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A physico-chemical basis for novel cementitious binders

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ABSTRACT

The drive towards sustainability in construction is shaping our attitudes towards alternatives to Portland cement. Although the cement and concrete industry is essentially sustainable with respect to raw materials supply, and concrete manufacture actually gives relatively low CO_2 emissions per unit volume compared to most competitive construction materials, the current focus on climate change has led to concerns about cement industry-generated CO_2. Thus, there is interest in developing alternative cements with lower associated CO_2 emissions. This paper seeks to provide a context for innovative development through a review of what is meant by a hydraulic cementitious binder, identification of key physico-chemical properties of successful binders and how novel systems generally rely on similar factors. Concepts such as reactivity, availability of reactive species and physico-chemical drivers for the formation of cementitious systems are discussed as a basis for introducing and reviewing recent developments in the search for ever more environmentally sustainable cements.

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1. Introduction

This paper reviews novel potential alternatives to conventional Portland-clinker-based hydraulic cements as inexpensive and environmentally sustainable oxide-mineral-based hydraulic binders for general use in construction. As a basis for this, some fundamental physico-chemical aspects of cement hydration processes are also reviewed, to provide context and to enable relationships between raw materials selection, mix composition and performance to be better understood.

The very low use-cost of conventional Portland-based cement systems is due to the great natural abundance and widespread distribution of the raw materials (calcium carbonates, aluminosilicates and calcium sulphates) coupled with a manufacturing process which has been highly optimised for energy- and cost-efficiency over the last few decades. However, it is not yet optimised in terms of CO_2 emissions, and the current global perspective on sustainability will probably require this to be done over the next few decades, due mainly to the enormous volumes of cement used worldwide.

CO_2 is one of several gases that are known to have a positive effect on the retention of heat by the Earth's atmosphere, and thus have the potential to increase average global surface temperatures. Since increases in the emissions of such "greenhouse gases" (GHG) are mainly due to human activity, their emissions are likely in future to be regulated on a global level. This is currently a major long-term concern for all heavy industries, even though no strong international measures are yet in place that will force major GHG-emitting industries to change their technologies on a global basis. The main problem for the cement industry is that all conventional construction cements are based on "clinkers" (products of thermal sintering or melt processes) containing basic calcium compounds, for which the major raw material is limestone (calcium carbonate). The decarbonation of limestone results in the release of "fossil CO_2" into the atmosphere, which currently accounts for about half of the cement industry's CO_2 emissions; and this problem is even greater for the lime industry. While both hardened cements and hardened limes do slowly re-absorb their emitted fossil CO_2 from the atmosphere by carbonation during the life of the structures made with them, and also after demolition, this re-absorption generally occurs on a timescale of hundreds of years and is thus not currently taken into account in most models of the rate of change of atmospheric CO_2 levels due to human influence. Thus, if we are to tackle this perceived problem, energy-efficient ways must be found to produce hydraulic binders that emit significantly less fossil CO_2 during manufacture.

In addition to the choice of raw materials, the choice of manufacturing process, and especially the choice of fuel and power sources, is an important sustainability issue. Clearly, the way in which "biomass-derived fuels," "waste fuels" and "industrial by-products" are treated during any sustainability evaluation can have an important bearing on the apparent sustainability of the overall process and thus of the potential economic value or cost of the product. And transportation to market is another major sustainability factor that clearly cannot be ignored.

1.1. What do we mean by "sustainability" with respect to cement technology?

The definition of sustainability is to some extent arbitrary, in the sense that we currently have no good models to predict whether or not "developed" human society as we now know it is itself sustainable for any significant number of generations. We can perhaps define an industry as being sustainable if it can continue to produce and sell its products over many generations. Factors that will influence this are the availability of the raw materials, including energy, as well as the availability of skilled manpower. For the Portland cement industry, manpower needs are relatively low, so it is raw materials and energy that dominate. There is no global shortage of suitable raw materials or energy sources, so the industry is inherently sustainable with the exception of its high CO_2 emissions.

The global average CO_2 emission per tonne of cement manufactured is estimated to be about 0.83 tonnes [1], which is actually quite low compared to most other manufactured products. Compare it, for example, to steel, at up to about 3 tonnes of CO_2 emitted per tonne produced, or to aluminium, at up to about 15 t/t. Moreover, cement is not the end product for any major application. Almost all cement is used to make concrete, in which it is typically diluted by a factor of 5–10 by aggregates and water, both of which have very low associated CO_2 emissions. Thus, concrete is actually a relatively low-CO_2 construction material, coming in well below most fired-clay products (e.g. bricks or tiles) and even some processed wood products on a manufacturing CO_2 emissions-per-unit-volume basis, (although the way in which CO_2 emissions are estimated for wood depend strongly on how it is grown and how it is treated before use).[1] Note also that the steel reinforcement used in most structural concretes contributes a very significant fraction of the total manufacturing CO_2 emissions of such concretes. The main issue, of course, is simply that concrete is the largest-volume manufactured product on earth, apart from processed water. Current estimates put global concrete production at around 10 km^3 per year, and this number continues to increase due to massive urban and national infrastructure development all over the world. So, simply because of the enormous volumes of concrete produced globally every year, it is clear that any positive action that the cement manufacturing industry could take to reduce its specific CO_2 emissions would make a significant global contribution to the goal of reducing overall global GHG emissions.

Thus, some cement companies, as well as independent R&D organisations, are developing and evaluating alternative cement technologies in anticipation of possible regulations. The main difficulty at the moment lies in knowing how to put a cost on emitted GHGs, since it is very difficult to estimate the environmental damage that they may cause in financial terms. And even after some such cost estimation is agreed, it will still be difficult to get anything equivalent to a GHG "emissions tax" universally accepted by the major emitters worldwide. Thus, in the absence of any global agreement or standards that might regulate this issue, the best that we can currently do is to compare novel low-CO_2 technologies in terms of the potential CO_2 emissions-cost at which they might become cost-competitive with conventional technologies that make products of equivalent performance. This is clearly a somewhat artificial situation, since in most cases the new processes do not yet exist on an industrial scale, and the new products do not exist in large enough quantities to be tested by real end-users to determine whether or not they might be acceptable on the open market, and at what price. Not surprisingly, the publicly available technical information on all of the novel cements to be discussed in this paper is very limited and has often not been subjected to independent or unbiased evaluation.

1.2. What do we mean by "cementitious matrix"?

The term cement can be used for almost any type of binder or glue, with formulations ranging from totally organic to totally inorganic. Organic glues were, historically, made from plant extracts, the most common being polysaccharides, e.g. starches; or latexes, e.g. natural rubber. The oldest true inorganic cements are almost certainly gypsum plasters, although mud, which is clearly much more ancient,

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[1] There are no generally agreed figures for overall CO_2 emissions, but there are many studies of embodied energy available in the literature. We used a single source which compared many different materials: http://www.victoria.ac.nz/cbpr/documents/pdfs/ee-coefficients.pdf. We then converted the embodied energy to CO_2 equivalent on the assumption that it was derived from coal, and finally added the estimated fossil CO_2 contribution from the raw material (in the case of cement).

can also be considered to be a binder when dried. Traditionally, the role of a "glue" is to bind solid materials together at surfaces. However, it may also have a role as a filler in its own right, in which case the term "cement" seems more appropriate, although this distinction is not universally applied. Traditionally, organic binders are more often used as glues, in the sense that only a very thin layer is required to bind together surfaces that are essentially flat, i.e. have only moderate roughness or porosity. The best examples of this class are probably the cyanoacrylates, which work best as extremely thin films. On the other hand, latexes are often used in cases where relatively thick but flexible joints are required. In this case, the hardened latex serves as both a glue and a filler — which can be very important on surfaces which are inherently very rough or porous. Inorganic binders that act as glues in thin films are less common, but water–glass is a good example. Clearly, thin-film binders must be made either from liquids that can solidify (e.g. polymerize), usually in the presence of a catalyst (e.g. hydroxyl ions in the case of cyanoacrylates); or else from solids that are essentially completely soluble at fairly high concentrations in a liquid carrier medium. Both give liquids which can, before hardening, completely wet the surfaces to be bound together and effectively fill in as much as possible of the residual surface roughness or porosity; but reaching the full adhesive effect in a solvent-based glue also requires at least partial removal of the solvent, e.g. by evaporation or by adsorption by the solid substrates. In both types, the resulting fine layer of newly formed solids bonds to the surfaces on both sides via short-range solid–solid forces. But, even though the actual surface adhesive forces at work may be intrinsically weak, e.g. often only van der Waals forces, the high effective contact area obtained by good initial liquid–solid wetting can still lead to a reasonably high average bond strength at the interface. The thinner the layer of adhesive, the less its own bulk mechanical properties are important for the overall performance of the joint.

Although the above explanations can be applied to both organic and inorganic cements, the subject of this paper is oxide-mineral-based hydraulic binders. It is thus important to point out that essentially all of the cements of interest for construction applications are used in the form of aqueous dispersions of poorly soluble powders, rather than as true solutions. The presence of fairly large solid particles (typically of the order of tens of microns in diameter) in the fresh "cement paste" (the term traditionally applied to the initial concentrated aqueous cement dispersion) means that the cement paste must inherently have a very significant filler effect. The particle size distribution of the cement, when freshly dispersed in water, is also critical in determining the initial rheological properties of the paste and its ability to fill in defects on the surfaces that it is intended to bond together. It is this initial aqueous dispersion, the "fresh cement paste," that gives rise, on hardening, to what we may call the "hardened cementitious matrix."

1.3. What do we mean by "hydraulic binder"?

The water-activated cements used to make modern construction concretes are commonly referred to as "hydraulic binders," both because they harden by a reaction that requires water, and also because they can set and harden under liquid water, i.e. they do not require the removal of excess water in order to harden. The term also implies that they can, under suitable conditions, be used for underwater concreting. However, the definition of the term "hydraulic binder" can give rise to somewhat arbitrary distinctions between binders that are more or less suited for use in various types of humid environment. For example, gypsum plasters can set and harden in a moderate excess of water, but suffer from poor long-term performance under humid conditions, probably because of the high water-solubility of the hydrated cement matrix (gypsum). Sorel cements behave similarly. But in both cases the hardening process involves a reaction with liquid water to produce stable solid hydrates, and the presence of some excess water at early ages does not impede the process. This clearly shows that the main bonding mechanism is not capillary forces, as is sometimes wrongly assumed. We will therefore use the term "hydraulic binders" to include all water-dispersed binders that can harden initially under a moderate excess of liquid water, even though not all of them are suitable for long term use under water, or in conditions of high humidity. Other processes may also be at play in many non-hydraulic water-dispersed binders, such as atmospheric carbonation in the case of limes, or polymer-interdiffusion (film formation) in the case of latexes; but physical removal of water from the material is always a necessary part of the early hardening process for such binders.

1.4. Outline of the hydration chemistry of oxide-mineral-based hydraulic binders

The term "oxide-mineral-based hydraulic binder," as used here, refers to relatively inexpensive inorganic cements derived essentially from common oxide mineral raw materials. The Earth's crust is made up mainly of minerals based on the oxides of silicon, aluminium, magnesium, calcium, iron, sodium and potassium. Other important oxides found mainly very near the surface are carbon dioxide, sulphur trioxide and water, which occur in common minerals as carbonates, sulphates, and hydroxides or hydrates, respectively. Most of the relevant elements occur at the Earth's surface in only one oxidation state, except for iron, carbon and sulphur, which can occur in various different states. But in cement chemistry it is reasonably assumed that all elements occur as oxides in their equilibrium oxidation states under 1 atmosphere of air at 25 °C, unless specified otherwise. This is the basis of the "oxide notation" used generally as a shorthand notation in cement chemistry.

In order to make a mineral-oxide-based hydraulic binder it is necessary to use a combination of oxide phases that is metastable in the presence of liquid water, and thus will tend to convert to a more stable phase assemblage when wet. It is generally assumed that the more stable phase assemblage will always contain more chemically bound water than the initial phase assemblage. However, the case of calcium carbonate binders appears to be an exception to this rule [2]. We now believe that the binding capacity of a hydraulic binder is mainly related to the fact that the new solid phases can precipitate from a supersaturated aqueous solution in such a way as to create a significant area of solid–solid bonding interfaces in a space that was previously filled only with liquid water. This is certainly the case for gypsum plasters, as explained in [3,4], and there is reason to believe that all oxide-mineral-based hydraulic cements bind by basically similar mechanisms. The binding mechanism is thought to be due to the formation of significant areas of solid–solid "grain boundaries" that are attractive even in water, and so do not readily re-disperse [3,4]. It is this aspect that in practice differentiates hydraulic cements from non-hydraulic mineral-based binder pastes such as clay-rich soils of the type used to make mud brick or rammed-earth construction products.

Apart from the bonding aspect, there is a second aspect of most hydraulic cements that plays a major role in most important applications, and that is the enhanced volume-filling effect that usually occurs due to the fact that conversion of some of the initially liquid water to solid hydrate phases results in a net increase in solid volume during paste hydration. This increase in solid volume fraction in the paste enhances the natural filler properties of the initial fresh paste, often very significantly, and this factor can often compensate for the intrinsically weak hydraulic bonding capacity of many of the solid phases present in the hardened matrix. In most cases of practical interest the reaction of the common anhydrous oxide phases with water at atmospheric pressure is exothermic and also results in a net decrease in total condensed-phase (i.e. total solid plus liquid) volume

[5]. However, the specifics of the phase changes involved can differ greatly between cements.

1.5. Outline of the manufacturing chemistry of lime-based hydraulic binders

Cements of practical interest for most construction applications must be made from very abundant and inexpensive raw materials, which represents a major chemical limitation [6]. Most common hydraulic cements are based on easily hydrated basic calcium compounds produced from limestones (rocks based mainly on $CaCO_3$) which represent very abundant and widely distributed sources of calcium oxide (lime), together with clays, which are very abundant sources of silica and alumina.

Quicklime was produced initially by burning lumps of limestone with any available fuel. The products were observed to react violently with water to give a fine water-dispersible powder that was called "slaked lime," and this product was found to have valuable applications in plasters and mortars. Once this ancient technology became widespread it also became apparent that the qualities of the limes produced in different locations were in fact very different, certain of them being far more suitable for use in situations where water-resistance was necessary, e.g. lining water conduits. The Romans greatly advanced lime technology, e.g. by adding reactive aluminosilicates in the form of volcanic ashes ("pozzolana") or particles of crushed brick, etc., to give cements with greatly improved hydraulic properties. Things didn't evolve much further until the early 19th century, when cements rich in highly basic calcium silicates and aluminates were developed, which gave better strength development and water-resistance than ordinary hydraulic limes. Thanks to the marketing genius of Joseph Aspdin, such cements are now generically known as "Portland cements." However, their underlying chemistry was not really well understood until over a century after their initial development [7]. Thus, early Portland cements also differed greatly from location to location depending on the type and proportions of the raw materials as well as the process technology used, both of which were usually well-guarded local secrets. It was the inception and development of national technical standards over the last century or so that led the cement industry to analyze and describe its products more accurately and openly. This process is still continuing, with technical standards becoming ever more international.

In addition to the need for abundant raw materials, the manufacturing process should be as energy-efficient as possible, since energy costs are usually a major part of the variable costs. However, each mole of CaO in limestone carries with it one mole of "fossil" CO_2, captured from the atmosphere millions of years ago when the limestone was originally precipitated from the oceans. Thus, production of easily hydrated compounds based on CaO requires emission of large volumes of fossil CO_2 back into the atmosphere, where it is nowadays considered undesirable due to its role as a greenhouse gas. Moreover, the enthalpy of decarbonation of $CaCO_3$ (and also of most other carbonate minerals) is very high – about 4GJ per tonne of CO_2 emitted – which implies that, if the process is powered by a carbon-rich fuel, such as coal or coke, roughly another 0.4 tonnes of CO_2 will be emitted just by the fuel required to accomplish the decarbonation reaction, (i.e. an additional 40%,) even in an ideal process with 100% thermal efficiency. Thus, it is clear that the content of limestone-derived reactive CaO in any cement will be a major factor in determining its manufacturing energy requirements and CO_2 emissions.

Most of the energy used in Portland cement manufacture is heat required for clinker formation, i.e. the decarbonation of limestone and the subsequent reaction of lime with the other ingredients, such as clay minerals, quartz and iron oxides. The main endothermic reactions are decarbonation of calcite at about 900 °C and the dehydration of the raw materials at lower temperatures. Due to the practical difficulties of recovering heat from humid exhaust gases below about 100 °C, the gross thermal energy requirement of even the best modern cement kiln systems is rarely less than 160% of the theoretical value of about 1.8 GJ per tonne for an OPC clinker made from dry raw materials [6]. However, the actual thermal performance of a modern cement plant can be better than this because the raw materials are often wet and so some of the waste heat can be used to dry them.

The other main energy requirement is electric power, e.g. for crushing, grinding and homogenizing the raw materials, powering fan and kiln motors, and especially for the fine grinding of clinker and the other ingredients required in the finished cement. An efficient cement plant requires about 100 kWh per tonne of cement, which, if produced from coal, would involve the emission of about 100 kg of CO_2 by the electric power producer. To this must be added the fuel required for the transportation of raw materials to the cement plant and of the product to market. Due to cement's low cost per tonne, shipping costs can easily become a very significant proportion of delivered costs, especially for overland transport; and they may also be important in terms of energy consumption.

1.6. Durability issues

This review will not deal in any great detail with the subject of durability, but it is an issue of great importance with regard to the sustainability of the products and structures that result from the use of hydraulic binders. Clearly, the main application of hydraulic binders is in the manufacture of concrete, and it is thus the subject of concrete durability that is of most relevance here. This is a very complex subject, because there is an enormous range of possible concrete compositions potentially available even with conventional Portland-based hydraulic binders, let alone the novel binders that are the subject of this paper. It thus makes little sense to talk about the durability of the binder itself. What is important is to understand how the binder is likely to be used and how its physical and chemical properties are likely to influence the durability of the resulting products under the exposure conditions to which they are likely to be subjected. Only if the novel binder paste is to be used as essentially a 1:1 volume replacement for a Portland-based cement paste in a volumetrically fixed concrete formulation can the performance of the hardened paste on its own (relative to the hardened Portland-based cement paste control specimen) be taken as an indication of the relative durability potential. And even under these conditions, the sensitivity of the binder pastes to curing conditions may be a critical factor in the durability of the resulting concrete. For example, many standard concrete and mortar tests compare specimens that are cured under water for a long time before testing, even though this is atypical of actual concrete practice on most construction sites. In the real world, very little concrete is moist-cured for more than a few hours, and thus the test conditions used to evaluate both mechanical performance and its durability should take into account the likelihood that the concrete will probably not be fully cured in practice.

A further issue of great importance when discussing concrete durability is that of reinforcement. Concrete is fundamentally a composite material, consisting of the hydraulic binder paste diluted with coarse and fine aggregates which usually serve to a significant extent as reinforcements in compressive loading. Thus, the physical and chemical interactions between the paste and the aggregates can have a significant impact on the overall performance and durability of the concrete. However, it is relatively rare for there to be a major durability problem associated with the aggregates, and the most common example, expansive alkali-aggregate reaction, is now reasonably well understood for Portland based concretes and so can be relatively easily assessed for alternative binders, many of which contain low alkali-metal levels and are thus inherently less likely to give this problem. But, beyond this, most structural applications of concrete also involve the use of steel as tensile reinforcement. In fact, modern concrete construction depends to a very large extent on the excellent synergy between steel and Portland cement pastes in both the physical and the chemical sense. In the physical sense, even ordinary steels have very high elastic moduli, are extremely strong in tension, and are also very tough and ductile, undergoing very large plastic deformations before rupture. This makes steel the ideal reinforcement for most concretes, which also have fairly high elastic moduli (if dense aggregates are used) but have very low tensile strengths and suffer essentially brittle failure at very small tensile elongations. In addition to this excellent mechanical synergy there is also a chemical synergy that is just as important, namely, the fact the Portland cements produce a strongly alkaline hydrated matrix which has the ability to passivate mild steel against corrosion. The fact that inexpensive mild steels can be used to reinforce inexpensive Portland cement based concretes to give good overall mechanical performance and durability is one of the main reasons why concrete is such a widely used building material. Thus, one important durability issue with any alternative cementitious matrix will be its ability to passivate inexpensive steels against corrosion. The precise range of pH needed to keep steel in a passive state in the presence of liquid water and normal atmospheric oxygen levels depends to some extent on the presence of other ions in the aqueous phase. In general, pH values above about 12 are considered to be necessary to protect steel in concrete, but higher pH values are required if chloride ions are present [8]. Portland cement-based concretes generally maintain a pH well above 12.5 due to the presence of some solid portlandite ($Ca(OH)_2$) in the matrix that acts as a buffer, and the presence of alkali metal ions in the pore solution; but the portlandite reacts slowly with atmospheric CO_2 to form calcite, and, once it has all been consumed, the pH can drop significantly as the C–S–H gel also begins to carbonate. Thus, atmospheric carbonation of reinforced concrete structures can in some cases dictate their effective working lives, if other factors do not damage them first. The ability of many of the alternative cementitious matrices discussed in this paper to protect steel from corrosion in structural applications has not yet been well assessed, and so remains an important subject for research. While some applications of concrete do not require steel reinforcement, e.g. blocks and bricks, the market for unreinforced concretes is smaller than that for reinforced concrete and is more easily subject to substitution by other products (e.g. fired clay products). It is therefore also of interest to consider the possibility of alternative types of tensile reinforcement for hydraulic cement matrices that do not have the capacity to passivate steel for a significant length of time. However, this subject goes beyond the scope of the present paper.

2. Overview of key physico-chemical drivers

Before specific cement systems are discussed in detail, it seems beneficial to review the principal physico-chemical factors which underlie the important cementing processes and how these can be used in practice in cement formulation.

2.1. Chemical potential gradients in reactive cement systems

The reactivity of primary solids in the presence of an activating liquid, whether in a hydrating Portland cement or in the hydrolysis of aluminosilicate glasses, is driven by the reduction in chemical potential (molar free energy) differences as the reactants convert to products. In many cementitious systems, the chemical potentials of reactants can be correlated with their "Lewis basicity." It is important to distinguish this from the more familiar concept of acid–base properties of aqueous solutions in which pH provides a numerical indicator of the concentration of the hydrogen ion in solution. Lewis basicity (or acidity) measures the ability of a chemical species to donate (or accept) an electron pair. In general, the larger the difference in Lewis basicity between two reactant species, the stronger is their tendency to form a covalent bond. Conveniently, Duffy and Ingram [9,10] defined the *optical* basicity scale in 1971, a numerical correlation of Lewis basicity, which embraces concepts such as ion polarisability, with composition and its use was Illustrated for cement-relevant oxides by Dent-Glasser and Duffy in 1987 [11].

The optical basicity of a medium composed of various oxides AO_a, BO_b, etc., is given by:

$$\Lambda = \chi(AO_a)\,\Lambda(AO_a) + \chi(BO_b)\,\Lambda(BO_b) + \;\ldots\ldots$$

where $\chi(AO_a)$, $\chi(BO_b)$.... etc. are the equivalent fractions of the oxides with respect to the total number of oxide species, and $\Lambda(AO_a)$, $\Lambda(BO_b)$....etc., are their optical basicities. The optical basicities for a range of oxides have been defined from spectroscopic and refractivity data and are listed for selected oxides in Table 1 [11–14]. Consequently, optical basicities for compounds of these oxides can be calculated, e.g. for C_3S, or $3CaO.SiO_2$; $\Lambda_{Ca_3SiO_5} = \frac{3}{5}\Lambda_{CaO} + \frac{2}{5}\Lambda_{SiO_2} = 0.792$, and superimposed on a compositional diagram, such as indicated in Fig. 1, to highlight chemical gradients.

Fig. 1 shows basic oxides towards the bottom left of the diagram and acids towards the right and top. The potential for an acid–base reaction between any two oxide compositions in the diagram increases with the distance between the iso-basicity lines on which they appear. Thus, the thermodynamic basis for many cement reactions, such as those between highly basic portlandite ($Ca(OH)_2$; $\Lambda = 0.7$) and relatively acidic glassy (alumino)silicates such as rice husk ash (RHA), metakaolin, fly ash, or BFS, can be represented by their separation across iso-basicity lines.

The optical basicity concept has shown considerable versatility in the areas of glass and metallurgical slag chemistry and, although not

Table 1
Optical basicity data for several oxides, adapted from [11–14] and $Ca(OH)_2$. * Optical basicity is dependent on ion co-ordination number. The value for Al_2O_3 used in Fig. 1 is estimated for 4-co-ordinate Al^{3+}. More detailed discussion of co-ordination effects is given for Al^{3+}, Fe^{3+} and Fe^{2+} in [14].

Oxide	Λ	Oxide	Λ
SO_3	0.33	CaO	1.0
P_2O_5	0.48	Li_2O	0.81
B_2O_3	0.4	BaO	1.23–1.43
SiO_2	0.476 (4), 0.32 (6)	Na_2O	1.105
Al_2O_3	*0.6 (4)**, 0.4 (6)	K_2O	1.32
MgO	0.78	H_2O	0.4
		$Ca(OH)_2$	0.7

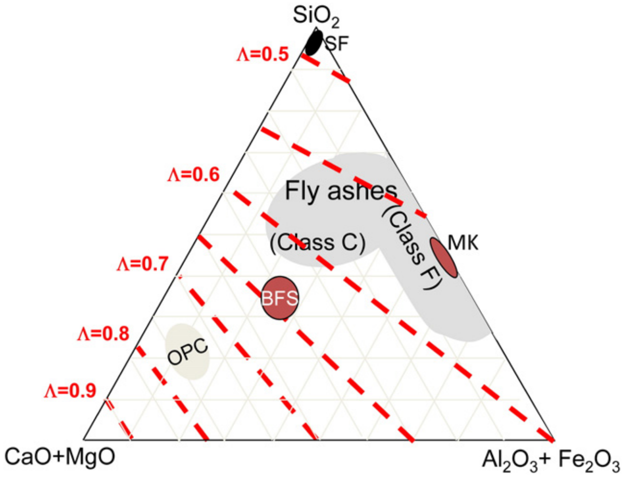

Fig. 1. Compositional diagram showing the positions of Portland cement and selected SCMs. Isobasicity lines are superimposed to illustrate chemical gradients available for exploitation in reacting cementitious systems.

yet fully developed for hydrated systems such as cements, it has already proved helpful in providing explanation for structural anomalies in cement phases [15] and for guiding control of the aesthetic properties of cements [16,17]. The preliminary assessments on reaction pathways given here offer some insights into the further possibilities to be derived simply from phase composition information.

2.2. The importance of solubility

While chemical potential differences are the thermodynamic representation of the driving forces for all chemical reactions, the rates of reactions depend on their detailed reaction mechanisms and thus can vary over many orders of magnitude for the same chemical potential change. Direct solid–solid reactions are generally slow relative to reactions involving at least one liquid phase, due to the greater mobility of species dissolved in liquids. As is well known, the "activity" of any conserved chemical component in a solvent increases with its chemical potential, so a chemical potential gradient in a solvent is generally roughly equivalent to a concentration gradient, along which the relevant component will diffuse. The total diffusive flux of a mobile dissolved species is roughly proportional to the product of its chemical potential gradient and its mean concentration, so higher solubility results in a greater flux. This is why reactive solids that are highly soluble in water tend to hydrate more rapidly than less soluble solids, regardless of the solubility of the final products.

A simple example of a well-characterized through-solution hydration reaction is that of plaster of Paris (calcium sulphate hemihydrate, $CaSO_4.½H_2O$), a reaction in which the component "$CaSO_4$" is conserved throughout (note that this statement is true in the purely thermodynamic sense, despite the fact that the solution actually contains various different calcium and sulphate-containing species, e.g. Ca^{2+} and SO_4^{2-} ions). $CaSO_4$ in plaster has a higher chemical potential than $CaSO_4$ in gypsum ($CaSO_4.2H_2O$), which implies that an aqueous phase in equilibrium with plaster will contain a higher concentration of $CaSO_4$ than one in equilibrium with gypsum. However it also implies that a plaster solution is metastable with respect to precipitation of gypsum; thus, plaster dissolves and then gypsum precipitates (after nucleation). Thus, the diffusion flux goes from dissolving plaster particles to growing gypsum particles, while the precipitated gypsum behaves as a cementitious product [4]. There is good proof that the reaction goes entirely through solution [18].

Hydration processes involving acid–base reactions also usually occur via through-solution processes. For example, $Ca(OH)_2$ and glassy SiO_2 do not react significantly when mixed together as dry powders, but in the presence of liquid water $Ca(OH)_2$ dissolves appreciably and the alkalinity of the resulting solution is sufficient to promote hydrolysis of the silica; the reaction between calcium and silicate ions in alkaline solution is then rapid, precipitating calcium silicate hydrate (C–S–H) gel. This highlights the importance of the *availability* of reactive species; their presence does not necessarily mean that they are available for reaction. For example, most natural silicas and aluminosilicates are quite insoluble in water at close to neutral pH, and are therefore unreactive even in the presence of dissolved aqueous calcium or magnesium ions. But, with increasing alkalinity their solubility increases, promoting greater aqueous silicate and aluminate concentrations [19,20], and increasing reaction rates [21]. Therefore the solubility characteristics of the reactants in the aqueous phase have a major influence on the rates of cement hydration reactions.

Clearly, the solubility of the final hydrated phases of a hydraulic binder will have an influence on the durability of the hardened product in water, as was discussed earlier for the case of gypsum plasters. It is thus worth pointing out that the similarly moderate solubility of $Ca(OH)_2$ (portlandite) as a hydration product can be shown to be a negative factor for Portland cement paste durability [22] in much the same way. This underlines one advantage of removing the excess portlandite by the use of supplementary cementitious materials (SCMs) that will react with it to produce far less soluble products such as C–S–H. C–S–H also has excellent pore-filling characteristics which can greatly reduce paste permeability. Note, however, that the durability of reinforced concrete usually depends more on the corrosion rate of the steel than the durability of the cement paste. Thus, the excess of portlandite in hydrated Portland cement pastes contributes to the durability of reinforced concretes because it provides a pH buffer at high enough values (≈ 12.5) to keep steel in a passive state. In addition, atmospheric carbonation of portlandite converts it to calcite with a net increase in solid volume, which helps reduce the porosity and permeability of the carbonated "skin" of the concrete.

2.3. Surface reactions

All cement hydration reactions involve the disappearance (usually by dissolution) of at least one solid "cement" phase and the formation (usually by precipitation) of at least one new solid "hydrate" phase. Dissolution and precipitation are both surface reactions, i.e. they occur at the boundary between the solid phase of interest and the surrounding solvent phase, which is usually liquid water. However, some hydration processes do appear to proceed by a "topochemical" mechanism, e.g. as has been suggested in the case of the hydration of reactive calcia [23]. Topochemical reactions are reactions that occur at the interface between two nominally solid phases, where one of the solid phases (the hydration product) must effectively be a solid solution containing water, and can thus be considered to play the role of the "solvent." Indeed, this model was proposed to account for the distinction between 'inner' and 'outer' product based on an NMR study on C–S–H [24].

The kinetics of surface reactions can be very complex, so it is not our intention to discuss them in detail here. However, there are several different types of surface reaction that must be mentioned even for the simplest cases of the dissolution and precipitation of solid phases in a liquid solvent.

1. The mechanism of dissolution of a solid depends on the characteristics of the specific solid surface undergoing dissolution and the degree of undersaturation of the liquid phase. Recent work [25] suggests that (mineral) dissolution rates can change by more than an order of magnitude on passing from simple "step retreat" at low undersaturations to generalized pit ("vacancy island") nucleation at high undersaturations. Thus, dissolution rates of crystalline solids cannot be assumed to vary linearly with the free-energy decrease occurring upon their dissolution in undersaturated solutions. Likewise, the growth rates of such solids from their supersaturated solutions at existing growth surfaces cannot be assumed to vary linearly with the free energy decrease occurring on precipitation.
2. The precipitation of a new solid phase not initially present requires the creation of a new interface, which is a nucleation process. The kinetics of nucleation is a complex subject and nucleation rates vary in an extremely non-linear manner with supersaturation [26]. Generally, very high supersaturations are required for pure homogeneous nucleation. Thus, heterogeneous nucleation is usually more likely as there are almost always some surfaces present. Rates of heterogeneous nucleation also vary in a very non-linear way with supersaturation but the probability of nucleation also depends on the nature of the surfaces already present, and can be increased greatly by the presence of suitable surfaces [27] (e.g. "germs" or "nuclei").
3. Certain solutes can accelerate the steady-state dissolution or growth of solid phases without necessarily being incorporated

into the products, i.e. they can act as catalysts. It is well known that aqueous chloride ions catalyze alite hydration and aqueous potassium ions catalyze the hydration of gypsum plasters. The detailed mechanisms of these processes are not known, but it is clear that they are not related to homogeneous nucleation [28].

4. Dissolution and precipitation process of well-ordered ("crystalline") solids are inherently somewhat different to those of disordered, (i.e. "amorphous" or "glassy") solid phases. In particular, the precipitation of a disordered phase is most likely to occur at relatively high supersaturations with respect to a more stable and closely related ordered phase that cannot nucleate or grow fast enough under the given conditions. This is related to "Ostwald's step rule." Thus, precipitations of disordered phases are often closer to homogeneous nucleation processes rather than heterogeneous growth processes. It is less common to find disordered phases that grow regularly at low supersaturations and whose growth is also susceptible to heterogeneous nucleation, e.g. by the addition of surfaces of the same disordered product. However, the growth of C–S–H during Portland cement hydration appears to be one such case.
5. Polymerization reactions occurring in solution can be considered somewhat equivalent to homogenous nucleation processes because, if the polymer becomes insoluble once it reaches a certain molecular weight, it may precipitate as a "glassy" solid phase. If it still contains active polymer growth sites at its surface, growth can also continue at the liquid–solid interface. Thus, a polymerization reaction can constitute a mechanism for the steady growth of a "glassy" solid phase from a solution phase at low supersaturations. The reverse process, i.e. the dissolution of a glassy phase by depolymerisation, can also occur, e.g. by hydrolysis in the case where the polymer phase is bonded via a condensation reaction. This may well be relevant to the precipitation both of C–S–H and of alkali-aluminosilicate "gels," both of which are "amorphous."

3. New understanding pertinent to well-established cementitious systems

3.1. Hydrolysis and condensation mechanisms involved in "pozzolanic" reactions

The hydration of aluminosilicates is an extremely important issue with respect to the sustainability of hydraulic cements, since these are amongst the most abundant minerals at the surface of the Earth that have the potential to be used as cementitious materials. Volcanic ashes usually cool rapidly enough so as to contain significant amounts of glassy aluminosilicates; they thus can show "pozzolanic" activity provided that they haven't already hydrated naturally before extraction. Clay minerals are non-reactive hydrated acidic aluminosilicates that can be activated either by fusion followed by quenching to a glass (e.g. as occurs during coal combustion, to produce fly ash), or, in some cases, by dehydration at temperatures low enough to avoid crystallisation (e.g. metakaolin). Addition of lime prior to the fusion and quenching processes produces more basic and thus more hydraulically active aluminosilicate glasses, the best known case being granulated blast furnace slag.

The hydration of acidic aluminosilicate glasses is generally accelerated by basic solutions, preferably solutions with $\text{pH} > 12$ and containing calcium and/or alkali metal ions. This acceleration is not purely catalytic, since the metal cations are usually incorporated to some extent into the solid hydration products. However, since (divalent) calcium ions are usually more strongly bound than (monovalent) alkali metal ions, alkalis can potentially catalyse the formation of C–A–S–H hydrates.

Initial mixing of Portland cement with water leads to a rapid increase in the alkalinity of the mix water, providing pHs in excess of 12.5 within a few seconds of mixing. This alkalinity is sufficient to initiate several simultaneous hydrolysis reactions, notably of silicate and aluminate surfaces. These processes may be schematically described as in Fig. 2, (see also Duxson, et al. [29]) and are analogous with the reactions described by Dent-Glasser and Kataoka [30] in their description of the alkali-aggregate reaction.

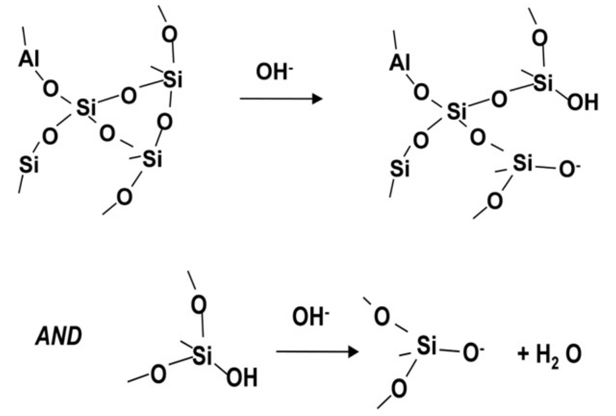

Fig. 2. Schematic illustration of alkaline hydrolysis of a (alumino)silicate indicating the formation of negatively charged surfaces.

Provided sufficient reactants are available, it can be expected that continuing hydrolysis of –Al–O–Si– and –Si–O–Si– bonds will lead to aqueous monomeric species, i.e. $[AlO_n(OH)_{4-n}]^{(1+n)-}$ and $[SiO_n(OH)_{4-n}]^{n-}$ provided concentrations do not exceed approximately 10^{-2} M [31]; higher aluminosilicate oligomers may be present if conditions permit considerably higher [Si] (>600 mM [32]). Aluminium and silicon hydroxides are only weak acids and so will remain partially protonated. It is through these protonated *aluminol* or *silanol* groups that the development of bonded networks can be established as shown in Fig. 3. These hydrolyses–condensation steps were discussed in more detail recently by Sharp et al. [33].

3.2. Influences of polarising cations

The dominant binding phase in all Portland-based cements is calcium (alumino)silicate hydrate gel, C–(A)–S–H, a poorly ordered phase of variable composition based on short, linear (alumino)silicate chains. The principal binding phase in alkali-activated fly ash or metakaolin ("geopolymer") systems is a sodium (or potassium) aluminosilicate hydrate gel, (N,K)–A–S–H, also poorly ordered but based on three-dimensional open frameworks typical of zeolites. A basis for the development of "cemented" silicate and aluminosilicate networks has been given above and in [33] but differentiating between the "structure-forming" properties of the 1-dimensional C–A–S–H and 3-dimensional N–A–S–H systems requires some consideration of the effect of the cations available during the aluminate and silicate condensation stages.

It may be recalled that the hydrolysed silicates and aluminates will have exposed negative charges. The ability of hydrated cations to

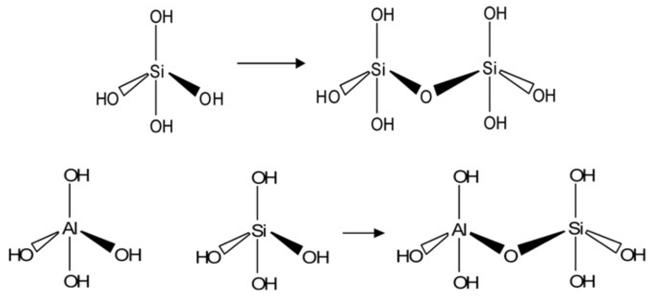

Fig. 3. Condensation of *silanol*/*aluminol* groups to reform –Si–O–Si- or –Si–O–Al- linkages in the formation of bonded networks.

Table 2
Cation characteristics relevant to hydration chemistry in cementitious systems.

	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Radius, Å	0.68	0.97	1.33	0.66	0.99
Z/r	1.47	1	0.75	3	2
$\Delta H^o{}_{hydn}/kJmol^{-1}$	−519	−406	−322	−1921	−1577

associate formally with these charges depends on how strongly the charges are hydrated. Table 2 summarises ion size and charge information and shows the expected correlation between charge density (Z/r) and hydration enthalpy, $\Delta H^o{}_{hydn}$, a measure of how strongly the positive charge of the ion interacts with the negative charge associated with the oxygen of the hydrating water molecules (see Fig. 4). Where a cation is able to release one of its hydrating water molecules, its positive charge is more exposed to the negative charge on the silicate. A further effect on charge screening is associated with hydrolytic dissociation, an effect enhanced by increased pH which more strongly polarises the M–O bond [34]. As Fig. 4 illustrates, this weakens the O–H bond until dissociation occurs. The released proton is readily consumed in the alkaline media and may even associate with negatively charged surfaces to facilitate condensation. Consequently, ion charge density and pH can be expected to influence condensation, and hence gelling mechanisms. In fact, Depasse and Watillon [35] showed that the critical charge density for stabilisation of a silica sol is intermediate between K^+ and Na^+; K is able to form an ion pair with the negative silicate surface through an electrostatic association, blocking condensation through this bridging oxygen, but Na is not. Consequently, sol coagulation is enhanced with increasing pH in the presence of Na but not with K, the larger ion more easily releasing a hydrating water molecule and binding with the negatively charged silicate oxygen to locally inhibit further condensation. Silica sols represent a reasonable model for cement-related systems in which the reactive surface is only partially dissolved but the same chemistry may be expected even when suspended solids are fully solubilised. Indeed, from NMR data, McCormick et al. [36] concluded that the tendency to form ion pairs with aqueous silicate ions increased with increasing alkali metal cation radius. The difference in gelling behaviour of K and Na systems already offers some suggestions for the observed differences between geopolymer systems activated by Na and K hydroxide/silicates [37,38].

The much higher charge density of Ca^{2+} (Table 2) presents an opportunity to differentiate the behaviour of lime-based from lime-free systems. At the pH of interest, the M–O bond is sufficiently strong that a water molecule on $Ca^{2+}(aq)$ dissociates, releasing a proton ($H^+(aq)$). By considering this mechanism (Fig. 4) and the appropriate formation constants for $[NaOH(OH_2)_5]_{(aq)}$, $[CaOH(OH_2)_5]^+{}_{(aq)}$ and $[MgOH(OH_2)_5]^+{}_{(aq)}$ as $10^{-0.4}$, $10^{1.36}$ and $10^{2.01}$ respectively, the quantitative significance of undissociated ion pairs can be calculated (Fig. 5). Deprotonation of hydrated Ca^{2+} begins to become significant at pH > 11, and this offers a route to condensation from which precipitation of portlandite or basic calcium silicate hydrates may result (Fig. 6(a)); see also [34]. Note that the high charge density of Ca^{2+} also contributes to the lattice energy stabilising the precipitated solid. By the same mechanism, precipitation of low Ca/Si C–(A)–S–H gels can begin at pH < 12 (Fig. 6(b)).

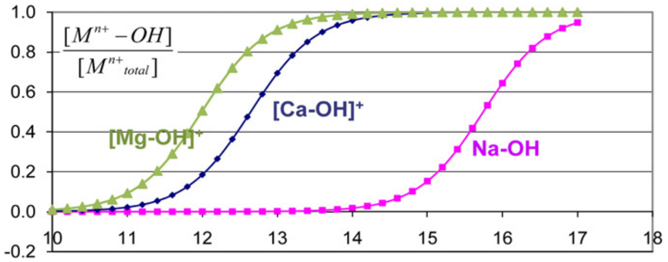

Fig. 5. Formation of M–OH ion pairs as a function of pH.

The tendency for strong polarisation and co-ordination by small multivalent cations accounts for the dominant precipitation role displayed by Ca in conventional cementitious systems. It limits the formation of the more highly polymerised silicates and aluminosilicates that are observed in alkali-metal-rich hydrate systems. The high stability of basic magnesium compounds in cement-based systems can also be explained by this chemistry.

3.2.1. Activation of aluminosilicates (SCMs and geopolymers)

The range of activation process in cement systems extends from the conventional application of SCMs in blends with Portland cement, e.g. [39], to alkali-activated aluminosilicate systems [40]. The fundamental chemical concepts addressed in the preceding section are considered central to the hydration of most hydraulic cements, but they do not occur in isolation or sequentially across the cement. Hydrolysis and condensation processes can be expected to occur simultaneously throughout the reacting system. Microstructure development can lead to isolated porosity incorporating pockets of aqueous phase in *localised* equilibria different from those established elsewhere. Consequently, real cements, particularly immature systems, present challenges in testing mechanistic hypotheses. Nevertheless, schematic and mathematical descriptions of this process have been developed by various authors and provide some interesting pointers [41–43].

The "conventional" activation of SCMs in Portland cement pastes occurs essentially via a portlandite-saturated aqueous phase, (which usually has a pH a little above 13 due to the presence of some soluble alkalis,) while their activation in alkali-activated aluminosilicate systems occurs essentially via concentrated alkali hydroxide solutions with pH well in excess of 14 . This difference has implications for the availability of the aluminate and silicate species for reaction [19,20]. For a given activator, reactivity is also dependent on the characteristics of the aluminosilicate (composition and thermal history). In a comparison of alkali-activated blast furnace slags (BFS) and metakaolins (MK), Li [44] addresses both composition and glass content as measures of reactivity and, based on [45] concludes that in the case of BFS, glass content, although important, gives a poor correlation with reactivity. Duxson focuses instead on the depolymerisation ratio, DP, [29] within the glass, where:

$$DP = \frac{n(CaO)-2n(MgO)-n(Al_2O_3)-n(SO_3)}{n(SiO_2)-2n(MgO)-0.5n(Al_2O_3)}.$$

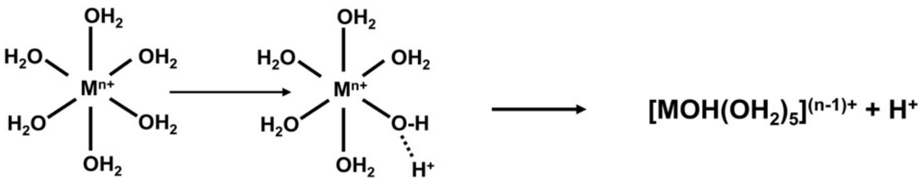

Fig. 4. Schematic illustration of hydrolytic dissociation and Brønsted acidity.

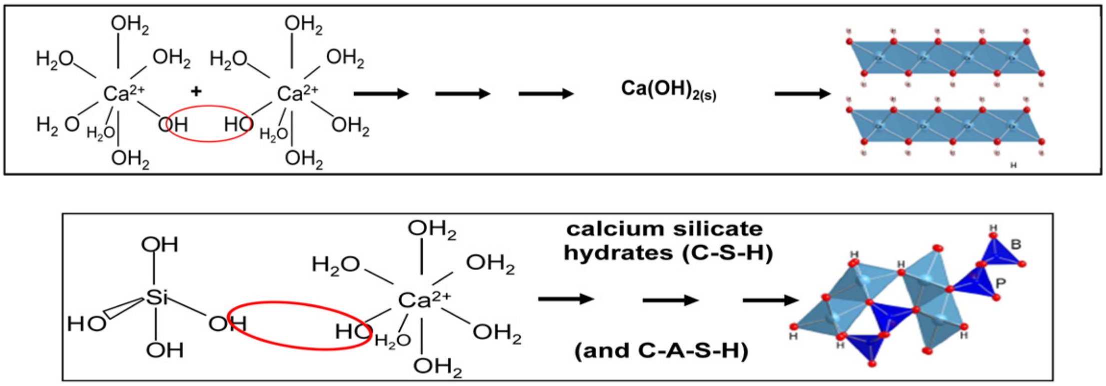

Fig. 6. Condensation as a possible mechanism for (a) $Ca(OH)_2$ and (b) C–A–S–H formation; $Ca(OH)_2$, C–S–H/C–A–S–H structures taken from [88].

Higher values of DP indicate a more depolymerised and therefore more reactive glass. This expression of local glass "structure" addresses the importance of non-bridging oxygens (NBOs), i.e. terminal oxygens in polymerised chains, usually associated with network modifying cations, as a measure of reactivity. Recently, as part of an assessment of synthetic SCMs, Moesgaard et al. [46,47] modelled *intermediate range* structural characteristics for synthetic calcium aluminosilicate glasses in the compositional range $C_{1.63}AS_{3.63}$ to $C_{3.31}AS_{3.38}$ [48] and proposed a quasi-two-phase structure consisting of regions rich in highly polymerized AlO_4 and SiO_4 units and other regions rich in highly depolymerised SiO_4 units. The reactivity of these glasses in cementitious systems may therefore be reasonably associated with this heterogeneity, specifically with the more energetically favourable hydrolysis of –Al–O–Si- bonds [19] initially [49].

To appreciate the increased reactivity of –Al–O–Si- over –Si–O–Si- linkages, it is useful to consider the acid–base properties of aluminates and silicates. In tetrahedral co-ordination, Al^{3+} and Si^{4+} have radii of 0.39 and 0.26 nm respectively [50]. Consequently, Si^{4+} has a Z/r more than twice that of Al^{3+} and is correspondingly more acidic. It can therefore more strongly polarize the electron density on its neighbouring oxide ions. Consequently, in an aluminosilicate mineral or glass, it would be expected that, where an oxide ion bridges between an Al^{3+} and a Si^{4+} ion, the –Si–O- bond will be strongest. Since –Al–O–Al- linkages are relatively rare in most common SCMs, which have low Al/Si ratios, the –Al–O–Si- linkages are likely to offer the easiest site for hydrolytic attack in these materials. This can account for the dissolution behaviour observed for aluminosilicate minerals [19,20] in which hydrolysis of –Al–O–Si- bonds preferentially releases Al into solution, leaving a Si-rich surface layer.

Indeed, the increased reactivity and performance of Class F fly ashes associated with higher alumina contents as reported by Duxson [29,51] is likely to be associated with an increase in the number of "reactive" –Al–O–Si- linkages in the aluminosilicate glass. This would contribute reactive monomeric $Al(OH)_4^-$ (aq) as observed by Weng and Sagoe-Crentsil [52] after 2 h in a study on metakaolin activation, and account for the initially Al–rich N–A–S–H gel ($Si/Al = 1.0$) observed by Fernandez-Jimenez et al. [53] in a study of fly ash activation. The Al-rich gel initially precipitated was considered to have formed coatings on the residual fly ash particles which contributed to early strength. But the remaining fly ash continued to dissolve in the activating solution and so the gel compositions became significantly more Si-rich by 7 days. This highlights the importance of *reactive species availability* with respect to the sequence of hydrate formation [51].

In activated BFS binders or Portland-cement-activated aluminosilicate binder systems, appreciable amounts of Ca are available from the beginning of hydration. The role of Ca in the formation of geopolymers for example has been addressed in the review by Li [44] but in principle, the chemistry described in Section 3.2 is applicable and accounts for precipitation of Ca as C(−A)–S–H or $Ca(OH)_2$ at high pH. In NaOH- or sodium silicate-activated metakaolins and fly ashes, the principle hydration product is a N–A–S–H gel; but in BFS systems, co-precipitation of C–A–S–H gels with N–A–S–H gels has been observed [54,55]. In a study of the influences of Ca additions on N–A–S–H gels and on Na and Al additions to C–S–H gels, Garcia-Lodeiro et al. [56,57] were unable to observe precipitation of $Ca(OH)_2$ but significant alteration of both gel types was reported even at relatively low pH. However their subsequent studies of phase equilibria in the Na_2O–CaO–Al_2O_3–SiO_2–H_2O system [58] suggests that pH *is* important in defining the distribution of Ca between C–A–S–H and N–A–S–H gels. At pHs typical of Portland or slag-based cements (i.e. above about 12) N–A–S–H and C–A–S–H gels can only co-exist at equilibrium if the C–A–S–H gel has a very low Ca/Si ratio. The reactivity of Ca at these pHs is considered to destabilise the 3D N–A–S–H structure by a mechanism similar to that illustrated in Fig. 6. However, Ca is less aggressive at lower pHs, due to the greater stability of its hydrated layer (see Fig. 5), and may associate with N–A–S–H gels by ion exchange, displacing Na^+ or K^+ [58]. In this case the gel can retain its 3D structure while adsorbing Ca^{++} until surface sites are saturated.

BFS activation has been discussed above in the context of glass characteristics. Alkalinity is necessary to access the reactive constituents, but this can also be achieved by indirect methods, e.g. via sulphates. For example, calcium or sodium sulphate sources dissolve to release sulphate ions that can be incorporated into stable hydration product (AF_m and AF_t phases). To balance charge, OH^-(aq) is released into the pore water raising the pH. This is also true for sodium carbonate activation. This mechanism enables BFS-based cements to develop strength with very little Portland cement and in fact provides the basis for supersulphated cements, which were first introduced in the early 1900s. The main hydration products are ettringite and C–S–H, with lesser amounts of hydrotalcite [59,60].

4. Comparisons of novel cementitious binders systems

A recent review article by Juenger et al. [59] addressed some sustainable alternatives to Portland-based cement systems. Four systems were identified, namely calcium aluminate cements, calcium sulphoaluminate-based systems, alkali-activated cements and supersulphated cements. The reader is referred to this article for details of historical context, compositions and reaction mechanisms. The remainder of the present paper reviews more recent progress in the development of low-CO_2 binder systems, making use of the physicochemical principles established in the previous sections.

4.1. Belite–calcium sulphoaluminate–ferrite (BCSAF) cements

Many types of calcium sulphoaluminate-based cement have been developed over the past few decades for a wide range of possible applications, especially in China, although relatively few are actually produced industrially [61]. There have also been many attempts to develop reactive belite cements in order to reduce the temperature and energy costs of clinkering in Portland cement kilns [62–64]. One approach being investigated by Lafarge is to combine the two above approaches to make intermediate clinker compositions containing belite, calcium sulphoaluminate (ye'elimite) and calcium aluminoferrite solid solution as the three principal phases, (given in decreasing order of content), and also including certain combinations of minor elements in order to stabilize the belite in the more reactive ά form [65]. Such "BCSAF" clinkers can produce cements with similar performance to Portland cements (OPCs) while in principle being manufactured in conventional Portland cement plants with the emission of 20–30% less CO_2 than the equivalent OPCs [66]. More recently, Lafarge has adopted the name "Aether™" for cements produced using this technology, which is now the subject of a European Community "Life+" development project. The hydration path of Aether™ cements is very different to that of OPCs, as it is the hydration of the ye'elimite phase (together with added calcium sulphate, e.g. as anhydrite) to give ettringite plus an amorphous aluminium hydroxide gel (AH_3) that accounts for most of the strength development during the first day [66]. This reaction can be represented as follows:

$$C_4A_3\bar{S} + 2\,C\bar{S} + 38\,H \Rightarrow C_6A\bar{S}_3H_{32} + 2AH_3 \tag{1}$$

Even on these short timescales, the importance of reactive species availability is highlighted in the study by Sahu et al. [67], which shows that the rate of ettringite formation and its subsequent impact on the reaction kinetics is dependent on the solubility (rate) of the calcium sulphate phase used.

Once the readily soluble calcium sulphate has been exhausted, ye'elimite can continue to hydrate to give a monosulphoaluminate AFm phase plus additional AH_3:

$$C_4A_3\bar{S} + 18\,H \Rightarrow C_4A\bar{S}H_{12} + 2AH_3. \tag{2}$$

After the first day, most of the additional strength development is due to hydration of the belite and ferrite phases, although their initial hydration products are different from those produced by essentially the same phases in OPC, which is not surprising given the ions available for precipitation. The latest evidence shows that belite initially hydrates mainly together with the consumption of AH_3, as shown below, to give crystalline strätlingite (C_2ASH_8) rather than C–S–H as usually formed in OPCs.

$$C_2S + AH_3 + 5\,H \Rightarrow C_2ASH_8. \tag{3}$$

The ferrite phase also apparently hydrates with consumption of some belite to produce katoites (siliceous hydrogarnets) covered by the general formula $[C_3(A,F)S_xH_{6\text{-}2x}]$ where the A/F ratio is unknown but x is probably not greater than 1 [68]. Thus, by 14 days the main hydrates all appear to be crystalline. This implies that it is not necessary to rely on amorphous phases such as C–S–H or AH_3 for strength generation in such cements. However, C–S–H does begin to form later on, typically at ages beyond about 14 days, as belite continues to hydrate after all of the AH_3 has been consumed, (at which point strätlingite also begins to be consumed by reaction with lime produced by belite hydration, giving more katoite) [69,70]. It is interesting to note that the compressive strengths of moist-cured concrete specimens made from BCSAF cements in 2006 continued to increase steadily over at least several months, and did not exhibit major bulk volume changes, despite the major changes in the hydrate phase assemblage that we may now assume to have taken place [71].

4.2. Partially prehydrated C–S–H-based binders

It is generally accepted that C–S–H is the most important binder phase in hydrated Portland cement pastes. Researchers at the Karlsruhe Institute Technology (KIT) have recently developed a new class of binder, called "Celitement™," that reportedly makes use of these binding properties in a more energy-efficient way, avoiding the need to produce Portland clinkers, and resulting in significantly lower CO_2 emissions for equivalent concrete performance [72]. 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. The precursor phase is typically formed from α-C_2SH, a calcium silicate hydrate produced by reaction of lime and silica under autoclave conditions. Crystalline α-C_2SH is not hydraulically reactive, but it can be activated by intergrinding it with a hard and relatively unreactive silica-rich filler such as quartz. Reportedly, the α-C_2SH becomes amorphous (and probably also 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, leading to C–S–H-mediated bonding between the filler particles. The manufacture of Celitement thus typically requires three fundamental steps: (1) the calcination of limestone to make quicklime; (2) reaction of lime, silica and water in an autoclave at about 200 °C to produce α-C_2SH, and (3) drying and intergrinding of α-C_2SH with a siliceous filler such as quartz. The net CO_2 emissions may reportedly, in favourable cases, be as low as 50% of those of CEM I OPCs. This is mainly because the binder contains a high content of a relatively inert filler such as quartz. It is reported that certain Celitement compositions can give mortar compressive strengths of up to 80 MPa after 28 days of humid curing, and also can give a low permeability matrix which might be helpful in retarding steel corrosion. On the other hand, the high filler content of most Celitement binders implies that they will probably require significant dosages of dispersants (superplasticizers) in order to achieve such performance [72].

4.3. Magnesium oxy-carbonate cements

MgO-based cements are not new. Sorel cements, invented over 140 years ago [73], are based on the hydration of MgO in concentrated solutions of either magnesium chloride or magnesium sulphate to precipitate hydrated magnesium oxy-chlorides or oxy-sulphates, respectively [74]. There are several well-defined binary hydrate phases (such as $5MgO.MgCl_2.13H_2O$) that can occur in these systems, but all of them have appreciable water solubilities, with a strong tendency to lose $MgCl_2$ or $MgSO_4$ to the solution by leaching, leaving brucite ($Mg(OH)_2$) as the main residual product, because it is very insoluble under neutral or basic conditions. This makes such cements too water-sensitive for most outdoor applications, in which respect they are rather similar to gypsum plasters. The performance of Sorel cements is also strongly dependent on the ratios of the main ingredients as well as the reactivity of the MgO used [75]. However, they generally set and harden very rapidly, can give considerably higher mechanical strengths than gypsum plasters, and also have good fire resistance. So, despite their relatively high cost, they have some good specialty applications, mainly for use in dry environments. Despite their high basicity, Sorel cements usually carbonate only very slowly in use, probably due in part to the formation of complex oxy-carbonate hydrates at the surface. It is also reported that the water-resistance of hardened Sorel cement products can be improved significantly by treating them with soluble phosphate salts [74].

Another important class of MgO cements is based on magnesium phosphates [74,76]. Magnesium forms sparingly soluble hexahydrated binary orthophosphates with either ammonium or potassium. The ammonium salt is called "struvite" ($MgNH_4PO_4.6H_2O$) and it has an isomorphous potassium-substituted equivalent. The hydration reaction is usually accomplished by adding solid MgO to a concentrated aqueous solution of the di-hydrogen phosphate salt of the monovalent cation, (e.g. a solution of KH_2PO_4). It is a rapid exothermic acid–base reaction in which the MgO first dissolves in the acidic solution and then the double salt crystallizes. This type of cement can set and harden very quickly, and can also give very high strengths. Moreover, since struvite has only about one tenth the solubility of gypsum, magnesium phosphate cements have good water resistance, especially under neutral or basic conditions. Its low solubility is one reason why it can sometimes be a major cause of discomfort for people and their pets, as it is a common component of urinary-tract stones in both!

Both Sorel cements and magnesium phosphate cements generally make use of MgO (periclase) powders made by calcination of magnesite ($MgCO_3$). The reactivity of the MgO powder is an important aspect of the quality control of such cements, and is mainly controlled by the calcination temperature used. Higher calcination temperatures and times allow the periclase crystals to grow larger and thus lead to reduced reactivity. Magnesium phosphate cements in particular require relatively unreactive ("dead burned") MgO powders in order to give long enough working times, and it is also often necessary to add set retarders such as soluble borates.

Despite the fact that magnesium is one of the most common elements on the surface of the earth, the two classes of MgO-based cements described above are restricted to specialty applications, mainly because of the relatively high cost of pure MgO. This is due partly to the scarcity of the main raw material, (relatively pure) magnesite, which is far less common than limestone or dolomite. Note also that (a) magnesium phosphate cements suffer from a more severe sustainability problem due to the global scarcity of phosphate ores and their priority application in fertilizers, and (b) it is possible to make a kind of Sorel cement from partially calcined dolomite, or "soft-burned dolime," which is essentially an intimate mixture of $CaCO_3$ and MgO and is less expensive than pure MgO. But the performance of such cements is poor due to their dilution with calcite [74].

It is also well known that magnesium is abundant in the oceans. Average seawater contains about 1290 ppm of Mg^{++}, which is equivalent to about 2.2 g/l of MgO, but it is present in an essentially fully neutralized form (the present-day average surface pH being about 8.07 due to saturation with respect to atmospheric CO_2). Thus, MgO can only be separated from seawater by the addition of a strong base, e.g. lime (CaO or $Ca(OH)_2$) or "hard-burned dolime" (fully calcined dolomite, an intimate mixture of CaO and MgO), to precipitate brucite, which is then dried and calcined to give periclase. But this is, overall, a more energy-intensive and expensive process than the calcination of magnesite.

However, the average content of MgO in surface rocks is very great. Thus, over the last decade, several fresh attempts have been made to try and develop more sustainable cement technologies based on magnesium oxide. An Australian company called "Tec-Eco" developed and patented a series of binders incorporating various amounts of reactive MgO produced by calcining magnesite at low temperatures [77]. The inventor, John Harrison, claimed that the low-temperature calcination of magnesite required less energy and emitted less CO_2 than the manufacture of Portland cements, and that adding reactive MgO to Portland–pozzolan cements could improve their performance and also increase their capacity to absorb atmospheric CO_2 [78]. Other researchers have since investigated the details of such systems but have not observed any remarkable benefits due to the incorporation of MgO [79]. In any case, Harrison's proposition that MgO-based cements were inherently more sustainable than CaO-based cements was not supported by the evidence, because (a) MgO derived from natural magnesite or from seawater releases more fossil CO_2 per unit mass than calcination of limestone to make lime (or OPC clinker), and must also accomplish this highly endothermic reaction by the combustion of fossil fuels[2]; and, (b) brucite probably carbonates less rapidly than hydrated Portland cement under most exposure atmospheric conditions. The possibility also exists that one could make prefabricated articles by deliberately carbonating wet MgO under an elevated partial pressure of CO_2, and that this might allow one to develop a strong microstructure based on metastable hydrated magnesium carbonates such as "nesquehonite" ($MgCO_3.3H_2O$), as suggested in [78]. But it is in any case well known that one can produce strong precast products by the carbonation of Portland cement concretes, and some conventional concrete block makers already do this, so it is still not clear why carbonated precast products made from MgO that itself is derived from $MgCO_3$ should be any more sustainable than those made from lime or OPC.

However, the above situation has changed significantly over the last three years, due to the research of Vlasopoulos and Cheeseman at Imperial College, London. They developed and patented a new class of MgO-based hydraulic binders which include magnesium oxy-carbonate hydrates such as, for example, hydromagnesite ($MgO.4MgCO_3.5H_2O$) as important constituents [80]. But, more importantly, they also noted that it should in theory be possible to extract reactive MgO from common magnesium silicate rocks with acceptably low energy requirements and CO_2 emissions, and this important observation is the basis of a start-up company called "Novacem™" which is currently conducting the R&D needed in order to determine how to make such cements in industrial quantities. Evidently, much of this work is still confidential, but the summary given here is based mainly on a recent public presentation [81].

The important difference between the Novacem approach and previous approaches is the idea that MgO might be extracted from common basic magnesium silicate rocks, such as peridotites or serpentinites, with overall CO_2 emissions low enough to render the overall process sustainable. The advantages of using basic magnesium silicates as raw materials are twofold: firstly, they are very abundant on a global basis, despite the fact that they are not as well-distributed over the Earth's surface as limestone or clays; and, secondly, they contain essentially no fossil CO_2. The Earth's mantle is roughly 70% magnesium orthosilicate (Mg_2SiO_4), and this occurs as surface deposits in the form of olivine. Partial hydration of such rocks near the Earth's surface usually leads to the formation of serpentine ($Mg_3Si_2O_5(OH)_4$). Since neither of these minerals contains fossil CO_2, the main industrial problem is how to efficiently extract reasonably pure MgO from them with acceptably low costs and CO_2 emissions associated with the energy used. Novacem's approach is to make use of supercritical carbonation in a high-pressure reactor. This decomposes magnesium silicate into magnesite and amorphous silica, which can then, if necessary, be separated. The magnesite can be calcined in the usual way to give a reactive periclase, and the resulting CO_2 gas can be recaptured and returned to the autoclave, so it essentially serves only as a "catalyst" in the process.

A second important feature of Novacem's approach is the deliberate inclusion of certain types of magnesium carbonate in the cement formulation itself, in order to control the setting and hardening properties [80]. This is also shown in the bottom half of Fig. 7. If these magnesium carbonates are obtained by consumption of CO_2 from the atmosphere or from other industrial processes during the manufacture of the Novacem cement, and are included in sufficient amounts in the cement composition, the manufacture and use of such cements could in theory even be net CO_2-negative. Thus, the Novacem approach does not specifically require that the binder absorb atmospheric CO_2 during its working life (e.g. in hardened concrete structures) in order for it to be

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[2] It is true that the calcination of magnesite is significantly less endothermic than the calcination of calcite (about 2.5 vs. 3.9 GJ/t of CO_2 emitted) and that it occurs rapidly at significantly lower temperatures (500 °C vs. 900 °C). However, this is far from being sufficient to compensate from the large amount of fossil CO_2 emitted.

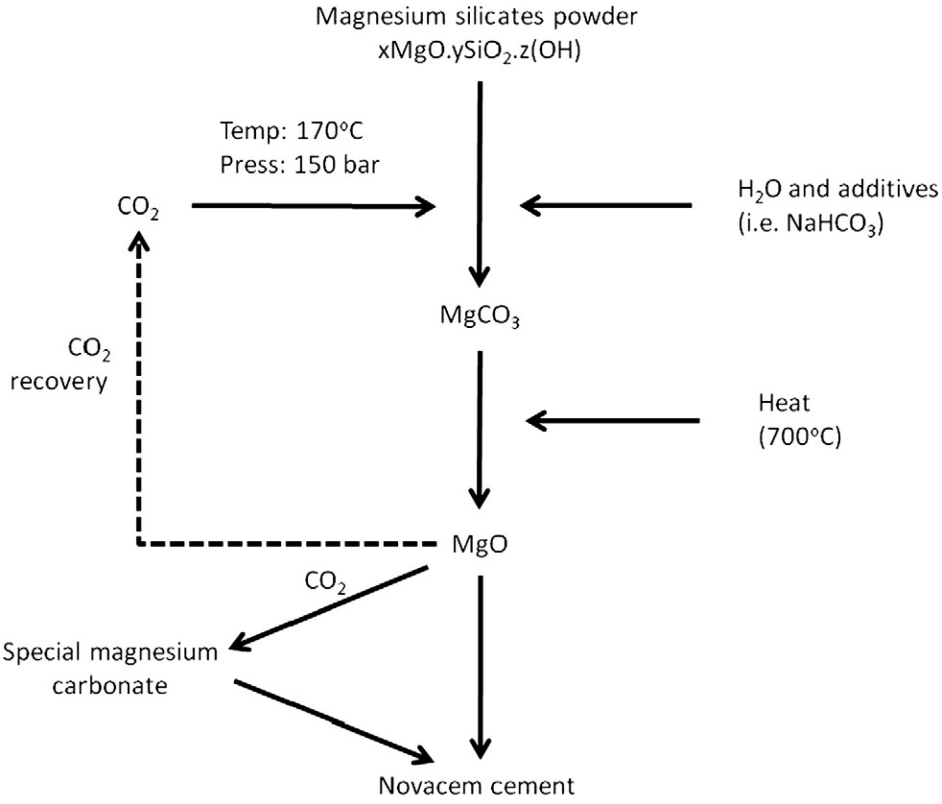

Fig. 7. Outline of the Novacem process.
Taken from Ref. [81]). Note that the definition of "special magnesium carbonate" is given in [80].

considered a "low-CO_2" cement. However, any such absorption would, of course, be an additional bonus.

Recent results [81] suggest that Novacem binders are capable of giving good-enough compressive strength development for a wide range of potential concrete applications. However, it is currently too early to determine whether or not the manufacture of Novacem will be industrially feasible at an acceptable cost and whether or not the desirable theoretically predicted CO_2 balance can be achieved in practice. Moreover, even if the approach is ultimately successful in the above terms, there will also still be much work to be done to establish the quality and reliability of such cements for major construction applications. One important issue will presumably be that of reinforced concretes, as magnesium hydroxides are far less basic than calcium hydroxides, implying that MgO-based cementitious matrixes will probably only be capable of buffering the pH of their pore solutions at values close to 10, which is too low for the conventional passivation of steel. However, this problem is not unique to Novacem. Many of the low-CaO binder systems discussed in this paper are likely to have difficulty in maintaining a high-enough pH for the passivation of steel over long periods of exposure to the atmosphere, because of their tendency to carbonate rapidly. In this respect, the high CaO content of Portland cements is still a major durability advantage in most structural applications unless the permeability of the paste matrix of low-CaO binders can be made so low as to limit steel corrosion rates to acceptable levels by restricting transport of ions and/or oxygen.

4.4. Calcium carbonate cements

As was noted in the introduction, calcium carbonate, in the form of limestone, is one of the most globally abundant raw materials for the manufacture of hydraulic binders. Clearly, it would be of great interest to be able to use it as a major binder ingredient without the need to decarbonate it first, thus avoiding the release of its fossil CO_2 into the atmosphere. Currently, limestone powders are used in various classes of Portland cement concretes, and it is known that calcite can actually react chemically with the aluminates in cement to form calcium carboaluminate hydrates which are classed as "AFm" phases, and may also contain some Fe^{3+} ions substituting for Al^{3+} [82]. The more reactive alumina available, the more carboaluminate hydrates can form, and some of this reactive alumina can come from SCMs such as slags or fly ashes (e.g. [83,84]) However, calcium carbonate cements have already been clearly demonstrated on a laboratory scale for use in the field of biomaterials, i.e. as potential bone-repair cements [2,85]. The approach used was to precipitate reactive amorphous calcium carbonate (ACC) powders by mixing solutions of calcium chloride with solutions of sodium bicarbonate. In order to stabilize amorphous forms of $CaCO_3$, magnesium or strontium ions were included in the chloride solution. It was shown that mixtures of ACC with vaterite would react in water to precipitate calcite or aragonite, and that this reaction gave a hardened product. A strength of 13 MPa was obtained in one paste, at a water/solid ratio of 0.4.

The importance of the above work is that it shows clearly that hydraulic binders can be made from relatively pure calcium carbonates without any decarbonation. It is especially interesting to note that the "hydration" reaction essentially involves no binding of water, since both the initial binder phase (ACC + vaterite) and the final "hydration" products (aragonite or calcite) are ostensibly anhydrous forms of $CaCO_3$. This appears to confirm the mechanism proposed by Shchukin and Amelina [3] for the development of strength in crystalline binders, i.e. the formation of "bridging" contacts when crystals growing from a supersaturated solution come into contact with one another.

The work of Combes et al. [2,85] was aimed at biological applications, rather than binders that might be more suitable for construction applications. However, Brent Constantz of the Calera Corporation of California has recently suggested that carbonate-based binders or aggregates might potentially be produced in large quantities and at an acceptable cost by the carbonation of sea water or various brines in the presence of suitable sources of alkalinity [86]. Apparently, the alkalinity could potentially be produced at an acceptably low energy cost by a proprietary new low-voltage "electrodialysis" process in which salt water can be separated into two separate solutions rich in NaOH and HCl, respectively, without producing significant amounts of unwanted gaseous products such as hydrogen or chlorine as occurs in the conventional "Chlor-Alkali" process widely used in the industrial production of NaOH and chlorine. The excess HCl produced by this new process could presumably be neutralized by dissolving basic minerals, as suggested by House et al. [87]. This could constitute a novel approach to the sustainable capture of anthropogenic CO_2 emissions and their conversion into industrially useful products, although little detailed technical information on such products or the manufacturing processes involved has yet been published.

5. Concluding remarks

Despite a growing societal awareness of environmental issues, and in particular, impacts of human activity on CO_2 emissions and global warming, the conveniences of a modern built infrastructure and the growth in developing countries is globally driving demand for concrete. Correspondingly, the pressure on the cement industry is to produce adequate binders whilst reducing their CO_2 emissions, currently around 0.8 tonnes per tonne of Portland cement produced. The search for low-CO_2 cements as partial replacements or complete alternatives has prompted innovative thinking in the development of new binders and a review of existing systems for greater efficiencies. This paper has attempted to outline a framework for approaching alternative binders by reviewing:

- What is meant by a cementitious binder, and
- What are the key physico-chemical properties of proven successful binders.

The paper has addressed bonding mechanisms, differentiating between systems which rely only on capillary forces for strength development, e.g. mud products, and hydraulic cements. Here the focus is on surface chemistry. Hydraulic cements react with water by releasing ions to solution from which new phases, usually incorporating water in some form, precipitate and do not readily disperse. These attractive adhesive/cohesive interparticle forces define successful cementitious binders. The initial precipitation chemistry, occurring through nucleation and growth mechanisms, and also defined by surface energies, provides the basis for microstructure development.

The type of phase precipitating is conditioned by chemistry, initially the hydrolysis/dissolution chemistry of the primary solid binder, and subsequently, the tendency for product growth (product crystallisation, polymerisation). The thermodynamic basis for these processes has its origins in the energetics of ion interactions and the optical basicity concept has been introduced as a potential tool for visualisation of acid–base gradients and prediction of reactivity gradients. The role of hydrated ions has also been discussed in the context of conditioning reaction products. Under the relatively high pH conditions typical of common cement systems, the strongly polarising influence of $Ca^{2+}(aq)$, relative to $Na^{+}(aq)$ drives the formation of the layer-structured C–(A)–S–H family of products rather the open-framework zeolite-type structures arising in Ca-free systems. These observations are applicable equally to conventional OPC-SCM systems as well as alkali-activated aluminosilicate systems and similar themes based on ion polarisability have been developed to discuss the reactivity of SCMs themselves.

With the foregoing themes as a basis, the final part of the paper is devoted to a review of four important classes of 'novel' binder systems that are currently under development with the objective of providing general-purpose hydraulic binders with lower CO_2 emissions than Portland-cement-based binders. Unfortunately, there is very little detailed verifiable scientific information available on these systems because of commercial constraints and patenting issues. However, we have used what little information is currently available in order to try and fit them into the scientific framework developed in the first part of the paper.

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