Title

A review of alternative approaches to the reduction of CO_2 emissions associated with the manufacture of the binder phase in concrete

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Abstract

In this review we discuss a wide range of alternative approaches to the reduction of CO_2 emissions associated with the manufacture of the binder phase in concrete. They are classified broadly as follows:

(1) Use alternative fuels and/or alternative raw materials in the manufacture Portland-based cements.

(2) Replace Portland clinker with "low-carbon" supplementary cementitious materials (SCMs) in concrete.

(3) Develop alternative low-carbon binders not based on Portland clinkers.

The first approach mainly represents incremental improvements that can be achieved fairly easily and cheaply as long as suitable raw materials can be found. The second approach ranges from incremental improvements, if low levels of SCM substitution are used, all the way to major innovations for binders with very high Portland clinker replacement levels. The third approach is the most risky but also holds the greatest promise for truly significant CO_2 reductions if it can be implemented on a large scale.

Keywords: Alternative binders, Blended cement (D), Cement manufacture (E), Hydration (A)

1. Introduction

The subject of this paper is mineral-based binders which, in their intended use, (but not necessarily considering their whole usage life cycle), result in the emission of a significantly lower CO_2-equivalent volume of greenhouse gases (GHG) than the equivalent amount (as required for the intended use) of conventional Portland-cement-based binders. In practice, the only greenhouse gas of concern here is CO_2, as only very small amounts of other greenhouse gases are emitted in cement manufacture. However, there is an important unresolved issue regarding the full life-cycle analysis, relating to in-use CO_2 uptake. It is well known that Portland cement based concretes absorb atmospheric CO_2 in service, the rate of this carbonation being dependent on the porosity of the concrete and the cross section of the concrete members, as well as the exposure conditions. Unfortunately, due to the variability of actual carbonation rates and the fact that excessive carbonation of steel-reinforced structural concrete is usually considered undesirable for durability reasons, it is difficult to determine the best way to take into account delayed carbonation of the binder in use. Thus, comparisons are generally done by excluding any consideration of long-term CO_2 uptake by the final product (concrete) over its use lifetime, and regulations relating to CO_2 emissions do not take this re-absorption into account. However, in this article we will make an exception to this rule by considering, in addition to hydraulic binders, certain binders that harden principally by carbonation. But it will be understood that such binders are primarily intended for use in precast products due to the need to provide a concentrated CO_2 atmosphere for the curing process; and also that such products will typically be either unreinforced or else reinforced with materials that do not corrode significantly in a matrix at pH values typically well below the range needed to passivate mild steel. These two constraints currently limit the types of construction product that can be made by means of carbonation hardening.

In 2013, about 4 billion tons of Portland-based hydraulic cement was used globally, (about half of it in China) [1], and CO_2 emissions from the cement industry amounted to over 5% of global anthropogenic CO_2 emissions [2]. The principal use of cement is to make concrete, and the CO_2 emissions associated with all of the other inputs to concrete can usually be neglected relative to that of the cement. Concrete is amongst the most energy- and carbon-efficient of all man-made materials on a volume basis; however, given the well-established association between global anthropogenic CO_2 emissions and global environmental changes, we expect there to be a continuing societal need for reductions in industrial CO_2 emissions, and the cement industry will certainly not be exempted from this [3].

Faced with this need, the Portland cement industry has several options, listed below in order of ease:

(1) Use alternative fuels and/or alternative raw materials to reduce CO_2 emissions for the manufacture of Portland-based cements.

(2) Replace Portland clinker to the greatest extent possible with low-carbon Supplementary Cementitious Materials (SCM) in concrete (whether added with the cement or directly into the concrete mix).

(3) Develop alternative low-carbon binders not based on Portland clinkers, (and requiring new standards).

(4) Capture and sequestrate the CO_2 emitted by cement plants.

Note that the first two options can each be split into two subsets, depending on whether or not the final product conforms or not to existing cement and concrete norms or standards in the country concerned. The question of standards is a complex one, because major reductions in CO_2 emissions are likely to require significant changes in cement and concrete norms, but such changes are likely to be slow, mainly because of the need to prove the durability of the resulting concretes in service.

There is one other important approach not listed above that can be considered if one looks at the use of concrete on a functional basis: the use of ultra-high-strength concretes to produce structures which achieve performance equivalent to that of more conventional concrete structures but use a significantly smaller volume of concrete. But, for simplicity, we will restrict the discussion in this paper to reducing the carbon footprint of concrete on a volumetric performance-equivalent basis.

Inclusion of the use of alternative fuels under the heading "low-carbon" is somewhat questionable on scientific grounds, because it does not necessarily reduce CO_2 emissions per unit of product; but it is one of the least costly approaches available to the cement industry, and it is permitted by carbon emissions regulations in certain circumstances, so it has been included here. The use of alternative raw materials in kiln feeds reduces specific CO_2 emissions mainly in cases where a significant fraction of the necessary calcium for the clinker is provided in a de-carbonated form, but sources of such alternative raw materials are very limited, so, on a global basis, this approach is unlikely to have a large impact.

In most parts of the world, the conventional approach to reducing the carbon footprint of concrete (per unit volume) remains the partial replacement of Portland clinker with SCMs. This can reduce the specific CO_2 emissions of concrete provided that the SCM is a low-carbon material (e.g. an industrial waste product such as fly ash) or a natural raw material requiring little processing (e.g. a natural pozzolan). But the local availability of such materials of adequate quality is also very limited, so there may well be a need to make equivalent materials (e.g. calcined clays as artificial pozzolans) provided that their manufacture is low enough in CO_2 emissions compared to Portland clinker.

Note also that the subject of alkali-activated binders, which also falls under option (3), will not be treated here, as it will be the subject of a separate review paper in this issue. Option (4) is also considered to be beyond the scope of this article. In the remainder of this article, section 2 deals primarily with approaches that attempt to keep the resulting cements as close as possible to what is covered by existing standards, while section 3 mainly covers approaches that require us to go well beyond existing norms.

2. Alternative fuels and raw materials for the manufacture of Portland-based cements

In Japan, use of waste tires as alternative fuel started in 1980 or around that time [4]. Alternative fuels commonly used in cement manufacturing include tires, sludge, waste oil, plastics, fabrics and biomass, etc. Heat can be recovered from waste oil, plastics or other wastes, which were previously simply incinerated, by recycling as heat source. Use of alternative fuels leads to reduction of CO_2 emissions in the sense of reduced use of fossil fuel.

Replacement of conventional fuels in the cement industry with biomass or wastes is in progress in many countries. The replacement ratio is close to 100% at advanced manufacturing facilities. As shown in Fig.1 [5], there is highly variable level of replacement ratios among countries and periods. According to the Cement Technology Roadmap 2009 by the IEA and WBCSD [2], the alternative fuel ratio was 16% in developed countries and 5% in developing countries in 2006 and is expected to increase to 40% to 60% and 10% to 20%, respectively, by 2030.

The amount of CO_2 produced by decarbonation of limestone in cement kiln feed can be reduced by increasing CaO input from alternative raw materials, if suitable CaO-rich materials can be found locally. The use of CaO-rich wastes and by-products as raw materials in the cement industry leads not only to reduced CO_2 emissions but to prolonged life of landfills as well as preservation of natural resources. Recent figures suggest that alternative raw materials and alternative fuel ash account for 3% to 4% of kiln-feed raw materials in Europe [6].

Fig.2 shows the alternative raw materials ratio and the clinker/cement ratio of some cement companies.

The values in Fig.2 were determined by the WBCSD procedure [7] and were reported on the companies' websites. "The alternative raw materials ratio" is consumption of alternative raw materials as a percentage of total raw materials (including SCM) for cement production. "The clinker/cement ratio" is calculated based on total clinker consumption and cement production (%). The companies in category I in Fig.2 are considered to be producing mainly Portland cement using conventional raw materials. The companies which are producing a certain amount of blended cement with SCM such as fly ash and blastfurnace slag, are considered to be in category IV. Also, the companies which are producing a certain amount of blended cement with conventional raw materials such as limestone powder, are considered to be in the category III. On the other hand, the companies in category II are producing mainly Portland cement with a certain amount of wastes and by-products. This tendency is particularly notable in the Japanese company.

The use of wastes and by-products in cement production is very high in Japan, reaching 320 kg/t of Portland cement in 2011 [8]. The amount of waste and by-products received by the Japanese cement industry in 2011 was 27 million tons (Table 1 [9]), which was equivalent to about 7% of the total industrial waste production of the same year, 381 million tons [10]. Recycling the wastes which are difficult for use in other industries will significantly contribute to environmental protection as well as to CO_2 emission reduction. Further discussion is necessary to express these contributions to reduce wastes of cement industry properly. With recent efforts in environmental protection, the recycle rates of many types of wastes have been increased. The increase in recycle rates was significant especially in sewage sludge, waste plastics and coal ash in Japan. This increased level of demand for recycling has even caused competitive situations to arise in the acquisition of some wastes and by-products [11].

Burning fuels produces residues containing mainly SiO_2 and Al_2O_3 from coal and mainly Fe_2O_3 from steel in waste tires. However, these can be again recycled as main components of the raw materials in cement production, without leaving any by-products from the waste use. The other advantage is that organic matters contained in alternative fuels and raw materials are degradable at high temperatures. On the other hand, alternative fuels or raw materials may sometimes contain minor elements or heavy metals. In addition, burnability of alternative raw materials is different from that of natural raw materials and thus changes the burning pattern in the kiln. Careful control is required because such factors as minor elements and burnability may affect quality performance of cement. The following section describes influences of minor elements and some alternative raw materials.

2.1 Influences of minor elements

Waste and by-products recycled as alternative fuels or raw materials can contain minor elements that have adverse effects on quality of cement or the environment. Minor element contents and their influences must be assessed precisely in determining practical usability, requirements for use and control methods for waste and by-products. Many studies have already been done [12] and more studies are under way [13] [14] on the influences of minor elements which do not allow general prediction due to their variations depending on many factors including the amounts, types and combinations of minor elements as well as main components of clinker raw materials.

Minor elements can also affect the mineral proportions of clinker. The conventional method for predicting the mineralogical composition of clinker is calculation by the Bogue equations. However, it has been pointed out that discrepancy between the actual mineral contents and those obtained by Bogue calculation becomes larger with the increase in minor element input (e.g., P_2O_5 and SO_3) from the increased waste and by-products in cement raw materials, or with the change in cooling conditions [15] [16]. As a solution to this problem, XRD/Rietveld analysis has been introduced at many plants for quantitative analysis of minerals. In addition, trials have been made for applying the XRD/Rietveld analysis results to quality prediction and analysis at production sites. For example, there are reports on development of a system which enables efficient control of production operation conditions and prediction of cement properties through an original analysis flow using data from XRD/Rietveld analysis and other process parameters [17][18]. With this system it is now possible, at the time of production, to predict changes the compressive strength of the cement and other test data which are usually not available until a certain age is reached. This system is also capable of providing rapid prediction of changes in product quality with the use of new fuels and raw materials at a given cement plant. When put in practical operation at production facilities, this kind of system will greatly contribute to enhanced consistency of cement quality.

Although the mineral composition of a cement can be obtained by XRD/Rietveld analysis, it is more difficult to evaluate the reactivities of the individual clinker phases. The reactivity of belite is an important factor for the usability of belite rich cement, which is produced from with a kiln feed with a lower limestone content than normal. Recently, some studies were reported about how the reactivity and crystal structures of pure alite and belite would change when different types of impurities (minor elements) were added in different quantities [19][20]. Durgun et al. reported that quantitative analysis results on the charge localization revealed that some impurities or some combinations of them could have favorable effects on belite reactivity (e.g., Li, K, Be, Sr, B, Al, B+P, Al+P and Li+P) [19]. From the comparison between the crystal energy and the cement characteristics, Sakurada et al. considered that a β-C_2S crystal in which a Ca(2) atom having 8-fold coordination is substituted by one K atom or one Sr atom is less stable compared with the structure in which a Ca(1) atom having 7-fold coordination is substituted by one K atom or one Sr atom in (Table 2) [20]. There will be practically an unlimited number of combinations of impurities, so a very large number of such analyses is needed if one follows this approach. It is expected that further analytical research on crystal structures and other factors in addition to experimental approach will lead to some practical proposal about the influence of minor elements and their effective use. A quality control technique combined with a conduction calorimeter was recently proposed for direct evaluation of reactivity of minerals [21]. More investigation is needed for the development of new analytical techniques.

2.2 Municipal waste incinerator ash

Municipal waste is treated in many different ways. In the EU in 2008, 19.5% was incinerated, 41.0% was recycled directly, and 39.5% was sent to landfills [11]. Annual generation of municipal waste in Japan was 45.4 million tons in 2011, with most of it incinerated for reduction in volume. Incineration for volume reduction accounted for 93.6% of the total generation, with 8.7 million tons of incinerator ash produced [22]. Incinerator ash directly sent to final disposal amounted to 4.8 million tons. As shown in Table 3 [23], the main components contained municipal waste incinerator ash are CaO, SiO_2, Fe_2O_3 and Al_2O_3, but in proportions very different to those of cement kiln feeds. The content of CaO in incinerator ash is highest in cases where CaO is blown into an incinerator to control HCl gas generation. Some reports are available about the use of municipal waste incinerator ash as cement raw material [24][25]. The major issues in using municipal waste incinerator ash as a cement kiln feed component are as follows: ratio of Al_2O_3 is high for a main component compared to clay in natural raw materials; chloride ions contents are often very high; and some heavy metals are also present. Pre-treatment of ash is proposed as a solution to the problems of chloride ions and heavy metals [26][27]·

Incinerator ash consists of bottom ash and fly ash. The content of chloride in bottom ash is only about 0.4 to 3%, while that in the fly ash is about 5 to 20% [27]. Therefore, the fly ash cannot be directly used as a cement raw material but needs to be pre-treated for desalting. When fly ash is desalted simply by washing, the chloride removal rate remains low due to the chloride ions present as Friedel's salt. However, Friedel's salt can be degraded by blowing in carbon dioxide derived from kiln exhaust gas which decreases pH to about 7.2 to 10.1 [27]. As a result, chloride ion concentration of fly ash is reduced to around 0.5% after washing. Calcium ions eluted from Friedel's salt bond with carbonate ions to form calcium carbonate. Fig 3 shows these process flows of a plant [28]. Filtrate from the washing and desalting process is neutralized using kiln exhaust gas [29]. Bottom ash is used as alternative to clay in cement raw materials after removing metals and debris. The Kumagaya plant in Saitama prefecture, Japan, installed the ash washing facility in 2001 and is capable of accepting 60,000 tons of bottom ash and fly ash every year, about a quarter of the total municipal waste incinerator ash discharged from Saitama prefecture. When 67.2 kg/t-cement of cement raw material is replaced by municipal waste incinerator ash, the amount of CO_2 emitted by the cement production process is decreased by 22.3kg/t-cement, but producing the ash itself accounts for CO_2 emissions of 6.14kg/t-cement, so the net CO_2 emissions are reduced by 16.2kg/t-cement by this process [30].

2.3 Pulverized waste concrete

Concrete accounts for about 45% of construction waste [31]. Many studies have been made on waste concrete recycling, and standards have been established for separated and recycled aggregate (e.g. JIS A 5021:2011). However, pulverized concrete from the aggregate recycling process has not been re-used efficiently. Cement paste, which is a major conponent of pulverized concrete, contains high concentrations of CaO, as shown in Table 4 [32]. Reusing it as clinker raw material will contribute to CO_2 emission reduction. NEDO conducted a comprehensive study related to CO_2 reduction techniques in cement industry in 2010 [33]. The study reported that factors that limit CO_2 reduction by reuse of pulverized concrete include alkali derived from aggregate and CO_2 generated during transport. The heat treatment and abrasion method currently provides the lowest possible aggregate content in pulverized concrete (aggregate content: 33.0%; CaO content 31.0%). However, use of pulverized concrete obtained by this method results in not more than about a 2% reduction in CO_2 emissions. The reduction rate will increase to about 10% if a new technique is made available that can reduce the aggregate content in the pulverized concrete to 2.4% (CaO content: 45.2%). Choi et al. [34] recently reported a technique for easy separation of aggregate from cement paste by applying inorganic materials such as cement and pozzolanic materials to the aggregate surfaces and employing microwave heating to manufacture recycled aggregate. This technique enables reducing CO_2 emissions from aggregate recycling to about one third those by conventional methods. The other effective approach is to promote use of concrete using limestone aggregate with low contents of alkalis and SiO_2. This approach allows for using most part of waste concrete including aggregate as clinker raw material. However, it is only available for those areas that have abundant limestone.

2.4 Modified Portland cement made using municipal waste incinerator ash as main raw material

Standards for modified Portland cements made using municipal waste incinerator ash as a major raw material were established in Japan in 2002. Municipal waste incinerator ash contains high concentrations of chloride, as mentioned in 2.2. However, the “Ecocement” manufacturing process uses municipal waste incinerator ash in a large volume as clinker raw material, without requiring any pre-treatment like washing [35]. Chlorine contained in incinerator ash is utilized as a primary mineral component ($C_{11}A_7 \cdot CaCl_2$) in Rapid Hardening Ecocement. The rapid hardening properties of the cement are provided by the high hydration reactivity of $C_{11}A_7 \cdot CaCl_2$. Ordinary Ecocement was developed on the basis of the manufacturing know-how of rapid hardening Ecocement, adjusting volatile-element contents and removal of chloride ions in the manufacturing process. Ordinary Ecocement consists of similar mineral components to OPC. Table 5 [23] shows an example of mix proportions of raw materials of Ordinary Ecocement. Although mineral compositions are similar, limestone content in Ordinary Ecocement is lower than that in OPC by about 26% as shown in Table 5 due to the presence of CaO in municipal waste incinerator ash.

Dioxins brought in raw material with incinerator ash are completely decomposed at above 800°C. Kiln exhaust gas needs to be cooled rapidly to below 250°C to prevent re-formation of dioxins. Heavy metals brought in with incinerator ash can be removed as chlorides in the process of volatilization and removal of chloride ions during the manufacturing of Ecocement. These heavy metals from chloride-containing dust are recovered by attached equipment (HMX) [36] and reused at a refinery, leaving no waste from this process. Since aggregation of chloride can lead to clogging and blockage of a cyclone, raw material of Ecocement is fed directly into a rotary kiln, without using a suspension preheater (Fig.4). This difference in processes results in a larger heat demand of the Ecocement manufacturing. As a result, despite the low limestone content in raw materials, CO_2 production per ton of Ecocement is almost equal to that of OPC [37]. It is expected that combination use of some other desalting technique will enable more effective energy conservation and CO_2 emission reduction in the production of Ecocement by allowing using more energy efficient manufacturing process.

Due to higher contents of Al_2O_3 in municipal waste incinerator ash than those in clay, C_3A content in the

Ordinary Ecocement clinker is slightly higher than that in OPC as shown in Table 6 [23]. Ordinary Ecocement which satisfies the JIS requirements for OPC, except for its slightly higher SO_3 content (about 3.5%) and presence of chloride ions (about 500 ppm), has a wide range of applications [38]. Actual quality values of Ordinary Ecocement are equivalent to those of the 42.5 N/mm^2 class specified in EN197-1:2000, proving its adequate performance as general purpose cement that satisfies the international standard requirements. The high C_3A clinker which is the base material of Ordinary Ecocement not only enables large quantity use of the waste-derived alternative raw materials in its production, but it also reportedly achieves reduction of porosity and densification of microstructure through generation of carboaluminate hydrates in reaction with limestone powder of additives, contributing to enhanced strength development [39]. Some recent research focuses on this reaction to use the high C_3A clinker as base material of limestone filler cement with SCM [40]. Well-balanced design can be established by using such cements, achieving both effective use of waste as clinker raw materials and reduction in cement-related CO_2 emissions. Further verification will be made to put it into practical use in future. The reaction between C_3A and $CaCO_3$ will be treated in more detail in 3.1

Ecocement is defined as a cement using 500 kg or more of waste per ton of production (JIS R 5214:2009). The amount of waste actually used in the manufacturing of Ordinary Ecocement is usually more than 600 kg/t-cement which is very much larger than that used for OPC. Ecocement also provides a new business model of cement where small-scale production less than one tenth the conventional system is established in suburban locations with a good balance between waste disposal cost and manufacturing cost. This presents an example of how future cement manufacturing could be. To make an Ecocement plant commercially feasible, more than 50,000 tons of municipal waste incinerator ash must be available annually in its vicinity [41]. A Ecocement plant operated in Nishitama, Tokyo, is capable of accepting about 94,000 tons of municipal waste incinerator ash which was equivalent to waste from a population of about 3,800,000 and is manufacturing about 130,000 tons of Ordinary Ecocement annually.

2.5 Belite-melilite clinker – a modified Portland clinker or a novel class of SCM?

Although coal ash and sewage sludge ash can be used as alternative to clay in Portland cement clinker raw materials, they tend to be higher in Al_2O_3 content and lower in SiO_2 content compared to natural clay. If they are used to manufacture Portland cement clinker, the resulting clinker will have an unusually high C_3A content, increasing its potential for problems both at early ages (for example, poor concrete rheology) and at later ages (for example, reduced sulfate resistance). Such cements also fall outside the existing norms in many countries. There are two rather different ways of tackling this problem. The first requires that the excess Al_2O_3 content be rendered effectively inert at early ages. This approach is dealt with in this section. The second approach is to try and take full advantage of the excess Al_2O_3 content of the alternative raw materials to make cements which can use this Al_2O_3 more effectively to generate strength. The latter approach will be treated in section 3.3 of this paper.

To counter the increase of Al_2O_3 in clinker resulting from the use of alternative raw materials, new clinkers are being developed in which the Al_2O_3 is fixed in melilite. Early reports claimed that melilite could provide densification of the concrete microstructure through carbonation, thereby contributing to strength enhancement at later ages [42][43], but carbonation hardening, which will be treated in more detail in section (3), is not equivalent to hydraulic hardening. More recently, belite-melilite clinkers obtained by burning asbestos-containing slate boards have been shown to be effective as an SCM which can be substituted for up to 20% OPC clinker without causing problems in cement quality [44]. Another study investigates synthesis and evaluation of belite-melilite cement made using lignite fly ash as raw material [45]. That experimental study tested various mineral compositions in the specimens, finding all of them inferior to OPC in strength development. On the other hand, another report argues that strength development equivalent to OPC can be achieved with compositions in a similar range by adding alkali and cooling with water after burning [46].

Belite can coexist with melilite in the system CaO-SiO_2-Al_2O_3 at clinkering temperatures. Kurokawa et al. carried out analyses on belite-melilite clinkers of a wide range of composition manufactured at a commercial plant [47]. As shown in Fig.5, they found that generation of a calcium silicate phase plus melilite was strongly dependent on the C/S ratio in the clinker, and that clinker consisting mainly of belite and melilite could be obtained at a C/S ratio of 1.7 to 1.9. The generation of calcium aluminates increased at C/S ratios of over 1.9, but it was successfully suppressed by increasing Fe_2O_3. As shown in Fig.6, mixing belite-melilite cement with OPC at a ratio of 20% or below provided strength development of the 52.5 N/mm^2 class, and mixing belite-melilite cement at a ratio of 30% or below provided strength development of the 42.5 N/mm^2 class. At a belite-melilite cement mix ratio of below 30%, strength equivalent to OPC was obtained after moist curing for about one year.

As mentioned before, the reactivity of belite-melilite cement can be improved by the addition of certain minor elements. Kurokawa et al. reported that increasing P_2O_5 content in belite-melilite clinker resulted in activated belite and enhanced strength especially after the age of 91 days[47]. The other finding was the concentration of P_2O_5 in belite which was thought to have contributed to the improved strength development of belite-melilite cement. It was also found that strength development equivalent to OPC could be obtained even with belite-melilite cement mixed at 10% in base OPC which had a Blaine specific surface area about 300 cm^2/g larger than that of OPC. This technique is reported to increase the amount of waste per ton of cement as raw materials by about 30 kg [48]. The amount of limestone used per ton of cement is thus expected to decrease by a similar amount.

Since Al_2O_3 in belite-melilite clinker is mostly fixed in melilite, reduced fluidity and other problems of cement quality are reduced even with an increase in the Al_2O_3 content of clinker raw materials. These clinkers can be made in conventional cement kilns, and the absence of alite permits a burning zone temperature about 150°C lower than for OPC [49], which is expected to save energy.

2.6 Portland clinkers burned at low temperatures by the use of mineralizers

Some of the minor elements derived from alternative fuels and raw materials as described in 2.1 can help lower clinker burning temperatures. For example, fluorine contained in sludge acts as a mineralizer and thus lowers clinker burning temperature. On the other hand, an increase in fluorine content in clinker was thought to cause delays in setting, decreases in early strengths and other quality problems in the cement [50][51]. It was found in the 1970s that this issue could be solved by combinations of fluorine compounds with sulfates, and many related papers were published during 1980s. Practical applications using existing kilns have been reported since 1990. Effect clinker burning temperature reductions in actual kilns has been demonstrated by Aalborg Portland. Using a semi-dry two-stage NSP ("new suspension preheater") kiln with a daily output of 5,000 tons, burning temperature was successfully lowered from 1500°C to 1350°C, with heat consumption reduced by about 3% [52]. As described later, a recent study investigates the addition of mineralizer as a technique for energy saving cement manufacturing [40]. It is reported that clinkers using mineralizer tend to be pulverized or powdered due to the decreased viscosity of liquid phase or similar causes. Also, the nodule sizes of C_2S rich clinker (low heat Portland cement clinker) tend to be smaller mainly because of lack of liquid phase. A study is being made on a technique for accurate burning point measurement under such conditions by measuring the spectrum inside the kiln [40]. There is also a study for estimation and control of clinker nodule sizes which are known to have an influence on the cooling efficiency at the cooler, based on the contents and viscosity values of liquid phase components.

Although many minor elements have been reported to have potential as mineralizer or fluxing agent [53], other mineralizers than F and SO_3 are not likely to have been put in actual use. Fluorine is available cheaply in some natural raw materials and also in industrial wastes, while sulfur is available cheaply in high-SO_3 petroleum cokes. However, Helmy et al. reported that use of granulated slag as alternative raw material of clinker showed significant effect as mineralizer [54]. This suggests that not only minor elements but also types of raw materials (degree of crystallization) influence the burnability of clinker.

2.7 Evaluation of heat consumption of several new cement clinkers

In relation to the low temperature burned clinker described in 3.3, it has been pointed out that ratio of heat consumption reduction with the decrease in burning temperature should be evaluated with not only the rotary kiln but the whole cement manufacturing process taken into account in calculation[55]. Suemasu et al. developed a new simulator based on a rotary kiln simulator KilnSimu by expanding the range of calculation to include the processes of raw material preheating, clinker burning and cooling so that the whole clinker manufacturing process could be taken into account [56]. They further enhanced the simulator capable of more precise reproduction of the phenomena inside an actual kiln by coupling the thermal fluid analysis program Fluent. These studies related to the use of mineralizer for energy saving cement manufacturing are conducted as a project by the Ministry of Economy, Trade and Industry (METI) of Japan [40].

Table 7 shows quantitative evaluation of heat consumption of some of the new clinkers described in this Chapter. In this evaluation, the heat consumptions were calculated on the assumption that cements were produced in a conventional kiln. Little heat reduction effect was found when C_3A content was increased by 4% from a conventional level. However, 7.6% reduction was expected in heat consumption with F = 0.2% and SO_3 = 4.0% as mineralizers. Belite sulfo-aluminate cements with 40% and 60% of ye'elimite were estimated to provide reduction of 21.1% and 24.8%, respectively, in heat consumption. When raw materials contain volatile components such as F and SO_3, attention needs to be paid to the influence of the increased amount of sulfur circulating within the kiln which causes increased sulfate deposits on the walls and affects stable operation of the kiln. The difference in performance between a new clinker and OPC is likely to be larger as the difference in their chemical compositions is larger. In investigating practical application of new materials, due consideration should be given not only to CO_2 emissions and heat consumption but also to stable operation of the manufacturing process and performance of the products.

3. What can be done to make even more carbon-efficient hydraulic binders?

3.1 How might we increase the efficiency of Portland-SCM combinations?

Optimization of the replacement of Portland clinker with SCMs involves four main scientific issues:

(i) How do the properties of the hardened binder depend on its composition and microstructure?

(ii) What should the ideal proportions be, from a thermodynamic (equilibrium) viewpoint?

(iii) How might these proportions be modified in practice by reaction rate (kinetic) issues?

(iv) How might these proportions be modified in practice by fresh concrete placement issues?

Clearly, the above questions cannot be completely separated, as all of the issues become intertwined in practice. But they must all be answered to some extent in order to provide the industry with a set of effective rules to help it design optimal or near optimal binder compositions in order to minimize carbon footprint (and/or other parameters, such as unit cost,) when using a given basis set of locally-available raw materials.

Considering that most applications of hydraulic binders are predicated on achieving the desired long-term mechanical properties, (e.g. compressive strength of concrete after curing, etc.,) it seems important to deal with issue (i) in the above list first. For many decades, the relationship between mechanical strength and hydrated cement composition for Portland cement based concretes has been treated reasonably well by Powers' "gel-space ratio" (GSR) approach [57], in which it is assumed that the combined hydration products of a Portland cement can be considered to be a homogeneous "gel" which fills the "capillary" spaces between the residual anhydrous cement grains and other non-reacting solid particles (fillers or aggregates) that may be present after hydration for any given time. In this case, the GSR value is the fraction obtained by dividing the total volume of all the cement hydrates (V_h) by the sum of itself plus the total residual "capillary" space, $Ø_{cap}$, between all unreacted solid particles, (including aggregates, fillers, and unreacted cores of partly hydrated cement particles):

$$GSR = V_h/(V_h + Ø_{cap})$$

Powers' observed that the compressive strengths of hydrated Portland cement-based pastes, mortars or concretes varied in proportion to $(GSR)^x$, where x is a positive exponent. Only two constants are required in this relationship: the value of x, and the (hypothetical maximum) strength at GSR=1.

However, it is found that different calibration constants are required for this relationship for cements that are somewhat different to conventional Portland cements. This complicates the use of GSR to predict strengths, especially for modern complex binder systems incorporating significant fractions of SCMs. But it has recently been shown [58] that the general form of this relationship can still be used if the volumes and roles of the various hydrates are correctly taken into account. By means of a homogenization approach (explained in detail in ref. [59]) it was shown that, for hydrated binder systems containing major volume fractions of C-S-H, the best correlations with strength can be obtained by treating the C-S-H plus the porosity as a continuous, percolating porous binder phase, or “foam,” while all of the other solid phases, including all of the observed crystalline hydrates (e.g. portlandite, ettringite, AFm phases, etc.,) and also anhydrous phases (residual unhydrated clinker, calcium carbonates, and other unreactive phases found in fillers or aggregates,) can be treated as simply as solid inclusions dispersed in this “C-S-H foam.” What this means is that C-S-H tends to be the most finely-divided solid phase in the microstructure, and the porosity is effectively “well-mixed” with the C-S-H. So a porous C-S-H phase (“foam”) percolates the spaces between the other, more crystalline (and thus coarser and also usually stronger) solid phases. This porous C-S-H foam is essentially the glue that holds everything together; but it is also the weakest link in the system, from a mechanical viewpoint, which is why it dominates the relationship used to calculate the strength. It is, however, very important to note that this type of relationship does not imply that the crystalline hydrates do not contribute to strength. Their contribution is all the more important to the extent that they increase the hydrated solid volume by binding large amounts of water. It is just that they appear in the GSR in a different place than the C-S-H, because they serve to reduce the residual capillary porosity, $Ø_{cap}$.

Although this new GSR approach is not yet fully validated for all of the binder systems of potential interest here, and especially for systems with very low Portland clinker contents in which the binding matrix itself may be very different from that found in ordinary Portland cement pastes, it nevertheless opens up the possibility that one may, in the near future, be able to make fairly accurate predictions of the compressive strength (as a function of degree of hydration and initial water/binder ratio) for Portland-cement binders with a very wide range of SCM types and clinker replacement levels.

The second issue to deal with is the question of the "ideal" phase assemblage. From a durability viewpoint, we would like the hardened cement paste to comprise only stable phases over the whole range of environmental conditions to which we expect the final product (concrete) to be exposed. There is a reasonably complete thermodynamic data base covering the main hydrates in the system CaO-SiO_2-Al_2O_3-Fe_2O_3-SO_3-H_2O at temperatures of 0-60°C [60], and the chemical effects of the main secondary components that we usually encounter, (MgO, Na_2O, K_2O, CO_2,) are also reasonably well understood. However, the issue of true thermodynamic stability remains a difficult one, because several apparently metastable phases seem to persist indefinitely in practice. For example, the amorphous C-S-H phase, which is the dominant hydrate phase in Portland-based binder systems, is theoretically metastable with respect to a mixture of crystalline tobermorite and portlandite over the temperature range of interest. So, in thermodynamic calculations, formation of tobermorite must be specifically forbidden in order to get realistic predictions. Part of the problem may be related to the fact that Al_2O_3 has significant solubility in C-S-H, so the true amorphous percolating hydrate is actually C-S(A)-H; but full thermodynamic data on this solid solution are not yet available. The distribution of Al between the major phases is also apparently subject to strong kinetic limitations, because in many Portland-based cement systems certain members of the large range of possible hydrogarnet solid solution phases {of general composition $C_3(A_{(1-x)}F_x)(S_yH_{(6-2y)})$} appear to be thermodynamically stable over a wide range of temperatures, but in practice they do not form to any great extent, so they too must be artificially excluded from the calculations. But both hydrogarnets and tobermorites form far more readily in cements cured at temperatures well above 60°C, so it appears that crystal growth kinetics is a very important but still poorly understood factor in Portland-SCM systems.

Regarding crystalline aluminate hydrates, the amount of water bound in solid form per mole of Al_2O_3 varies very widely amongst the possible products, being highest in ettringite (H/A = 32), intermediate in AFm phases (H/A = 11-19), and low in hydrated alumina and hydrogarnet phases (H/A ≤ 3). Thus, from the viewpoint of converting liquid water into space-filling solid phases, and thereby increasing GSR, the formation of ettringite would appear to be the most efficient way to use the aluminium in the binder. In hydrating Portland-based cement systems at normal exposure temperatures, ettringite is stable relative to aluminate phases with lower H/A ratios as long as sufficient soluble calcium sulfate is still available. In practice, however, we are unable to take advantage of this fact for kinetic reasons. This is because the addition of the amount of (calcium) sulfate needed to convert all of the aluminium to ettringite (i.e. to give a Š/A molar ratio of 3 in the binder) results in strongly retarded hydration of the aluminate phases (C_3A and C_4AF) in Portland clinker, with the result that most of the ettringite forms very slowly over a long period of time, well after a rigid skeleton is formed with C-S-H as the main binder; and this slow ettringite formation is usually expansive and often leads to strength loss (which we refer to here as the "ettringite formation problem.") Thus, all norms for Portland-based cements contain tight limits on sulfate content in order to protect users from this problem; but this comes at the expense of a rather inefficient use of sulfates and the aluminate phases in such binders. This is all the more true in cases where a significant fraction of the aluminate is contained in SCMs, (as it often is,) since the sulfate limits on such cements have been developed for Portland cements with fairly low total aluminate contents; and also because the aluminate in the SCMs itself also reacts too slowly and thus cannot be used to make more useful (strength-giving) ettringite – another manifestation of the ettringite formation problem.

The realization that the aluminates are not being used to their greatest potential in modern blended Portland cement binders has, over recent years, forced a rethinking of our approach to reducing the carbon footprint of hydraulic cements. One approach has been to redesign clinker compositions to try and avoid the ettringite formation problem. This approach was initially inspired by the observation that one well-known class of calcium aluminosilicates-based binders - supersulfated blast-furnace slag cements - manages to avoid the problem of expansive ettringite formation. Such cements contain essentially all of their aluminate intimately mixed with silicate and calcium oxide in the ground granulated slag - a uniform glassy anhydrous phase with relatively low C/(A+S) and high A/S ratios compared to those of Portland clinker. It is observed that supersulfated cements can be hydrated together with sufficient calcium sulfate to give ettringite plus a relatively low-lime amorphous C-S-H as the two main hydrate phases, and such cements show no problem of either slow expansion or strength loss. This may be due to the simultaneous formation of ettringite and C-S-H throughout the hydration process and/or the lower ettringite supersaturation produced by slag-gypsum mixtures. However, such binders have at least two practical disadvantages: (1) they gain strength relatively slowly; and (2) suitable granulated slags, available as industrial by-products and thus having a relatively low carbon footprint, are currently in high demand for other applications, typically as SCMs in more standard blended Portland-cement based binders. Unfortunately, the direct manufacture of calcium aluminosilicate glasses similar in composition to granulated blast-furnace slags would be prohibitively expensive because of the need to use a melting furnace, and the resulting product would have a far higher carbon footprint than ordinary Portland cement, so this is not a good solution. However, these observations led to renewed interest in clinkers comprising ye'elimite ($C_4A_3\check{S}$) as the main reactive aluminate phase, as it was thought that they potentially offered a more kinetically-efficient route to the formation of an ettringite/C-S-H binder [61]. This subject will be dealt with in more detail in section 3.4.

Instead of considering making alternative clinkers which can use sulfates more effectively, an easier approach, especially from the normalization viewpoint, is to find ways of increasing the overall H/A ratio of Portland-SCM-based binders while keeping the total sulfate content low. Recent work in this area has focused on the fact that carbonate-AFm phases are very stable and can be formed readily and inexpensively by the introduction of finely-ground limestone into the cement. Formation of these phases avoids the decomposition of ettringite once all of the available calcium sulfate has been consumed, and thus allows, on average, a higher bound water content per unit of clinker. This is demonstrated by the following simplified comparison, which assumes a fairly typical sulfate content in the cement ($\check{S}/A = 0.6$), and ignores any uptake of alumina by solid solution in the C-S-H phase. It also treats all of the aluminate as being present as C_3A, whereas some will actually be contained in C_4AF; but that aluminate also reacts in a very similar manner.

A) Hydration of C_3A with 0.6 moles of gypsum and lime to give typical AFm phases:

$$C_3A + 0.6\,C\check{S}H_2 + 0.4\,CH + 10.8\,H \Rightarrow 0.6\,C_4A\check{S}H_{12} + 0.4\,C_4AH_{13}$$

$$270 + 103 + 30 + 194 \Rightarrow 373 + 224 \quad \text{(g/mol)}$$

$$89 + 45 + 13.2 + 194 \Rightarrow 185.4 + 109.6 \quad \text{(ml/mol)}$$

Solid volume ratio (hydrates/cement) = 2.00

B) Hydration of C_3A with 0.6 moles of gypsum plus excess calcite:

$$C_3A + 0.6\,C\check{S}H_2 + 0.8\,C\check{C} + 14\,H \Rightarrow 0.2\,C_6A\check{S}_3H_{32} + 0.8\,C_4A\check{C}H_{11}$$

$$270 + 103 + 80 + 252 \Rightarrow 251 + 454 \quad \text{(g/mol)}$$

$$89 + 45 + 29.6 + 252 \Rightarrow 141.4 + 209.6 \quad \text{(ml/mol)}$$

Solid volume ratio (hydrates/cement) = 2.15

One can see that addition of excess limestone leads to a higher bound water content per unit cement, which results in a higher volume of solid products. It also avoids the consumption of lime to produce hydroxyaluminate AFm phase (usually found as a solid solution with monosulfoaluminate), leaving more lime available for the pozzolanic reaction. But this is just the baseline case, in the absence of SCM additions to the cement. In the presence of pozzolans or slags containing reactive alumina (as well as reactive silica), much of the reactive alumina from the pozzolanic reaction will end up in AFm phases, (although some will also end up in the C-S-H). However, if this reactive alumina (“A”) is not balanced by a suitable amount of reactive calcium carbonate, the presence of this excess alumina plus excess lime will lead to the conversion of ettringite to monosulfoaluminate, with significant loss of hydrate volume:

C) Hydration of reactive alumina with portlandite plus ettringite to give monosulphoaluminate:

$$C_6A\check{S}_3H_{32} + 6\,CH + 2\,\text{“A”} \Rightarrow 3\,C_4A\check{S}H_{12} + 2H$$

$$1254 + 444 + 204 \Rightarrow 1866 + 36 \quad \text{(g/mol)}$$

$$707 + 198 + 52 \Rightarrow 927 + 36 \quad \text{(ml/mol)}$$

Solid volume increase (products - reactants) = -30 ml/mol = -15 ml/mol of “A”

D) Hydration of reactive alumina with portlandite plus calcite to give monocarboaluminate:

$$C\check{C} + 3\,CH + \text{“A”} + 8H \Rightarrow C_4A\check{C}H_{11}$$

$$100 + 222 + 102 + 144 \Rightarrow 568 \quad \text{(g/mol)}$$

$$37 + 99 + 26 + 144 \Rightarrow 262 \quad \text{(ml/mol)}$$

Solid volume increase (products - reactants) = +100 ml/mol of “A”

(Note: the molar volume used for “A” in the above two equations is that of corundum. Its value in actual raw materials will be different, but that will not change the results of the comparison, which are relative).

The above equations show that it is preferable to have an excess of reactive calcium carbonate present whenever reactive alumina is available from any source (e.g. a pozzolan or a slag) to react with excess lime in the cement paste. If insufficient calcium carbonate is available and reaction (C) occurs instead of reaction (D), one loses about 115 ml of solid phase per mol of A reacted, which is a significant loss, although the maximum loss would be limited by the total (potential) amount of ettringite present in the paste. Note also that we have shown the reactions as giving monocarboaluminate AFm phase, but, in fact, the hemicarboaluminate AFm phase, $C_8A_2\check{C}H_{24}$, is similarly stable and can produce the same type of effect with only half the amount of calcium carbonate. In volume terms, the hemicarboaluminate is actually preferable, as it has a greater volume per mol of "A" than the monocarboaluminate. But, since calcium carbonate fillers are usually very cheap and also help to accelerate early-age alite hydration by providing nucleation sites for C-S-H growth, it is usually preferable to have an appreciable excess of calcium carbonate in the system just to be sure that reactions (B) and (D) predominate. In such cases hemicarboaluminate forms first but is ultimately replaced by monocarboaluminate as more calcite reacts.

3.2 Portland-based binder systems with greatly-increased SCM contents

Recent developments in composite Portland cement technology reflect the above theoretical analysis. The application of this theory to explain the observed synergetic effect of adding limestone as well as reactive alumina was first clearly demonstrated in a thorough study of Portland-slag-limestone blended cements by Hoshino et al [62] in 2006, but it took some time before others investigated it seriously in systems containing low-lime SCMs such as fly ashes and calcined clays. A family of patent applications starting in 2009 and assigned to Aalborg cement [63] claims blended cements based on Portland cement with additions of both mineral carbonates (e.g. ground limestone) and calcined clays, and highlights the synergies of the coupled addition. It was shown that, for a 35% level of clinker replacement, maximal 28-day strengths were typically obtained from blends in which from about one half to about three quarters of the total SCM addition was in the form of a calcined clay, the rest being in the form of ground limestone. De Weerdt et al. [64][65] demonstrated that this approach could be used to optimize blended cements with coupled fly ash and limestone substitution, while Moesgaard et al. [66] showed that the same approach could be used to good effect when an artificial lime-alumina-silica glass was used instead of fly ash. More recently, Antoni et al. [67] showed that the same approach could be used to permit very high levels (up to 45%) of OPC replacement by using a 2:1 blend of metakaolin and limestone, while still obtaining strengths at least as good as those of the control OPC at 7 and 28 days. They also pointed out that even better results could be obtained by slightly increasing the calcium sulfate addition levels in such blends, consistent with the volume-filling theory; but the optimum sulfate level was still quite low, presumably for the reasons discussed earlier.

Although the approach of coupled limestone-alumina source SCM substitution holds great promise for the development of a wider range of Portland-based hydraulic cements with lower carbon footprints, the full industrial exploitation of these advances is likely to be slow because many of the most desirable compositions fall outside existing norms. Thus, a considerable amount of testing will be required to demonstrate that the new compositions are durable and robust enough for practical use. The main durability issue is likely to be the increased carbonation rate arising from the lower lime content and thus lower carbonation buffering capacity of the cement paste, thus reducing its ability to protect mild steel from corrosion. This is an unavoidable consequence of the need to reduce CO_2 emissions by reducing the amount of "carbonatable CaO" (CaO capable of reacting with atmospheric CO_2 after the cement has been hydrated, i.e. in hardened concrete), and it is an issue for essentially all of the low-CO_2 binder systems being proposed. However, with the application of good concrete design for the intended use, good quality control procedures and good workmanship (especially good curing), this should not stop the widespread application of such binders, as there are many applications where carbonation rate is not a durability issue.

Other issues that may also have to be dealt with relate to the stability of the hydrate assemblage over a wide range of temperatures. Reactions (A) – (D) are thermodynamically favored under humid conditions at temperatures typical of standard test procedures, but at significantly higher temperatures the carboaluminate/ettringite couple becomes less stable relative to monosulfoaluminate plus calcite, and formation of (siliceous) hydrogarnets may also become more likely. These effects might have some durability implications, so a considerable amount of careful work is still needed to demonstrate the performance of these new ultra-high SCM replacement binders under the whole range of conditions which may occur in their intended concrete applications. As with any binder system, there are bound to be certain applications to which they are less well-suited than other binder systems, and this will have to be taken into account in future norms.

We have not tried to deal in any general way with the fourth issue listed at the beginning of this section, namely, how blend proportions might be influenced by fresh concrete placement issues. This usually depends strongly on the details of the raw materials used in the blended cement, and also of their particle size distributions. It is, therefore, very complex and very dependent on local issues, and so is not easily dealt with by a theoretical approach. Some common observations are useful, however. Clays calcined at low temperatures (or, even worse, not calcined at all) can significantly increase the water demand of a blended cement. Fly ashes are very variable and so can give either very low or very high water demands depending on circumstances. But ground limestone generally has a lower water demand than OPC unless it happens to contain very significant levels of clay minerals. Thus, combinations of calcined clays and ground limestone are almost always preferable to calcined clays alone in terms of overall water demand, and this can be helpful in keeping the water content of the concrete low. But the control of concrete water content is still an important quality issue which must be dealt with locally.

3.3 Belite-Ye’elimite-Ferrite cements

Belite-rich Portland cements are well known, reasonably well understood, and largely covered by existing cement and concrete standards. However, they are not widely used, primarily due to their low early age strengths, mainly due to the low dissolution rates of belites (compared to alites). In addition, manufacture of belite-rich Portland clinkers results only modest reductions in CO_2 emissions, because (a) the manufacture of belite instead of alite only reduces CO_2 emissions by about 10%, and in any case alite is not usually completely eliminated; and (b) the aluminate is present as C_3A or C_4AF and thus still has a fairly high associated CaO content. But much work has been done over the past few decades, especially in China, to develop "CSA" cements, based on clinkers rich in the calcium sulfoaluminate phase, ye'elimite ($C_4A_3\check{S}$) [68]. Such cements are capable of giving very rapid early strength development because, unlike C_3A and C_4AF hydration, ye'elimite hydration is not strongly retarded by the presence of gypsum, and this allows ettringite + hydrated alumina gel formation to be used to give early strengths:

$$\begin{array}{lcccccccccl} \text{E)} & C_4A_3\check{S} & + & 2\,C\check{S}H_2 & + & 34\,H & \Rightarrow & C_6A\check{S}_3H_{32} & + & 2\,AH_3\textit{(amorphous)} & \\ & 610 & + & 344 & + & 612 & \Rightarrow & 1254 & + & 312 & \text{(g/mol)} \\ & 234 & + & 149 & + & 612 & \Rightarrow & 707 & + & 64 & \text{(ml/mol)} \end{array}$$

Solid volume ratio (hydrates/cement) = 2.01

Due to the moderate liquid phase content during clinkering, the manufacture of CSA-rich clinkers is possible in rotary kiln systems that are essentially the same as used for manufacturing Portland clinkers. This is an advantage, industrially, if one compares CSA cements to their close cousins, calcium aluminate cements (CAC), which usually require melt-processing and thus need a different type of kiln, typically with lower energy-efficiency. But manufacture of both CSA and CAC cements generally requires large fractions of bauxite in the kiln feed, which adds greatly to the cost of the raw materials, and which in turn results in both CSA and CAC being sold only as specialty cements with relatively high prices and thus relatively small market volumes compared to Portland-based cements.

In an attempt to circumvent these disadvantages while still taking advantage of the low-CO_2 emissions of alumina-rich cements, recent studies, mainly in Europe, have focused on systems that are intermediate between “classical” CSA cements and belite-rich Portland cements [69]. Such cements have in the past been referred to by the rather clumsy name of “Belite-Calcium Sulphoaluminate-Ferrite” (BCSAF) cements, but are now preferably referred to as “Belite-Ye’elimite-Ferrite” (BYF) cements. The composition range of such binders is not yet formally defined by any standards, but they can be said to lie at or below the low-CSA end of the range of binders recognized in the Chinese CSA cement norms. More importantly, the major phase (“B”) in BYF clinkers is based on dicalcium silicate: either one or more of the polymorphs of belite, or a mixture of belite(s) and ternesite ($2C_2S\cdot C\check{S}$) [70]. The other two main phases are always ye’elimite (“Y”) and a calcium aluminoferrite solid solution phase (“F”), and the order of phase abundance is B>Y>F. BYF cements generally comprise BYF clinker plus calcium sulfate (e.g. anhydrite or gypsum) plus other ingredients such as SCMs similar to those used with Portland cements. The theoretical advantages of BYF cements were initially proposed based on the following rather idealistic assumptions:

(i) Early-age strengths develop rapidly due to ye’elimite hydration together with added calcium sulfates, giving an initial rigid framework of ettringite + AH_3 “gel”

(ii) Later-age strength development continues due to belite, ternesite and ferrite phase hydration, producing various phases (e.g. stratlingite, monosulfoaluminate, siliceous hydrogarnets and C-S-H) [71]. The key to this later-age strength development is ensuring that the calcium silicate phase(s) hydrate effectively, which can be done by the inclusion of belite activators such as borates [72], or by the presence of ternesite formed at relatively low kiln temperatures [73].

(iii) By choosing an appropriate B:Y:F ratio, the kiln feed required to make BYF clinkers may not need an excessively high fraction of bauxite. Other less expensive sources, such as alumina-rich fly ashes and clays, can provide much of the alumina (and iron) needed.

(iv) Due to their high aluminate and low lime contents, the sulfate contents in BYF cements can be significantly higher than for Portland-based cements without any risk of expansion or strength loss. The extra added calcium sulfate, (which, if available locally, is generally “low-carbon,”) can make an important contribution to strength by forming a stable ettringite framework.

As for Portland cements, however, the kinetics of hydration reactions often limit what can actually be achieved relative to what might be hoped for in theory. Reaction (E) effectively limits the amount of ettringite that can be formed at early ages to an amount equivalent to one third of the aluminate contained in the ye’elimite phase, plus the small fraction of the ferrite phase that reacts at early ages. Much more ettringite could be formed, in theory, if the excess lime contained in the belite phase could be made available to react with the AH_3 formed at early ages; but, in practice, it is found that the presence of the extra calcium sulfate required for this reaction has a negative effect on belite reactivity for reasons that are not yet fully clear [74]. However, the use of ternesite, instead of belite, provides an interesting route to supplying both the extra lime and the extra sulfate at the same time, which may be one reason why the ternesite phase appears to be more reactive than usual when incorporated into BYF cements [75].

The development of BYF cement technology is still at a relatively early stage, and relatively little has yet been published in peer-reviewed scientific journals on the long term mechanical and chemical durability of concretes made from such binders. Initial concrete durability test results from the EU-funded "Aether" project are encouraging [76]. However, many of the potential durability issues facing BYF-based concretes are quite similar to those that face concretes made from Portland-based binders with high SCM replacement levels. Thus, comparisons between the two approaches would be helpful. An initial attempt at this is made in the next section.

3.4 Comparison of high-SCM Portland-based cements with BYF cements as a means of reducing CO_2 emissions and other aspects of the environmental impact of hydraulic binders.

One of the major motivations for the development of ultra-high SCM-substituted Portland-based binders based on OPC/calcined-clay/limestone blends was the observation that conventional (natural or by-product) SCMs of adequate quality for use with Portland cements are already in short supply in many places, and are not likely, in the long term, to be available in anything like the quantities required to have a major impact on the cement and concrete industry's global specific CO_2 emissions [67]. This is essentially the same motivation that initially led to the development of BYF-type binders [61]. Both approaches are based on the assumption that the most abundant raw materials suitable for making hydraulic binders will remain calcium carbonates and aluminosilicates such as clay minerals, but that it is possible to reduce the calcium content of the hardened binder significantly and still get adequate strength development rates if one changes the cement chemistry appropriately. In fact, the main difference between the two approaches is related to the pyroprocessing step. For making BYF clinkers, a mixture of limestone plus an alumina-rich clay (ideally, kaolinite) can be burned together in a rotary kiln to make a clinker containing all of the reactive phases needed in the final cement apart from the calcium sulfate (either additional calcium sulfate must be added with the kiln feed, or a sulfur-rich kiln fuel must be used). Limestone fillers can also be added to the BYF cement if desired, and carboaluminate phases will in theory form similarly to those formed in the Portland-SCM binders; but this is less necessary than with OPC because significantly higher sulfate contents can be used in BYF binders. On the other hand, the ultra-high SCM-based binders require an alumina-rich clay (again, ideally, kaolinite) to be calcined in a separate kiln at low temperatures and then blended or inter-ground with a conventional Portland cement, together with finely-ground limestone, (typically at a mass ratio of about 2 parts metakaolin to limestone). The similarity of the two approaches in terms of overall cement composition is shown in Table 8 for a simplified system containing only the five major oxides. It can be seen that a BYF clinker, (assumed to contain only its three major phases) is, in this case, equivalent, in terms of its content of the five major oxide components, to a mixture of an OPC with metakaolin, in this case only at a 14% replacement level.

Note that the 14% replacement level of metakaolin shown here is not necessarily unrealistic when one considers that it has been assumed that well under half of the added “metakaolin” in a 55:30:15 OPC:MK:limestone blend will react by 90 days [67]. The remainder of the calcined clay will presumably behave as an inert filler. Note also that the addition of limestone (especially for the OPC/calcined clay binder) or of extra calcium sulfate (especially for the BYF binder) is not included in the table, but in both cases will allow the clinker phases to be further diluted while at the same time producing useful volumes of hydrates.

The above results serve to show that one can obtain either a blended OPC/MK cement or a BYF cement with effectively the same elemental composition, i.e. effectively starting from the same raw materials in the same proportions. This tells us immediately that the CO_2 emissions associated with decarbonation of limestone will be the same in both cases; and we know that this decarbonation reaction also accounts for the major part of the enthalpy of clinker formation. Thus, the only real differences in terms of cement manufacturing process will be the need to calcine the clay in a separate kiln (for the OPC/MK approach), and to add it to the cement during grinding. It is thus likely that the overall energy efficiencies will also be similar for both approaches. The main difference is more likely to be one of practical convenience. Making BYF clinker requires very careful control of kiln feed composition and kiln operating conditions, whereas the OPC/MK approach allows the use of a standard OPC of the type that is already in production and thus very easy to obtain. So the OPC/MK approach is far easier to adopt in the short term. One disadvantage, however, is that the OPC/MK approach requires that a suitable kaolinite-rich clay deposit be available for calcining, whereas the BYF clinker approach broadens the range of raw materials that can in principle be used to make the clinker to include other aluminium-rich industrial wastes, as discussed in section 2 of this paper. Thus, the choice of approach is likely to depend on circumstances such as the local availability of suitable kilns and of suitable raw materials.

They calculation in Table 8 also serves to show that one may well arrive at fairly similar final equilibrium hydrate phase assemblages by using either the OPC/calcined clay approach with high levels of clinker replacement (e.g. with limestone additions), or the BYF clinker approach, (which can also potentially be combined with the addition of conventional SCMs or limestone). This observation is important because it suggests that the long-term durability issues for both approaches may well be very similar.

3.5 Carbonation-hardening systems based on calcium silicates

Carbonation hardening of lime (in air) has been used for many centuries, and carbonation-assisted curing of Portland cement concrete (often using flue gases as a source of heat, humidity and CO_2) is well known and practiced to varying degrees in precast concrete manufacture. The concept of accelerated hardening of various calcium silicates, both hydraulic and non-hydraulic, by carbonation in an atmosphere artificially enriched in CO_2 is certainly not new, as was pointed out by Bukowski and Berger in 1979 [77]. However, it has not, to date, become a commercially viable approach to the production of concrete products. But this situation may change if political pressures to reduce the concrete industry's carbon footprint increase, or if technical improvements lead to better and more commercially attractive performance attributes.

There is some reason to believe that this is now the case with the technology being developed by Solidia, a US-based start-up company that was originally based on the research of Riman and Atakan at Rutgers University, New Jersey, USA [78]. Solidia's current approach is described in a recent paper [79]. It involves the use of an essentially non-hydraulic binder based primarily on wollastonite or pseudo-wollastonite ($CaSiO_3$). Clinkers close to this composition can be manufactured in conventional cement kilns, requiring significantly less energy and giving a significantly lower carbon footprint than the manufacture of Portland cement clinker: the reduction in CO_2 emissions can be as great as 30%. Clinkering temperatures can be as low as 1200°C, which may make it easier to use increased amounts of alternative fuels with relatively low heating values; and the clinkers can also be easier to grind than typical Portland clinkers. The CO_2-curing process is a counter-diffusion process in which CO_2 gas replaces water inside the pores of the concrete and reacts with the anhydrous calcium silicate phases to produce calcium carbonate and silica. Curing is typically done at atmospheric pressure in a sealed chamber with gas circulation, using CO_2 concentrations of 60-90% and a temperature of about 60°C, but the carbonation reaction is itself highly exothermic, and is thus capable of providing most if not all of the latent heat required to evaporate the water from the pore system and maintain the concrete at the desired temperature. By means of an appropriate control system the conditions in the curing chamber can be maintained at the optimal values for rapid carbonation, which can give full curing in a few hours to a day or so, depending on sample size and geometry. A typical concrete made with 16 mass% Solidia binder will sequester CO_2

equivalent to about 5% of its total mass, i.e. for every tonne of Solidia binder used, the amount of CO_2 consumed by the concrete will be about 300 kg.

The mechanical properties of concrete products made from Solidia Cement are reportedly similar to those of Portland cement concrete products [80], but the chemical properties are clearly different, the pH of the residual pore solution falling to well below 10 after carbonation [81]. This implies that Solidia concretes will not directly protect mild steel from corrosion; but they could either be used without reinforcement, or else with other forms of reinforcement, e.g. galvanized steel, or glass fibers, or polymer fibers, that perform well at moderate pH values. The final binder phase assemblage of well-carbonated (fully-hardened) Solidia cement pastes consists primarily of calcium carbonate (usually mainly present as calcite) plus a silica-rich amorphous phase which usually contains some calcium, and which may be considered to be either amorphous silica containing adsorbed Ca, or else a low-lime form of C-S-H [77]. Its microstructure is also very different to that of hardened Portland cements. A recent microstructural study of carbonated wollastonite pastes [82] showed them to contain two principal classes of porosity: micropores, below about 2nm in diameter, which only empty at relative humidities below about 40%; and capillary pores, mostly well above 10nm in diameter, most of which are already empty at relative humidities below about 95%. These results can be explained by a microstructure in which the original grains of wollastonite are replaced by relict grains of porous amorphous silica (or low-lime C-S-H), while the $CaCO_3$ formed from the calcium leached out of the original grains deposits around them in the original capillary spaces, bonding together the relict-grains in a matrix of finely-crystalline calcium carbonate, as shown diagrammatically in Fig. 7. It appears that the calcium carbonate phase is the percolating phase responsible for the mechanical cohesion of the hardened paste, and this phase slowly fills the large inter-granular capillary pores during carbonation. However, even with wollastonite pastes made at an initial water/solid mass ratio as low as 0.2, the residual porosity after a high degree of carbonation was still above 20% by volume, of which over 80% was in the form of large capillaries empty below 95% RH [82]. Thus, it appears that further carbonation curing should still be possible under these conditions, as there is a percolating network of large capillaries that should allow fairly rapid exchange of water vapor and CO_2 between the inside of the hardened specimen and the external curing atmosphere.

A generalized reaction pathway for the water-catalyzed carbonation of alkaline-earth silicate minerals was represented diagrammatically by Gartner et al. [83], as shown in Fig. 8. It is known that direct carbonation in the absence of water is extremely slow at temperatures below several hundred °C, so only water-catalyzed carbonation need be considered for Solidia-type binders. The main steps in the process are believed to be:

(i) Dissolution of the alkaline earth silicate in "liquid" water (even though this water may only be present as a thin film on the surfaces of the solid phases present; and thus the species dissolved in it may have reduced mobility compared their mobility into bulk liquid water).

(ii) Dissolution of CO_2 gas in the same aqueous phase.

(iii) Slow hydrolysis of dissolved CO_2 to give dissolved carbonic acid, followed by its rapid dissociation into solvated ions: $H_2CO_3(aq.) \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^=$

(iv) Transport of dissolved species from their “source phase” to their “sink phase” by diffusion processes in the aqueous phase (arrows in Fig. 8 indicate net fluxes).

(v) Growth of alkaline earth carbonates, which may be either hydrated or anhydrous, and either amorphous or crystalline.

(vi) Growth of silica, (or, possibly, silica-rich intermediate phases), which are usually amorphous but may be either hydrated or anhydrous.

The microstructure resulting from this type of process will be strongly influenced by the relative solubilities of the reacting phases in the aqueous phase. Typically, we would expect the aqueous phase to have a fairly low pH due to the presence of carbonic acid, and thus to be a rather poor solvent for silica but a much better solvent for the alkaline earth carbonate (which is effectively dissolved as a bicarbonate). Thus, we would expect the silica-rich product to precipitate closer to the uncarbonated mineral silicate phase than the carbonate-rich product; and this is consistent with the microstructural observations. It also suggests that, in order for carbonation to continue at an appreciable rate, the pores in the silica-rich product must maintain a significant content of aqueous phase in order for them to continue to transport alkaline-earth metal ions towards the more CO_2-rich zone where the alkaline-earth carbonate precipitates. Thus, while carbonation continues, there will always be a certain concentration of alkaline-earth ions in the process of traversing the silica-rich phase, some of which may be adsorbed on its surfaces. It is also conceivable that an intermediate phase, such as a calcium silicate hydrate phase, could precipitate first, in which case it would be expected to occupy a zone between the alkaline earth silicate and the silica-rich precipitate; but there is apparently no indication of this in the recent study on wollastonite carbonation [80].

There is as yet little data available on the durability of Solidia concretes, although "chemical common sense" dictates that they should not be susceptible to alkali-aggregate reactions or sulfate attack. An initial study of the freeze-thaw and salt-scaling resistance of air-entrained Solidia concretes has shown results that are comparable with or better than those of air-entrained Portland cement-based concretes with a moderate level (20%) of fly-ash replacement [84].

3.6 Hydraulic cements based on magnesium silicate raw materials

From the viewpoint of reducing global carbon dioxide emissions, magnesium silicates hold out a tantalizing promise. They constitute enormous reserves of highly basic raw materials theoretically capable of capturing CO_2 in stable solid form as magnesium carbonate. Global reserves of ultra-basic magnesium silicate minerals are more than sufficient to capture all anthropogenic CO_2 emissions for the foreseeable future [85]. These minerals are close to the composition of the Earth's upper mantle, i.e. close to M_2S (di-magnesium orthosilicate, which crystallizes as olivine) with about one in ten magnesium (Mg^{++}) ions being replaced by a ferrous ion (Fe^{++}). At the surface, deposits of rocks derived from these magnesium silicates (peridotites) tend to become partly hydrated, leached and oxidized, producing mainly magnesium serpentine ($M_3S_2H_2$). This is because forsterite (magnesium olivine, M_2S,) the magnesium equivalent of belite, is relatively reactive with water compared to most minerals found in igneous rocks. However, it is still nowhere near reactive enough to be directly useful in hydraulic binders or even in carbonatable binders, nor indeed in direct CO_2 capture from industrial flue gases. Olivines are very hard minerals (Mohs 6.5-7) and thus require a lot of energy to grind, especially to the very high finesses that would be required to overcome their low reactivity at ambient temperatures and pressures. In nature, slow hydration of olivines near the surface results in formation of serpentines, which, with Mohs hardnesses typically closer to 4, are far easier to grind than olivines. But they are even less reactive with water or CO_2.

Interestingly, a thermodynamic analysis of typical seawater, taking into account dissolved CO_2, shows it to be significantly supersaturated with respect to both main classes of magnesium silicate hydrates, (serpentine and talc) but significantly undersaturated with respect to forsterite. This is presumably because the ocean floor is rich in basic magnesium silicate rocks, which dissolve continuously, but the magnesium silicate hydrates that should precipitate as a result of this hydration reaction do not crystallize easily at ambient temperatures. Seawater appears to be only slightly supersaturated with respect to both common forms of $CaCO_3$ (calcite and aragonite), a bit more supersaturated with respect to magnesite ($MgCO_3$), and even more supersaturated with respect to dolomite ($CaCO_3 \cdot MgCO_3$). It is notable that sedimentary rocks based on calcite or aragonite are far more common that magnesite or dolomite, and this can perhaps be attributed to the fact that many marine organisms can make use of calcite or aragonite to form their skeletons, but not magnesite or dolomite, (although a small amount of Mg can replace calcium in aragonite and calcite). It appears that the catalysis of calcium carbonate crystal growth by marine organisms evolved quite early and has never been superseded by a biological mechanism for crystallizing magnesite or dolomite, despite the greater supersaturation of these phases and greater abundance of magnesium in seawater (which has an Mg/Ca atomic ratio of about 5). These observations suggest that absorption of atmospheric CO_2 by carbonation of basic rocks can continue to occur via the oceans, but it seems likely that most of the carbonate precipitates as calcite or aragonite, rather than as magnesite or dolomite. Thus, in the oceans, carbonation of magnesium silicates is a rather inefficient process, and much of the magnesium may well precipitate as silicates rather than carbonates.

Given that natural carbonation of basic magnesium silicates seems to be too far slow to deal with the short-term problem of rapidly increasing atmospheric CO_2 from anthropogenic sources, it is reasonable to look for practical ways in which we might accelerate this process, while of course ensuring that the overall system remains a net sink for CO_2. For this reason, the concept of making binders from basic magnesium silicates seems attractive. Thus, at the time of the previous ICCC, there was great interest in the Novacem approach [86], which proposed to use as its first step the known high pressure water-catalyzed reaction between supercritical CO_2 and finely-ground magnesium silicate rocks to give primarily magnesite plus amorphous silica as products:

For forsterite olivine: $Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$ (1a)

For antigorite serpentine: $Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$ (1b)

Much of the prior work on such high-pressure processes had been done in the context of attempts to develop processes for using carbonation of basic magnesium silicate rocks for permanent CO_2 storage [87], for which separation of the magnesite and silica was not necessary. But the initial Novacem approach required separation of the two products, because the second step was low-temperature (≈700°C) calcination of magnesite to give a reactive periclase (MgO):

$$MgCO_3 \quad \rightarrow \quad MgO \quad + \quad CO_2\uparrow \qquad (2)$$

Any residual silica in the products of reaction (1) could potentially cause a problem here, because it might recombine with the MgO during calcination to form a magnesium silicate, thus defeating the purpose of the reaction cycle. Thus, a reasonable degree of separation was thought to be needed between steps (1) and (2). This was to be achieved by running reaction (1) at sufficient dilution to permit all of the $MgCO_3$ to dissolve in the liquid phase as “magnesium bicarbonate”:

$$MgCO_3 \quad + \quad CO_2 \quad + \quad H_2O \quad \rightarrow \quad Mg^{++}(aq.) \quad + 2HCO_3^{-}(aq.) \qquad (3)$$

Under these conditions, SiO_2 was to be separated by filtration or sedimentation, and solid $MgCO_3$ then recovered by reducing the CO_2 partial pressure, thus reversing reaction (3). However, a recently published Novacem patent application [88] suggests that the idea of separating the silica prior to calcining the magnesite was not pursued, perhaps because the degree of formation of magnesium silicates during calcination was found to be too small to justify what would be a rather difficult separation step. It may also be related to the fact that the presence of some reactive silica in the cement appears to be desirable, according to two other recently-published patent applications [89][90].

Regarding the composition and hydration mechanism of the cement itself, there is still relatively little information available in print. This can be attributed in part to the fact that Novacem itself went out of business in 2012, and also that, as far as can be determined from the level of publications, no-one else is currently continuing to do research on the type of binder that Novacem had been trying to develop. So the only source of information on the subject comes from the patent applications that have been published over the last two years (even though there may be no active research going on.)

Recent process developments in the area of mineral CO_2 capture by magnesium silicate carbonation, and life-cycle analyses (LCA) of their overall thermodynamic and CO_2 efficiencies, are discussed by Nduagu et al. [91]. In the "NETL process" (developed over two decades ago at the US National Energy Technology Laboratory, and used by Novacem as the basis for their approach,) a pressurized stream of pure CO_2 is reacted with the ground minerals (in the form of a concentrated slurry in a sodium bicarbonate/chloride solution) under the following reaction conditions: $T = 185°C$, $P(CO_2) = 150$ bars, $P(H_2O) = 6.5$ bars. These are not too different from the conditions proposed by Novacem. However, Nduagu et al. [91] conclude that the NETL process is not the most competitive process for industrial CO_2 mineralization using magnesium silicates, in large part because of the need to purify CO_2 from flue gases prior to its pressurization. They conclude that their own more recent "ÅAU" process is, overall, more efficient than the NETL process for CO_2 capture. The ÅAU process involves a closed-loop chemical cycle in which the magnesium silicates are first reacted directly with ammonium sulfate or bisulfate at about 400°C to form magnesium sulfates plus ammonia, and then re-absorbing the ammonia gas into aqueous solution at low temperatures and using it to precipitate magnesium hydroxide (brucite) by its reaction with magnesium sulfate. Brucite is then used to scrub CO_2 directly from compressed flue gases in a fluidized bed reactor operating at 500-550°C and "only" 20 bars total pressure, giving magnesite. Both the NETL and ÅAU processes require significant levels of gas pressurization in order to catalyze the carbonation of basic magnesium silicates, and the electrical energy required for this is substantial. More recently, researchers at Lafarge [83] have outlined a novel process that operates at atmospheric pressure, and makes use of a cycle involving alkali carbonates to catalyze the process. However, the work on this cycle is not yet complete and so there has as yet been no LCA study of this approach, so its CO_2-efficiency cannot yet be compared quantitatively with the NETL or ÅAU processes.

Regardless of the issue of the unproven industrial practicality of the various processes that have been developed to date for the carbonation of basic magnesium silicate rocks, the LCA data given by Nduagu et al. [91] on both the NETL and ÅAU processes can allow us to make an initial estimate of the energy and CO_2 balances required to make magnesite from natural magnesium silicate rocks, which is the first step in the Novacem process. The calculated energy requirements of both processes, if run with full heat recovery, are similar: 3.4 and 3.6 GJ per tonne of flue-gas CO_2 mineralized, respectively. However, the net CO_2 capture efficiency, which takes into account the equivalent CO_2 value of all the GHGs emitted in order to operate the process, is reportedly significantly higher for the ÅAU process (0.483) than for the NETL process (0.317), which implies that the ÅAU process effectively consumes 7.5 GJ of primary energy per net tonne of CO_2 captured, whereas the NETL process consumes 10.7 GJ. These are rather large numbers, which at first seem discouraging. Putting them into the context of manufacturing a

"Novacem-like" cement, and assuming that one tonne of CO_2 captured is equivalent to the production of about one tonne of MgO-based cement after additional processing (which requires additional energy, principally for decarbonation of the magnesite), it looks like a very high primary energy requirement per tonne of cement. However, this calculation is probably too pessimistic for three reasons. Firstly, these very high primary energy requirements are mainly required to make the capture process CO_2-neutral. Secondly, the CO_2 cycle in the Novacem manufacturing process could be more efficient because the CO_2 can be produced in a concentrated stream from the calciner, and thus the gas concentration step can be avoided, which makes quite a big difference if we use the NETL approach. Thirdly, if we instead use the ÅAU process, the intermediate product, brucite, could be dehydrated directly to MgO at moderate temperatures and fairly modest additional energy consumption, thus avoiding the need for the pressurized fluidized bed reactor. So it seems likely at a first glance that a "Novacem-like" cement could be manufactured with zero net CO_2 emissions for a primary energy requirement perhaps in the 7 GJ/tonne range. This could well be energy-competitive with Portland cement, if we consider that, to make Portland cement with zero net CO_2 emissions we would have to add a gas scrubbing system (with either mineral capture or underground sequestration) to the Portland cement plant. The MgO-based cement would also have some potential for further CO_2 absorption during use – but then so does Portland cement. So it is still too early to say whether or not the manufacture of a "Novacem-like" magnesium hydroxy-carbonate cement (possibly with additional siliceous components) from magnesium silicate raw materials might theoretically be an effective way to reduce the cement industry's net specific CO_2

emissions. Additional research on more efficient production cycles, coupled with careful and realistic LCA calculations, is needed.

4. Summary of main points

This review has covered a wide range of alternative approaches to the reduction of the CO_2 emissions associated with the manufacture of binder phase in concrete. These range from the relatively straightforward and easily implementable use of alternative raw materials and fuels for the manufacture of standard Portland-based cements, all the way to the as-yet unproven technology for the manufacture of totally non-standard novel binders based on magnesium hydroxy-carbonates derived from basic magnesium silicate raw materials. In addition to highlighting the need for the optimization of the manufacturing technologies involved in producing hydraulic binders, it is also made clear that the efficient use of known hydraulic binder components is a very important issue in terms of environmental impact. Currently, existing norms for hydraulic binders are very conservative in order primarily to try and protect the users of the final hardened products against errors resulting from poor workmanship and the use of the wrong product for any given application. More energy- and CO_2-efficient binder systems may already exist which would be quite suitable for certain applications, but which are not yet normalized, so their use involves a higher risk and requires a greater level of education on the part of the users. Thus, even without the development of any more new technologies, progress is needed both in the normalization process and in user-education, if we wish to progress more rapidly towards greater sustainability.

Finally, it is clear that the industrial development of the more novel (and thus more expensive to develop) approaches to CO_2 emissions reduction will depend on the economic and regulatory landscape at the global level. Without fairly strong globally-binding agreement on limits to cement- and concrete-related CO_2 emissions, only the relatively simple and immediately cost-effective approaches, such as increased use of wastes as raw materials, are likely to be implemented. But it is important for legislators to know that many other potentially more effective options (in terms of total global CO_2 emissions reduction) exist and at least some of them could be implemented on a large scale with a decade or so if the regulatory incentives were put in place to encourage their development.

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