

The potential for carbon dioxide reduction from the cement industry through the increased use of industrial pozzolans.

*Mark Tyrer**

Mineral Industry Research Organisation, Solihull, B37 7UQ

Christopher Cheeseman, Rosemary Greaves

Centre for Environmental Control and Waste Management, Department of Civil and,
Environmental Engineering, Imperial College London, SW7 2AZ

Peter Claisse, Eshmaiel Ganjian

School of Science and Environment, Coventry University, Priory Street, Coventry CV1 5FB

Martin Kay

PIRA International. Pira House, Cleeve Road, Leatherhead, Surrey KT22 7RU

Jonathan Chrchman-Davies

CarbonAided Ltd., Grosvenor Gardens House 35-37 Grosvenor Gardens London SW1W 0BS

Correspondence Address*: Dr. M. Tyrer. MIRO, Concorde House, Trinity Park,
Birmingham, B37 7UQ. Phone: 0121 635 5225 E-Mail: m.tyrer@miro.co.uk

Extended Abstract: Cement and Concrete Science, University of Manchester, Manchester,
15-16th September 2008

Introduction

The construction industry employs over 10% of the European workforce and is greatly dependent on the supply of cements for the production of structural concrete. World-wide, mankind produces over a cubic kilometre of cement per year (over ten times the combined volume of all other man-made products) and this is made into a cubic mile of concrete. The strategic importance of this material cannot be overstated. It must be noted however, that each tonne of cement produced, releases a little under a tonne of carbon dioxide, approximately half from calcination of limestone, the remainder resulting from energy use in firing and grinding the material. After power generation and transport, cement production is the third largest source of greenhouse gas, accounting for some 5% of global anthropogenic CO₂.

There has been a long-recognised need for this industry to increase its efficiency, indeed the World Business Council for Sustainable Development reviewed this industry in 2002. They reported that inadequate R&D investment was a weakness of the industry and *Action No.6* recommends a major collaborative R&D effort focused on long-term CO₂ reduction. Since that time, some estimates of global CO₂ emissions from cement production have risen to 2,500 Mtpa.

This presentation considers the potential for atmospheric carbon reduction in the cement industry through resource-efficient use of pozzolanic materials. Traditionally, the market for industrial pozzolans has been dominated by pulverised fuel ash (PFA) and blast furnace slag (BFS). In the long term, these resources are in decline; most of the world production of suitable blast furnace slag is already destined for use in the cement industry and it would seem timely to consider other options for blended cement production.

Background

Gartner [1] reviewed possible routes to CO₂ reduction in 2004 and estimates that the energy requirements of a modern cement plant (dry process) may be as low as 3.06 GJ per tonne of Portland cement clinker, but notes that this is commonly exceeded. His discussion includes (relatively) low energy clinker production, such as belitic cements and the calcium sulphoaluminate clinkers, noting that although these interesting technologies offer some potential in CO₂ reduction, they are unlikely to make a significant change to the industry in the foreseeable future. The review compares the CO₂ derived from raw materials during the production of a range of cement types, reporting that as a mass fraction of the cementitious binder, this varies from around 22% (C₄A₃S) to 110% (magnesite-derived cements). The use of supplementary cementitious materials (SCM) to replace some of the binder in a blended cement reduces its CO₂ emission considerably as none is derived from the raw materials and relatively little CO₂ is associated with processing. It must be borne in mind however, the parent processes of both these materials is highly carbon intensive. More recently, Damtoft *et al.* [2] estimate that if all the suitable, but currently unused BFS and PFA were to be blended with cement clinker (1:1 wt./wt.) the corresponding reduction in CO₂ from this industry would be around 17%. They go on to consider the energy implications of each stage of the service life of cement materials, illustrating where practical energy savings may be made. Worrell *et al.* [3] observe that “*The global potential for CO₂ emission reduction through producing blended cement is estimated to be at least 5% of total CO₂ emissions from cement making (56 Mt of CO₂) but may be as high as 20%*”. It seems that the increased use of supplementary cementitious materials offer the most readily achievable means of reducing the greenhouse gas from the industry, yet practically, the location of many under-used materials is often remote from their potential markets, limiting their economic re-use.

Options to increase the use of supplementary cementitious materials

The global cement industry recognises the need to source and blend supplementary cementitious materials. They are not seen as a commercial threat, displacing conventional cements from their traditional markets, but as a practical means of producing high performance materials, with reduced environmental impact of the final products. The inclusion of around 5% calcium carbonate in Portland cement as a reactive component (hydrating [4] to Ca₄Al₂(CO₃)(OH)₁₂·5H₂O) is now commonplace, producing a durable product through porosity closure. Similarly the addition of silica fume, originally considered as a rheology modifier, produces such high-strength and durable concrete that demand outstrips supply. A wide range of other materials have been studied as potential CRM components and some currently under investigation are described below.

Non ferrous slags have been studied as cement replacement materials as they may contain both glassy pozzolanic components and hydraulic phases. Originating from a wide range of sources (Cu, Zn, Pb refining *etc.*) their recent application has been reviewed by Shia *et al.* [5]. Although widely studied, their applications in cements is limited for two reasons: Often the material is very hard, requiring considerable grinding energy [6]. Of greater concern is the potential for leaching heavy metals from the slag during service. As such materials are variable (even from a single source) this reduces user confidence in the sustainability of a consistent supply.

Metakaolin and burned oil shale are similar materials in that they are denatured clays, comprising poorly ordered alumino silicates. Metakaolin is formed during high temperature processing of kaolinite at 500-800 °C. This highly disordered material is highly reactive in the alkaline chemical environment of cement pore solutions and readily hydrates to form a

durable product [7]. Burned oil shale (the bottom ash from oil shale combustion), is subjected to much higher temperatures and partially recrystallises to produce new phases, some of which (especially C₂S) are hydraulic [6, 8].

Container glass seems an attractive pozzolan as it is wholly glassy, requiring only grinding to produce a reactive material. The alkali content of the glass however is high (10 – 15% Na₂O) in order to lower the glass transition temperature to around 570 °C for processing. This poses an obvious problem in that it greatly exceeds the maximum alkali content permitted under current standards, yet the body of work on this material continues to grow [9, 10]. Although much glass is collected for recycling into new glass products, a fraction is rejected and landfilled. This raises the possibility of using it in blended cements in which the total alkali content is compliant with standards, especially in complex blends containing other glasses deficient in sodium.

Paper Mill sludge Ash. The paper industry is undergoing a quiet revolution, largely as a result of changing environmental legislation. Formerly, paper mill sludge (the waste slurry rich in filler materials and short cellulose fibres) was filtered and landfilled, but rising waste management costs limit this as a disposal option. The partially dried material comprises ~50% solid and 50% water and of the solid phase, cellulose fibre and mineral filler – mainly kaolinite- are present in equal amounts. The calorific value of the fibre is sufficient to burn the waste in energy-from-waste plants, which reduces its volume considerably. The resulting ash contains disordered aluminosilicate phases derived from clay minerals and is both pozzolanic and moderately alkaline [11].

Incinerated sewage sludge ash contains relatively insoluble metal phosphates along with pozzolanic aluminosilicate phases. In addition, soluble sulphates, minor alkali oxides and a range of trace metals are also present. The use of this material and its potential as a cement addition is reviewed by Cir *et. al* [12] who notes the initial retarding effect of liberated heavy metals during the early stages of hydration. This, combined with lower compressive strengths than those of other cements, may limit the use of what is a widely available and low cost material.

Municipal Waste Incinerator Bottom ash is another widely available material of potentially no cost. From a single source, its composition is relatively consistent and it contains some pozzolanic glassy components, hydraulic minerals (largely gehlenite, C₂AS and mayenite, C₁₂A₇.) along with relatively unreactive components such as wollastonite. Aluminium metal is one component which limits the ready use of this material in cementitious systems. Hydrolysis under alkaline conditions releases hydrogen gas and dissolves the aluminium metal as aluminat ions. The gas release persists for many hours, often extending beyond the setting time, making consolidation into a high strength material very difficult. Thermal pre-treatment [13,14,15] initially applied to oxidise residual organic components, increases the quantities of the hydraulic components and partially oxidises the residual aluminium. Subsequent hydration in the presence of calcium hydroxide shows that both densified (hydrated under compression) and lightweight products may be produced.

Discussion

Practical limits of time and space preclude a detailed discussion here. Perhaps the most useful questions to ask are how the cements research community can best help the production and construction industries to meet their obligations to reduce its carbon emissions. The realisation that only those materials, which comply with current standards and codes of practice, are ever likely to be adopted by the construction industry defines the first questions:

- *To what extent does addition of a new blending component change the composition and properties of a material and at what point does the “new” material fail to comply with the appropriate governing standards?*

The second, but no less important question is commercial:

- *How are the economics of the material changed by inclusion of a supplementary cementitious material? Do changes in production costs or in the properties of the material warrant a change in its price? Does the reduced carbon footprint have a definable value?*

Lastly, an important question must be asked by the practitioner (design engineer, architect, site engineer *etc.*)

- *What specification of concrete is most appropriate for this application?*

We respectfully suggest that this question is often answered from a perspective of confident over-specification. A design, which specifies the same concrete mix throughout, may well be operationally very cautious (at the expense of both the client and the environment!) Should the concrete binder contain pozzolanic material and the overall mix design be targeted at a specific strength or durability, considerable savings in the CO₂ emissions may be made. It is the opinion of at least two of the authors that most concrete is considerably over specified.

References

- [1] Gartner., E. “Industrially interesting approaches to low-CO₂ cements” (2004) Cement and concrete research V34 pp1489-1498
- [2] Damtoft., J.S ; Lukasik., J. ; Hertford., D.; Sorrentino., D. Gartner., E.M. (2008) “Sustainable development and climate change initiatives” Cement and concrete research V38 pp115 – 127
- [3] Worrell.,E.; Price.,L; Martin., N.; Hendriks.,C and Meida., L.O. (2001) “Carbon dioxide emissions from the global cement industry” Annual Review of Energy and the Environment. Volume 26, Page 303-329, Nov 2001
- [4] Matschei.,T.; Lothenbach., B. ; Glasser F.P. (2007) The role of calcium carbonate in cement hydration Cement and Concrete Research, V37, pp 551-558
- [5] Caijun Shia, Christian Meyerb and Ali Behnood (2008) Utilization of copper slag in cement and concrete. Accepted for publication in: Resources, Conservation and Recycling
- [6] Dhir R K (1994) Additional materials and allowable contents in cement. Pp 57-68 In: Euro-Cements: Impact of ENV 197 on Concrete Construction. Ed. Ravindra K. Dhir, M. Roderick Jones. Publ. Taylor & Francis, 1994
- [7] N. J. Coleman, C. L. Page (1997) Aspects of the pore solution chemistry of hydrated cement pastes containing metakaolin Cement and Concrete Research, V27 pp 147-154
- [8] G. Habert, N. Choupay, J.M. Montel, D. Guillaume, G. Escadeillas (2008) Effects of the secondary minerals of the natural pozzolans on their pozzolanic activity Cement and Concrete Research, V38 pp 963-975
- [9] Yixin Shao Thibaut Leforta, Shylesh Morasa and Damian Rodriguezb (2000) Studies on concrete containing ground waste glass. Cement and Concrete Research V30 pp 91-100
- [10] Ahmad Shayan Aimin Xu (2004) Value-added utilisation of waste glass in concrete. Cement and Concrete Research V34 pp 81-89
- [11] J. Bai, A. Chaipanich, J. M. Kinuthia, M. O’Farrell, B. B. Sabir S. Wild, and M. H. Lewis. (2003) Compressive strength and hydration of wastepaper sludge ash – ground granulated blast furnace slag (WSA – GGBS) blended pastes. Cement and Concrete Research, 33, , pp. 1189-1202.
- [12] Martin Cyr, Marie Coutand, Pierre Clastres (2007) Technological and environmental behavior of sewage sludge ash (SSA) in cement-based materials Cement and Concrete Research, V37 pp 1278-1289
- [13] X.C. Qiao, B.R. Ng, M. Tyrer, C.S. Poon, C.R. Cheeseman (2008) Production of lightweight concrete using incinerator bottom ash. Construction and Building Materials, Volume 22, Issue 4, April 2008, Pages 473-480
- [14] X.C. Qiao, M. Tyrer, C.S. Poon, C.R. Cheeseman (2008) Novel cementitious materials produced from incinerator bottom ash Resources, Conservation and Recycling, V52 496-510
- [15] X.C. Qiao, M. Tyrer, C.S. Poon, C.R. Cheeseman (2008) Characterization of alkali-activated thermally treated incinerator bottom ash Waste Management, Volume 28, Issue 10, 2008, Pages 1955-1962