		SINTEF REPORT		
SINTEF Building and Infrastructure COIN – Concrete Innovation Centre Address: NO-7465 Trondheim NORWAY Location: Richard Birkelands vei 3 Telephone: +47 73 59 52 24 Fax: +47 73 59 71 36 Enterprise No.: NO 948 007 029 MVA		TITLE COIN P1 Advanced cementing materials SP 1.1 F Reduced CO2 - emissions Principles of making cement with reduced CO2 emission State of the art		
		AUTHOR(S) Harald Justnes CLIENT(S) Aker Kværner Engineering and Technology, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Spenncon AS, Unicon AS, Veidekke ASA and The Research Council of Norway		
REPORT NO.	CLASSIFICATION	CLIENTS REF.		
SBF BK A07019	Unrestricted	Terje F. Rønning		
CLASS. THIS PAGE	ISBN	PROJECT NO. NO. OF PAGES/APPENDICES		
Unrestricted	978-82-536-0982-9	3D006010 14		14
ELECTRONIC FILE CODE		PROJECT MANAGER (NAME, SIGN.)	CHECKED BY (NAME, SIGN.)	
		Harald Justnes	Hedda Vikan	
FILE CODE	DATE	APPROVED BY (NAME, POSITION, SIGN.)	-	
ABSTRACT	2007-10-15	Tor Arne Hammer, Centre Manager		

ABSTRACT

A review of literature has been made with respect to making cements with less CO₂ emission.

It seems that the most viable alternative on a short term basis to make cement with less carbon dioxide (CO_2) emission is to replace parts of the clinker with supplementary cementing materials and limestone already available at the factory. However, reaching a replacement level of 30% may reduce early strength and hamper building productivity unless counteracted by finer grinding or admixtures.

The use of alternative fuels that are at least partly CO_2 neutral will also help, but this is to a large extent already exploited today.

Alternative raw materials to limestone that are rich in calcium are hard to find, but Wollastonite $(CaSiO_3)$ may be interesting to look into due to its abundance in Scandinavia.

Among the alternative clinkers, calcium sulphoaluminate cements are interesting in terms of their much lower CO₂ emission (in the order of 30%) than OPC and potentially very rapid strength development (depending on composition) possibly enhancing building productivity. It is recommended to keep an eye on this technology internationally.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Materials Technology	Materialteknologi
GROUP 2	Concrete	Betong
SELECTED BY AUTHOR	Cement production	Sementproduksjon
	Carbon dioxide	Karbondioksid
	Alternative fuel and raw materials	Alternative brennstoff og råmaterialer



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

SINTEF

TABLE OF CONTENTS

1	INTRODUCTION	4
2	OBJECTIVE	4
3	PRINCIPLES OF MAKING CEMENT WITH LESS CO2 EMISSION	5
	3.1 Alternative clinkers	5
	3.1.1 High belite cement	5
	3.1.2 Calcium sulphoaluminate cement	
	3.2 Alternative fuels and raw materials (AFR) for Portland cement manufacturing	8
	3.2.1 Alternative fuels (AF)	8
	3.2.2 Alternative raw materials (AR)	
	3.3 Cements with less clinker content (blended cements)	10
4	FUTURE RESEARCH	11
5	CONCLUSION	12
6	REFERENCES	12
7	ABBREVIATIONS	14

🕥 SINTEF

1 INTRODUCTION

The topic of CO_2 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 biofuels 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 electing 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.

The cement industry world wide is estimated to emit about 5% of the total global anthropogenic carbon dioxide (CO₂) emissions (Hendriks *et al.*, 1998). The general estimate is about 1 ton of CO₂ emission per ton clinker produced if fossil fuel is used.

Cement is clinker ground together with gypsum for setting regulations, other additives and sometimes supplementary cementing minerals like blastfurnace slag, fly ash etc. Portland cement clinker is generally composed of 63-70% CaO, 19-24% SiO₂, 3-7% Al₂O₃ + TiO₂ and 1-5% Fe₂O₃ and forms the main mineral phases Ca₃SiO₅, Ca₂SiO₄, Ca₃Al₂O₆ and Ca₂AlFeO₅ (or Ca₂Fe₂O₅) when burnt at about 1,450°C. The usual components in the raw meal fed to the kiln are limestone (for CaO), clay or slate (for Al₂O₃ and SiO₂) as well as iron ore (to adjust Fe₂O₃). For an average composition of the cement clinker feed with a lime saturation factor (LSF = CaO/{2.80·SiO₂ + 1.18·Al₂O₃ + 0.65·Fe₂O₃}) of 0.95, coal as the fuel with calorific value of 29.3 MJ/kg and a carbon content of 85% by mass, a kiln with a fuel energy consumption of 3,200 kJ/kg clinker will give carbon dioxide emission fractions of 335 kg/ton clinker from the fuel and 535 kg/ton clinker from the dissociation of limestone (Locher, 2006);

$$CaCO_3 = CaO + CO_2 (g)$$
^[1]

The ratio between raw material derived CO_2 and fuel derived CO_2 may of course differ in practice, but the rough 60/40 share show the path to reduction in CO_2 emissions. The ways to make Portland cement with less CO_2 emission can then be to 1) make clinker with less calcium, 2) make clinker with another calcium source than carbonate, 3) use fuel without CO_2 emission (i.e. quota regulated), 4) make cement with less clinker content and 5) a combination of measures 1-4.

2 OBJECTIVE

This report is state-of-the art report no. 1 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.

Although the objective of the task states that the principle of less clinker content in cement is to be followed, the present report evaluates all principles that may lead to achieving the objective. The options may be good to know for future reference and as argument for the given choice.

🕥 SINTEF

3 PRINCIPLES OF MAKING CEMENT WITH LESS CO₂ EMISSION

3.1 Alternative clinkers

The most interesting alternative clinkers to Portland cement clinker with respect to reduced CO_2 emission seems to be high belite cement clinker and sulphoaluminate cement clinker as described in the following sub-sections. Calcium aluminate cement clinkers are also emitting less CO_2 during their production as the main cementing mineral is $CaAl_2O_4$ (CA in short hand) forming $CaAl_2O_4 \cdot 10H_2O$ (or CAH_{10}) at low temperature hydration. Later, at temperatures above +23°C, this hydration product can undergo the following transformation;

$$3 \text{ CAH}_{10} = \text{C}_3 \text{AH}_6 + 2 \gamma \text{-AH}_3 + 18 \text{ H}$$
[2]

Reaction 2 will theoretically give 48 vol% less solid products than reactant. The resulting porosity increase leads to a loss in strength often referred to as *strength retrogression*. The released water volume (55 vol%) is also somewhat larger than the porosity increase and pressure stresses therefore arise in the hardened paste making the situation worse than the porosity increase alone. A few structural failures due to strength retrogression have made this cement type prohibited for structural use and it is thus not further treated in this report.

3.1.1 High belite cement

High belite cement is essentially a Portland cement where the content belite, C_2S , is much higher (45-60%) than that of alite, C_3S (20-30%), or quite the opposite of an ordinary Portland cement (OPC). The lower calcium level should then give less CO_2 emission providing the source is limestone. In addition, this cement requires about 100°C lower kiln temperature than OPC, requiring less fuel and hence somewhat lower CO_2 emission also for this reason. High belite cement is harder to grind than OPC and will require some extra energy in this respect.

Gartner (2004) made an estimate of CO_2 savings changing from a modern OPC with 65% C₃S to a high belite cement with little or no C₃S and found that the overall reduction in limestone consumption in total would not be more than 8 %. Even allowing for the ensuing reductions in burning temperature, he pointed out that the likely maximum total CO_2 emission savings only would be in the order of 10%. He also said that this has to be balanced against the fact that high belite clinkers are very hard to grind and thus require more energy. Very low rates of strength development are also considered unsatisfactory by most costumers.

Chatterjee (2003) reviewed the status of high-belite cement and concluded that the interest in it has grown over the three last decades due to its anticipated multidimensional benefits like lower energy consumption, raw materials conservation and constructional durability of the resultant concrete. However, the product and its manufacturing technology are yet to be of extensive commercial significance as there are still no viable technologies to substantially enhance the intrinsic low reactivity of the belite phase and to generate large surface area for the cement at a reasonable energy input to achieve a higher degree of hydration in concrete.

It seems that high belite cement in practice is produced in Japan, India and China (Sui and Yao, 2003) and that the application first and foremost is as low heat cement in massive structures like dams. However, low heat can be also be obtained by for instance using large content of supplementary cementing materials as blast-furnace slag and fly ash in the concrete.



For the sake of cement with less CO_2 emission it does not seem like high belite cement is worth pursuing with its low savings potential (about 10%), in particular when bearing in mind the low strength development rate that would have hampered building productivity.

3.1.2 Calcium sulphoaluminate cement

Calcium sulphoaluminate cement has recently been promoted as the cement for sustainable development (Alaoui et al., 2007) as a typical cement composition is 53% C₄A₃ \bar{S} , 18% C₂S, 12% C and 15% C₄AF (2% residual). According to their comparison with Ordinary Portland cement reproduced in Table 1, the CO₂ emission is in theory not only less for calcium sulphoaluminate cement (-43%), but also the specific heat consumption during clinkering (-14%) due to lower temperature, as well as lower crushing energy (-40%) since the minerals are more friable.

Table 1 Comparing CO_2 emission (from raw materials) and energy of making ordinary Portland cement with that of sulphoaluminate cement (Alaoui et al., 2007)

Parameters	Ordinary Portland clinker	Sulphoaluminate clinker
CO_2 emitted per ton clinker	535 kg/t	305 kg/t
Specific heat consumption during clinkering ¹	3.845 GJ/t ²	3.305 GJ/t
Energy for crushing ³	45 - 50 kWh/t	20 - 30 kWh/t

¹Popescue et al. (2002), ²BAT is 3.1 GJ/t, ³Janotka and Krajci (1999)

Gartner (2004), however, discussed the sulphoaluminate system as follows: "There are many practical problems with ettringitic cementing systems such as sulphoaluminate cements, especially the problem of controlling the expansion associated with the reaction. If one wishes to make use of ettringite as a major cementing phase, there is an older technology that still has great interest: that of "supersulfated" slag cements. Such cements, based on ground granulated blastfurnace slag (GGBFS) with fairly large amounts (10-20%) of gypsum or anhydrite, plus a very small amount of lime or Portland cement as a catalyst, can give volume-stable concretes in which ettringite and C-S-H are the main hydrate phases. However, their strength development is slow compared with that of Portland cements, and the concretes are more easily carbonated, sometimes leading to strength loss and corrosion of reinforcing steel. As a result, they have fallen out of favour with concrete users and most of the available GGBFS is instead currently used in blends with Portland cement. Nevertheless, given that GGBFS is an industrial by-product and can thus be considered to have zero associated CO₂ emissions, supersulfated cements still appear to be a promising area for additional research. Although calcium sulphoaluminate-based cements are increasingly being used in specialised applications where high early strengths and self-stressing or shrinkage compensation are required, their more general application to concrete is limited to China, where a wide range of $C_4A_3\bar{S}$ -based cements have been developed and normalised under the name of the "Third Cement Series", TCS (Zhang et al., 1999). In the Chinese literature, it is stated that these cements, which are based on clinkers containing C_4A_3S , belie and ferrite in various proportions as their major phases, can be used in a wide variety of applications depending on their different phase compositions and on the amount of gypsum or anhydrite interground to make the final cement. However, as far as we are aware, the TCS technology currently practiced in China is based mainly on clinkers with fairly high $C_4A_3\bar{S}$ contents (60-70%), aimed at the



prestressed concrete sector in which the rapid strength development at moderate curing temperatures, plus self-stressing, are economic advantages. Such cements must usually be manufactured using bauxite as a principal raw material, and this makes them relatively expensive compared with Portland cements. It should be noted that the same comment applies to the more traditional calcium aluminate cements, such as the classic "Fondu" cement, which is rich in monocalcium aluminate and thus has a fairly low raw material derived CO₂ emission. However, in addition to its higher raw materials cost, Fondu clinker is made by a melt process, which is not very energy efficient compared with the Chinese TCS approach (which makes use of conventional rotary kilns). The TCS approach has also been re-examined recently in some eastern European countries (Palou et al., 2003), with the objective of making energy-efficient sulphoaluminate-belite cements with lower C₄A₃\$ contents and higher belite contents than those produced in China. However, published results are disappointing apparently due to the same problem of low belite reactivity that affects belite-rich Portland cements, so it is not yet clear whether TCS cements are really capable of offering very significant global CO₂ savings".

Later Li, Walenta and Gartner (2007) are acknowledging the great potential of calcium sulphoaluminate cement in reducing CO_2 emission by at least 20 - 30% compared to an OPC of equal performance providing the clinker is produced in a modern rotary kiln. They also added that a great deal further careful study will be required to fully understand the hydration of these interesting and novel cements in order to better optimise their compositions and thereby further decrease manufacturing CO_2 emissions for equal concrete performance.

Valenti et al. (2007) also pointed out a few other environmentally friendly aspects of calcium sulphoaluminate cements: Firstly, industrial wastes and by-products difficult to reuse and dispose can be used as raw materials for its clinker production, such as fluidized bed combustion waste, red mud, low-quality pulverized coal fly ash and chemical gypsum. Secondly, the intergrinding of large amounts of gypsum with the clinker enables reduced clinker content and enhanced chemical gypsum utilization, in particular flue gas desulphurization gypsum generated world wide in increasing amounts.

Pèra and Ambroise (2004) listed the following advantageous applications of sulphoaluminate cements:

- Development of concrete with high early strength: 40 MPa in 6 h and > 55 MPa at 24 h
- Design of self-levelling screed with limited curling when unbounded to its support
- Design of self-levelling topping mortar presenting the following properties: time of workability > 30 min, set within 75 min and low drying shrinkage (< 250μ m/m)
- Glass fibre reinforced cement (GFRC) composites that can be demoulded 4 h after casting and present high ductility and durability after aging in different weathering conditions

Quillin (2001) acknowledged a very good sulphate resistance of sulpho-aluminate-belite cement, but the chloride diffusion was higher than Portland cement, and especially the carbonation rate. However, he admitted that the durability may have been improved using a suitable plasticizer to achieve a lower w/c (used w/c = 0.56).

Glasser and Zhang (2001) evaluated the durability of 14 year old reinforced concrete pipes (w/c = 0.25) exposed to the tidal zone in China, and found that the mild steel mesh reinforcement was without corrosion. This may have been due to a dense matrix and rapid self-desiccation that is difficult to re-saturate.

The aspects concerning durability has made applications of calcium sulphoaluminate cement outside China limited to for instance rapid repair mortars and self-levelling screeds. In China with



its $> 10^6$ t/year production it is also used in construction, but apparently in low performance structures as in in-door housing etc. However, this makes quite a bit of the total concrete market in a society, so this cement may be worthwhile looking further into due to its large saving potential in CO₂ emission and considering the fast strength development enabling faster building processes.

3.2 Alternative fuels and raw materials (AFR) for Portland cement manufacturing

Alternative fuels and raw materials (AFRs) in cement clinker manufacturing may be difficult to separate completely as many of the alternative fuels (AF) may have an ash component that will end up as an integral part of the cement clinker and thereby can be judged as alternative raw material (AR). However, AF is here defined as a kiln feed being used mainly for its calorific value (energy component) even though it often is a material that should be destroyed in a safe manner. AR is a kiln feed that mainly will contribute to the clinker, but may also have a calorific value, and can also be special category waste to be disposed in a safe manner.

3.2.1 Alternative fuels (AF)

Tokheim and Brevik (2007) recently said that the philosophy of Norcem in reducing CO_2 emission from their cement production up to now has been to replace fossil fuels with waste derived fuels that are partly CO_2 neutral. An overview of fuels used at Norcem, Brevik, is reproduced in Table 2.

Fuel	H _j ^a (GJ/t)	Gross CO ₂ emission factor (kg CO ₂ /GJ)	$\begin{array}{c} Gross CO_2 \\ emission \\ factor \\ (t CO_2/t) \end{array}$	Fossil fraction (%)	Net CO_2 emission factor, e_j (kg CO_2/GJ)	Net CO ₂ emission factor, e_j' (t CO ₂ /t)
Coal	29.3	96.0	2.8	100	96.0	2.8
Petcoke	33.9	92.8	3.1	100	92.8	3.1
Diesel	42.8	74.0	3.2	0	0.0	0.0
Waste Oil	34.0	74.0	2.5	100	74.0	2.5
Plastic	37.7	75.0	2.8	100	75.0	2.8
Solid hazardous waste	14.9	74.0	1.1	100	74.0	1.1
Liquid hazardous waste	15.7	74.0	1.2	100	74.0	1.2
Refuse derived fuels	13.5	87.0	1.2	10	8.7	0.1
CCA waste wood	12.6	110.0	1.4	0	0.0	0.0
Animal meal	16.8	88.0	1.5	0	0.0	0.0
Wood	15.7	110.0	1.7	0	0.0	0.0

Table 2 Waste fuels commonly used in the cement industry (Tokheim and Brevik, 2007)

^aSpecific heat



Since the concept of alternative fuels (AF) is so well exploited in Norway and in Europe as a whole (Scheuer, 2003), there seems little to gain further with this approach and other approaches are therefore focused on in this report. However, it is interesting to notice that according to the Environmental Declaration Forms ISO/CD 14025 Type III found on the homepage of Norcem, their "Anlegg", "Industri", "Standard", "Standard FA Brevik" (blended) and "Standard FA Kjøpsvik" (blended) cements are emitting 767, 767, 774, 656 and 668 kg CO₂-equivalent/t cement, respectively, in 2006. The low values for the pure clinker cements are likely due to AF.

3.2.2 Alternative raw materials (AR)

Calcium sources other than limestone can, in theory, be used as raw materials, but it turns out that there are not really any other sufficiently wide spread and sufficiently concentrated sources of calcium available (Gartner, 2004). Calcium sulphates (gypsum and anhydrite) are abundant in some locations and have historically been used to make portland cement, but the major complication is that the principal by-product in this case is not CO_2 as shown by the oversimplified equations for formation of tricalcium silicate (major component in Portland cement), but rather sulphuric acid (H₂SO₄);

$$3 \text{ CaCO}_3 + \text{SiO}_2 = \text{Ca}_3 \text{SiO}_5 + 3 \text{ CO}_2$$
 [3]

 $3 \text{ CaSO}_4 + \text{SiO}_2 + 3 \text{ H}_2\text{O} = \text{Ca}_3\text{SiO}_5 + 3 \text{ H}_2\text{SO}_4$ [4]

The process sketched in reaction 4 was, in fact, practiced industrially primarily as a means of producing sulphuric acid, with the by-product being portland cement clinker, but it fell out of favour relative to other less complicated and less expensive methods of sulphuric acid manufacture. As with all processes that attempt to obtain 2 useful products at the same time, relative economic fluctuations in the raw materials supply and in the market for both products made it difficult to operate profitably for long periods of time. In addition, the overall thermal efficiency and environmental impact of the cement-sulphuric acid process were considerably worse than that of normal cement manufacturing process. The total global demand for Portland cement is roughly an order of magnitude greater than that of sulphuric acid, meaning that it would never be meaningful to produce more than a fraction of Portland cement in this way. Moreover, good deposits of calcium sulphate are less abundant than good deposits of limestone, making this an important issue in locating a factory. Nevertheless, the process could be looked at again for suitable locations, if the market conditions were also right (Gartner, 2004).

However, it will also help to replace *parts* of the calcium with other minerals than limestone, not necessarily *all* of it.

Aïtcin (2007) discussed the possibility of using slag, ASTM class C fly ash or even the mineral anorthite (CaAl₂Si₂O₈) as they contain a substantial amount of calcium as shown in his ternary phase diagram reproduced in Fig. 1. He claimed that using slag instead of clay could save 22% CO₂ outlet, but he did not take into account that the alumina content may limit the use of these alternative raw materials since they might create an unacceptably high C₃A content in the clinker. Norway has by the way a good deposit of pure anorthite in Gudvangen should it be of interest.

Hassan (2001) suggested basalt rock as an alternative raw material for Portland cement clinker, but as a replacement of clay, not limestone, since it has relatively low calcium oxide content (9.7%).

🕥 SINTEF



Fig. 1 A simplified ternary phase diagram of CaO-Al₂O₃-SiO₂ (C-A-S) comparing composition ranges of Portland cement clinker with those of clay, Class C and F fly ash, slag and anorthite after Aïtcin (2007).

From the author's point of view, Wollastonite (CaSiO₃ or CS in short hand notation) ought to be relatively interesting as an alternative raw material since it is quite abundant with a few good locations as close as Sweden. At least if new cement plants are to be built since it often occurs together with limestone. Furthermore, if one looks at the pure binary phase diagram of C-S in Fig. 2, it can be seen that CS is melting congruently at about 1600°C. Impure Wollastonite will probably melt at the operating temperature of a cement kiln (about 1450°C) and may thus ease the formation of the main clinker minerals C_3S and C_2S . There should be a potential of saving at least 20% raw material derived CO₂ emission by using Wollastonite, making it maybe worthwhile looking into on a longer term basis. A quick search revealed that Wollastonite already has been patented (e.g. Zhong, 1993) as a fluxing agent in dosages of 1-10% of the raw meal claiming to reduce the clinkering temperature by 100°C. However, as an AR much higher dosages should be of interest, exceeding the claims of the patent.

3.3 Cements with less clinker content (blended cements)

There is a number of blended cement defined in the European Standard EN 197-1 (2000). Norcem has for instance their Standard FA cement with up to 20% ASTM Class F fly ash interground being classified as an CEM II A-V. If the supplementary material used for blending is CO_2 neutral, one will automatically reduce the CO_2 emission with the same amount providing that the grinding energy is not increased or it comes from hydropower without CO_2 emission.

Replacement levels of clinker up-to 35% is allowed for the CEM II B series. Depending on the nature of the supplementary cementing material, the early strength may, however, be reduced to a level that does not comply with an all-round cement with at least 30 % less CO₂ emission as the target of activity 1.1 within COIN. Lower strength can however partly be compensated by finer grinding or so called "quality-improvers".





Fig. 2 The binary phase diagram of CaO-SiO₂ showing amongst other phases the behaviour of pure Wollastonite (CS).

However, making cements where clinker is replaced with supplementary cementing materials seems to be the easiest to implement the less clinker approach on a short term basis as long as the cement can be defined within EN 197-1 (2000). However, that is the content of the second state-of-the-art report in activity 1.1 within COIN and interested readers should consult this.

4 FUTURE RESEARCH

It is clear from the review that the most viable solution to make cement with less CO_2 emission on a short term is to reduce the clinker content by grinding a fraction of clinker together with other cementitious materials without CO_2 emission or where the CO_2 already have been accounted for in another industry. It is recommended to try to develop an all-round cement with at least 30% less CO_2 emission along these lines, in particular utilizing ternary blends that may have synergic effects on strength development.



On a longer term basis one could always look for alternative raw materials rich in calcium but without carbonates; examples are Wollastonite (e.g. CaSiO₃). However, such alternative raw materials should be relatively close to a cement plant to make it economical.

It is recommended to follow closely the development of calcium sulphoaluminate cements as there seems to be a renewed interest in them due to their large potential saving in CO_2 emission relative to OPC coupled with their fast strength development enabling high building productivity.

5 CONCLUSION

A review of literature has been made with respect to making cements with less CO₂ emission.

It seems that the most viable alternative on a short term basis to make cement with less carbon dioxide (CO_2) emission is to replace parts of the clinker with supplementary cementing materials and limestone already available at the factory. However, reaching a replacement level of 30% may reduce early strength and hamper building productivity unless counteracted by finer grinding or admixtures.

The use of alternative fuels that are at least partly CO_2 neutral will also help, but this is to a large extent already exploited today.

Alternative raw materials to limestone that are rich in calcium are hard to find, but Wollastonite $(CaSiO_3)$ may be interesting to look into due to its abundance in Scandinavia.

Among the alternative clinkers, calcium sulphoaluminate cements are interesting in terms of their much lower CO_2 emission (in the order of 30%) than OPC and potentially very rapid strength development (depending on composition) enhancing building productivity. It is recommended to keep an eye on this technology internationally.

6 REFERENCES

Aïtcin, P.-C. : The Use of Blast furnace Slag and Class C Fly Ash as a Source of Raw Material to Decrease Significantly the Amount of CO₂ during the Fabrication of Portland Cement Clinker", Proceedings of Terrence C. Holland Symposium on Advances in Concrete Technology, Ed. George C. Hoff, held in conjunction with the 9th CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Warszawa, Poland, 21-25th May, 2007, pp. 175-189.

Alaoui, A. Feraille, A., Steckmeyer, A. and Le Roy, R.: "New Cements for Sustainable Development", Proceedings of the 12th International Congress on the Chemistry of Cement, July 8-13, 2007, Montreal, Canada, paper 258 (W3-11.3) 8 pp.

Chatterjee, A.K.: "High-Belite Portland Cement - An Update on Development Characterization and Applications", Proceedings of the 11th International Congress on the Chemistry of Cement (ICCC); "Cement's Contribution to the Development in the 21st Century" (Eds. G. Grieve and G. Owens), Durban, South Africa, 11-16 May 2003, pp. 31-40 (ISBN 0-9584085-8-0).

EN 197-1 "Part 1: Composition, Specifications and Conformity Criteria for Common Cements", CEN, 2000.



Gartner, E.: "Industrially Interesting Approaches to "Low-CO₂" cements", Cement and Concrete Research, Vol. 34 (2004) pp. 1489 - 1498.

Glasser, F.P. and Zhang, L.: "High-Performance Cement Matrices based on Calcium Sulphoaluminate-Belite Compositions", Cement and Concrete Research, Vo. 31 (2001) pp. 1881-1886.

Hendriks, C.A., Worrell, E., Price, L., Martin, N., Ozawa Meida, L., de Jager, D. and Riemer, P.: "Emission Reduction of Greenhouse Gases from the Cement Industry", Proceedings of the 4th International Conference on Greenhouse Gas Control Technologies, Interlaken, Austria, August 30th - September 2nd,, IEA GHG R&D Programme, 1998, UK

Janotka, I. and Krajci, L. "An Experimental Study on the Upgrade of Sulphoaluminate-Belite Cement Systems by Blending with Portland Cement", Advances in Cement Research, Vol. 11 (1999) pp. 35-41.

Li, G.S., Walenta, G. And Gartner, E. "Formation and Hydration of Low-CO₂ Cements based on Belite, Calcium Sulphoaluminate and Calcium Aluminoferrite", Proceedings of the 12th International Congress on the Chemistry of Cement, July 8-13, 2007, Montreal, Canada, paper 398 (TH3-15.3) 12 pp.

Locher, F.W.: "Cement - Principles of Production and Use", Verlag Bau+Technik, Düsseldorf, 2006 (ISBN 3-7640-0420-7), pp. 165

Lukasik, J., Damtoft, J.S., Herfort, D., Sorrentino, D. and Gartner, E.M: "Sustainability and Climate Change Initiatives", Proceedings of the 12th International Congress on the Chemistry of Cement, July 8-13, 2007, Montreal, Canada, paper 540 (MPL-1) 28 pp.

Palou, M., Majling, J., and Janotka, I.: "The Performance of Blended Cements based on Sulphoaluminate-Belite and Portland Cements", Proceedings of the 11th International Congress on the Chemistry of Cement (ICCC); "Cement's Contribution to the Development in the 21st Century" (Eds. G. Grieve and G. Owens), Durban, South Africa, 11-16 May 2003, pp. 1896-1902 (ISBN 0-9584085-8-0).

Pèra, J. and Ambroise, J.: "New Applications of Calcium Sulphoaluminate Cement", Cement and Concrete Research, Vol. 34, 2004, pp. 671-676.

Popescu, C.D., Muntean, M. and Sharp, J.H. "Industrial Trial Production of Low Energy Belite Cement", Cement and Concrete Composites, Vol. 25, 2002, pp. 689-693.

Quillin, K.: "Performance of Belite-Sulphoaluminate Cements", Cement and Concrete Research, Vol. 31, 2001, pp. 1341-1349.

Scheuer, A.: "Utilization of alternative fuels and raw materials" Cement International, Vol. 1, No. 1, 2003, pp. 52-66.

Sui, T. and Yao, Y.: "Recent Progress in Special Cements in China", Proceedings of the 11th International Congress on the Chemistry of Cement (ICCC); "Cement's Contribution to the Development in the 21st Century" (Eds. G. Grieve and G. Owens), Durban, South Africa, 11-16 May 2003, pp. 2028 - 2032 (ISBN 0-9584085-8-0).



Tokheim, L.A. and Brevik, P.: "Carbon dioxide emission reduction by increased utilization of waste-derived fuels in the cement industry", Proceedings of the International Symposium on Sustainability in the Cement and Concrete Industry, Edited by S. Jacobsen, P. Jahren and K.O. Kjellsen, Lillehammer, Norway, 16-19 September, 2007, pp. 263-273

Valenti, G.L., Marroccoli, M., Montagnaro, F., Nobili, M. and Telesca, A.: "Synthesis, Hydration Properties and Environmentally Friendly Features of Calcium Sulphoaluminate Cements", Proceedings of the 12th International Congress on the Chemistry of Cement, July 8-13, 2007, Montreal, Canada, paper 254 (W3-11.2) 12 pp.

Zhang, L., Su, M., and Wang, Y.: "Development and Use of Sulpho- and Ferro-aluminate cements in China", Advances in Cement Research, Vol. 11, 1999, p. 15

Zhong M. Zhang: "Modified Flux Composition for Cement", US Patent 5183506, 1993.

7 ABBREVIATIONS

- A = Cement chemist short hand notation for aluminium oxide, Al_2O_3
- AF = Alternative Fuels
- AFR = Alternative Fuels and Raw materials
- AR = Alternative Raw materials
- BAT = Best Available Technology
- C = Cement chemist short hand notation for calcium oxide, CaO
- F = Cement chemist short hand notation for ferric oxide, Fe_2O_3
- H = Cement chemist short hand notation for water (hydrogen oxide), H_2O
- K = Cement chemist short hand notation for potassium oxide, K_2O
- M = Cement chemist short hand notation for magnesium oxide, MgO
- N = Cement chemist short hand notation for sodium oxide, Na_2O
- OPC = Ordinary Portland Cement
- S = Cement chemist short hand notation for silicon dioxide, SiO_2
- \bar{S} = Cement chemist short hand notation for sulphur trioxide, SO₃