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SINTEF REPORT

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COIN P1 Advanced cementing materials
SP 1.1 F Reduced CO₂ - emissions

Making cements with less clinker content

State of the art

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CLIENT(S)

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ABSTRACT

A review has been made on how to make cements with reduced clinker content to achieve the goal of minimum 30% reduced CO₂ emission and still let these cements be defined as common cements by the European standard EN 197-1.

There is a recent trend to make ternary cement blends in Germany based on clinker - blastfurnace slag - limestone to be within the class CEM II/B-M (S-LL) with up to 35% clinker replacement in accordance with EN 197-1.

There exists a ternary cement based on a clinker - blastfurnace slag -silica fume on the market in USA and one based on clinker - siliceous fly ash -silica fume in Canada. In both cases silica fume is used to secure reasonably early strength. These cements would have been classified as CEM II/B-M (S-D) and CEM II/B-M (V-D), respectively, by EN 197-1.

It is recommended to focus further research in COIN on developing a CEM II/B-M (V-L) or (V-LL) replacing 35% clinker with siliceous fly ash and limestone to fulfil the minimum objective of 30% reduced CO₂ emission and to exploit the potential synergy of the two clinker replacements (i.e. calcium carbonate forming calcium carboaluminate hydrate with extra water binding in reaction with some of the pozzolanic products from the fly ash).

The goal may be significantly exceeded (up to 50% reduced CO₂ emission) by developing a CEM IV/B (Q) where the clinker replacement is a clay containing sufficient calcium carbonate to exploit the carboaluminate concept and where it is calcined at only 700-800°C leaving the calcium carbonate intact.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Materials technology	Materialteknologi
GROUP 2	Concrete	Betong
SELECTED BY AUTHOR	Cement	Sement
	Fly ash	Flygeaske
	Limestone	Kalkstein

Foreword

COIN - Concrete Innovation Centre - is one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfill this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently 5 projects:

- Advanced cementing materials and admixtures
- Improved construction techniques
- Innovative construction concepts
- Operational service life design
- Energy efficiency and comfort of concrete structures

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %). The present industrial partners are:

Aker Kværner Engineering and Technology, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Spenncon AS, Unicon AS and Veidekke ASA.

For more information, see www.sintef.no/coin

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1 INTRODUCTION

The topic of CO₂ emission is taken seriously by the cement industry and was recently one of the key-note papers at the latest International Congress on the Chemistry of Cement (ICCC). Lukasik et al. (2007) argued in this paper that the cement and concrete industry is contributing positively to the Climate Change Initiative by:

- Continuously reducing CO₂ emission from cement production by increased use of bio fuels and alternative raw materials as well as introducing modified low-energy clinker types and cements with reduced clinker content.
- Developing concrete compositions with the lowest possible environmental impact by selecting the cement type, the type and dosage of supplementary cementitious materials and the concrete quality to best suit the use in question.
- Exploiting the potential of concrete recycling to increase the rate of CO₂ uptake.
- Exploiting the thermal mass of concrete to create energy-optimized solutions for heating and cooling residential and office buildings.

Cements with reduced clinker content (last point in first bullet above) or cements blended with supplementary cementing materials (SCMs) are a well established technologies as for instance demonstrated by Müller (2006) for (in particular) binary systems (clinker + one SCM) and are defined in the European standard as outlined in Chapter 3. Binary blended cements are well established in Norway as Norcem's Standard FA with up to 20% siliceous fly ash and Embra's "Miljøsement" with about 30% ground blast furnace slag.

However, there is now a new trend of making ternary blends (clinker with 2 SCMs), but as pointed out by Lukasik et al. (2007), the definitions in the current ENV 197-1 may prohibit further development and full exploitation of these possibilities. In order to be able to elaborate on this, the content of EN 197-1 is reviewed in Chapter 3.

2 OBJECTIVE

This report is state-of-the art report no. 2 in task 1.1f within COIN, which have the overall objective of developing cement based on the principle of less clinker content that will have at least 30% less CO₂ outlet and still can be used as all-round cement.

The specific objective of this report is to demonstrate how the overall goal is achievable using blended cement that still is defined within the European standard EN 197-1, and in particular synergic ternary blends.

3 CLASSIFICATION OF CEMENTS

EN 197-1 classifies cements based on calcium silicate hydrates for hardening and which are for general use. The constituents for these cements are:

1. Portland cement clinker (K)
2. Granulated blastfurnace slag (S)
3. Pozzolanic material (P and Q)
4. Fly ash (V and W)
5. Burnt shale (T)
6. Limestone (L, LL)
7. Silica fume (D)
8. Minor additional constituents
9. Calcium sulfate
10. Additives

The constituents of cement are sub-divided into main and minor additional constituents. Main constituents are the substances listed above from 1 to 7, provided their content in the cement exceeds 5% by mass. Minor additional constituents can be all the substances listed under 1 to 8, provided they have a maximum content of 5% by mass in the cement, as well as inorganic mineral substances from clinker production. The data concerning the cement composition, and also concerning the proportions of calcium sulfate and additives, always relate to the total of all main and minor additional constituents in the cement without taking the calcium sulfate and additives into account.

1. Portland cement clinker (K)

Portland cement clinker is also known as cement clinker or just clinker. At least 2/3 of it consists of the two calcium silicates, namely tri- and di-calcium silicate, which are richest in CaO and can react with the mixing water and harden reasonably rapidly. Portland cement clinker is therefore a hydraulic substance.

2. Granulated blastfurnace slag (S)

Granulated blastfurnace slag is a granulated, rapidly cooled, and therefore predominantly glassy, basic blastfurnace slag. It is a latent hydraulic substance because it reacts only slowly with water, but when mixed with activators, such as cement clinker, it reacts and hardens relatively rapidly with the formation of calcium silicate hydrates. It must consist of at least 2/3 by mass of glassy slag and at least 2/3 of CaO, MgO and SiO₂ in order to be defined as blastfurnace slag by EN 197-1.

3. Pozzolanic material (P and Q)

Pozzolanic materials are natural or industrial substances which, because of their content of reactive silicon dioxide, SiO₂ react when finely ground in the presence of water at normal ambient temperature with dissolved calcium hydroxide, form calcium silicate hydrates, and as a result can harden hydraulically. Reactive silicon dioxide, which is present either as free SiO₂ or combined in aluminosilicate, is therefore essential for the pozzolanic hardening. Calcium aluminate hydrates, which can also contribute to the

strength formation, are also formed. The proportion of reactive CaO is unimportant. The content of reactive SiO₂ content must be at least 25% by mass. Although fly ash and silica fume have pozzolanic properties they are dealt with separately in points 4 and 7.

Natural pozzolanas (P) are usually materials of volcanic origin or sedimentary rock of suitable chemical and mineralogical composition. This also includes trass.

Industrial pozzolanas (Q) can be thermally treated and activated clays and shales, and air-cooled slags from the extraction of lead, copper or zinc, provided they contain sufficient concentrations of reactive SiO₂.

4. Fly ash (V and W)

Fly ash is obtained by electrostatic or mechanical precipitation of dust particles from the exhaust gases from furnaces. It may only be used for cement production if it comes from a furnace fired with pulverized coal. The fly ash is either an aluminosilicate or a calcium silicate depending on how the silicon dioxide is chemically combined. Because of the content of reactive silicon dioxide both types have pozzolanic properties, and calcium silicate fly ash also has hydraulic properties. In order to limit the content of incompletely burnt substances the loss on ignition must not exceed 5.0% by mass.

Siliceous fly ash (V) is a fine powder, consisting predominantly of spherical and glassy particles, which has pozzolanic properties. It must contain less than 5% by mass of reactive CaO and at least 25% by mass of reactive SiO₂.

Calcareous fly ash (W) is a fine powder with hydraulic and/or pozzolanic properties. The content of reactive CaO must be $\geq 5\%$ by mass. Calcareous fly ash, containing between 5 and 15% by mass of reactive CaO, must contain more than 25% by mass of reactive SiO₂.

5. Burnt shale (T)

Burnt oil shale has particular importance as a constituent of hydraulic binders. It is produced in a special furnace at temperatures of approximately 800°C. Because of the content of calcium carbonate and sulphur in the natural starting material the burnt oil shale contains clinker phases, mainly dicalcium silicate and monocalcium aluminate, as well as small quantities of free CaO and calcium sulfate and larger proportions of pozzolanic substances. In a finely ground state such burnt shales therefore exhibit not only hydraulic properties, such as those of Portland cement, but also pozzolanic properties.

During strength testing in mortar after moist storage, finely ground burnt oil shale must reach a compressive strength of 25.0 N/mm² at 28 days. It must also be sound (i.e. pass the expansion in the Le Chatelier test) when mixed with 70% by mass of Portland cement.

6. Limestone (L and LL)

Limestone must meet the following requirements:

- a) The limestone must contain at least 75% by mass of CaCO₃ calculated from the CaO content.

- b) The clay content, determined by the methylene blue adsorption on the pulverized limestone, must not exceed 1.20 g/100 g limestone.
- c) The total content of carbon (TOC) as a measure of the content of organic constituents must not exceed 0.2% by mass for limestone LL and 0.50% for limestone L.

7. Silica fume (D)

Silica fume consists of very fine spherical particles with a content of amorphous silicon dioxide SiO_2 of at least 85% by mass. Silica fume must meet the following requirements:

- a) The loss on ignition must not exceed 4.0% by mass.
- b) The specific surface area (BET) must be at least $15 \text{ m}^2/\text{g}$.

8. Minor additional constituents

Minor additional constituents are natural or synthetic inorganic mineral substances which, after appropriate preparation, improve the physical properties of the cement, e.g. its workability or water retention, through their particle size distribution. They can be inert or have slightly hydraulic, latent hydraulic or pozzolanic properties. However, no requirements are set for them in this respect. They must be correctly prepared, i.e. selected, homogenized, dried and comminuted to suit their state of production or delivery. They must not increase the water demand of the cement appreciably, impair the resistance of the concrete or mortar, or reduce the corrosion protection of the reinforcement.

9. Calcium sulfate

Calcium sulfate, in the form of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or β -anhydrite ($\beta\text{-CaSO}_4$), or as a mixture of these compounds, is added in small quantities to the cement during its manufacture to control the setting. β -anhydrite is the naturally occurring modification of water-free CaSO_4 , and is also known as anhydrite II. α -anhydrite (anhydrite I) is the high-temperature modification of CaSO_4 and is stable only at temperatures above 1180°C . If part of the water content of gypsum is removed, hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) is formed, while complete dehydration produces "soluble" γ -anhydrite ($\gamma\text{-CaSO}_4$) also known as anhydrite III. The hemihydrate occurs in two forms, known as α - and β -hemihydrate. They both have the same crystal lattice and differ only in the way they are formed, and are therefore not polymorphic modifications. The more coarsely crystalline α -hemihydrate with lower water demand is formed when gypsum is dehydrated in an autoclave, and β -hemihydrate with a substantially greater specific surface area and higher water demand is formed by "dry" dewatering in rotary kilns, boilers at temperatures from 120°C to 180°C or simply due to the heat in the mill where the constituents and gypsum are ground to cement.

Gypsum and β -anhydrite occur naturally, but the calcium sulphates which are generated in various industrial processes can also be used as setting regulators. This applies in particular to chemical gypsum, which is generated during the extraction of phosphoric acid from calcium phosphates (phosphogypsum) or during the extraction of hydrofluoric acid from fluor spar (fluogypsum) as well as to FGD gypsum (i.e. gypsum from flue gas desulphurization plants) mainly in power stations.

10. Additives

For the purpose of the European and German standards cement additives are constituents which are used to improve the manufacture or properties of cement, e.g. grinding aids. The total quantity of these additives should not exceed 1% by mass, and the dry content of organics shall not exceed 0.5%. If this value is exceeded the precise quantity must be stated on the packaging and/or on the delivery document. These additives must not promote corrosion of reinforcement or adversely affect the properties of the cement or the concrete or mortar made from that cement.

EN 197-1 contains cements for general use, and not cements with special properties. It differentiates between the following five main categories:

CEM I Portland cement

CEM II Portland-composite cement

CEM III Blastfurnace cement

CEM IV Pozzolanic cement

CEM V Composite cement

The subdivision of these five main categories into a total of 27 types of cement together with their designations is shown in Table 1.

CEM I is Portland cement containing at least 95% by mass of Portland cement clinker. The main category CEM II covers cements which, in addition to clinker, contain one or more main constituents in a proportion of between 6 and 35% by mass (silica fume up to a maximum of 10% by mass). This proportion is subdivided again at 20% by mass. The cement with the lower proportion is designated as A and the cement with the higher proportion as B. CEM III is the designation for three types of blastfurnace cement A, B and C containing between 36% and 95% by mass of granulated blastfurnace slag with subdivisions at 65% and 80% by mass of granulated blastfurnace slag. CEM IV denotes two types (A and B) of pozzolanic cement containing between 11 and 55% by mass of pozzolana, with a subdivision at 35% by mass of pozzolana. These cements must pass the pozzolana test. CEM V comprises composite cements which, in addition to cement clinker (K), contain 36% to 80% by mass of granulated blastfurnace slag (S) and/or pozzolana of natural (P) and/or industrial (Q) origin and/or siliceous fly ash (V), and are subdivided into A and B at 60% by mass.

The different categories of cement are also associated with 3 strength classes; 32.5, 42.5 and 52.5, based on the standard strength measured at 28 days as outlined in Table 2. The three classes are further sub-divided on the basis of the initial strength into normal hardening (code letter N for normal) and rapid hardening (code letter R for rapid).

EN 197-1:2000

Table 1- The 27 products in the family of common cements

Main types	Notation of the 27 products (types of common cement)		Composition [proportion by mass ¹⁾]										Minor additional constituents	
			Main constituents											
			Clinker	Blastfurnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone*			
K	S	D ²⁾	P	Q	V	W	T	L	LL					
CEM I	Portland cement	CEM I	95-100	-	-	-	-	-	-	-	-	-	-	0-5
	Portland-slag cement	CEM II/A-S	80-94	6-20	-	-	-	-	-	-	-	-	-	0-5
CEM II/B-S		65-79	21-35	-	-	-	-	-	-	-	-	-	0-5	
Portland-silica fume cement	CEM II/A-D	90-94	-	6-10	-	-	-	-	-	-	-	-	0-5	
	Portland-pozzolana cement	CEM II/A-P	80-94	-	-	6-20	-	-	-	-	-	-	-	0-5
CEM II/B-P		65-79	-	-	21-35	-	-	-	-	-	-	-	0-5	
CEM II/A-Q		80-94	-	-	-	6-20	-	-	-	-	-	-	0-5	
CEM II/B-Q		65-79	-	-	-	21-35	-	-	-	-	-	-	0-5	
CEM II	Portland-fly ash cement	CEM II/A-V	80-94	-	-	-	-	6-20	-	-	-	-	-	0-5
		CEM II/B-V	65-79	-	-	-	-	21-35	-	-	-	-	-	0-5
		CEM II/A-W	80-94	-	-	-	-	-	6-20	-	-	-	-	0-5
		CEM II/B-W	65-79	-	-	-	-	-	21-35	-	-	-	-	0-5
Portland-burnt shale cement	CEM II/A-T	80-94	-	-	-	-	-	-	-	6-20	-	-	0-5	
	CEM II/B-T	65-79	-	-	-	-	-	-	-	21-35	-	-	0-5	
Portland-limestone cement	CEM II/A-L	80-94	-	-	-	-	-	-	-	-	6-20	-	0-5	
	CEM II/B-L	65-79	-	-	-	-	-	-	-	-	21-35	-	0-5	
	CEM II/A-LL	80-94	-	-	-	-	-	-	-	-	-	6-20	0-5	
	CEM II/B-LL	65-79	-	-	-	-	-	-	-	-	-	21-35	0-5	
Portland-composite cement ³⁾	CEM II/A-M	80-94	<----- 6-20 ----->										0-5	
	CEM II/B-M	65-79	<----- 21-35 ----->										0-5	
CEM III	Blastfurnace cement	CEM III/A	35-64	36-65	-	-	-	-	-	-	-	-	-	0-5
		CEM III/B	20-34	66-80	-	-	-	-	-	-	-	-	-	0-5
		CEM III/C	5-19	81-95	-	-	-	-	-	-	-	-	-	0-5
CEM IV	Pozzolanic cement ³⁾	CEM IV/A	65-89	-	<----- 11-35 ----->							0-5		
		CEM IV/B	45-64	-	<----- 36-55 ----->							0-5		
CEM V	Composite cement ³⁾	CEM V/A	40-64	18-30	-	<----- 18-30 ----->					0-5			
		CEM V/B	20-38	31-50	-	<----- 31-50 ----->					0-5			

1) The values in the table refer to the sum of the main and minor additional constituents. 2) The proportion of silica fume is limited to 10%.

3) In Portland-composite cements CEM II/A-M and CEM II/B-M, in Pozzolanic cements CEM IV/A and CEM IV/B and in Composite cements CEM V/A and CEM V/B the main constituents besides clinker shall be declared by designation of the cement.

* L : total organic carbon (TOC) shall not exceed 0.5% by mass; LL: TOC shall not exceed 0.20% by mass.

Table 2 Strength classes of cements as defined in EN 197-1

Strength class	Compressive strength (N/mm ² or MPa)			
	Early strength		Standard strength at 28 days	
	≥ at 2 days	≥ at 7 days	Minimum	Maximum
32.5 N	-	16	32.5	52.5
32.5 R	10	-	32.5	52.5
42.5 N	10	-	42.5	62.5
42.5 R	20	-	42.5	62.5
52.5 N	20	-	52.5	-
52.5 R	30	-	52.5	-

EN 197-1 also specifies some physical and chemical requirements to the common cements. The initial setting tested in accordance with EN 196-3 must not start before 75, 60 and 45 minutes for the strength classes 32.5, 42.5 and 52.5, respectively. There is no limit for the final setting time. The soundness must not exceed 10 mm expansion during the Le Chatelier test defined in EN 196-3. The chemical requirements to be fulfilled by the cements complying with EN 197-1 are listed in Table 3.

Table 3 Chemical requirements for the cements as defined in EN 197-1

Property	Test method	Cement type	Strength class	Requirement (%)
Loss on ignition	EN 196-2	CEM I and III	All	≥ 5.0
Insoluble residue	EN 196-2 ¹	CEM I and III	All	≥ 5.0
Sulfate content (as SO ₃)	EN-196-2	CEM I CEM II ² CEM IV CEM V	32.5 N 32.5 R 42.5 N	≥ 3.5
			42.5 R 52.5 N 52.5 R	≥ 4.0
		CEM III ³	All	
Chloride content	EN 196-2	All ⁴	All	≥ 0.10 ⁵
Pozzolanicity	EN 196-1	CEM IV	All	satisfies test

¹Determination of the residue insoluble in hydrochloric acid as well as sodium carbonate solution

²Cement type CEM II/B-T may contain ≤ 4.5 % SO₃ in all strength classes

³Cement type CEM III/C may contain ≤ 4.5 % SO₃

⁴Cement type CEM III may contain $> 0.1\%$ Cl⁻, but in that case the content must be declared on the package

⁵For application in the manufacture of prestressed concrete elements, cements with lower chloride content may be produced. In such a case the lower value shall replace 0.1% and be declared in the delivery note.

According to the classification system for EN 197-1 outlined in the preceding text, the established binary blended cements in Norway; Norcem's Standard FA with up to 20% siliceous fly ash and Embra's "Miljøsement" with about 30% ground blast furnace slag, are denote CEM II/A-V 42.5 R and CEM II/B-S 52.5 N, respectively.

4 BLENDED CEMENTS

4.1 Binary systems

It is beyond the task of this state-of-the art report to review all binary cement systems, but CEM II is in fact now the dominating cement class in Europe (Müller, 2006) according to the 2003 distribution shown in Fig. 1, and the CEM II market share has probably only increased until today. As the second component to clinker, limestone (LL) was

dominating in 2004/2003 both in Germany and EU as a whole, while slag (S) came second in Germany and M was second choice in EU (Fig. 2 from Müller, 2007) when the lower strength class 32.5 was referred to. Category M (mixed) is Portland-composite cement where all components are allowed mixed together and is most likely a ternary system (i.e. clinker + 2 SCMs) and belongs to chapter 4.2.

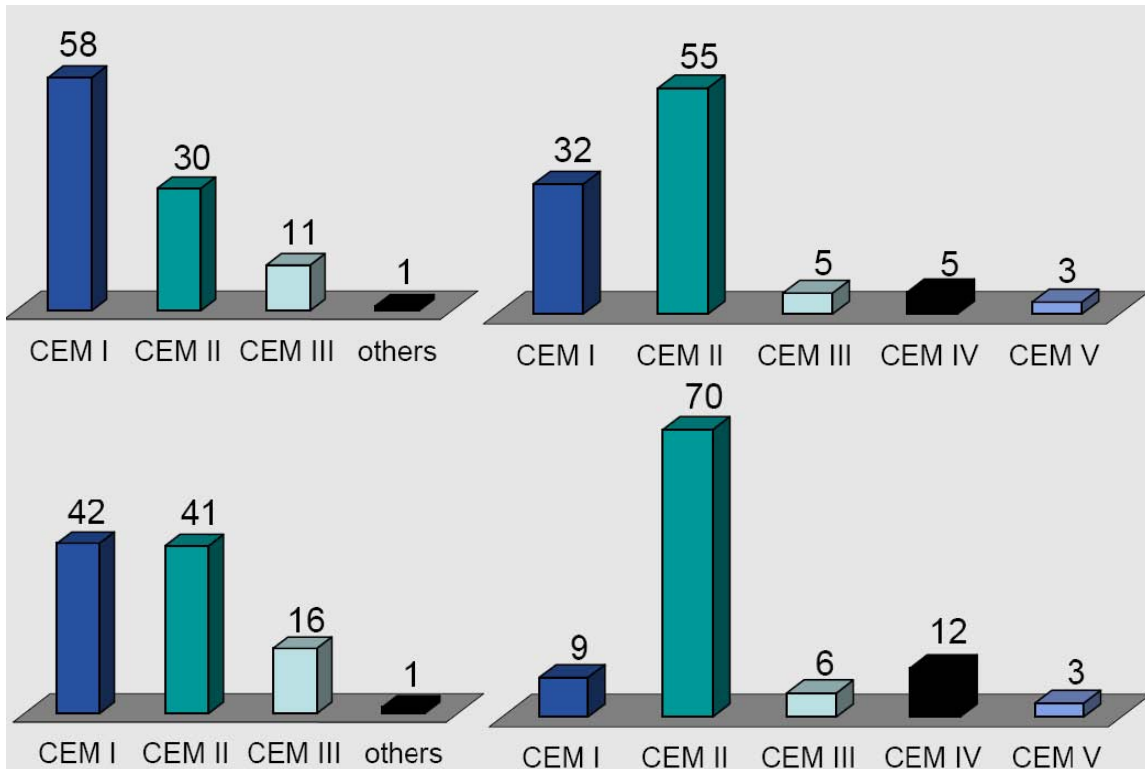


Fig 1 The market share in 2003 of the different cement types in Germany (left) and EU (right) with reference to all strength classes (upper) and to strength class 32.5 (lower) after Müller (2006).

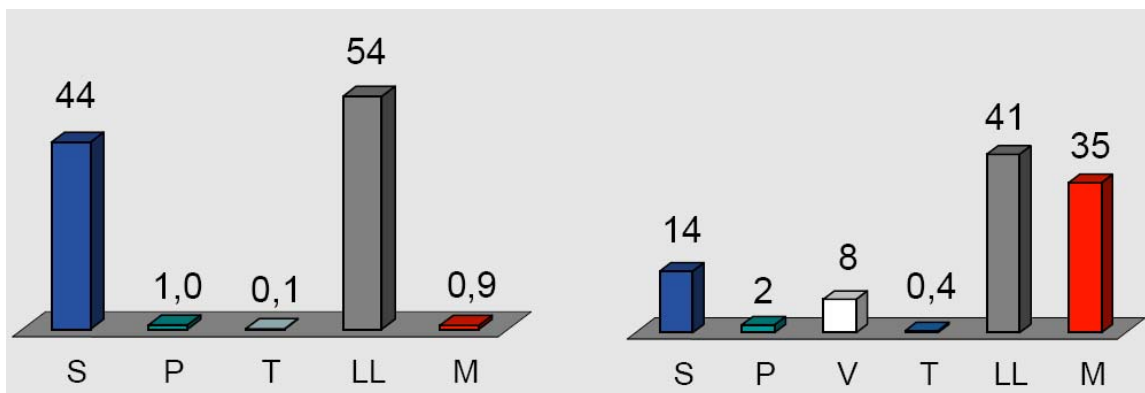


Fig. 2 The market share in 2004 for Germany (left) and for 2003 in EU (right) for the second component in CEM II cements with reference to strength class 32.5.

4.2 Ternary systems

Following the established binary cement systems, there seems to be a recent trend towards development of ternary cementitious systems that at least utilize the combined effect of two SCM clinker replacements, if not planned synergy between them.

Müller (2006) seems to focus on the CEM IIB-M class and especially on ground blastfurnace slag (S) and quality limestone (LL) mixes (e.g. 10% S and 25% LL). He gave an overview of the CEM II/A-M and CEM II/B-M cements under development in Germany as referred to in Table 4, confirming the impression that slag-limestone (S-LL) combinations are in fashion in Germany.

Table 4 The situation for Portland-composite cements in Germany per October 2005

Cement type	Inspection by VDZ ²	Technical approval placed	On-going trials for technical approval	Total
CEM II/A-M (S-LL)	1	-	-	1
CEM II/B-M (S-LL) ¹	13	13	9	35
CEM II/B-M (V-LL) ¹	2	-	-	2
CEM II/B-M (S-D)	1	-	-	1
Total	17	13	9	39

¹As a rule minimum 2 strength classes per cement/plant.

²Verein Deutsche Zementwerke (eng. Association of German Cement plants)

In Fig. 3 reproduced from Müller (2006) the porosity and some pore size distributions are shown for mortar based on CEM II/B-LL (25% LL), CEM III/A-S (50% S), Cem IV/B-V (40% V) and CEM II/B-M (10% S and 25% LL) relative to CEM I. The chloride diffusion coefficients for some of the same mortars are shown in Fig. 4. It can be noted that the coarse porosity ($> 0.1 \mu\text{m}$) is much higher (2x) for CEM II/B-LL (25% LL) than for CEM I, while the chloride migration coefficient has about the same magnitude. The CEM III/A-S (50% S) had the lowest value for these two parameters among those tested, while surprisingly enough the CEM II/B-M (10% S and 25% LL) performed better than the CEM I with 70% of its coarse porosity and half the chloride migration coefficient.

The good performance by CEM II/B-M (10% S and 25% LL) with respect to coarse porosity and chloride migration, but also for other durability properties tested by Müller (2006) not referred to here, might not only be a result of improved particle packing by the ternary blend (not discussed by Müller, 2007), but also a synergic chemical reaction between hydration products from slag and limestone.

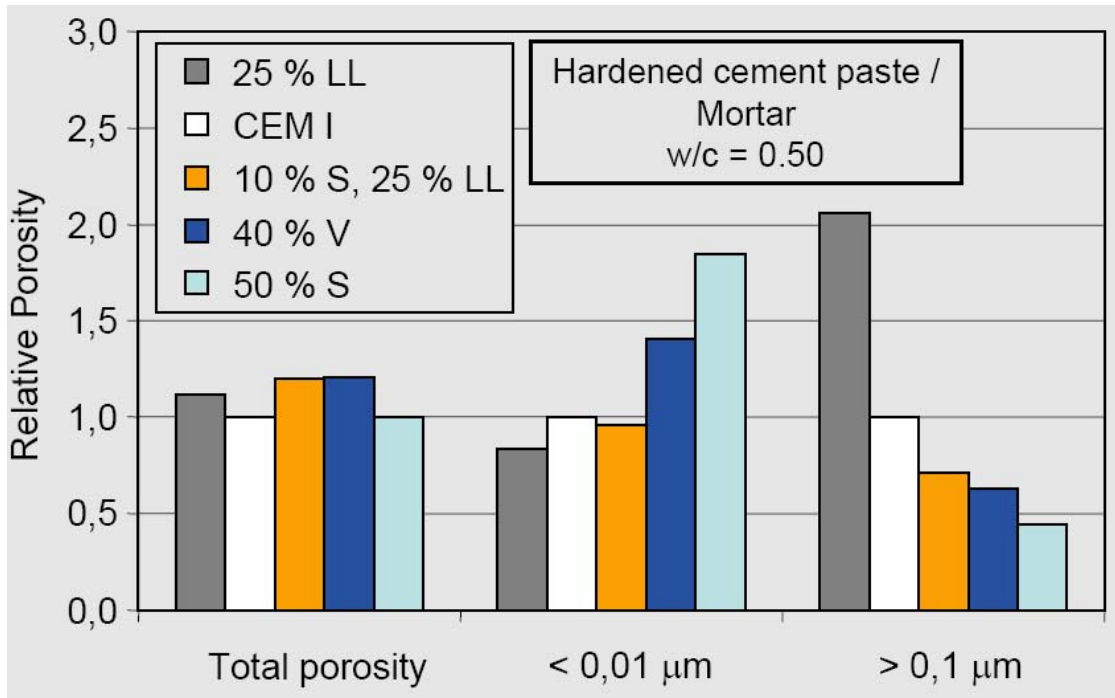


Fig. 3 Total porosity and porosities < 0.01 μm and > 0.1 μm for mortar based on CEM II/B-LL (25% LL), CEM III/A-S (50% S), Cem IV/B-V (40% V) and CEM II/B-M (10% S and 25% LL) relative to CEM I (= relative value 1) from Müller (2006).

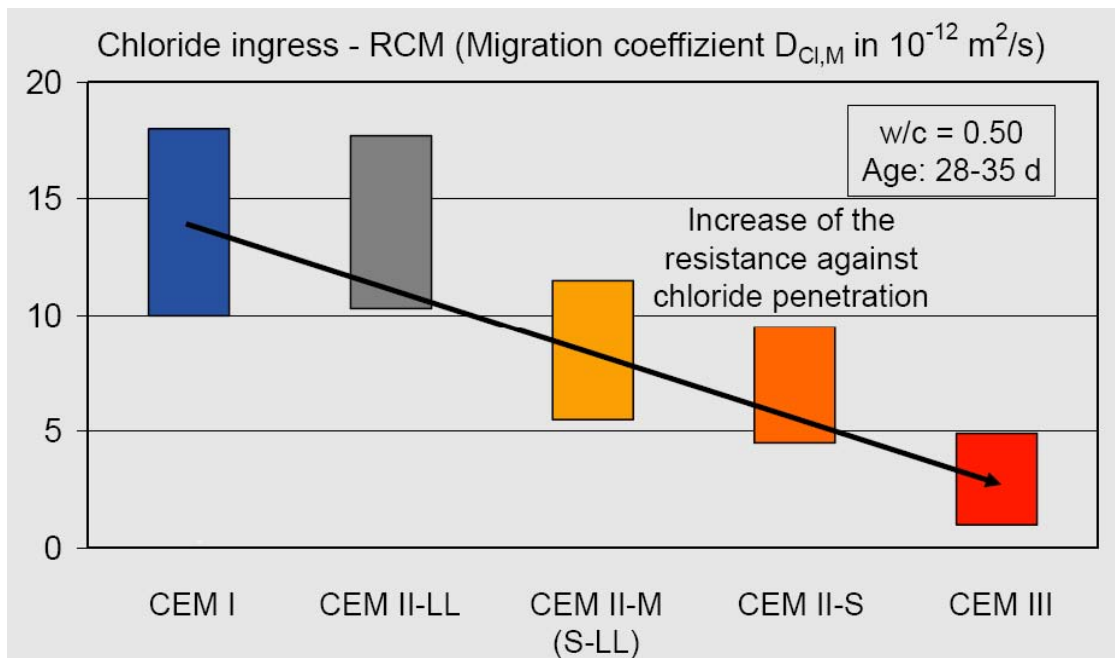
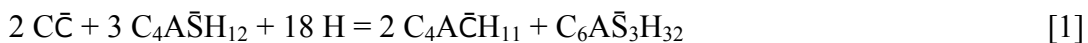


Fig. 4 Chloride migration coefficients for mortar based on CEM II/B-LL (25% LL), CEM II/B-S (30% S), CEM III/A-S (50% S), and CEM II/B-M (10% S and 25% LL) relative to CEM I (= relative value 1) from Müller (2006).

Blast furnace slag has a typical composition of 47% CaO+MgO, 35% SiO₂ and 12% Al₂O₃. When activated with gypsum together with cement, the hydration products are generally the same as for ordinary Portland cement (OPC); CSH-gel, Ettringite and monosulphate, are produced during the continued hydration (Schmolczyk, 1965, and Uchikawa, 1986). The formation of Strätlingite (C₂ASH₈) is only to be expected if alkali hydroxide is added to the slag cement (Richartz, 1966) or if the blast furnace slag is activated with alkali hydroxide (Regourd, 1980, and Forss, 1983). According to Matschei et al. (2007a, b and c), limestone will only react with calcium aluminate hydrates (e.g. C₃AH₆) or monosulphate (C₄AH₁₀) and not Ettringite (C₆A \bar{S} ₃H₃₂). I assume that in slag cement, the aluminates will be as a mix of monosulphate and Ettringite and not free calcium aluminate hydrate. The reaction of a fraction of the aluminate in a blastfurnace slag will then be

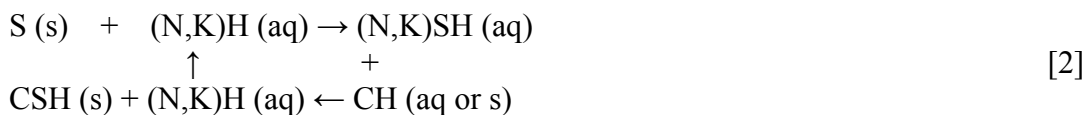


where C = CaO, \bar{C} = CO₂, A = Al₂O₃, \bar{S} = SO₃ and H = H₂O. In short, calcium carbonate reacts with monosulphate and liberates sulphates that in turn will react with monosulphonate to form ettringite involving substantially extra volume water transformed from liquid to solid hydrates. This may help reduce the porosity and permeability of the ternary system, although the available aluminate may be small in slag cement. It might have been better to add something producing more aluminates together with limestone, but unfortunately EN 197-1 exclude limestone in the classes CEM IV (pozzolanic cements) and CEM V (composites cement) that could be formulated to produce more calcium aluminate hydrates.

St. Lawrence cement (www.stlawrencecement.com) promoted their new ternary cement called TerC³ “Ternary for a Century” during the 12th International Congress on the Chemistry of Cement (July 2007). Cement clinker is replaced by 25-30% of a mix of siliceous fly ash (ASTM Class F) and silica fume.

Another ternary cement is on the market in USA based on the combination cement-slag-silica fume (Fidjestøl, 2007). Apparently the role of silica fume is to increase the early strength due to its faster reactivity than slag or fly ash.

The combination of silica fume with other pozzolanas was initially surprising to the author of this report since silica fume will keep the alkalis needed to activate slag or fly ash busy for a while as shown for the reaction loop proposed by Justnes (2007);



using cement chemist’s short hand notation; C = CaO, S = SiO₂, N = Na₂O, K = K₂O and H = H₂O. However, since the alkalis apparently only are catalytic they will be available for activation of slag or fly ash when all silica fume has reacted. As shown in Fig. 5 for sealed curing of paste with 8 and 16% silica fume replacement of cement, about 40 and

20% silica fume have reacted in 1 day, respectively. Thus it is likely that about 80% would have reacted for a 4% replacement and the alkalis made available for slag or fly ash activation in a couple of days.

Although there may not be a chemical synergy, but more an additive effect of slag or fly ash with silica fume, there might be a physical synergy in particle packing. Justnes (2007) investigated the porosity of cement paste for oil well applications with or without silica fume and found that silica fume alone reduced average pore size openings from about 250 nm to 25 nm as plotted in Fig. 6.

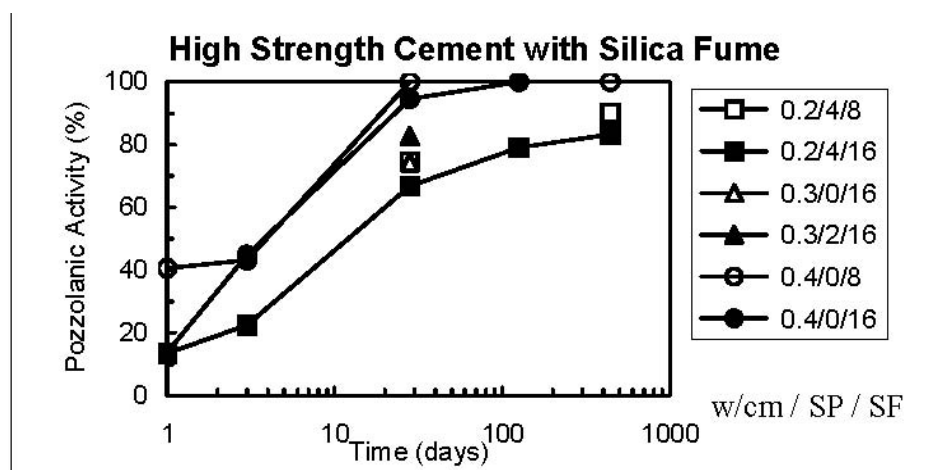


Fig. 5 Pozzolanic activity progress of silica fume in HSC with 8 and 16 % silica fume (SF) replacement at moderate to low w/cm with and without super-plasticizer (SP) according to ^{29}Si MAS NMR (Justnes, 2007).

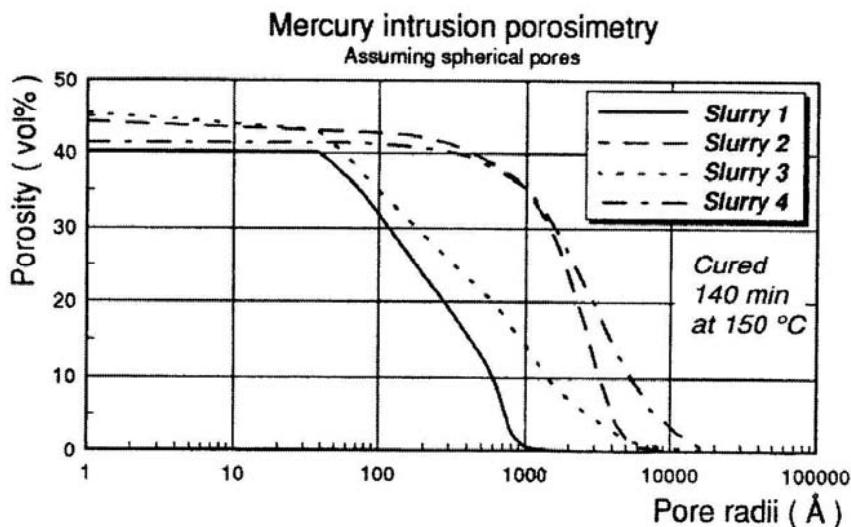


Fig. 6 Pore size distribution of oil well cement slurries immediately after set at 150°C: 1) full composition, 2) lacking SF, 3) lacking weight material and 4) lacking both SF and weight material (Justnes, 2007).

However, in the brochure of the ternary cement TerC³ it is only referred to the 3 days strength as the earliest strength, which could indicate there are some problems of reaching satisfactory 1 day strength for such a blended system. Reported values are 20-25, 25-30 and 35-40 MPa compressive strength after 3, 7 and 28 days curing, respectively.

5 FUTURE RESEARCH

For the sake of practicality it is recommended to focus further research on developing a portland-composite cement (CEM II/B-M) where the 35% clinker replacement allowed is based on a mixture of siliceous fly ash (V) and limestone (L or LL). Up to 5% of the 35% may be used for an alkali rich minor component that will accelerate the fly ash (e.g. clinker kiln dust, CKD, or alkali carbonates). The reasoning behind this is that the pozzolanic reaction of the fly ash consisting of a glassy aluminosilicate (AS) phase form a mixture of calcium silicate hydrate (CSH) gel, Strätlingite (C₂ASH₈) and calcium aluminate hydrates (e.g. C₃AH₆) in reaction with calcium hydroxide (CH). The reaction is unbalanced since there are too many unknowns;



The calcium carbonate (C $\bar{\text{C}}$) will in turn be able to react with the calcium aluminate hydrate and form calcium carboaluminate hydrate transferring even more liquid water into hydrates and thereby lowering porosity and increasing strength;



Reaction 4 is quite fast as Matschei et al. (2007c) synthesized pure C₄A $\bar{\text{C}}$ H₁₁ by letting stoichiometric amounts of C₃A and C $\bar{\text{C}}$ hydrate together for 14 days.

One of the benefits with a ternary blend as recommended above is that siliceous fly ash (V), limestone and CKD already are available at Norcem's cement plants. A second advantage is that these components are easier to grind than clinker, unlike slag, and will thus further contribute to energy saving. Thus, the minimum 30% saving in CO₂ emissions is within reach as well as the objective of the project providing that satisfactory early strength is achieved. Another advantage of fly ash in this respect is that the aluminate content is higher than in blastfurnace slag (20-30% vs. 12% in average) and that sulphate is not used as activator as for slag. Thus, a large fraction of the aluminate hydrates formed might be made available for reaction with calcium carbonate in a CEM II/B-M (V-LL) compared to a CEM II/B-M (S-LL) with equal contents of V and S.

One advantage of using common potassium carbonate (K₂CO₃ or K $\bar{\text{C}}$ in short), or sodium carbonate (Na₂CO₃) for that matter, is that they are safe to handle and will form high pH *in situ* by reaction with calcium hydroxide from cement hydration;



and at the same time form calcium carbonate with high surface area that probably is faster reactive with calcium aluminate hydrates than limestone powder. Such *in situ* forming accelerators were utilized by Justnes (1995 and 1996) making lime-pozzolan mortars with high early strength. The disadvantage may be that alkali carbonates may retard the setting of cement too much and give somewhat lower long term strength depending on total alkali content.

Although not available today at Norcem, common clay calcined at 700-800°C (Østnor, 2007) should be evaluated as a replacement for siliceous fly ash. Both because of its availability and since fly ash might be hard to get in the future, but also because common clays in general have relative high aluminate content (in average 18%). The pozzolanic reaction of calcined clay is further believed to be in analogy with siliceous fly ash described in reaction 4, as will the further reaction with limestone outlined in reaction 5. Calcined clay is also defined in EN 197-1 as a major component of type Q (see Table 1). Some clays may also contain calcium carbonate, which does not decompose before 900°C. Calcining such clays at 700-800°C may thus render a ready mix of a pozzolan producing calcium aluminate hydrates and calcium carbonate to react further with them. Finding a suitable clay one could thus still exploit the carbonate-aluminate concept and allow higher clinker substitutions (up to 55%) making a pozzolanic cement, CEM IV/B (Q) defined in EN 197-1 (see Table 1), providing the clay consist of at least 25% reactive SiO₂. With this concept the minimum target of reduced CO₂ emission could be exceeded, maybe up to 45% with a 55% replacement taking into account that calcining the clay also generates some CO₂ by burning fuel. Carbon dioxide emission from calcination of clay is only assumed to be 20% of the clinker it replaces since there will be no CO₂ from decomposition of limestone in the clay ($\approx 60\%$ of the CO₂ from cement clinker) and only half of the fuel derived CO₂ ($\approx 40\%$ of the CO₂ from cement clinker) due to the much lower temperature of calcination (700-800°C) versus clinkerization (1450°C). On the other hand, if bio fuel or waste fuel with zero net CO₂ emission factors used for clay calcination, the full effect of clinker calcination reduced carbon dioxide emission can be exploited. It is realistic that 50% of fuel for calcination of clay is with zero net CO₂ emission factor, and then about 90% of the clinker replacement can be accounted for as reduced CO₂ emission, leading to a maximum of 50% reduction for a CEM IV/B (Q). However, special measures may have to be taken in order to achieve satisfactorily early strength for cement with such a high clinker replacement.

6 CONCLUSIONS

A review has been made on how to make cements with reduced clinker content to achieve the goal of minimum 30% reduced CO₂ emission and still let these cements be defined as common cements as classified by EN 197-1.

There is a trend to make ternary cement blends in Germany based on clinker - blastfurnace slag - limestone to be within the class CEM II/B-M (S-LL) with up to 35% clinker replacement in accordance with EN 197-1.

There exists a ternary cement based on a clinker - blastfurnace slag - silica fume on the market in USA and one based on clinker - siliceous fly ash - silica fume in Canada. In

both cases silica fume is used to secure reasonably early strength. These cements would have been classified as CEM II/B-M (S-D) and CEM II/B-M (V-D), respectively, by the European standard EN 197-1.

It is recommended to focus further research in COIN on developing a CEM II/B-M (V-L) or (V-LL) replacing 35% clinker with siliceous fly ash and limestone to fulfil the minimum objective of 30% reduced CO₂ emission and to exploit the potential synergy of the two clinker replacements (i.e. calcium carbonate forming calcium carboaluminate hydrate with extra water binding in reaction with some of the pozzolanic products from the fly ash).

The goal may be significantly exceeded (up to 50% reduced CO₂ emission) by developing a CEM IV/B (Q) where the clinker replacement is a clay containing sufficient calcium carbonate to exploit the carboaluminate concept. The assumptions are that the clay is calcined at only 700-800°C leaving the calcium carbonate intact and that some 50% bio fuel or waste derived fuel without CO₂ emission is used for the calcination.

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