Potential for carbon dioxide reduction from cement industry through increased use of industrial pozzolans


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 CO2 per unit mass when compared with metals, glasses and polymers. Conversely, it is made in such vast quantities, that it is responsible for over five percent of anthropogenic CO2. 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 inclusion of supplementary cementing materials. This article reviews some of the options currently under investigation, especially from the UK perspective, and highlights that some of the research needs to be satisfied before such materials are more widely adopted.

Keywords: Carbon dioxide reduction, Industrial pozzolans

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Introduction

The construction industry employs over 7% of the UK workforce1 and is greatly dependent on the supply of cements for the production of structural concrete. Worldwide, mankind produces around 2.5 Gt per year2 (often described as over a cubic kilometre of cement per year: more than 10 times the combined volume of all other man made products) and most of this is made into concrete. The International Energy Agency estimates that something between 6 and 10 km3 of concrete were produced in 2006.2 The strategic importance of this material cannot be overstated. It must be noted, however, that each tonne of cement releases a little under a tonne of carbon dioxide, approximately half from calcination of limestone, the remainder resulting from energy used 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 CO2.3

There has been a long recognised need for this industry to increase its efficiency; indeed the World Business Council for Sustainable Development reviewed the cement industry in 2002.4 They reported that inadequate R&D investment was a weakness and recommended 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 2500 Mtpa.5

This article 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 and fly ash are already destined for use in the cement industry and it would seem timely to consider other options for blended cement production.

Background

Gartner5 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%

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(C₄A₃S) to 110% (for magnesite derived cements) (note that the nomenclature of describing cement compounds uses abbreviated oxide composition: C=Ca, S=SiO₂, A=Al₂O₃, S=SO₃, etc.). The use of supplementary cementitious materials (SCM) to replace some of the binder in blended cements reduces CO₂ emission considerably, as none is derived from the raw materials and relatively little CO₂ is associated with processing.

This raises the question of how best to account for the embodied CO₂ in such materials. Is it appropriate to consider the CO₂ associated with their manufacture? Many industrial pozzolans are by-products of highly energy intensive processes and consequently represent a considerable amount of embodied CO₂. Conversely, they are by-products and were never the intended product from their industrial production. It is fortuitous that they have a value as pozzolans, as they are effectively removed from the waste inventory of their parent processes. It may be argued that as the primary intention of the producer was to form another product, no embodied CO₂ should be associated with industrial SCMs. Conversely, one may apportion the CO₂ output of the entire parent process, weighting this between the various products according to their mass, saleable value or other criteria.

It must be borne in mind, however, that the parent processes of both these materials are highly carbon intensive. More recently, Damtoft and et al. estimate that if all the suitable, but currently unused BFS and PFA were to be blended with cement clinker (1:1, w/w), 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. 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 offers the most readily achievable means of reducing greenhouse gas from the industry, yet practically, the location of many underused materials is often remote from their potential markets, limiting their economic reuse.

**Options to increase 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 to Ca₄Al₂(CO₃)₂(OH)₁₂·5H₂O] is now commonplace, producing a durable product through porosity reduction. Where clinker is blended with aluminous components such as blast furnace slag, the potential exists to include proportionately more limestone flour reducing the energy (and therefore CO₂) associated with production of such cementitious binders. Similarly, the addition of silica fume, originally considered as a rheology modifier, produces high strength and durable concrete, yet supplies are limited and the market price remains high. Excellent concrete is produced from inclusion of an alternative source of silica, rice husk ash, which is available in much larger quantities, although in the rice growing regions of the tropics, particularly Southeast Asia. A wide range of other materials have been studied as potential CRM components and some currently under investigation are described below.

**Non-ferrous slags**

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 Shi et al. Although widely studied, their applications in cements in limited for two reasons. Often the material is very hard, requiring considerable grinding energy the cost of which may outweigh any commercial benefit. 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.

Metallurgical slags (granulated and air cooled) are disposed of as wastes from the ferro-manganese and ferro-manganese–silicon alloys manufacturing plants. They find little use as SCM in comparison with blast furnace slags from steel plants. In recent decades, however, considerable research and development on metallurgical slags have been carried out. In Canada, some alloy steel converter slags are used as an additive in cement raw materials and the effects on cooling rate of structures in which the cements blended with those slags was used are reported. Plasma treatment has also been used on metallurgical slag and is used to reduce copper, nickel and cobalt levels in the treated slag. Microwave treatment of ferrous slag is reportedly used to control the heating rate of slag due to addition of carbon and magnetite, with potential applications in the recovery of iron from slag as well as in the modification of slag in order to produce a more saleable byproduct. Vitrification of slag is also being carried out with electric arc furnace dust, using a sol–gel process. Cement–metallurgical slag blended cements give compressive strengths in the range of 15–30 MPa. However, notwithstanding, the efforts cited above, there remains a big gap between the generation and use of metallurgical slags produced by the industries concerned.

**Metakaolin and burnt oil shale**

Metakaolin and burnt oil shale are similar materials in that they are denatured clays, comprising poorly ordered aluminosilicates. Metakaolin is formed during high temperature processing of kaolinite at 500–800°C. This highly disordered material is very reactive in the alkaline chemical environment of cement pore solutions and readily hydrates to form a durable product. Burnt 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 C₃S) are hydraulic.

**Container glass**

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) included 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.²⁸ 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.

Glass’s dissolution in alkaline pore solution is somewhat slower than the hydration of clinker, which requires practical methods for increasing its reactivity as a supplementary cementing material. Shi and Day²¹ effectively used salts as chemical activators to increase the reactivity of natural pozzolans, as well as several other methods, including mechanical and thermal treatments.²² A comparison of the methods by Shi and Day indicated that the most effective method for developing reactivity in natural pozzolans was chemical activation, which improved both the initial reaction rate and the final strength. The reactivity of the treated pozzolanic material was measured in terms of the compressive strength and total hydration of the material. It is reasonable to expect that some success may be achieved by applying similar treatment to waste glass in order to improve its pozzolanic properties. The properties which influence the pozzolanic behaviour of waste glass, and most pozzolans in general, are fineness, composition and the pore solution chemistry. Based on observed compressive strengths, Meyer et al.²³ postulated that below 45 μm, glass may become pozzolanic. The pozzolanic properties of glass are first notable at particle sizes below ~ 300 μm. Below 100 μm, glass can have a pozzolanic reactivity which is greater than that of fly ash at low percent cement replacement levels and after 90 days of curing.⁹

The use of lithium compounds has been explored for alkali–silica reactivity (ASR) mitigation as well as promoting pozzolanic reactivity. Some of the compounds which have been explored include lithium carbonate (Li₂CO₃),²⁴ lithium hydroxide (LiOH),²⁵ lithium nitrate (LiNO₃),²⁶ lithium chloride (LiCl)²⁷ and lithium fluoride (LiF).²⁸ Lithium is unique among the alkali metals because it has the smallest atomic radius to possess the large hydrated radius and polarising power.²⁹ The properties of concrete and mortar specimens containing other alkalis has been explored include lithium carbonate, Lawrence and Vivian²⁶ were able to demonstrate that silica was slower to dissolve in the presence of lithium, and the product had different properties than that in the presence of other alkalis. This low dissolution rate was accompanied by a lack of repolymerisation of the silica species and the presence of a microcrystalline lithium silicate precipitate (Li₂SiO₃). Both silica dissolution and lack of repolymerisation, as well as aggregation of particles, were observed by Kurtis and Monteiro.²⁸ While several authors have observed a decrease in dissolved silica in the presence of various lithium compounds, using LiOH specifically can result in an increase in dissolved Si while still mitigating ASR expansion.³⁰ The lack of repolymerisation and the formation of aggregated or crystallised products are hypothesised to be related to the lack of ASR expansion in the presence of lithium. Primary challenges still facing the use of lithium treatments include the absorption of large amounts of added lithium into the early hydration product, which, once absorbed, may not be available in later life; the increase in hydroxyl ion concentration,¹² and the concerns of safety when working with reactive materials. Lithium, although widespread in nature, is expensive to refine and commands a high price in other industries, especially battery production. On balance, although interesting, this approach is unlikely to offer a commercially viable route to reuse of waste glass in cement.

**Paper mill sludge ash**

The paper industry is undergoing a quiet revolution, partly 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 either landfilled or land spread (as a soil conditioner), but rising waste management costs and possible restrictions on land spreading limit these as disposal options. Currently, two UK paper mills (in Deeside and Kent) operate combined heat and power (CHP) plants in which the sludge is burnt and it is likely that more CHP operations will be commissioned in the future. The resulting ash contains disordered aluminosilicate phases derived from clay minerals (dominantly metakaolin) and is both pozzolanic and moderately alkaline as it contains some free lime (CaO). Paper manufacturing (which uses significant quantities of recycled fibre) generates a paper sludge byproduct, which after pressing comprises ~ 50 wt-% solids. The solids phase comprises cellulose fibre which is not retained in the paper web together with mineral filler (e.g. kaolins, carbonates and talcs) and ink. The quantity of paper sludge generated is significant. UK paper recycling mills generate nearly 1 million tonnes of wet paper sludge annually, the majority of which is spread on land to recover its organic value. The calorific value of the fibre is sufficient to burn the waste in energy from waste plants, which reduces its volume considerably. Over 270 000 t of paper sludge is incinerated generating around 120 000 t of paper sludge ash (PSA) annually. The composition of PSA varies between mills according to the input materials. Mills burning only paper sludge produce ash with high calcium oxide (lime) content, while those cocombusting with plastics can produce PSA with a relatively high chlorine content, making it unsuitable for cement manufacture. Ash from a single source is, however, highly consistent in composition, reflecting the stringent controls required in CHP incineration and this makes it an attractive material for use in blended cements. Frias et al.³¹ have characterised such ashes and demonstrated the large influence of thermal history on their pozzolanic behaviour.

The use of paper mill sludge ash in cement has been investigated as a pozzolanic activator for blast furnace slag³² with some success. In addition, (uncalcined) sludge has been used in co-combustion with coal as fuel for electricity generation. The fly ash produced from such operations proved to be similar in performance to...
conventional fly ashes, suggesting that this material deserves closer examination by the cement industry.

**Incinerated sewage sludge ash**

Incineration has become an important method for disposal of sewage sludge following the ban on sea disposal in 1998. Although land application of sewage sludge is an alternative, there are concerns over the accumulation of potentially toxic elements in soils, and regions may have insufficient appropriate agricultural land. Approximately 1–6 million tonnes of sewage sludge dry solids were produced in England and Wales in 2007 of which ~15% was incinerated. Dewatered sewage sludge with 25–30% dry solids content normally has sufficient calorific value for autothermal combustion. Although incineration evaporates water and oxidises organic matter to CO₂, CO₂, NOₓ and SOₓ gases, the removal of exhaust gas fines by electrostatic precipitators or bag filters produces incinerator sewage sludge ash (ISSA).

There are currently seven sludge incinerators operating in the UK and these produce ~97 000 t per year of ISSA. It is estimated that ~1.2 million tonnes per year of ISSA are produced in North America with a similar quantity from the EU, with the vast majority sent to landfill.

XRD data of ISSA shows that the major crystalline phases present are quartz, SiO₂, the calcium magnesium phosphate mineral whitlockite Ca₅Mg₃(P₂O₇)₄ and some hematite Fe₂O₃. 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 was reviewed by Cir et al. who noted the initial retarding effects 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**

The aim of municipal solid waste (MSW) management should be to extract value by maximising the recycling of waste components. However, there is clearly a limit to what can be viably recycled, and combustion of the residual non-recyclable MSW in modern energy from waste (EWF) plants represents a safe and effective way of obtaining further value from MSW, both in terms of the energy generated and further extraction of materials such as metals. National policy recognises EWF as an important source of biomass energy and it is expected to have an increasing role in the waste management of industrialised countries such as the UK. EWF plants also produce incinerator bottom ash and this typically represents about 10 vol.-% and 30 mass-%MSW being processed. As produced bottom ash is fairly difficult to handle and it is normally left to carbonate before ferrous and non-ferrous metals are extracted and it is sorted into different size fractions normally for use as aggregate. The overall composition is relatively consistent and it contains a significant fraction of potentially pozzolanic components, hydraulic minerals such as gehlenite, C₂AS and mayenite, C₁₂A₇, along with relatively unreactive components such as wollastonite. Trace levels of aluminium metal tend to remain in the ash and this has limited the use of this material in cementitious systems due to the resulting production of hydrogen gas from hydrolysis under alkaline conditions as aluminium metal forms aluminate ions. The gas release persists for many hours, often extending beyond the setting time, making consolidation into a high strength material very difficult. Thermal pretreatment, 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 hydrated under compression and lightweight products may be produced.

Extensive work completed in Japan that has reported the production of different types of ecocements made from incinerator bottom ash. These have used up to 50% of incinerator ashes as raw materials in a manufacturing process similar to that used for Portland cement.

**Discussion**

Perhaps one of the most important issues is the way in which we recognise the carbon and climate change benefits of new blending materials. At present, cements can be specified which result in lower construction carbon intensity, but these benefits are extremely dependent on the precise blend and the supply chain chosen. Tying down the construction benefit at the individual project level requires good traceability along this supply chain. Choice of materials not only relates to cement blends, but also to other materials such as aggregates and structural components, all of which may have higher or lower carbon footprints. In addition to embodied constructional carbon, it is now widely accepted that the overall footprint of the project includes operating energy consumption and the destination of the materials in the project at the end of its service lifetime. The interplay between these life cycle phases, their carbon footprints and the choices made during design and material selection is not simple and requires careful balancing. The role of appropriate cementitious materials as enablers for reusing wastes and giving low operational carbon designs is being increasingly appreciated in mainstream construction. The future of cements lies in their ability to be flexibly designed and to offer longevity and end of life flexibility. If correctly directed, this future can be extremely bright.

In conclusion, there are very many industrial pozzolans which are underused by the cement industry and deserving of further study. It must be recognised, however, that many are not available in large quantities from a single source and that logistics of their efficient supply and reuse poses at least as great a challenge as does the underlying science and technology.

**References**


