Options for CO_2 reduction in the European Cement Industry Observations from a European Science Foundation Workshop

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Abstract

Concrete is the most widely used material on earth, eclipsing the combined volumes of all other man-made materials by a factor of ten. In terms of its embedded carbon, it is a benign product, being associated with relatively little CO_2 per unit mass when compared with metals, glasses and polymers. Conversely, it is made in such vast quantities, that it is responsible for around five percent of the earth's anthropogenic CO_2.

The UK hosted a European Science Foundation Exploratory Workshop (EW08-142) on this theme last summer, which was attended by 24 experts from the cements, metals and environmental industries and from seven leading universities. This article records some of the outcomes of this workshop, highlighting the needs in applied research, in resource efficiency and in technology development. Despite recent advances in kiln design and alternative, low-energy clinkers, it seems likely that the greatest carbon savings from the industry are likely to be made by the increased use of supplementary cementing materials.

Introduction

The European Science Foundation (ESF) is an association of 79 member organisations devoted to scientific research in 30 European countries. Since its establishment in 1974, it has coordinated a wide range of pan-European scientific initiatives, of which the Exploratory Workshops are just one example. They must address a topical scientific subject and these small, interactive group sessions are aimed at opening up new directions in research to explore new fields with a potential impact on developments in science. The workshops, which usually last 1-3 days, have a wide participation from across Europe and should involve mature scientists as well as young, independent researchers and scholars with leadership potential.

Technical Themes

Space precludes reporting of individual contributions here, but the meeting focused on five technical themes:

The current state of CO_2 emissions in the European cement industry
Options for CO_2 reduction
Current trends for CO_2 reduction in cement manufacturing
Current research and emerging trends
Case studies and a discussion on future collaborative research

The presentations highlighted the following points:

- Concrete is the most widely used man-made material on earth. In terms of its embedded carbon, it is a benign product, being associated with relatively little CO_2 per unit mass when compared with metals, glasses and polymers. Despite this, concrete produces roughly 150kg/t of CO_2, compared to, say, 2000 for glass and 3000 for steel, Conversely, it is made in such vast quantities, that it is responsible for over five percent of anthropogenic CO_2.
- It is expected that the cement production will grow by 3- 4 percent per annum in the next 10 years, such that CO_2 generation will become more dominant if nothing else changes.
- On European average, the market share of Portland composite cements (EN197-1 CEM II) is more than 50% with increasing tendency. In contrast the market share of Portland cement (CEM I) continuously decreased during the last 15 year to a current level below 30%.
- Raw material in clinker production accounts for about 0.53t CO_2/t at present, compared to 0.38t CO_2 /t for fuel demand.
- Changing from the wet to the dry manufacturing process has reduced energy consumption from 5.5 to 3.0GJ/tonne. Some estimates suggest a reduction to 2.8GJ/tonne may be possible in future.
- Less than 10% of all current cement could be served by presently available granulated blast furnace slag, so slag alone is not the sole solution – fly ash has much larger reserves and potential for re-use and other low-energy

cements will also need to play a part. Limestone reserves are huge if it could be made more reactive, for example, by increasing the aluminium content of clinkers.

- Switching from coal (95kg CO_2) to oil (78) to gas (56) improves fuel CO_2 efficiency at kiln, confirming that fuel type has a role to play in CO_2 reduction.
- In summary, a common belief is that the CO_2 agenda is not critical yet – CO_2 generation will need to become much more expensive to make a worldwide economic impact. It may need to be as high as £50-100 / tonne to force the carbon agenda such that its impact on cement production forces a step-change.
- The three key issues are currently: *carbon reduction, primary energy reduction* and *whole life cycle costing* (to include transport costs of all materials and fuels).
- Carbon capture and storage is a significant research challenge. Capture and re-use of CO_2 in the flue gases in cement manufacture is addressed in a recent patent by Mori (1995) in which CO_2 is reacted with limestone :

$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$ The calcium bicarbonate solution is benign and suitable for discharge to the sea.

N.B. Calcium bicarbonate is not stable as a solid at atmospheric temperature and pressure.

- An option was reported to intensify CO_2 in the flue and combine with O_2 (as used in the glass industry) raising the question of whether captured CO_2 be safely and economically stored.
- Ternary cements, with mixed constituents introduce more possibilities. For example, clinker- fly ash-limestone combinations will produce and aluminium rich *CASH* gel and CAH that can react with limestone to form calcium carboaluminate hydrates leading to more chemical bound water resulting in higher strength and lower permability of concrete produced thereof.
- Fluidised bed technology with calcined clays can reduce CO_2 by about 26 percent, but it is recognised this depending greatly on the mineral composition of clay.
- Improving the grinding technology is as important to this industry as it is to many other industries.
- Use zero clinker cement (e.g. alkali activated pozzolans) is to be encouraged for low strength applications.

There were two primary results of the meeting; the first was a detailed exchange of ideas and the second was a discussion of the needs of the industries represented and partners present and recommendation of how best to collaborate.

1) **The needs of the cement producers** are two-fold. First there is an obvious need to lower CO_2 emissions whilst maintaining the profitable production of cement and the quality of the concrete structures. Much research has and continues to be funded directly from the industry and this divides into four broad categories:

i. **Blended or Composite Cements.** The cement industry has invested heavily in blended cements research over several decades. Commercially mature, this technology focuses on various material streams, including: Coal combustion ash / Pulverised fuel ash / Fly ash / Burnt oil shale / Ground, Granulated Blast furnace Slag / Limestone / Silica Fume / Rice Husk Ash / Calcined clays (including metakaolin) and Natural Pozzolans

Of these, the cement producers felt that the last two (calcined clays and natural pozzolans) offer the greatest and most immediate impact on CO_2 reduction in the foreseeable future. Research on thermally processed clays and natural pozzolans has, for the most part been concerned with their chemical and physical properties as supplementary cementing materials. Work on their reactions in ternary and higher-order mixtures remains incomplete and there is a need to collect and review extant work and to close the knowledge gaps. Of more immediate concern however, is the lack of knowledge at either a national or European level as to the extent of these resources, their locations, quantities and properties.

ii. **Efficiencies in processing**. Several contributors referred to advances in kiln design, grinding technology and especially in heat integration, through improvements in the use of pre-heaters and efficient use of low grade heat. Although this information was of interest to the audience, it described technologies away from the expertise of most participants. Consequently, this is not an area in which this group intends to attempt a future influence.

iii. **Low energy clinker development**. This has been a very active area of research in recent years and the principal groups of clinker types are:

- Belite – aluminate clinkers. Also known as porsol cements, this phase assemblage is dominated by CA ($CaO.Al_2O_3$) $C_{12}A_7$ ($12CaO.7Al_2O_3$) and β-C_2S ($2CaO.SiO_2$). Formed from an appropriate mixture of bauxite, limestone and clay, the clinker is formed at relatively low temperature (1250-1300°C) largely by solid state diffusion, thus avoiding formation of the more thermodynamically stable phase gehlenite (C_2AS).
- Sulpho-aluminate clinkers ($3CaO.3Al_2O_3.CaSO_4$) were originally developed in China (1975) and are attractive clinkers as they form at some 100-200°C lower than conventional Portland cements. Formed from calcining limestone, bauxite and gypsum at around 1350°C, the clinker mineral assemblage is principally C_2S, C_4AF and yeelemite ($4CaO.3Al_2O_3.SO_3$). Unlike Portland cements, the hydrate assemblage is dominated by ettringite, rather than CSH and the degree of expansion associated with this phase may be controlled by the quantity of free portlandite interground with the product.
- Sulpho-belite clinkers (variously, sulpho-belite / sulphoaluminate-belite etc.) are a family of low energy clinkers whose essential constituents are belite (C_2S) and tetracalcium trialuminate sulphate (C_4A_3S). Depending on their composition, these clinkers may be designed to produce expansive binders or non-expansive binders offering high early strengths. Also produced at around 1350°C, these clinkers may be formed from raw meals containing borax and phosphogypsum; noticeably reduce the reaction temperature necessary for clinker formation.
- Ferrite clinkers (usually ferrite rich clinkers) are formed during the calcination of limestone, magnetite and bauxite at 1300°C or greater and are dominated by phases in the C_4AF to C_6AF_2 range. In some ways analogous to aluminate-rich clinkers, their hydration is somewhat sluggish, but may be accelerated by fine grinding or chemical activation, for example with citrate and potassium carbonate. Although the subject of considerable research, they pose a processing difficulty in that they are comparatively hard and therefore expensive to grind.

iv. Use of alternative fuels and raw materials. Alternatives to fossil fuels have been used in cement manufacturing for some decades. Incorporation of tyre crumb into the fuel has proved a valuable means of disposal of otherwise waste rubber, with considerable energy benefits. Similarly, the co-combustion of waste solvents was reviewed. Comparisons were made between the cement industry in European and North America, showing the importance of understanding the elemental composition of alternative fuels, especially limits on halogens (particularly in solvents) and sulphur present in oils, tyre crumb and in some biofuels.

Alternative raw materials are important in cement manufacture, for two reasons. First it is uneconomic to transport materials over large distances when a suitable alternative is available and secondly, many low energy clinkers require alternative materials for their feedstocks. Considering conventional clinker production, blastfurnace slag can (at least in part) be used as a source of calcium, where transport of limestone is only marginally economic. Similarly, coal fired power station fly ash may replace clay, as a source of both silica and alumina and spent foundry sands are regularly used as a silica source in clinker production. The possibility of replacement of mined iron (oxide) ore by roasted pyrite is attractive, where a suitable route to capturing the SO2 emissions is economic. The Cembureau estimate (C. Lorea, 2006) is that approximately 6.5 % (14 Mtonnes) of the raw meal used in Europe is derived from alternative feed stocks. The PCA report "Beneficial Reuse of Materials in the Cement Manufacturing Process" (PCA 2007) list the major alternative materials in use in North America in terms of the elements of benefit to clinker manufacture:

Filter cake (element varies)
Cracking catalysts (Si,Al)
Blast furnace slag (Si, Fe, Al)
Foundry sand (Si)
Petroleum contaminated soil (Si, Al)
Bottom ash (Fe, Si, Al)
Water treatment sludges (Al, Si)
Fly ash (Fe, Si, Al)
Refractory brick (Al, Si)

2) **The needs of the mineral industries** are a fine balance between the profitable and sustainable recovery of raw materials with an equally sustainable strategy for waste minimisation. Throughout the wide and varied operations in the European mineral sector, the issue of waste management is recurrent. The possible re-use of mineral fines would have economic, societal and environmental benefits reaching far outside this industrial sector. Considering the surplus minerals with most potential for use by the cements industry, six were discussed at length: Clay-soil overburden *("scalpings")* moved during quarrying and mining operations ; Clay-rich washing from aggregate

cleaning and rock processing ; Shale and slate waste with an otherwise limited market ; Rock cutting and crushing fines ; Limestone flour ; Processed mineral wastes such as burnt oil shale ; combustion ashes and harbour dredgings.

The view of the minerals industry representatives is (as with the cements producers) that a comprehensive review is needed on a regional, national and European level of the locations, quantities and compositions of the mineral by-products available for re-use. This should address the sustainability of supply (*i.e.* current operations) and assess the legacy wastes from previous operations, which my usefully be recovered.

3) **The needs of the metals producers** are analogous to those of the mineral sector: A requirement exists for the economic and environmentally sustainable re-use of the by-products of metals smelting and refining. Three principal by-products are of concern: (i) Blast furnace slag (most BFS is destined for use in construction either as glassy slag used as a supplementary cementing material or as air-cooled aggregate). (ii) Steel converter slags. By-products from the basic oxygen process (*BOS slags*) and the electric arc process (*EAF dust*) are the greatest issue for the metals industries in terms of their scale. The limitation is the variability of supply and variability of composition, compounded somewhat by the high density of the material and the hardness of BOS slag. (iii) Non-Ferrous slags. These materials are highly variable in composition and owing to the geochemical associations of elements present in many non-ferrous ores, commonly pose a toxicity hazard. Additionally, the slagging process varies between different metals, so the bulk chemistry of the slag varies between metal types (*e.g.*, borate-, halide-, carbonate-based slags). Consequently, it seems unlikely that they will make significant impact in the cements market and as the available quantities are low (in comparison with the needs of the cement producers) only very localised use is envisaged.

4) **The needs of the waste management industry** reflect both of those above, in that safe and sustainable re-use of waste materials is of critical importance to quality of life. Minimising the volumes of materials sent to landfill throughout Europe has raised new issues in waste management, as increased quantities of material are processed through *Energy-From-Waste* plants. The combustion products from various waste streams all have potential as components in blended cements. Some are surprisingly variable from a single source or within an industry, whilst others show a high degree of uniformity. Those of greatest interest to this Workshop were: Municipal waste incinerator ash ; Sewage sludge ash ; Paper mill sludge ash ; Road gully wastes and Harbour and canal dredgings.

Conclusions

General agreement was reached that new directions in blended cements research is needed. Although there are many gaps in the scientific knowledge, relatively few attempts have been made to draw together the wealth of high quality science underpinning CO_2 efficiency in cement manufacture. It was the view of the participants that a networking activity would form the most efficient basis on which to identify the knowledge gaps and that mobility grants present a means to pursue this. Scientifically, six areas were identified in which additional knowledge is required:

i. Optimisation of existing material blends to maximise material performance
ii. An increased understanding of the systems under investigation; essentially bridging the gap between the chemical sciences and physical and engineering sciences in cement and concrete
iii. Focused research into the hydration and performance of ternary and higher-order cement blends
iv. Development of predictive methods by which the combined performance of new materials may be assessed with defined confidence
v. An increased understanding of the speciation of transition metals in cements and their hydrates, allowing a knowledge-based decision to be made about their effective safety in construction materials
vi. Research into means by which the reactivity of latently hydraulic materials may be increased

From an engineering standpoint there were three strongly recommended actions which are important in shaping the direction in which the field should develop:

i. There is a need for universally agreed methods of acceptance-testing by which new materials may be screened rapidly and their suitability for use in blended cements assessed.
ii. As the majority of all cement produced world-wide will be used in structural concrete, there is a need to maintain the current level of durability of cementitious binders with the possible new cement types.

iii. There is a need to influence both the development and use of standards and codes of practice. The relationship between acceptance testing and standards could be better defined. The dichotomy between performance-based standards (potentially taking a very long time before new materials may enter a market) and compositional-based standards (potentially increasing risks to safety and commerce) should be addressed.

Lastly, there were three recommendations in the political, educational and legal arenas:

i. The types of cement manufactured are likely to diversify as market demands become more specific. There is a need for educational activities to ensure this increases resource efficiency and reduced CO_2 impact from the engineering practitioners.
ii. There is a need to work with experts in economics or economic geography in making best use of scientific and engineering research resources. For example, costs (energy, environmental and economic) associated with transport, storage and processing are often inadequately defined in practice, resulting in poor predictions of the actual gains made in an operational change.
iii. The scientific community needs to make greater effort to communicate effectively with political and economic decision makers. This is reflected in the very low (and largely declining) degree of research funding in cement science over the last two decades. If we are to enjoy continued global development, the provision of sustainable buildings must be optimised in terms of their environmental impact and this must be addressed in policy terms as well as by science, engineering and commerce.

More details of this workshop and references can be found at:

http://www.esf.org/activities/exploratory-workshops/workshops-list/workshops-detail.html?ew=7995