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The environmental credentials of hydraulic lime-pozzolan concretes

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Abstract:

This research considers the compressive strength, embodied CO_2, embodied energy and binder intensity of hydraulic lime-pozzolan concretes, in comparison with those of Portland-cement based concretes of equivalent 28-day compressive strength.

Production of a lime-pozzolan concrete with a 28-day cube strength of approximately 50 MPa and an elastic modulus of 20GPa has demonstrated the feasibility of producing modern, structural grade hydraulic lime-pozzolan concretes. Furthermore, construction and testing of two reinforced lime-pozzolan concrete beams has demonstrated the possibility of producing structural elements with a finished appearance and flexural behaviour similar to Portland cement concrete. This paper reflects on the value of this new material's technological progress in the context of the industry wide search for low carbon cements.

Results of the research reported in this paper demonstrate that the use of aluminosilicate by-products, specifically ground granulated blastfurnace slag and silica fume, in combination with naturally hydraulic lime can realise savings in environmental impact; but that the savings are both future-orientated and highly dependent on the boundaries of the analysis. When considering only the secondary impacts of ground granulated blastfurnace slag and silica fume production, a ternary combination was observed to result in a lime-pozzolan concrete with a 28-day cube strength of 33MPa and an embodied-CO_2 of 95 $kgCO_2/m^3$, 64% lower than a CEMI, and 41% lower than a CEMIII/A concrete of equivalent strength. Both mass and economic allocation procedures were, however, shown to have a very detrimental effect on the environmental credentials of silica fume and thus also on hydraulic lime-concretes containing this pozzolanic addition.

It is recognised that technical performance alone cannot be used to assess or compare the merits of any new material. This paper focus on the production, environmental impact and long-term availability of individual constituents of this novel binder, with a view to addressing important questions about the viability and desirability of re-producing this novel cementitious system in a commercial setting. Such information is acknowledged to be critical in the dialogue about the potential adoption and development of this emerging binder technology.

Keywords: *Sustainability, hydraulic lime-pozzolan concrete, binder intensity, embodied CO_2, embodied energy*

Highlights

- Embodied impacts of lime-pozzolan concretes compared with Portland cement concretes.
- Embodied CO_2 up to 64% lower than Portland cement concretes of equivalent strength.
- Lime-pozzolan binder efficiency seen to increase with increased compressive strength.
- Identification of 'greenest' binder determined by choice of allocation methodology.

Frequently used abbreviations:

C_e	Economic allocation coefficient
CEMI	Portland cement
C_m	Mass allocation coefficient
CO_2	Carbon dioxide
EC	Embodied CO_2
EE	Embodied energy
$f_{cm,28}$	Mean compressive cube strength after 28 days
$f_{cyl,28}$	Cylinder strength after 28 days
GGBS	Ground Granulated Blastfurnace Slag
LCCs	Low carbon cements
NHL	Natural Hydraulic Lime
NHL5	Natural Hydraulic Lime 5
PCE	Polycarboxylate ether
SF	Silica Fume
SP	Superplasticiser
t	Tonnes
w/b	Water to binder

1 Introduction

In 2012 over 3.7 billion tonnes of cement were produced worldwide (Van Oss, 2013) enough to produce over 12 billion m^3 of concrete or 1.7 m^3 for every man, woman and child on the planet. As the principal binding constituent of concrete, cement continues to be a key driving force of human development.

The manufacture of Portland cement (CEMI) is a carbon and energy intensive process and is widely acknowledged to be responsible for 5-9% of the total global anthropogenic carbon emissions (Shi et al., 2011 & Harrison, 2013) and 2-3% of primary energy use (Juenger et al., 2011). The actual energy demand and energy related emissions vary significantly between production facilities, due to differing processing technology and national energy generation strategies. Japan pioneers

energy-efficiency in cement kiln technology and boasts dry-process kilns with suspension pre-heaters and pre-calciners requiring less than 3000 MJ/t clinker (Japanese Cement Association, 2011). This is less than half the heat requirement of the older wet-kiln technology that demand up to 6300 MJ/t (Boesch and Hellweg, 2010).

Despite pressure to reduce its environmental impact, the global cement industry must continue to invest in capacity expansion programmes in order to meet the growing demand. Investment in modern production technologies both minimizes the environmental impact and maximizes profitability for the cement producer. However with an upper limit on the overall kiln efficiency, the returns associated with the investment in the best available technologies (BAT's) are diminishing. Production efficiency is therefore not the only strategy for reducing the impact of cement manufacture on the natural environment. Other strategies include alternative fuel sources, carbon-capture and storage and the development of alternative cements (International Energy Agency, 2009).

The aim of this study was to investigate the embodied CO_2 (EC) and embodied energy (EE) of modern lime-pozzolan cements, as well as to evaluate the viability of this 'novel' cementitious system. This paper starts with detailed introduction to this alternative binder technology and its constituents, in order to contextualise the findings of this research.

1.1 Alternative cements

One of CEMI's greatest advantages as a cement has been the widespread availability of raw materials for global production and the wide scale applicability of the material in use. With no other single cement technology set to replace it, a shift in product mix is anticipated with a number of 'second generation', 'low-carbon' cements being developed (Gartner, 2009). Potential second-generation cements that are in different stages of research and development include: calcium sulfoaluminate cements (CSAC) (Ioannou et al., 2014), supersulfated cements (SCC) (Ioannou et al., 2013), alkali activated cements (AAC) and geopolymers (Heath et al., 2013), magnesium oxide cements (Liska et al., 2012), high volume slag cements (Saleh et al., 2012) and ternary cements (De Weerdt et al., 2011); as well as hydraulic lime-pozzolan cements (Grist et al., 2013a).

With a total installed capacity of 3.2 billion tonnes of clinker (Van Oss, 2013) and modern concrete construction practice entirely geared to the production and use of CEMI, novel cements face a very difficult route to market. It is however appreciable that it is the compressive strength, durability and ease of placement of concrete that is so fundamental to construction and not the nature of the cementitious binder itself.

Rising fuel costs, carbon reduction targets and a growing demand for more sustainable alternatives are driving change and forward-thinking cement manufacturers are preparing to respond with new product technologies. Commenting

on emerging low carbon cements (LCCs), Chana (2010) argued, *"there is a future for new or novel cements…but there really is a long way to go before they can make substantial inroads into the market"* (Mineral Products Association, 2010). To envisage the 'post-Portland cement age' material scientists, contractors and consumers alike, need the ability to make sense of the benefits of alternative technological solutions. Against this backdrop this paper specifically reflects on the sustainability credentials of lime-pozzolan cements as an alternative to CEMI- based cements.

1.2 Background and materials

1.2.1 Hydraulic-lime concrete

Lime-pozzolan binders have a long history; a lime-concrete floor slab discovered in Southern Israel in 1985 was dated back to 7000BC (Bensted and Coleman, 2003). However, the research reported in this paper does not represent a return to a former technology, as it exploits carefully produced and controlled pozzolanic materials and takes advantage of significant modern advances in the development of concrete technology, specifically the performance of the latest generation of water reducing admixtures. That said, the considerable precedence for the use of this binder in construction is a significant advantage in comparison to other novel cements; therefore its long history, which is a testament to the durability of this material, should not be disregarded.

In the 1770's the civil engineer John Smeaton conducted extensive testing on lime-pozzolan concretes in a search for a suitable hydraulic concrete for construction of the foundations of the third Eddystone Lighthouse off the coast of Plymouth, UK (Blezard, 1988). The mix Smeaton specified for this project consisted of blue lias slaked lime, pozzolanic trass and some copper slag (Bensted and Coleman, 2003). More recently Cachim et al. (2010) attained a mean cube strength after 28-days ($f_{cm,28}$) of 17 MPa with 20% of the hydraulic lime replaced with metakaolin, a synthetic pozzolan.

The hydraulic lime-pozzolan concretes discussed in this paper should not be confused with 'Limecrete' a commercially available lime-concrete suitable for low-grade structural applications. Rather the concretes presented in this paper have a $f_{cm,28}$ of up to 50 MPa and can be cast into reinforced elements with a similar finished appearance and structural behaviour to CEMI concrete elements (Grist et al., 2013c).

1.2.2 Hydraulic lime production

Until the advent of CEMI in the 1800's, hydraulic lime was the principal binder for use in construction (Kenny and Oates, 2000). Both hydraulic lime and CEMI are synthetic materials manufactured by the thermal decomposition of a source of calcium carbonate (typically limestone) at high temperatures. At kiln temperatures in excess of 900°C calcium carbonate ($CaCO_3$) disassociates, with carbon dioxide (CO_2) being

driven off to produce calcium oxide (CaO), commonly known as quicklime. The hydraulic set of both hydraulic lime and CEMI results from the presence of active calcium silicates phases, which are formed in the reaction of quicklime (CaO) with silica, alumina or iron oxide (Boynton, 1980). These minerals are either added to the raw feed as a controlled blend of clay impurities in the case of CEMI and Hydraulic Lime; or are inherent in the original siliceous or argillaceous limestone deposit in the case of Natural Hydraulic Lime (NHL).

Different calcium silicate phases form at different kiln temperatures and in different parts of the kiln. CEMI typically includes four primary calcium silicate minerals of which alite (Ca_3SiO_5) is the most predominant (Odler, 1988). Alite forms at kiln temperatures of above 1300°C and is responsible for the rapid set of CEMI. Natural Hydraulic Lime (NHL5), a building lime with a characteristic compressive strength ≥ 5MPa at 28 days and classified in accordance with BS EN 459, by comparison contains only a trace amount of alite (<0.7%) and the dominant compound (43%) is belite (Ca_2SiO_4), which forms at 900°C (CESA, 2006b). The mineralogical composition of NHL5 is shown alongside a typical CEMI (Dhir et al., 2001) in Table 1.

Compounds	Typical NHL5, % by mass	Typical CEMI, % by mass
Insoluble content	4	trace
Free lime, $Ca(OH)_2$	21	2
Unburnt calcium carbonate, $CaCO_3$	23	0
Alite, Ca_3SiO_5	trace	58
Belite, $(CaO)_2.SiO_2$	45	13
Tricalcium aluminate, $3CaO.Al_2O_3$	2	9
Gehlenite, $Ca_2Al(AlSiO_7)$	2	0
Calcium aluminoferrite, $Ca_2(Al,Fe)_2O_5$	2	8
Gypsum, $CaSO_4$	trace	5
Other	1	5

Table 1: Mineralogical composition of NHL5 in comparison to CEMI

CO_2 and energy savings associated with the production of NHL, as opposed to CEMI, are evident when one compares the stoichiometric reactions describing the production of alite and belite (see equations 1 and 2).

Production of alite

$$3\ CaCO_3 + 1\ SiO_2 \xrightarrow{\sim 1400°C} 1\ Ca_3SiO_5 + 3\ CO_2$$

300.3 *60.1* *228.3* *132.0*

Equation 1

Production of belite

$$2\ CaCO_3 + 1\ SiO_2 \xrightarrow{\sim 900°C} 1\ (CaO)_2SiO_2 + 2\ CO_2$$

200.2 *60.1* *172.3* *88.0*

Equation 2

Expressed in terms of mass, every tonne of alite produced liberates 579 kg of CO_2, whereas every tonne of belite produced liberates 511 kg of CO_2. This suggests a potential 12% saving in the raw-material CO_2 (RM-CO_2). In addition, there is CO_2 produced from the heat generation; but this 'fuel-derived' CO_2 (FD-CO_2) is dependent on the efficiency of the kiln and type of fuel used. Since belite forms at a lower kiln temperature than alite, further energy and carbon savings result from reduced kiln temperatures that require less fuel. The vertical-shaft kilns used for production of NHL5 tend to operate at 1000°C (CESA, 2006b). This is substantially lower than the 1450°C which is needed for the calcination of limestone to produce the alite in CEMI; although some of the additional energy needed for the extra temperature may be recovered in the form of preheated air for fuel combustion (Bye, 2011). Equations 1 & 2 also demonstrate the raw-material savings. One tonne of calcium carbonate, appropriately clinkered with silica, yields 860 kg of belite or 750 kg of alite.

Disintegration of the sintered lumps of quicklime during slaking substantially reduces the demand for finish grinding of NHL in comparison to CEMI, with only 25% of the slaked lime coming out of the hydrator requiring further grinding to achieve a particle size of 0.09 mm (CESA, 2006b). In Europe the total electricity consumption per tonne of CEMI is reported to be between 90-120 kWh, of which around 40% of this total (36-48 kWh) is required for grinding the clinker (Boesch and Hellweg, 2010).

1.2.3 Aluminosilicate mineral additions

Although there are a number of aluminosilicate materials that can be used in lime-pozzolan concrete mixes, the use of ground granulated blastfurnace slag and silica fume have been determined to be the most promising in initial studies (Grist et al., 2013a). These synthetic materials are both by-products of current industrial processes.

1.2.3.1 Ground Granulated Blastfurnace Slag (GGBS)

GGBS is a latent-hydraulic Type II addition, permitted to replace CEMI by up to 80% by mass in structural concreting applications in Europe (BS EN 197-1, 2011) and by up to 95% by mass in concretes specified for maximum strength, such as secant piles. It is sold as a high quality, environmentally friendly material that improves many aspects of performance and reduces the EC of concrete (Mineral Products Association, 2011). GGBS is a by-product of the reduction of iron ore to produce

metallurgical iron. It is estimated that 242 Mt of iron slag is produced worldwide each year, of which 82% is GGBS suitable for use in the concrete industry (Heath et al., 2014). Even if all blastfurnace slag could be sold as GGBS for cement replacement, it would still amount to less than 7% of the total annual demand for CEMI. Although it is difficult to determine the extent to which physical and economic factors will limit future production levels, it is clear that cementitious systems based on high replacement levels of GGBS will not be able to meet the total global requirement for sustainable binders. It is evident that in the development of LCCs a diversification of raw material utilization is essential.

The Mineral Products Association reports that GGBS has an EC of 52 $kgCO_2/t$ (Mineral Products Association, 2011). This figure includes the CO_2 associated with the secondary processes, namely granulation of the slag, transport to the slag grinding plant and CO_2 derived from drying and grinding. An EE of 1300 MJ is reported to include the production and distribution of electricity associated with these processes. It has been argued that the impacts of the iron-making should not be taken into account because the slag evolves irrespective of whether or not it is used (Higgins, 2007). Whilst it is agreed that the evolution of slag is inevitable, as the market for GGBS has grown the probability of this increasingly high-value product not being utilized has fallen, and thus the validity of this approach can be challenged. As a consequence a number of authors (Chen et al., 2010 & Van den Heede and De Belie, 2012) have questioned whether some of the environmental impact of iron production should be assigned to the GGBS and thus allocated to the concrete producer.

There are five slag grinding plants in the UK and it is estimated that a third of all UK ready-mix concrete deliveries include GGBS (Jones, 2011). In the UK the most commonly used blastfurnace cement has a GGBS content of 50% by mass, designated CEMIII/A; this has been calculated to result in a 40% reduction in CO_2 emissions and a 30% reduction in primary energy, in comparison to CEMI concrete (Higgins, 2007).

1.2.3.2 Silica fume (SF)

SF consists of spheres of amorphous silicon dioxide (SiO_2) that form as smoke-particles during the production of metallurgical grade silicon and ferrosilicon alloys. SF is a highly-reactive pozzolanic material that improves both the rheology of fresh concrete and the strength and durability of the hardened material. Appreciation of the benefits of the use of SF as a supplementary cementitious material in the production of high strength concrete has seen the transition of this material from a polluting waste-product to a valuable high-performance concrete addition (Fidjestol and Magne, 2008). Such is the market demand for SF today that plants run to produce SF during a down-turn in alloy sales. Indeed high-purity, refractory grade SF is routinely produced with silicon-metal as a by-product (Myhre, 1996).

The suitability of industrial by-products as constituents of LCCs is questioned by those concerned about the long-term security of supply, which is governed by the longevity of the primary industry. The raw material for the production of silicon,

quartz or quartzite, is abundantly available. As a by-product of the silicon metal and ferrosilicon alloy industries, the future availability of SF can reasonably be assessed by the projected demand for these two materials. Although novel materials such as graphene might in time impact silicon production in the consumer electronics market, the production of silicon metal and ferrosilicon alloys is principally driven by metal foundry industries, with ferrosilicon being a critical alloying component of iron in the production of steel (Holappa, 2010) and silicon used similarly in the production of aluminium alloys. The graph in Figure 1 shows the strong growth of global silicon production in the last fifteen years.

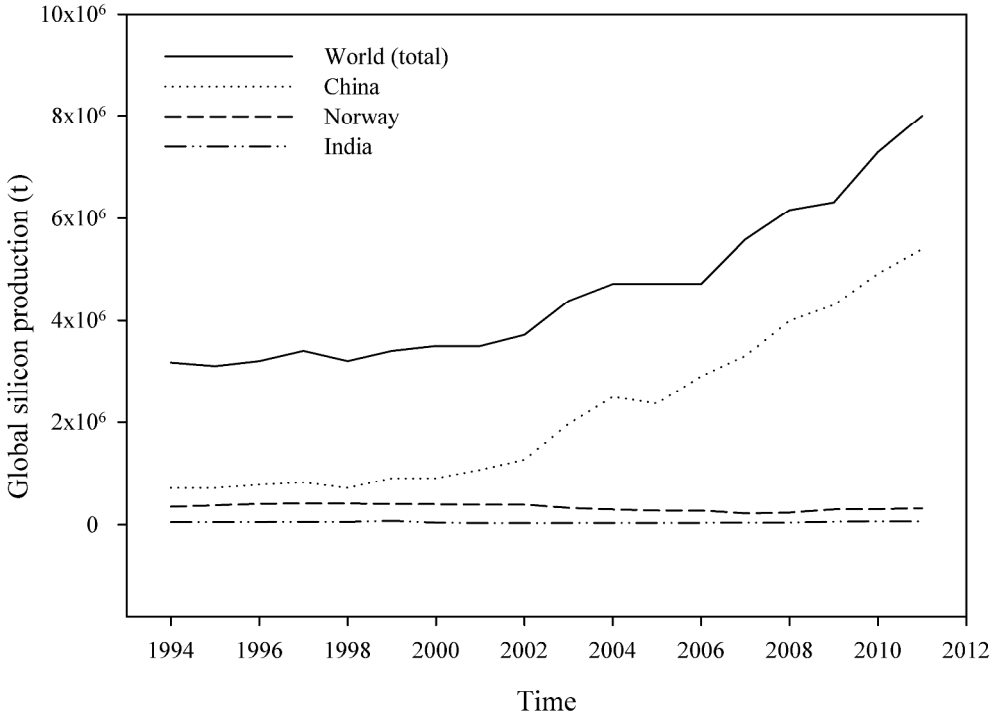


Figure 1: Trends in global silicon production (USGS, 2012)

1.2.4 Long-term security of supply of industrial by-products

It is worth noting that continued production is not the only determinate of availability of SF and GGBS for use as cementitious additions. As Van Oss (2012) highlights, Environmental Protection Agencies, and other bodies involved in the classification of materials, wield significant influence over the market. When industrial by-products are classified, or re-classified (Van Oss, 2013), as 'hazardous wastes' demand can change dramatically. Changes in disposal legislation, or stigmatisation, can threaten sales regardless of whether or not scientific evidence is able to demonstrate the safe stabilisation of these materials in concrete (Chen et al., 2009). The desire to utilise waste materials in concrete varies between national markets due to variable availability and status (Togerö, 2006). Such potential market risks are a good argument for developing cementitious systems based on geological resources, such as naturally occurring pozzolanic materials. Further research should be done to look at

the potential substitution of GGBS for naturally occurring pozzolanic materials such as regional volcanic ashes.

A carbon foot-printing exercise commissioned by a silicon manufacturer and performed by a third party consultancy reports an EC of 14 $kgCO_2/t$ of SF slurry (Enviros Consulting, 2009). This figure includes collection and secondary processing of the SF as well as transportation of the slurry to the UK. The EC associated with the industrial production of SF in Norway is low due to the country's hydroelectric power generation. An EE figure of 18 MJ/t is reported for SF produced in Norway (ELKEM, 2013). This figure includes the energy associated with processing, packaging and storing SF until it leaves the factory gate. It does not include collection of the SF, which has been a legal obligation in Norway since 1974 when legislation was introduced to reduce air pollution (Myhre, 1996).

1.3 Calculation of embodied CO_2 and energy

When calculating the EC and EE of blended cements incorporating supplementary cementitious materials that are by-products of other industrial processes, great care has to be taken in the collection and allocation of the data (Ekvall and Finnveden, 2001).

It is a relatively common practice in environmental impact studies to classify these materials as 'waste products' and thus attribute them with zero EC and EE; on the basis that these emissions arise whether or not the materials are then diverted from landfill for use (Habert and Roussel, 2009 & Damineli et al., 2010). Others attribute only a small EC and EE to these materials on the basis that they require some degree of additional secondary processing, storage and handling before they are ready to be sold at the factory-gate (Kawai et al., 2005 & Flower and Sanjayan, 2007). Still others highlight that these materials can no longer be classified as 'waste-products' (Habert and Roussel, 2009 & Van den Heede and De Belie, 2012). As useful by-products of other industrial processes, there is an argument that it is appropriate to allocate part of the total environmental impact of the primary process to the material and thus to the concrete producer (Chen et al., 2010, Van den Heede and De Belie, 2012 & Habert, 2013).

This is more than just a debate about nomenclature, as it affects the way that the environmental impact of the main process is allocated. Since 2008 GGBS and SF having been officially classified as 'by-products' in line with a new European Directive 2008/98/EC (European Union, 2008), but to date no allocation procedure has been decided upon. The effects of a number of different allocation procedures have been being considered by policy makers in an attempt to rule out procedures that would unfairly disadvantage the different industries. This study considered two common allocation procedures: mass allocation and economic allocation. In the case of mass allocation the overall environmental impact of an industrial process is divided between the primary product and the by-product(s) on the basis of the relative mass of

the products, whereas in economic allocation impacts are attributed based on the relative monetary value of the products.

2 Methodology

2.1 Goal of the study

Recent research considering the properties of a range of binary and ternary lime-pozzolan binders has demonstrated that the pozzolanic reaction, resulting from the inclusion of aluminosilicate additions, substantially enhances the compressive strength of resultant mortars or concretes (Grist et al., 2013a). Such additions not only improve the material properties but also are a determinate of its environmental impact. A detailed life-cycle assessment of all the constituent components of this innovative composite material is beyond the scope of this paper as these are specific to the mix design, location and intended use. Rather, this paper offers the reader an opportunity to step back and consider the bigger picture, facilitating a high-level comparison of the relative environmental impact of this novel concrete technology.

The investigation into the environmental impact of lime-pozzolan concretes comprised two studies. The first study compared the EC and EE of lime-pozzolan concretes produced in the laboratory, with two reference CEMI-based concretes of equivalent $f_{cm,28}$. The second study explored the sensitivity of the environmental impact analysis to methodological choices.

2.2 Embodied CO_2 and energy comparison

In this study the embodied impacts of four alternative hydraulic lime-pozzolan concretes were calculated. The lime-pozzolan binders investigated in this study were all ternary combinations of NHL5, GGBS and SF. The embodied impact of an NHL5-only concrete was also calculated for comparison.

Given that GGBS has a substantially lower environmental impact than NHL5 (considering secondary processing impacts only), it was decided to investigate how varying the ratio of NHL5 to GGBS affected the $f_{cm,28}$, and thus also the binder efficiency, of the resulting ternary lime-pozzolan concretes. The addition of SF was fixed at 12% of the total binder content in each case, based on previous findings (Grist et al., 2013c). Each of the three ternary NHL5-GGBS-SF concretes had a total binder content of 465 kg/m^3 and a water to binder (w/b) ratio of 0.42. They were designated concretes (I) – (III):

- 53% NHL5, 35% GGBS and 12% SF (I)
- 38% NHL5, 50% GGBS and 12% SF (II)
- 23% NHL5, 65% GGBS and 12% SF (III)

In order to investigate the effect of the total binder content on the eco-efficiency of the resulting lime-pozzolan concrete, one further NHL5-GGBS-SF concrete was also analysed in this study. This lime-pozzolan concrete, produced in a previous study (Grist et al., 2013c), had an overall binder content of 546 kg/m^3 and a w/b ratio of 0.35. This concrete had a $f_{cm,28}$ of 49 MPa and is designated concrete (IV).

- 50% NHL5, 40% GGBS and 10% SF (IV)

A control mix of 100% NHL5, designated mix (0), was also produced to establish the contribution of the pozzolanic reaction to compressive strength.

- 100% NHL5 (0)

CEMI-based concretes were also analysed in this study to provide a frame of reference when interpreting the results. The mean compressive cube strength after 28 days ($f_{cm,28}$) was selected as the unit of functional performance when comparing the environmental impact of the alternative concretes. Specifically, CEMI and CEMIII/A (50% CEMI & 50% CEMIII/A) concretes, of equal $f_{cm,28}$ strengths, were extrapolated from the work of Dhir et al. (2001) to enable a like-for-like comparison. The required w/b ratio of comparable concretes was determined theoretically by studying the empirical strength results of concretes prepared and tested by Dhir et al. (2001) at a range of w/b ratios.

When calculating the EC and EE of the concretes, only the impacts associated with the secondary processing of the aluminosilicate additions, GGBS and SF, were assumed. EC and EE data for all the constituents of the lime-pozzolan and CEMI-based concretes are shown in Table 2.

	Embodied CO_2	Embodied energy
	kgCO_2/t	MJ/t
CEMI	930	3,800
NHL5	635	2,721
GGBS	52	1,300
SF	14	18
Water	0.3	10
Aggregate	4	100
SP	220	18,300

Table 2: EC and EE of constituent materials assuming minimal secondary processing of 'waste' materials (CESA, 2006a, European Federation of Concrete Admixture, 2006, Enviros Consulting, 2009, Mineral Product Association, 2011, ELKEM, 2013)

Using these figures the EC and EE of all the concretes was calculated and compared, as were the carbon and energy intensity indices in accordance with the work of Damineli et al. (2010).

2.3 Materials

To produce concretes comparable with concrete (IV), the constituent materials and procedures for proportioning the aggregates, specimen production and curing, were all identical to those employed in the earlier work (Grist et al., 2013c). An NHL5 conforming to BS EN 459-1:2010 was used. The SF was obtained in the form of a slurry, with a SF:water ratio of 50:50 by mass, and conformed to BS EN 13263-1:2005. The GGBS conformed to BS EN 15167-1:2006.

The mix design process for concrete described by Teychenné et al. (1997) was used as the basis for proportioning aggregates. The coarse aggregate comprised a 5-10 mm and 10-20 mm carboniferous limestone. The fine aggregate was 50% Marlborough grit and 50% fine building sand by mass. The particle size distributions (PSDs) of all the aggregates were determined in accordance with BS 933-1:2012 and the results are shown in Table 3.

	% passing			
Sieve size (mm)	Coarse aggregate	Fine aggregate	Marlborough grit	Building sand
40	100	100	100	100
28	100	100	93	100
20	87	100	54	99
14	25	100	38	96
10	1	87	17	93
6.3	0	22	0	82
4	0	0	0	10
2	0	0	0	1
1	0	0	0	0

Table 3: PSD of aggregates

The mix constituents of each of the concretes are given in Table 4. The slump is also presented for the lime-pozzolan concretes, which was tested in accordance with BS EN 12350-2:2009.

Mix description	Free water content	Total binder content	w/b ratio	CEMI	NHL5	GGBS	SF	Coarse aggregate	Fine aggregate	SP	Slump
	kg/m³	*kg/m³*		*kg/m³*	*kg/m³*	*kg/m³*	*kg/m³*	*kg/m³*	*kg/m³*	*kg/m³*	*mm*
Lime-pozzolan concretes:											
(0)	197	465	*0.42*	0	465	0	0	930	770	4.8	140
(I)	197	465	*0.42*	0	246	163	56	930	775	4.0	150
(II)	197	465	*0.42*	0	177	233	56	930	780	3.7	130
(III)	197	465	*0.42*	0	107	302	56	930	785	3.5	130
(IV)	190	546	*0.35*	0	273	218	55	885	750	6.5	140
CEMI reference concretes:											
CEMI (49 MPa)	175	365	*0.48*	365	0	0	0	1315	515	0	n/t
CEMI (33 MPa)	175	273	*0.64*	273	0	0	0	1295	640	0	n/t
CEMI (13 MPa)	175	175	*1.00*	175	0	0	0	1260	920	0	n/t
CEMIII/A (49 MPa)	175	461	*0.38*	230	0	230	0	1315	450	0	n/t
CEMIII/A (33 MPa)	175	307	*0.57*	154	0	154	0	1315	575	0	n/t
CEMIII/A (13 MPa)	175	213	*0.82*	107	0	107	0	1285	735	0	n/t

Table 4: Concrete mix constituents

The concretes were prepared in a rotary pan mixer according to the standard procedure detailed in BS EN 1881-125:2013. Each lime-pozzolan concrete was dosed with the minimal quantity of polycarboxylate ether (PCE) superplasticiser (SP) to produce concretes with a target slump of 140 mm (see Table 4 for the measured slump values). By comparison the CEMI-based reference concretes did not contain any SP and the slump of these concretes, being extrapolated from empirical test results, was not tested (n/t) and expected to have varied due to the variation in w/b ratio. Due to the high embodied impact of the SP (see Table 2), the embodied impacts of the lime-pozzolan concretes have been reported with and without the addition of SP (see Table 12). The concretes were cured under polythene sheeting for 24-hours and then in a conditioning lab maintained at 20±0.5°C and 60-65% RH, in accordance with BS EN 12390-2:2009, until testing.

The compressive strength of concretes (0-III) was measured in accordance with BS EN 12390-3:2009 at 2, 7, 28 and 56 days. The static modulus of elasticity in compression of the lime-pozzolan concretes was also determined in accordance with the method described in BS EN 1881-121:1983 at 28-days.

2.4 Sensitivity analysis

The analysis used in the first study assumed only minimal EC and EE values when quantifying impacts associated with the production of the GGBS and SF. In this study mass and economic allocation methodologies were used to define an environmental impact envelope for lime-pozzolan concretes. A mass allocation coefficient (C_m) of 19% and an economic allocation coefficient (C_e) of 2% were adopted for GGBS in this study as reported by Chen et al. (2010). Furthermore the methodology for deriving these coefficients was used to calculate the equivalent coefficients for SF.

2.5 Calculation

2.5.1 GGBS

The embodied impact of the co-product ($\vec{F}_{co-product/waste}$) has been calculated using Equation 3, in which $\vec{F}_{primary\ process}$ is the impact of manufacturing the primary product and $\vec{F}_{secondary\ process}$ the additional impact associated with the secondary processing (for example collecting, drying, grinding) of the co-product. The allocation coefficient, determined by the choice of methodology, is denoted C.

$$\vec{\mathbf{F}}_{\mathbf{co-product/waste}} = \mathbf{C}.\vec{\mathbf{F}}_{\mathbf{primary\ process}} + \vec{\mathbf{F}}_{\mathbf{secondary\ process}} \qquad \textit{Equation 3}$$

In this analysis, $\vec{F}_{primary\ process}$ has been assumed to equal the EC, or EE, of virgin iron production as reported by Hammond and Jones (2009). The EC and EE of GGBS, including either mass or economic allocation of the primary production of the steel, are shown in Table 5.

	Units	Primary Process (Iron)	Secondary Process (GGBS)	Total (mass allocation)	Total (economic allocation)
EC	$kgCO_2/t$	1,900	52	420	96
EE	MJ/t	25,000	1,300	6,139	1,885

Table 5: EC and EE of GGBS on the basis of mass and economic allocation

2.5.2 Silica Fume

As SF is a by-product of two distinct industrial processes, namely the production of silicon metal (>95% Si) and the production of ferrosilicon alloys (<95% Si), both industrial processes need to be considered separately. Typical masses of SF arising from silicon and ferrosilicon production are reported in Table 6 (Fidjestol and Magne, 2008). Table 6 also shows the mass allocation coefficients (C_m) for the two processes, which were calculated using Equation 4 as described by (Chen et al., 2010).

$$\mathbf{C_m} = \frac{\mathbf{m_{by-product}}}{\mathbf{m_{main\ product} + m_{by-product}}} \qquad \textit{Equation 4}$$

Product	Typical mass produced (kg)	Allocation by mass, C_m
Silicon	1000	69%
SF	450	31%
Ferrosilicon	1000	82%
SF	225	18%

[a.] *Considering the production of FeSi75%*

Table 6: C_m for Si and SiFe75%

Assuming that ferrosilicon production accounts for 80% of the total global production of silicon-metal products (on a gross-weight basis) (USGS, 2012), then the mass allocation coefficients for the production of SF from silicon metal and ferrosilicon results in an overall weighted mass coefficient (C_m) of 21%.

A notable disadvantage of economic allocation procedures is that the market price for the primary and secondary products is highly variable between regions and over time. Minimum allocation coefficients have been calculated for SF production based on maximum and minimum annual spot prices for ferrosilicon (75%), silicon metal and SF in four global markets: US, China, India and Europe (see Table 7). Due to the lack of available data, the price of silicon in India was estimated based on the average ratio of silicon metal to ferrosilicon in the other three global markets (1:0.62). The price of SF in the US was assumed to be the same as in Europe. Results are shown in

Market	SF derived from Si metal		SF derived from FeSi75%	
	$C_{e(min)}$	$C_{e(max)}$	$C_{e(min)}$	$C_{e(max)}$
India	7.0%	10.8%	7.0%	10.8%
US	3.7%	5.8%	3.5%	5.1%
China	3.0%	7.3%	3.4%	7.4%
Europe	4.3%	6.8%	4.5%	6.8%

Table 9. Global prices were converted into Euros/t (€/t) according to the currency conversion rates shown in Table 8.

Market	Si (>95%)		FeSi75%		SF	
	Min	Max	Min	Max	Min	Max
	€/t	€/t	€/t	€/t	€/t	€/t
India	1345	1681	840	1050	*320*	400
US	2109	2460	1511	1634	240	320
China	1260	1512	781	819	120	*240*
Europe	1800	2100	1120	1250	240	320

Table 7: Maximum and minimum dealer import prices for Fe, FeSi75% and SF (2010) based on monthly averages from Platts Metals Week.

1 US$	0.797 €
1 INR	0.014 €
1 RNB	0.126 €

Table 8: Currency conversion rates assumed [1 INR = 1 Indian Rupee and 1 RNB = 1 Chinese Yuan]

Based on these figures minimum and maximum economic coefficients were calculated according to equations 5 & 6, modified from (Chen et al., 2010), where €.m is the price per tonne (€/t) multiplied by the number of tonnes produced in the process.

$$\mathbf{C_{e(max)}} = \frac{(€.\mathbf{m})_{\mathbf{by-product\ (max)}}}{(€.\mathbf{m})_{\mathbf{main\ product(min)}} + (€.\mathbf{m})_{\mathbf{by-product\ (min)}}} \qquad \textit{Equation 5}$$

$$\mathbf{C_{e(min)}} = \frac{(€.\mathbf{m})_{\mathbf{by-product\ (min)}}}{(€.\mathbf{m})_{\mathbf{main\ product(max)}} + (€.\mathbf{m})_{\mathbf{by-product\ (max)}}} \qquad \textit{Equation 6}$$

Market	SF derived from Si metal		SF derived from FeSi75%	
	$C_{e(min)}$	$C_{e(max)}$	$C_{e(min)}$	$C_{e(max)}$
India	7.0%	10.8%	7.0%	10.8%
US	3.7%	5.8%	3.5%	5.1%
China	3.0%	7.3%	3.4%	7.4%
Europe	4.3%	6.8%	4.5%	6.8%

Table 9: Calculated maximum and minimum C_e for SF from Si and SiFe75%

Both C_m and C_e were then applied to the impacts associated with the primary processes, which were identified from literature.

The total emission factor reported by the Intergovernmental Panel on Climate Change (IPCC) for ferrosilicons is 3.91 tCO_2/t FeSi(75%) (IPCC, 1996). The IPCC have based their emission factors on FeSi75%, considered representative of ferrosilicons produced in Norway, the largest producer in Europe. Sjardin (2003) reports a lower value of 2.93 tCO_2/t FeSi(75%) . This study considered the two values as a range: 2.9-3.9 tCO_2/t FeSi (75%).

For silicon metal the IPCC reports a value of 4.3 tCO_2/t Si (IPCC, 1996). Sjardin (2003) however, considers a slightly higher value of 4.49 tCO_2/t Si, from the work of Olsen et al. (1998), more representative of silicon production in Norway. Again these two values are presented here as a range 4.3-4.5 tCO_2/t Si. These CO_2 emission figures are based on the carbon content of the raw materials, namely the reducing agents (typically coal or coke) and the electrodes (typically produced from a paste of petroleum coke and coal-tar pitch) (Sjardin, 2003). These figures, which do not include CO_2 emissions associated with electricity production, are indicative of Scandinavian production, where energy production is primarily from renewable forms of electricity generation. The EC in other regional markets will be higher.

Hammond and Jones (2009) give the EE for the production of silicon as 2355 MJ/kg. They acknowledge that this figure is only from a single source and the origin of this data is not given. In the absence of a more reliable figure, this value had been assumed for the EE of silicon. The EE of ferrosilicon is also not known; for this analysis it has been assumed to be 2041 MJ/kg, based on the same ratio as the EC values given for silicon and ferrosilicon production. Table 10 shows the calculated EC and EE for SF based on mass and economic allocation of impacts associated with silicon metal (a) and ferrosilicon production (b). In the case of economic allocation, maximum and minimum global spot prices have been used to calculate upper and lower values. Part (c) tabulates weighted values for SF production based on the reported ratio of the two primary silicon-metal products.

(a) Silicon production

	Units	Primary Process	Secondary Process	Impact based on mass allocation (C_m = 31%)	Impacts based on minimum economic impact ($C_{e\ (global\ min)}$ = 3.0%)	Impacts based on maximum economic impact ($C_{e\ (global\ max)}$ = 10.8%)
EE	MJ/t	2,355,000	18	730,100	72,500	254,800
EC	$kgCO_2/t$	4,300	14	1,300	100	500

(b) Ferrosilicon production

		Primary Process	Secondary Process	Total based on mass allocation (C_m = 18%)	Impacts based on minimum economic impact ($C_{e\ (global\ min)}$ = 3.4%)	Impacts based on maximum economic impact ($C_{e\ (global\ max)}$ = 10.8%)
EE	MJ/t	2,041,000	18	367,400	69,400	221,000
EC	$kgCO_2/t$	2,900	14	500	100	300

(c) Weighted silicon metal production (80% Ferrosilicon, 20% Silicon)

		Weighted total for SF, based on mass allocation	Weighted total impacts for SF based on $C_{e\ (global\ min)}$	Weighted total impacts for SF based on $C_{e\ (global\ max)}$
EE	MJ/t	439,900	70,000	227,800
EC	$kgCO_2/t$	700	100	300

Table 10: EE and EC of SF on the basis of mass and economic allocation

2.6 Effect of Allocation Method on EC and EE

To understand the sensitivity of the analysis to alternative methodological assumptions the data in tables 2, 5 & 10, was used to build four alternative environmental impact cases for lime-pozzolan concrete (IV) with a 28-day compressive strength of 49 MPa. The four comparative cases were:

(1) GGBS and SF considered having zero embodied impacts.
(2) GGBS and SF as 'waste' in which only impacts associated with secondary processes are considered.

(3) Environmental impacts of SF and GGBS assigned by mass allocation.
(4) Environmental impacts of SF and GGBS assigned by economic allocation.

The embodied impact of the CEMI concrete of equivalent strength was clearly unaffected by the choice of methodological assumption, as it did not contain any aluminosilicate by-products, but the same analysis was undertaken for the CEMIII/A concrete (containing 50% GGBS) for comparison.

3 Results and discussion

3.1 Mechanical properties of lime-pozzolan concretes (0-III)

The compressive strength development of the four new lime-pozzolan concretes prepared for this study is shown in Figure 2.

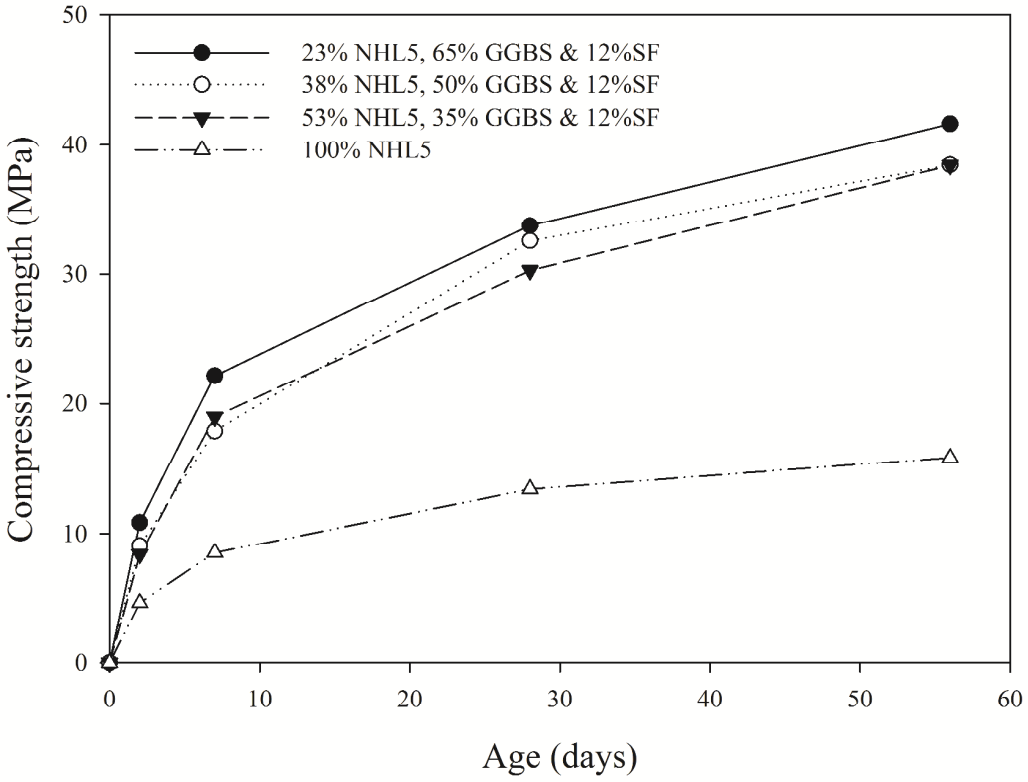


Figure 2: Lime-pozzolan concrete compressive cube strength development

It was observed that varying the ratio of NHL5:GGBS had minimal impact on the compressive strength development of the resulting lime-pozzolan concretes. The ternary binder comprising 23% NHL5, 65% GGBS and 12% SF resulted in the highest cube strengths at all ages, but was only 2.5-3.5 MPa higher than the lowest strength mix, which at 28-days was 53% NHL5, 35% GGBS and 12% SF. All three ternary lime-pozzolan concretes substantially outperformed the lime-concrete control, which attained a $f_{cm,28}$ of 13.4 MPa. The rate of strength gain in the ternary lime-

pozzolan concretes was observed to be greater than in the control lime-concrete at all ages. All the concretes showed a substantial strength increase between 28 and 56 days and would be expected to continue to gain strength after 56 days (Massazza, 1993).

Early age strength gain of lime-based concretes has previously been of particular concern (Yallop, 2013). It can be observed from the results in Figure 2 that these lime-pozzolan concretes gained around 60% of their $f_{cm,28}$ in the first 7 days. Approximately 30% of the $f_{cm,28}$ was attained in the first 2 days after casting. The strength development of these lime-pozzolan concretes may be classified as 'slow-medium', in accordance with BS EN 206-1:2000. As would be expected, the $f_{cm,28}$ of these three lime-pozzolan concretes was substantially less than that of lime-pozzolan concrete (IV), which had a higher overall binder content.

The cylinder strength ($f_{cyl,28}$), elastic modulus (E_c), compressive strain at the maximum stress (ε_{c1}) and ultimate strain (ε_{cu1}) for each of the four lime-pozzolan concretes are shown in Table 11.

	$f_{cyl,28}$	E_c	ε_{c1}	ε_{cu1}
	MPa	GPa	%	%
100% NHL5 (0)	12.0	17.4	0.0029	0.0098
53% NHL5, 35% GGBS & 12% SF (I)	27.1	32.5	0.0014	0.0014
38% NHL5, 50% GGBS & 12% SF (II)	27.7	28.4	0.0015	0.0015
23% NHL5, 65% GGBS & 12% SF (III)	29.0	17.4	0.0028	0.0028

Table 11: 28-day elastic properties of NHL5 and lime-pozzolan concretes

Although the $f_{cyl,28}$ of the three ternary lime-pozzolan concretes were observed to be similar, the results show that the ratio of NHL5 to GGBS has a marked impact on the E_c. It can be seen that reducing the proportion of GGBS in the ternary combination, increased the E_c and reduced ε_{cu1} of the composite concrete. The observed reduction in E_c, associated with a higher content of aluminosilicate additions, agrees with the findings of Nassif et al. (2005) in CEMI-based concretes.

The E_c of lime-pozzolan concretes (I-III), with $f_{cyl,28}$ of around 27 MPa, are reasonably accurately predicted by equation 7 for CEMI-based concretes given in Eurocode 2 (EC2), (BS EN 1992-1-1, 2004) which would predict an elastic modulus of 30 GPa.

$$E_{cm} = 22\,[f_{cm}/10]^{0.3} \qquad \textit{Equation 7}$$

In EC2, for concrete classes ≤ C50/60, the lowest value of ε_{c1} assumed for ultimate limit state design is 0.0024. Two of the lime-based concretes in Table 11

demonstrated a strain at failure less than 0.0024 and would therefore require a more conservative elastic design approach.

Given the similarity in the strength development of the three ternary lime-pozzolan concretes, they have been assumed to be of equal strength ($f_{cm,28}$ = 33.0 MPa; the mean 28-day cube strength of the three ternary compositions), to facilitate a comparison with CEMI and CEMIII/A reference concretes of a single strength. The control lime-concrete, having a substantially lower compressive strength ($f_{cm,28}$ = 13.5 MPa), has been compared with equally low-strength CEMI and CEMIII/A concretes.

3.2 Embodied CO_2 and energy comparison

Table 12 shows the calculated EC and EE of the lime-pozzolan concretes, alongside that of the CEMI and CEMIII/A reference concretes of the same $f_{cm,28}$.

Concrete	$f_{cm,28}$	w/b ratio	EC	EE	CO_2 Intensity, ci_{cs-28}	Energy Intensity, Ei_{cs-28}
	MPa		$kgCO_2/m^3$	MJ/m^3	$kgCO_2/(m^3$ Mpa)	$MJ/(m^3$ Mpa)
NHL5-concrete (inc. SP[a]) (0)	13.5	0.40	305	1275 (1365)	22.6	94.4 (101.1)
CEMI	13.5	1.00	170	675	12.6	50.0
CEMIII/A [50% CEMI & 50% GGBS]	13.5	0.82	115	550	8.5	40.7
53% NHL5, 35% GGBS & 12% SF (inc. SP[a]) (I)	33.0	0.40	175	890 (965)	5.3	27.0 (29.2)
38% NHL5, 50% GGBS & 12% SF (inc. SP[a]) (II)	33.0	0.40	135	795 (860)	4.1	24.1 (26.1)
23% NHL5, 65% GGBS & 12% SF (inc. SP[a]) (III)	33.0	0.40	95	695 (755)	2.9	21.1 (22.9)
CEMI	33.0	0.64	265	1045	8.0	31.7
CEMIII/A [50% CEMI & 50% GGBS]	33.0	0.58	160	790	4.8	23.9
50% NHL5, 40% GGBS & 10% SF (inc. SP[a]) (IV)	49.0	0.35	195 (195)	1190 (1310)	4.0 (4.0)	24.3 (26.7)
CEMI	49.0	0.48	345	1570	7.0	32.0
CEMIII/A [50% CEMI & 50% GGBS]	49.0	0.38	235	1355	4.8	27.7

[a] *Including addition of SP at the dosage required to produce a hydraulic lime-pozzolan concrete with a target slump of 140mm.*

Table 12: Embodied impact comparison

The results shown in Table 12 demonstrate the critical importance of comparing mixes of equal functional performance. Despite NHL5 having a lower EC than CEMI and CEMIII/A binders on a mass-for-mass basis, the results show that the CO_2 intensity of the NHL5 (only)-concrete (0) is almost twice that of the equivalent strength CEMI and almost three times that of the equivalent strength CEMIII/A concrete. This refutes the use of NHL5 with no pozzolanic additions as a low CO_2 alternative to CEMI (although other performance benefits are relevant in many applications).

On the other hand the calculated CO_2 intensity, that is the amount of CO_2 emitted in the delivery of 1 MPa of compressive strength at 28-days (Damineli et al., 2010), of each ternary lime-pozzolan concrete is shown to be lower than CEMI concretes of the same $f_{cm,28}$, demonstrating that NHL is effective in conjunction with appropriate

pozzolanic additions. Furthermore lime-pozzolan concretes (II), (III) and (IV) are seen to have lower carbon intensities than the best practice CEMIII/A concretes of equivalent $f_{cm,28}$. The CO_2 intensities of all the concretes tested, except the NHL5-only concrete, fell within the range 1.5 to 15 kg $CO_2/(m^3$ MPa) reported in literature (Damineli et al., 2010).

Considering the lime-pozzolan concrete with a $f_{cm,28}$ of 49 MPa, it can be seen that the EC of this 'high-strength' concrete is 43% lower than the CEMI and 17% lower than the CEMIII/A concrete of equivalent $f_{cm,28}$. The necessary addition of SP, at a dosage of 1.2% by mass of binder in this case, was shown to have no significant impact on the EC of the lime-pozzolan concrete (IV). The addition of SP has, however, been shown to have a substantial impact on the EE of the resultant lime-pozzolan concrete (as seen in Table 12). Including SP the EE of lime-pozzolan concrete (IV) is around 17% lower than the equivalent CEMI concrete; excluding SP it is 24% lower. The EE of the lime-pozzolan concrete, excluding SP, is seen to be 12% lower than that of the CEMIII/A concrete, and including SP, marginally lower (3% reduction).

The concrete with the lowest EC is lime-pozzolan concrete (III), which contained a high proportion of aluminosilicate minerals. This concrete had an EC of 95 $kgCO_2/m^3$, 64% lower than a CEMI, and 41% lower than a CEMIII/A concrete of equivalent $f_{cm,28}$.

The EE data is presented with and without an allowance for SP in the case of each lime-pozzolan concrete. All four lime-pozzolan concretes had energy intensities less than the comparative CEMI concretes, even with an allowance for SP, but only mixes (III) and (IV) had energy intensities less than the best-practice CEMIII/A concrete.

The binder intensity (bi_{cs-28}), or total amount of binder to deliver 1 MPa of compressive strength at 28-days (Damineli et al., 2010), of lime-pozzolan concretes (I), (II), & (III), having a typical $f_{cm,28}$ of around 33 MPa and requiring 465 kg/m^3 of binder, is 14.1 $kg/(m^3$ MPa). Whereas the binder intensity of lime-pozzolan concrete (IV), having a $f_{cm,28}$ of 49 MPa and requiring 546 kg/m^3 of binder, is 11.0 $kg/(m^3$ MPa). This demonstrates that the lime-pozzolan binder was more efficient at higher compressive strengths and agrees with the findings of Damineli et al. (2010) in CEMI-based concretes.

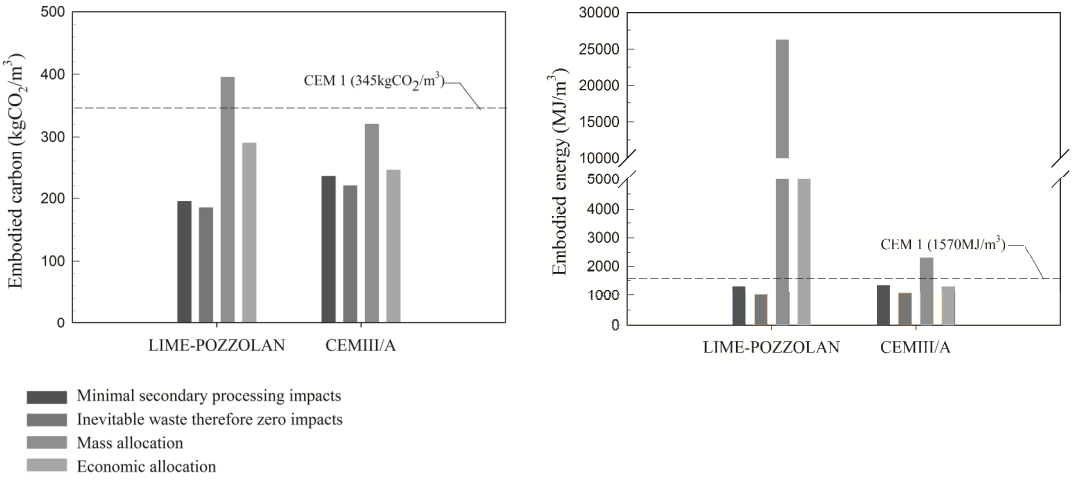
Although these binder intensity values are located within the range of results reported by of Damineli et al. (2010), it is difficult to compare these efficiencies with external data as the $f_{cm,28}$ of each concrete is not only a function of the efficiency of the binder, but also of other mix design and methodological choices. For instance the resultant $f_{cm,28}$ is also a function of the nature and grading of the aggregates, the particle packing of the binder, the use of SP and the curing conditions. Given that the use of SP and inclusion of 6-10% SF are recommended as ways to improve the efficiency of CEMI-concrete mix designs, the scope for improving the efficiency of lime-pozzolan concretes may be limited. Other strategies for increasing the efficiency of lime-pozzolan binders will no doubt include: optimising the ratio of constituent binders

both for chemical composition and/or particle packing, tailoring a blended SP, selecting suitable aggregates and identifying optimised curing conditions.

Combining these results we can postulate that a lime-pozzolan concrete containing a high proportion of GGBS, as in binder (III), and an increased overall binder content is likely to yield a concrete with a lower still CO_2 and energy intensity.

3.3 Sensitivity analysis

Figure 3 graphically compares the EC (a) and the EE (b) of lime-pozzolan, CEMIII/A and CEMI concretes of the same strength ($f_{cm,28}$ = 49 MPa) based on four alternative allocation methodologies.



(a) **(b)**

Figure 3: Effect of four different allocation procedures on the EC (a) and EE (b) of three alternative concretes ($f_{cm,28}$ =49 MPa)

This study demonstrates the pronounced effect of selecting different allocation methodologies in calculating the environmental impacts of cementitious binders including mineral 'by-products'. Choice of allocation procedure would have a fundamental effect on the selection of the 'greenest' binder.

Figure 3 shows that if GBBS and SF are considered waste materials, being assigned zero or nominal secondary processing impacts only, both the lime-pozzolan and the CEMIII/A concrete offer savings in EC and EE in comparison to the CEMI concrete. Furthermore, the lime-pozzolan concrete is shown to be the lowest carbon solution.

However, if either a mass or economic allocation coefficient is adopted in calculation the impacts of GGBS and SF, the CEMIII/A concrete is shown to have the lowest impact. This can be attributed to the very detrimental effect of both mass and economic allocation procedures on the environmental credentials of SF, which is only

present in the lime-pozzolan concrete. This is particularly pronounced in the calculation of EE, owing to the energy intensity of the manufacture of silicon and ferrosilicon alloys. When economic allocation is assumed the lime-pozzolan concrete is calculated to have an EE of around 5000 MJ/m^3, three times that of the CEMI concrete. Moreover, if the mass allocation is assumed the EE of the lime-pozzolan concrete is calculated to be sixteen times that of the CEMI concrete.

It is important that issues of nomenclature do not unintentionally undermine the sensible and sustainable closed-loop utilization of materials as the allocation of impacts has no effect on global environmental impacts. Rather interoperable systems that promote the flow of materials and prevent waste must be designed and protected (Desrochers, 2004). Two extreme scenarios can be imagined that would indicate failure of the overall system: clearly it would have failed if the use of these materials was abandoned by the cement industry and these materials tended once again towards 'waste'; equally the production of silicon metal as a by-product of the industrial production of aluminosilicates for 'green' cement manufacture is clearly an example of high-level system failure. Although these scenarios represent extreme cases, they serve to highlight the consideration that needs to be given to the regulation of allocation procedures.

Standard methodologies are clearly needed to prevent manipulation and engender confidence in the results of Life Cycle Assessments (LCAs), however standardisation of allocation procedures is proving hugely challenging and controversial for policy makers (Heijungs and Guinée, 2007, Reap et al., 2008 & Yellishetty et al., 2009) especially in the concrete industry (Chen et al., 2010 & Van den Heede and De Belie, 2012). One recent model that might warrant further consideration in the case of lime-pozzolan technology is that proposed by Habert (2013), which considers the economic behaviour of energy-intensive industries subject to the European Union Greenhouse Gas Emission Trading Scheme (EU-ETS). The objective of this allocation methodology is to fairly distribute economic gains and losses, associated with CO_2 emissions, between the industries producing mineral additions as by-products and the concrete industry.

Although care has been taken to compare the EE and EC of concretes of equivalent functional performance (in this case $f_{cm,28}$), it is recognised that this analytical approach assumes temporal equivalence, that is that the durability of the concretes is also identical. Further testing is required to assess the relative durability of lime-pozzolan, and other novel concretes, so that their embodied impacts could be amortised over their anticipated life-cycles. Given the life-cycle of concrete structures is highly influenced by physical and chemical interactions with other materials, the nature of the environment in which they are used and meteorological and social events, temporal phenomena dramatically increase the complexity of the analysis. Nonetheless, testing is necessary to compare the performance of NHL5 and CEMI-based concretes subject to aggressive exposure conditions and other accelerated durability tests. The risk of sulphate attack and alkali-silica reaction (ASR) in

hydraulic lime-pozzolan concretes are both anticipated to be low due to the low content of tricalcium aluminate (C_3A) and Na+ and K+ cations respectively. Rigorous testing is needed to substantiate these predictions and quantify the durability of lime-pozzolan concretes, to inform their appropriate use and sustainability.

While this paper has focused on EE and EC, further research is needed to assess the broader environmental impacts of lime-pozzolan concretes. Given that future lime-pozzolan concrete technology is likely to be predicated on the combination of ecological and technical performance benefits, this work should be undertaken in conjunction with research investigating the breathability, permeability and durability of lime-pozzolan concretes; and how these properties are affected by the nature and proportion of aluminosilicate mineral additions. Specifically, future testing might consider the technical and ecological performance of lime-pozzolan concretes based on alternative synthetic or naturally occurring pozzolanic materials.

Given the considerable investment that the CEMI industry has made in improving kiln efficiencies, it is recognised that the CO_2 emission reductions seen in this paper are unlikely to be realised across the board without similar investment in efficient lime-kiln technologies. Although the NHL5 utilised in this research programme was reported to have a lower EC and EE than CEMI on a mass-for-mass basis, the ecological benefits associated with lime and lime-based materials should generally be regarded as future-orientated. Given that the production of NHL5, like CEMI, is based on the calcination of limestone, it is suggested that similar or improved kiln efficiencies are possible in this industry. The availability of the raw material, the familiarity of the manufacturing process and the possibility of achieving the necessary kiln temperatures using alternative fuels, such as biomass (Marias & Bruyères, 2009), is thought to make lime-technology in construction interesting from both a historical and future perspective.

4 Conclusions

This paper reflects on the value of lime-pozzolan concrete technology in the context of the industry wide search for LCCs. The results of these three studies are thought to be valuable in the dialogue about the desirability and viability of this emerging lime-pozzolan binder technology. Furthermore, the results are interesting more generally in the formulation of low-carbon cementitious binders and the shaping of LCA allocation policies.

- A comparison of the embodied impacts of a NHL (only)-concrete with that of a CEMI concrete of equivalent $f_{cm,28}$ has revealed that the use of NHL5 alone as a ‘green’ alternative binder to CEMI is not practical.
- The use of NHL5 in conjunction with pozzolanic materials has been shown to be a viable ‘low-carbon’ alternative to CEMI or CEMIII/A in certain circumstances.

- A lime-pozzolan concrete with a binder comprising 23% NHL5, 65% GGBS & 12% SF, with a $f_{cm,28}$ of 33MPa has an EC 64% less than a CEMI concrete of equivalent strength. The EC of this concrete is also around 40% less than an equivalent strength CEMIII/A concrete. The EE of this lime-pozzolan concrete is 28-33% lower than that of the CEMI concrete (depending on inclusion of SP) and 4-12% lower than that of the CEMIII/A concrete.
- Although this paper demonstrates that the use of aluminosilicate by-products, specifically GGBS and SF, in combination with NHL5 can realise savings in environmental impact, it has also shown that the 'savings' are highly dependent on the choice of allocation procedure.
- Whereas, in the case of GGBS it has previously been shown that economic allocation procedures maintain environmental benefits in comparison to CEMI; both mass and economic allocation procedures are shown to have a very detrimental effect on the environmental credentials of SF.
- This study has also shown that the mix design, and resulting compressive strength, has an effect on the environmental performance of lime-pozzolan concretes. Specifically the binder intensity of the lime-pozzolan concrete was found to vary between 11.0 kg/(m^3 MPa) for a $f_{cm,28}$ of 49 MPa and 14.1kg/(m^3 MPa) for a $f_{cm,28}$ of 33 MPa, demonstrating that the binder is more efficient at higher compressive strengths.

This study of the EC and EE of lime-pozzolan concretes suggests that these concretes could reasonably be advocated as a low-carbon alternative to CEMI concretes. Given that the ecological performance of these concretes has been shown to be influenced by the source of NHL5, the choice of allocation methodology, the ratio of constituent materials, the total binder content and the use of SP, it is recommended that caution is exercised by those promoting or specifying this novel technology purely on the basis of its 'green' credentials. That said there is scope for the careful design, specification and production of lime-pozzolan concretes that could realise substantial CO_2 emission savings.

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