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Concrete: An eco material that needs to be improved

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Abstract

Concrete is the largest volume material used by man and is irreplaceable for innumerable large infrastructure developments. From the point of view of natural resources, ecology and economy, it is virtually impossible to imagine substituting concrete by any other material. However, because of the large volumes used, its total energy and CO_2 footprint is important. This material therefore needs to be improved and small steps can have a big impact, once again because of the large volumes involved. This review paper examines some of the routes that may be followed to further improve the environmental performance of concrete.

Keywords: Concrete; Cement; Sustainability; CO_2; Chemical admixtures

1. Introduction

Concrete is the largest volume material used by man and is irreplaceable for innumerable large infrastructure developments. From the point of view of natural resources, ecology and economy, it is virtually impossible to imagine substituting concrete by any other material.[1] Because of this, volumes used are colossal, reaching presently about 10 km^3/yr. For comparison, the amount of fired clay, timber, and steel used in construction represent, respectively about 2, 1.3 km^3 and 0.1 km^3.[1] The success of concrete comes from, on the one hand the broad availability and low cost of its components, and on the other hand, the ease with which it can be prepared. In concrete relatively low cost components are transformed by reactions with water from a flowable, and castable slurry into a load bearing, strong durable rock-like material.

As a result of the large volumes of concrete used, the production of Portland cement, the main binder of concrete, contributes 5–8% of all man made CO_2.[2] This is mainly due to limestone decarbonation, which is essential to the chemistry of Portland cement. Modifying this binder therefore represents a major objective that is driving research and development in this area. Various solutions under investigation are summarized in this paper, covering wide combinations of risk to benefit.

This paper does not however, deal with the technological issues of cement production itself as this is already an advanced industry and recent reviews on the subject can be consulted for further information.[3,4] On the other hand we touch on other issues dealing with the material formulation. For example, at a lower priority level than cement modification, it can also be noted that demolition of existing concrete structures generates huge amount of wastes (crushed concrete) whereas, simultaneously, our non-renewable resources of natural aggregates are, in most developed countries, almost extinguished. While there is proven solutions for recycling such material both in concrete for the coarse particles and in cement kilns for the fines,[4] the recycling of the fines faces logistic problems.[1]

One of the issues using recycled aggregates in concrete is to control its rheology. This holds in a broader sense for concrete formulations having reduced cement content. Indeed, while one can produce concrete with equivalent strength and durability, while reducing the cement content, the control of rheology becomes more challenging. A section of this paper is therefore dedicated to presenting a synthetic overview of recent progress in understanding and controlling the flow of this complex material.

Finally, an important section is dedicated to chemical admixtures. These are substances, which added in small amount produce large changes in important macroscopic parameters,

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including: flow, hydration, shrinkage, etc. Such additives are already widely used, but they will certainly have increasing importance in concretes of reduced environmental impact as well as in those using novel mineral binders.

In summary, society faces the challenge of reducing the environmental impact of concrete without compromising people's need for housing and infrastructure. From a concrete materials point of view, the main possible solutions are largely known and include:

1. Partial cement (clinker) replacement by supplementary cementitious materials
2. Development of alternative binders
3. Broader use of concrete mix designs that limit cement content
4. Recycling of demolished concrete in new concretes
5. Enhancement of durability (designing new infrastructures for longer service life)
6. Rehabilitation of existing infrastructures (extending the service life of existing infrastructures)

These are the only solutions with real potential of having a large-scale impact in this sector. This paper proposes a brief review of some of the solutions included in the first four points listed above because they share issues that can be more easily grouped together.

More specifically the topics discussed were selected based on their apparent realism in terms of large-scale feasibility and in some cases because of the more radical change they propose. It is important to remember that any of these solutions will ultimately need to be relatively robust to material variations whether geographical, temporal and/or seasonal. In practice, a given solution will almost always require some degree of local adaptation, such as a change in mix design, cement or admixture formulation. For reasons of cost effectiveness, these adaptations must be identifiable with as little work as possible. Performance predictability is therefore an area of real practical interest and one to which academic research can contribute important building blocks. For this reason we have also included a brief section on the perspectives opened by various modelling approaches for predicting concrete properties.

Finally, in order to place concrete research in a broader context, we have highlighted some challenges that are shared with other communities such as medical research, rheology, geochemistry and molecular modelling. We hope this will provide stimulating thoughts and possibly new ideas, directions and approaches for reducing the environmental impact of concrete.

2. Concrete components

2.1. Today's cements

2.1.1. Historical note

A hydraulic binder is a mineral powder that can develop strength by reacting with water while remaining wet. The first mineral binders date back to the Roman Empire. At that time, it was found that this behaviour could be obtained if a source of amorphous silica was added to slaked lime. This led to substantially higher strength than pure slaked lime and also to a substantially faster rate of strength gain.

The product of the reaction between lime and amorphous silica is a calcium silicate hydrate, which is the main binding mineral of modern Portland cement. This is why, although the starting materials are different, it is often stated that cement has been used for more than 2000 years.

After the fall of the Roman Empire, this knowledge was however, lost and really only resurfaced around 1750s. A major step was then accomplished in 1824 when an Englishman by the name of Joseph Aspdin patented "Portland Cement". This name was given because it allowed the production of a material that was similar to Portland limestone, considered as a good construction stone. The first usage of this material concerned restoration and/or repair work rather than civil engineering.

The name "Portland cement" is still used today. However, the material has changed as the temperatures originally used would not have allowed formation of the phases that compose modern Portland cement. Later developments by Aspdin with one of his sons did however, use higher processing temperatures and chemical compositions that must have given phases more similar to modern Portland cement.

2.1.2. Portland cement

Portland cement is produced by first co-grinding a mixture of about 80% limestone and 20% clays. This is then calcined and subsequently burnt at temperatures reaching 1450 °C. The chemical decomposition of limestone is responsible for the large release of CO_2 in cement production. During the high temperature processing, the kiln conveys nodules of calcium and silicon oxides held together by a calcium aluminate melt. Their reactions lead to a material that is quenched and contains the four main phases shown in Table 1. In what follows, we use cement chemist notation. The material produced in the kiln is referred to as clinker. It is the grinding of this clinker, together with about 5% calcium sulphate (anhydrite or dihydrate) down to a powder with a specific surface of 300–1000 m^2/kg that gives Portland cement.

Most of the strength development comes from the reaction of C_3S with water to form a compound of variable stoichiometry known as C-S-H (calcium silicate hydrate) which is nanostructured and poorly crystalline together with crystalline particles of CH (calcium hydroxide). Overall this hydration reaction leads to the formation of solids with twice the volume of the starting solids, although the total volume reduces since water is more tightly packed in the solids formed.

In reinforced concrete, both C-S-H and CH play a role in preventing corrosion of the steel reinforcement. The C-S-H forms a tortuous solid network. It has therefore a physical role in reducing the rate of ingress of chemically active species. In contrast CH can be viewed as a chemical sink for ingressing CO_2 as it reacts with it to precipitate calcite. This contributes to maintaining a high pH around the rebars and preventing their corrosion.

Overall, the production of Portland cement is highly optimized in all parts of the manufacturing process. For a recent review of the engineering aspects of this subject readers are referred to.[3] While there is still room for improvements the

Table 1
The four main phases found in Portland cement, their approximate chemical composition, name and role.

	Chemical composition	Cement chemist notation	Name of impure phase	Role
Tricalcium silicate	Ca_3SiO_5	C_3S	Alite	Provides most of the early and late strength
Dicalcium silicate	Ca_2SiO_4	C_2S	Belite	Contributes to very late strength
Tricalcium aluminate ferrite	Ca_3Al2O_6	C_3A	[a]	Contributes significantly to very early strength
Part of the melt during burning				
Calcium aluminate ferrite	Ca_2 (Al,Fe)O_5	C_4AF	[a]	Part of the melt during burning
Responsible for the grey colour				

[a] The term Celite is used sometimes and refers to the mixture of C3A and C4AF that dates back to before those phases could be distinguished.

remaining margins are however, low. The area with greatest potential is seen as the reduction in clinker[3,5] namely by the use of blended cements as discussed in Section 2.1.3.

2.1.3. Blended cements

Despite the chemical sink for CO_2 provided by CH, its presence in large amounts throughout the material could be viewed as the result of unnecessary CO_2 release during cement manufacturing. In fact, this CH can be effectively used to react with materials containing amorphous silica such as fly-ash, slag, silica fume, calcined clays or natural pozzolans. These pozzolanic reactions are very similar to those in Roman cements.

It is therefore possible to replace part of the clinker in cement by various materials that are referred to as Supplementary Cementitious Materials (SCMs). This already happens to a large extent and there has been much progress in rationalising the impact SCMs on the chemical and physical characteristics and the overall reactivity of blended cements.[6]

In practice, these blended cements are integrated into norms defining cement types. In Europe, CEM I corresponds to Portland cement and CEM II to a blended cement with degrees of replacement that can be as high as 35% depending on the SCM type. This type of cement is still referred to as Portland cement and represents today the largest part of cements manufactured in most markets.

Clinker replacement therefore represents an important way of reducing the environmental impact of concrete. However, the extent of replacement is limited by the following problems:

- Reduced early strength
- Limited amounts of reactive SCMs
- Limited replacement by non-reactive SCMs (such as limestone) without compromising final strength

It must be stated here that limestone can react to some extent with the aluminate phases of Portland cement and this can give a slight strength increase.[7,8] However, the range of substitutions in which this can be exploited is relatively limited. In particular, at high cement replacement levels, most of the limestone can be considered as non-reactive, although it may affect hydration rates depending on its fineness.

One area in which blended cements still have margin for expansion is in composite cements, also referred to as type M cements in Europe. In this class of cements it is possible to include different SCMs. In particular one could include a reactive and a non (poorly) reactive SCM. This increases the total amount of limestone that could be used, while accommodating for the limited resources of reactive SCMs. In the case of limestone addition to fly-ash cements it is also observed that the extent of reactivity of the limestone is increased because of the alumina contained in the fly-ash.[9] One challenge in this area is to enhance early strength. Another is that by increasing the number of components the quality control requirements also increase.

2.2. Tomorrow's possible cements

In this section we examine various cements currently being considered as potential alternatives to the more traditional cements discussed above. Their nature and degree of development varies significantly. For example, alkali activated alumina silicates have been used for decades, but have not really achieved significant market penetration. Nevertheless, this subject is being intensely investigated, judging by the very high number of publications and citations earned in this field. In contrast, other systems are based on recent discoveries and new concepts, while one of these alternatives has reached the level of pilot testing in a full-scale cement kiln.

Most of these solutions have been discussed also in other recent reviews and readers are referred to these as complimentary information.[1,2] Here we attempt to give a brief overview in relation to the other aspects discussed in the present paper.

As a general remark before discussing these different cements, it should be recalled that the Portlandite reserve in Portland cement is beneficial in terms of corrosion resistance for rebars, but that this is reduced when reactive SCMs are used. Alternative cements having a low alkaline buffering capacity should therefore probably be compared to blended cements rather than Portland cement. Comparisons then become difficult, but probably critically important in terms of the industrial cost efficiency of the process and life-cycle assessment. Moreover, all new cements are challenged by the lack of standards, something that promoters of novel cements are trying to change.

2.2.1. Alkali activated alumino-silicates

Alumino-silicates either do not react with water, or do so too slowly. However, provided these materials have a high amorphous content and are placed in an alkaline medium, they will hydrolyse and condense, forming new inorganic polymers that can develop load-bearing capacity. In cement these materials benefit from the natural alkalinity of the system and of the Portlandite reserve to fulfil these reactions.

Without Portland cement, alumino-silicates can be activated by adding strong bases. In this case the pH is raised to values in the range of 14 rather than 13 as found in cement. As summarized by Gartner this has important consequences in terms of the availability of alumina and silicate species for reaction.[1,2] The reactivity is however, strongly influenced by the structure of these alumino-silicates, and much research has been devoted to this issue.[10,11]

Alkali activated alumino-silicates can be classified in two groups depending on their calcium content. High calcium content raw materials are mainly prepared with blast furnace slag that can react at room temperature producing a main hydration product noted C-A-S-H. This is similar to the C-S-H from Portland cement but contains substantial substitution in linking tetrahedral, giving longer chains that may also be cross-linked depending on the activator used.

Those containing low amounts of calcium are sometimes also referred to as geopolymers. These have been used in a number of applications[12,13,14] and have been the subject of much research and interest in the last decade. Geopolymers are formed by a two-stage reaction in which suitable alumino-silicate starting materials are mixed with a highly alkaline medium in which reactive silicate and aluminate groups dissolve. The aluminates and silicates dissolve and poly-condense into short-range ordered and cross-linked chains that form a cementitious gel and provides the binder phase in these materials.[15]

Suitable geopolymer starting materials must possess high quantities of reactive silicate and aluminate groups. Commonly used starting materials are metakaolin, produced by calcination of kaolin clay at around 750 °C and coal fly ash. In all cases, geopolymers are reported to have lower embodied energy and have reduced CO_2 emissions compared to Portland cement.[10,16,17]

Unlike the calcium silicate hydrate (C-S-H) gel formed during Portland cement hydration, geopolymers form an alumino-silicate network consisting of tetrahedral coordinated SiO_4 and $AlO_4{}^-$ groups.[18,19] Such structures have a negative charge associated with the aluminium ion which is balanced by Na^+ or K^+ cations from the alkali activation solution, forming N-A-S-H of K-A-S-H gel depending on the counter ion present.

Alkali activated systems are being commercially used to form concretes by Zeobond in Australia who aim to provide a practical and realistic solution by creating a sustainable alternative to the manufacture of cement. The most readily available raw materials containing aluminium and silicon are coal fly ash and blast furnace slag from the steel industry, and these are the materials that Zeobond use to produce low carbon emission geopolymer binders. The properties of geopolymer cement, when used to make concrete, have been repeatedly and independently shown to be equivalent to other cements in terms of the structural performance of the resulting geopolymer concrete.

In terms of future and large-scale use, alkali activated alumino-silicates can be expected to become challenged in terms of overall applicability by:

- High sensitivity to alkali concentration and temperature
- Reduced reaction rates at low temperature
- Quality control of materials that have a highly variable composition, not only by location but also by production date in some cases
- Competition with blended cements
- Limited volumes of readily available alumino-silicates relative to Portland cement
- Handling of the highly alkaline activator on job sites
- Cost and environmental footprint of the activator

It appears that these issues will be critical to determine if alkali activated alumino-silicates are to find large-scale application in construction.

2.2.2. Belite-rich cements containing calcium sulfo aluminate and ferrite phases

An interesting approach to new clinkers is the one followed by Lafarge and registered as Aether®. It consists of a combination of various known chemical reactions of cementitious systems, but overall leads to very different reactivity from Portland cement. Publically available information on this subject can be found in Refs. [1,2,20,21].

In the first day, strength development comes from formation of ettringite ($C_6A\bar{S}_3H_{32}$) and amorphous aluminium hydroxide (AH_3) from the reaction ye'elimite ($C_4A_3\bar{S}$) with anhydrite ($C\bar{S}$) in the presence of water. Once the anhydrite is exhausted, further reaction of ye'elimite yields monosulfoalumintate ($C_4A\bar{S}H_{12}$) and AH_3. Interestingly, belite seems to react with AH_3 to yield strätlingite (C_2ASH_8), which occurs until about 14 days. Until this point in time, no C-S-H or CH are formed, so that the main hydrates are very different to Portland cement systems. After this, further reaction of belite does yield C-S-H and CH.

It is claimed that despite these various changes in solid phase assemblage, no detrimental dimensional changes take place. Moreover, the testing of this cement is now the subject of an EU project that will include full scale production trials (http://www.aether-cement.eu/). This material is claimed to deliver similar performance to Portland cement but is associated with a 20–30% reduction CO_2 emissions.

2.2.3. Celitement

Celitement is a hydraulic cementitious binder developed by Karlsruhe Institute of Technology. The raw materials are similar to those used in the manufacture of conventional cementitious binders, CaO from limestone and various types of silicates that are blended at Ca:Si molar ratios between 0.5 and 2. The raw materials and water are transformed into calcium silicate hydrates using an autoclave at temperatures between 150 °C and 300 °C. The hydrothermal product is then blended with a second silicate component and milling activates the phases and controls product properties. This produces Celitements, which are hydraulically active calcium hydrosilicates. Additives are used to control hydration reactions and the properties of the final product. The molar ratio of Ca to Si can be much less than 2 and therefore the calcium carbonate used and the corresponding carbon dioxide emissions are significantly reduced.[22]

The CO_2 emissions associated with Celitement are reported to be approximately 50% those of normal CEM I Portland cement and compositions are reported to give low permeability mortars with compressive strengths up to 80 MPa after 28 days curing. A test plant with a capacity of 100 kg per day became operational in 2011, and although significant barriers remain this represents an exciting potential technology for the manufacture of low carbon cement and concrete.

2.2.4. *Cements from magnesium silicates*

Another interesting approach to manufacturing low carbon cements is being developed by Novacem, a spin out company from Imperial College London. This uses magnesium silicates such as olivine and serpentine as the basic raw materials for binder production. Worldwide reserves of magnesium silicates exceed 10,000 billion tonnes,[23] much of which is potentially extractable using open pit surface mining in a similar way and at a similar cost to limestone.

Novacem aims to develop cementitious binders with performance and cost similar to Portland cement, but with significantly reduced carbon footprint. The use of magnesium silicates combined with a low temperature production process and with the addition of hydrated magnesium carbonates enables production of a low carbon cementitious binder. The Novacem cement is a mix of MgO, pozzolans and hydrated magnesium carbonates. There are several potentially suitable hydrated carbonates that can be used and these include artinite ($MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$), hydro-magnesite ($4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$), dypingite ($4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$), barringtonite ($MgCO_3 \cdot 2H_2O$), nesquehonite ($MgCO_3 \cdot 3H_2O$) and lansfordite ($MgCO_3 \cdot 5H_2O$), and these are produced using specialised reactor technology.

The addition of hydrated magnesium carbonates controls strength development by changing the MgO hydration mechanism and the physical properties of the hydration products. Their addition also decreases the carbon footprint due to the absorption of 300–500 kg CO_2 per tonne of carbonate used.

The Novacem production process involves three stages. During the first stage magnesium silicates are carbonated under elevated levels of temperature and pressure (i.e. 170°C/15 MPa) to produce magnesium carbonate and SiO_2. In the second stage magnesium carbonate is heated at low temperatures (~700 °C) to produce MgO, with the CO_2 generated being recycled for use in the first stage. During the final stage some of the MgO formed is used to produce hydrated magnesium carbonates using either the CO_2 contained in the flue gases from the fuels used to power the production process, or external CO_2. Current efforts are concentrated on the construction and optimization of a reactor system that can be increased to industrial scale and Novacem cements are not currently commercially available. However, this does represent an alternative high volume cement binder technology with potential to produce low carbon concrete products.

2.3. *Sand and aggregates*

Although the sand and aggregate used in concrete are not normally considered to be manufactured materials, the enormous volumes used mean that they also have a significant overall environmental impact that needs to be carefully considered when discussing concrete as an eco-material. There are unavoidable CO_2 emissions associated with all the raw materials used to form concrete and this includes the cement, aggregate, water and the various organic additives that might be required.

Aggregate is generally used to include different types of mineral additives used to form concrete including gravel, crushed rock, sand and potentially natural or manufactured lightweight aggregates. The primary energy (0.083 kJ/g) and carbon emissions (11.0 kg CO_2/m^3) normally reported for aggregates are low in comparison with all other manufactured materials. However, the scale of aggregate production is enormous. Data shows that in 2009 the UK produced 170 million tonnes of aggregate for use in construction, of which 51 million tonnes was land-won sand and gravel, 15 million tonnes was marine dredged sand and gravel and 105 million tonnes was crushed rock.

A number of major sustainability and economic issues are associated with aggregate supply. These materials are often produced significant distances away from where concrete is used and therefore the cost and environmental impacts of transporting vast amounts of aggregates is a major concern. In addition there are the inevitable environmental issues associated with aggregate extraction and the subsequent processing to form suitable product and available sources may be limited. It should also be noted that aggregates containing amorphous or cryptocrystalline silica are subject to alkali aggregate reaction (AAR) often also known as alkali silica reaction (ASR). This reaction leads to expansive forces that can lead to cracking, which increases the rate of other degradation mechanisms as: corrosion, freezing, sulphate attack. Those "concrete illnesses" are what can be "fatal" for a structure and not ASR itself. As a result, it is sometimes said that ASR is to concrete what AIDS is to people.

Legislative drivers such as the aggregate tax are having a major impact on business development and innovation in construction materials and the drive to produce concrete as an eco-material. This is promoting the development of more sustainable aggregate materials and secondary aggregates derived from recycled materials with particular emphasis on low carbon sources. Legislative and economic drivers are therefore absolutely fundamental to increased innovation and the move towards more resource efficient sand and aggregate in concrete.

2.4. *Chemical admixtures*

Chemical admixtures present a great opportunity to achieve significant effects with small additions to concrete or other particulate systems. They can be described as the "chemical spices" of concrete. They operate by modifying interfacial properties in

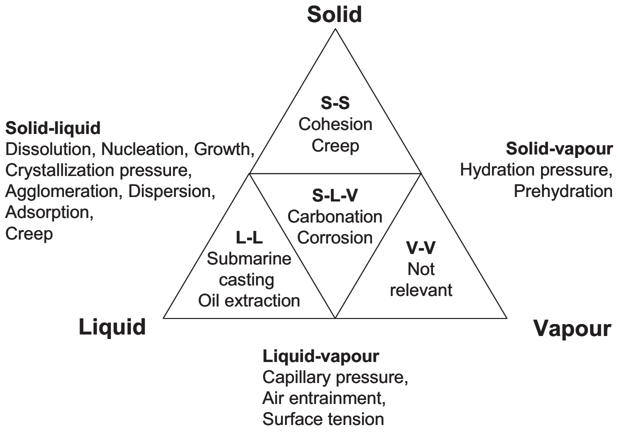

Fig. 1. Illustration of the role played by different interfaces in the system. S–S, solid–solid, L–L, liquid–liquid, V–V, vapour–vapour and S–L–V, solid–liquid–vapour.

the system. This is illustrated in Fig. 1, where the properties influenced by the different phases in the system are presented in a ternary diagram for the solid, liquid and vapour phases present in concrete both in its fresh and hardened state.

The interfaces of greatest interest are those between solids and liquids. As is well known in ceramic science, these interfaces control the state of flocculation as well as the adsorption of dispersants that in turn strongly impacts the rheology of particulate systems as concrete.

Among the chemical admixtures used in concrete, dispersants (superplasticiser) constitute a major class, with about 800,000 tonnes being used worldwide every year. In relation to these admixtures, many basic issues in this field have been clarified over the past few years. For example the conformation of comb-copolymer dispersants in their adsorbed state[24] and the link from admixture structure to yield stress in well-dispersed systems[25] could be measured and rationalised. However, several unknowns remain as for example:

- The performance at low dosages (case mostly found in practice)
- The behaviour admixture blends (case of most commercial products)
- And the behaviour in composite cements

These issues are very relevant to practice and their underlying scientific questions cover a variety of very interesting and basic issues as the competitive adsorption of organic admixtures in relation to their molecular structure.[26,27,28,29,30]

One factor that perturbs the working mechanisms of dispersants is their interaction with the hydration reaction of tricalcium aluminate, the most reactive phase in cement.[31,32] One possible mechanism for this is the incorporation into a calcium aluminate layered double hydroxide.[33,34] However, the extent of this intercalation depends on the sulphate concentration so that the relevance of intercalation to real systems is probably quite variable depending not only on composition but also addition time.[34,35]

Another case where layered minerals are an issue is that of clays. It has been known for many years that superplasticiser containing polyethylene oxide (PEO) side chains loose their efficiency in presence of swelling clays. This has been explained by an adsorption (or intercalation) of these side chains into (onto) the surface of these clays.[36]

Another area where solid–liquid interfaces have recently been found to be more important than previously suspected is in (early) hydration kinetics.[37] There it was found that the surface of anhydrous minerals can develop etch pits during the initial dissolution phase. This can enhance the rate of the subsequent reaction and the time at which the material starts to develop load bearing capacity. A modification of this process could be one explanation for the retardation that most chemical admixtures have on cement hydration.[36] Alternative explanations as a modification of either the nucleation or growth rates of the hydrates also involve the solid–liquid interfaces.

A challenge for research here is to push the degree of comprehension of these phenomena down to the molecular level and understand for example how chlorides enhance slag reactivity. Such work would provide new insight into alternative ways of how to enhance the reactivity of blended cements, which could involve molecular design of organic admixtures.

The liquid–vapour interfaces have also been used for decades to entrain air in an effort to enhance freeze-thaw resistance.[38] Later, modifications of the same interface have been exploited to reduce drying shrinkage and the cracking that can result.[39,40] This is traditionally explained by a reduction of the surface tension and thereby of the capillary pressure. Let alone, this is insufficient to explain the dosage response performance of these admixtures. This can however, be explained if one takes into account the fact that the internal liquid vapour interface area increases during the hydration and subsequent drying of cementitious systems.[41] It can also be noted that entrained air has an effect on rheology and can deliberately be used for this purpose. Former controversy in the literature on this subject has recently been clarified. Indeed, at low shear rates, the entrained air behaves as non deformable inclusions, leading to an increase in viscosity. However, at higher shear rates, relevant for pumping, entrained air may be deformed, so that it can contribute to reducing viscosity.[42]

While taken individually, the use of such technologies is relatively well understood, but a real challenge appears when attempting to combine them. Problems are also reported to arise in some blended cement systems. In particular, Jolicoeur et al.[43] reported on the loss of freeze thaw resistance in some systems containing fly-ash cement. They identified that air bubbles were destabilized by the inclusion in the surfactant layer of small carbonaceous particles. They also identified molecules that can remedy this problem. Beyond this specific problem and solution, one can envision here that approaches from surfactant science may be used to understand and control at a molecular level such undesired interactions.

Finally, it should also be noted that solid–air interfaces should not be neglected since they impact agglomeration in the dry state. This is of great technological importance during the grinding of mineral powders or simply their handling. Moreover, the cement industry is shifting to using additives strictly defined as grinding aids to ones referred to as cement improvers. In addition to improving the grinding, these admixtures are also intended to positively affect later stage properties such as rheology or strength.[36] A key contribution in this area was to relate the effectiveness of amino-alcohols as cement improvers to their ability to complex iron, thus enhancing the solubility of calcium alumino ferrite, an otherwise poorly reactive phase.[44,45]

3. Concrete properties and role of mix design

Since the beginning of its industrial use at the end of the 19th century, concrete mix design has been empirical. Most mix design methodologies rely on more than one century observation of already built structures and are based on norms not specifying any target property requirements but only target components proportions that have proven, through the years, to guarantee adequate performances of the material. Only recently, approaches correlating components physical properties with the macroscopic properties of the mixture were developed.[46] However, because of the environmental pressure on the material, it can be expected that concrete mix design will evolve faster than ever in the coming decades. With such an innovation rate and the upcoming use of binders less known than Portland cement, the above norms will have to change at the same rate without compromising the safety of concrete structures.

It can moreover be expected that, in a short-term perspective, two major changes will occur in the mix design of this unavoidable construction material. First, the binder turning the granular skeleton into an artificial stone will progressively be replaced by products with lower environmental impacts (Cf. previous section). This trend will allow for a reduction in the energy consumption and CO_2 emissions of the material. Second, the granular skeleton itself will evolve and incorporate more and more recycled aggregates coming from demolished concrete structures. This will allow for a reduction in the amount of wastes generated at the end of the concrete life cycle and a reduction of the consumption of non renewable resources such as river sand or more generally natural aggregates. These trends will have consequences both on the hardened and fresh properties of the material.

Another important lever is simply to reduce the volume of paste without changing the ratio of water to cement. This strongly penalizes the flowability of the material, but does not compromise most of the engineering properties. Moreover, the yield stress can be reduced by a combination of superplasticizer use and improved size grading of the aggregates.[47] There is thus still much potential for making good concrete with reduced cement content.

3.1. Hard state

Concrete is mostly used for its high compressive strength and its durability in aggressive environments. The replacement of traditional cement by alternative binders and the use of recycled concrete aggregates will have strong consequences on the two above properties.

Predicting the life time of a concrete structure has always been a complex issue. Various chemical species such as chloride, CO_2, and acids propagate in a reactive porous medium. Simultaneously, drying and wetting cycles modify the water content of the hardened concrete changing the apparent permeability of the medium. Most chemical reactions occurring in the material are strongly coupled and the resulting behaviour can only be correctly modelled in the simplest cases. At present engineers are mainly using very basic and empirical diffusion laws. This provides them with an approximate time for aggressive chemical to reach the reinforcing steel bars, which is then used as an estimate of the service life of a concrete structure.

Recent results have shown that it seems possible to produce durable concrete with alternative binders. This however, involves in most cases a strong reduction in the water proportion added during mixing. This allows for a strong reduction in the material permeability suppressing the need for the understanding of the behaviour of these alternative binders when in the presence of aggressive chemical species.

Similarly, it seems possible to mix design concrete with these alternative binders showing similar mechanical strengths. Here again, it is a decrease in water content that allows for a fast growth in strength preventing any early age cracking due to drying or shrinkage.

It can also be expected that the use of recycled concrete aggregates could further increase the durability issue by adding into the material far less chemically inert and more porous aggregates. Moreover, as the elastic modulus of these inclusions is, in most cases, lower than the one of natural aggregates, the rigidity of the final composite could be decreased leading to increased shrinkage or creep.

Finally, concerning concrete containing low volumes of cement paste, as mentioned above, most engineering properties are not altered if the water to cement ratio is kept constant.[67]

3.2. Soft state

Behaviour of fresh concrete in steady state is often described by a yield stress Bingham model.[48] From a practical point of view, yield stress may be related to filling capacity and more generally to whether or not concrete will flow or stop flowing under an applied stress whereas plastic viscosity may be associated to the velocity at which a given concrete will flow once flow is initiated.

Yield stress is often considered as the most important parameter for formwork filling in practice.[49] If we consider for instance the casting of a wall, a purely viscous fluid (i.e. no yield stress) would self level under the effect of gravity. Gravity would indeed induce a pressure gradient in the fluid if the upper surface of the material is not horizontal. This pressure gradient would generate a shear stress in the material that creates a shear rate and forces the material to flow until the upper surface becomes horizontal and until the pressure gradient at the origin of flow has disappeared. The viscosity of the material will only play a role on the time needed to obtain a horizontal surface. In the case of a yield stress fluid such as concrete, gravity and pressure gradient also generate a shear stress. However, if this shear stress, which is a complex function of the formwork thickness and the local density of steel reinforcements, becomes lower than the yield stress of the concrete, flow stops before the concrete self levels or before the formwork is entirely filled.

The plastic viscosity of the material is of the order of 100 Pa s and conditions pumping processes and casting rates. High viscosity concretes are difficult to use and require additional effort from the workers at the building site. However, although yield stress can strongly vary from a modern Self compacting Concrete that almost self levels under its own weight and a traditional vibrated concrete, plastic viscosity has, through the last century, been kept almost constant by the mix design engineers.

The reduction of the water proportion in concrete allowing for adequate setting time, early age properties, mechanical strength and durability of future concrete will have some major consequences on concrete rheological properties. Such an increase in solid content will generate both an increase in yield stress and plastic viscosity. Although delicate in the case of new binders (Cf. previous section), use of adsorbing polymers shall allow for a reduction in the inter-particle colloidal forces preventing any prohibitive increase of the yield stress of the mixture. However, the increase in solid content will generate an increase in plastic viscosity that polymer technology is not able to counter so far. Moreover, the replacement of natural round aggregates with almost spherical shapes by crushed recycled aggregates will strongly affect the packing fraction of the granular skeleton increasing further the viscosity of the mixture.

Plastic viscosity of concrete results from a complex interplay between viscous dissipation in the interstitial water amplified by direct contacts between cement grains and coarse particles. It will be in the field of dense rigid particles suspensions[50] that a solution to this increase in plastic viscosity could be found.

4. Outlook

4.1. Promising developments

In the preceding sections we have presented various aspects of concrete composition and mix design. In each of them we have highlighted promising developments where by we see important possibilities of improving the sustainability of concrete. These include:

- *Blended cements*: This is the most traditional route, but one with still substantial potential. Ternary blends can be expected to grow in importance as well as the role of admixtures acting on the hydration. The types of blends used will vary a lot depending on the local availability, but the amounts of limestone will probably grow everywhere.
- *Belite-rich cements containing calcium sulfo-aluminate and ferrite phases*: Based on a combination of existing cement chemistries this approach is broadly usable. Preliminary results are promising and pilot level production has begun.
- *Magnesium silicate derived cements*: These have the potential to be supplied in the significant volumes required to compete with Portland cement. They offer unique scope for very low carbon construction products although major production issues remain.
- *Low cement concrete*: Enlightened mix design of concrete, using existing technology at its best can reduce the need of cement in concrete.
- *Chemical admixtures*: Already widely used, these are the spices of today and tomorrow's concrete. They can help to improve properties, but are not (no more) sufficient alone. Their robustness in systems of growing complexity will probably have to be improved. Generally one can expect that they will be increasingly requested to resolve short comings of any of the above solutions.

4.2. Robustness

From the above, it is highly probable that the future of concrete will not come from one but many solutions, so that the range of compositions and in particular of binders will increase. As a result, concrete may become more sensitive to variations in the proportions or composition of its components. Robustness will therefore become a subject of greater concern.

Moreover, as most alternative binders are less efficient than clink Portland, it can be expected that the water proportion in the system shall decrease.

In addition, as concrete compositions broaden, the range of chemical admixtures will probably also have to increase. Here again robustness will be a growing concern. Another issue about admixtures, is that as one attempts to optimize concrete more and more, we can expect that the number of chemical admixtures in a given mix will increase. We may therefore see a growing number of issues of inter-admixture compatibilities arise. Overall, many of these issues will be tackled, as today, by a combination of polymer design and product formulation.[51] However, a deep understanding of the physico-chemical mechanisms will be increasingly helpful in saving time by more rapidly defining the range of potentially working solutions.

In terms of ordinary concrete, we may see the advent of ultra-low cement mix designs. In all these cases rheology becomes a major issue and in particular the grading of aggregates. Here there is probably a greater potential than usually expected. An example is Eco-SCC®, a self-compacting concrete containing less than 315 kg/m^3 of binder, which is 2–3 times less than normal mix designs.[52] In all these cases variations in any of the components is more critical than in highly optimized systems and efficient ways of dealing with this risk will have to be established.

4.3. Modelling

In the face of the complexity of concrete computational models appear as a seducing option because of their ability to handle complex systems and address questions that are not easy or even possible to study experimentally. There are numerous approaches to modelling various properties of cementitious systems and it is far beyond the scope of this paper to review these. Rather we indicate a couple areas where substantial progress has or still needs to be done.

4.3.1. Reactivity and microstructure build-up

Recent reviews have been published on cement reactivity and its modelling.[53,54] For the purpose of this article, we just want to emphasize that the hydration kinetics of cement are not given by the superposition of the hydration kinetics of its components taken individually. This is because dissolution, nucleation and growth all depend on the solution composition and that in a mixture of reactive components, each solid phase is having an influence on the aqueous phase. Recent models take this into account and are therefore much more successful in relating reaction kinetics of individual phases to that of mixtures.[55,56] These models also develop a microstructure that can be used to simulate other properties of the matrix as: capillary porosity (volume and approximate sizes), diffusivity, chemical shrinkage, internal relative humidity, elastic modulus, etc.[57,58,59] A longer standing model that does not provide a microstructure is the Gibbs Energy Minimization Similuations (GEMS), which is a thermo-kinetic model borrowed from geosciences[60,61] and much developed for cementitious systems.[7] It is very successful at predicting the long-term phase assemblage of cementitious systems. At the present stage, all these approaches seem challenged by their ability to reliably accommodate SCMs. The fundamental problem seems to lie more in limited understanding on the reactivity of these components, so that more targeted work on the experimental side seems to be necessary at this stage.

Understanding the reactivity of minerals at the atomistic scale may provide complimentary information needed by those models. Such work has only just begun. It mainly addresses the role that substitutions in the belite structure have on its reactivity. Two main paths can be distinguished. The first relies on calculating free energy states of reactants and products to compute the reaction energy by their difference. The second approach investigates electron density distribution to infer the reactivity differences.[62]

4.3.2. Interfaces

As explained previously, interfaces play an essential role in cementitious systems. In particular, they present the greatest lever by which one can modify properties with chemical admixtures. Unfortunately, atomistic modelling of these surfaces is quite challenging. In particular, it should be noted that interfacial energies depend on the square of the partial charges that atoms are attributed in force fields. Recent progress in the definition of force fields with soundly based atomic charges has however, been made.[63,64,65] A similar approach has recently been used to simulate tricalcium silicate and the solid–vapour interfacial energy obtained is in agreement with experimental data.[66] Provided one has a reliable model for interfacial properties, it is then possible to simulate the behaviour of organic additives as grinding aids.[67] Extending such approaches to liquid–solid interfaces is possible and has been done for gypsum.[68] However, here the computational time increases and becomes problematic with molecules of increasing size, so that other approaches may need to be also considered.[69] The modelling of interfaces is also called to play an important role in understanding the cohesion of cementitious systems.

4.3.3. Rheology

The matrix behaviour is certainly the most complex part of concrete rheology. It involves colloidal interactions, hydration reaction and admixture adsorption. So far, modelling has only really been successful with inert systems. In particular, a physically based model is now capable of dealing with high volume fractions of solids, random shapes and interparticle forces as well as broad particle size distributions, which are all very important features of our systems.[70,71,72] However, the incorporation of aging is still lagging behind. The recent findings relating this to nucleation of hydrates may help to define computationally efficient ways of quantifying the phenomena.[73]

At the macroscopic level, computational modelling of fresh concrete flow has proven in the last years its efficiency when trying to tailor a casting process to a given material and application[59,74] Most industrial tests such as slump or slump flow have been modelled. Computational fluid dynamics techniques were also used to predict the filling of complex formwork allowing for the identification of the minimum fluidity needed for a given casting process. It can be expected that, in the next years, computational modelling could become the tool that will bring rheology from research and development into the field of practical applications. New models are developed in numerous research teams around the world. They will allow in the future the predictions of e.g. the segregation of the coarsest particles, the orientation of fibres and, from a more general point of view the consequences of the casting process on the properties of the structural element in its hardened state.

4.3.4. Mechanical properties and durability

Mechanical properties and durability are macroscopic characteristics that depend on the microstructure of concrete. They require therefore almost by definition multi scale modelling. At present, it appears that engineering models are extending into the microstructural levels. An example is the inclusion of hydrate orientation into a multi scale engineering mechanics model.[75] Conversely, microstructural models are being extended to provide input parameters at larger scales as for example the elastic modulus of cement paste and of the interfacial transition zone between aggregates and cement paste.[58]

Service life predictions are even more challenge by their multi scale nature. This is a broad and complex subject of which we can only mention a couple of specific issues. The first point to emphasize is that concrete durability is mostly linked to the corrosion of the steel rebars in reinforced concrete. As mentioned before, rebars are stable in the high pH initially provided by concrete. This can change because of carbonation or chloride ingress.[76] In both cases, it is necessary to properly model the transport phenomena.[74] Particularly in the case of chlorides (from deicing salts or sea water) there is a need to go beyond simplified engineering models based on Fick's laws and account for the ion specific interactions involved.[77] Despite much progress in this area, the coupling to microstructural models and micromechanics of damage remains insufficient. In other important modes of degradation the situation is largely similar.

In the case of corrosion, another major question remains poorly resolved. It is the determination (or handling) of the critical chloride content at which corrosion of steel reinforcement starts.[78] The literature shows much scatter on such values and recent research suggests this must be related to the probabilistic nature of the problem.[78] Consequently there is a need to combine adequate new experimental approaches with modelling approaches that will be able to tackle the probabilistic nature of chloride-induced corrosion. Eventually, this must be linked to an evaluation of the structural safety and be delivered in a form that is useable by a structural engineer.

4.4. Research beyond construction materials

As we have seen concrete is a multi component and multi scale material of which the properties result from the complex interplay among its components. In this sense concrete research shares a number of methodological challenges with medical research.

Indeed, both areas greatly benefit from pushing their research down to smaller and smaller scales. However, they must also deal with the fact that interactions among components, possibly at larger length scales, can dominate the overall system response. From this point of view, there is still a lot to do on the research methodology, not only bridging length scales, but dealing with large number of active components.

Another probably unexpected area where we see a merging of research challenges is the modelling of rheology. Here arguably, concrete research faces the challenge of dealing with the motion of aggregates in a rebar network. As mentioned before, a full solution to the problem is challenged in situations where aggregates are not much smaller than the rebar spacing.[79,80] An analogue case might be that of microfluidics with colloidal dispersion or even blood flow in small veins.

Another example concerns molecular modelling. In particular this could become an essential tool to access crucial information concerning the interfaces that are so important in cementitious systems. Phenomena as adsorption or cohesion can be examined without having to include reactivity. Despite this simplification, the inhomogeneity of cementitious systems means that subsystems must be defined to keep computational times within reasonable ranges. Other computational problems include the ionic composition of the aqueous phase that calls for large simulation box sizes. This is also the case for simulating polymeric admixtures as superplasticiser. Determining efficient computational approaches and ways in which to best address the multicomponent nature of cementitious systems represents therefore a major challenge that is shared with many other real systems from material science to medicine.

5. Conclusions

The components of good concrete are extremely simple: cement, sand, aggregate, mineral additions, admixtures and water. However, as stated by Neville the components of bad concrete are the same and the difference lies in the know-how.[81] The first step towards a sustainable use of resources is to make durable concrete. Today this is not so much an issue for research as of implementation in practice.

The second step towards reducing the environmental impact of concrete is to modify its composition. Here the subject becomes much more challenging and the know-how needs to be further developed. It must also be reminded that concrete already has a very good environmental performance.[1] Its most energy intensive component and the one with the largest footprint is cement. However, its manufacturing is already a highly optimized process.[3,4] Improving this material is therefore challenging, as the starting point is good and involves materials that are widely available around the earth.

Nevertheless there are potential solutions that have a real potential of finding large-scale applications. Some of them have been outlined in this paper. They range from better use of existing know-how to development of alternative binder chemistries. The future will probably be made of a variety of solutions. They will remain multicomponent systems, which is specifically one of the factors that make their understanding complex. It is because of this that numerical modelling based on solid physics and chemistry can become very important for research in this area. In particular, predicting durability of novel systems would facilitate their acceptance and radically change the “time to market” in this area. For the time being, minor modifications to well known systems appear the best solution as they can be covered by existing experience and norms. Chemical admixtures in particular have a great role to play in making it possible to “stretch” the mix design range of concrete and mineral binders to their limits.

Finally, it should be noted that the performance of cements would eventually have to be evaluated by including the resistance that they can offer against the corrosion of steel reinforcement. Because of their reduced carbonation buffering capacity, some cements may turn out to have to be compared to blended cements rather than Portland cement. This, together with raw materials availability, ease of production and use may eventually be decisive factors in their possible acceptance. It is an essential question for which reliable durability testing and modelling will be necessary.

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