and ENCI Maastricht.

In fact, by maximisation of the ARMs in the alternative CCMs of CBR Lixhe and ENCI Maastricht, loam and sabulous clay were completely replaced (**Table 10.4.**). Maximisation of the different ARM materials in the CCMs of CBR Antoing was lower than for the two foregoing factories due to the fact that CBR Antoing does not use a real SiO_2-source. Because the necessary SiO_2 is delivered by their two limestone sources, especially the poor limestone (CRM/Ant/CP) (**Table 3.4.**), the dosage of CRM/Ant/CP was decreased but on the other hand by lack of sufficient CaO *[wt%]* in the ARMs, the dosage of CRM/Ant/CR was increased.

The only limiting factor for the maximisation of the ARMs was the SiO_2 *[wt%]* of the CCM itself by which the ARM with the highest SiO_2 *[wt%]* was dosed the least. In the case of ARM/CTP and ARM/KHD, the dosages were much higher than the classic SiO_2-sources. This is due to the higher CaO *[wt%]* and lower SiO_2 *[wt%]* which results in a significant decrease of the limestone CRM of CBR Lixhe and ENCI Maastricht. This increased dosage of ARM/CTP and ARM/KHD compared to ARM/ADR, was also seen in the alternative CCMs of Antoing.

The CCMs were prepared and sintered as described in **paragraph 3.4.** The physical and chemical analysis of these CCMs as well as the chemical and mineralogical analysis of the final clinkers will be discussed in the following sections.

Table 6.5. Table 10.4.: Compositions of the alternative clinker meals with ARM/CTP and ARM/KHD

	CRM+ARM	**Quantity** (wt%)		**CRM+ARM**	**Quantity** (wt%)		**CRM+ARM**	**Quantity** (wt%)
CCM/Ant/ADR	CRM/Ant/CP	38.13	CCM/Ant/CTP	CRM/Ant/CP	34.78	CCM/Ant/KHD	CRM/Ant/CP	33.22
	CRM/Ant/CR	51.81		CRM/Ant/CR	53.22		CRM/Ant/CR	54.51
	CRM/Ant/FA	7.11		CRM/Ant/FA	6.57		CRM/Ant/FA	6.65
	CRM/Ant/IC	0.84		CRM/Ant/IC	0.81		CRM/Ant/IC	0.73
	ARM/ADR	2.11		ARM/CTP	4.62		ARM/KHD	4.90
	Sum	100.00		Sum	100.00		Sum	100.00
CCM/Lxh/ADR	CRM/Lxh/Tu	78.44	CCM/Lxh/CTP	CRM/Lxh/Tu	75.24	CCM/Lxh/KHD	CRM/Lxh/Tu	75.46
	CRM/Lxh/Lo	0.00		CRM/Lxh/Lo	0.00		CRM/Lxh/Lo	0.00
	CRM/Lxh/FA	13.31		CRM/Lxh/FA	11.23		CRM/Lxh/FA	11.39
	CRM/Lxh/IC	1.61		CRM/Lxh/IC	1.53		CRM/Lxh/IC	1.35
	ARM/ADR	6.64		ARM/CTP	12.00		ARM/KHD	11.80
	Sum	100.00		Sum	100.00		Sum	100.00
CCM/Maa/ADR	CRM/Maa/Ma	79.09	CCM/Maa/CTP	CRM/Maa/Ma	74.86	CCM/Maa/KHD	CRM/Maa/Ma	75.11
	CRM/Maa/SC	0.00		CRM/Maa/SC	0.00		CRM/Maa/SC	0.00
	CRM/Maa/FA	10.69		CRM/Maa/FA	8.76		CRM/Maa/FA	8.83
	CRM/Maa/IC	1.62		CRM/Maa/IC	1.50		CRM/Maa/IC	1.27
	ARM/ADR	8.60		ARM/CTP	14.88		ARM/KHD	14.79
	Sum	100.00		Sum	100.00		Sum	100.00

10.8.4. Chemical and TGA analysis

The fact that in the Benelux, cement can be composed out of clinker, slag, fly ash and limestone filler in various concentrations, indicates that the chemical variation of the recycled fines could be large. Based on the chemical compositions of a CEM I and a CEM V cement, CaO could vary from 65 wt% to 45 wt% and SiO_2 from 20 wt% to 30 wt%. Also the origin and the mineralogy of the used aggregates can influence the chemical composition as well as the chemical variation of the fines. The aggregates could come from the sea, a river or a quarry and can consist out of pure quartz, calcite and dolomite and even feldspar and hornblende **(Section 6.2.)** if porphyry is taken into account.

Table 10.5. Average, minimum and maximum values of individual chemical compounds out of ten recycled fines fractions

ARM		Minimum	Average	Maximum
CaO	(wt%)	18.50	25.12	29.92
SiO_2	(wt%)	41.55	48.15	62.50
Al_2O_3	(wt%)	2.99	5.50	9.27
Fe_2O_3	(wt%)	1.50	2.70	4.06
K_2O	(wt%)	0.70	0.86	1.30
Na_2O	(wt%)	0.12	0.39	0.69
SO_3	(wt%)	0.97	1.47	2.71
MgO	(wt%)	0.39	1.25	2.61
LOI 975°C (O_2)	(wt%)	3.64	13.61	19.89

As already mentioned in **section 3.2.**, it wasn't possible to sample a big batch of these fines. Nevertheless it was possible to collect a small batch of fines samples (**Table 10.5.)** which were sampled over the past two years, made of different concrete waste materials as well as generated by different separation techniques. These samples were not used for the investigation of the fines coming out of recycled concrete but nevertheless demonstrate the chemical variation that could be expected if these fines are used as ARM for Portland clinker production.

The chemical analysis of the final clinkers presented in **table 10.6.** shows that the alternative CCMs out of the used ARMs and CRMs were properly assessed by the simulation program and have a comparable chemical composition as their reference (**Table 3.7.**). Only both alternative clinkers of ENCI Maastricht had a SiO_2 *[wt%]* that was slightly higher than the reference**.** By using Bogue equations **[29]**, predictions can be made for the expected mineralogy of the reference and alternative final clinkers.

Table 10.6.: Chemical analysis and Bogue calculations of the Final Clinkers with ARM/ADR and ARM/CTP produced in a static kiln

Clinker		CL/Ant/ ADR	CL/Ant/ CTP	CL/Lxh/ ADR	CL/Lxh/ CTP	CL/Maa/ ADR	CL/Maa/ CTP
CaO	(wt%)	66.31	66.53	66.41	66.21	66.80	66.17
SiO_2	(wt%)	22.62	22.75	22.37	22.49	22.47	22.89
Al_2O_3	(wt%)	4.08	4.00	4.21	4.15	4.23	4.22
Fe_2O_3	(wt%)	2.88	2.83	4.03	3.96	3.61	3.65
K_2O	(wt%)	0.39	0.39	0.12	0.15	0.11	0.14
Na_2O	(wt%)	0.16	0.17	0.15	0.16	0.19	0.17
SO_3	(wt%)	0.62	0.53	0.14	0.20	0.08	0.13
MgO	(wt%)	1.74	1.64	1.29	1.33	1.35	1.45
TiO_2	(wt%)	0.25	0.24	0.27	0.26	0.25	0.25
P_2O_5	(wt%)	0.20	0.20	0.23	0.24	0.07	0.07
Cl	(wt%)	-	-	-	-	0.17	0.16
LOI 975°C (O_2)	(wt%)	0.31	0.35	0.40	0.45	0.34	0.36
DoS-factor		115.20	96.17	47.33	59.85	26.60	38.39
Alite (C_3S)		66.45	66.97	66.24	65.02	67.54	61.79
Belite (C_2S)		14.73	14.72	14.17	15.44	13.49	19.03
Aluminate (C_3A)		5.94	5.81	4.34	4.30	5.10	5.01
Ferrite (C_4AF)		8.76	8.61	12.26	12.05	10.99	11.11

TGA analyses of the three ARM samples used in the different alternative CCMs are presented in **figure 10.12.** The analyses clearly show that the ARMs have mass losses due to dehydration of hydration products between 100 and 650°C, as well as small but quantifiable decarbonation peaks around 700°C when heated up. The hydration products result from the reacted cement whereas the carbonated products probably come from limestone or carbonation products originating from the used aggregates or reacted cement present in the recycled concrete. These mass losses resulting from dehydration and decarbonation reactions could vary based on the composition of the recycled concrete as explained.

TGA analysis (**Figure 10.12.**) shows that both the dehydration and the decarbonation mass losses are larger in ARM/CTP and ARM/KHD compared to ARM/ADR which is also undersigned by the measured Loss Of Ignition (LOI) in **table 10.3.** This proofs that percentage wise more hydrated cement as well as limestone is present in ARM/CTP and ARM/KHD compared to ARM/ADR which is also confirmed by the chemical composition of both ARMs presented in **table 10.3.**

As shown in **table 10.4.**, limestone CRM dosages decreased by maximising the different ARMs in the alternative CCMs of Antoing, Lixhe and Maastricht. TGA analyses visualised in **figures 10.13.** and **10.14.** and evaluated in **table 10.7.** show small but significant decreases in decarbonation mass loss between the reference and alternative CCMs.

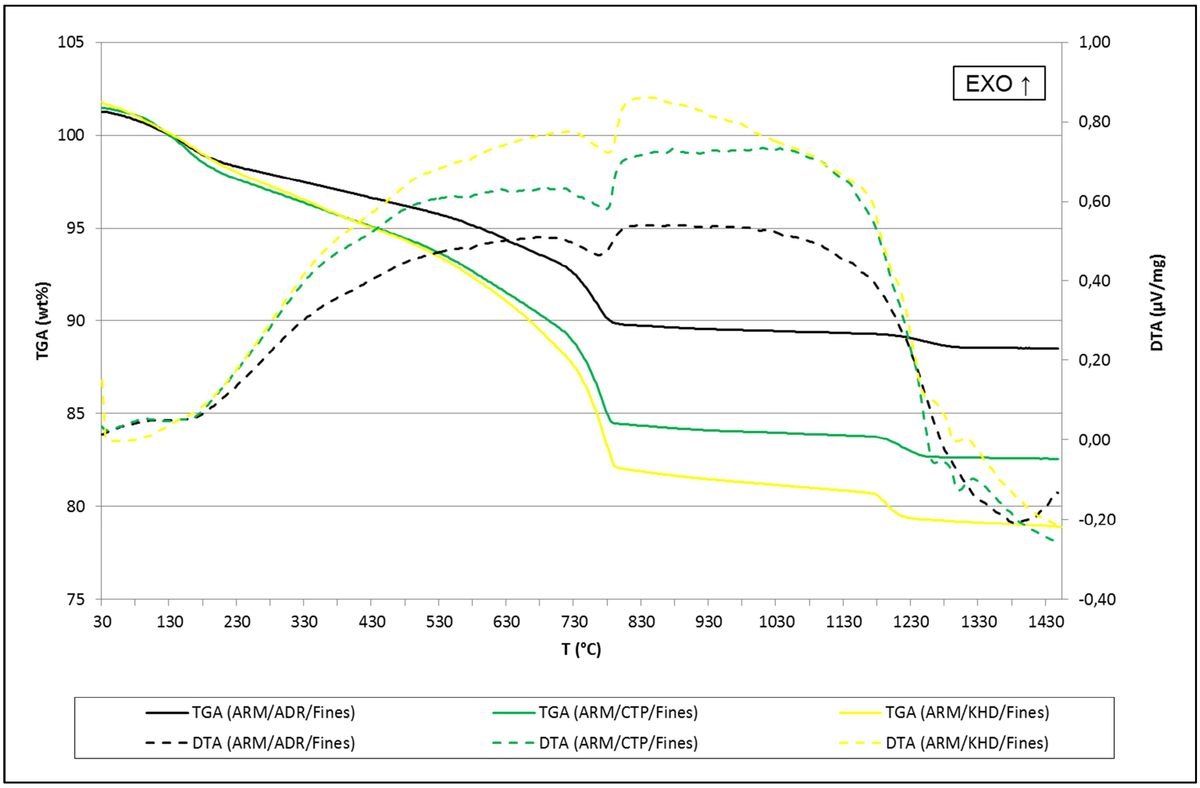

Figure 10.12.: TGA/DTA analysis of the three selected ARM fines for CCM and final production

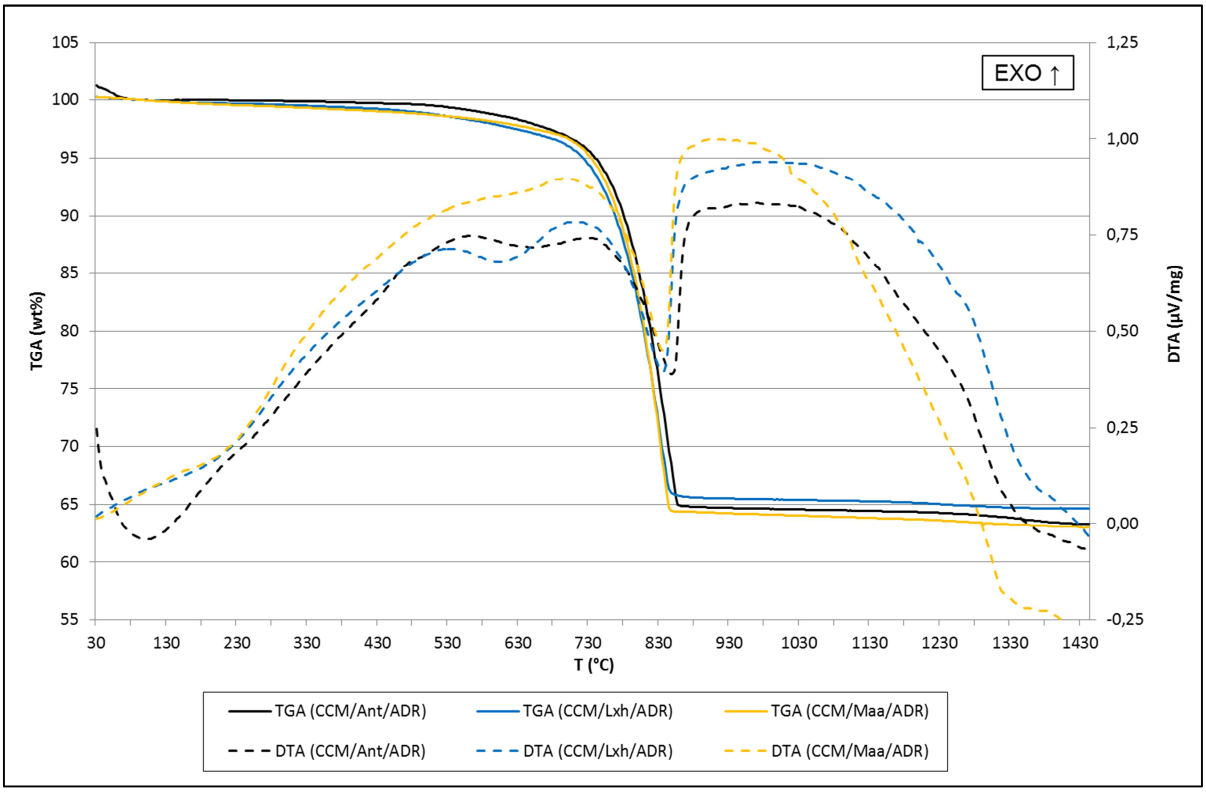

Figure 10.13.: TGA/DTA analysis of the CCM produced
for the three clinker factories with ARM/ADR

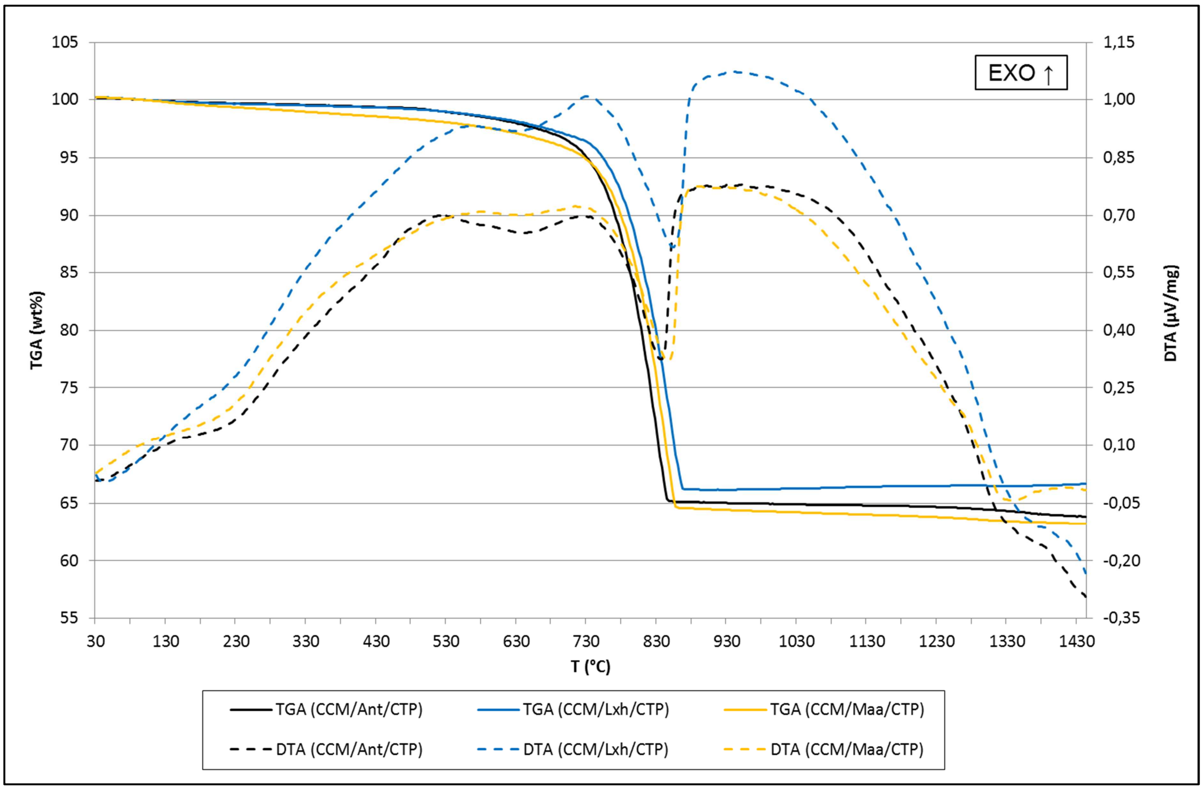

Figure 10.14.: TGA/DTA analysis of the CCM produced
for the three clinker factories with ARM/CTP

The difference between the intrinsic inorganic CO_2 based on the possible presence of CaO *[wt%]* and MgO *[wt%]* in carbonated form and the inorganic CO_2 measured by TGA (**Table 10.7**.), shows that using these ARMs could lower the inorganic CO_2 emission in Portland clinker production.

Table 10.7.: TGA/DTA evaluation of both alternative and reference CCMs
of CBR Antoing, CBR Lixhe and ENCI Maastricht

CCM	Inorg CO_2	Total CaO	Total MgO	Intrinsic Inorg CO_2
Mat	TGA Meas (wt%)	XRF Meas (wt%)	XRF Meas (wt%)	XRF Der (wt%)
CCM/Ant/Ref	34.0	43.48	1.10	35.32
CCM/Ant/ADR	31.8	43.89	1.07	35.61
CCM/Ant/CTP	31.5	44.35	1.05	35.95
CCM/Lxh/Ref	32.5	45.26	0.88	36.48
CCM/Lxh/ADR	30.7	44.77	0.88	36.09
CCM/Lxh/CTP	30.8	45.36	0.93	36.61
CCM/Maa/Ref	34.2	44.79	0.97	36.21
CCM/Maa/ADR	31.7	45.18	0.93	36.47
CCM/Maa/CTP	30.3	44.37	0.94	35.85

This is quite logical because the decreased limestone CRM dosages have a much bigger impact on the decarbonation mass loss of the final alternative CCM than the carbonated material brought by the different ARMs into the alternative CCMs.

10.8.5. XRD Analysis and the grindability of the different ARMs

Because the chemistry of the alternative clinkers was comparable with this of their reference as mentioned in **paragraph 10.8.4.**, Bogue equations based on the chemical analysis of the final clinkers were quite similar (**Tables 3.6.** and **10.6.**). The raw meal fineness will have its influence particularly on the formation of the liquid phase and the growth rates of silicate crystals **[30]**.

Out of **figures 10.15.** and **10.16.**, it is clear that the coarsest of the fines ARM, ARM/ADR, will have sufficient grindability to replace CRM/Lxh/Lo and CRM/Maa/SC as SiO_2-sources in the alternative CCM. The grindability of ARM/ADR is comparable with that of CRM/Lxh/Lo and although ARM/ADR has to be dosed 3 times more than CRM/Ma/SC (**Table 10.4.**) which has a worser grindability than the two others, their grindability as a function of SiO_2 *[wt%]* will be comparable.

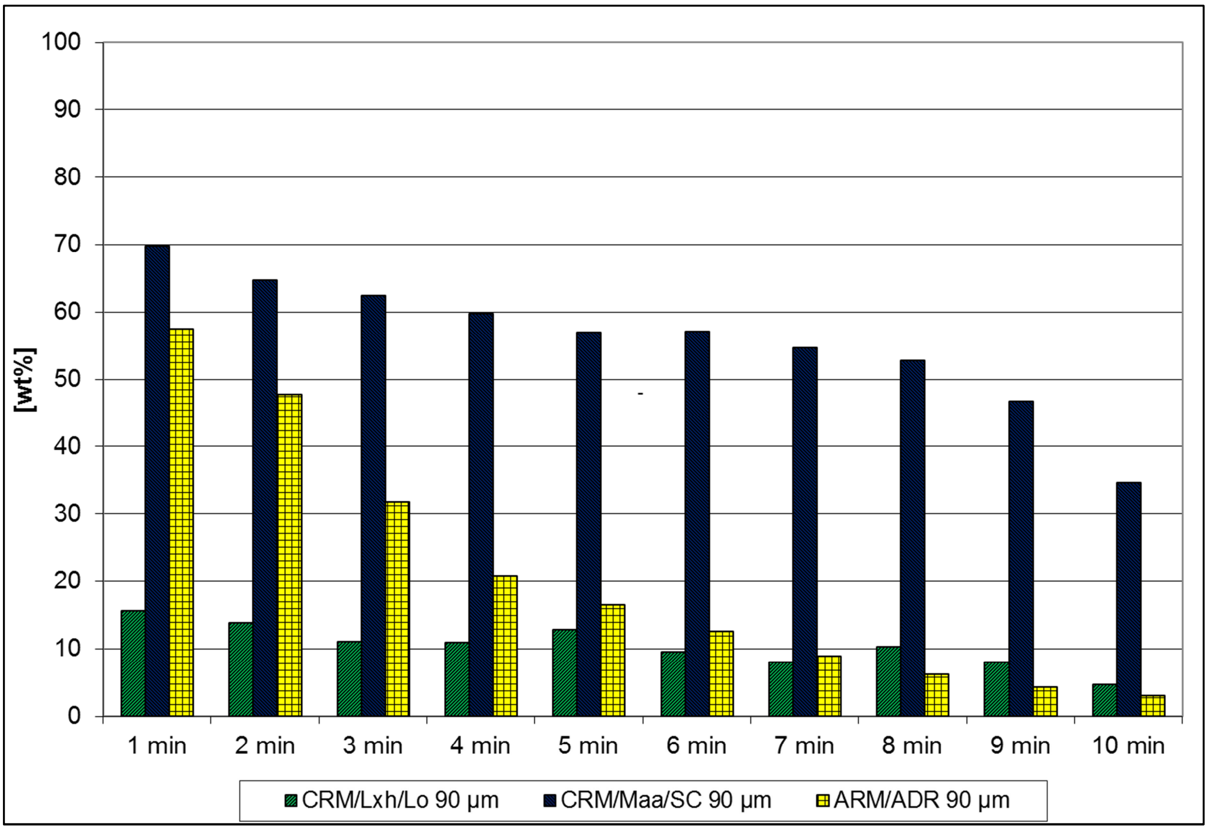

Figure 10.15.: Residue on the sieve of 90 µm for classic SiO_2-sources and the ARM/ADR after 1-10 minutes grinding time

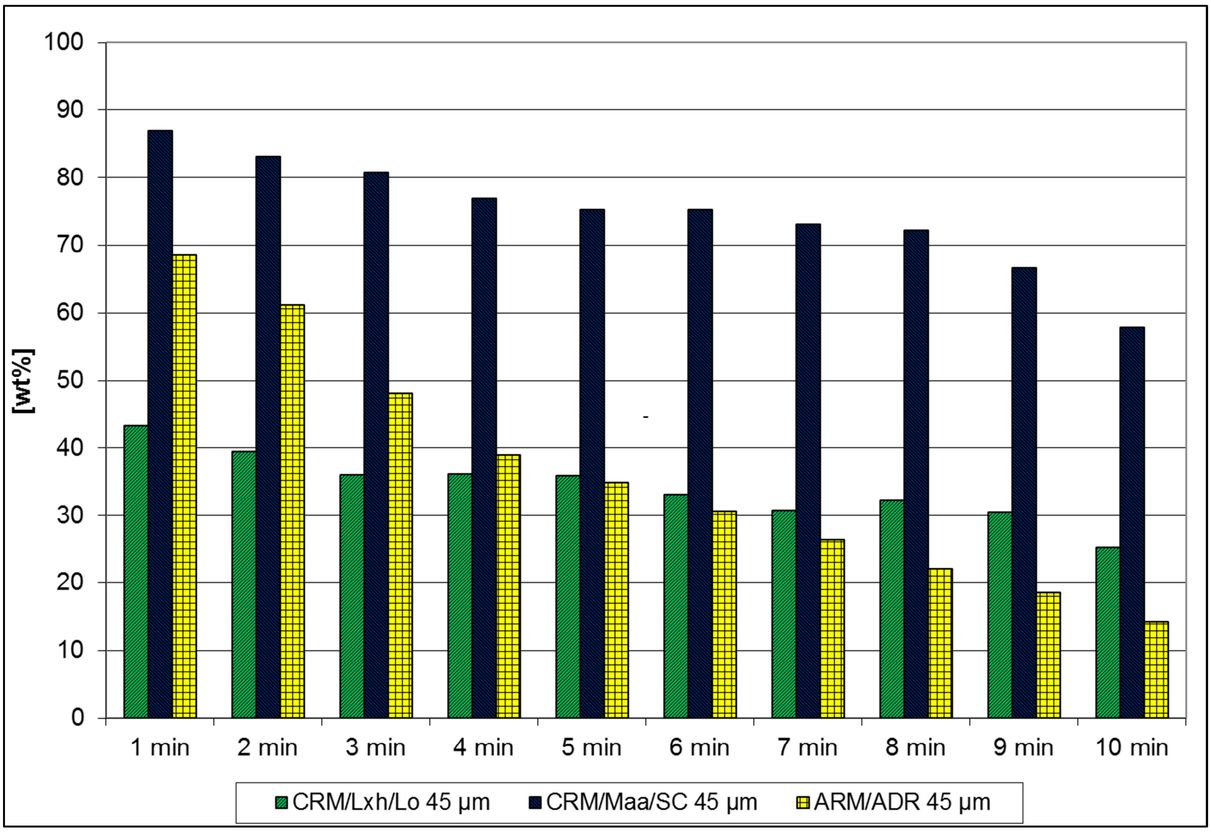

Figure 10.16.: Residue on the sieve of 45 µm for classic SiO_2-sources and the ARM/ADR after 1-10 minutes grinding time

The fineness of quartz is found to have a very strong effect on the CCM burnability **[32-33]**. In fact the maximum permissible particle size of quartz is recommended to be 45 µm **[31]**, as described in **section 2.8.**, although these values are not used in clinker factories as steering parameters. Target finenesses of the CCM are described to be maximum 12 wt% residue on a 90 µm sieve and 2.6 wt% on a 211 µm sieve **[32]**. This explains why residues on the sieves of 45 µm and 90 µm were chosen to evaluate the grindability of the ARM.

The grinding time is a relative parameter with as only reason, to compare the different SiO_2-sources and ARM mutually. This is demonstrated by the burnability of the alternative CCM undersigned by the low free CaO *[wt%]* of their corresponding clinkers (**Table 10.8.**).

The XRD analysis with Rietveld refinement of the reference clinkers presented in **table 3.8.** and the final alternative clinkers presented in **table 10.8.**, show mineralogical weight percentages that are comparable with those calculated by the Bogue equations but nevertheless have significant differences. The reason can be found in the DoS-factors of the alternative CCMs.

Table 10.8.: Mineralogical analysis by XRD of the Final Clinkers with ARM/ADR and ARM/CTP

Clinker		CL/Ant/ ADR	CL/Ant/ CTP	CL/Lxh/ ADR	CL/Lxh/ CTP	CL/Maa/ ADR	CL/Maa/ CTP
Alite (C_3S)	(wt%)	66.56	65.90	57.56	66.34	61.48	55.91
Belite (C_2S)	(wt%)	18.45	19.74	24.22	15.81	21.42	26.25
Aluminate (C_3A)	(wt%)	1.85	2.25	3.04	3.41	4.31	2.99
Ferrite (C_4AF)	(wt%)	12.50	11.63	14.43	14.83	12.11	14.30
Free Lime (CaO)	(wt%)	0.11	0.07	0.34	0.51	0.22	0.03
Periclase (MgO)	(wt%)	0.26	0.25	0.22	0.05	0.37	0.28
Arcanite (K_2SO_4)	(wt%)	0.07	-	-	-	-	0.01
Aphthitalite	(wt%)	0.10	-	0.09	-	-	0.13

(Full XRD analysis of Cl/Maa/ADR in Figure A.7. (Appendix A))

Although all CCMs were designed to have DoS-factors between 80 and 120, many of the final clinkers didn't achieve this goal. The lower the DoS-factor, the bigger the difference between the alite *[wt%]* measured by XRD and the alite *[wt%]* calculated by Bogue which was already extensively explained in **section 2.6.** As of the moment free alkali are present in the hot clinker because no sufficient SO_3 *[wt%]* is available to combine all alkali into sulfates, viscosity of the melt is increased resulting in a decrease the alite formation **[29]**. The reason of this unbalance between alkali and SO_3 *[wt%]* is due to the different volatility of Cl, SO_3 and alkali in a static lab furnace compared to a real clinker kiln (**Section 3.3.**). The alternative clinkers of CBR Antoing, both attained DoS-factors between 80 and 120 and had identical alite *[wt%]* measured by XRD and calculated with Bogue. For both the alternative clinkers of CBR Lixhe and ENCI Maastricht, DoS-factors were lower than 80. This resulted in alite *[wt%]* measured by XRD lower than these calculated by Bogue for both alternative clinkers of ENCI Maastricht and the CL/Lxh/ADR. Because ARM/CTP consists out of more SO_3 *[wt%]* than ARM/ADR, the DoS-factor was apparently sufficient high in CL/Lxh/CTP to have comparable alite *[wt%]* in XRD analysis and Bogue calculation.

Nevertheless, it can be concluded that in case DoS-factors were maintained between 80 and 120, the investigated ARM wouldn't influence the mineralogy of the clinker in a negative way.

10.9. Ecological benefit

The use of fines coming out of recycled concrete aggregates production as ARM for Portland clinker production could have different positive ecological advantages in line with Cement Sustainability Initiative but which have to be quantified in a LCA-study to be objectively evaluated. Based on the guidelines of the LCA process (**Section 4.4.**), different principles as cradle to grave, cradle to cradle or cradle to gate, can be used to demonstrate the possible ecological benefit by using recycled fines or sludge out of recycled concrete aggregates production as ARM in Portland clinker production. As demonstrated in **section 10.8.**, the used technique to separate the fines from the recycled aggregates fraction will influence differently the raw materials composition of the CCM.

- EPD of Portland clinker (cradle to gate):

  Recycled concrete fines could reduce the required volume of limestone as well as the used SiO_2-source based on their chemical composition. The lower the SiO_2 *[wt%]*, the higher the maximisation of the fines will be. As demonstrated in **section 10.8.**, an increased replacement of the limestone by the fines results in a lower inorganic CO_2 emission as well as a decreased required decarbonation energy. Nevertheless the introduction of hydrated cement derivatives by the fines will increase the chemical bound H_2O *[wt%]* in the CCM. This means that by an increasing decarbonated CaO *[wt%]* coming from the cement derivatives, a related increase of chemical bound H_2O *[wt%]* will be present, reducing the energy savings. This means that the chemical as well as the mineralogical composition of the fines will have a direct influence on the LCA of the Portland clinker production. Furthermore the EPD of the fines has to be balanced with the EPDs of the limestone and the SiO_2-source which the fines will replace.

- EPD’s of the other related processes (cradle to gate):

  An improved EPD of Portland clinker will have a positive impact on the EPD of Portland cement. Nevertheless, industrial practice will be necessary to fine-tune the EPD calculation of Portland cement. The influence of the PSD of the SiO_2 coming from the recycled concrete fines on the clinker burnability and therefore the clinker quality have to be quantified as well as the influence of minor components as SO_3, alkali, MgO, ZnO, etc. on the sintering of the clinker and the hydration reactions of the Portland cement. These parameters will have their influence on the required grinding energy and required fineness of the final Portland cement necessary to obtain the same characteristics as the classic Portland cement in terms of strength development and others. Also the EPDs of other cement types which EPD’s will be less but still considerably influenced by the Portland clinker, have to be investigated.

  Valorisation of the recycled concrete fines in Portland clinker could also improve the EPD of recycled concrete aggregates. The biggest improvement will come from skipping landfill by the reuse and the improved valorisation of the concrete demolition waste. Nevertheless, the EPDs of both recycled concrete fines and aggregates will also be strongly influenced by the used separation technique and the possible upgrade it represents for both Portland clinker and concrete applications. Energy will be spent during demolition, collection, transport and treatment of the concrete waste. The required energy for an improved valorisation of the different recycled concrete fractions should therefore be in balance with the impact it will represent to the EPDs of the alternative Portland clinker and concrete.

  For example, out of **section 10.8.** it was clear that the improvement of the recycled concrete fines and aggregates was less effective with the ADR separation technique than for both CTP and KHD techniques. On the other hand, the ADR installation can be fed with a much coarser wet aggregate fraction by which extra separation and drying energy is avoided.

Therefore, realistic EPDs of these recycled concrete fines and related aggregates fractions can only be objectively calculated with industrial practice which takes in account energy spent on demolition, collection, transport and treatment but also the upgrade of the recycled concrete aggregates as a function of the improvement of the ecological footprint, they represent in the related concrete.

- Cradle to grave / Cradle to cradle:
  The use of recycled concrete fines in Portland clinker and recycled concrete aggregates in concrete, demonstrates that cement as well as primary aggregates are recyclable, which shifts the use of these materials from a cradle to grave towards a cradle to cradle assessment. The required energy to produce a primary aggregate could therefore be divided over a longer life span which could improve the ecological impact of the primary aggregates production. Also the decarbonation energy necessary to deliver decarbonated CaO for Portland clinker could be seen as a one-time investment if recycled concrete fines are re-entered in the Portland clinker production. Whether or not these ecological benefices will be retained, will depend of the target definition and scope of the LCA calculation (**Section 4.4.**).

Based on the results of this study and the cited influences on the LCA calculation, it cannot yet be concluded that the use of recycled concrete fines as ARM for Portland clinker production will be ecologically beneficial. Nevertheless, the use of these fines is in line with the Cement Sustainability Initiative (**Section 4.2.**). The recycled concrete fines will have their influence on two of the five Key Performance Indicators of the Cement Sustainability Initiative: Climate change management as well as fuels and materials use.

10.10. Conclusions

By this study, it was shown that the fines fractions generated out of concrete recycling could be used as an Alternative Raw Material (ARM) for Portland clinker production. However, a homogenisation phase adapted to the chemical variation of the recycled fines will be crucial. Nevertheless, the way these fines fractions are generated, will have a direct impact on the particle size distribution, the chemical composition and the generated quantity of the ARM and therefore also on their intrinsic properties as ARM. It was demonstrated that the smaller the fines fractions are cut from the sand fraction, the better they are suited as ARM for Portland clinker production.

The way these fines fractions are separated also influences the final quality of the treated sand fraction and therefore also its use in concrete as well as asphalt applications.

It was shown that the three generated ARM could replace Classic Raw Materials (CRM), primarily SiO_2-sources, but also limestone CRMs by an increasing CaO *[wt%]* of the ARM. The physical and chemical bound H_2O, which is present at a larger extent in the ARM than in the CRM, will consume more energy during evaporation. The possible energy gain coming from the lowered decarbonation energy as well as the decrease in inorganic CO_2-emission, will be quite small because of the small replacement capacity of these ARM due to their high SiO_2 *[wt%]* and the presence of limestone coming from the aggregates or fillers used in the recycled concrete. Together with the energy consumption needed for the liberation of the chemically bound H_2O, energy gain by using these ARMs will be negligible.

No major influence on the mineralogy of the final clinker was demonstrated by using these specific recycled fines as alternative raw material. The positive effect on the ecological impact of Portland clinker production is that a primary natural material could be replaced by a secondary recycled material.

Furthermore, an upgrade of recycled aggregates could be established which is an advantage as a function of their practical use. Therefore, the use of fines extracted from recycled concrete should be considered as a way to get in line with the Cement Sustainability Initiative, together with the already available alternative fuels and raw materials.

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Chapter 11

Conclusions and perspectives

The importance of sustainable living has become an integral part of our society. Hybrid cars, solar panels, windmill parks, energetic friendly housing are all efforts where industry and society tries to decrease their ecological impact on environment. Sustainability has indeed to be a collaboration between industry, society and environment **[1]**. This collaboration is visualised in a simple and well-known diagram in **figure 11.1.**

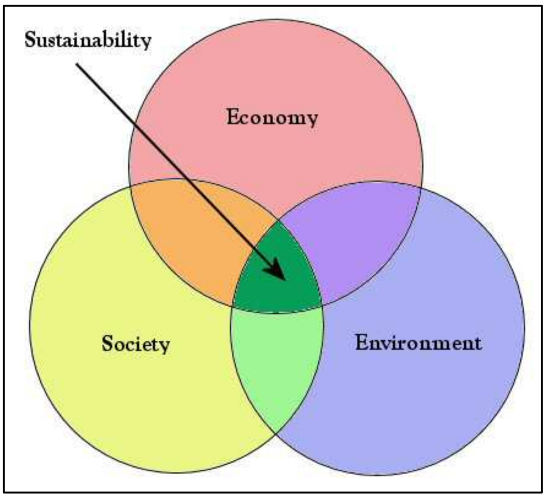


Figure 11.1.: Sustainability as collaboration model **[1]**

Nevertheless sustainability cannot be seen as a trade-off between these three pillars because they are not equivalent.

Economy emerges from society whereas environment is influenced but not directly related to economy or society.

Nevertheless economy and society are underpinned by environment which underlines the importance of the collaboration between those three pillars.

The resources available on earth, the capacity of the biosphere to absorb pollutants and the impact of human activity on ecosystems or species, present limits for human activities which implies that sustainable development becomes more and more an ethical question. This importance is gradually taken up by several industries. Companies, even when they are not adapting voluntarily, are obliged by economic necessity or by governmental pressure to decrease their ecological impact.

In this view, the European Union have set binding regulations to meet some ambitious climate and energy targets for 2020. These targets, known as the "20-20-20" targets, set three key objectives which are also visualised in **figure 11.2.**:

- A 20% reduction in EU greenhouse gas emissions from 1990 levels.
- Raising the share of EU energy consumption produced from renewable resources to 20%.
- A 20% improvement in the EU's energy efficiency.

The EU is even offering to increase its emissions reduction to 30% by 2020 if other major economies in the developed and developing worlds commit to undertake their fair share of a global emissions reduction effort.

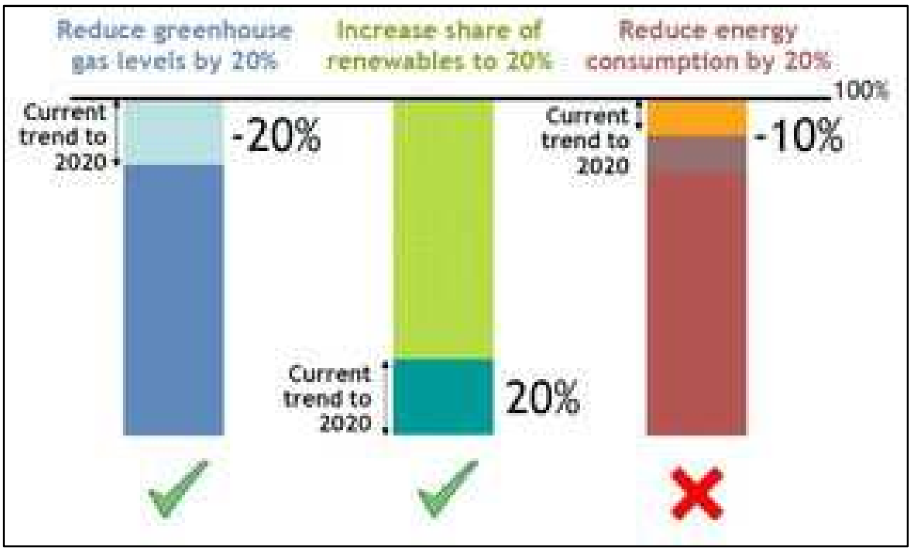


Figure 11.2.: EU 20-20-20 targets (Ref. http://geospatial.blogs.com [cited 2014 Aug 27])

Also the European cement industry is adapting in this direction.

Cembureau for example, describes in their document about co-processing of alternative fuels and raw materials in the Cement Industry **[2]**, the interaction between the cement industry, society and ecology (**Figure 11.3.**).

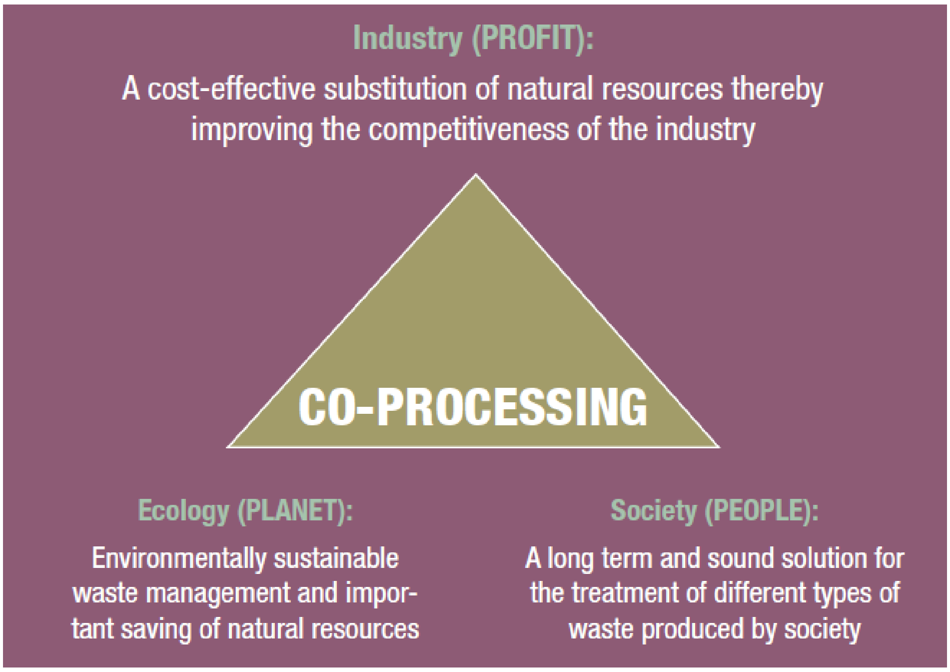


Figure 11.3.: Co-processing model of Cembureau **[2]**

This document describes indeed that sustainable development can be economically beneficial and could deliver durable solutions for different types of wastes without altering the final cement quality.

Another example of how the cement industry is coping with its ecological impact is by the cement sustainability initiative which was developed at international level in cooperation with the WBCSD **[3]**, as was already extensively explained in **section 4.2.**

Both examples clearly show that the use of alternative fuels and raw materials is one of the key factors in the ecological strategy of the cement industry. The use of these alternative resources could provide numerous benefits as a reduced need for quarrying, an improved environmental footprint and reduction of landfill by waste which has his benefits for economy, society and environment.

Nevertheless as demonstrated in this PhD study, the use of Alternative Raw Materials (ARMs) in the Cold Clinker Meal (CCM) although in line with the cement sustainability initiative, is not always ecologically beneficial. The key issue in using recycled materials or by-products is the energy it would cost to generate a useful raw material and the impact it will have on the production process and final Portland clinker quality. Objective ecological calculations as for example a Life Cycle Assessment (LCA) have to be made to unveil whether or not the use of an ARM will have a positive ecological impact on the Portland clinker process and the other related processes.

These ecological calculations have to incorporate some typical parameters which were raised during this PhD study and which demonstrate their fitness for Portland clinker production (**Section 4.3.**). These parameters could be defined as basic rules based on which future materials could be evaluated for use as Alternative Raw Material.

- Chemical variation:

  When using ARMs in Portland clinker production, their chemical variation is very important for the preparation of the alternative CCM. As could be noted out of **sections 2.2.** and **2.5.**, the dosages of the different raw materials have to be closely monitored to guarantee a stable chemical composition of the CCM. To guarantee this stable chemical composition, clinker factories have defined minor and major limits for the variations of the four major metal oxides: CaO, SiO_2, Al_2O_3 and Fe_2O_3 (**Table 2.2.**).

  The maximum chemical variation that can be accepted of an ARM is in direct relationship with its foreseen dosage *[wt%]* that will induce an acceptable chemical variation for the alternative CCM. When investigating the fitness of an ARM, a realistic estimation of this chemical variation is the first parameter that has to be checked based on which the maximum dosage can be defined.

  A long sampling period, a big amount of collected samples and sometimes a geographical dispersion for the sampling makes it possible to have a good interpretation of the chemical as also the mineralogical variation of the sludge samples in an objective way.

  Based on their chemical variation, it could be concluded that fibrecement out of production waste, porphyry fines and clean cellular concrete could be used as ARM in significant dosages. After a homogenisation phase, also dolomitic limestone, polluted cellular concrete and recycled concrete fines could be suited for Portland clinker production. Probably fibrecement will also need a homogenisation phase when recycled out of a demolition waste stream but this has to be further investigated. Concrete sludge can up to this moment be catalogued as unsuited for Portland clinker production although a hypothesis was set which states that when the SO_3 *[wt%]* of concrete sludge could be closely monitored, the collection out of the sludge basin could be performed in a way which would lower the chemical variation of the concrete sludge to an acceptable level suited for use as ARM for Portland clinker production.

- Organic constituents:

  The presence of organic constituents, although better avoided, is not insurmountable in an ARM. Nevertheless the amount of organic constituents as well as the targeted dosage of the ARM will have their influence on the place where these ARMs can be introduced in the Portland clinker kiln to avoid clogging and exceeding emission limits. These ARMs should be introduced at a hot point in the process, e.g. a pre-calciner or a pre-heater, to ensure full thermal degradation.

  The potential energy loss by skipping the cyclone tower as energetically most profitable way to heat up this type of materials will be related to the endothermal energy needed to heat up the ARM. The required decarbonation and dehydration energy will be therefore decisive for the ARMs fitness for Portland clinker production. Whether or not an ARM, containing partly organic constituents, can be used in a Portland clinker kiln, will be related to the specific technical installation and/or the emission limits valid for the country or region where the kiln is located. Nevertheless, the possibility of a kiln to manage organic constituents in its ARM creates the possibility to accept materials which cannot be recycled in another way due to the presence of these organic constituents and/or which would have a big ecological impact if disposed as landfill.

  The valorisation of such materials could have a big ecological advantage and would also be beneficial for society. Examples of these materials are fibrecement which contains organic constituents partly consisting out of biomass in the form of cellulose. It was demonstrated that FC lowers the total required energy compared to the use of classic raw materials by the exothermal decomposition of organic fibres and the decreased decarbonation energy without compromising neither on physical, chemical nor mineralogical properties.

  Also cellular concrete is an example that together with inorganic recycled demolition waste also organic materials as plastics, glues, wood, etc. could be introduced in the Portland clinker production which will have an influence on the fitness as ARM.

- Chemical composition:

  Naturally the chemical composition of the ARM will play an important role in the fitness of a specific material as ARM, but also on its maximisation in the Portland clinker process. An important part of the ecological benefit will be the presence of decarbonated CaO and the related decrease in inorganic CO_2 emissions as well as decarbonation energy.

  As mentioned in **section 2.2.**, four major metal oxides have to be in balance to create a Portland clinker after sintering. In most cases, a Portland kiln will use four Classic Raw Materials (CRM) that are specifically chosen because of their excess in one of the four metal oxides. In most ARM, comparable CaO *[wt%]* and SiO_2 *[wt%]* are present, supplemented with smaller quantities of Al_2O_3 *[wt%]* and Fe_2O_3 *[wt%]* instead of an excess in one of the four metal oxides. This means that maximisation of these ARMs will be limited mostly by the present SiO_2 *[wt%]* as was demonstrated in the different chapters.

In the case the ARM cannot replace one of Classic Raw Materials (CRM) completely, an additional raw material for the CCM will be created. Technical adaptations or investments will in most of the cases be necessary to incorporate ARMs in the Portland clinker process.

Secondly, when using ARMs containing cement derivatives, significant levels of SO_3 *[wt%]* will be brought in the Portland clinker process. A was explained in **paragraph 2.3.2.**, increased levels of SO_3 *[wt%]* can be managed to a greater or lesser extent in a Portland clinker kiln but will nevertheless act as additional limit for the maximisation of ARMs in the CCM. Also minor metal oxides as MgO *[wt%]*, ZnO *[wt%]* and others have to be monitored closely, being also the case for all classic raw materials. In the sludge from the water treatment system of concrete plants for example, the finer fractions of the various raw materials of the concrete are specifically gathered by which the cement content in the sludge samples and their specific fines fractions is much higher than in normal recycled concrete.

Thirdly, also the presence of physical and chemical bound H_2O will be an important parameter as a function of the required energy during dehydration and evaporation.

The chemical composition of an ARM will therefore be crucial for its fitness as ARM and the possible ecological improvement it could create as a function of energy consumption, CO_2 emissions and possible fluxing effects within a Portland clinker process.

Within the current research of the five ARMs, the air-cured fibrecement materials had the best chemical composition for ARM maximisation, but also as a function of a decreased decarbonation of the required CaO. On the other hand, porphyry fines showed a possibility to replace an expensive and pozzolanic raw material and could also generate a fluxing effect in specific situations. Most of the ARMs had more or less, physical and chemical H_2O present in their chemical composition.

- Particle Size Distribution as a function of the mineralogical composition:

  As could be noted out of **chapters 2**, **6**, **8** and **9**, not only the particle size distribution but also the mineralogical composition of each of the different particle size fractions will be of great importance to the fitness of a material as ARM for Portland clinker production. The mineralogical composition of the CCM will determine the energy necessary to grind the CCM to sufficient fineness. As was demonstrated in **section 2.8.**, a direct relationship can be noted between the burnability of the Portland clinker and the fineness of each of the four major metal oxides. Especially the SiO_2 fraction has to be ground the finest which presents the biggest struggle for most ARMs collected out of construction materials due to the presence of quartz sand.

Quartz has the property to be difficult to grind which will require additional grinding energy for CCM preparation as well as higher targeted finesses to guarantee optimal Portland clinker reactivity.

Most CCMs are prepared with target values for the fractions smaller than 200 and 90 µm (**Section 2.8.**) where the biggest part of SiO_2 *[wt%]* has to be ground smaller than 45 µm to guarantee good burnability of the Portland clinker. It can be stated that monitoring CCM fineness by residues on 90 µm and 200 µm is not sufficient to guarantee good burnability when using ARMs with poor grindability as a function of their SiO_2 *[wt%]* which replaces CRMs as SiO_2-source in Portland clinker production. In that case, monitoring CCM fineness by residues on 45 µm and 63 µm sieves will be a necessity.

The additional grinding energy consumption and/or impact on the Portland clinker reactivity or the required energy of a possible preparation phase to reduce the presence of the coarse quartz fraction, have to be taken in account during the objective evaluation of the ecological benefice of an ARM.

Within this research, cellular concrete, recycled concrete and concrete sludge showed difficulties regarding the fineness of their SiO_2 fraction.

- ARM preparation:

  By using a specific preparation phase, an ARM out of a recycled material or by-product can be adapted and even improved as a function of its chemical variation, the presence of organic constituents, chemical composition as well as its particle size distribution. It is very important to evaluate the efficiency of these preparation phases for the property that is supposed to be altered. From an ecological point of view, a preparation phase will consume energy which has to be valorised in an improved fitness of the resulting ARM for Portland clinker production, to be ecologically beneficial. Techniques demonstrated prosperous for example to create an ARM out of recycled concrete, were not successful for concrete sludge. When a separation technique was used on 250 µm, it was demonstrated that a separated fines fraction on 250 µm does not have an improved chemical composition and variation in case of concrete sludge in comparison with recycled concrete. Nevertheless, an improved burnability within the alternative Portland clinker was noticed.In the case the particle size distribution of the SiO_2 fraction was too coarse, a separation phase on 250 µm gave good results as a function of the burnability of the Portland clinker. The same technique also decreased the chemical variation in the recycled concrete by collecting specifically the cement derivatives as ARM in the fraction < 250 µm as well as improved the fitness of the fraction > 250 µm as raw material for concrete as well as asphalt applications.

  Homogenisation phases, specific collection strategies as well as pre-grinding showed all to be efficient methods to improve the ARM fitness.

- Fluxing effects:

  Fluxing effects can have a beneficial effect on Portland clinker production by decreasing the energy consumption of the kiln or improve the Portland clinker reactivity. When these minor constituents can be brought in the CCM by an ARM, it can not only be ecologically but also economically beneficial. Nevertheless these minor constituents can also have a negative impact on the Portland clinker process when present in excess and should therefore be monitored closely.

  Within this PhD study, MgO was investigated as a cheap and effective mineraliser that can be brought in by by-products of porphyry and dolomitic limestone aggregates production or by recycled concrete if porphyry or dolomitic limestone should be present.

  It was demonstrated that in combination with alkali and SO_3, a decrease of the liquid formation temperature is noticeable by which equal mineralogical composition can be attained at 1350°C which could safely be considered in combination with the increased alite formation at 1450°C. The combined fluxing effect is not as distinct as this of CaF_2 but at the other hand easier and cheaper to introduce in a clinker kiln by the ARMs. The fact that it is harder for clinker producers to attain too low than sufficient SO_3 *[wt%]* and alkali *[wt%]* will be beneficial to induce this combined fluxing effect. The fine-tuning of MgO up to 2.0 - 2.5 wt% in Portland clinker could therefore be recommended to fully benefit the mineralogical advantages.

The evaluation based on the foregoing parameters made clear that three out of five investigated materials could be interesting alternative raw materials for Portland clinker production. Porphyry and to a lower extent dolomitic limestone by-products could replace fly ash and limestone with a preceding homogenisation phase in the case of dolomitic limestone. By a similar homogenisation phase, fibrecement could be a valuable ARM if introduced at a hot point in the Portland clinker process. When dosed in significant dosages, fibrecement could generate an inorganic CO_2 emission reduction as well as a related energy gain. Also, recycled concrete fines could replace classic SiO_2-sources and limestone by an increasing CaO content if preceded by an adequate homogenisation and separation phase. On the other hand, nevertheless it was proven that cellular concrete could replace classic SiO_2-sources in the raw material mix, the energy necessary to grind its coarse quartz sand fraction will limit its use as ARM due to energetic and qualitative restrictions. Also concrete sludge can be classified as an infeasible ARM due to insurmountable limitations based on the foregoing parameters. The extended conclusions for each of the five ARMs individually were already expressed in their assigned chapters.

Additionally, the hydration heat of Portland cement samples artificially made out of the reference and alternative Portland clinkers typically simulated and produced for CBR Lixhe, were measured by Tam Air analyse (**Section 3.7.4.**). Out of **figure 11.4.**, it was clear that there is an impact of the different ages of the Portland clinker samples due to prehydration by which the oldest Portland clinker samples had the lowest heat peaks. Nevertheless the similar dormant periods and hydration peaks demonstrate that there are no major impacts by the use of the ARMs on the hydration energy of the Portland cement and on the reactivity of the Portland clinker.

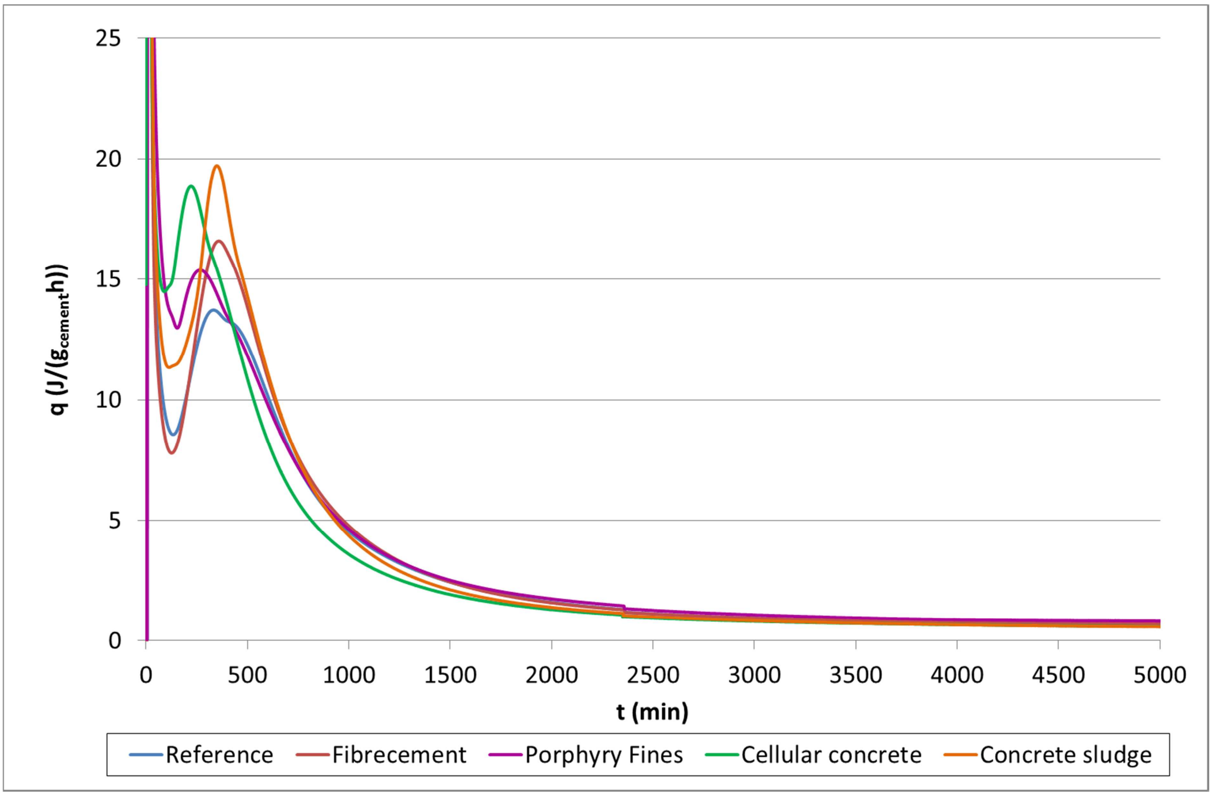


Figure 11.4.: The hydration heat during the first 7 days by an isothermal calorimetric test at 20°C on Portland cement samples made out of the reference and alternative Portland clinkers of CBR Lixhe

The major conclusion out of this PhD study is that the use of ARMs can be ecologically beneficial if they are selected, prepared and/or transported in the most efficient way and their impact on the Portland clinker process and the final Portland clinker quality is evaluated objectively by an ecological impact evaluation. It was demonstrated that using specific by-products or waste materials coming from the production and demolition of building materials as raw material for clinker production could lower the total required energy compared to the use of classic raw materials, without compromising neither on physical, chemical nor mineralogical properties. It is foreseen that in the next decades, the use of such materials will gradually increase and they will become a significant part of the raw material mix.

References

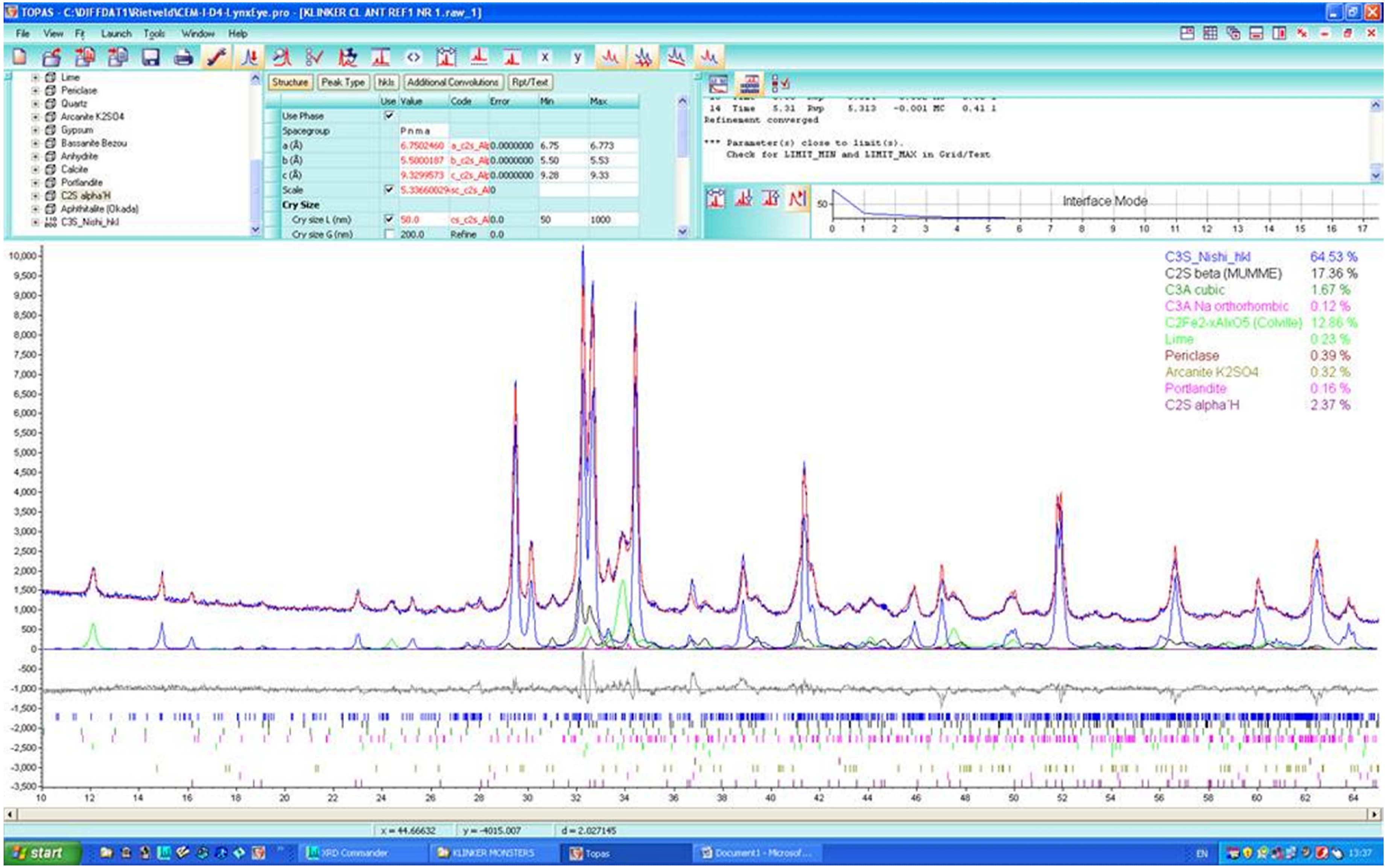
[1] W.M. Adams,The Future of Sustainability: Re-thinking Environment and Development in the Twenty-first Century, W.M. Adams,University of Cambridge, UK, Report of the IUCN Renowned Thinkers Meeting, 29-31 January 2006

[2] Sustainable cement production: Co-processing of Alternative Fuels and Raw Materials in the Cement Industry: CEMBUREAU, January 2009

[3] J.S. Damtoft, J.Lukasik, D. Herfort, D Sorrentino, E.M. Gartner, Sustainable development and climate change initiatives, Cement and concrete research 38 (2008) 115-127.

Appendix A

XRD analysis of some of the artificial made Portland clinkers



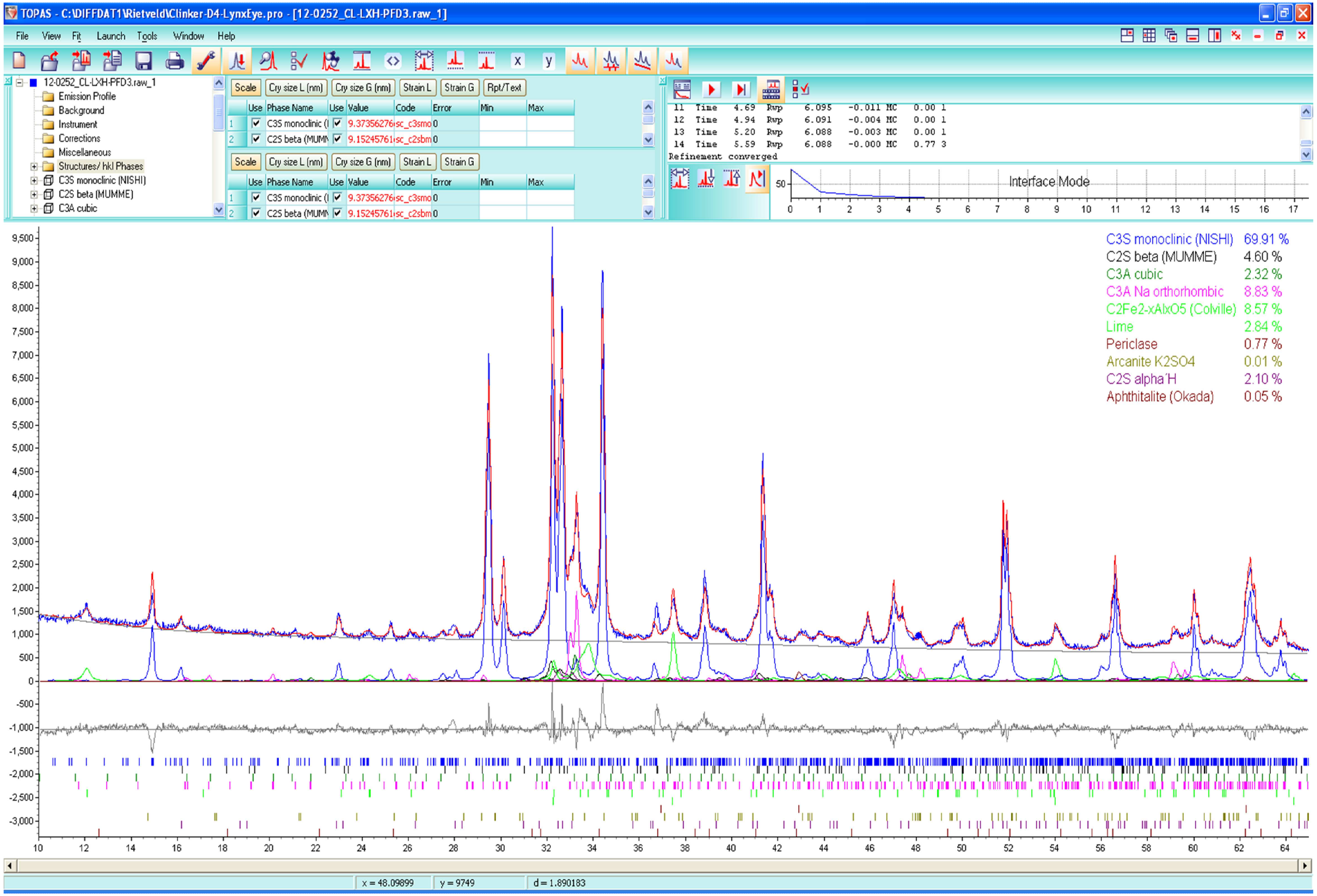
	Use	Value	Code	Error	Min	Max
Use Phase	☑					
Spacegroup		Pnma				
a (Å)		6.7502460	a_c2s_Al	0.0000000	6.75	6.773
b (Å)		5.5000187	b_c2s_Al	0.0000000	5.50	5.53
c (Å)		9.3299573	c_c2s_Al	0.0000000	9.28	9.33
Scale	☑	5.33660029	sc_c2s_Al	0		
Cry Size						
Cry size L (nm)	☑	50.0	cs_c2s_Al	0.0	50	1000
Cry size G (nm)	☐	200.0	Refine	0.0		

```
 14  Time    5.31  Rwp    5.313    -0.001 MC    0.41 1
Refinement converged

*** Parameter(s) close to limit(s).
    Check for LIMIT_MIN and LIMIT_MAX in Grid/Text
```

C3S_Nishi_hkl	64.53 %
C2S beta (MUMME)	17.36 %
C3A cubic	1.67 %
C3A Na orthorhombic	0.12 %
C2Fe2-xAlxO5 (Colville)	12.86 %
Lime	0.23 %
Periclase	0.39 %
Arcanite K2SO4	0.32 %
Portlandite	0.16 %
C2S alpha'H	2.37 %

Figure A.1.: XRD-analysis of Cl/Ant/Ref



TOPAS - C:\DIFFDAT1\Rietveld\Clinker-D4-LynxEye.pro - [12-0252_CL-LXH-PFD3.raw_1]

- 12-0252_CL-LXH-PFD3.raw_1
  - Emission Profile
  - Background
  - Instrument
  - Corrections
  - Miscellaneous
  - Structures/ hkl Phases
  - C3S monoclinic (NISHI)
  - C2S beta (MUMME)
  - C3A cubic

	Use	Phase Name	Use	Value	Code	Error	Min	Max
1	☑	C3S monoclinic (I	☑	9.37356276	sc_c3smo	0		
2	☑	C2S beta (MUMN	☑	9.15245761	sc_c2sbm	0		

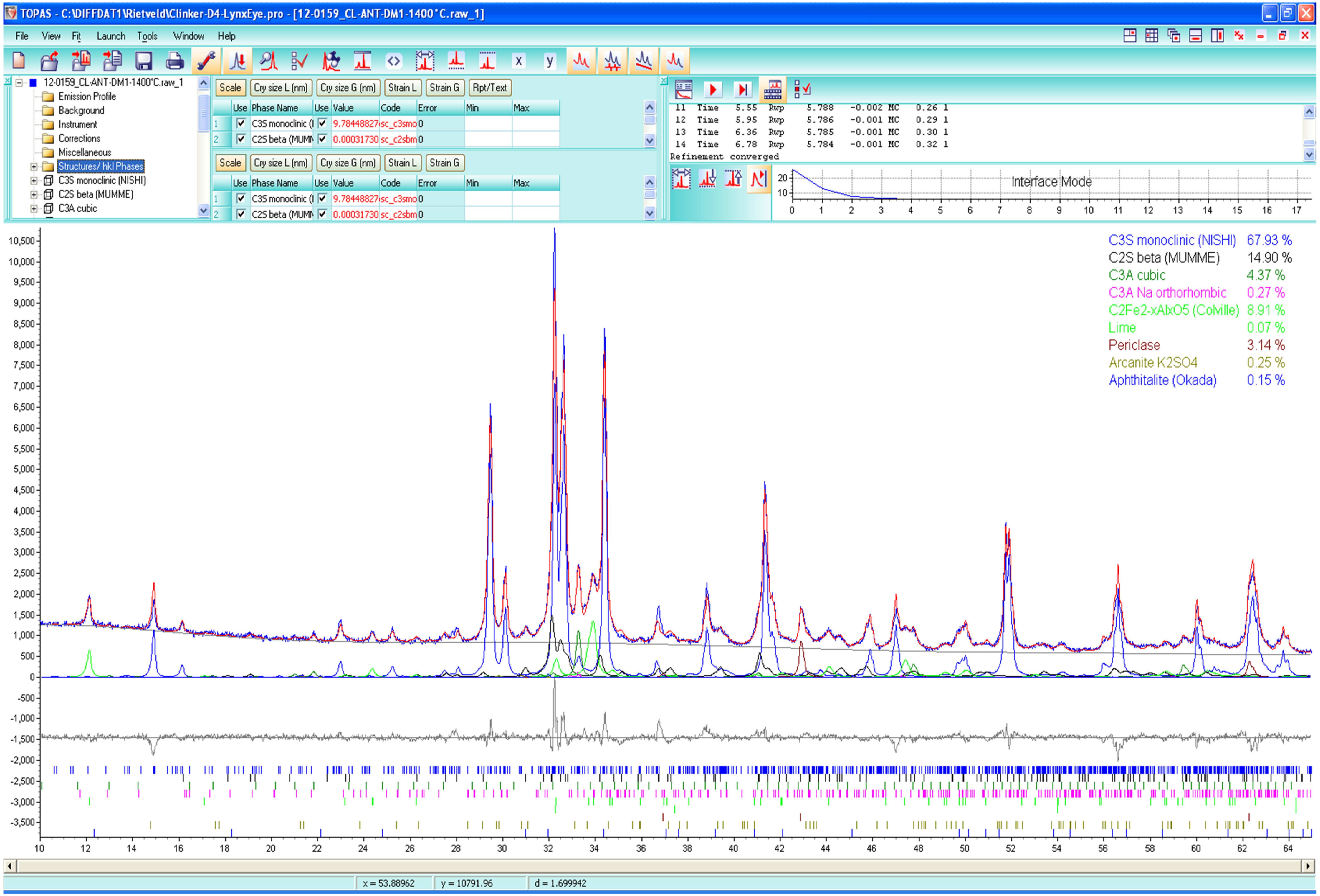
	Use	Phase Name	Use	Value	Code	Error	Min	Max
1	☑	C3S monoclinic (I	☑	9.37356276	sc_c3smo	0		
2	☑	C2S beta (MUMN	☑	9.15245761	sc_c2sbm	0		

```
 11  Time   4.69  Rwp    6.095   -0.011 MC   0.00 1
 12  Time   4.94  Rwp    6.091   -0.004 MC   0.00 1
 13  Time   5.20  Rwp    6.088   -0.003 MC   0.00 1
 14  Time   5.59  Rwp    6.088   -0.000 MC   0.77 3
Refinement converged
```

C3S monoclinic (NISHI)	69.91 %
C2S beta (MUMME)	4.60 %
C3A cubic	2.32 %
C3A Na orthorhombic	8.83 %
C2Fe2-xAlxO5 (Colville)	8.57 %
Lime	2.84 %
Periclase	0.77 %
Arcanite K2SO4	0.01 %
C2S alpha´H	2.10 %
Aphthitalite (Okada)	0.05 %

x = 48.09899 y = 9749 d = 1.890183

Figure A.2.: XRD-analysis of Cl/Lxh/PpF

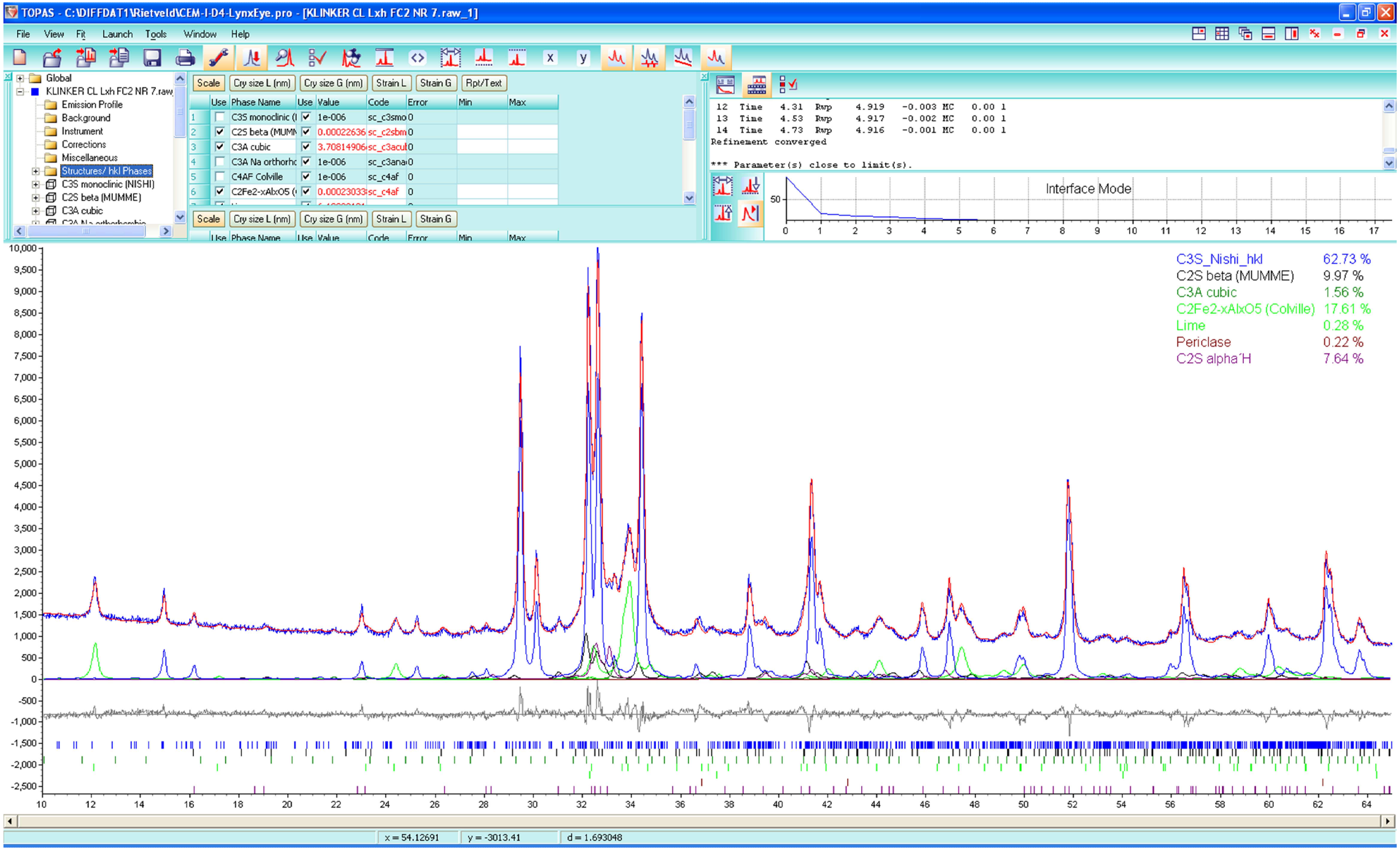


	Use	Phase Name	Use	Value	Code	Error	Min	Max
1	☑	C3S monoclinic (I	☑	9.78448827	sc_c3smo	0		
2	☑	C2S beta (MUMM	☑	0.00031730	sc_c2sbm	0		

	Use	Phase Name	Use	Value	Code	Error	Min	Max
1	☑	C3S monoclinic (I	☑	9.78448827	sc_c3smo	0		
2	☑	C2S beta (MUMM	☑	0.00031730	sc_c2sbm	0		

```
11  Time   5.55  Rwp    5.788   -0.002 MC   0.26 1
12  Time   5.95  Rwp    5.786   -0.001 MC   0.29 1
13  Time   6.36  Rwp    5.785   -0.001 MC   0.30 1
14  Time   6.78  Rwp    5.784   -0.001 MC   0.32 1
Refinement converged
```

Figure A.3.: XRD-analysis of Cl/Ant/DL



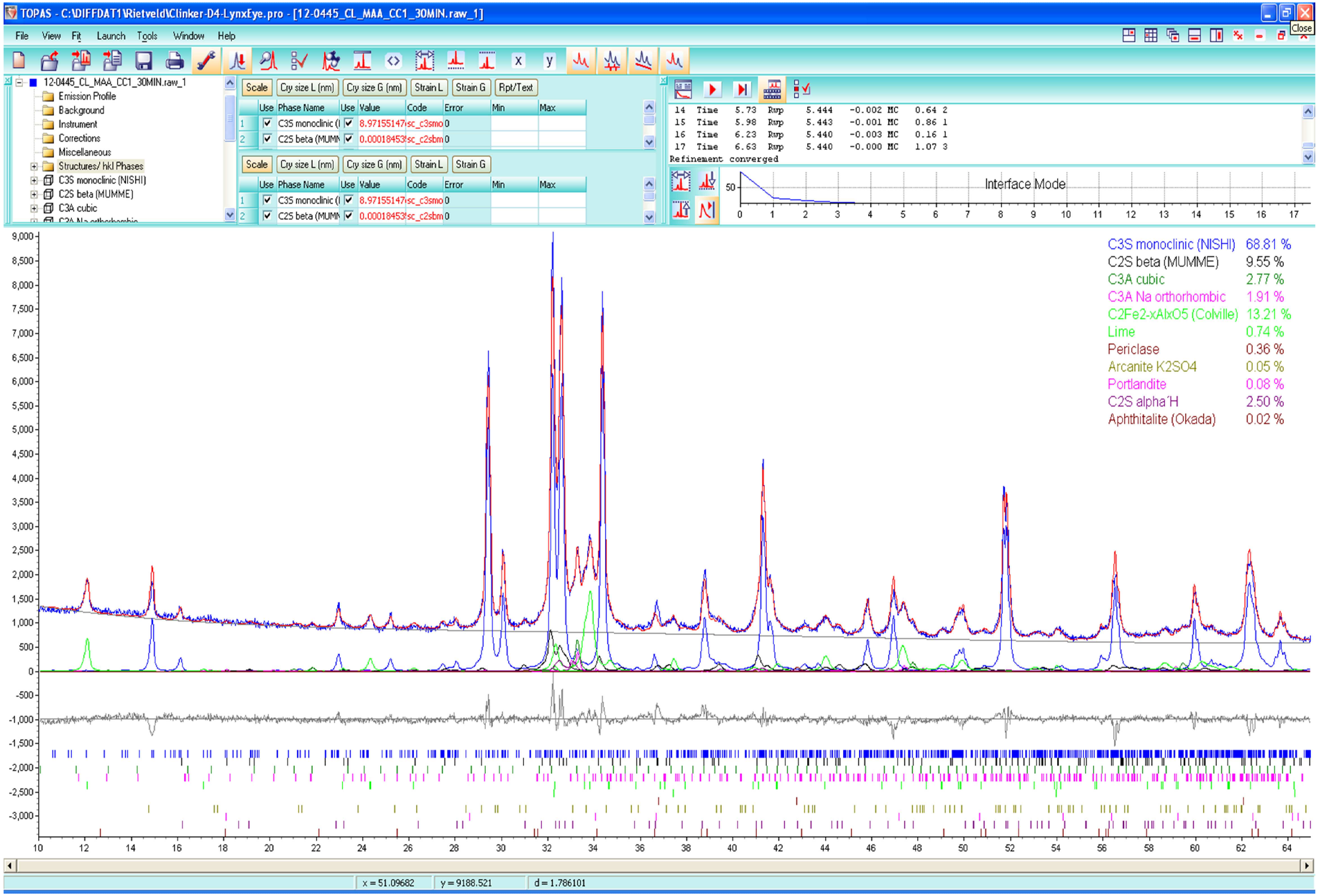
	Use	Phase Name	Use	Value	Code	Error	Min	Max
1	☐	C3S monoclinic (I	☑	1e-006	sc_c3smo	0		
2	☑	C2S beta (MUMM	☑	0.00022636	sc_c2sbm	0		
3	☑	C3A cubic	☑	3.70814906	sc_c3acul	0		
4	☐	C3A Na orthorhc	☑	1e-006	sc_c3ana	0		
5	☐	C4AF Colville	☑	1e-006	sc_c4af	0		
6	☑	C2Fe2-xAlxO5 (	☑	0.00023033	sc_c4af	0		

```
 12  Time   4.31  Rwp    4.919   -0.003 MC   0.00 1
 13  Time   4.53  Rwp    4.917   -0.002 MC   0.00 1
 14  Time   4.73  Rwp    4.916   -0.001 MC   0.00 1
Refinement converged

*** Parameter(s) close to limit(s).
```

C3S_Nishi_hkl	62.73 %
C2S beta (MUMME)	9.97 %
C3A cubic	1.56 %
C2Fe2-xAlxO5 (Colville)	17.61 %
Lime	0.28 %
Periclase	0.22 %
C2S alpha´H	7.64 %

Figure A.4.: XRD-analysis of Cl/Lxh/FC


TOPAS - C:\DIFFDAT1\Rietveld\Clinker-D4-LynxEye.pro - [12-0445_CL_MAA_CC1_30MIN.raw_1]

- 12-0445_CL_MAA_CC1_30MIN.raw_1
  - Emission Profile
  - Background
  - Instrument
  - Corrections
  - Miscellaneous
  - Structures/ hkl Phases
  - C3S monoclinic (NISHI)
  - C2S beta (MUMME)
  - C3A cubic

	Use	Phase Name	Use	Value	Code	Error	Min	Max
1	☑	C3S monoclinic (I	☑	8.97155147	sc_c3smo	0		
2	☑	C2S beta (MUMM	☑	0.00018453	sc_c2sbm	0		

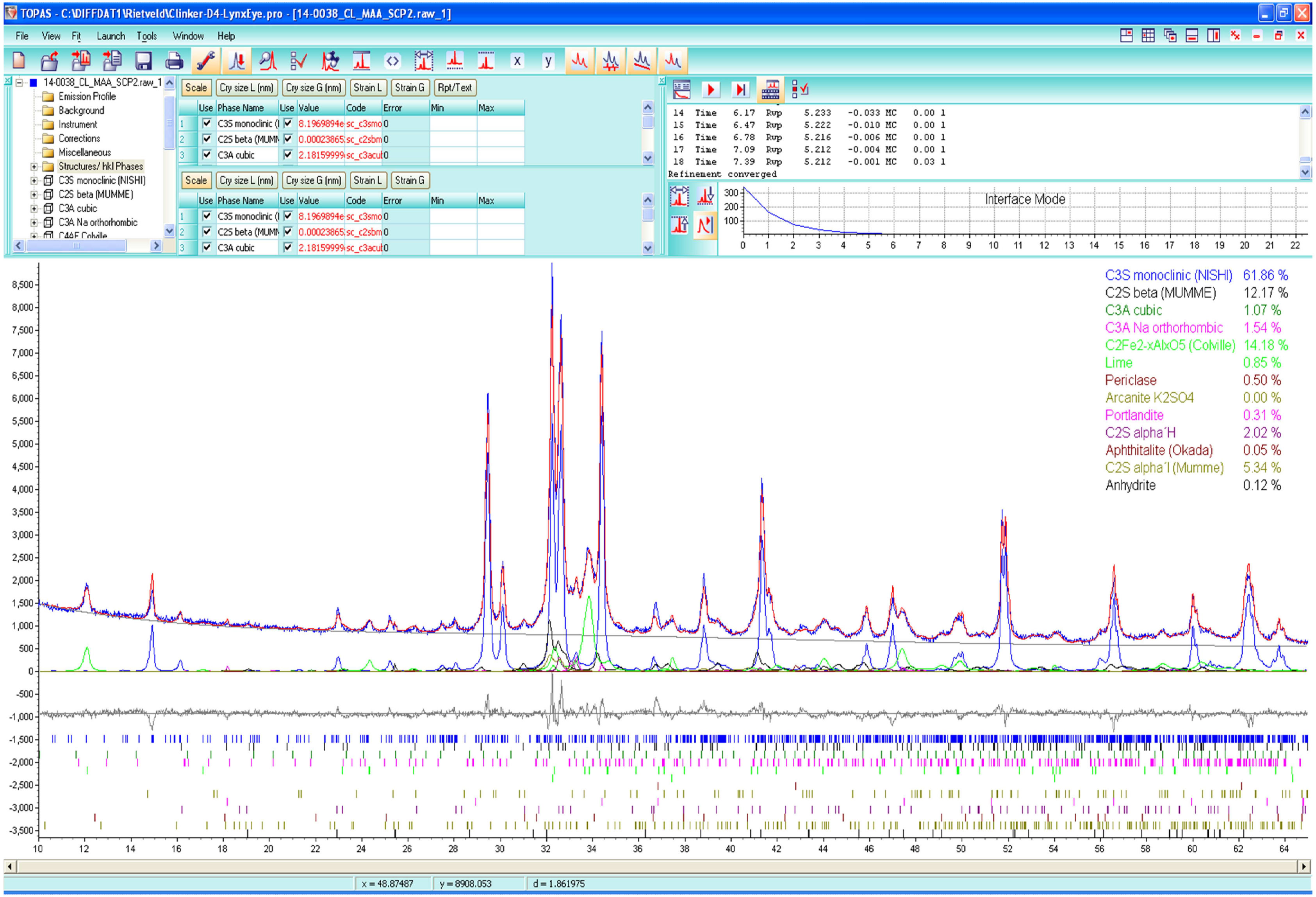
	Use	Phase Name	Use	Value	Code	Error	Min	Max
1	☑	C3S monoclinic (I	☑	8.97155147	sc_c3smo	0		
2	☑	C2S beta (MUMM	☑	0.00018453	sc_c2sbm	0		

```
14  Time   5.73  Rwp   5.444  -0.002 MC   0.64 2
15  Time   5.98  Rwp   5.443  -0.001 MC   0.86 1
16  Time   6.23  Rwp   5.440  -0.003 MC   0.16 1
17  Time   6.63  Rwp   5.440  -0.000 MC   1.07 3
Refinement converged
```

C3S monoclinic (NISHI)	68.81 %
C2S beta (MUMME)	9.55 %
C3A cubic	2.77 %
C3A Na orthorhombic	1.91 %
C2Fe2-xAlxO5 (Colville)	13.21 %
Lime	0.74 %
Periclase	0.36 %
Arcanite K2SO4	0.05 %
Portlandite	0.08 %
C2S alpha´H	2.50 %
Aphthitalite (Okada)	0.02 %

x = 51.09682 y = 9188.521 d = 1.786101

Figure A.5.: XRD-analysis of Cl/Maa/CC



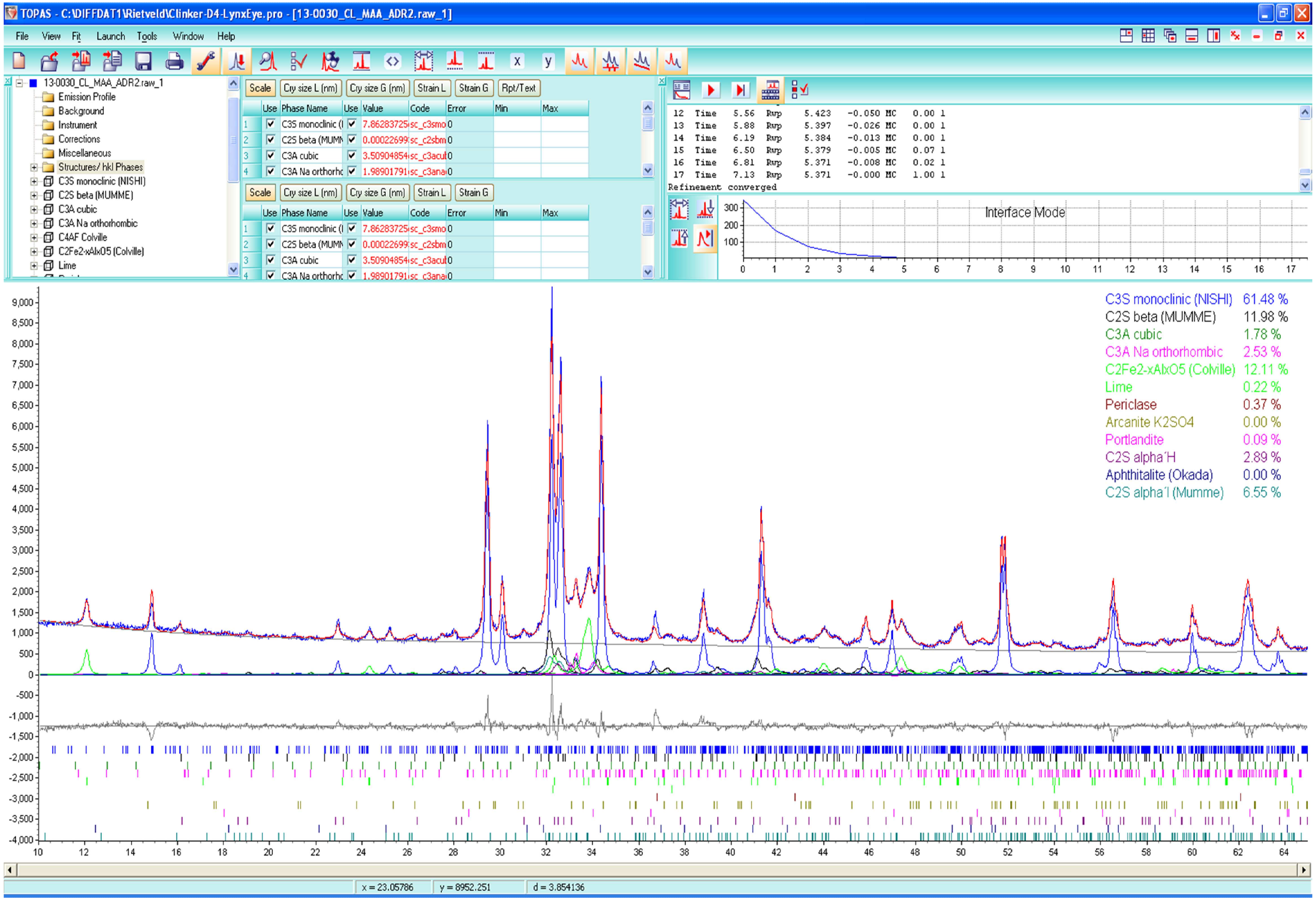
	Use	Phase Name	Use	Value	Code	Error	Min	Max
1	☑	C3S monoclinic (I	☑	8.1969894e	sc_c3smo	0		
2	☑	C2S beta (MUMN	☑	0.00023865	sc_c2sbm	0		
3	☑	C3A cubic	☑	2.18159999	sc_c3acul	0		

	Use	Phase Name	Use	Value	Code	Error	Min	Max
1	☑	C3S monoclinic (I	☑	8.1969894e	sc_c3smo	0		
2	☑	C2S beta (MUMN	☑	0.00023865	sc_c2sbm	0		
3	☑	C3A cubic	☑	2.18159999	sc_c3acul	0		

```
14  Time   6.17  Rwp    5.233   -0.033 MC   0.00 1
15  Time   6.47  Rwp    5.222   -0.010 MC   0.00 1
16  Time   6.78  Rwp    5.216   -0.006 MC   0.00 1
17  Time   7.09  Rwp    5.212   -0.004 MC   0.00 1
18  Time   7.39  Rwp    5.212   -0.001 MC   0.03 1
Refinement converged
```

x = 48.87487 y = 8908.053 d = 1.861975

Figure A.6.: XRD-analysis of Cl/Maa/SCP



	Use	Phase Name	Use	Value	Code	Error	Min	Max
1	☑	C3S monoclinic (I	☑	7.86283725	sc_c3smo	0		
2	☑	C2S beta (MUMM	☑	0.00022699	sc_c2sbm	0		
3	☑	C3A cubic	☑	3.50904854	sc_c3acul	0		
4	☑	C3A Na orthorhc	☑	1.98901791	sc_c3ana	0		

	Use	Phase Name	Use	Value	Code	Error	Min	Max
1	☑	C3S monoclinic (I	☑	7.86283725	sc_c3smo	0		
2	☑	C2S beta (MUMM	☑	0.00022699	sc_c2sbm	0		
3	☑	C3A cubic	☑	3.50904854	sc_c3acul	0		
4	☑	C3A Na orthorhc	☑	1.98901791	sc_c3ana	0		

```
12  Time   5.56  Rwp    5.423   -0.050 MC   0.00 1
13  Time   5.88  Rwp    5.397   -0.026 MC   0.00 1
14  Time   6.19  Rwp    5.384   -0.013 MC   0.00 1
15  Time   6.50  Rwp    5.379   -0.005 MC   0.07 1
16  Time   6.81  Rwp    5.371   -0.008 MC   0.02 1
17  Time   7.13  Rwp    5.371   -0.000 MC   1.00 1
Refinement converged
```

C3S monoclinic (NISHI)	61.48 %
C2S beta (MUMME)	11.98 %
C3A cubic	1.78 %
C3A Na orthorhombic	2.53 %
C2Fe2-xAlxO5 (Colville)	12.11 %
Lime	0.22 %
Periclase	0.37 %
Arcanite K2SO4	0.00 %
Portlandite	0.09 %
C2S alpha´H	2.89 %
Aphthitalite (Okada)	0.00 %
C2S alpha´l (Mumme)	6.55 %

Figure A.7.: XRD-analysis of Cl/Maa/ADR

Appendix B

EPDs for CEM I, CEM II and CEM III cements (Febelcem)

Environmental Product Declaration for Belgian Cement - Cembureau EPD Format

Cement CEM I 52.5 N

In compliance with ISO 14020, ISO TR 14025 and ISO 14040-43

according to EN 197-1 (2000)

Aim and Scope

This Environmental Product Declaration (EPD) is mainly intended for Business-to-Business (B2B) communication and its prime purpose is to provide measurable and verifiable input for the environmental assessment of construction works.

As the applications of cement as an intermediate material are numerous, a unique *functional unit* cannot be defined and therefore this EPD is based on a *declared unit* .

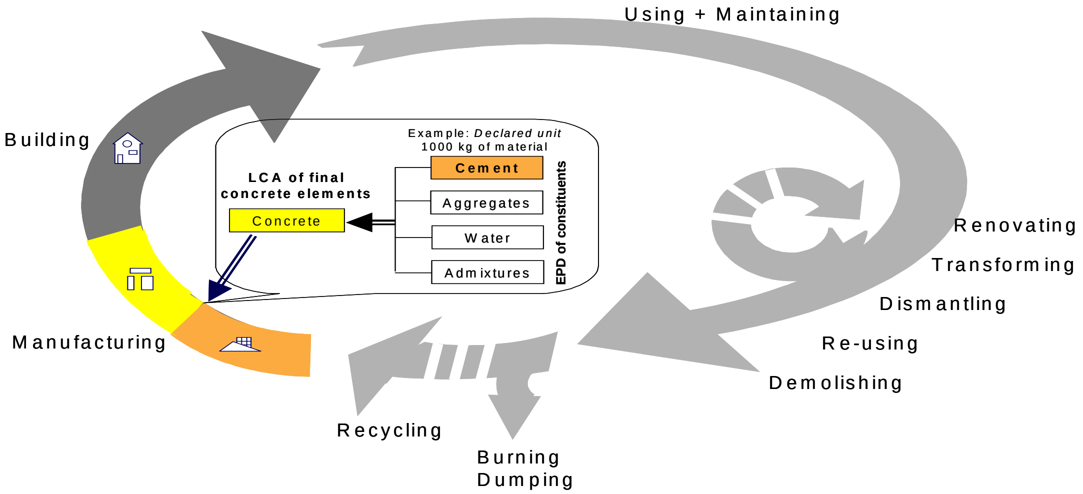
This EPD has been specifically prepared for the cradle-to-gate life stages of cement.

This is illustrated in the figure hereafter.

See Users' Guide for more information.

Key information

Declared unit *:*
1 000 kg of cement
Issue date *:*
February 07, 2012
Revision date *:*
n.r.
EPD owner:
Febelcem
Contact person *:*
A. Jasienski
a.jasienski@febelcem.be
Author:
SGS INTRON BV
Third party reviewer
IVAM UvA BV



This EPD includes information related to the cement manufacturing only

Cement production process and System boundaries

Production process
The main processes in cement production are:
- Quarrying and acquisition of material resources
- Production of raw mix
- Burning of clinker
- Grinding of cement
- Storage of cement / dispatch

<u>Material resources</u>

Natural raw materials for the clinker manufacture are in the first place calcareous materials like limestone or marl, sand and argillaceous materials like clay or shale, which are abundantly present in the earth. Alternative materials such as fly ash, blast furnace slag and other process residues may also be used as partial replacement for the natural raw materials.

<u>Production of ground raw materials</u>

Production of ground raw materials occurs by a wet or dry process. In the wet process a slurry of the raw materials is prepared prior to burning. The slurry is homogenised in basins and pumped to the wet long kiln. In the dry process, drying and grinding to the desired fineness of the raw mix usually takes place in one step in the raw mill. The residual heat of the flue gases of the kiln is utilised for drying.

<u>Burning of clinker</u>

The raw mix is preheated using the residual heat of the flue gases and burned in a rotary kiln at about 1450°C.

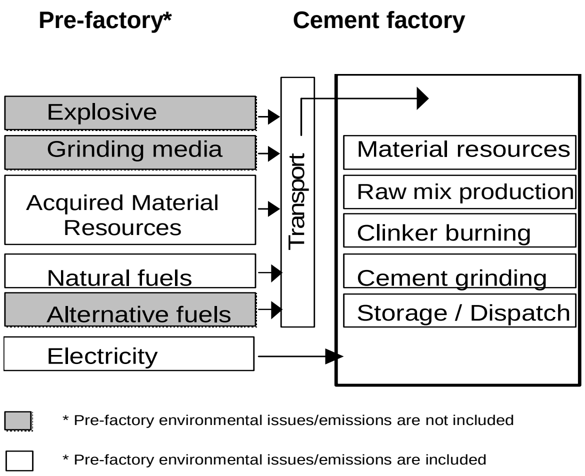
Major natural fuels used in the cement industry are coal, lignite and natural gas. The most important alternative fuels are derived from different types of waste. The percentage of alternative fuels varies highly within Europe.

<u>Grinding of cement</u>

Finally, clinker is ground together with gypsum and possibly other constituents to produce cement.

System boundaries

The system boundaries are shown in the figure.



* Pre-factory: processes outside the cement factory boundary but still within the system boundaries. For more details on cut-off rules see INTRON report R20085203

Use of resources without energy content: Raw materials

	Pre-factory kg/1000 kg	Cement factory kg/1000 kg	Total kg/1000 kg	Comments
Natural resources				
Renewable*	0,00	0,00	0,00	All major raw materials are in the system boundaries for the cement factory; the other materials are almost all secondary, and resource use is cut-off.
Non-renewable	0,00	1443	1443	
Secondary (alternative)				
Renewable*	0,00	0,00	0,00	
Non-renewable	0,00	199	199	
Total	0,00	1642	1642	

* If relevant

Use of resources: Water

	Pre-factory kg/1000 kg	Cement factory kg/1000 kg	Total kg/1000 kg	Comments
Water	162	0,86	163	water consumption for hydropower turbines has been excluded from the pre-factory data

Use of resources with energy content

Thermal energy MJ/1000 kg	Pre-factory	Cement factory	Total	Comments
Natural resources				A small part of renewable energy from electicity generation has been neglected for pre-factory data, it is included under non-renewable
Renewable	70,4	4,74	75,2	
Non-renewable	2437	2778	5215	
Secondary (alternative) resources				
Renewable	0,00	409	409	
Non-renewable	0,00	1451	1451	
Total	2507	4643	7150	

Other indicators

The electricity consumption in the manufacturing process per 1000 kg of cement corresponds to:

0,12 MWh

Impact categories

	Unit	Pre-factory	Cement factory	Total	Comments
Global warming	kg CO_2 eq / 1000 kg	85,5	824	909	All factory impacts are included under cement factor, except from fossil fuels used outside the clinker operations; being, the emissions related to the use of diesel and gas consumption for grinding.
Acidification	kg SO_2 eq / 1000 kg	0,56	1,92	2,49	
Ozone depletion	kg CFC-11 eq / 1000 kg	0,00	0,00	0,00	
Photochemical oxidant formation	kg C_2H_4 eq / 1000 kg	0,07	0,19	0,26	
Eutrophication	kg PO_4 eq / 1000 kg	0,09	0,40	0,49	

Toxicity impact

- At present time, there are no internationally recognised models for the assessment of the toxicity impact.

- Whenever an accepted national model for the determination of the toxicity impact exists, it may be used.

Generated waste for disposal

	Pre-factory	Cement factory	Total	Comments
	kg/1000 kg	kg/1000 kg	kg/1000 kg	
Non hazardous waste	6,44	8,96	15,40	
Hazardous waste	128,21	32,18	160,39	

Additional information

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The production of cement is subject to National and European legislation, which address all relevant environmental effects like the excavation of natural raw materials, the rehabilitation of quarries, the recovery of energy and material from wastes and the emission of noise, dust and hazardous substances (NOx, SO_2, heavy metals, etc.).

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Additional references

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WBCSD	www.wbcsdcement.org - Information on LCA tools for the cement industry.

Environmental Product Declaration for Belgian Cement - Cembureau EPD Format

Cement CEM II B/M 32.5

In compliance with ISO 14020, ISO TR 14025 and ISO 14040-43

according to EN 197-1 (2000)

Aim and Scope

This Environmental Product Declaration (EPD) is mainly intended for Business-to-Business (B2B) communication and its prime purpose is to provide measurable and verifiable input for the environmental assessment of construction works.

As the applications of cement as an intermediate material are numerous, a unique *functional unit* cannot be defined and therefore this EPD is based on a *declared unit* .

This EPD has been specifically prepared for the cradle-to-gate life stages of cement.

This is illustrated in the figure hereafter.

See Users' Guide for more information.

Key information

***Declared unit** :*
1 000 kg of cement
***Issue date** :*
February 07, 2012
***Revision date** :*
n.r.
EPD owner:
Febelcem
***Contact person** :*
A . Jasienski
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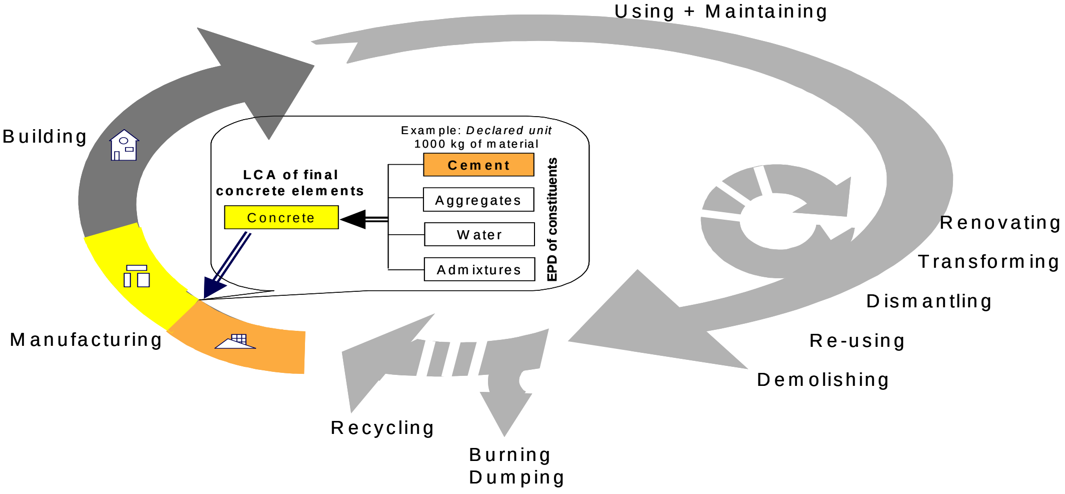
Author:
SGS INTRON BV
Third party reviewer:
IVAM UvA BV



This EPD includes information related to the cement manufacturing only

Cement production process and System boundaries

Production process
The main processes in cement production are:
- Quarrying and acquisition of material resources
- Production of raw mix
- Burning of clinker
- Grinding of cement
- Storage of cement / dispatch

Material resources

Natural raw materials for the clinker manufacture are in the first place calcareous materials like limestone or marl, sand and argillaceous materials like clay or shale, which are abundantly present in the earth. Alternative materials such as fly ash, blast furnace slag and other process residues may also be used as partial replacement for the natural raw materials.

Production of ground raw materials

Production of ground raw materials occurs by a wet or dry process. In the wet process a slurry of the raw materials is prepared prior to burning. The slurry is homogenised in basins and pumped to the wet long kiln. In the dry process, drying and grinding to the desired fineness of the raw mix usually takes place in one step in the raw mill. The residual heat of the flue gases of the kiln is utilised for drying.

Burning of clinker

The raw mix is preheated using the residual heat of the flue gases and burned in a rotary kiln at about 1450^{o}C.

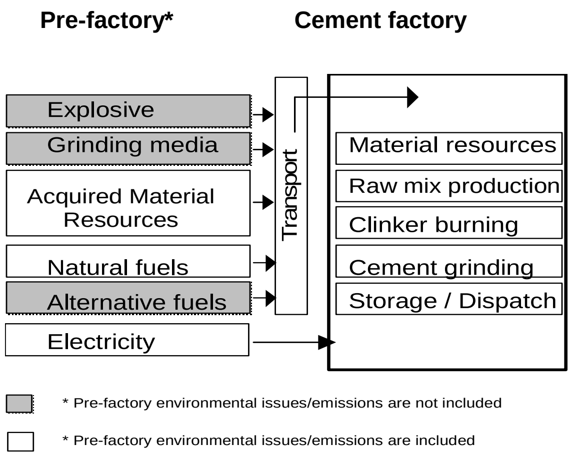
Major natural fuels used in the cement industry are coal, lignite and natural gas. The most important alternative fuels are derived from different types of waste. The percentage of alternative fuels varies highly within Europe.

Grinding of cement

Finally, clinker is ground together with gypsum and possibly other constituents to produce cement.

System boundaries

The system boundaries are shown in the figure.



* Pre-factory: processes outside the cement factory boundary but still within the system boundaries. For more details on cut-off rules see INTRON report R20085203

Use of resources without energy content: Raw materials

	Pre-factory	Cement factory	Total	Comments
	kg/1000 kg	kg/1000 kg	kg/1000 kg	
Natural resources				
Renewable*	0,00	0,00	0,00	All major raw materials are in the system boundaries for the cement factory; the other materials are almost all secondary, and resource use is cut-off usign economic allocation.
Non-renewable	0,00	1244	1244	
Secondary (alternative)				
Renewable*	0,00	0,00	0,00	
Non-renewable	0,00	291	291	
Total	0,00	1535	1535	

* If relevant

Use of resources: Water

	Pre-factory	Cement factory	Total	Comments
	kg/1000 kg	kg/1000 kg	kg/1000 kg	
Water	170	36,85	207	water consumption for hydropower turbines has been excluded from the pre-factory data

Use of resources with energy content

Thermal energy MJ/1000 kg	Pre-factory	Cement factory	Total	Comments
Natural resources				A small part of renewable energy from electicity generation has been neglected for pre-factory data, it is included under non-renewable
Renewable	82,8	7,85	90,7	
Non-renewable	1986	2592	4578	
Secondary (alternative) resources				
Renewable	0,00	256	256	
Non-renewable	0,00	723	723	
Total	2068	3578	5647	

Other indicators

The electricity consumption in the manufacturing process per 1000 kg of cement corresponds to:

0,06 MWh

Impact categories

	Unit	Pre-factory	Cement factory	Total	Comments
Global warming	kg CO_2 eq / 1000 kg	73,1	640	714	All factory impacts are included under cement factor, except from fossil fuels used outside the clinker operations; being, the emissions related to the use of diesel and gas consumption for grinding.
Acidification	kg SO_2 eq / 1000 kg	0,48	1,52	2,00	
Ozone depletion	kg CFC-11 eq / 1000 kg	0,00	0,00	0,00	
Photochemical oxidant formation	kg C_2H_4 eq / 1000 kg	0,06	0,15	0,21	
Eutrophication	kg PO_4 eq / 1000 kg	0,08	0,34	0,42	

Toxicity impact

- At present time, there are no internationally recognised models for the assessment of the toxicity impact.

- Whenever an accepted national model for the determination of the toxicity impact exists, it may be used.

Generated waste for disposal

	Pre-factory	Cement factory	Total	Comments
	kg/1000 kg	kg/1000 kg	kg/1000 kg	
Non hazardous waste	6,05	12,60	18,64	
Hazardous waste	133,73	43,74	177,47	

Additional information

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The production of cement is subject to National and European legislation, which address all relevant environmental effects like the excavation of natural raw materials, the rehabilitation of quarries, the recovery of energy and material from wastes and the emission of noise, dust and hazardous substances (NOx, SO_2, heavy metals, etc.).

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Environmental Product Declaration for Belgian Cement - Cembureau EPD Format

Cement CEM III/A 42.5 N LA

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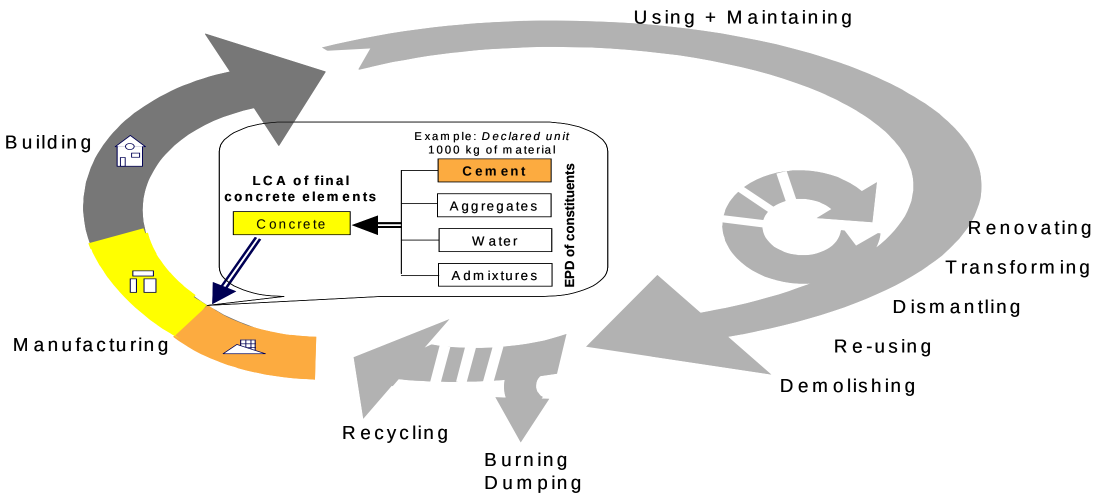
Third party reviewer:
IVAM UvA BV



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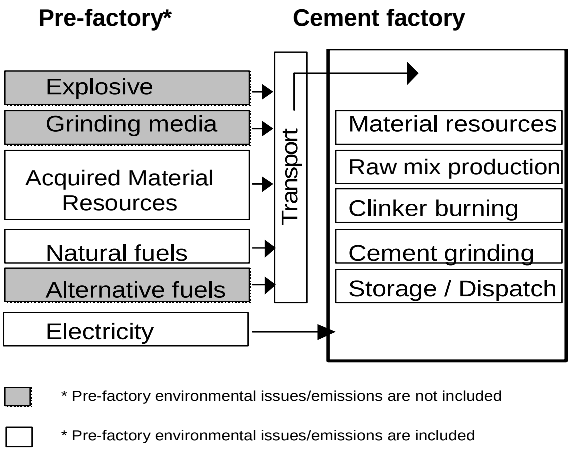

* Pre-factory: processes outside the cement factory boundary but still within the system boundaries. For more details on cut-off rules see INTRON report R20085203

Use of resources without energy content: Raw materials

	Pre-factory	Cement factory	Total	Comments
	kg/1000 kg	kg/1000 kg	kg/1000 kg	
Natural resources				
Renewable*	0,00	0,00	0,00	All major raw materials are in the system boundaries for the cement factory; the other materials are almost all secondary, and resource use is cut-off usign economic allocation.
Non-renewable	0,00	895	895	
Secondary (alternative)				
Renewable*	0,00	0,00	0,00	
Non-renewable	0,00	476	476	
Total	0,00	1371	1371	

* If relevant

Use of resources: Water

	Pre-factory	Cement factory	Total	Comments
	kg/1000 kg	kg/1000 kg	kg/1000 kg	
Water	107	25,84	133	water consumption for hydropower turbines has been excluded from the pre-factory data

Use of resources with energy content

Thermal energy MJ/1000 kg	Pre-factory	Cement factory	Total	Comments
Natural resources				A small part of renewable energy from electicity generation has been neglected for pre-factory data, it is included under non-renewable
Renewable	45,8	4,49	50,3	
Non-renewable	1630	1572	3201	
Secondary (alternative) resources				
Renewable	0,00	200,88	200,88	
Non-renewable	0,00	811	811	
Total	1675	2588	4264	

Other indicators

The electricity consumption in the manufacturing process per 1000 kg of cement corresponds to:

0,09 MWh

Impact categories

	Unit	Pre-factory	Cement factory	Total	Comments
Global warming	kg CO_2 eq / 1000 kg	60,0	415	475	All factory impacts are included under cement factor, except from fossil fuels used outside the clinker operations; being, the emissions related to the use of diesel and gas consumption for grinding.
Acidification	kg SO_2 eq / 1000 kg	0,31	0,99	1,29	
Ozone depletion	kg CFC-11 eq / 1000 kg	0,00	0,00	0,00	
Photochemical oxidant formation	kg C_2H_4 eq / 1000 kg	0,04	0,10	0,13	
Eutrophication	kg PO_4 eq / 1000 kg	0,05	0,27	0,32	

Toxicity impact

- At present time, there are no internationally recognised models for the assessment of the toxicity impact.

- Whenever an accepted national model for the determination of the toxicity impact exists, it may be used.

Generated waste for disposal

	Pre-factory	Cement factory	Total	Comments
	kg/1000 kg	kg/1000 kg	kg/1000 kg	
Non hazardous waste	4,23	8,68	12,91	
Hazardous waste	83,51	31,28	114,79	

Additional information

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WBCSD	www.wbcsdcement.org - Information on LCA tools for the cement industry.

About the candidate

Joris Schoon was born on November 29th 1975 in the city of Aalst. He received his high school degree in Natural sciences – Mathematics from the “Sint-Jan Berchmanscollege” in Brussels. He obtained the degree of master in chemistry with emphasis on polymer chemistry, with distinction from the “Vrije Universiteit Brussel”.

After some minor work experiences, Joris Schoon started his career in 2000 at CBR, a cement manufacturing company, part of the Heidelbergcement group, one of the world’s largest building materials manufacturers. First he was active as quality manager for CBR Gent, a cement producing plant, and later on additionally for CBR Antoing, a Portland clinker producing plant.

In 2007, he joined the commercial department of CBR as consulting engineer. In 2011 he started working for Sagrex, the aggregate producing company within the Heidelberg Cement group as quality advisor.

In 2001, he received his degree of concrete technologist from the Belgian Concrete Group (BBG/GBB), an a second one as concrete technologist from the Dutch Concrete Association in 2008.

In the academic year 2010-2011, Joris Schoon started his PhD study at the Faculty of Engineering and Architecture at Ghent University. Within the Magnel Laboratory for Concrete Research, part of the Department of Structural Engineering, he joined the Concrete and Environment research group of Prof. dr. ir. Nele De Belie. There, he studied the possibility to valorise non-marketable by-products out of aggregate and concrete production as well as recycled materials out of building and demolition waste, as alternative raw material for Portland clinker production. On this topic, he was the first author of five peer reviewed journal publications and three papers in international conference proceedings. At the Concrete Innovation Conference 2014 in Oslo, he was nominated for the innovation award.

In 2013, he received also the Creative Entrepreneurship Award of Heidelberg Cement Benelux as recognition for his contribution to the improvement of the technical processes.

Scientific publications

A1

J. Schoon, L. Van der Heyden, P. Eloy, E. M. Gaigneux, K. De Buysser, I. Van Driessche, N. De Belie, Waste fibrecement: An interesting alternative raw material for a sustainable Portland clinker production, Construction and Building Materials 36 (2012) 391–403

J. Schoon, A. Vergari, K. De Buysser, I. Van Driessche, Nele De Belie: Fines extracted from porphyry and dolomitic limestone aggregates production: MgO as fluxing agent for a sustainable Portland clinker production: Construction and Building Materials, 43 (2013) 511-522

J. Schoon, K. De Buysser, I. Van Driessche, N. De Belie: Feasibility study on the use of Cellular Concrete as alternative raw material for Portland clinker production, Construction and Building Materials, 48 (2013) 725–733

J. Schoon, K. De Buysser, I. Van Driessche, N. De Belie: Fines extracted from recycled concrete as alternative raw material for Portland clinker production: Fineness as determinant factor, Cement and Concrete Composites, Accepted

J. Schoon, K. De Buysser, I. Van Driessche, N. De Belie: Feasibility study on the use of concrete sludge as alternative raw material for Portland clinker production, Journal of Materials in Civil Engineering, Accepted

Conference proceedings (International conferences)

J. Schoon, L. Van der Heyden, I. Van Driessche, N. De Belie: Fibrecement recycling as raw material for Portland clinker production, IALCCE 2012 : Proceedings of the third international symposium on life-cycle civil engineering, Vienna, p.1189-1195, (2012)

J. Schoon, K. De Buysser, I. Van Driessche, N. De Belie: MgO as fluxing agent for a sustainable Portland clinker production, 2013, Proceedings of the 1st International conference on Chemistry of Construction Materials, Berlin, p.35-38 (2013)

J. Schoon, K. De Buysser, I. Van Driessche, N. De Belie: Fines extracted from recycled concrete as alternative raw material for Portland clinker production, CIC 2014: Proceedings of the Concrete Innovation Conference 2014, Oslo, p.151 (2014)