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Research needs for cementitious building materials with focus on Europe

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Abstract

The needs for research on cementitious materials are reviewed with a focus on Europe. These are considered under 8 topics: clinker production, alternatives to Portland cement, composite cements based on Portland clinker, concrete, admixtures, durability, recycling, digitisation in concrete construction, and, carbon capture and use or storage; finally, the key research questions and their potential for CO_2 reduction are summarised in a "Watermelon" diagram with a list of 30 key questions to be addressed (see Appendix).

Keywords: Europe; Research Needs; Cement

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1 Introduction: why do we need research on cementitious building materials: trends, needs and stakes in the European construction sector for the coming decade?

This letter looks at the main research and development challenges facing cementitious building materials from a European perspective (as other RILEM Technical Letters deal with other continents), although much of the content is of global relevance. We discuss, from both academic and industrial viewpoints, the most important research topics related to clinker and cement production, alternatives to Portland cements, composite cements based on Portland clinker, admixtures, concrete mix designs and new

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functionalities, durability and recycling. The topics identified are summarised in graphics at the end of the paper focusing on the potential for reducing environmental impact and identifying 30 critical research questions.

Today, the most critical challenge facing the construction industry in Europe is sustainability, but other important issues are: improvement in construction efficiency, urbanisation, improvement in housing comfort, digitalisation... European citizens continue to aspire to a better and more comfortable life. But, higher comfort cannot come at any cost and will only continue with a major shift towards a net-zero (CO_2) future.

With concretes and mortars representing about 5% of the continental CO_2 emissions [1], the cement industry has no other choice but to reinvent itself. The cement and concrete industry must contribute not only to a very low carbon economy, but also to a circular one. It uses more than one-third of the total materials extracted from the ground in Europe. In addition, the European construction sector produces close to one billion tons of waste per year, the largest waste stream by volume, representing 30% of all waste generated [2]. The management of construction/demolition waste recycling can probably be improved in several European countries. The aim is to avoid, minimise and reuse waste at all stages, from quarries (both for cement and aggregates production) to building sites.

The European Union has pioneered strong and stringent policies to protect the environment. During the first quarter of 2020, the European Commission adopted three pillars of the Green Deal: the EU Industrial Policy [3], the European Climate Law [4] and the 2nd Circular Economy Action Plan [5]. These three documents lay the foundations for the forthcoming legislative framework that will impact the assets, the products and the markets of the cement and concrete industry in Europe, as they range from inscribing the principle of climate-neutrality in EU law to outlining a strategy for the built environment and construction products. Specific initiatives will be developed concerning: requirements for recycled content, Life Cycle Analysis (LCA) in public procurement, environmental & carbon footprint declaration, material recovery for construction and launch of a strong “renovation wave”.

The ambitious goal to be carbon neutral by 2050 highlights the urgent need for construction materials to dramatically decrease their environmental footprint (especially CO_2 emissions) and to increase and develop more complete circularity concepts.

Europe has an ancient and close relationship to concrete, which was twice born on this continent (first Roman cement based on lime-pozzolan blends invented two millennia ago, then Portland cement patented by Aspdin in 1824 in the UK) [6].

European universities house many research groups on cementitious building materials. These universities are developing an increasingly wider range of competencies (inorganic and organic chemistry, physico-chemistry, physics, rheology, mix-designing, durability, modelling techniques, engineering, artificial intelligence, construction techniques and economics, robotics, life cycle analysis…) to be able to work at every level from nanometre to building scale.

Famous European architects have pushed the limits of concrete and made it evolve to meet their architectural needs over the past 130 years. Today and in the near future, architects are looking for innovative construction solutions to further improve the concrete characteristics in terms of aesthetics, flexibility, versatility, comfort for the end-users and sustainability.

On their side, European contractors have various expectations about what future building materials can bring: lower construction costs, fewer expensive delays on job sites and increased productivity (integration into Building Information Modelling, ease of placement, optimising the shape of a structure by robotic means, lighter precast elements, modular construction, sensors embedded in concrete…).

The expectations of the European cement and concrete industry for R&D on cementitious building materials are very high and its common vision leads to the following features for the concrete of the future:

- extremely low CO_2 footprint, through (for instance) new low CO_2 concrete mix designs, large amounts of fillers or innovative admixtures to mitigate lower early age strength or higher viscosity
- use of local and recycled materials to save natural resources
- easy and cheap to produce and deliver while ensuring a very high level of consistency throughout the year, with predictable performance, thanks to innovative admixtures, artificial intelligence and sensors
- higher early age strength to ensure production cycle optimization (precast & onsite)
- very long-term durability without apparent cracks, a high ability to re-carbonate and be recycled.

In this paper the focus is on research questions linked to the cementitious materials, not about structural design of concrete (for which a similar detailed review could be useful in the future). The questions are presented at the end of each section and summarized in the Appendix. Nevertheless, we try to give some consideration to the entire chain of steps in the production and use of cementitious materials with the “5Cs”: clinker, cement, concrete, construction, carbonation. The production of clinker and cement is the start of a chain in the use of these materials. This extends through the use of cement and other cementitious materials in concrete to the use of these materials in buildings and infrastructure and then the way that these buildings are used, re-used or demolished, or whether the infrastructure needs repair and maintenance. Realising all the efficiency improvements at each step could lead to a reduction of CO_2 emission from cement in Europe in 2050 of about two thirds of the 1990 level [7]. Nevertheless, it will never be possible to produce cementitious materials with zero CO_2 emissions unless there is some amount of CO_2 capture which is subsequently either used or stored.

2 Clinker production

The production of clinker is the first step in the production process of cementitious construction materials. Around 90% of the final CO_2 emissions associated with the final materials come from this step and most of these (>60%) are from the decomposition of limestone: $CaCO_3 \Rightarrow CaO + CO_2$.

Around 99.8% of clinker produced worldwide is based on "Portland cement" clinker. Calcium aluminate cements and Calcium sulfoaluminate or Ye'elimite based cements are the only two other cement types produced in significant quantities, each with productions around 1000 times less than Portland types. The overwhelming dominance of Portland cement clinker is an inevitable consequence of the chemistry and geology of the earth. Eight super-abundant elements: O, Si, Al, Fe, Ca, Na, K, Mg make up more than 98% of the earth's crust. The fundamental principle of hydraulic cements is to have anhydrous minerals which dissolve in water, but which then produce new combinations with water (hydrates) that have low solubility and so precipitate as solids that fill the spaces between the cement grains and "glue" the fine and coarse aggregates together to form concrete. The high solubility of sodium and potassium salts and the low solubility of Fe and Mg in alkaline solutions, mean that hydraulic cements need to be based in the system of the three oxides - lime (CaO), silica (SiO_2) and alumina (Al_2O_3). In this system there are only 2 regions (Figure 1) where hydraulic minerals exist: the calcium silicates which form the basis of Portland cement and the calcium aluminate / sulfoaluminate region. Calcium aluminate and sulfoaluminate contain stoichiometrically less calcium in their main reactive minerals (CA, $C_{12}A_7$, $C_4A_3\$$) and so can produce cements with lower CO_2 emissions, however to produce these minerals, sources of alumina without much silica are needed. The expense and comparative rarity of such raw materials account for the fact that the production of these alternative clinkers is only a few tenths of a % today and is unlikely to increase significantly in the future as will be further discussed in section 3.2.

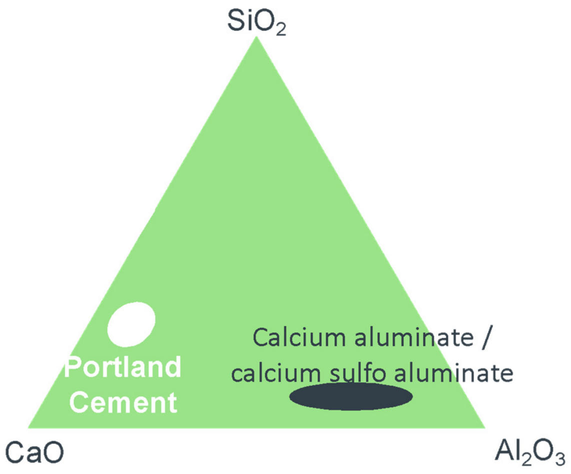

Figure 1. CaO-SiO_2-Al_2O_3 phase diagram showing two regions of cementitious phase, Portland cement, containing mainly Calcium Silicates C_3S and C_2S and Calcium Aluminate / Sulfoaluminate.

It is well known that Portland cement clinker is composed of 4 main anhydrous phases: Alite (impure C_3S); belite (impure C_2S); aluminate (impure C_3A) and Ferrite (impure $C_2(A,F)$), but its complexity goes far beyond this and is not well appreciated by most users and academics. Some additional factors are:

- Minor phases particularly alkali sulphates and free lime
- Minor elements and polymorphism of the main clinker phases
- Crystallite size and defects.

On the materials side these may all be affected by aspects, such as the type of raw materials, the binder mix design, presence of fluxes and mineralizers, material fineness (especially of limestone and the silica source) and homogeneity. On the process side, there are the kiln design (with or without preheater, cyclones, etc.), kiln dimensions, speed of rotation, fuel mix, burner set-up, kiln dwell time and temperature profiles, gas concentration and composition, clinker granulation and heat transfer, the formation of build-ups, cooler design and efficiency, air flow and intake, etc. Even this simplified list demonstrates that all possible interactions cannot be well captured in ordinary lab-scale or even pilot-scale experiments. It is well known that the reactivity of industrial clinkers may differ significantly from laboratory or pilot scale clinkers produced with the same raw meal, but the reasons for these differences in reactivity are far from being well understood [8].

Only in the last few decades has it even been routinely possible to quantify the amounts of the 4 main clinker phases due to the extensive use of Rietveld analysis for X-ray diffraction. We are far from having rapid and reliable methods to quantify all relevant additional factors that govern clinker reactivity.

Despite the obstacles, better understanding the link between the process parameters and the clinker performance would be a great advantage in two important respects:

- ability to produce clinkers with predictable and regular properties, not merely from the point of view of strength development, but also regarding early age behaviour such as rheology and interaction with admixtures
- ability to optimise the reactivity of the clinker as a means to maximise clinker replacement by substitutes such as supplementary cementitious materials (SCMs).

This challenge is made particularly difficult by the increasing use of alternative fuels and raw materials (AFR). We will consider first the challenges brought by AFR, then discuss two important aspects where improved understanding of clinker is needed and finally look at the prospects for using machine learning.

2.1 Alternative fuels and raw materials

Increasing the use of alternative fuels and raw materials in clinker manufacture can make an important contribution to sustainability and the circular economy.

Traditionally, the firing of clinker is done with fossil fuels: coal, natural gas, fuel oil, pet coke (a by-product of oil refinement). Alternative fuels are waste materials, their use for clinker production reduces the need for virgin fossil fuels and also provides a safe and effective route for their disposal. This is of great importance not only for the manufacturers but also for society.

Alternative fuels used by the cement industry are, for example, old car tyres, sewage sludge, animal residue, waste oil, paper residue, plastic, textile and lumpy materials. These fuels still emit CO_2, but all of their calorific value can be efficiently used. Fuel CO_2 is only reduced through the use of biomass. However, there are limited supplies of biomass. Relatively clean and easy to use biomass is probably more efficiently used in other applications, while otherwise hard to exploit sources, such as municipal waste and oil contaminated sawdust can be used in cement kilns. In a few European cement kilns, 100% substitution has been achieved. In other markets the substitution rates are still low, mainly due to legislative reasons, such as low cost of disposal in landfill or lack of a good network for collection. This is a major social challenge to ensure that waste is disposed of safely and its residual calorific value used most efficiently.

Some practical limitations for fuel substitution are the introduction of minor elements such as phosphorus, alkalis and heavy metals (e.g. chromium, copper, nickel, zinc, etc.). The amount and type of minor elements can influence the clinker formation as well as the properties of the clinker produced. This highlights the need for research to understand the influence of minor elements. Furthermore, many wastes will produce ash whose composition must be considered when designing the raw mix composition.

While the use of alternative fuels is well established, the use of alternative raw materials is on a much smaller scale (up to 10-15% in only some plants). Alternative raw materials (ARM) can reduce the need to extract minerals from the earth. The raw mix for clinker is around 80% limestone and 20% argillaceous (e.g. clay) with minor adjustments of iron oxide, alumina or silica. It is becoming increasingly difficult to open new limestone quarries so alternative sources (such as ARMs), particularly for lime, are of great interest. Even more interesting is the possibility to use non-carbonated sources of lime, which directly reduce the chemical emissions from the decarbonation of limestone. In addition, the use of wastes as alternative raw materials reduces demand for landfill and develops the circular economy. A good example is the use of synthetic gypsums, such as from the desulfurization of flue gas from burning coal to produce electricity. Other examples are fly ashes and blast furnace slags which have low reactivity as SCMs. There are also a wide variety of steel slags and by-products potentially available, but these may contain toxic metals, such as Pb, Cu, Ni, which may limit their use. Fines, from the demolition of old concrete and production of recycled aggregate (CDW), are another source of alternative raw materials, which is being increasingly considered and used. Clearly these have similar composition to clinker, and much of the CaO may be uncarbonated.

As with alternative fuels, the main problem and consequent research needs are the introduction and varying levels of minor elements. This underlines the need for better understanding of the impact of these on clinker chemistry and microstructure. Particularly complex, is the impact on the formation of the liquid phase during clinkering. In this regard the contamination of CDW with chloride and sulphate (such as from old roads or plaster) is particularly problematic as it influences the firing and may lead to build-up of material on the kiln lining. It may also influence the kiln atmosphere and the control of emissions.

In a nutshell, further research regarding alternative fuels and raw materials is needed to determine the criteria and limits on minor elements and hazardous components, to be able to enlarge the scope of usable by-products.

2.2 Understanding clinker reactivity

A better understanding of clinker reactivity is a key research need, which goes far beyond a simple quantification of the 4 major clinker phases. It is well known that alite is the most important phase in Portland cement, which plays the main role in strength development for the first few weeks. A general trend in the past few decades has been to maximise the amount of this phase. Since the 1960s it has risen from around 50-60% to 60-70% in many parts of the world. In some regions, notably India, the high content of silica in most limestone deposits means that it is still difficult to have alite contents above 60% and contents around 50% are typical.

2.2.1 Alite

There have been numerous studies of alite alone and in Portland cements, but misleading conclusions have often been drawn, due to the failure to appreciate the complexity of factors affecting reactivity. A good example of this is the question of polymorphism. Crystallographically, alite can exist with 3 types of symmetry: Rhombohedral, monoclinic and triclinic. The rhombohedral phase is stable at temperatures above about 1070°C, i.e. during the clinkering reactions. The lower temperature polymorphs are closely related to the rhombohedral structure by small distortions of the lattice. During clinkering various ions, like Mg, Al, etc. are incorporated into the structure in solid solution and these impact the polymorphs which are found in the final clinker after cooling. Therefore, differences in reactivity are more likely related to the ions in solid solution and the defect density than the specific polymorph. For example, Bazzoni et al.[9] studied the reactivity of alite doped with either magnesium or zinc. The magnesium doped sample exhibited a different polymorph to the reference but had very similar reactivity. In stark contrast, the zinc doped sample had a much higher reactivity, but the same polymorph, as the reference.

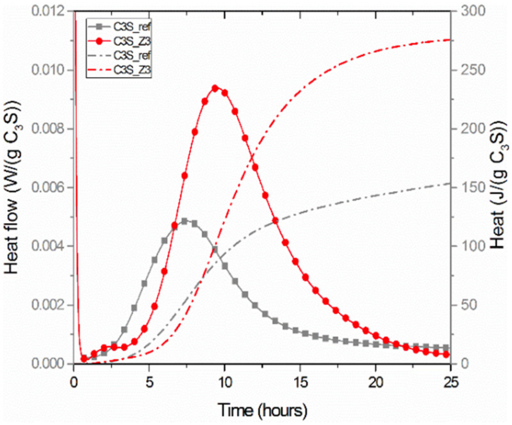

Figure 2. Calorimetry of C_3S with and without ZnO doping from [10]. The grey curves are for the reference pure C_3S, while the red curves are for C_3S doped with 3% zinc. In each case the solid curve is the heat flow (left axis) and the dotted curves the cumulative heat (right axis). Further details on the sample preparation are in the original paper.

The study of zinc doping in alite also illustrates that the whole idea of anhydrous phases having an intrinsic *reactivity* is misleading.

Comparison of C_3S and alite with and without addition of zinc (Figure 2) indicates that the presence of zinc extends the induction period, but once the acceleration period starts the rate of reaction is dramatically accelerated [10].

As discussed in detail elsewhere [11], the induction period is believed to be controlled by the rate of dissolution of alite, linked to the under saturation of the solution, while the main heat evolution peak is related to the growth of C-S-H. So, zinc appears to slow down dissolution, but speed up the growth of C-S-H. A similar dichotomy is seen with the impact of annealing [12]: the induction period, controlled by dissolution, is dramatically prolonged, while the main heat evolution peak related to C-S-H growth is hardly affected. What most people usually mean by *reactivity* is the rate of strength development as this is usually the only thing measured. Even at one day this will combine the two stages of alite reaction (induction period and main heat evolution peak) but also the reaction of the aluminate and ferrite phases.

Following the work of Sulovsky [13] it is widely assumed that the two monoclinic polymorphs M1 and M3 contribute differently to strength development. However, this assumption has not been studied in detail. M1 and M3 polymorphs synthesised in the laboratory did not have significantly different reaction rates, when normalised for surface areas [14]. Similarly, there was no significant difference in the degree of reaction of these two polymorphs within a single cement. This indicates that there are multiple factors affecting strength development and differences cannot be simply attributed to the existence of different polymorphs. For example, it is possible that the minor elements which favour one polymorph over another may also influence the crystal size of the alite, which is clearly an important factor in the rate of reaction.

Another good example of complexity and the danger of studying phases in isolation is the case of fluorine. There are reports of fluorine doping retarding alite hydration without changing the polymorph[15]. However, fluorine can be added as a mineraliser to commercial cement clinkers, without any adverse effects on strength development [16]. This indicates that retardation effects vanish when other minor elements and minerals are present in a real clinker, even though in such cases the polymorphism of the alite may be changed. These observations show that studies should focus on the effect of defects, crystallite sizes and porosity, in other words accessible surface area on the reactivity of clinkers rather than just polymorphism.

2.2.2 Interstitial phases and importance of cooling regime

The interstitial phases, usually denoted as aluminate (C_3A solid solution) and ferrite (usually referred to as C_4AF, but really $C_2(A,F)$ solid solution) form during cooling by solidification of the liquid present during clinkering. For this reason, they are even more susceptible to variations brought by the materials and process than the calcium silicate phases. For example, impurities, such as chlorine and fluorine, lead to the formation of glassy and ill crystalline fast reactive aluminate phases (e.g. mayenite present in white cement). The presence of such amorphous interstitial phases requires the modification and optimisation of calcium sulphate types and dosages added during grinding. This in turn may require further adjustments regarding the type and dosage of concrete admixtures.

Controlled clinker cooling is very important for clinker quality. It is also important for heat recovery and the energy efficiency of the production process.

Fast cooling is essential to stabilise the alite phase which is thermodynamically unstable below 1250°C and may decompose into belite and (sub-microscopic) free lime during slow cooling. Fast cooling also leads to the crystallisation of fine-grained aluminate phases instead of large crystals. This facilitates the control of hydration kinetics during setting, as well as early age strength development. This results in an improved cement strength, compared to a slowly cooled clinker. It increases the probability of elements (e.g. Mg, Al, Fe) and other minor elements being kept in the crystal structure of the clinker silicate minerals (i.e. avoiding the exsolution). These substitutions, generally, lead to increased strengths and shortened setting times. Fast clinker cooling also means that any MgO present forms as small crystals, reducing the likelihood of cement unsoundness. However, too fast cooling may lead to solidification of the liquid phase as micro crystalline or amorphous glass with the problems of calcium sulphate adjustment and admixture interaction.

These discussions on alite, interstitial phases and cooling, all highlight the complexity of factors affecting clinker "reactivity" and also the difficulty to study under laboratory conditions.

2.3 Prospects for machine learning

Given the complexity of clinker it would seem an area where the application of machine learning (part of artificial intelligence) could be of benefit [17]. However, one must be aware of the limitations intrinsic to such approaches:

- machine learning is based on “interpolation”, i.e. the model does not work outside of the data range used for learning
- the model needs training data covering the actual production processes
- it is a mathematical function by definition, i.e. identical variables must lead to identical values, and otherwise, data will be identified as an outlier. Data might be correct, but an important variable is missing. Therefore, classification as an outlier will depend on the variables selected
- it does not know the cement and production process; it just treats numbers. Therefore, the user always needs to judge the significance of the output of the model.

At present, the data collected during clinker manufacture is mainly to ensure the stability of the process, not the reactivity of the clinker. “Strength” data as a proxy for quality is only collected once or twice a day. While fuels may vary according to supply, it is not common to adjust the chemical composition of the raw meal and even if this were done the complexity of the interactions makes it difficult to link cause and effect. It is therefore of considerable interest to link more traditional scientific investigations with these data driven tools.

2.4 Alternative calcination technologies

The main research focus in alternative calcination technologies is lowering the amount of CO_2 emitted from fuel, for example by electrification of the process and/or the capture of the CO_2, through oxy-fuel, carbon scrubber technologies, direct separation:

- oxy-combustion or oxy-fuel is where pure oxygen rather than air is used for combustion [18]. The flue gas consists only of water vapour and CO_2, plus small amounts of other substances. Once compressed the flue gas is composed of nearly pure CO_2, suitable for transport, use, and storage;
- a carbon dioxide scrubber is a piece of equipment that treats exhaust gases from industrial plants and absorbs carbon dioxide (CO_2) [19]. The CO_2 is then desorbed and stored. Sorbent deactivation must be assessed under realistic conditions involving high CO_2 concentrations in the calciner;
- direct separation technologies would enable the efficient capture of the unavoidable process emissions from lime and cement production by indirectly heating the limestone via a special steel vessel. It enables pure CO_2 to be captured when released from the limestone, since furnace exhaust gases are kept separate. It requires minimal changes to the conventional processes for cement, replacing the calciner in the preheater-calciner tower.

There are several research questions related to the application of these technologies. At present many of them are only available as lab or semi-industrial prototypes. These technologies will affect the atmosphere during the clinkering process, and the impact of such changes on clinker reactivity (e.g. oxyfuel) is not known. The changes in the kiln atmosphere may also affect the volatilisation of minor elements and the phase stability. In other words, all key process parameters mentioned above are interrelated.

2.5 Conclusions on clinker production

To put this section in perspective, there are many outstanding questions related to clinker production. These are important not only to optimise the production but also to enable the reduction of associated CO_2 emissions.

In particular, it is important to understand:

- what are the consequences and limits of substitution of fuels and raw materials?
- can the “reactivity” of the clinker be improved?

As discussed in section 4, clinker reactivity is now the main technical limitation to increase the level of clinker substitution, which is the most effective strategy to lower CO_2 emission.

Minor elements play a key role in both questions and new ways for fast but accurate measurement of these in both atmosphere and incorporated in the clinker are needed. However, a major obstacle to better understanding the clinker formation process, is the large number of interacting factors and therefore the difficulty of studying industrially relevant systems in the laboratory. Nevertheless, studying the important parameters at the lab and pilot-scale under well-controlled conditions can provide quantitative data to help relate process parameters to clinker phase composition and cement performance. To achieve tangible results, comparable to hydration studies where methods are well established, the different studies on clinker formation need to develop a set of experimental basics/protocols/reports to enable a comparison of results and enlarge the amount of available information.

The integration of experiments and thermodynamics should be reinforced to develop tools that are capable to predict the process of Portland cement clinker production (including bypass, emissions, etc.) including the kiln atmosphere influence, the composition of phases including solid solutions, phase equilibrium, and enthalpy balance with higher accuracy before transfer to the plant quality control concept.

The modelling should be developed with the target to build a thermodynamic framework with a self-consistent database and relate this with industrial practice.

This will help to better understand the reactions taking place in the industrial kiln systems using new calcination technologies as well as traditional ones.

A. Clinker - Priority research topics & key questions

Topics	N°	Key research questions to be solved
Alternative raw materials	1	Determine criteria and their limits to enlarge the scope of by-products used as ARM and ARF (minor elements impact, thresholds for hazardous components)
Alternative calcination	2	Understand impacts and reduce the cost of calcination with electrification
	3	Determine the most promising and cost-effective processes for CO_2 purification (kiln oxy-fuel combustion, calciner CO_2 separation)
Clinker reactivity	4	Better understand the link between process parameters and clinker performance like rheology, interaction with admixtures and reactivity to maximise substitution
	5	Model the impact of clinkering and cooling conditions on clinker reactivity
Clinker consistency	6	Develop laboratory methods to simulate real industrial kiln conditions
	7	Develop tools to improve clinker consistency, for example machine learning

3 Alternatives to Portland cement

Having discussed the research needs for Portland clinker, we need to consider if there are realistic alternatives to Portland based cements. Over the past decades substantial research efforts have been invested in alternative binders, with negligible impact in the field. We need to understand the reasons for this lack of success.

Here we consider:

- Belite rich Portland clinker
- Hydrothermal synthesis of C_2S
- Ye’elimite based binders (CSA / BYF)
- Alkali-activated binders
- Magnesium-based binders.

The hardening of binders by carbonation will be considered later in the overall context of CO_2 mineralisation.

The chemical constraints imposed by the composition of the earth, have already been highlighted in section 2. In addition, the scale of production and the very low cost of clinker production must also be kept in mind.

3.1 High belite cements, by clinkering

The saving of CO_2 between alite and belite is relatively modest. A simple stoichiometric calculation indicates that the “chemical” CO_2 emissions from the breakdown of limestone to form belite are 512 kg/tonne, 11.6% less than the 579 kg/tonne for alite [20]. Much is discussed about the lower clinkering temperature, but with the high efficiency heat recycling in modern kilns this leads to very modest savings.

Overall, considering that the calcium silicates are typically 80-90% of the clinker, the CO_2 saving for high belitic Portland cements is at best 10%. This must be offset against the much slower reaction rate of belite. Broadly speaking if belite does not react at least to 90% of the level of alite, any CO_2 savings will be wiped out in the final application. Much research has sought to “activate” belite, but with limited success. The activation by boron in Ye'elimite based cements and active C_2S produced by hydrothermal synthesis are discussed below. A further problem is that the reaction of belite appears to be inhibited by any faster reacting component: by alite in Portland cement and by metakaolin and slag in blended cements. In Portland based systems the reaction of belite is negligible for at least 10 days and even for more than a month in blended systems [21,22]. Belite also produces proportionally less calcium hydroxide than alite, so there is a lower potential for pozzolanic reaction with the addition of supplementary cementitious materials.

In short, increasing the proportion of belite relative to alite in Portland type clinker does not save CO_2. Just the opposite, increasing the proportion of alite will allow higher levels of SCM substitution, which *can* save CO_2. Of course, Portland type cements with high belite content have advantages in applications where lower heat is important, such as massive structures like dams or in oil well cements. However, in the case of massive structures, a blended cement with a high level SCM may be as good from a technical standpoint and even better from the point of view of CO_2 emissions.

3.2 Hydrothermal synthesis of C_2S

The production of C_2S by hydrothermal synthesis provides a means to overcome the slow reaction of belite produced by classical sintering. The development of these materials is based on the activation of a precursor α-C_2SH either by grinding or annealing [23]. α-dicalciumsilicate hydrate is obtained by autoclaving a mixture of calcium oxide and silica. The hydrothermal treatment is mainly done at temperatures between 150-200°C for up to 16h. This precursor, the crystalline α-C_2SH, is not hydraulically reactive and must be activated either by grinding or by annealing.

α-C_2SH can be activated by an energy intensive grinding process with quartz. Researchers at the Karlsruhe Institute of Technology (KIT) have recently developed this new class of binder, called “Celitement™” [24]. Their approach is to produce a coating of a C–S–H precursor phase on the surface of particles of a relatively unreactive substrate such as quartz (tribochemical process) and use a grinding step to activate the material. As a result, the α-C_2SH becomes amorphous, dehydrates to some extent as it is ground, and thus forms a reactive coating on the filler particles that can hydrate in water at ambient temperatures.

However, there are several disadvantages to activation by grinding. The structural water bound in α-C_2SH is partly released during grinding and can lead to coating and agglomerates on grinding equipment. A special mill is required, but up-scaling a new milling concept to an industrial scale is not trivial. Furthermore, α-C_2SH is only partly dehydrated during grinding and the capability to combine the mixing water in new hydrates is lower compared to pure C_2S binders. This means low water/binder ratios are necessary to form materials with low porosity.

Ishida [25] reported that the dehydration of α-C_2SH starts at temperatures between 390 and 490 °C and produces low-crystalline β-C_2S and an intermediate phase. This intermediate phase is a new type of dicalcium silicate which Miyazaki [26] later named *x*-C_2S. The hydration of such binders is relatively fast.

It was reported that a C_2S binder prepared at 600 °C was completely hydrated after 28 days (water/solid = 0.5, 25 °C) [27]. Annealing of α-C_2SH leads to a multiphase binder consisting of an X-ray amorphous phase, x-C_2S, γ-C_2S and after annealing at temperatures greater than 600°C also β-C_2S. The most important parameters of the annealing process are temperature and vapour pressure of the atmosphere in the annealing process devices.

As the entire manufacturing process will be different from that used for OPC, new process facilities need to be developed for these technologies, particularly for production of the precursor. Rotary kilns or flash calcination can be suitable technologies for the annealing step.

The lack of large-scale production means that there is very little information available on the performance of these materials in concrete or mortar, so there is no clear picture on the advantages and drawbacks compared to OPC. These binders should in principle be suitable for most types of conventional concrete applications due to their relatively high hydraulic activity. Most importantly the hydrates formed are similar to those from Portland cement, i.e. mainly C-S-H. However, the content of Portlandite (desirable for reinforced concrete) is low. As with conventional high belite clinkers the potential reduction in CO_2 is far from obvious. The calcium oxide needed to make the pre-cursor will still need to come mainly from the decarbonation of limestone.

3.3 Ye'elimite based cements

A common feature of calcium sulfoaluminate cements [28] and the more recently named BYF (Belite Ye'elimite Ferrite) cements [20] that the first reacting phase controlling set and strength development for the first days, is Ye'elimite; $C_4A_3\$$. The chemical CO_2 emissions from this phase are only 216kg/ton, 37% of that of alite, so clearly there is potential for CO_2 savings with these cements, roughly in proportion to the Ye'elimite content. In addition, the clinkering temperature is lower, but as explained for high belite cements this has minimal effect. They are also easier to grind (consume less energy to reach the same particle size distribution).

The main issue hindering the wider use of these materials is the relative scarcity and higher cost of raw materials with much higher alumina than silica contents. The mineral bauxite is the best raw material, but this is mainly used to produce aluminium metal. It is estimated that about 90% of the world's bauxite reserves are located in just 10 countries. The relative scarcity of this mineral and the competition from the production of aluminium means that even BYF cement, containing only 20-40% Ye'elimite, have production costs more than 20% higher than Portland cement clinker. High Ye'elimite CSAs, with around 70% or more Ye'elimite, which are used in dry mixed mortars, are in the same price range as calcium aluminate cement, that is to say 3-5 times the price of Portland cements.

This price reflects not only the higher production costs, but also the much smaller scale of production, transportation costs and technical support.

Considerable work has been done on the preparation of CSA materials from high alumina wastes[29, 30]. This has demonstrated the feasibility of production from waste if the overall chemistry of the raw meal is correct. However, the amounts of such wastes are also not particularly large, and they may be quite variable. Another issue with Ye'elimite based cements has been the variation of the onset of setting and hardening. The work of Bullerjahn [31] shows that this is determined by the presence of a small amount of mayenite ($C_{12}A_7$). There would also be a need to develop new types of admixtures to control the kinetics and rheology in a cost effective manner.

A major problem of these systems is the slow reaction of belite. This can be solved by the addition of Boron [32–34] but this is not an abundant element (0.001% or earth's crust) and adds considerably to the cost.

Overall, despite intensive research in recent years, real advantages of Ye'elimite based cements for general use in concrete have failed to materialise. Production costs are considerably higher, and larger amounts of CO_2 may be saved by going to higher levels of substitution with SCM (such as with LC3). Consequently, we do not see a significant need for further research on these materials outside their niche applications as a component of specialty mortars.

3.4 Alkali activated binders

Over the past half-century extensive research effort has been invested in alkali activated materials (AAMs), also known as geopolymers, with objectively little impact in the field. Most alkali activated materials use slag or high calcium fly ash. The supplies of these materials are limited and decreasing. Reactive slags and fly ashes are almost 100% used by the cement industry today to lower their CO_2 footprint. They are already contributing to CO_2 reduction. Any other use out of the traditional way (composite cement and low clinker concrete) is a cannibalization of these sources and could even result in a net increase in CO_2 emissions due to the activators, which usually have a high carbon footprint. The development of AAMs as a route to lower the CO_2 emissions requires finding raw materials other than those that are in use for traditional cement and concrete applications.

3.4.1 Alternative raw materials for AAM and geopolymers

The development of alternative raw materials for geopolymers / AAMs lies in technological innovations to exploit untapped resources such as industrial waste streams and metallurgical by-products (e.g. ladle slags, red-mud, Ca fly ashes with high free lime content, etc.). For example, opportunities may come from optimising processing technologies for extracting base and critical metals from industrial residues and making use of the remaining processing residues in the construction sector.

The gradual conversion of steel production from the integrated blast furnace/LD converter route, which has been used for about 70% of steel production so far, to a direct reduction/electric furnace-based route planned for the next decades will inevitably lead to by-products (e.g slags) that have completely different chemistries and mineralogies.

Artificial glasses and kaolin/metakaolin which are produced in a controlled process could also be a source for AAM production, but these require high amounts of CO_2 intensive activators [20]. Even if new sources of raw materials can be found, there still remain the following technical obstacles which have not been solved:

3.4.2 Issues of workability and consistency

AAMs generally present poor rheology and currently there are hardly any effective superplasticizer for these products. Furthermore, AAMs use by-product materials which come from different sources. Any minor components present can have different effects on their rheology and interaction with SPs. The by-products used for AAMs can be quite variable, which makes it difficult to define SPs that can work for a large range of these systems.

Additionally, any change of the production process at the industrial site might affect the quality of the by-product without any traceability or power to change it. Moreover, local conditions, activator intensity and minor components lead to variable setting time and the extent of reaction. Even if the AAM binder composition is known, the presence of any minor components can lead to unpredictable performance and properties.

3.4.3 Hardened properties and durability

Another problem for AAMs is shrinkage, which becomes worse as the Ca content is reduced. AAMs with low Ca content increase the quantity of water in the hydrates that is required to prevent shrinkage. This increases the sensitivity of pastes to drying shrinkage. This problem is further exacerbated by increasing the Na content (needed for low calcium systems). Another issue is that the soluble alkali content, higher than conventional cement, can be a source of efflorescence, which can be a significant issue when the products are exposed to humid air or in contact with water. The efflorescence is mainly sodium carbonate. There is a dilemma: to prevent shrinkage, these materials need to be maintained in a humid environment to keep structural water above certain content but this in its turn will lead to the efflorescence problem.

As AAMs become lower in calcium, they have no buffer to carbonation and carbonation may lead to dusting of the materials [35].

We do not encourage further research on these materials as being cost effective in terms of the CO_2 reductions which can be realised.

3.5 Magnesium based cements

Recently there has been a growing interest in cementitious materials based on magnesium compounds. Magnesium is the eighth most abundant element in the earth crust (2.1% compared to 3.6% for calcium), however the distribution of magnesium rich minerals is much more heterogeneous. What is more interesting is that a substantial proportion of magnesium rich minerals are not carbonates. Getting magnesium oxide from magnesium carbonate (magnesite) makes no sense from a CO_2 perspective. Due to the lower atomic weight of magnesium almost twice as much CO_2 per tonne is emitted from the calcination of magnesium carbonate as from calcium carbonate (limestone).

Ultramafic and mafic rocks, mainly found at the boundaries between tectonic plates, contain magnesium silicate minerals such as olivine, $(Mg,Fe)_2SiO_4$. Obtaining MgO from such sources, would involve the emission of no “chemical” CO_2. However, no energy-efficient industrial scale process has been developed to do this so far. A recent publication [36] proposes a new process based on acid dissolution.

MgO and $Mg(OH)_2$ are able to produce materials which harden with the absorption of CO_2 When mixed with water and exposed to CO_2, hydrated Mg-carbonates such as:

- nesquehonite ($MgCO_3{\cdot}3H_20$),
- dypingite ($Mg_5(CO_3)_4(OH)_2.5H_2O$), and
- hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$)

form. Consequently, such materials can be net carbon negative. Unfortunately, these materials do not have an alkaline pore solution which would protect reinforcing steel and the strengths reported so far have been quite modest [37]. Another issue is that the size of elements produced is limited by the need for CO_2 to access all the material (as discussed later for carbonation hardening materials based on calcium silicate).

Nevertheless, they could be suitable for making masonry blocks. Another interest of the process proposed in [36] is the potential to produce amorphous silica as a by-product, which could be used as an SCM in blended materials.

Globally, the issues with cement from magnesium silicates are the distribution of the raw materials and finding an economically viable process to convert magnesium silicates to magnesium oxides on a large scale. Furthermore, it is questionable whether reinforcing steel can be protected in conventional applications.

To summarise this section on alternatives hydraulic binders, we do not see strong potential for CO_2 reduction coming in the short term from alternatives to Portland cement-based materials. The table below highlights the only outstanding research question, which is considered to have some potential.

B. Alternative hydraulic binders - Priority research topic & key question

Topics	N°	Key research questions to be solved
Alkali-activated materials	8	Only for precursors other than slag or fly ash, understand and mitigate the issues of AAM slump loss, short setting & shrinkage

4 Composite cements based on Portland clinker

The previous sections highlight that the composition we know as "Portland" cement, is an inevitable consequence of the composition of the earth and there are no alternatives which can be produced on the same scale and at the same cost, with equivalent performance. For these reasons, Portland based cements will remain, in the future, the basis of the overwhelming majority of cementitious construction materials. But this is very far from saying that nothing can be done to lower the environmental impact of cement-based materials. The strategy, which has already led to very significant reductions in the embodied CO_2 emissions of cement (19% since 1990), and has the potential to go much further, is to replace as much as possible of the Portland cement clinker by supplementary cementitious materials (SCMs). Of course, this strategy is not new, we have been using blended cements successfully for many decades now. Figure 3 shows the evolution of clinker substitutes in Europe (Cembureau members) since 1990[a]. After a rise of roughly 5% between 1990 and 2010, the average level of substitution has fallen back in recent years.

This is mainly due to the relatively limited amounts of slag and fly ash available. In Europe, ground granulated blast furnace slag (GGBS) is the most used cement substitute. Today the amount of blast furnace slag available world-wide is around 8% of cement demand. This will decline further as more steel is recycled and the iron and steel industry looks for alternative, less energy and CO_2 intensive ways to obtain iron from ore. Fly ash is the result of burning coal to produce electricity, which currently accounts for 30% of worldwide CO_2 emissions. Consequently, it is a first priority to reduce electricity production from coal. Coal fired power stations are already closed, or planned to close in many European countries so the supply of fly ash will decrease, it already represents less than 2% of clinker substitutes in Europe [38].

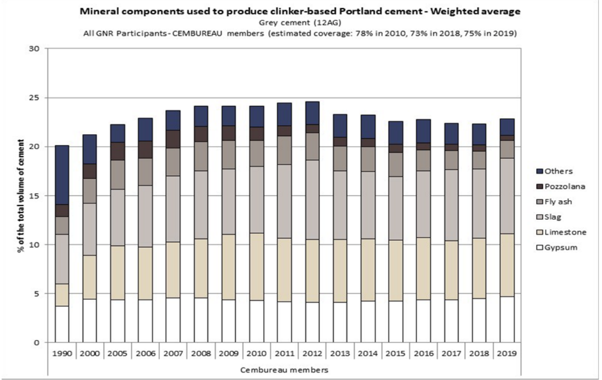

Figure 3. Evolution of clinker substitutes in Europe from GCCA, "getting the numbers right" database [38] readers are referred to the GNR web site in reference for more details.

Limestone is an important clinker substitute and it is abundant at all sites of clinker production. It is now well established that calcium carbonate will react with aluminate ions to form calcium carboaluminate hydrates, which contribute to space filling and strength development [39, 40]. In typical Portland cements the amount of alumina (in C_3A and the $C_2(A,F)$) is quite limited such that the usual maximum 5% of limestone relative to the clinker can react. This means that although low additions of limestone will improve strength and other properties, for additions above about 15%, limestone acts purely as a diluent.

SCMs containing alumina can increase the amount of limestone reacting and this synergy has led to the development of ternary blends where clinker is substituted by a combination of aluminosilicate SCM (e.g. slag, fly ash or calcined clay) and limestone [41–43].

In the light of the shortage of classic SCMs (slag and fly ash) the material which can radically increase the substitution level of clinker and so lead to extensive reductions in emitted CO_2 is calcined clay. When kaolinite clays are calcined (heated in the range 750-850°C) they become highly reactive materials. Due to their high alumina content, calcined clays work particularly well in combination with limestone, which is the synergy behind the LC3 (limestone calcined clay cement) technology. High grade metakaolin is a very expensive product, partly due to the high requirements on colour and homogeneity imposed by the other applications in which it is used (such as paper coating and ceramics). For use as SCM in cement, clays need only have a kaolin content of around 40%

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[a] The data presented in Figure 3 shows the % volume substitution. Generally, in research papers substitutions by mass are used. As the densities of SCMs and clinker are not all the same, there are slight difference between mass and volume, but these difference are not pertinent to the general points being made here.

and such clays are very abundant worldwide – frequently as wastes from other mining operations. Kaolinitic clays are available in Europe, even if the typical kaolin content of clays found in Europe tends to be lower than those found in tropical and subtropical regions.

Given that the most effective route to reducing CO_2 emissions for cement is to maximise the addition of SCM, what is the research needed to support this strategy? The most important needs can be grouped under several headings discussed further below:

- quantify SCM reactivity to facilitate the formulation of cements with desired strength development
- increase the early strength to maximise the amount of replacement possible. Possible routes are better grinding strategies, increasing clinker reactivity and perhaps other additives or admixtures, including seeding
- optimise the workability and robustness of mixtures through the use of admixtures and particle packing
- develop methods to assure good performance for the required service life.

Within each of these broad headings are a number of basic scientific questions which need to be better understood and many of these relate back to the most abundant hydrate phase C-S-H as will be discussed.

4.1 Quantification of SCM reactivity

When considering the aluminosilicate SCMs (fly ash, slag, natural (uncalcined) pozzolans, and calcined clays) the rates of reaction seen in blended cement systems are very different. This is well illustrated in Figure 4 [44] where binary (65% clinker, 30% SCM, 5% gypsum) and ternary (50% clinker, 30% aluminosilicate SCM 15% limestone and 5% gypsum) with either calcined clay, slag or fly ash as the aluminosilicate SCM are compared. The blends with calcined clay rapidly catch up with the strength development of the OPC and have typically higher strengths at 7 days, the slag binary blend surpasses the OPC strength at 28 days, while the fly ash blends need 90 days to surpass the OPC strength. In the long term (180 days) all the blends have similar strengths 10-20% higher than the OPC reference.

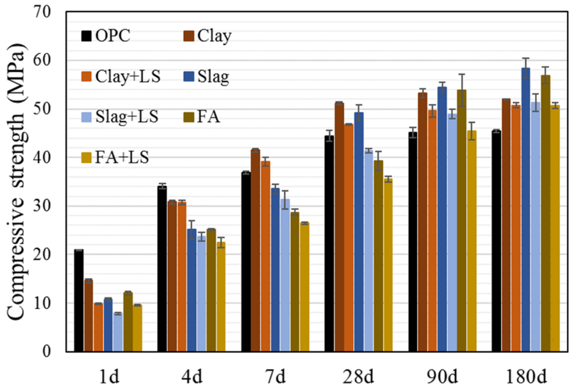

Figure 4. Comparison of strength development in binary and ternary mixes of Portland cement with either calcined clay, slag or fly ash without and with limestone [44].

The most common way to assess the reactivity of SCMs is so called “strength activity index tests”. The best example of such a test is ASTM C311 [45] in which a mortar with 20% SCM addition should achieve more than 75% of the reference strength. There are several problems with such tests. The main problem is that as the mortars are mixed to a constant workability, the water to solid ratio will change. It is claimed that this represents the reality in the field, but a well-designed concrete mix will have very different flow properties from a mortar, especially in the case of the ASTM test where the sand prescribed is very fine. A second problem is the variability of the reference cements used. It is sometimes assumed that relative strengths should be similar even if absolute strength values are different, but this is not the case. In [46] by RILEM technical Committee TC-267 TRM 10 different SCMs were tested with 6 different cements (all sold under the designation CEM I 42.5R). The relative strength varied in some cases by more than 100%. In this study the blends were made at constant water to cement ratio with a substitution of the CEM I by SCM of 30%. It should be noted that the relative strength of the quartz blends (quartz is assumed inert) is just over 30% lower than the reference cement, a roughly 1:1 strength reduction to substitution level. It is therefore clear that almost any substituent can meet the 85% threshold for relative strength at the 20% substitution level in the ASTM standard unless it has a very negative effect on workability and so induces a big increase in the water to solid ratio.

The R3 test (rapid, relevant and reliable) was developed to avoid the issues discussed above [47–49]. Here chemically pure Portlandite is used to react with the SCM and a small amount of KOH, K_2SO_4 and limestone are added to better simulate the solution composition existing in a typical cement. Measurements of strength are inherently complicated by issues of particle packing, casting and compaction. In the R3 test the heat evolved or the water combined in hydrate other than Portlandite are used as direct measurements of the degree of reaction of the SCMs. The R3 test shows good agreement with the compressive strength across a wide range of materials and has now been adopted as a standard by ASTM C1897 [49].

This new standard marks a big step forward with the estimation of reactivity, but it still takes up to 7 days to get a result. Therefore, the development of even more rapid methods to assess reactivity would be desirable, especially in the context of controlling the quality of processed SCM (such as calcined clay) and assessing the quality of individual batches of SCM like fly ash, or uncalcined pozzolans.

4.2 Increasing early strength

As seen in Figure 4, many blends, even with only 50% clinker can reach good strengths in the long term, but usual construction practice means that there are also requirements for minimum strengths at 1-3 days to allow demoulding operations and not slow down the construction process. Therefore, early strength is often the main factor limiting the level of clinker substitution. For this reason, there is considerable interest in increasing early strengths, which are controlled mainly by the reaction of the clinker, and particularly the alite component.

Before looking in more detail at ways to improve the clinker reactivity, it is interesting to consider why the rate of reaction slows so dramatically after the first day.

Figure 5 shows a typical heat evolution (calorimetry) curve for a Portland cement.

Setting and the start of strength development are brought about by the main reaction of alite between a few hours and about one day.

About 50% of the alite reacts during this main peak.

Superposed on this main alite peak is a subsidiary peak corresponding to the main reaction of the aluminate and ferrite phases; up to 100% of the aluminate phase and around 50% of the ferrite phases react in this peak.

There has been considerable research into the reasons for the slowdown in reaction rate of alite after about 10 hours (at 20°C). These are discussed in detail in [11]. Contrary to previous assumptions, it does NOT correspond to the onset of diffusion control. Instead, the weight of evidence indicates that its origin lies in the growth of the C-S-H phase.

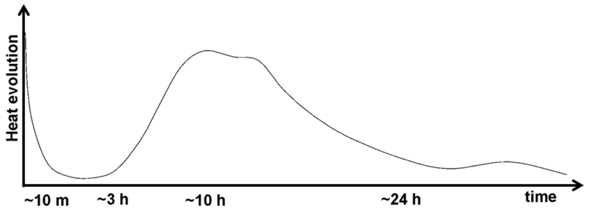

Figure 5. Typical heat of hydration curve for a Portland cement at 20°C.

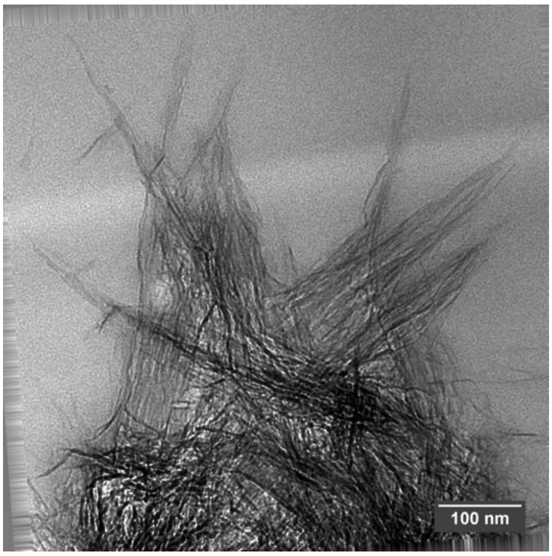

Figure 6. TEM micrograph of C-S-H, showing sheet like structure within "needle" like growth.

C-S-H is now known to be nanocrystalline (rather than amorphous) and to have a sheet-like structure based on a highly defective tobermorite (see figure 6). At the end of the induction period these sheets agglomerate and grow out from the surface of pre-existing solids (alite, but also other surfaces, such as quartz and limestone). These spiky agglomerates have been referred to as needles [50].

These needles initially grow fast, but after they reach a certain length, the rate of growth slows dramatically and this leads to the deceleration in reaction rate [9, 50]. Consequently, there are fundamentally two ways in which the amount of reaction in the main heat evolution peak can be increased:

- increase the amount of surface on which the "needles" can grow
- increase the length to which the needles grow, before the rate of growth slows down.

4.2.1 Increasing the surface available for growth

The easiest way to increase the surface for the growth of C-S-H is to grind the cements finer. However, this has the downside of increasing water demand (water needed for a given consistency) and also the energy needed for grinding. However, in multi component blends the clinker is only one constituent and the water demand can be maintained at reasonable levels, by grinding and blending strategies which maximise the clinker component in the fine fraction, while keeping the overall particle size distribution similar. In order to optimise the relative particle sizes of the different components, separate grinding followed by blending will often give better results [51]. The use of grinding aids is another important factor in obtaining good particle size distributions with the least possible energy.

The other strategy to increase surface area is to introduce fine particles. Limestone is particularly effective as a surface for C-S-H nucleation [52]. In [53] it was shown that if limestone is fine enough, similar strength can be obtained up to 7 days, even with 20% replacement of clinker by limestone.

Another strategy to promote the nucleation of C-S-H is the use of seeding discussed further in section 6 on admixtures.

4.2.2 Increasing the critical length for fast growth

The original work, identifying the critical length for fast growth [9] arose from a study of the effects of zinc doping on alite. It was found that a small percentage of zinc in alite led to longer needles and higher degrees of hydration during the main heat evolution peak. This impact of zinc on the growth of C-S-H needles has been confirmed subsequently [10]. Unfortunately, it is not easy to translate the beneficial impact of zinc from alite to Portland cement. During the clinkering process most of the zinc goes into the liquid phase, where it increases the likelihood of amorphous aluminate and ferrite phases forming, whose reaction is difficult to control, and little zinc is left in the alite phase.

In fact, comparison of the hydration of pure alite and Portland cement, indicates that calcium sulphate and possibly alumina also enhance the hydration during the main heat evolution peak [54,55]. This indicates that there are more factors behind the optimal adjustment of the calcium sulphate addition (optimum gypsum) than just the correct control of the reaction of the aluminate phase.

4.2.3 Role of alkalis

Since the 1970's it has been shown that additions of alkali can increase early strength [56]. Unfortunately, alkali additions also have a negative influence on later strength and the cross over from positive to negative effect may occur after only a few days. An important question, still to be answered, is whether it is possible to improve early strength without negative consequences for the long term.

Early hypotheses for poor later strength revolved around a less optimal packing of hydrates in the microstructure, but such hypotheses are not supported by the experimental evidence, which indicates that at the same degree of hydration [57] the materials with alkali have, if anything, higher strengths, but they have a lower degree of hydration in the long term. Ongoing work indicates that this may result from the fact that alkalis lower the water activity.

Based on this discussion the following areas for research can be identified as promising:

- improved grinding, blending strategies, including grinding aids. However, such aspects are difficult to study under laboratory conditions
- better understanding of factors controlling C-S-H growth
- better understanding of the interaction between the alite hydration and the sulphate and aluminate phases during the first days.

4.3 Longer term strength development

In the study of hydration kinetics, the mechanism controlling reaction after one day has been sadly neglected. Between 1 and 28 days a typical concrete develops about 75% of its design strength. Until recently it was widely assumed that after the first day or so, kinetics are controlled by diffusion through a thickening layer of hydrates around the cement grains. However, the study of hydration at different water to cement ratios shows that this assumption is certainly incorrect. In the work of Ouzia [58], the hydration of the same alite was studied at w/c 0.35 and 0.5. At a certain point the cumulative heat curves suddenly diverge, with hydration continuing at a higher rate for the higher w/c ratio. This clearly contradicts the hypothesis of diffusion control, as at a higher degree of hydration the product layer will be thicker and so the rate of hydration should be lower.

These results also highlight the importance of the w/c in controlling kinetics after the main hydration peak. This is related to the way the filling of the porosity by solution develops. In a sealed system, which is close to the practical case, as soon as the cement paste sets, gas filled voids will develop due to the overall reduction in volume on hydration (chemical or Le Chatelier shrinkage). As hydration is a through-solution process, hydrates can only form in pores filled by solution. As hydration continues the maximum size of the solution filled pores becomes smaller, reflected by the decreasing internal relative humidity. At a relative humidity of 90%, the maximum size of solution filled pores is around 10 nm. At the same time the saturation of the solution controls the smallest pores in which hydrates can continue to form. These two constraints are responsible for the dramatic slowing of the rate of reaction after a few days [59, 60].

Nevertheless, it seems that hydration does continue at a very slow rate. It is suggested that this slow, on-going hydration, which may continue for years, is due to the growth of hydrates in a water film on the otherwise gas filled pores [60].

In order to achieve good long-term performance, it is important to have a dense microstructure with limited porosity. Control of water to cement ratio is clearly the prime factor in achieving this, but (as discussed further in section 7 on Durability) the different ingredients in a blended system may contribute differently to densifying the microstructure and this needs to be further studied to obtain the best materials from the point of view of both early and long-term performance.

C. Composite cements based on Portland clinker - Priority research topics & key questions

Topics	N°	Key research questions to be solved
Low clinker cements	9	Develop reliable and rapid reactivity tests for SCMs
	10	Model the sulphate-silicate-aluminate-alkalis balance to understand the hydration-rheology link with high SCMs content binders
	11	Enhance hydration in main peak, for example by: understanding limitations of C-S-H growth and impact of alkalis
	12	Understand the long-term behaviour: reaction limitations and performance
	13	Extend range of clays & carbonates and improve early age strengths for calcined clays/filler/clinker binders
Grinding & Blending	14	Develop more efficient mills, blending techniques to optimise the particle size distributions of the different components in multicomponent blends

5 Concrete

If cement is the key ingredient, concrete remains the main end product. This material has become, in the span of a century, the backbone of our civilization thanks to its good mechanical performance, durability and extremely low cost. The downside is that enormous amounts are now used each year resulting in a significant global CO_2 footprint. Most pressure in recent years has been on CO_2 reduction at the clinker and cement stage.

The issues related to decreasing the clinker content in multicomponent blends have been discussed in the last section. However, gains made at the cement level may be more than wiped out at the concrete level as shown in Figure 7 [61].

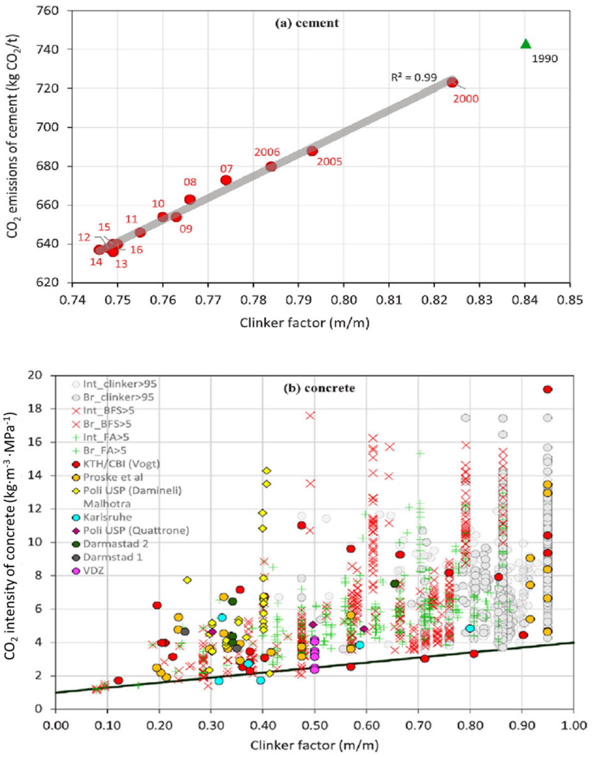

Figure 7. Correlation of CO$_2$ emission/intensity with clinker factor in a) cement and b) concrete, reproduced with permission from [61]. CO$_2$ emissions and the clinker factor are linearly correlated whereas this is not the case for concrete due to the large variety of possible mix designs. The black line in Figure (b) represents what could be technically achieved without considering rheological properties. Readers are referred to the original publication for more details.

One can see that while the impact of the clinker factor correlates linearly with associated CO$_2$ emissions for cement, the relationship (in kg.m^{-3}.MPa^{-1}) is far less clear for concrete.

The lower back line shows that if the concrete is well designed the savings in the cement can be translated to concrete, but that poorly designed concrete may have embodied carbon content more than 4-5 times this ideal!

The main challenge at the concrete level is to reduce the amount of cement per unit volume, or more precisely the amount of clinker. The obstacles to reducing cement content are not only technical, but also concern questions of incentives, economics, norms and knowledge transfer. Here we try to identify where there are still research questions to be addressed.

Range of concrete types

Concrete is not a unique product; a whole range of formulations are available to give strengths from less than 10 MPa to well over 100 MPa. Nevertheless, in Europe, as worldwide, the overwhelming majority of concrete used (>80%) has a design strength in the range 25-35 MPa. One of the main advantages of the European concrete markets is that most of the concrete is produced through the ready-mix plant network, which is, in many areas, often dominated by a few large companies. This should make progress towards lower carbon concrete easier than in parts of the world, such as India, where the majority of concrete is produced on site from cement in bags. As discussed in [20] the sale of cement in bags leads to much higher wastage rates and so wasted CO$_2$.

5.1 Importance of paste volume / aggregate grading

Provided that the concrete can be well placed and compacted, reducing the volume of paste has numerous advantages: reduced risk of thermal cracking, shrinkage, cost & environmental impact, and improved durability.

The most effective way to reduce the paste volume is to optimise the aggregate granulometry. It has been well appreciated since the early days of concrete technology and the studies of Féret and Bolomey over 100 years ago showed that the use of a range of aggregate sizes allows smaller aggregate to fill spaces between large ones and minimise the remaining volume to be filled by paste. We do NOT think that more research is needed on this. The practical tools developed by Bolomey, De Larrard [62], Andreasen, etc. work very well. Unfortunately, this is probably not an area where computational models can make a significant contribution due to the range of typical aggregate sizes from sub mm to tens of cm. If aggregates are digitised, the number of voxels scales as cube of size and it is only practical to cover size ranges of about 1:5 not 1:1000.

5.2 Importance of workability

Almost all concrete has to meet criteria on workability / placeability as well as criteria on strength (and maybe also durability). These demands are somewhat antagonistic, as simplistically adding more water improves workability, while lowering strength. However, this interplay has become more complex in the past few decades thanks to advances in admixture technology.

Unfortunately, the European norms for concrete were conceived at a time when admixtures were not so effective and link a maximum water cement ratio – necessary to achieve the required strength and durability, with a minimum cement content to ensure good workability without admixtures. For this reason, a large fraction of concrete in Europe uses very little or no admixtures and could probably be made with significantly less cement (so less CO$_2$) with the same or better performance.

Rheological difficulties may become more marked as the volume of paste decreases. This all indicates that an important research area is improvement in rheology especially for low volume paste volumes, where concretes have the tendency to be more sticky, flow more slowly (higher viscosity) and if not properly admixed, may have a tendency to segregate. Here again we stress the importance of having an optimized grading curve to achieve a good workability from the beginning and avoid therefore to solely on admixtures for flow corrections. This would reduce issues of robustness arising from material fluctuations.

In general terms, the description of the rheological behaviour of concrete is a multiscale as well as a multi timescale problem. Indeed, the proportioning of the various materials, known as the concrete mix design, includes physical macroscopic parameters (such as the maximum size of the aggregates, their shape and distribution for example) that will lead to a specific rheological behaviour of the formulated concrete. On the other hand, at the microscale (paste level) flocculation or dispersion of particles suspended in the pore solution for a given volume fraction will impact the rheological properties at the concrete level. Moreover, these processes of flocculation and dispersion dominate at short timescale while the overall hydration process irreversibly leads to the transition of a granular fluid to a fully percolated solid over a longer time frame [63]. This is discussed further in the section on admixtures below.

5.3 Sand and aggregates

The aggregate sector is the largest non-energy extractive industry with a capacity in Europe of around 3 Gt/y [64]. Minimal processing is required to achieve the different size classes required for concrete production and therefore the CO_2 footprint associated with these materials is minimal. Since sand and coarse aggregates constitute the largest material fraction in concrete, this contributes to the relatively low CO_2 footprint of a cubic meter of concrete.

In recent years, various publications in the media have reported that sand is considered as the third scarcest resource worldwide after oil and water. At the European level, it seems that this scarcity is mainly due to the difficulty to access sources that are economically viable or because legislation prohibits extraction at some locations. The authorization to open a new quarry is becoming more difficult to obtain in densely populated areas, where such industrial processes are usually not welcomed by the local population.

The scarcity of natural river sand, where particles are well rounded, pushes towards the increased use of fines from crushed aggregates (often called manufactured sand), which may require some reformulation of mix designs. Furthermore, less optimal aggregate sources may contain impurities such as clay minerals or coarse aggregate coatings. The negative impact of these impurities on the concrete workability is well documented [63, 65–68].

5.4 Conclusions on concrete

It is clear that the concrete industry has the potential to reduce its amount of clinker per cubic metre of concrete and significantly decrease the CO_2 footprint of the concrete sector. Today, since the CO_2 pressure is essentially put on the cement industry, there is no constraint on the maximum content of cement per cubic metre of concrete and the cement used in concrete may consequently be (much) higher than necessary.

Low paste concrete represents an effective way to lower the clinker content per cubic metre without negatively impacting its compressive strength and with the benefit of lower shrinkage, reduced thermal cracking and the same or better durability. This will however come at the cost of workability and it is therefore crucial that improvements on admixture technology in conjunction to proper mix design are made to facilitate their ease of use.

In the case of certain applications (e.g. self-levelling or compacting concrete) where high volumes of paste are necessary, one should find ways to decrease the clinker content as for example by the use of blended cement with higher replacement rate or by the addition of filler material. These options may result in slower strength development, where ways to accelerate hydration kinetics would be desirable as discussed in the previous section. Furthermore, it should not be forgotten that lowering the water to cement ratio, facilitated by the use of modern admixtures, will also improve the rate of strength development at high levels of clinker replacement.

Perhaps most important is to avoid strength development specifications that do not reflect the real speed of construction and overshoot the structural requirements resulting in a waste of material consumption.

D. Concrete - Priority research topics & key questions

Topics	N°	Key research questions to be solved
Low cement content	15	Develop mix-design methodologies for concrete with low cement or low paste content to improve workability and early-age strength robustness
Poor quality aggregates	16	Find ways to mitigate the effects of using poor quality sands, containing too many or not enough fine particles and/or clay.
2 other questions regarding Concrete digitalization, N° 17 and 18, are presented in Chapter 9		

6 Admixtures

6.1 Research needs in superplasticizer technology: polycarboxylate ether copolymer (PCE)

As mentioned previously, there are important needs to improve and better control the workability of concrete. With respect to superplasticizers, it is important to avoid unexpected variations in dosage that could result in undesired retardation and extra cost.

Due to their success on the application side, superplasticizers have received much more dedicated research than any other admixtures. This ranges from the comprehension of their adsorption behaviour [69, 70] to their mode of action [71–73] through their impact on hydration kinetics [74, 75]. A subject that has been the focus of recent research deals with the so-called “PCE-cement incompatibility” [76, 77] which may be even more exacerbated by low paste concrete. This robustness issue originates from organo-mineral interactions between PCEs and early aluminate hydration products which as consequence induces fluctuations of the rheological behaviour as a function of PCE dosage. Studies have focussed on the consumption of superplasticizers (SPs) in the AFm phases and it has also been reported that ettringite can be modified by the presence of PCEs [78–81]. Impact of SCMs on this early fast reaction is also an area that hasn't really been tackled. The fact that these interactions happen during the first minutes, if not seconds, of hydration makes its study experimentally challenging. However, new concepts, such as non-classical nucleation theory [82], may bring fresh insights.

An often-overlooked parameter is the polydisperse nature of PCEs. Such heterogeneity can arise from the synthesis method (free radical copolymerization (FRC) vs polymer analogous esterification (PAE)) and within each method, from the synthesis route applied as shown in [83]. Such polymer reactions result in a cocktail of polymers having both variations in grafting densities and masses especially with the FRC route which is the main industrial route for PCE production. At present, we are still unable to properly characterise these two parameters simultaneously. This implies that targeting the performance of PCEs obtained through the FRC method is essentially empirical or at best developed through the help of design of experiment (DOE). A better characterization of such polydisperse cocktails, or synthesis methods which reduce polydispersity, could help in defining which molecular structures may preferentially adsorb and interact with specific surfaces and further optimise this class of admixture.

Nonetheless to be effective such knowledge requires characterisation methods to determine where different molecules adsorb during the course of hydration or in other words being able to measure the spatial-temporal evolution of the competitive adsorption of organic molecules present in the pore solution. Competitive adsorption between different polymer structures remains a relatively unexplored field in cement hydration [74, 80, 84]. The few studies which have been made indicate that competitive adsorption is not only the result of the affinity between the adsorbing molecules and the substrate but also a function of surface coverage.

Cross-polarisation NMR techniques appear to be a promising method to determine the interactions between molecules and substrates. Such techniques have been used to study the spatial distribution of sucrose during hydration [81, 85]. But, more knowledge of temporal evolution is required, along with a proper characterization of the interfaces on which these molecules adsorb. Such studies would be valuable in developing PCEs or other dispersants adapted to specific phases. For instance, the work of Picker on C-S-H [86, 87] has shown that a proper selection of the anchoring groups derived from phase display experiments could lead to a modification of its growth. Similar approaches could be envisioned for other important cementitious phases, including high specific surface SCMs (calcined clays) and fillers, especially to reduce the viscosity of low CO_2 concretes having low clinker and high filler contents.

More generally, it remains extremely important to further characterise the hydration process and the potential interaction admixtures may have on the different processes such as dissolution, nucleation and growth. This constitutes a relevant area of research that needs to be pursued as robust admixtures are essential for the productivity at the concrete plant but also due to the introduction of new blends of SCMs with probably even higher substitution levels in the coming years. Furthermore, future admixture development will certainly need to go beyond the traditional PCE and have specific molecules that would interact preferentially with certain phases. In that respect competitive adsorption studies as well as knowing specific organo-mineral interaction are essential to develop new admixture formulation concepts.

Another important area, in which better understanding is needed, is the problem of "stickiness" (slow viscous flow), which can take place at low w/c ratio as well as for low paste concrete. Lowering the apparent viscosity of such concretes would improve their ease of use and improve their acceptance on the application side. For the time being, it is not clear what the factors responsible for this undesirable consistency are, nor is there an easy way to measure this property and it remains therefore difficult to properly tackle this issue.

Finally needs arise from the increasing use of non-optimal aggregate containing clay materials discussed earlier. Some clay minerals, even present at low level, may adsorb a significant fraction of the superplasticizer resulting in increased dosages. Various commercial products do already exist on the market, but demand for lower cost and more effective products is likely to increase.

6.2 Accelerators and strength enhancing admixtures

Accelerators have been used for decades in the construction business to help adjust concrete setting and hardening and facilitate the production process. They represent the second most important admixture type by volume after water-reducers/superplasticizers. The need for acceleration of setting or hardening will undoubtedly increase due to higher levels of clinker replacement in multicomponent blends. The requirements depend on applications and climate conditions.

For precast, medium/large scale building and infrastructure projects, prestressed and post-tensioned concrete, fast repair for roads or airport runways applications, the initial mechanical strengths (typically 4 to 12 hours) are critical for profitability through rapid demoulding – for early release of cable pre-stresses; for cables post-tensioning or for quick traffic opening. Cement fineness and temperature are the two most important parameters governing the rate of strength development, so it is common practice to use heating in precast plants (hot water, self-heating, electric resistance, steam injection, microwave, etc.). In such applications, accelerators can reduce energy costs and speed up stripping, handling and curing processes. For standard ready-mix concrete, accelerators are used according to the ambient temperature, the aim being to have roughly the same open time (two hours window between the cement-to-water contact and the concrete being poured) and mechanical strength around 16-24 hours, all year round.

In addition, the general trend of using "low-Portland clinker-content cements or concretes" generates new needs for improved early strengths, especially if curing requirements are not perfectly respected on site. Mix-design optimization usually takes care of final strength, but rheology and early strengths are still to be improved. Considering such blended cements, one major area of research deals with the activation of the SCMs that can be seen as the acceleration of their ability to react and participate in the phase assemblage. Apart from pH increase, new routes of activation still need to be identified.

The two current technologies of hardening acceleration are based on soluble salts and on seeding technology:

- salts: Except sodium thiocyanate and nitrate, the most relevant salts used as accelerators are based on calcium (chloride, formate, nitrate and nitrite). They present the following major drawbacks: sensitivity to the mineralogy of cement, toxicity, regulatory constraints (especially on chloride for reinforced concrete), and negative impact on long-term strength.
- seeding technology: This is the use of nanoparticles for acceleration purposes, providing additional surface area for heterogeneous nucleation and possibly pozzolanicity. Among the different candidates, C-S-H seeds appear to be one of the most efficient because they are ideal nucleation substrates for C-S-H products and their specific surface area is enormous [88, 89].

C-S-H seeds can be obtained by different routes (precipitation method, pozzolanic/hydraulic methods or sol-gel method) with potential additional specificities (mechano-chemical treatment, presence of polymers, ultrasound, and pH control).

The final motivation is to control the composition of the C-S-H (Ca/Si ratio) as well as their particle size. The latter is known as a crucial factor, while the former is still under debate and some clarification will be welcome.

Their specific drawbacks are mainly their lower efficiency at low temperature and with less reactive cements, and often, the increased demand for water or superplasticizer.

The use of polymers during the synthesis of C-S-H is indeed a very promising solution to control the size of the particles via the inhibition of the agglomeration and the Ostwald maturation.

The final C-S-H / polymer composite shows improved performance despite a sharp increase in costs, as well as reaction times.

Although the analysis of such composite materials remains complex because of their extreme sensitivity to drying and/or carbonation, further research on seeding technology should focus on mitigating these disadvantages.

There is also need for progress in the following areas, which are common to both the acceleration technologies discussed above:

- acceleration is not maintained over time, which means that the benefits of accelerators may be lost at longer ages, even within the first day Figure 8 [89]; an accelerator that could tackle this would undoubtedly be highly desirable
- accelerated concretes often exhibit excessive strengths at older ages (which is the main indirect reason why high strength concretes with significantly lower water/binder ratio are used today...); this "needed early but useless long-term strength" observation is becoming a rising issue as environmental concerns increase and this should be studied and mitigated, too.

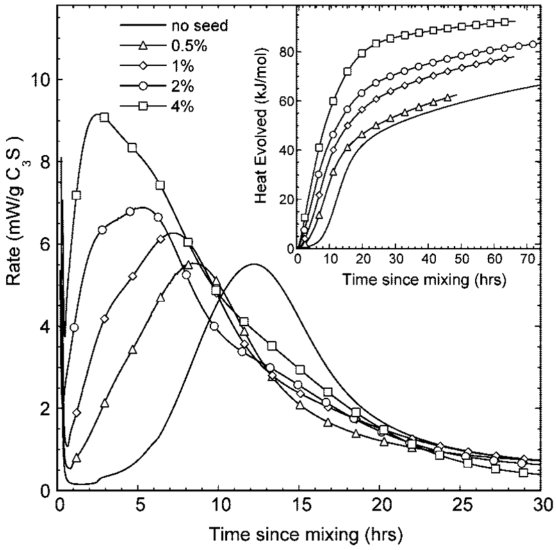

Figure 8. Effect of C-S-H seed made with a molar ratio Ca/Si of 1 on the early hydration kinetics of C_3S hydration. The seed amounts refer to the mass of solid C-S-H per mass of C_3S. Reproduced with permission from [89].

For special applications like classical wet shotcrete, bi-component 3D printing or 3D shotcreting, very specific setting accelerators are added at the nozzle. These accelerators are usually based on sodium or potassium silicate (liquid), aluminium sulphate (liquid) or calcium aluminate cement (powder). Rates of addition are usually high (5 to 7%) so the impact on the cost and final strength is significant.

Even if significant improvements occurred in the 2 past decades (mainly for safety and health reasons to avoid high pH admixtures) there is still room for optimization regarding cost, health, impact on final strengths and usage flexibility for prospective future solutions based on "setting-on-demand" concept.

6.2.1 "Nano" strength enhancers

In the last several years, a number of materials (carbon nano-fibres, carbon nano-tubes, graphene, graphene oxide, boron nitride nano-tubes, cellulose nano-fibres...) have been proposed and studied with claims about strength and cracking enhancement of cementitious materials, thanks to their dimension, the nanoscale pretending to bring a quantum leap to product performance [90–93]. The authors do not think this is a priority for further academic research.

Although some start-ups and academic papers claim outstanding performance (even though other academic ones are more negative), these claims have never been confirmed by industrial experience, in terms of strength or cracking control at a reasonable cost per m^3 of concrete. In addition, nano-materials are potentially carcinogenic, mutagenic or toxic to reproduction and their use is subjected to stringent legislation, and increasingly so, requiring specific handling methods that are outside of reach for our industrial operations or very uneasily dispersed in water.

Some improvements in terms of electrical conductivity have been indicated with some concrete containing carbon nanotubes or graphene, on very small samples, but the potential use of this enhanced feature would need to be economically and technically demonstrated before further research.

6.3 Drying shrinkage: shrinkage reducing admixtures and internal curing

Shrinkage reducing admixtures (SRA) have been available for several decades now and have proven to be effective at reducing drying shrinkage issues. However, their main limitation is the high dosages (and hence cost) required to become effective. The mechanisms behind drying shrinkage have been a source of debate for many years between the capillary pressure theory and the disjoining force theory [94]. Some researchers consider that only the theory of disjoining forces can account for the impact of SRA as well as the need for large dosages. The thermodynamic view of shrinkage can be summarised as a change of Helmholtz free energy upon drying where interface creation is compensated by deformation energy. Therefore, by reducing the energy cost for the creation of liquid gas interfaces, less deformation energy is required to achieve equilibrium for a given relative humidity (RH). Finally, since the ratio of water filled pores to exposed liquid-gas interface of a cement paste can decrease by about 6 orders of magnitude as the cement paste evolves from a water saturated state to a dried one [95], it can easily be understood why such high dosage are required, i.e. large creation of internal surface area upon drying due to the nanoscopic nature of C-S-H.

Internal curing strategies such as the use of superabsorbent polymer (SAP) aiming at modifying the rate of water removal (from external drying imposed by environmental conditions as well as self-desiccation) have also proven to be effective to mitigate shrinkage [96, 97] and more efficient than SRAs in terms of dosage requirements.

Novel strategies as well as cost efficient material would be desirable to ensure a wider use of such admixtures especially for binders with high substitution levels by materials such as pozzolan and calcined clay, which have a high specific surface areas. Improved durability performance through the mitigation of volume deformation and cracking by modification of water removal over time will for sure see an increasing demand in coming decades and be part of an overall strategy to diminish the environmental impact of concrete. However, in this respect, self-healing does not appear as a cost-efficient strategy nor does it solve the intrinsic issue of volumetric deformation.

6.4 Air entraining admixtures

Air entraining agent encompasses several technologies ranging from amphiphile molecules, organic microcapsules to gas forming materials. The comprehension of their mode of action and the required propertied of the formed pore network is well known and defined.

Their application is, however, not always straight forward due potential incompatibilities with other admixtures present in the concrete formulation. Moreover, impurities as well as some supplementary cementitious materials have shown some negative impact on the stability of the entrained air especially with amphiphile molecules which may require the development of more robust molecules.

Despite all the various factors mentioned above and the fact that this list far from exhaustive, generally a trial and error approach is needed obtain the desired network of entrained air bubbles for the concrete to become freeze-thaw resistant.

6.5 Corrosion inhibitors

Finally, we would like to add a short note on corrosion inhibitors, before discussing corrosion in the durability section. This is restricted to the use of admixtures added to the fresh concrete with the purpose to increase the service life of reinforced concrete. For a more detailed discussion of the subject, readers are invited to consult [98]. The main characteristics of such inhibitors should be to compete with aggressive ions such as chlorides at the steel interface and/or modify the local pH condition to prevent steel depassivation.

Ideally inhibitors should prolong the initiation stage but also decrease the rate of corrosion once initiation has ended. While there is good evidence that inhibitors can modify the length of the initiation stage, there is limited evidence that the efficacy extends to the period of active corrosion.

Here again, similar concepts as outlined previously involving competitive adsorption and interfacial properties are keys to come up with new effective solutions. Nonetheless, it should be stressed that corrosion inhibitors remain a second order parameter in the quest of preventing corrosion as the quality of the concrete is by far the most important factor.

E. Admixtures - Priority research topics & key questions

Topics	N°	Key research questions to be solved
Superplasticizers	19	Develop SP processes to control polydispersity
	20	Develop methods to determine spatial/temporal competitive absorption mechanisms, with phase specificity (including high specific surface SCMs)
Accelerators & strength enhancers	21	Improve early age strength of low CO_2 concretes without negative impact on workability or late strength evolution
Air entrainment agents	22	Understand and improve air entrainment stability with SCMs and impurities

7 Durability

Concrete structures are expected to last for many decades. Design service lives of 50 or 100 years are typical. Nevertheless, very few concrete structures are demolished because they are no longer serviceable due to durability issues. Most buildings are typically demolished to make way for new buildings.

The most important research needs with regards to durability are related to the need to demonstrate that new “low carbon” concrete can deliver the required service life.

The main requirement here is for reliable test methods which can demonstrate sufficient durability in a relatively short time, able to predict the field performance with a high level of confidence.

In almost all structures the question of ensuring good performance over the service life relates to the structural design “Eurocode”; the definition of exposure classes and the European Concrete Standard – EN 206.

Table 1 shows the exposure classes used in Europe, which identify 5 types of attack: carbonation corrosion, chloride corrosion; freeze thaws and chemical (including sulphate) and 18 sub classes.

Table 1. Exposure classes in EN206

Designation	Environment	No. of subclasses
XO	No risk or corrosion (inside buildings with low air humidity)	1
XC	Corrosion of reinforcement induced by carbonation	4
XD	Corrosion of reinforcement by chlorides other than from sea-water	3
XS	Corrosion of reinforcement by chlorides from sea-water	3
XF	Freeze-thaw attack with or without deicing salt	4
XA	Chemical attack	3

Together these make a very complex landscape to negotiate and it is well accepted that the situation today is not conducive to innovation or to the minimisation of environmental impact. While there are research needs (as outlined here), many of the issues militating against progress towards structures with lower embodied carbon are linked to questions of ingrained habits, policy, obtaining consensus between different stakeholders and reluctance to change. Some of these issues include:

- specification of concrete to the most severe exposure class in a structure, even when a majority of concrete may be in a much lower exposure class. For example, most of the interior concrete in a building would be in XC1 class, but a higher class, XC2 or XC3 may be specified due to the environment of some external concrete
- a link between maximum w/c (which generally is important to obtain the required performance) and minimum cement content (which is not) taken from concrete without admixtures (as highlighted in section 5)
- non-harmonisation of the concrete code, which leads to a huge diversity of permitted cement types and minimum cement contents in the different countries following EN 206.

For several years the sector has been aware of these issues and there are on-going discussions to move from purely prescriptive standards (specifying cement types, maximum w/c and minimum cement content, etc.) to performance tests which measure (for example) the resistance to carbonation or chloride ingress.

However, moving to performance based approaches is can be complex when rapid, reliable and relevant tests are not yet available.

The main degradation issues affecting durability of concrete are:

- reinforcement corrosion due to chloride ingress
- reinforcement corrosion due to carbonation
- freeze / thaw cycles
- alkali-silica reaction (ASR)
- sulphate attack.

These are listed in rough order of their importance in terms of field damage. Exact figures are hard to obtain, but issues relating to reinforcement corrosion probably account for around 90% of problems in the field, with chloride induced corrosion being overwhelmingly dominant. Freeze/Thaw cycles and ASR probably account for most of the remaining 10%.

7.1 Carbonation

From the point of view of moving to concretes with lower embodied CO_2, corrosion due to carbonation is the main limiting issue as almost all concrete is considered to fall under one of the XC exposure classes according to EN 206 and most concretes with lower embodied CO_2 emissions will usually carbonate faster than plain Portland cement. The rate of carbonation is dominated by the reaction of CO_2 in the atmosphere with calcium containing compounds, not only calcium hydroxide but the calcium oxide in all hydrates and anhydrous phases. Decarbonation of limestone to produce clinker is the main source of CO_2, so low CO_2 concrete will have less calcium oxide to react with CO_2 during use. This link between calcium content and carbonation rate is illustrated by the results in [99].

The major research question is therefore: how much can the clinker content of cement and concrete be lowered and still provide good service life with respect to reinforcement corrosion due to carbonation? The first question is how to measure carbonation rates in a short time. The only test currently accepted throughout Europe is to measure the carbonation rate for concrete stored at 60% RH, with atmospheric levels of carbonation, which takes at least one year. Accelerated tests, which are accepted in some countries (for example the Swiss standard [100] which uses 4% CO_2 concentration), can take several months and the concrete carbonated during such tests is only a few millimetres deep, which may not be representative of the “covercrete” protecting the reinforcement as a whole. This is one consideration which has impeded the development of accelerated tests. How can samples be prepared in a short time where the outer surface has a microstructure of field concrete carbonating over many years?

The issue surrounding testing is linked to the question of the extent to which the lower capacity of low carbon concrete to absorb CO^2 can be mitigated by the preparation of such concrete, particularly better curing and limitations on water to cement ratio. Resistance to gas flow has been proposed as a method of assessing the “quality” of a concrete with respect to carbonation, but such measures are made on non-carbonated concrete, whereas the penetration of CO_2, in reality, occurs through the carbonated zone.

These considerations make it clear that we need a better understanding of resistance to carbonation in low carbon concrete, how this evolves over the lifetime of structures and how it is affected by the process parameters: w/c, curing and surface treatments.

There is another, perhaps more important question, which has received much less attention up till now: *Is steel in carbonated concrete actually going to corrode in real situations?* As recently highlighted by Angst et al. [101] the internal relative humidity of concrete is critical. Corrosion in carbonated concrete only occurs at a significant rate when liquid water is present at the steel interface [102], which will be rare in the field in concrete with a reasonable cover depth. Further work is needed to well identify the situations in which active corrosion due to carbonation will occur and the other situations where it is very unlikely.

7.2 Chlorides

Chloride ingress provoking reinforcement corrosion is by far the major cause of poor concrete durability. Here, fortunately, the use of SCMs generally leads to improvements, with blended cements having higher resistance to chloride penetration. Here the main need is to better understand the mechanisms behind these improvements and integrate these into a predictive framework.

Conventionally the pore structure of concrete is regarded as the main parameter controlling the ingress of ions such as chloride, leading to the prescriptive standards based on control of water to cement ratio. However, blended materials at relatively high w/c ratios (~0.5) can have much higher resistance to chloride ingress, than plain Portland systems at much lower w/c (~0.3) Figure 9, [103]. It is emerging that other parameters play a major role, which are hidden behind what is usually termed “formation factor”. The formation factor is defined as the ratio of conductivity of the pore solution to the conductivity of the saturated cement paste or concrete containing that pore solution.

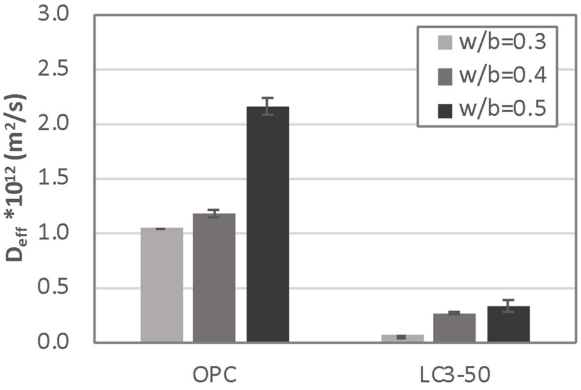

Figure 9. effective chloride diffusion coefficients for OPC and LC3-50 systems at different water to cement ratios adapted from [103].

This point is well illustrated by the study of Wilson comparing pastes of systems with different SCMs at different w/c [104]. Pastes were used to avoid issues due to the concrete formulation. The effective chloride diffusion coefficients of LC3 (for example) were around 10 times lower than the reference OPC, such that the D_{eff} of LC3 at w/c of 0,5 is still about 3 times lower than that of the reference OPC at 0.3. Such a big difference cannot be explained by changes in binding capacity or pore structure alone. Increased chloride binding is often thought to be the reason aluminosilicate SCMs (calcined clay, slag and fly ash) have improved resistance to chloride ingress [105].

While it is true, they generally contain larger amounts of calcium aluminate, AFm phases (monosulfate or nowadays more likely mono or hemi carbonate), which can immobilise chloride by forming Friedel’s salt, they contain less C-S-H due to the lower amount of clinker.

In [44] it was seen that there was little difference in chloride binding capacity of the blends shown in Figure 4 (section 4.1) at chloride concentrations typical of sea water. The decrease of pore solution pH in a blended system also seems to be important and this can be intuitively understood as there are less positive ions (Na^+, K^+) to counterbalance the incoming negative chloride ions. However, there appear to be additional factors which we think are linked to the movement of ions close to charged surfaces. After a few weeks the pore structure of concrete is dominated by narrow channels around 10 nm in size between the C-S-H hydrates, named *interhydrate* pores [95]. Many people talk about "tortuosity" increasing, but tortuosity, formation factor, etc. are terms defined from porous rocks to express the ratio between transport of ions in a material and transport of the same ions in free solution. Saying the "tortuosity" is correlated to transport is effectively a circular argument as the "tortuosity" is defined from the transport in the first place. Understanding better the transport of ions in small pores is clearly of considerable importance.

7.3 Alkali-silica reaction

As with chloride ingress, aluminosilicate SCMs (fly ash, slag, calcined clay, silica fume) are all effective at reducing the risk of deleterious expansion due to alkali silica reaction.

The expansion is mitigated by several factors:

- the use of SCM (as long as they do not themselves contain soluble alkalis) dilutes the alkalinity from the cement. This effect is generally rather minor
- SCM (both pozzolanic and slag) reduces the Ca/Si ratio of the C-S-H, which increases its capacity to absorb alkali and further lowers the pH of the pore solution. The capacity to reduce the pore solution pH is effective even if extra alkalis are added to the mix of the SCMs themselves contain soluble alkalis (providing this is not extremely high (above about 1%)) [106, 107]
- SCM containing alumina releases aluminium ions into the pore solution, which act directly on the dissolution rate of the aggregates. This mechanism is particularly effective in the case of calcined clays containing metakaolin [108, 109].

The main issue, and research need, is for reliable tests and predictive methods to determine the amount of a particular SCM in the blend which is needed to suppress alkali silica reaction (ASR) for a particular aggregate. The concrete prism test ASTM C1293 [110], is generally regarded as one of the best to determine aggregate reactivity.

However, in this method extra alkalis are added to the mix to counteract their leaching over time and it is not clear how these added alkalis affect the first two mitigation mechanisms listed above.

The group at LMC, EPFL [107] have pioneered a method of storing prisms in solutions matching the pore solution. However, experience with a wider range of aggregate and in more labs would be needed to establish this as a standardised method.

7.4 Freeze-thaw

An important durability concern in many Northern European countries is linked to freeze-thaw and its consequent damage on concrete resulting in costly repair and maintenance work. We can distinguish two types of damage due the exposure of concrete to freeze-thaw cycles: internal damage and salt scaling:

- internal damage occurs when water freezes and expands within the concrete pores and leads to concrete cracking
- frost salt scaling originates from the interaction between brine-ice and the concrete surface in the presence of de-icing salts and results in the flaking of the concrete surface.

Extensive experimental research has been dedicated to determining the relevant parameters affecting the frost durability of concrete and to developing adequate mitigation methods. For instance, the effects of concrete mix, water to cement ratio, concrete saturation, surface drying, type of de-icing salts, permeability and porosity of materials have been studied and the magnitude of damage associated with them has been identified.

Mitigation methods to reduce the damage likelihood were developed with air-entraining agents being the most practical and widely used method to increase the resistance to frost.

However, even in air-entrained structures, damage can still sometimes occur showing that air-void does not grant an ultimate protection to the structure, if the produced bubbles have neither the right size nor the right repartition within the cement paste. Having a certain quantity of entrained air is today necessary to get the right tiny bubbles (diameter <50µm) network, with a spacing factor (average half-distance edge to edge distance between 2 bubbles) below 200µm. This usually leads to a strength loss, which is detrimental to concrete and often implies to modify the concrete mix design and increase the environmental footprint. Research is needed to solve this issue, aiming at improving freeze-thaw resistance without jeopardising mechanical strength.

The mechanisms resulting in frost damage are still not clearly understood. The lack of a comprehensive understanding of the mechanisms involved in frost damage and the complexity of these physical, chemical, and mechanical processes hindered the development of predictive models and of reliable and relevant accelerated test methods.

Some physico-mechanical models have been developed to explain and quantify these phenomena at micro and macroscale.

The internal damage, can now modelled fairly successfully via the thermo-hydro-mechanical models [111].

Frost salt scaling remains however a difficult task. To-date two conflicting approaches offer explanations of the phenomenon:

- the glue-spall model [104, 112] attributes scaling to the thermo-mechanical mismatch between the ice and the concrete
- the cryogenic suction model [113] considers the frost salt scaling as a result of the uptake of unfrozen brine by ice crystals to form continuous ice growth in capillary pores.

These two approaches describe most of the important observations during a frost salt scaling experiment. Recent studies however indicates that none of the proposed theories can account for the full body of experimental observations reported in the literature, justifying the need for a more comprehensive experimental and modelling framework to better understand the frost damage mechanisms.

Notwithstanding, the extensive research effort into freeze-thaw damage, there are areas that need more research in the coming years:

- recent investigations within a Nanocem project [114] have brought new insights on frost salt scaling, revisiting the glue spall theory and showing that the ice microstructure plays a detrimental role in salt scaling. For instance, saline ice contains porosity which is referred to as brine pockets or channels.

  Based on thermo-viscoelastic analysis of ice/concrete bilayer materials, it is suggested that scaling is located at the level of the brine channels. Furthermore, the changes of these brine channels size and distribution affect the magnitude of tensile stresses which generate the scaling.

  This new way of viewing the frost salt scaling phenomena as a result of the evolving ice microstructure could explain the various experiment observations and could offer the opportunity to control the scaling by controlling the ice microstructure
- the lack of understanding of frost-induced deterioration mechanisms is strongly impeding the design of relevant testing methods. Various standards are being used in different countries, generating very diverse results. There is an urgent need to unify the testing approaches so that the results obtained in different countries and laboratories can be successfully exploited
- the freeze-thaw durability of concrete containing certain SCMs must be assessed. On one hand, air entrainment in slag-containing concrete is still forbidden in some countries like Germany (but not in many other parts of Europe) and the reasons need to be understood and clarified. On another hand, with the increasing efforts to reduce the CO_2 a new generation of materials is being developed, some of them showing a refined porosity (like calcined clay-containing concretes) which improves their durability to ions ingress (e.g. chlorides) but their durability to freeze-thaw and scaling needs to be confirmed.
- air-entrainment to resist frost always leads to strength loss. Used in particular applications (stiff, extruded or sprayed concrete, usage of high amount of slag), hollow microspheres or microfibers, which are deformable solid elements can replace the 4-8% entrained air to ensure good durability of concrete under freeze-thaw cycles, without jeopardising the mechanical performance. These microspheres are extremely small, hollow, highly resilient, tough but flexible, with acrylonitrile polymeric shells, providing stress relief zones for the expansion of freezing water within concrete and enhancing its long-term durability [115]. But, in order to try to generalise their use, research is needed to significantly reduce their dosage (3-7 kg/m^3) and cost.

7.5 Sulphate attack

The main issue regarding sulphate attack is that the test methods which exist do not correspond well to what happens in cases of degradation in the field [116].

Most test methods look at the expansion of small mortar prisms, under full immersion in a solution with sulphate concentration much higher than found in the field.

In contrast, the rare cases of poor durability linked to sulphate ions which do exist seem to be related to concrete partially immersed in soil. The deterioration seems to be concentrated just above the soil line and can be linked to the wicking of sulphate ions through the concrete – sometimes referred to as “physical” sulphate attack. In addition, extensive work in the EN standardisation committee has failed to identify a test method which has a good reproducibility between labs, let alone a proven relevance to field cases. Consequently, the present European standard is a hodgepodge of different country standards: all accept low C_3A cement, but the acceptance of slag or fly ash cement varies from country to country and newer SCMs (e.g. calcined clays) have not even been considered. This situation needs to be resolved.

F. Durability - Priority research topics & key questions

Topics	N°	Key research questions to be solved
Corrosion	23	Develop more relevant quick test methods and service life models to move from standards imposing minimum cement content to performance standards
Alkali-Silica reaction	24	Determine the SCM content optimum with quick relevant tests and address the risk of recycled aggregates
Frost	25	Develop a reliable scaling resistance test and establish a clear theory about scaling mechanisms

8 Recycling concrete more sustainably

Construction waste management is part of the European Commission’s ambitious Circular Economy Package. According to Eurostat [117], 819 million tons (MT) of non-hazardous construction and demolition waste (CDW) has been produced in 2018 in the EU alone. Recycling is one of the responsible ways of dealing with CDW. CDW yields multiple product streams that could potentially find varied applications. Concrete is one of the major constituents of CDW. Officially in Europe, about 130 MT of concrete is recycled every year. A very small share (roughly 5%) of this recycled concrete goes back into mainstream concrete. The rest is either used in road sub-base or goes to landfill.

Better CDW management is important for a sustainable circular economy. While there are opportunities for effectively utilising CDW, there are challenges primarily related to sustainable sourcing and sorting, technical obstacles (e.g. the need to increase the paste content to offset the water absorption which is detrimental to the CO_2 footprint), client acceptance, standards, policies and legislation. Ready mix concrete returned to the plant also needs recycling.

An important obstacle is the cost of logistics. Cooperatively establishing circular recycling platforms at centrally accessible locations seems to be a way of dealing with products generated through CDW recycling. In order to ensure a constant supply, the systems need to be able to predict the inventory of recyclable buildings and infrastructure.

The Life Cycle Assessment (LCA) and Life Cycle Cost Assessment (LCCA) can help to assess the environmental and economic merits of recycled aggregates versus natural resources. In turn, this will help in choosing the best technology to deal with CDW, improve its management and select techniques which could be tested for industry scale-up.

Concrete is made up of aggregates and hydrated cement paste; the separation of the two is the main challenge to deal with when it comes to recycling concrete.

Recycled concrete may be used in following ways (from most common today to most novel):

- materials for roads, (commonly regarded as down cycling)
- masonry sands
- recycled coarse aggregate
- recycled fine aggregate that is intentionally produced and not just as by-product of crushing
- fines used in the production of clinker and/or cement.

When considering recycled concrete, two products can be of high relevance for more valuable concrete applications: coarse aggregate (typically > 5mm) and fines (typically < 5mm). Recycled fines, constitute roughly half of recycled concrete, in non-optimized crushing processes and may be very heterogeneous.

The higher surface area of the fine aggregates and sand than the coarse fraction have high volumes of hydrated cement (or binder) attached to their surface. The fines could potentially be used to produce clinker or cement with recycled content (alternative raw materials, supplementary cementitious materials - especially if carbonated). The main research needs are to reduce the fines generated during crushing and/or make better use of them.

8.1 Better separation of aggregates from paste and mitigation of water absorption

Due to the adhered mortar, the mechanical and physical properties of recycled aggregates are usually worse and more variable than those of natural aggregates. The main properties affected are density, absorption (higher and more prolonged) and porosity, these may cause inconsistent concrete performance (fresh state, strength and durability). The amount of absorbed water depends on the abundance and continuity of the pores within the particle, whereas the kinetics of absorption depends on the size and continuity of these pores. Research is needed to define the kinetics of absorption of aggregates and estimate adequately the quantity of water needed for the concrete mix, but also to create a reliable model for the specified time for the whole saturation of recycled aggregates depending on the concrete types and recycled concrete aggregate types.

The water absorption issue in the finer fraction of recycled concrete is much more challenging. A crucial point is the use of crushers that are designed for crushing rocks with substantially higher compressive strengths (60 - 350 MPa) for crushing recyclable concrete (barely in the range of 15 - 30 MPa, average). Developments in crusher technology (smart crushers) can better separate the coarse aggregate and should facilitate reuse in concrete [118]. Other promising process avenues, but which need additional research, development and scale-up, are the following:

- better and more cost-effective separation technologies, to avoid unwanted fractions for concrete applications (and find solutions for the rejected waste such as plasterboard, wood chips or bricks);
- soft and adapted mechanical rubbing for paste separation from the aggregate;
- carbonation of the recycled aggregates (fine and coarse), to reduce absorption and help separation from the paste [119];
- characterisation of waste concrete before it enters processing to dynamically and flexibly adjust the process parameters.

While reuse of coarse aggregates is well established, there remains the issue of the fine fraction (fRCA) consisting of sand and paste. There are examples of concrete made of 100% recycled aggregates.

The performance of these are encouraging with respect to durability. However, most codes restrict and even prohibit the use of the fine fraction of recycled aggregates in concrete production, due to a perception of unsatisfactory performance. However, a critical review of more than 170 scientific publications concludes that there are no general limits on the use of fine recycled concrete aggregates (fRCA) in the concrete mix, the optimal percentage of fRCA being found to be 25%, which had no effect on the strength of concrete [120]. Recent and on-going progress in both admixtures (in order to get adequate concrete workability without jeopardising the long-term properties) and on-going mix design research can and will help. Furthermore, research should focus on finding solutions (additives or special treatment of fines) to minimise the detrimental effects on compressive and tensile strength, modulus of elasticity, shrinkage, carbonation and chloride penetration. Research should go beyond the question of fines being usable or not and should focus on how we can improve their quality to close the loop of the circular economy. Research should target advanced recycling technologies that allow adequate separation of sand and hardened cement paste. This will facilitate the reuse of the sand fraction for concrete production.

8.2 Carbonation of recycled aggregates as a carbon capture usage & storage approach

The fine fraction contains a large amount of cement paste, which is largely uncarbonated. One relatively straightforward way to benefit from the content of uncarbonated CaO is to use fines as a raw material for clinker production as already mentioned in section 2.

There are potentially other ways to exploit the potential of this CO_2 sink. Recently, it has been suggested that the fine aggregates from recycled concrete can be carbonated and used as an alternative SCM for concrete production [121, 122].

Recycled concrete fines carbonate easily due to their high surface area, so carbonation by the direct use of waste gases from the cement plant is possible, which means CO_2 capture and mineralization in a single step. While scientifically this appears attractive, the co-location of such facilities, infrastructure for carbonation, process speed and transportation costs still remain challenging. The carbonation mechanisms of the recycled cement paste and the behaviour of the carbonated material in reacting cementitious matrices should be better understood. Such research will provide the fundamentals for industrial process optimization and acceleration.

8.3 Conclusions on Recycled Concrete

In a developed region such as Europe, the amount of concrete being demolished is of the same order of magnitude as new concrete. Improvement in concrete recycling is a must for the industry. Research is needed to develop knowledge about feasibility, applicability, durability and environmental benefits.

There is then a need to look at policies, legislation, LCA and LCCA rules, codes and standards in order to increase the quantity of coarse and fine recycled aggregates allowed, based on concrete strengths and exposure classes.

In addition, there is considerable potential to use recycled concrete fines, as raw material for clinker or (after carbonation) as an alternative SCM at the cement or concrete level.

This could make a major contribution to the circular economy.

G. Recycling - Priority research topics & key questions

Topics	N°	Key research questions to be solved
Recycled concrete aggregates	26	Develop cost-efficient solutions to block their porosity and absorption
	27	Improve, accelerate and reduce the cost of treating recycled aggregates by carbonation
Recycled concrete fines	28	Determine the most efficient process to treat RCF in order to produce reactive SCMs

9 Digital tools in concrete construction

9.1 Digital tools for design optimisation

Structural engineering faces significant challenges today to improve the sustainability of construction. Tomorrow's design will go well beyond conventional structural analysis. The European design approach should address the challenges of sustainability, including its social and environmental impacts.

Structural engineers with the help of materials engineers should be responsible to offer the society the best possible solutions.

Current structural design practice is predominantly concerned with minimising a building project's construction cost and timeline, while ensuring that the structure meets the criteria for safety and serviceability. Due to the environmental and economic challenges, new policies will be required to help promote the economic incentives for sustainability.

The construction industry is in general quite conservative and often reproduces similar designs in its projects. In addition, material choice tends to happen late in the process, usually after the design stage. Ideally digital tools could provide a seamless integrated process spanning from conception/design to fabrication, which would:

- customise the design to fully achieve the required performances
- take into account the project specificities in order to avoid over-design
- shift the selection of materials to an earlier stage so that the design can fully integrate their performances.

Digital innovations could lead to: topology optimization (e.g. bridges and complex building shapes)[123], fully in compression structure design for optimised slabs and floors thanks to 3D-printed formworks leading to savings of material [124], the ability of robotized construction to deposit the right material exactly at the right place instead of pouring conventional rectangular shapes (just because it is easier).

Globally, significant reduction of material usage can be reached, with corresponding CO_2 savings up to around 50% [125, 126]. Studies have even proposed that novel design approaches can lead to buildings with an embodied carbon an order of magnitude lower than conventional building structures today, by choosing low carbon materials and optimising the structural efficiency of buildings [127].

Future research programs must develop a more holistic view of engineering design. Achieving more sustainable design will require a concerted effort from researchers and practitioners to reduce material consumption, and to maintain good quality of life for people at affordable prices and environmental impact. Structural design concepts should as well consider the interaction of the new structures with time including the modularization of the structure to accommodate change over time. Concrete material scientists should promote the adaptability of their product. Designers should include new recyclable materials with improved durability, and so reducing necessary repairs and replacement.

A key-digital tool to help to achieve these targets will be the Building Information Modelling (BIM) approach. It has been possible for a few years to find BIM tools with an integrated Life Cycle Analysis (LCA) tool plugged in. But it is today used once the design is done, or during (or even after) the construction. The evaluation and optimisation of life cycle performance of buildings in early design stages are clearly needed but the application of LCA is however restrained by some important uncertainties linked to the design and the material decisions at this stage. Some academic studies recently showed the possibility of environmental impact assessment using Building Information Modelling [128–130] which hopefully will in a near future stimulate the use of an adequate LCA tool for the pre-design phase, plugged into the most used BIM tools.

Other potential important opportunities for digital tools in concrete-based construction are to develop sensors and Artificial Intelligence solutions to improve the global quality and robustness of:

- concrete mix design methods
- traceability
- concrete production
- concrete transportation
- field monitoring.

9.2 Digital construction: concrete 3D printing and other digital tools

Digital construction may also contribute to saving quantities of waste (e.g. moulds), while allowing total freedom in customization thanks to its integrated process from design to manufacturing.

One must however recognize that this new technology will give rise to a rather limited number of applications and not immediately.

This technology could lead in the future to some CO_2 reduction for complex construction projects, if academic R&D focus only (and maybe in a more limited number of universities than today) on the following aspects of concrete additive manufacturing:

- develop alternative design solutions to make more (performance) with less (materials), as discussed generally in the previous paragraph. Some authors have highlighted the primary influence of the design for efficient digital fabrication, with a need to focus on structural optimization and to combine it with multi or increased functionality [131].
- As most academic research on digital fabrication focuses today on walls and columns, other building or infrastructure applications and functional integrations must also be studied (slabs, floors, insulation, reinforcement...);
- develop lower carbon footprint materials for digital construction, acknowledging that today, most digital cementitious “ink” mixes have higher paste contents using high clinker content cements, which may offset the benefit of material-efficient designs [132].
  On one hand, it is needed to develop low carbon mixes with low carbon binders, on another hand it is crucial, each time it is feasible, to develop materials solutions and processes to move from printing paste or mortar to “real” concrete containing coarse aggregates, allowing a dramatic reduction of the paste content, hence of the carbon footprint. Additionally, it is important that these future low carbon 3D printed concrete will allow a consistent and robust production while building in a varying environment;
- improve and develop the 3D shotcreting approach allowing easy-to-embed reinforcement [133].

Overall, we feel the potential of digital construction lies much more in the development of tools to optimise the design process, improve concrete production and construction than in 3D printing per se.

In the field of 3D printing there is probably more potential in 3D printing formwork than the concrete itself, given the difficulties to lower paste content and incorporate reinforcement.

D'. Concrete (digitalisation) - Priority research topics & key questions

Topics	N°	Key research questions to be solved
Concrete digitalisation	17	Develop tools to improve concrete mix design methods, traceability, concrete production & field monitoring. For example sensors and Artificial Intelligence.
	18	Make Digital Fabrication carbon friendly: with low carbon binder, use of real concrete with coarse aggregates, 3D-shotcreting to embed reinforcement

10 Carbon capture use & sequestration: potential of mineralisation versus other forms of storage

Despite the potential CO_2 reductions which can certainly come from the research areas discussed in the rest of this paper, there is no such thing as zero $C0_2$ concrete. Even though traditional levers such as energy efficiency, clinker factor and alternative fuels can be pushed still further, CO_2 capture and use or storage (CCUS) will be a necessity in the coming decades to reach the 1.5°C increase scenario.

Various roadmaps indicate the need for CCUS to reach this target to be from 48% [134] to 36% in the most recent roadmap issues by the GCCA (Global Cement and Concrete Association) [135].

A more European angle to emphasise the importance of CCUS in achieving the 2050 goal is given in the Cembureau report "Cementing European Green Deal" [7], shown in Figure 10:

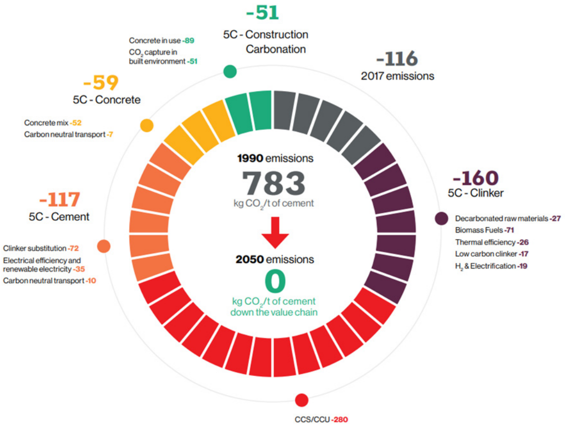

Figure 10. Levers to reduce CO_2 emissions from Cementitious Materials to zero from Cembureau report [7].

10.1 Carbon capture and use

For carbon capture, a cement plant can choose between two technologies depending on its layout:

- a post-combustion technology, like wet amine carbon dioxide scrubbers, dry sorbent-based adsorption process, membrane separation, cryogenic distillation, direct CO_2 separation (indirectly heating the limestone via a special steel vessel and enabling pure CO_2 to be captured in the preheater-calciner tower)
- or an oxy-combustion technology, where nearly pure oxygen is used at the burner instead of air, leading to a much more concentrated CO_2 flue gas and an easier way to capture CO_2.

The needs in terms of R&D for clinker CO_2 capture are numerous: increasing the capture efficiency while decreasing the cost, decreasing the energy consumption, upscaling to industrial size, assessing sorbent deactivation under realistic conditions, studying its impact on volatilisation of minor elements and on clinker reactivity.

Once captured, CO_2 can be used (refrigeration, welding, water treatment, greenhouse, medical, laser, fire extinguishers) and represents approximately 10 Mtpa (28Mtpa worldwide in 2018 [136]), to be compared to 117 Mtpa CO_2 emitted just by the European cement industry [137]. Hence an important part of the CO_2 has to be sequestrated, to avoid being released into the atmosphere.

Further R&D is necessary to develop new CO_2 markets, such as:

- e-fuel (mainly methane / methanol / ethanol), but the huge need for hydrogen may be a barrier;
- chemical/plastics (derived from methanol, hence with the same amount of energy);
- microalgae: better productivity than the other biodiesel sources but TRL still low and cost still high
- agricultural greenhouses to increase their productivity;
- storage in BECCS (Bio-Energy with Carbon Capture and Storage), extracting bioenergy from biomass, then capturing the carbon and storing it by geologic sequestration in depleted gas/oil reservoirs, saline aquifers or other sealed and safe underground cavities, for which cost must be reduced [138].

10.2 Carbonatable cements using CO_2

Mineralisation approaches to produce building materials could pave the way for both CO_2 use and permanent storage. The idea of acquiring concrete strength through CO_2-induced carbonation instead of water-based hydration sounds appealing.

Carbonatable cements are new binders that harden by reaction with CO_2 rather than reaction with water. In this way they convert CO_2 into stable solid carbonates. This CO_2 mineralization can store some CO_2 from the clinker production industry and therefore reduce the footprint of the final product.

It has been found that the compounds which work best with carbonation hardening are phases like, wollastonite (CS), rankinite (C_3S_2), and γ-C_2S [139].

These phases already contain less calcium oxide than the alite in OPC and so the CO_2 emissions to produce reactant materials are lower. When the CO_2 consumed in the hardening reaction is also taken into account global savings of around 50-60% CO_2 versus OPC for a concrete of the same strength are possible. One particular benefit of these binders is their reaction kinetics with CO_2 and strength gain versus OPC. After only one or two days, they achieve final strengths equivalent to OPC after 28 days and more.

Nevertheless, the carbonation has to occur in closed curing chambers under strict temperature and humidity conditions and features a rather low pH (<10), limiting the applications to non-reinforced concrete precast markets. Furthermore, these binders suppress or at least limit efflorescence issues due to the reaction of CaO with CO_2, which makes their use highly interesting in terms of aesthetics.

Future R&D on carbonatable binders will have to take up the following challenges:

- create a complete set of standards since all existing norms only refer to hydraulic binders
- develop solutions for elements thicker than a few centimetres elements (allowing the CO_2 to penetrate)
- mitigate the lack of steel reinforcement protection to develop durable and easy-to use solutions for reinforced precast elements
- improve carbonatable binders to offer equivalent properties to OPC today for an equivalent cost, including the use of (industrial non-treated) CO_2 and the necessary curing chambers.

10.3 Recycled concrete aggregates for CO_2 sequestration

As discussed in section 8, recycled concrete aggregates also represent a potential CO_2 sink. The cement paste attached to these second-life aggregates has been decarbonated during its manufacturing and only partially recarbonated during its service life. Carbonating these construction-demolition waste (CDW) aggregates either with industry direct flue gases [140] or with purified CO_2 improves the performance of the recycled aggregates in fresh concrete due to a much lower porosity and also reduces the CO_2 footprint of concrete. However, far reaching developments in these carbonation technologies must be achieved by up scaling and improving ongoing small pilots installed in Europe; transportation and treatment extra costs must also be reduced.

In conclusion, CCUS has to be further developed to answer the industrial needs in terms of costs but also in terms of the mass balance between the CO_2 emissions and the potential use and storage scenarios.

Some CO_2 capture techniques already exist, some others have to be proven and confirmed by industrial pilots. New solvents, new absorbents that would reduce energy consumption will be welcome. Technologies have to be much more efficient energetically to be really significant. Mineralisation processes to produce CO_2 sequestering building materials like carbonatable cement-based concrete, carbonated CDW aggregates and other industrial wastes (like non-pozzolanic slags), could be a promising avenue in the future if costs are reduced, applications broadened and industrial flue gas directly used.

H. CO_2 Capture, Use & Storage - Priority research topics & key questions

Topics	N°	Key research questions to be solved
CO_2 capture	29	Understand and quantify the impact of process changes to facilitate CO_2 capture, on clinker reactivity and on volatilization of minor elements
Mineralisation	30	Determine possible industrial wastes for carbonation, by the use of industrial non-treated CO_2 flue gas

11 Conclusion

Understanding the many issues involved for the entire construction sector value chain in Europe and the robust definitions of the cement and concrete of the future help to pinpoint forthcoming needs in terms of research. By fostering closer ties with all the players in the sector, academic and industrial Research & Development teams, working together, aim to gain a deeper understanding of construction customers' and players' needs and to come up with innovative R&D strategies (see the mind map below) which will improve their businesses and their lives by developing the best ground-breaking solutions to meet these needs and solve potential problems. The most prominent among them is clearly the environmental footprint of cement and concrete, keeping in mind that reaching carbon quasi-neutrality in a few decades is a matter of life or death for this industry.

Portland cement-based solutions will undoubtedly still be used in the coming decades in Europe (and elsewhere) as it is the most efficient binder based on earth super abundant materials. However, CO_2 reduction is clearly the top priority, considering that Europe has today the most ambitious targets.

But European bodies must not be afraid of being slightly protectionist: European producers are very willing to tackle this major environmental challenge without being vulnerable to imports with higher carbon emissions.

In addition to the need of European significant incentives, we also wish to underline the importance of stimulating greater investment in R&D as targeted funding is undeniably an underlying factor for success in the field. We have to make funding agencies, both public and private, more aware of the fact that research funds for cementitious materials must focus on promising subjects, ambitious but realistic, that can be converted into industrial, cost-effective, massive, robust and easy-to-multiply solutions.

Appendix: Overview of topics where research is needed and key questions to be solved, in Europe for the ongoing decade, towards cementitious materials environmental neutrality

This appendix highlights the main topics where research is needed in Europe for the coming decade in order to reach cementitious materials environmental neutrality.

It consists of:

- a mind map below showing for each of the eight domains (clinker, multicomponent blends, alternative hydraulic binders, admixtures, concrete, durability, CCUS and recycling) the main topics of R&D to be covered. Each domain and each topic have a colour corresponding to its potential environmental impact: dark green for highest impact, medium green for medium impact and light green for a much lower impact.

– a list of scientific and technological key-questions to be solved thanks to academic research. It has been decided to highlight the 30 most important key-questions which have the main environmental impact, in order to suggest the European academic teams working on cementitious materials to focus on them. The authors strongly encourage the University researchers to spend their energy and resources to solve these major issues rather than some other trendy subjects having hardly a chance to be industrially and commercially developed.

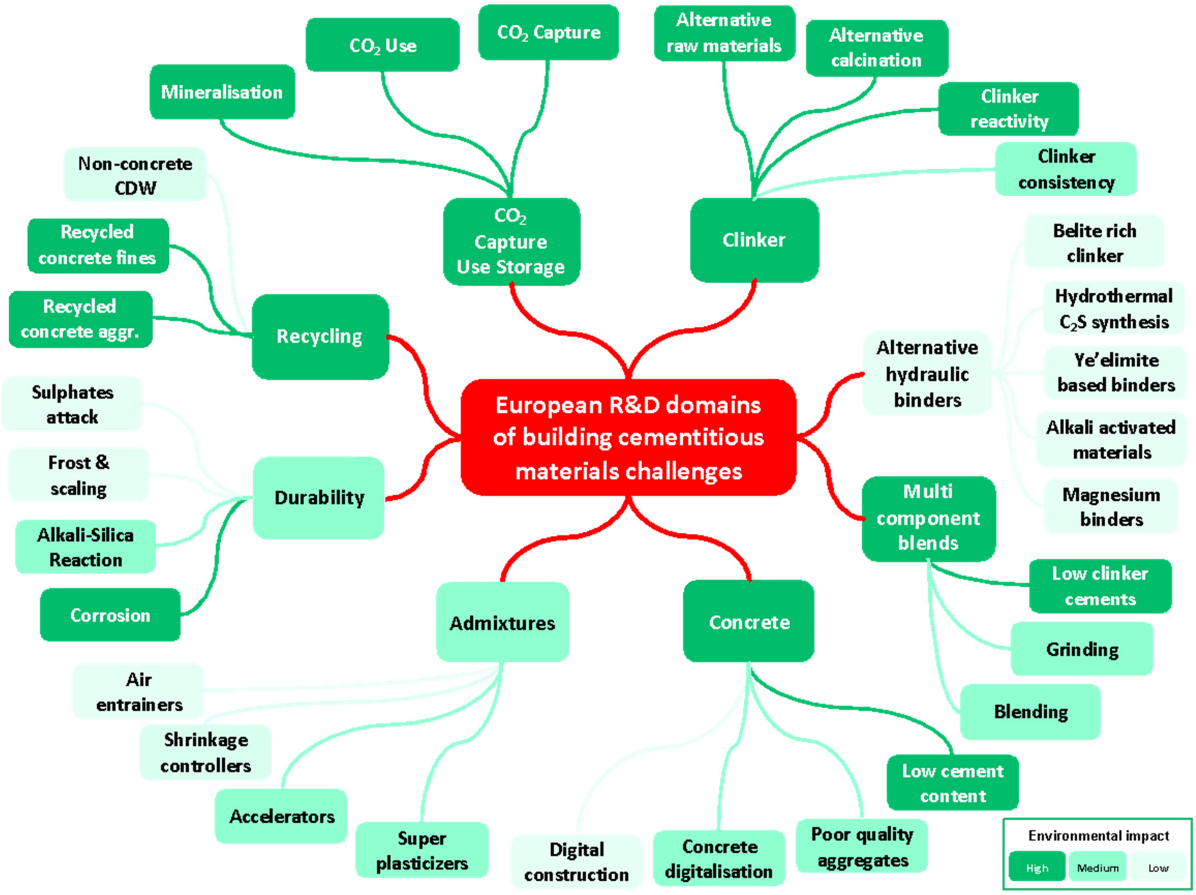

Figure A1. Mind map of the main research topics to be explored in Europe for the ongoing decad

A. Clinker - Priority research topics & key questions

Topics	N°	Key research questions to be solved
Alternative raw materials	1	Determine criteria and their limits to enlarge the scope of by-products used as ARM and ARF (minor elements impact, thresholds for hazardous components)
Alternative calcination	2	Understand impacts and reduce the cost of calcination with electrification
	3	Determine the most promising and cost-effective processes for CO_2 purification (kiln oxy-fuel combustion, calciner CO_2 separation)
Clinker reactivity	4	Better understand the link between process parameters and clinker performance like rheology, interaction with admixtures and reactivity to maximise substitution
	5	Model the impact of clinkering and cooling conditions on clinker reactivity
Clinker consistency	6	Develop laboratory methods to simulate real industrial kiln conditions
	7	Develop tools to improve clinker consistency, for example machine learning

B. Alternative hydraulic binders - Priority research topic & key question

Topics	N°	Key research questions to be solved
Alkali-activated materials	8	Only for precursors other than slag or fly ash, understand and mitigate the issues of AAM slump loss, short setting & shrinkage

C. Composite cements based on Portland clinker - Priority research topics & key questions

Topics	N°	Key research questions to be solved
Low clinker cements	9	Develop reliable and rapid reactivity tests for SCMs
	10	Model the sulphate-silicate-aluminate-alkalis balance to understand the hydration-rheology link with high SCMs content binders
	11	Enhance hydration in main peak, for example by: understanding limitations of C-S-H growth and impact of alkalis
	12	Understand the long-term behaviour: reaction limitations and performance
	13	Extend range of clays & carbonates and improve early age strengths for calcined clays/filler/clinker binders
Grinding & Blending	14	Develop more efficient mills, blending techniques to optimise the particle size distributions of the different components in multicomponent blends

D. Concrete - Priority research topics & key questions

Topics	N°	Key research questions to be solved
Low cement content	15	Develop mix-design methodologies for concrete with low cement or low paste content to improve workability and early-age strength robustness
Poor quality aggregates	16	Find ways to mitigate the effects of using poor quality sands, containing too many or not enough fine particles and/or clay.
Concrete digitalisation	17	Develop tools to improve concrete mix design methods, traceability, concrete production & field monitoring. For example sensors and Artificial Intelligence.
	18	Make Digital Fabrication carbon friendly: with low carbon binder, use of real concrete with coarse aggregates, 3D-shotcreting to embed reinforcement

E. Admixtures - Priority research topics & key questions

Topics	N°	Key research questions to be solved
Superplasticizers	19	Develop SP processes to control polydispersity
	20	Develop methods to determine spatial/temporal competitive absorption mechanisms, with phase specificity (including high specific surface SCMs)
Accelerators & strength enhancers	21	Improve early age strength of low CO_2 concretes without negative impact on workability or late strength evolution
Air entrainment agents	22	Understand and improve air entrainment stability with SCMs and impurities

F. Durability - Priority research topics & key questions

Topics	N°	Key research questions to be solved
Corrosion	23	Develop more relevant quick test methods and service life models to move from standards imposing minimum cement content to performance standards
Alkali-Silica reaction	24	Determine the SCM content optimum with quick relevant tests and address the risk of recycled aggregates
Frost	25	Develop a reliable scaling resistance test and establish a clear theory about scaling mechanisms

G. Recycling - Priority research topics & key questions

Topics	N°	Key research questions to be solved
Recycled concrete aggregates	26	Develop cost-efficient solutions to block their porosity and absorption
	27	Improve, accelerate and reduce the cost of treating recycled aggregates by carbonation
Recycled concrete fines	28	Determine the most efficient process to treat RCF in order to produce reactive SCMs

H. CO_2 Capture, Use & Storage - Priority research topics & key questions

Topics	N°	Key research questions to be solved
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Mineralisation	30	Determine possible industrial wastes for carbonation, by the use of industrial non-treated CO_2 flue gas

Credit Statement

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Patrick Juilland, original draft sections 5, 6, discussions;

Christophe Levy, original draft sections 1, 7.4, 9, 10, 11, appendix (diagram and 30 questions), discussions.

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