Innovations in Sustainable Development

THE FOLLOWING PROVIDES AN UPDATE ON THE DEVELOPMENT OF NEW TYPES OF CEMENT, CONCRETE, AND NEW MANUFACTURING TECHNOLOGIES FROM THE MAJOR PLAYERS AND FROM NEW ENTRANTS TO THE INDUSTRY.

Calix Catalytic Flash Calcination

Dr Mark Sceats, Chief Scientist, Calix Limited

Calix Limited is a minerals processing company that has developed its low carbon footprint Catalytic Flash Calciner (CFC) technology for manufacturing "activated" materials used by the cement and other related industries. Calix delivers solutions based on its CFC Reactors to enable its customers to produce a wide range of sustainable building products. These solutions have additional environmental benefits, beyond that of the low carbon footprint of the CFC process itself.

The CFC technology differentiates itself from conventional pyroprocesses for calcination by the

Figure 1. Calix CFC plant at Bacchus Marsh Victoria showing the production of drums of calcined magnesite from the 12 m CFC Calciner seen in the upper left.

Figure 2. Calix CFC plant showing the continuous feed of ground magnesite into the steam flow for injection into the CFC Calciner.

use of indirect heating and steam as a catalyst. This enables low temperature calcination, which minimises sintering to give high surface area products. The CFC technology can be applied to calcination of carbonates, and to flash dehydration of other minerals used by the cement industry. Careful design of the heat recuperation systems allows for a high energy efficiency.

The sustainability arises from a number of interrelated aspects.

- **Low emissions calcination:** When applied to the calcination of carbonates such as limestone, magnesite and dolomite, the indirect heating leads to the CO_2 being recovered as a pure gas stream, for geo- or bio-sequestration. Calix aims to scale up its process to large plants to supply lime for the lime and cement industries so that they can reduce their carbon footprint. For existing lime plants, the CFC can use the small limestone particles rejected as kiln feedstock, and can also beneficiate the lime kiln dust. The indirect heating also means that the products are not contaminated by impurities from the combustion process. In large scale plants, there is a potential for integration of the CFC process with cogeneration of power.
- **Fuel gas decarbonation:** The active lime produced by the CFC process is a CO_2 sorbent, and can be used to decarbonise fuel gases in an established process called calcium looping, which uses the reversibility of the calcination process. In this process, the lime extracts carbon from the fuel gas and produces a pure CO_2 stream when regenerated in the calciner. Calix uses a reactor scheme, called the Endex Reactor, in which the lime sorbent and the heat for calcination can be continuously recycled to give an energy efficient decarbonation process for fuels. When combined with the CFC process for lime production, a zero emissions process for cement manufacture is feasible with fossil fuels, and a carbon negative process with biomass fuel.
- **Portland cement substitution:** Calix has demonstrated that its CFC Calciner can produce active materials that can substitute for OPC. These products are high surface area metakaolin, caustic magnesia and gypsum hemihydrate. The high surface area can lead to enhanced strength of the cement product, providing an additional benefit. This application can reduce the carbon footprint of many cement and concrete formulations by lowering the amount of OPC used. This is a large existing market, and Calix is completing a series of long-term tests of the product strength.
- **Sustainable building products:** The calcined magnesite and dolomite products from the CFC can be used as binders to make formulations of magnesium oxide board for interior and exterior panels. The CFC Calciner can selectively calcine the magnesium in dolomite to produce Semidolime ($MgO.CaCO_3$), which imparts beneficial anti-weathering properties from the absence of lime. When used with the high surface area gypsum from the CFC as co-binder, a range of fast setting products can be manufactured for particular applications in the building industry. The CFC process provides for a low embodied energy in these products. Calix is developing applications in which the pure CO_2 stream from its CFC calciners is reinjected into the products to enhance strength and for lightweight panels.

The widespread application of CFC Reactors, including those in the Endex Reactors for carbon capture, will occur when the benefits to customers are demonstrably clear. Calix is developing and demonstrating the broad range of sustainable products to build the market for its CFC calciners.

Celitement

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What is Celitement?

Celitement is a new type of hydraulic cement, which is based on calcium silicates, as is ordinary Portland cement (OPC). It can be produced from common primary and secondary raw materials. Celitement can be utilised in a wide variety of applications, e.g. concrete, mortars and specialties. The benchmark for its performance is CEM I 52.5 according to the European standard EN-197-1. Upon its hydration, calcium silicate hydrates are formed similar to the hydration of OPC. Due to the low calcium content, however, no portlandite is present in hardened pastes. The proprietary production process uses previously calcined and milled raw materials. After mixing, an approximate molar CaO/SiO_2 ratio (C/S) between one and two is adjusted. The mixture is cured with water in an autoclave at conditions similar to the production of autoclaved aerated concrete (AAC). The dry autoclaved material is blended with an equivalent mass of silica-rich material, such as sand, and is finely ground. A pilot plant (100 kg/day) is under construction by Celitement GmbH, a start-up owned by KIT, the SCHWENK group and four inventors. Celitement has the potential to cut in half the process energy and the CO_2 emitted over the whole process chain of Portland clinker production. The process has been developed by the Karlsruhe Institute of Technology (KIT), a German university and national research centre.

Composition – hydration – hydration products

Celitement is made up from composite grains, measuring 1 – 20 μm dia. Each grain contains cores of a mechanically hard, silica-rich, non-hydraulic and chemically resistant material such as quartz, feldspar or glass. These cores are enclosed by a hydraulic shell made up from amorphous calcium hydrosilicates of various compositions. Depending on the C/S-ratio of the autoclaved material and the nature of the co-ground silica-rich component, the silica plus water content may rise up to 80 mass %. When water is added, the shell transforms to calcium silicate hydrates, the classic "glue" in all cements that are standardised in the EN 197-1. No other hydration product, especially no portlandite, is necessarily formed (Figure 1). If the cores are made up from pozzolanic material, such as blastfurnace slag (bfs), calcium aluminate hydrates may form.

Paste setting and hardening

By adjusting the composition of Celitement, mixing, setting and hardening properties can be controlled to closely match different classic cements. After wetting, a more or less pronounced dormant period follows, which is succeeded by a maximum of heat released between 3 to 20 hours. Stiffening is accomplished after 2 to 15 hours if desired. Compared to OPC, the overall water demand is somewhat reduced, due to the reactive shell that already contains chemically bound water. Thus, to achieve a good workability, in some cases the addition of a liquifier is necessary.

Properties of hardened paste

Due to the small capacity of the laboratory hydrothermal test facility (3 l) that is currently used, standardised test

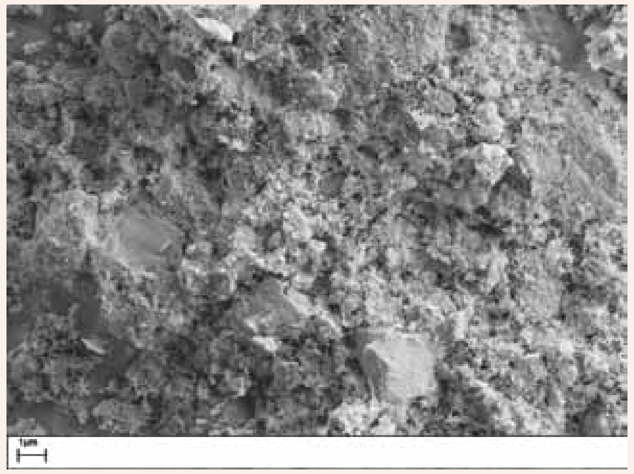

Figure 1. Cryo-REM image of a broken Celitement paste after 5 hours' hydration. Silica-rich cores are enclosed in hydrating rims of amorphous calcium hydrosilicate. Image width 22 µm.

Figure 2. Cryo-REM image of a broken Celitement paste after 7 days' hydration. A silica-rich core is enclosed in hydrated calcium silicate hydrate. Pore space is nearly closed. Image width 22 µm.

methods could only be applied on mortars of lime-rich types of Celitement, made up of 50 mass % of hydrothermally processed α-$Ca_2SiO_4.H_2O$ and bfs. Compressive strength developed to 60 and 80 MPa after 7 and 28 days, respectively. In contrast to OPC, hardening of Celitement formulations does not necessarily involve the crystallisation of phases other than calcium silicate hydrates. By effectively closing the capillary pore system, a dense microstructure results (Figure 2). Measurements by mercury intrusion porosity show a rapid decrease of pore diameters within the first 7 days.[1] First results on soundness prove a low shrinkage potential and a high freeze/thaw resistance. Celitement that is nearly white can be synthesised using raw materials of low iron content.

Potential use

As Celitement is based on the same chemical "glue" as OPC, namely CSH-phase, its potential use is as universal as standard cements. Applications span from specialties and mortars to reinforced concrete and precast structural elements. Hardened Celitement has a lower buffering capacity than OPC, due to the reduced $Ca(OH)_2$ content.

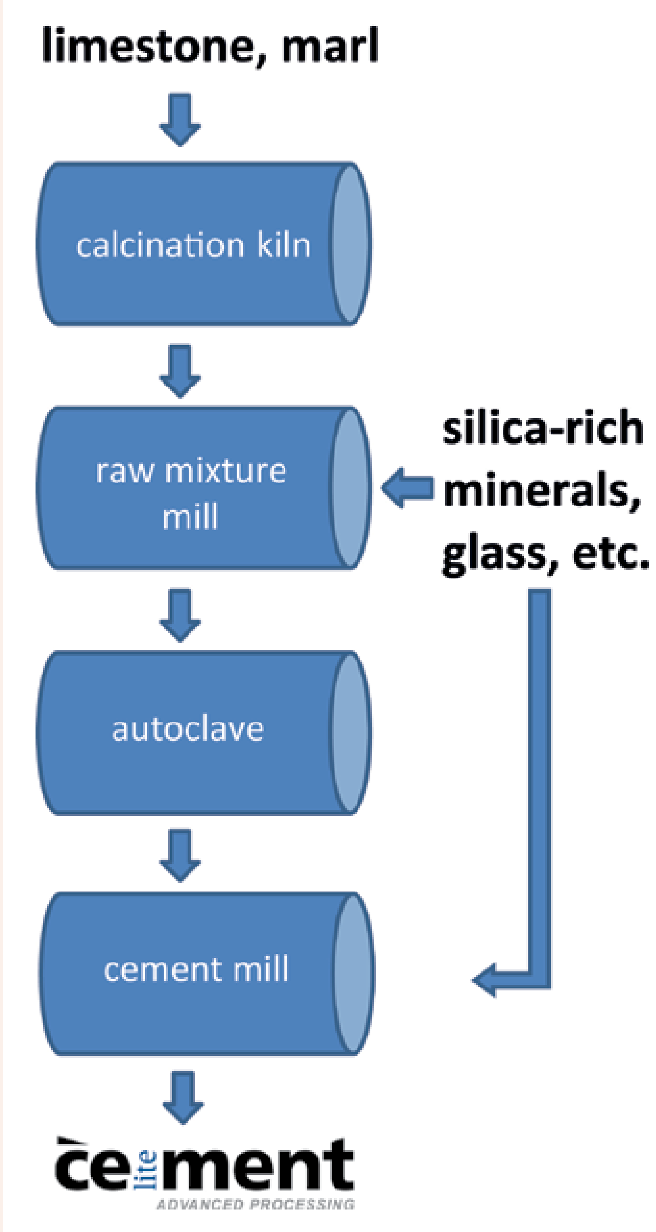

Figure 3. Schematic flow chart of the production of Celitement.

There were concerns about the possibility of accelerated attack by acid media in reinforced structures. However, in practice it is not the buffering capacity of a concrete structure alone that results in a high resistance against chemical attack, but also its structural density. For example, UHPC applications have a strongly reduced buffering capacity due to the addition of reactive silica, without losing their acid resistance.[2] Just like OPC-clinker, Celitement can be blended with different cementitious materials.

Making of Celitement

In principle, Celitement can be made of the same raw materials as OPC clinker, taking into account the lower lime content (Figure 3). The lime content may also be provided by limestone. Impurities are acceptable in a wide range. The limestone is calcined at around 1000 ˚C. Alternatively, even secondary raw materials such as crushed concrete were successfully tested. The product from calcination is further mixed with material rich in SiO_2 in order to achieve the desired CaO/SiO_2 ratio ranging from one to two. The mixture is finely ground and subsequently treated in an autoclave together with water at a temperature around 200 ˚C and saturated steam pressure. The process conditions resemble those common in the production of AAC. Calcium hydrosilicates or calcium silicate hydrates, respectively, are obtained. At normal conditions these hydrothermal products do not react when coming into contact with water. They are stabilised by a network of very strong hydrogen bonds.

In order to form a hydraulically reactive cement, the network of hydrogen bonds needs to be destroyed by mechanical activation. For this purpose the dry autoclave product is mixed and co-milled together with a mechanically hard silica-rich material, e.g. sand, bfs, rock flour or glass, until a specific surface of approximately 2 m^2/g is reached. The mechanical activation transforms the calcium hydrosilicates into an amorphous hydraulic phase, which coats the surface of the unreactive grains. Celitement and its production process are protected by several international patents.

Energy balance/CO_2 emissions

The energy needed to make Celitement has been estimated in two ways. First, the theoretical energy required for the chemical reactions from the raw material has been calculated from basic thermodynamic data.[1] This approach neglects efficiency factors and does not account for the energy needed for mining, transportation and milling of raw materials, for process control, fine grinding of the product, etc. On the other hand, it allows for comparison of technologies with different technological maturity. The energy needed for the formation of Celitement from limestone and quartz is dominated by the calcination of limestone. Thus it heavily depends on the composition of the reactive shell. For a composition high in calcium oxide (30 mass % CaO, 65 mass % SiO_2, 5 mass % H_2O) it amounts to 555 kJ/kg. Reducing the calcium content (20 mass % CaO, 70 mass % SiO_2, 10 mass % H_2O) results in an enthalpy of formation of 294 kJ/kg. This compares to OPC-clinker with an enthalpy of formation of 1761 kJ/kg.[3]

In a second approach, typical specific energy demands for each operational step in the making of Celitement were taken from literature and combined to estimate the cumulated specific energy.[1] All steps are common to the building materials industry, either in OPC or AAC plants. Except for the autoclave process, for which values from AAC plants were used, all specific energy expenditures were taken from OPC production, starting from the excavation of raw materials to the final milling. As this last step is not yet adapted to the special needs of the Celitement process, it was penalised by a factor of 2 with respect to the value for OPC plants. The calculation results in an overall consumption of primary energy of 3150 kJ/kg for high-lime Celitement and 2170 kJ/kg for low-lime Celitement. These values compare to 4360 kJ/kg for ground OPC-clinker (including electrical power).

The CO_2 emissions from both the Celitement process and OPC-clinker production are generated from two sources: from the calcination of raw materials and from energy consumption (thermal and electrical energy). With respect to both paths, the following emissions result: 910 kg/t finely ground OPC clinker; 483 kg/t high-lime Celitement; 350 kg/t low-lime Celitement.

With respect to the common raw materials, the low energy demand and the moderate investment in facilities, which are common in the building materials industry, production cost for Celitement should roughly equal those for OPC-clinker, if plants of equal size are compared. Special cost-effects, such as expenditures for CO_2 emissions or benefits from the use of secondary raw material, are not taken into account.

Process development, pilot plant and outlook

The Celitement process has been developed by KIT. It has been exclusively licensed to Celitement GmbH, a start-up of the SCHWENK group, KIT and four scientists. In order to allow for the development of market-ready applications of Celitement and to set up the scale-up of the process, a pilot plant with a projected output of 100 kg/day is currently being built at Karlsruhe. Its commissioning is scheduled for summer 2011. In 2015, the SCHWENK group plans a first industrial plant with an output of about 30 000 tpa of Celitement. Due to time-consuming standardisation procedures and the necessary up-scaling of the process, the market entry is expected in low-volume, high economic value applications.

Awards

The KIT received the material efficiency award 2010 from the German federal ministry of economics and technology for the Celitement technology.

References

1. STEMMERMANN, P; SCHWEIKE, U; GARBEV, K.; BEUCHLE, G.; and MÖLLER, H., 'Celitement – a sustainable prospect for the cement industry', *Cement International* 8 (5), (2010), pp. 52–66.
2. LUDWIG H.M., 'Bewertung ultrahochfester Betone unter dem Aspekt der Dauerhaftigkeit', *Beton- und Stahlbetonbau* 100 (2), (2005), pp. 116–123.
3. TAYLOR, H.F.W., *Cement Chemistry*, London: Academic Press (1990).

Holcim Optimo

Holcim (Switzerland) has already massively reduced CO_2 emissions by making changes to cement production and composition. Its new cement, Holcim Optimo, is another achievement in this line.

Optimising the manufacturing process…

The industry is constantly striving towards higher energy-efficiency and lower CO_2-intensity. The two main triggers to improve the environmental performance are optimisation of manufacturing processes and substitution of clinker. State-of-the-art filter plants reduce emissions of nitrous oxides; firing processes optimised down to the smallest detail minimise emissions of harmful gases. To reduce the use of fossil fuels, alternative materials such as waste oil, car tyres, and solvents are also combusted.

…and lowering the clinker factor

More CO_2 is saved by using less clinker. By 2009 the proportion of Portland cement had been reduced to 22%. The entry into force of standard SN EN 197-1 made this development possible, as in addition to "pure" cement, it allows for cements with additives. Aside from the technological advantages for concrete, which extended the range of applications, this advance also enabled significant reductions in CO_2 emissions. In recent years, the most popular cement has been a type of Portland limestone cement, which contains ground limestone as an additive. Other cements have admixtures of blastfurnace slag, and in the manufacture of concrete, flyash replaces part of the cement. These materials are suitable additives on account of their chemical reactivity; however, they are not always available in the same quantities or in a constant quality, which causes serious production problems. What is more, they have to be transported over long distances.

Figure 1. The shale deposits of Dotternhausen are unique in Central Europe.

Figure 2. Close-up view of shale.

Further solutions to increase productivity in construction

Another solution for the construction industry is Easecrete, a concrete mix developed by Holcim Singapore. Easecrete requires no vibration and at most very minimal compaction; as a result it reduces noise level by 21%. Unlike traditional self-compacting concrete, Easecrete is composed of less cementitious materials, making it both affordable and environmentally friendly.

It can be casted using workers in a ratio of 1:3. This speeds up the construction process by 46% and reduces overall construction time and material costs, including a 30% saving on manpower.

Flexible applications

Easecrete can be applied more easily for heavy and dense reinforced foundations, difficult to vibrate sections and other related specific needs. It can be easily pumped over higher and greater distances. Moreover, it has a greater flow rate of concrete mix than normal concrete mix and so allows for greater freedom and flexibility in structural shapes and design.

Another solution similar to Easecrete is Jetsetcrete, which has the unique advantage of high early strength and can at the same time be designed with very high flowability. This product is suitable for casting intricate shapes and sizes such as precast elements, as well as for pre- and post-tensioned slabs. Another excellent application is in the infrastructure works such as road repairs and airport runways, where it is crucial for concrete to gain strength as quickly as possible.

Burnt shale – an ideal clinker subsitute

Holcim embarked on a crossborder cooperation to improve the uncertain supply situation, replace the proportion of clinker in cement with a hydraulically effective additive of constant high quality, and shorten transport routes. The shale that can be found in the immediate vicinity of Holcim South Germany's Dotternhausen cement plant near Rottweil contains combustible components that are used to produce electricity. The burned shale is chemically reactive, i.e. it is capable of hydraulic and pozzolanic reactions. It is an ideal clinker substitute, to which shale cements already used in Germany impressively testify. Nevertheless, the properties of Holcim Optimo, a mixture of clinker, limestone and burned shale, were meticulously studied in a comprehensive range of pilot tests, which showed the positive impact of ground shale on several properties of concrete. The new Nano-T® technology increases the effective packing density, and thereby the density of the concrete structure. Holcim Optimo is certified to SN EN 197-1 for all applications of concrete.

Transport by rail

The transport of shale from the Swabian Alb to Holcim's Swiss plants also needed to be environmentally sustainable. This is why in recent years considerable sums have been invested in expanding the railway infrastructure, including a new loading silo in Dotternhausen, the upgrading of an entire section of railway line to connect the plant to the national railway network, the purchase of new rolling stock, and a number of structural adjustments and extensions at the Swiss plants.

Taking the lead

Holcim (Switzerland) is proud of the fact that the introduction of its new cement will reduce its CO_2 emissions – measured on the basis of its total cement production – by a further 10%, without in any way affecting sales to clients. Furthermore, Holcim Optimo can be used with all common additives.

Lafarge launches Project Aether

Gunther Walenta, CO_2 Project Manager and Ellis Gartner, Scientific Director, Chemistry, Lafarge Research Center

With the increasing need for concrete construction, particularly for housing and infrastructure in developing countries, it is expected that emissions of CO_2 from cement manufacture will double by the middle of this century unless technical changes can be implemented to reduce the CO_2-intensity of the hydraulic binders needed for such concretes.[1]

As part of its partnership with the World Wildlife Fund (WWF), Lafarge made a voluntary commitment in 2001 to reduce its net CO_2 emissions per t of cement worldwide by 20% between 1990 and 2010. It exceeded this objective one year early, reducing net emissions per t of cement by 20.7% between 1990 and the end of 2009. Up until now, efforts to reduce CO_2 emissions by Lafarge and the cement industry as a whole have mainly focused on modernising installations, substituting fossil fuels with alternative fuel sources and using additives such as pozzolan, slag and flyash to produce less carbon-intensive blended cements.

However, the combination of these three approaches can only go so far: a technological breakthrough is required to reduce the CO_2 emissions intrinsic to cement production.

Over the past few years, Lafarge researchers have investigated a number of different avenues and in 2003

Figure 1. Project Aether has received the support of the European Union's LIFE+ programme for the environment.

Figure 2. Two industrial trials will be carried out to test the feasibility of industrial-scale production of Aether clinkers.

began research into belite-rich clinkers containing calcium sulfoaluminate (ye'elimite) and calcium aluminoferrite as the other major phases. The belief was that cements based on these clinkers should be significantly less CO_2-intensive than cements based on Portland cement clinkers, as they require significantly less calcium carbonate in the kiln feed.[2]

Many types of calcium sulfoaluminate (CSA)-based cement have been developed in the past few decades for a wide range of possible applications.[3–8] However, China is so far the only country to have normalised such cements for use in construction. Two main classes are currently produced in significant volume, based either on 'sulfo-aluminate clinkers' (SAC) containing 55 – 75% ye'elimite ($C_4A_3\$$), 15 – 30% belite (C_2S) and 3 – 6% ferrite ($C_2(A,F)$); or on "ferro-aluminate clinkers" (FAC) containing 45 – 65% ye'elimite, 15 – 35% belite and 10 – 25% ferrite.[9,10] With different types and dosages of mineral admixtures, such as gypsum, anhydrite, limestone, etc., cements with a very wide range of performance characteristics can be made: for example, rapid-hardening, self-stressing, expansive, etc. However, these cements are adapted for specific niche applications; they do not represent a genuine alternative to Portland cement in general concrete construction.

Belite-rich cements are also well-known in the literature, and many of the CSA-based cements mentioned above also contain significant amounts of belite. However, the low reactivity of the belite in many of these cements remains a key problem, since efficient hydration of belite is needed for good long-term strength development. Thus, the challenge when Lafarge started research on this topic in 2003 was how to combine the benefits of both CSA and belite into a single clinker that could be produced efficiently and at an acceptable cost. This research led to the development of Aether™, an innovative new class of clinker, based not on tricalcium silicate (alite, the major phase in OPC), but instead using dicalcium silicate (belite) as the major phase, with calcium sulfoaluminate (also known as CSA or ye'elimite) and calcium alumino-ferrite (usually just called "ferrite") as the other two principal phases. Less limestone is required to produce Aether clinkers relative to conventional Portland cement clinkers, and they are also manufactured at lower temperatures (~1275 ˚C) using 15 – 20% less energy. This allows a reduction of 20 – 30% in total CO_2 emissions during the cement production process. Aether cements can be made from the same basic raw materials used for Portland cement manufacture: limestone, clay, iron ore, bauxite and gypsum, as well as other raw materials, such as industrial byproducts. They can be produced in existing industrial installations, using the same fuels, and with only minor process adaptations. Importantly, Aether cements are expected to offer similar performance to conventional Portland-based cements in a variety of concrete applications.

In 2010, Project Aether obtained the support of the European Union through the LIFE+ financial instrument for the environment. The LIFE+ funding has allowed the project to enter its development phase – to run until 2013 – with the organisation of two industrial trials to validate the feasibility of

Figure 3. Lafarge began research into the development of Aether clinkers in 2003.

Figure 4. Testing at the Lafarge Research Center.

Aether clinker production on a large scale, as well as testing on cements, concretes and mortars made with these new clinkers. The trials will be carried out at two Lafarge plants in Europe, with a pilot test before each trial at the Institute of Ceramics and Building Materials' (ICiMB) specialist cement-testing facilities in Krakow, Poland. ICiMB boasts a semi-industrial scale rotary kiln, which makes it possible to test certain parameters and predict conditions for Aether clinker production in real industrial installations.

An assessment of the trial results will then be made by BRE, the UK independent consultancy, testing and training organisation. BRE will carry out calculations to assess the total CO_2 emissions associated with the manufacture of cement from Aether clinker, compared to Portland cement. It will look at CO_2/t of cement, but also per t of concrete, based on specific mix designs, to provide concrete of pre-defined properties. BRE will then assess concrete and mortars made using the new Aether cement, compared to otherwise equivalent concrete and mortars made using Portland cement. BRE's experts will focus on strength development and long-term durability, essential in establishing the feasibility for use of Aether cements in construction. In terms of durability testing, BRE will look at issues such as the protection of steel in concrete, dimensional stability, chemical resistance and freeze/thaw. Specimens will be prepared for long-term exposure in a range of exposure conditions.

Finally, BRE will develop a roadmap for certification and normalisation of the new cements, outlining the steps that will need to be taken, and the barriers to be overcome, if they are to be widely used in the construction sector. It will also outline the essential requirements for wider materials testing and performance verification, and associated guidance and training needs for a range of stakeholders from specifiers to end users.

The overall aim of Project Aether is to demonstrate the industrial feasibility of Aether clinker production and, ultimately, to offer a viable, lower-CO_2 alternative to Portland cement in general concrete construction.

References

1. See website <http://www.epa.gov/climatechange/emissions/co2_human.html#industrial>
2. GARTNER, E., 'Industrially interesting approaches to "Low-CO_2" cements', *CCR*, 34, (2004), pp.1489–1498.
3. GIES, A.; KNOFEL, D.; and BUJAN, M., 'Influence of alkalis on the composition of belite rich cement clinkers and the technological properties of the resulting cement,' *CCR*, 16 (1986), pp. 411–422.
4. CHATTERJEE, A.K., 'High belite Portland cement – an update on development, characterization and applications', *11th ICCC* (Durban), vol. 1 (2003), pp. 31–40.
5. MIELKE, I.; MULLER, A.; and STARK, J., 'Active belite cement', *9th ICCC*, vol. 2 (1992), p. 399.
6. TONGBO, S.; SUIHUA, G.; KEZHONG, L.; JING W.; and YUN L., 'Research on high belite cement. Part I : Laboratory research - Part II : Cement properties,' *Proceedings of the 4th Beijing Internat. Symp. on cement and concrete* vol. 1 (1998), pp. 145–148.
7. SUI, T.; and YAO, Y.; 'Recent progress in special cements in China,' *11th Int. Congr. Chem. Cement*, Durban, vol. 4 (2003), pp. 2028–2032.
8. LI, G.S.; and GARTNER, E.M., 'High belite-containing sulfoaluminous clinker, method for the production and the use thereof, for the production of hydraulic binders,' WO2006/018569 (2006).
9. YANMOU, W.; MUZHEN, S.; and LIANG, Z., *Sulphoaluminate Cement*, Beijing Industial University Press (1999), p. 33.
10. JIANGJING, D.; ZHIJUN, X.; and QIUYING, Z., *Production and application of Sulfo-aluminate cement in China*, Beijing Industrial Construction Materials Press (2006), p. 29.

Researchers bring predictability to flyash-based geopolymer concrete

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Geopolymer concrete (GPC) is an emerging class of cementitious materials that do not need the presence of Portland cement as a binder. One of the main reasons for the growing interest in geopolymer concrete technology is its life cycle greenhouse gas (GhG) reduction potential.[1] The production of Portland cement, the most common construction material in the world, contributes about 5% of the total global manmade CO_2 emissions to the atmosphere. Unlike Portland cement, which requires calcite ($CaCO_3$) as its main raw material, geopolymer relies on flyash, a coal combustion byproduct (CCP). Thus, geopolymers are considered eco-friendly construction materials in two distinct ways: a) reducing the need for Portland cement, and the associated CO_2 emissions; and b) converting CCPs into beneficial construction materials, thus reducing landfill and disposal facility requirements. GPC technology is particularly attractive as it is not limited to class 'C' flyash (for which there is a high demand in the cement industry), but can also utilise class 'F' flyash (most of which is currently placed in landfills). Additionally, geopolymers can tolerate higher concentrations of ammonia and other impurities in the raw flyash compared with Portland cement. This is of particular importance in view of recent air emission regulations. Measures taken by coal-fired power stations to meet these new standards are expected to adversely affect traditional utilisation of coal flyash due to an increased level of impurities.

Table 1. Comparison of the equations derived by the researchers for Geopolymer concrete with these given in ACI-318-08[3]

	Geopolymer concrete	Portland cement concrete given by ACI
Flexural strength in terms of compressive strength	$f_r = 0.69 \sqrt{f_c'}$ *MPa*	$f_r = 0.62 \sqrt{f_c'}$ *MPa*
Elastic modulus in terms of density and compressive strength	$E_r = 0.037 (w)^{1.5} \sqrt{f_c'}$ *MPa*	$E_r = 0.043 (w)^{1.5} \sqrt{f_c'}$ *MPa*

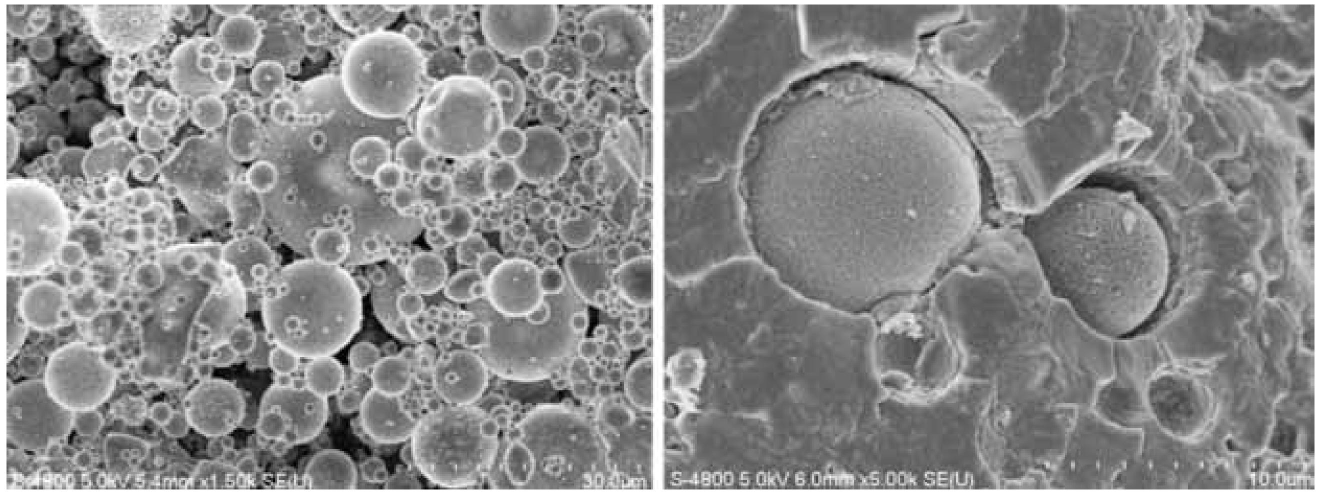

Figure 1. SEM micrographs of flyash before geopolymerisation (left) and after (right).

By comparison to ordinary Portland cement (OPC), GPC features higher resistance to acid and sulfate attacks. Because their chemistry is not based on calcium aluminates, these materials are practically inert to sulfate corrosion. Furthermore, the geopolymeric net does not show any affinity for a reaction with sulfate salts. GPC also offers a substantially higher fire resistance (up to 2500 °F), high compressive and tensile strengths, a very rapid strength gain and lower shrinkage. Alkali-aggregate reactions do not occur in geopolymer concrete and its nanoporous pore structure results in greatly reduced permeability and ionic diffusion. Setting times are controlled by the temperature of the process, but geopolymer concretes usually set in a few hours of the initiation of the reaction. Setting times as short as 5 min and as long as 30 h were achieved by the research team using different formulations.[2]

Figure 2. Dry cast geopolymer block.

Facing the challenges

One of the main challenges for the use of flyash as source material for geopolymer is its variability. The chemical properties of flyash depend on the type and composition of its precursor coal. Silica and alumina molecules contained in the flyash are the main components of the geopolymer network. Therefore, the amount and ratio of these influence the resulting mechanical properties of geopolymer.

While silica and alumina are the main precursors for the geopolymeric reaction, other factors seem to also play a significant role in the mechanical behaviour of geopolymer. Impurities, namely CaO, have a positive impact on the mechanical strength of the geopolymer matrix, but tend to reduce setting time. Another important characteristic of flyash is its crystallography, or the way the molecules are arranged within the flyash. Since amorphous compounds are easier to dissolve than crystalline compounds during the first step of geopolymerisation (dissolution of species), they yield higher amounts of reactive SiO_2 and Al_2O_3 to combine during the transportation/coagulation phase of the geopolymeric reaction. This results in a higher degree of geopolymerisation and consequently higher mechanical strength, as opposed to crystalline phases, which are harder to dissolve. A key physical characteristic is particle size distribution, determined mainly by the degree of pulverisation of the precursor coal. As a significant part of the reaction occurs at the particle-liquid interface, the finer the particles the greater is the surface area and the more reactive is the flyash. Another important parameter of ash quality is the efficiency of the burning process, as a poor burning process results in potentially significant percentage of unburned coal in the flyash, termed 'Loss on Ignition' (LOI). A high content of unburned carbon with high surface area adversely impacts the behaviour of the fresh mixture, creating a demand for the addition of activator solution well beyond what was needed to activate the source material, to obtain a workable mixture.

Figure 3. Selected applications of geopolymer concrete and grout.

Figure 4. Precast geopolymer concrete wall (8 ft. x 11 ft.) designed to hold back 300 t of soil.

An empirical approach

To tackle the variability issue, Dr. Erez Allouche and Mr. Ivan Diaz, a senior PhD candidate, collected 35 flyash samples from power plants around the US. Each flyash sample was analysed in terms of chemical composition, crystallographic properties and particle size distribution. The mechanical performance of geopolymer concrete made from each flyash sample was evaluated in terms of density, setting time, compressive and flexural strength, static elastic modulus and Poisson's ratio. The database was analysed to detect correlations between flyash characteristics and mechanical properties of GPC. Correlations within the elastic modulus, the compressive and flexural strengths of GPC were also sought and regression models were developed. The researchers showed that the elastic modulus, as well as the compressive and flexural strengths of GPC can be predicted with reasonable accuracy by analysing the chemical, physical and crystallographic properties of a given flyash. The prediction model is capable of predicting the mechanical characteristics of the geopolymer concrete within 10% of the actual value based on the attributes of the flyash for several common GPC mix designs. Additionally, the researchers found that the mechanical behaviour of GPC is similar to that of OPC-based concrete, suggesting that equations, akin to those given by the American Concrete Institute's building code, could be applied for GPC to determine its flexural strength and static elastic modulus.[3]

References

1. VAN DEVENTER, J. S. J.; PROVIS, J. L.; DUXSON, P.; and BRICE, D. G., 'Chemical Research and Climate Change as Drivers in the Commercial Adoption of Alkali Activated Materials,' *Waste and Biomass Valorization*, V. 1(1), (2010), pp. 145–155.
2. DIAZ, E. I.; ALLOUCHE, E. N.; and EKLUND, S. 'Factors Affecting the Suitability of Fly Ash as Source Material for Geopolymers,' *Fuel*, V. 89 (2010), pp. 992–996.
3. DIAZ, E. I.; ALLOUCHE, E.N.; and VAIDYA, S. 'Mechanical Properties of Fly Ash-Based Geopolymer Concrete,' *ACI Materials Journal*, V. 108(3), (2011).

A carbon negative cement for the construction industry

Dr Nikolaos Vlasopoulos and Dr John Prendergast, Novacem

Introduction

Novacem is developing a new cement that will offer performance and cost parity with ordinary Portland cement, but with a carbon negative footprint. Novacem cement is based on magnesium oxide (MgO) and is well positioned to reduce cement industry carbon emissions. The company was selected as a World Economic Forum Technology Pioneer for 2011 and has established a number of industrial collaborations that support the development of its technology, including with Lafarge and Laing O'Rourke.

Figure 1. Novacem blocks.

Cement and concrete properties

Any alternative to Portland cement faces the same challenges; it has to (i) be used in the same way as Portland cement, (ii) develop similar mechanical and durability properties at the same rate as Portland cement and (iii) develop its mechanical and durability properties through hydration rather than carbonation with CO_2.

Novacem cement is a novel blend of MgO with hydrated magnesium carbonates and pozzolanic materials. There are several potentially suitable hydrated magnesium carbonates that can be used with Novacem cement and Novacem has developed a specialised reactor for producing them.

Inclusion of hydrated magnesium carbonates in the cement composition has two advantages. Firstly, they control the cement hardening properties by modifying the MgO hydration mechanism and the physical properties of the resulting hydration products. Secondly, they decrease the cement's carbon footprint as they absorb CO_2 during their production and therefore have a carbon negative footprint (absorption of 300 – 500 kg CO_2/t of carbonate).

Novacem cement has undergone significant development during the last 18 months. During this time period the strength of cement paste samples has increased from 20 MPa to over 80 MPa and optimisation is ongoing to reach or surpass performance parity with Portland cement. Work by Laing O'Rourke at its Steetley precast concrete manufacturing facility has shown that Novacem concrete can achieve compressive strength development suitable for a wide range of applications. Work over the next 12 – 24 months will concentrate on the assessment of long-term properties and durability.

Production process

Magnesium is the eighth most abundant element and constitutes about 2% of the Earth's crust. Novacem's production process is based on accelerated carbonation of magnesium silicates to produce MgO. Novacem has focussed on design, construction and operation of a reactor system that can be scaled up industrially. Development of a laboratory pilot plant was undertaken during a 2-year £1.5 million project funded by the UK's Technology Strategy Board and including Laing O'Rourke. This led to construction and successful commissioning of a batch pilot plant in early 2010. In Autumn 2010, conversion of the initial batch plant to continuous was completed and the upgraded plant was successfully commissioned.

The Novacem production process has three steps. During the first step, magnesium silicates are carbonated under elevated levels of temperature and pressure (i.e. 170 ˚C/<<150 bar) to produce magnesium carbonate. In the second step, the magnesium carbonate produced is heated at low temperature (~700 ˚C) to produce MgO, with the CO_2 generated being recycled back into the first step. During the third step, part of the MgO produced is used to produce the hydrated magnesium carbonates required using either the CO_2 contained in the flue gases from the fuels used to power the production process, or CO_2 derived from external sources.

Novacem's production process can use feedstock with larger particle size than that of limestone for Portland cement without sacrifice in reactor performance. The process has no need for an energy intensive milling process. Suitable magnesium silicates, e.g. olivine and serpentine, are widely dispersed with accessible worldwide reserves estimated to exceed 20 000 billion t; there are known resources in at least 16 of the top 20 cement markets. Magnesium silicates are amenable to open pit surface mining and so can be extracted in a similar way to limestone and at a similar cost. The potential for low cost mining combined with the low energy consumption of the Novacem process means that Novacem cement can offer cost parity with Portland cement before taking account of any value attributable to carbon dioxide.

Energy and carbon footprint

The carbon footprint of Novacem cement is not dependent on carbonation during use. Its footprint is achieved during manufacture by the combination of the following features:

Figure 2. Operation of the Novacem laboratory pilot plant.

- Use of magnesium silicates minerals, which eliminates the CO_2 emissions from raw materials processing.
- Use of a production process that not only requires less energy but also lower temperatures and allows the use of fuels with low energy content or carbon intensity (i.e. biomass).
- Use of hydrated magnesium carbonates in the cement composition that absorb CO_2 during their production and therefore have a carbon negative footprint.

The final CO_2 balance will depend on the fuel mix used and the amount of hydrated magnesium carbonates included. Use of higher amounts of hydrated magnesium carbonates in the Novacem cement composition can further decrease its carbon footprint without adversely impacting cement performance. Current calculations estimate that the carbon footprint will be in the range of -100 kg CO_2/t cement to +100 kg CO_2/t cement; any point within this range is a step-change improvement compared to the emissions of conventional cement production.

Next steps for Novacem

Novacem is planning to scale up towards an industrial pilot plant in conjunction with cement industry partners such as Lafarge. The company aims to develop such relationships with a number of cement manufacturers who have the capability and appetite to contribute to the development and subsequent roll-out of the technology. The industrial pilot plant will produce up to 25 000 tpa of cement and will be used to take the first significant volumes of Novacem cement to market, most likely in concrete product applications. Novacem is already developing relationships with concrete products producers who have a focus on sustainability and could play leading early adopter roles.

Novacem is about to commence a second Technology Strategy Board project, this time in conjunction with BRE, the UK independent consultancy and testing organisation, and Laing O'Rourke. This £1 million project will run over three years with the aim of demonstrating strength and durability of Novacem concrete over an extended period and a wide range of tests.

Ultimately, Novacem aims to develop its technology for use in all cement applications as a cost-effective alternative to Portland cement, to roll-out the technology across the cement industry through licensing, and to create significant value for the industry through reduced CO_2 emissions.

Figure 1. Tokyo Tama Ecocement plant.

Forget landfill

Takahiro Kawano, Taiheiyo Cement Corp.

Through its experience in Japan, Taiheiyo can offer environmentally sound treatments for increasing utilisation of MSW through environmentally friendly technologies. The Japanese Ministry of Environment has long used incineration for MSW volume reduction and, in principal, local governments each have their own incinerators and landfill sites. Taiheiyo's technologies to utilise incineration ash in cement production make it possible for MSW management officers to "forget landfill".

With rapid economic growth, almost all the big cities in Asia are currently suffering from the same big headache: how to deal with increasing waste. As society obtains both affluence and convenience, we are constantly generating enormous quantities of municipal solid waste and, regretfully, impose the burden of this on the environment. Taiheiyo Cement Corporation has introduced environmentally friendly technologies from the perspective of diverting waste from landfill, which will help future generations reduce the rate of depletion of natural resources and allow the safe treatment of waste.

Municipal waste incineration ash contains the same elements (i.e. calcium, aluminium, iron and silicon) as the main components of clay used in cement production, and therefore it can be used as an alternative to clay. However, since municipal waste incineration ash contains more chlorine and heavy metals than natural clay, this is a problem that must be addressed.

The first difficulty encountered in cement production when using incineration ash is chlorine. Chlorine causes two problems: a cement quality problem, in which chlorine rusts steel reinforcing bars, and equipment failure due to the fact that chlorine becomes concentrated during circulation through the production process and, as a result, generates low-melting point compounds. The former problem was solved by washing soluble chlorine away before using ash (ash washing technology), and the latter by a technology that isolates the circulation of chlorine to bypass the burning process (the chlorine bypass).

As the chlorine problems were addressed with the above solutions and the use of municipal waste incineration ash in cement production increased, the heavy metal content in the cement rose beyond the range found in natural soils, resulting in the need to remove heavy metals during the production processes. The technology that solved this problem is Taiheiyo's Ecocement system. Some of the heavy metals are vaporised by a chloride volatility process using chlorine as a catalyst and attaching it to dust, which is removed from the system in the form of recycled resources (urban mines) by a wash treatment.

The Ecocement system utilises municipal waste incineration ash at high levels, more than 500 kg/t, to produce reliable quality cement that can be used in Japan Industrial Standard concrete. Mortar strength development is slightly slower than Portland cement but concrete mix design can be adjusted to meet high early strength requirements. The quality design of Ecocement has increased the use of incinerator ash in Japan and the high utilisation ratio means that, as ash treatment facilities, Ecocement plants can be more compact.

Modification for local needs

Different countries and cities have different conditions for waste treatment; whether they be water supply, industrial structure, cement quality standards or municipal solid waste treatment scheme (source separation, waste composition, waste treatment process, sanitary land filling or incineration). Taiheiyo can provide technologies to enhance recycling methods with minimum environmental impact by utilising incineration ash, with necessary modifications. For example, the company offers a modified Ecocement system, whose final product can easily be a substitute for OPC, a modified chlorine bypass system, hybrid bypass, etc. Taiheiyo can make existing cement plants more robust and efficient in the sense of treating municipal solid waste incineration ash. The company hopes to advance the possibility that incineration ash will become a commonplace input in OPC and maximise the potential to incorporate municipal waste ash in cement clinker production.

Currently, at Dalian cement plant in China, the Japanese Ministry of Economy, Trade and Industry is subsidising the introduction of Taiheiyo technology.

Figure 1. Air purifying street in Hengelo, the Netherlands.

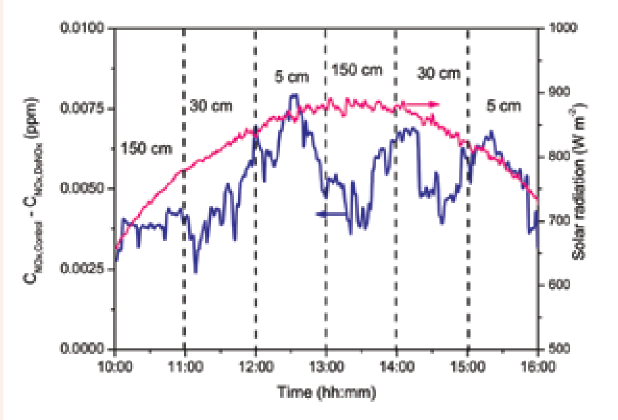

Figure 2. Air monitoring results in summer 2010: difference between the NO_x concentration in the control street and in the $DeNO_x$ street at different sampling heights vs. the solar radiation.

Concrete degrades NO_x

Dr. M.M. Ballari, Prof. H.J.H. Brouwers, Department of Architecture, Building and Planning at Eindhoven University of Technology

The authors have developed and tested a cement-based concrete paving material that actually reduces nitrogen oxides (NO_x), a hazardous air pollutant, implying it could soon become a crucial tool for improving air quality in urban areas.

The problem in many cities is that vehicle exhausts emit nitrogen oxides, which cause acid rain and smog that damages not only the environment, human health and quality of life, but also the fabric of buildings. The new concrete is coated with titanium dioxide (titania), which is a photocatalytic material, meaning it removes the nitrogen oxides and uses sunlight to convert them into harmless nitrate that is washed away by rain. This technology is a Japanese invention, but full-scale outdoor data proving that it is an efficient way to decontaminate air are still scarce.

Following extensive laboratory tests, the pollution-eating concrete has been trialed in the Dutch town of Hengelo, where 1000 square metres of the road's surface were covered with air-purifying concrete paving stones. As a control, another area of 1000 square metres was surfaced with normal concrete paving slabs. Samples were then taken from the air at between 0.05 and 1.5 m above the surface by NO_x chemiluminescence analysers in both the control and $DeNO_x$ street. In the air monitoring, the authors have found nitrogen oxide reductions of 35 to 40% in areas paved with the new concrete. It also provides a self-cleaning effect, meaning the new concrete has the additional advantage that it breaks down algae and dirt so its surface stays clean.

> The new concrete is coated with titanium dioxide (titania), which is a photocatalytic material, meaning it removes the nitrogen oxides and uses sunlight to convert them into harmless nitrate that is washed away by rain.

The concrete could be a very feasible solution for inner city areas where they have a problem with air pollution. Another advantage of this technology is that one can apply the titania very easily in the normal production of concrete pavement stones. Furthermore, it does not require any maintenance; it does not wear off with normal use. Predictably, the stone is around 50% more expensive than a normal concrete stone, but the authors are adamant that when the total cost of fitting is included, the overall increase in cost is only 10%.