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Advances in alternative cementitious binders

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ABSTRACT

There is a burgeoning interest in the development, characterization, and implementation of alternatives to Portland cement as a binder in concrete. The construction materials industry is under increasing pressure to reduce the energy used in production of Portland cement clinker and the associated greenhouse gas emissions. Further, Portland cement is not the ideal binder for all construction applications, as it suffers from durability problems in particularly aggressive environments. Several alternative binders have been available for almost as long as Portland cement, yet have not been extensively used, and new ones are being developed. In this paper, four promising binders available as alternatives to Portland cement are discussed, namely calcium aluminate cement, calcium sulfoaluminate cement, alkali-activated binders, and supersulfated cements. The history of the binders, their compositions and reaction mechanisms, benefits and drawbacks, unanswered questions, and primary challenges are described.

Contents

1. Motivation

Since the development of Portland cement over 175 years ago, it has become the dominant binder used in concrete for construction. Annual worldwide Portland cement production is approaching 3 Gt

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[1]. Praised for its versatility, durability, and economic value, Portland cement concrete is receiving increasing recognition for its relatively low embodied energy compared to other building materials, as shown in Fig. 1 [2], and for its use of local materials, thereby reducing energy and pollution costs associated with material transport.

However, Portland cement is not without problems. Because such vast quantities are produced, manufacturing of Portland cement consumes 10–11 EJ of energy annually, approximately 2–3% of global primary energy use. Furthermore, Portland cement production results in approximately 0.87 t of carbon dioxide for every tonne of cement produced [3]; this accounts for 5% of manmade CO_2 emissions [3]. The cement industry is under pressure to reduce both energy use and greenhouse gas emissions and is actively seeking alternatives to this familiar and reliable material.

Coupled with the interest in seeking low-energy, low-CO_2 binders is an interest in finding re-use for waste materials from other industries. Portland cement concrete already accommodates a wide variety of waste materials used as supplementary cementing materials, including fly ash from coal combustion, ground granulated blast furnace slag from iron production, and silica fume from ferrosilicon production. However, these are used to replace only a portion of the cement in concrete, typically on the order of 10–50% (although sometimes used in greater quantities). There is interest in pushing this envelope further, to create binders made entirely or almost entirely from waste materials.

Additional motivation for exploring alternatives to Portland cement can be derived from its shortcomings in certain applications and environments. For instance, rapid-repair applications demand a faster strength gain than Portland cement concrete can provide. Similarly, environmental conditions with high acidity or high sulfate concentrations can cause substantial degradation of Portland cement concrete. For such cases, there is a demand for Portland cement alternatives.

New binders are being developed for concrete that promise to reduce the environmental impact of construction, use a greater proportion of waste materials, and/or improve concrete performance. These materials represent a substantial departure from the traditional chemistry of Portland cement, and therefore do not benefit directly from the many years of research into its reaction mechanisms, property development and durability. Furthermore, new materials have difficulty finding acceptance in the construction industry, making implementation challenging. In this paper we discuss some of the alternative binders which are attracting increasing attention in research and practice, summarizing the current understanding, gaps in knowledge and challenges. This paper does not address all of the possible Portland cement alternatives that are being developed, studied, and used. Rather, we have chosen four materials that show particular promise as Portland cement alternatives: calcium aluminate cement, calcium sulfoaluminate cement, alkali-activated binders, and supersulfated cement.

The challenges facing new concrete binders are twofold. Primarily, there are many fundamental questions to be addressed with respect to processing, chemical and physical behavior, and performance. Secondly, after a strong basic understanding of the material is in place, it is important to establish standard composition and/or performance parameters for the materials and to incorporate them into building codes and specifications. In this paper the challenges of standardization and specifications are addressed jointly in the next section, and we then proceed to discuss the scientific challenges unique to each binder separately.

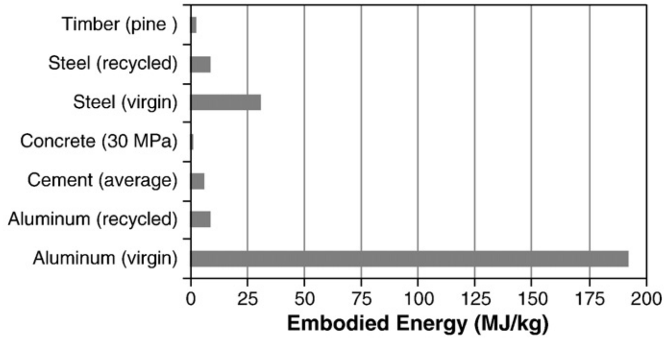

Fig. 1. Embodied energy of common building materials [2].

2. Specifying alternative binders

Specifications for building materials can generally be classified as either prescriptive or performance-based. Certainly, a prescriptive specification for Portland cement would preclude the use of an alternative binder. A performance-based specification, however, may provide sufficient flexibility to allow the use of a non-Portland cement binder. There are differing degrees of prescription in cement standards and specifications in place worldwide. In the United States, ASTM has parallel prescriptive (ASTM C150 [4]) and performance-based (ASTM C1157 [5]) standards for cement, but the acceptance of ASTM C1157 is not yet widespread among state regulatory authorities. ASTM C 1600 [6] has recently been adopted and covers the broader category of rapid-hardening hydraulic cements in a performance-based approach. In the European Union, EN 197-1 [7] is a predominantly prescriptive cement standard which is referenced by the concrete standard EN 206-1 [8], and this would appear to place some restrictions on the use of non-Portland cements in that region, unless product-specific Technical Approvals can be obtained. Each EU nation also has its own set of national appendices which sit beneath the EU Standards, and some of these are more permissive than others in terms of the scope for introducing alternative binder chemistries.

Other nations including Canada and Australia have good scope for acceptance of materials on a performance basis within existing legislative frameworks. There also exists in Ukraine a highly developed framework of prescriptive standards governing specific classes and formulations of non-Portland cements, which have been generated through 50 years of development of alkali activation technology.

International developments in standards for non-Portland cements are being driven and monitored by RILEM Technical Committee 224-AAM. This committee has a specific focus on alkali-activated binders, but the availability of performance-based standards is motivated by the desire to use performance rather than chemistry as the primary criterion for acceptance of a binder type, since composition-based criteria are necessarily binder-specific. The focus of the RILEM Committee does not specifically limit the applicability of its outcomes to alkali-activated materials.

Probably the most daunting challenge facing developers of performance-based standards is exactly how a testing regime may be designed which is sufficiently inclusive to enable its use to test and validate a wide range of binder systems, but which is also restrictive enough to ensure good performance of materials when they are mixed and placed under less-controlled real-world conditions. The selection of curing conditions (for example, whether lime–water curing is useful for non-Portland cement systems), whether the most critical tests are conducted on precursors, pastes, mortars or concretes, and the need to transfer as much as possible of knowledge from Portland cement and concrete technology to the new binder systems, are all essential areas which require input from both the commercial and research sectors if satisfactory outcomes are to be achieved.

3. Alternative binders

3.1. Calcium aluminate cements

Calcium aluminate cements (CACs) are a specialty class of cements containing primarily monocalcium aluminate (CA) and sometimes

$C_{12}A_7$ and/or CA_2. Silica may be present in small amounts in the form of C_2S and/or C_2AS (gehlenite). Small amounts of ferrite may also be present in the form of a C_4AF solid solution with variable A/F ratio [9]. Originally developed in the early 1900s, near La Teil, France by Jules Bied of the J. & A. Pavin de Lafarge company, CACs were invented to resist sulfate attack [9]. Calcium aluminate cement concrete has several distinct advantages over traditional Portland cement concrete, including rapid strength gain upon setting and enhanced resistance to abrasion, sulfate attack and alkali–silica reaction. Furthermore, production of CAC results in lower CO_2 emissions than Portland cement production. Currently, CACs are mainly used in refractory and building chemistry applications, such as floor screeds and rapid-hardening mortars [9]. However, CACs are gaining renewed interest in the construction industry due to their rapid hardening and enhanced durability properties compared to other cementitious binders.

Despite the fact that CAC was developed over 100 years ago and has many advantageous characteristics, it is not used as extensively as Portland cement. Widespread use of CAC is limited by two primary challenges. First, a process called “conversion” occurs in hydrated CAC over time, whereby metastable hydrates convert to stable hydrates, leading to an increase in porosity and subsequent decrease in strength. Several building collapses in the 1970s were initially attributed to CAC conversion, and many structural codes subsequently banned use of the material. Later investigations revealed that in one of the collapses, improper structural detailing was to blame, and other failures were a result of improper material usage despite manufacturer recommendations. Since this time, intensive research has provided a greater understanding of CAC chemistry and behavior. A report by the Concrete Society in 1997 provided improved guidance for predicting long-term properties, and, as a result, the technical concrete market has seen resurgence in interest and use of this alternative cementitious binder [10]. Secondly, CAC is expensive compared to Portland cement, with the cost related directly to the limited supply of bauxite, the main source of alumina in CAC production. Both of these challenges need resolution if this material is to gain acceptance as a viable Portland cement alternative.

3.1.1. Hydration and property development

In Portland cement the temperature history affects primarily the rate of reaction, whereas in CAC the temperature during hydration also impacts the phases that form and the rate of transition from metastable to stable hydrates (i.e. the conversion process). At low curing temperatures, metastable hydrates CAH_{10} and C_2AH_8 form. It is generally accepted that the predominant metastable hydrate formed at temperatures below ~15 °C is CAH_{10} [11]. As the curing temperature increases to 30 °C, C_2AH_8 is also formed; however, the formation of CAH_{10} is not thermodynamically favored and formation of C_2AH_8 is slow as temperatures approach 30 °C [12,13]. The conversion of these hydrates to the stable C_3AH_6 phase is accompanied by the formation of AH_3 gel and the release of water. This is a thermodynamically inevitable process. As a result of the conversion process, the paste increases in porosity and subsequently the strength of the material decreases. At higher curing temperatures (>70 °C) the stable hydrate C_3AH_6 is predominantly formed [9]. Fig. 2 shows a schematic of the conversion process and approximate temperature ranges for the formation of metastable and stable hydrates.

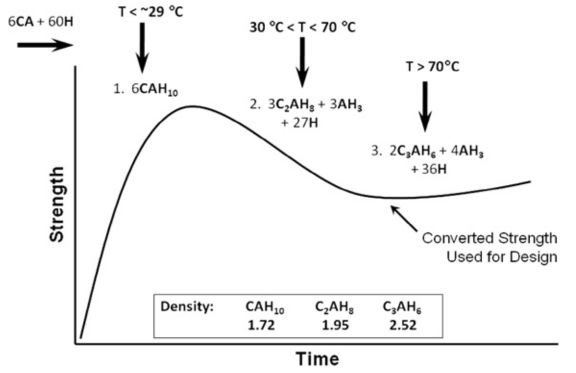

Fig. 2. Schematic of conversion implies densification of hydrates which leads to increased porosity and strength reduction.

While the conversion process may take years in the field, it can be simulated in the laboratory by curing at 38 °C immediately after casting. This leads to an accelerated formation of the stable hydrates, and the subsequent minimum in strength is typically realized within 5 days [10]. Fig. 3 shows scanning electron microscope images of CAC microconcretes cured isothermally at 20 °C and 38 °C, promoting the formation of metastable (higher strength) and stable (lower strength) hydration products, respectively. In Fig. 3a, despite the large amount of unreacted CA present, the microstructure is relatively dense, filled with hydration product (CAH_{10}) and discrete porosity similar to a traditional high-performance Portland cement microstructure. In sharp contrast, in Fig. 3b there is little unreacted CA. Additionally, the porosity that exists is evident throughout the entire microstructure, resulting in a lower strength material for 38 °C isothermal curing than for 20 °C isothermal curing.

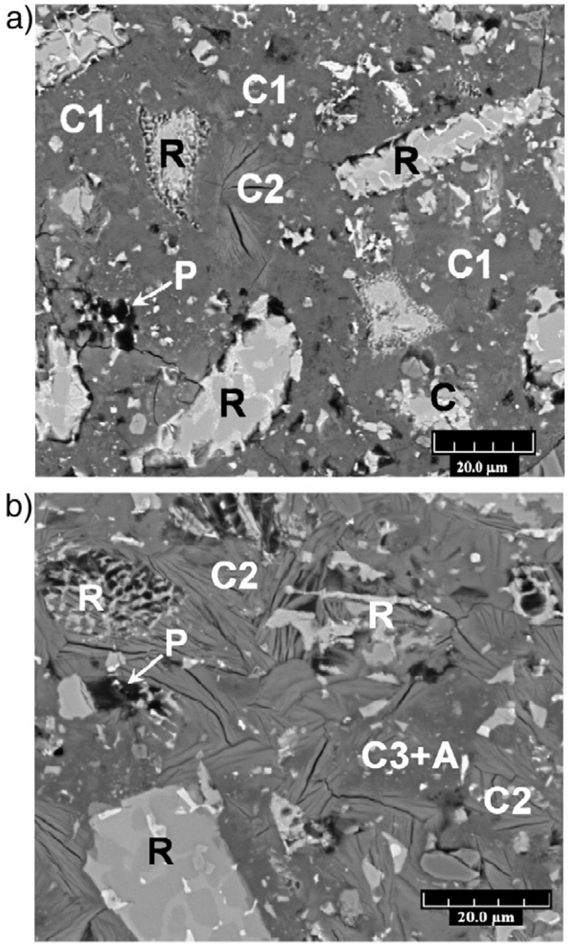

Fig. 3. SEM images of CAC microconcrete: a. unconverted, high strength; b. complete conversion, lower strength, increased porosity (both scale bars = 20 µm). C = unreacted CA, A = AH_3 gel, C1 = CAH_{10}, C2 = C_2AH_8, C3 = C_3AH_6, R = partially reacted CA grain, P = pore.

It is recognized that conversion is an inevitable process and research has shown that the best approach when using CAC concrete is to design for the lower, converted strength rather than for the maximum strength, thereby eliminating long-term problems post-conversion [10]. Recent research in CAC systems has focused less on strength development, but instead on characterizing and predicting dimensional stability in order to reliably predict field performance, as well as blending the cement with supplementary cementing materials in order to reduce the cost of concrete made from CAC.

Recent research efforts investigating calcium aluminate cements were highlighted in the 2008 Centenary Conference [14]. The proceedings include information specific to hydration, increased understanding of mechanical and volumetric properties, durability, refractory and building chemistry applications, and the use of fillers and reactive powders in conjunction with CACs.

Early-age microstructural development was investigated by Pöllmann et al. [15] using cryo-scanning electron microscopy (SEM) coupled with heat-flow calorimetry and in situ X-ray diffraction. Combining these techniques they were able to observe the transformation of AH_3 gel to crystalline AH_3 phases at early ages (up to 8 h after mixing). From 8 to 15 h, cryo-SEM showed an increasing density of CAH_{10} and the crystallization of layered, hexagonal crystals of C_2AH_8.

Ideker et al. [16,17] demonstrated the profound effect of curing temperature on early-age volume changes. Specifically, under isothermal curing, the formation of metastable hydrates (primarily CAH_{10}) was linked to shrinkage. Conversely, formation of stable phases (especially C_3AH_6) was linked to expansion of the material. The mechanisms governing these volume changes are not obvious. Simple volume change calculations of the hydrates for conversion from CAH_{10} to C_2AH_8 or CAH_{10} to C_3AH_6 show volume increases of 4.4 and 2.4%, respectively. This includes the release of water from CAH_{10} (if this is not done, an incorrect net shrinkage is calculated). The researchers have conjectured that the ability of the system to accommodate water release and subsequent water movement within the pore structure could be linked to expansion as a result of increased hydraulic pressure [16,17].

Lamberet et al. [18] and Alexander et al. [19] highlighted the improved performance of CAC in sewer tunnel linings compared to OPC. The presence of higher concentrations of aluminum ions in CAC systems combined with low pH levels prevalent in wastewater conveyance were shown to inhibit bacterial growth, thereby reducing damage in CAC-based mortar linings.

The reaction kinetics and long-term properties of Portland cement-dominated and calcium aluminate cement-dominated self-leveling flooring mortars were investigated by Kighelman et al. [20]. They found that CAC-dominated systems were more stable volumetrically due to early-age strength gain and a denser microstructural formation. They also found that the CAC-dominated systems showed improved abrasion resistance compared to OPC-dominated systems.

Gosselin [21] found that the incorporation of SCMs, in particular ground granulated blast furnace slag (GGBFS) and silica fume, created more space and available water for the hydration of CA. At early ages this resulted in further hydration of CA in these systems compared to pure CAC systems. Reactivity of SCMs was not observed until later ages (>1 day), similar to Portland cement systems, and as a result the incorporation of SCMs did not significantly enhance early-age strength gain. In field applications of CACs, an accelerator (typically Li_2SO_4-based) is commonly used to regulate setting time. In pure CAC systems Gosselin found that an accelerator actually reduced hydration of CA at early ages and decreased strength gain due to an increase in the formation of denser stable hydrates (C_3AH_6 and AH_3) at early ages. This finding has implications on the use of CAC in field applications, as it seems that the problem of strength loss associated with conversion may be partially mitigated through the use of SCMs and/or chemical accelerators.

Little work has been done on modeling the reaction kinetics of CAC, as research has generally focused on developing predictable mechanical behavior and gaining a better understanding of the formation of metastable and stable hydrates. More detailed investigations of hydration kinetics will be welcomed in the future and will further enhance our understanding of calcium aluminate cement systems and how to utilize them through avoidance of or proper characterization of conversion.

3.2. Calcium sulfoaluminate cements

Calcium sulfoaluminate (CSA) cements contain ye'elimite ($C_4A_3\overline{S}$) as a major constituent (30–70%). Ye'elimite was introduced as a cementitious phase in the 1960s, when it was patented by Alexander Klein as an expansive or shrinkage compensating addition to cementitious binders ("Klein's compound") [22]. While CSA cements are not widely used in Europe and the U.S., they have been produced, used and standardized in China for about 30 years [23–29], where they are known as the "third cement series." Two types of clinkers are defined, sulfoaluminate belite clinker (containing mainly ($C_4A_3\overline{S}$) and C_2S) and ferrialuminate clinker (containing mainly ($C_4A_3\overline{S}$), C_4AF and C_2S). The clinkers are interground with different levels of calcium sulfate in order to obtain rapid-hardening, high strength, expansive, or self-stressing cements. CSA cements have been used in China as a binder for concrete in bridges, leakage and seepage prevention projects, concrete pipes, precast concrete (e.g. beams and columns), prestressed concrete elements, waterproof layers, glass fiber reinforced cement products, low temperature construction and shotcrete [23,24,26,27,30]. In addition, due to their low pH, their low porosity and the ability of ettringite and AFm phases to bind heavy metals, calcium sulfoaluminate cements and their blends with Portland cement are of interest in the field of hazardous waste encapsulation [31–35].

CSA cements are receiving increasing attention because they promise to provide a low-CO_2 alternative to Portland cement [36]. Compared to alite, which releases 0.578 g CO_2 per g of the cementing phase when made from calcite and silica, calcium sulfoaluminate clinker releases only 0.216 g CO_2 per g of cementing phase when made from limestone, alumina and anhydrite. The firing temperature used to produce CSA clinker is typically 1250 °C, about 200 °C lower than that used for Portland cement clinker. In addition, this type of clinker is easier to grind than Portland cement clinker [23].

3.2.1. Raw materials and binder composition

CSA clinker can be produced from limestone, bauxite (iron-rich bauxite in the case of ferrialuminate clinker) and calcium sulfate (anhydrite or gypsum) [23–29,37,38]. The high cost of bauxite presents an economic challenge for CSA cements, just as for CAC. Therefore, a significant amount of effort has been put into exploring industrial by-products or waste materials such as fly ash, blast furnace slag, phosphogypsum, baghouse dust or scrubber sludge for the manufacture of calcium sulfoaluminate-based clinkers [39–42]. Generally, the same production process as for Portland cement clinker, either in shaft or in rotary kilns, can be applied [26], using a clinkering temperature between 1250 and 1350 °C.

Depending on the raw meal composition, CSA clinkers can contain various other hydraulic phases such as belite, calcium aluminoferrite, excess anhydrite or free lime, calcium aluminates, perovskite or gehlenite [24,38,43]. The latter two phases can be regarded as hydraulically inactive. To increase the reactivity of the belite phase, which is responsible for late strength development of sulfoaluminate belite cements, minor ingredients can be added to the raw meal [44].

Usually about 15–25 wt.% of gypsum is interground with the clinker for optimum setting time, strength development and volume stability. Depending on the level of calcium sulfate addition, CSA cements with different properties can be obtained [26,28,29]. CSA cements can also be used in blends with other cementitious materials including Portland cement, burnt oil shale or limestone [28,32,45–49] to improve their strength development or to formulate rapid setting/hardening binder systems.

3.2.2. Hydration

The kinetics of pure ye'elimite hydration and product development are influenced by the addition of calcium sulfate or calcium hydroxide [50–54]. With water alone, ($C_4A_3\overline{S}$) reacts with water according to Eq. (1) to form monosulfate and aluminum hydroxide, with the latter being usually X-ray amorphous. The kinetics of this reaction are quite slow, exhibiting a dormant period of several hours. The addition of gypsum or anhydrite accelerates the hydration kinetics, and ettringite is formed according to Eq. (2), together with aluminum hydroxide, instead of monosulfate. When the calcium sulfate is consumed, monosulfate is formed according to Eq. (1). The ratio between ye'elimite and calcium sulfate determines the ratio between ettringite and monosulfate in the final product. Above a calcium sulfate to ye'elimite molar ratio of 2, only the reaction according to Eq. (2) occurs. With the addition of calcium hydroxide, ye'elimite reacts very rapidly to form C_4AH_x, whereas the combined addition of calcium hydroxide and calcium sulfate leads to the rapid formation of ettringite according to Eq. (3).

In CSA cements, which generally contain several hydraulic phases, similar reactions take place [23,24,27,30,44,49,55–59]. Usually the ($C_4A_3\overline{S}$) is more reactive than the other accessory phases like C_2S, C_4AF or CA [29,44,58–60]. Depending on clinker composition, additional hydration products such as strätlingite (C_2ASH_8) (Eq. (4)), calcium silicate hydrates or CAH_{10} may form. Fig. 4 shows the phase development of a calcium sulfoaluminate cement containing belite with ongoing hydration, derived by thermodynamic modeling [58]. The water-to-cement ratio needed for complete hydration is determined by the amount of calcium sulfate added, and is at a maximum around an addition of 30% calcium sulfate [23,54]. This is higher compared to Portland cement, e.g. 0.78 for pure ye'elimite reacting with 2 molar equivalents of anhydrite [61], or around 0.60 for technical cements [23]. In comparison to Portland cement, cements based on calcium sulfoaluminate react faster, and most of the hydration heat evolution occurs between 2 and 24 h of hydration [59]. Typical values for heat of hydration are close to 400 J/g cement after 72 h by conduction calorimetry [58,62].

$$C_4A_3\overline{S} + 18H \rightarrow C_3A \cdot C\overline{S} \cdot 12H + 2AH_3 (\text{monosulfate formation}) \tag{1}$$

$$C_4A_3\overline{S} + 2C\overline{S}H_2 + 34H \rightarrow C_3A \cdot 3C\overline{S} \cdot 32H + 2AH_3 (\text{ettringite formation}) \tag{2}$$

$$C_4A_3\overline{S} + C\overline{S}H_2 + 6CH + 74H \rightarrow 3C_3A \cdot 3C\overline{S} \cdot 32H (\text{ettringite formation}) \tag{3}$$

$$C_2S + AH_3 + 5H \rightarrow C_2ASH_8 (\text{strätlingite formation}) \tag{4}$$

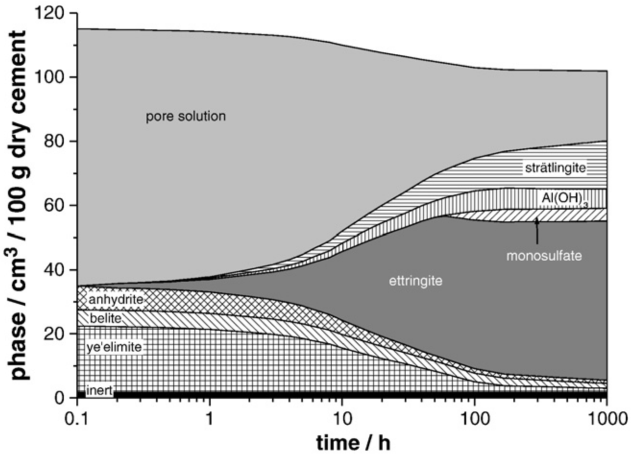

Fig. 4. Phase development of a CSA cement (water/cement = 0.80) as a function of hydration time calculated by thermodynamic modeling, taken from [58].

The hydration of calcium sulfoaluminate cements depends mainly on the amount and reactivity of the added calcium sulfate [23,29,54,57,58,63,64]. Therefore, a formula for the calculation of optimum sulfate level (Eq. (5)) to obtain the different types of CSA cements was developed in China, based on stoichiometric calculations [29]:

$$C_T = 0.13 \cdot M \cdot \frac{A}{\overline{S}} \tag{5}$$

where C_T = ratio gypsum/clinker, A = mass % of ye'elimite in the clinker, $\overline{S}$ = mass % of SO_3 in the gypsum, M = molar ratio gypsum/ye'elimite, and the value 0.13 is a stoichiometric factor containing all the conversions between mass and molar units. The value M (and also whether gypsum or anhydrite is used) is related to the type of CSA cement. $M = 0–1.5$ with a low-calcium sulfate content yields a rapid-hardening or high strength cement, which is also confirmed by the experimental data given in [57]. Higher sulfate levels are applied to formulate expansive ($M = 1.5–2.5$) and self-stressing cements ($M = 2.5–6$). Shrinkage compensating, expansive and self-stressing cements generate expansive (compressive) stresses in the final, dried paste, mortar or concrete, which are low (<1 MPa) in the case of shrinkage compensated and high (up to 8 MPa) in the case of self-stressed systems [65]. The latter have to be restrained by a suitable reinforcement in order to avoid excessive expansion and crack formation. Thus, according to Eq. (5), the properties of the CSA cements are directly related to the formation kinetics and to the total amount of the voluminous ettringite phase in the hardened system.

There are not many data available on pore solution chemistry in this system [27,44,58,66]. The liquid phase is dominated at an early age by Na, K, Ca, Al and sulfate, until the added calcium sulfate has been consumed. The pH value in this period is between 10 and 11. After consumption of the calcium sulfate, a strong decrease of calcium and sulfate concentrations and an increase of pH to about 12.5 occur. During the first hours of hydration, silicate concentrations in the pore solutions are lower than for OPC, wheras after several days they are comparable in both systems.

Microstructural investigations [24,27,57–59,67], Fig. 5, have revealed mainly the presence of space-filling ettringite needles, together with monosulfate, aluminum hydroxide, and calcium silicate hydrates and/or strätlingite, leading to a very dense, low porosity microstructure.

3.2.3. Properties

The setting times of CSA cements depends on their ye'elimite content, the kind and content of minor phases, and the amount and reactivity of the added calcium sulfate. Typical values are between 30 min and 4 h [23,27–29,44]. Compared to Portland cement, CSA cements in general reach higher early and late strengths [23,26–30,56,57].

CSA cements exhibit a chemical shrinkage, which is related to the fact that the apparent density of the water bound in the hydrated phases, such as ettringite, is higher than the density of free water. It can be calculated through thermodynamic modeling that CSA cements should have a theoretical chemical shrinkage of about 11 cm^3/g cement after 28 days [58], whereas a Portland cement reaches about 4–5 cm^3/g. Chemical shrinkage of CSA cement was experimentally found to be of the same order of magnitude as the predicted value [62]. It should also be noted that expansion may occur if ettringite forms in reasonable amounts after setting, which can be triggered by the amount of added calcium sulfate [29]. Calcium oxide and calcium hydroxide accelerate ettringite formation, and so can also lead to expansion [27,57]. Further, due to the high water/cement ratio needed for complete hydration, which is typically around 0.60, CSA cements tend to undergo self-desiccation, as a low water-to-cement ratio of 0.30–0.45 is typically used [23].

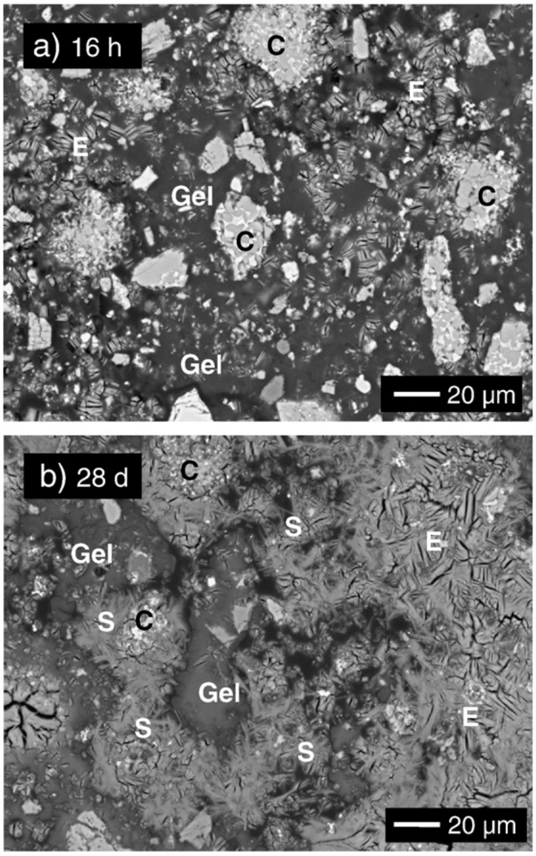

Fig. 5. Scanning electron micrographs (backscattered electron images of polished sections) of hydrated CSA cement after a) 16 h and b) 28 d, taken from [58]; C = CSA clinker, G = gypsum, E = ettringite, Gel = gel-like $Al(OH)_3$ and S = strätlingite.

The durability of building materials made from CSA cements, as derived from laboratory tests and from field studies, seems to be in general at least comparable to conventional Portland cement-based materials [23–26,28,29,42,56,67], however more data concerning long-term behavior are needed. CSA-based concretes can exhibit a high resistance to freeze–thaw and against chemical attack by seawater, sulfates, chlorides, magnesium and ammonium salts [23–25,28,29]. Much of this resistance could be due to the dense pore structures developed by CSA cements. Porosity measurements by mercury intrusion porosimetry have revealed that hydrated CSA cements exhibit mainly pores of a threshold radius below 25 nm [61] and only a minor content of larger pores forming an interconnected pore network [23,61], leading to high impermeability [25,26].

Carbonation depends on the water-to-cement ratio and appears to be more rapid than in Portland cement concretes, leading to the decomposition of ettringite, which may cause a moderate strength loss [30]. Despite that, the alkalinity of CSA cements is about 1 pH unit lower than for Portland cements, and the steel reinforcement seems to be protected from corrosion [23,29]. The low alkalinity also seems to be favorable concerning alkali aggregate reaction [25,28,29].

3.3. Alkali-activated binders

Alkali-activated binders are receiving increasing attention as an alternative to Portland cement because of their high strength and durability and low environmental impact. Alkali-activated binders are made by mixing solid aluminosilicate powders such as fly ash, blast furnace slag, or metakaolin with an alkaline activating solution. The reaction product, or gel, can have a network structure similar to those of organic thermoset polymers, and thus the binders are sometimes called “inorganic polymers” or “geopolymers”. Unlike Portland cement, the solid component of alkali-activated binders can be entirely waste-stream materials, particularly fly ash and blast furnace slag, used with very limited further processing. It has been estimated that substituting alkali-activated binders for Portland cement in concrete can reduce CO_2 emissions by more than 80% [68]. A significant body of research has demonstrated excellent physical properties of concrete using alkali-activated binders, often comparable to or exceeding those of Portland cement concrete [69].

Similar to the other alternative binders discussed, the fundamental technology used to make alkali-activated binders is not new; the reaction of an alkali source with an alumina- and silica-containing solid precursor to form a solid material with performance comparable to hardened Portland cement was first introduced by Purdon in 1940 [70]. Purdon activated blast furnace slags with alkaline solutions and lime, and achieved good rates of strength development and final strengths. He also noted the enhanced tensile and flexural strength of slag-alkali cements, the low solubility of the hardened binder phases, and low heat evolution, and commented that this method of concrete production is best suited to premixed and precast applications where activator dosage can be accurately controlled. However, sensitivity of the activation conditions to the amount of water added, as well as the difficulties inherent in handling concentrated caustic solutions were noted as potential problems. Experience over the following 70 years has shown that Purdon was correct in identifying these as issues of concern (see the comparable listing of difficulties presented by Wang et al. in 1995 [71], for example) but scientific and engineering solutions have been developed, and alkali activation technology has been used on significant scales in major infrastructure works and niche applications in Europe, the Americas, and the Asia-Pacific region [72–77]. The cost of activators has also been identified as a potential issue, although this is exacerbated by the lack of economies of scale as alkali activation technology is mainly applied in small operations at present.

3.3.1. Reaction mechanisms and binder structure

The detailed chemistry of alkali activation is still the subject of much discussion in the scientific literature and depends on the nature of both the solid precursor [78] and the alkali activator [79] selected. The focus here will be on aluminosilicate systems activated with alkali metal hydroxide, silicate, or possibly carbonate (for sufficiently reactive metallurgical slags) solutions. These materials generally form an alkali-containing X-ray amorphous gel binder, and follow a conceptually similar sequence of reaction pathways as depicted in Fig. 6 [80].

The precise nature of the binder gel is determined mainly by the level of calcium available for reaction. It should be noted that the amount of calcium present and the amount of calcium that can actually react often differ [81,82], so the superficial mix composition does not always provide an accurate prediction of reactive components. For example, a high-calcium alkali-activated binder (such as one derived from the activation of blast furnace slag) usually forms a primary binder phase of C–(A)–S–H gel that is amorphous to partially crystalline, relatively highly cross-linked, with a moderate degree of Al substitution and a low C/S ratio [83,84].

On the other hand, lower levels of calcium lead to the presence of what is widely referred to as a “geopolymer”-type gel [69,85], a highly cross-linked aluminosilicate gel which bears strong nanostructural resemblance to zeolite frameworks [86–88] but is generally lacking in long-range crystalline order. This gel contains a very low level of chemically bound water [89,90], which brings both advantages and disadvantages in performance; thermal (e.g. fire) resistance is generally excellent, but permeability can tend to be high. This type of gel is increasingly being described in the literature as N–A–S–H gel [91], but given the low bound water content, it may be more accurately indicated by N–A–S–(H), as in Fig. 6. Zeolite crystallization within the binder does tend to take place with high water content,

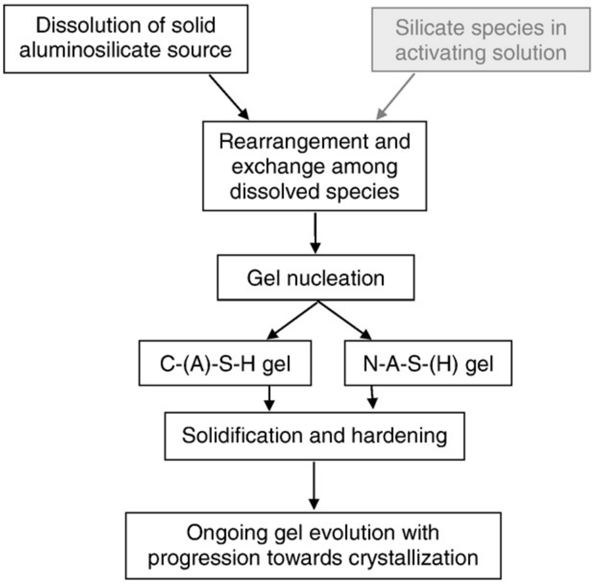

Fig. 6. Schematic representation of the alkali activation reaction process, after [81]. The mechanism is presented in its most general sense, with the possibility of additional silicate being supplied by the alkaline activator solution shown by the gray box. Either one or both of the gel types depicted will be formed, depending on the system composition.

high-temperature curing or extended ageing, and is more prevalent in hydroxide-activated systems [92].

Practical implementation of alkali activation technology can also utilize blends of high- and low-calcium precursors, or an intermediate-calcium precursor such as ASTM Class C fly ash, to obtain what is believed to be a coexisting mixture of the two types of gel, and ideally take advantage of the beneficial properties of each [74,78]. However, the exact natures of the coexisting gel phases, including the thermodynamic basis of gel coexistence, remain to be determined in detail [91].

Crystalline phases including hydrotalcite-like phases or zeolites can form as secondary phases, depending mainly on the activator selected. Carbonate activators tend towards hydrotalcite formation (particularly when the slag is rich in magnesium), and hydroxide activators can lead to zeolite formation. Silicate-activated binders are quite variable in secondary phase crystallite content and type, depending on the silica modulus (activating solution SiO_2/Na_2O ratio) and the solid precursor mineralogy.

3.3.2. Reaction kinetics

Understanding reaction kinetics in alkali activation necessitates the development of analytical techniques capable of measuring the rate of gel network growth, which (as in most cementitious systems) is far from a trivial task. Nonetheless, several approaches have been applied successfully and are summarized briefly here. The specific case of reaction kinetics in aluminosilicate "geopolymer" systems has been discussed in detail in a recent review of experimental and modeling approaches [93]; the kinetics of alkali-activated slag hydration are more amenable to analysis by the standard analytical techniques applied to Portland cement [94–97] due to the greater similarities in chemistry and higher heat release compared to low-calcium binder systems.

Time-resolved infrared spectroscopy, conducted both ex situ [98] and in situ [99], has provided probably the most detailed available information regarding both the kinetic and gel-structural effects taking place during alkali activation of low-calcium aluminosilicates, particularly fly ashes. It has been observed, by coupling this technique with other analytical methods, that the initial gel phase formed will differ structurally from the final gel phase observed after extended curing. The presence of moisture and heat will allow the gel to continue rearranging into a more thermodynamically favorable form, increasing in crosslink density [100], expelling the initially reasonably high levels of bound water [101], and with some formation of zeolitic crystallites [92,102]. These two stages of gel evolution, sometimes denoted "Gel I" and "Gel II" [69,98], are represented in a general sense by the "solidification and hardening" and "ongoing gel evolution" boxes in Fig. 6.

The fact that the key phases in both the reactants (metakaolin, fly ash and/or slag) and products (N–A–S–(H) and/or C–(A)–S–H gels) are all lacking in long-range order means that the application of diffraction-based techniques to alkali activation is challenging. Unlike the case of Portland cement hydration, where key reacting phases are crystalline and can be tracked using in situ diffractometry [103], similar studies of alkali-activated binders have only been carried out on very simple model systems. However, the formation of the "Gel I" phase from a metakaolin precursor has been identified and described using energy-dispersive X-ray diffractometry [104,105].

Reaction kinetic modeling of the alkali activation reaction processes has not yet been carried out extensively. For low-calcium systems, a detailed reaction kinetic model derived from the basic ideas presented in Fig. 6 has been developed from data obtained by in situ energy-dispersive X-ray diffractometry [80,105] and then applied successfully to data obtained by other in situ measurement techniques including impedance spectroscopy [106]. Kinetic and reaction path analysis of closely related systems, including lime-fly ash binders [107] and fly ash dissolution in alkaline environments designed to simulate cement pore solutions [108], may be able to provide additional information and insight to aid in the further development and validation of reaction models to describe these kinetic pathways, but much remains to be done in this area.

In higher calcium alkali-activated slag systems, the most detailed models available have been developed from a thermodynamic basis, then linked to reaction kinetics via parameters describing the extent of reaction and by pore solution chemistry [109,110]. These models utilize techniques which have been very successful in the analysis of Portland cement-based systems, providing insight into phase evolution as a function of time, but do not incorporate reaction engineering aspects such as rate-controlling processes [111] or other mechanistic details. The availability of sufficiently detailed thermodynamic data for N–A–S–(H) gels and related phases is currently hindering the application of such modeling approaches in the study of lower-Ca systems.

3.3.3. Primary challenges

The key unsolved question in the development and application of alkali activation technology is the issue of durability. Alkali-activated slag systems are known to be capable of showing very good durability [72,112–114], but it appears that this is strongly dependent on the application of adequate curing regimes. It should be noted that, contrary to the assertions of some researchers, high-temperature curing is not required for high strength development in alkali-activated materials. A correctly formulated alkali-activated binder can set and harden at room temperature or even below this, and this has been demonstrated on a large scale in Australia by the application of pre-mixed alkali-activated concretes in infrastructure projects [74]. Carbonation can be quite problematic in these systems, as there is no reservoir of available calcium to provide a pH buffer, and so durability performance is critically dependent on the development of a compact and refined pore structure [115].

There are complications in some applications due to the fact that many of the superplasticizing admixtures which are usually used in Portland cement concretes are not effective in enhancing the flow behavior of alkali-activated binders, as they are often degraded by highly alkaline activators [116,117]. This means that the usual water-reduction performance expected of these admixtures is not achieved, and so necessitates the use of a higher water/binder ratio to achieve the desired flow properties. Alkali-activated materials with higher water content also require more careful control of curing to achieve a favorable pore structure, meaning that the need for further research and development in this area is redoubled.

3.4. Supersulfated cements

Supersulfated cements are binders free (or almost free) of Portland cement clinker, generally comprised of blastfurnace slag, calcium sulfate and an alkaline activator. The alkaline activator is often Portland cement, in small relative quantity. The possibility to activate ground granulated blastfurnace slag by sulfates was first discovered by Hans Kühl in 1909 [118]. Basic slags (i.e., high CaO + MgO content) with a high Al_2O_3 content (at least 14–15%) were found to be suitable for the manufacture of supersulfated cements [118], as such materials exhibited a reasonable strength development. Their application increased after the Second World War [119,120] due to a shortage of Portland cement clinker and resulted in standardization of the binder in several countries like Germany and the United Kingdom [121,122]. Later, in Germany, changes in the iron manufacturing processes yielded slags which did not fulfill the minimum Al_2O_3 content requirement (13%) anymore. This led to a withdrawal of the former German standard DIN 4210 [122], and the use of the slags instead in blends with Portland cement (blastfurnace slag cement). However, it has been shown that slags with lower Al_2O_3 contents can successfully be activated and used as binders for rendering [123], injection [124] or masonry mortars [125] in aggressive environments such as in the presence of high sulfate concentrations.

Supersulfated cements are attracting new attention and are thought to have promising potential for industrial applications [36,126], partly due to the climate debate [3], but especially due to their very low heat of hydration and their good durability in chemically aggressive environments [118,119,127]. There are also various repair mortar applications reported, such as rendering, injection mortars or masonry mortars [122–124], where especially the high sulfate resistance has been the main driving force to use supersulfated cement. The renewed interest is illustrated by the fact that new products have recently come on the market and that a European standard for supersulfated cements [128] is now available.

3.4.1. Raw materials and binder composition

The main constituents of supersulfated cements are 70–90% ground granulated blast furnace slag, 10–20% calcium sulfate and generally low quantities (mostly <5%) of an alkaline activator, mainly Portland cement or clinker [120,129–137]. Generally, slags with high CaO, MgO and especially Al_2O_3 contents are suitable for the manufacturing of supersulfated cements [119,129,132,133,137]. The mixture composition for optimum properties is sensitive to the chemical composition of the slag. Those slags with high alumina contents generally require higher calcium sulfate additions [130]. The calcium sulfate is mainly gypsum or anhydrite, but binders containing hemihydrate are also reported in the literature [134,136]. The use of secondary sources of calcium sulfate like phosphogypsum [129,131], flue gas desulfurization gypsum [133] or fluoroanhydrite [129] is possible as well. Besides Portland cement or Portland cement clinker, other activators including calcium hydroxide [134,135], potassium hydroxide [132] or sodium carbonate [135] are reported. The latter two are favorable in the case of a low reactivity slag, as they increase the pH of the pore solution and thus favor slag dissolution. However, an overdose of such alkaline activators leads to a significant strength loss [133]. Too high a content of Portland cement clinker or calcium hydroxide has a negative impact on the volume stability of the binder, as these components may cause expansive reactions related to ettringite formation [119].

3.4.2. Hydration

The hydration mechanism is well described in the literature [129,130,132–136,138,139]. The alkaline environment of the pore solution promotes dissolution of the slag. The dissolved aluminum, calcium and silicon ions react with the added calcium sulfate to form ettringite and C–S–H phases. Compared to Portland cement, a higher amount of ettringite forms, and is mainly responsible for early strength development. Besides the main hydration products, being ettringite and C–S–H phases, minor hydrate phases like AFm phases or hydrotalcite also occur. Fig. 7 displays the phase composition of hydrated supersulfated cement as a function of the hydration degree of the slag as calculated by thermodynamic modeling [132]. The calculation predicts the consumption of anhydrous slag and gypsum and the formation of C–S–H, ettringite and hydrotalcite as the main stable hydrate phases.

The reaction kinetics are strongly dependent on slag chemistry and fineness as well as on the kind and amount of activator. In general, the hydration degree of slag is lower compared to the hydration degree of a Portland cement system. The hydration degree of blastfurnace slags in various supersulfated cements, determined from sealed samples at ages between 28 and 90 days, is reported to be in the range of about 15–25% [132,133,137]. At this age, the small slag particles (a few μm) have reacted fully, whereas the larger particles show only hydration rims [132]. The reaction kinetics of supersulfated cements have not been studied or modeled in a comparable way to Portland cement.

The pH values of pore solutions in supersulfated cements are generally much lower than in Portland cements. In systems activated by Portland cement or lime as the alkaline component, the pH during the first hours of hydration is around 12.5. At later ages, the pH drops to values between 11.5 and 12 [132,133]. If KOH is used as alkaline activator, high pH values occur at early ages (pH 13 after 8 h), but decrease at later ages (pH 12 after 28 days) [132].

The composition of the pore solution is dominated by sulfate, calcium and alkali ions at early ages (<1 day) [132,133]. At later ages, sulfate and calcium concentrations do not significantly change, whereas alkali concentrations increase due to release from the raw materials and a decrease of the volume of pore solutions. With increasing hydration degree of the slag, sulfide ions are released into the pore solution, which can be used as a semi-quantitative indicator of slag dissolution. Si and Al concentrations in the pore solution are generally low, depending on the pH value of the pore solution, and increase with increasing pH. From the pore solution analysis, saturation indices with respect to the relevant hydrate phases can be calculated [133]. The pore solution is saturated with respect to gypsum and oversaturated with respect to ettringite. Monosulfate is undersaturated with the exception of the first hours, and portlandite is always undersaturated.

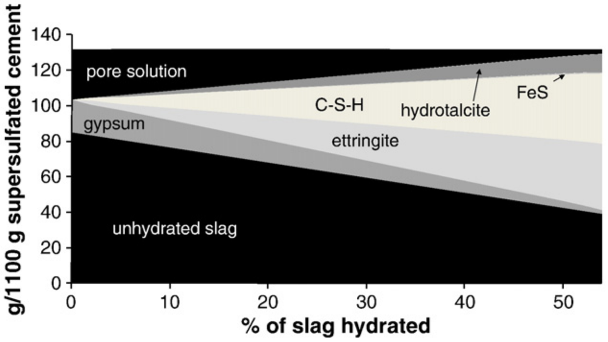

Fig. 7. Phase composition of supersulfated slag as a function of slag dissolved, calculated by thermodynamic modeling [132].

The microstructure of hydrated supersulfated cements [132,133, 135,140,141], Fig. 8, is generally characterized by large (several µm) ettringite crystals, which have precipitated from solution during the first hours of hydration and are responsible for setting and early strength development. Between the ettringite crystals, fibrous or plate-like C–S–H phases occur on the surfaces of the slag grains, forming rims around the slag particles. Matschei et al. [133] found two C–S–H reaction fronts around the slag grains, with an inner layer exhibiting lower Ca/Si ratios (about 1.2) than the outer layer (about 1.4).

3.4.3. Properties

The initial setting of supersulfated cements as required by EN 15743 [128] should be more than 75, 60, and 45 min for strength classes 32.5 N, 42.5 N, and 52.5 N, respectively. Initial setting times are often longer than for Portland cements [119]. Values reported in the literature are mostly between 1 h and 10 h [129,131,134–136], depending on the type and fineness of the slag and on the mixture design of the supersulfated cement. In the case of activation by hemihydrate, the application of retarders might be necessary in order to prolong the setting times [134,136]. Likewise, strength development [121,123,126,129,131,133,135,137] is slower compared to Portland cement. However, 28-day strengths are similar to Portland cements. The slow hardening during the first few days makes it necessary to apply a prolonged moist curing to building materials based on supersulfated cements [119]. Besides poor strength, insufficient curing may lead to dusting of the surface [119].

Supersulfated cements exhibit a low heat of hydration; values after 7 days of hydration reported in literature are about 90 J/g (using isothermal conduction calorimetry [133] or 130–170 J/g (using the heat of dissolution method [139]). The kinetics of heat release under isothermal conditions are characterized by an initial peak, a dormant period of several hours and a main hydration peak [132,133].

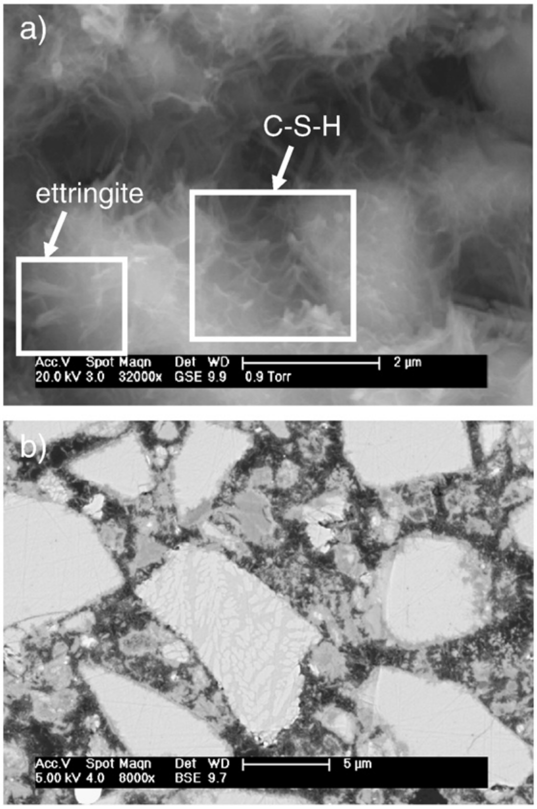

Fig. 8. Scanning electron micrographs of supersulfated slag pastes [132], a. secondary electron image of a fractured surface after 1 day of hydration and b. backscattered electron image of a polished section after 28 days of hydration.

Shrinkage of mortars and concretes based on supersulfated cement is in the same range as for Portland cement [124,125], provided that appropriate curing is applied. In comparison to Portland cement, supersulfated cements exhibit a lower capillary porosity as determined by mercury intrusion porosimetry [120], which is beneficial with respect to durability. Supersulfated cements provide an excellent resistance to sulfate attack [119,120,123–125,142,143], with the exception of $MgSO_4$. Chloride and seawater resistance are generally high, which is related to the low porosity and the high content of aluminate phases in the hydrate assemblages, which are able to bind chloride [120,131,142]. Generally, good frost resistance can be reached in supersulfated cement-based building materials [123,124].

One important issue of supersulfated cements is carbonation, especially when curing is not sufficient. Carbonation causes a decomposition of the ettringite [129] and leads to a strong increase of capillary porosity [133]. The result is a dusting or pulverization of the concrete skin [129]. This skin formation can be prevented by blocking the penetration of ambient air during early hydration (e.g. by wet curing) [129] or by using admixtures like polymer dispersions [125].

The use of a wide range of admixtures is reported in literature, e.g. superplasticizers [124,125,129], retarders [125,134,136], air entraining agents [123,124], methyl cellulose [125] or polymer dispersions [125].

4. Conclusions

Table 1 compares Portland cement to the four alternative binders explored in this paper in terms of the properties discussed herein, namely composition, energy use, CO_2 emissions, and performance. While there are obvious and substantial differences between these materials, remarkably they all have a period of fluidity to enable mixing and placement and substantial strength gains in the absence of applied heat, enabling use for the same applications.

While recent years have shown dramatic improvements in the performance of alternative cementitious binders and an increased understanding of their chemistries, reaction mechanisms and property development, these binders continue to only be used in niche applications and have yet to see widespread use. The primary hindrances to the adoption of alternative binders are the higher costs compared to Portland cement and the prescriptive nature of specifications for binders in concrete. As performance-based specifications become more prevalent, it is likely that the use of alternative binders will increase. Along with increased use will come further research in these systems, including in-depth investigations on reaction kinetics parallel to efforts in Portland cement.

Calcium aluminate cements offer rapid strength gain and good durability in high sulfate environments. However, they have suffered a poor reputation because of the loss in strength that occurs over time due to the conversion of metastable hydration products to more dense stable hydration products, increasing the porosity. Recent studies into the combination of calcium aluminate cements with supplementary cementing materials and chemical admixtures have resulted in a lower cost material that effectively eliminates the formation of metastable hydrates, in turn eliminating the problem of conversion.

Calcium sulfoaluminate cements are touted for their low CO_2 emissions and energy demand. They also have performance benefits over Portland cement, particularly their rapid strength gain and ability to bind heavy metals. The challenges facing these materials have primarily been the cost of bauxite, lack of understanding of phase formation and property development for materials with varied compositions, and the unknown long-term durability. These challenges are being met through further investigation into using wastes

Table 1
Comparison of alternative binders to Portland cement.

	Portland cement	Calcium aluminate cement	Calcium sulfoaluminate Cement	Alkali-activated binder	Supersulfated cement
Primary phases/materials	C_3S	CA	$C_4A_3\bar{S}$, C_2S, $C\bar{S}/C\bar{S}H_2$	Aluminosilicate, alkali	Slag, $C\bar{S}/C\bar{S}H_2$
Secondary phases/materials	C_2S, C_3A, C_4AF, $C\bar{S}H_2$	$C_{12}A_7$, CA_2,C_2S, C_2AS, C_4AF	C_4AF, CA, C_2AS		Alkali/Portland cement
Hydrates	C–S–H, CH, AFt, AFm	CAH_{10} (m*), C_2AH_8 (m), C_3AH_6, AH_3	AFt, AH_3, AFm, C_2ASH_8, C–S–H	Gel (N–A–S–(H) and/or C–(A)–S–H), zeolites, hydrotalcite	AFt, C–S–H, AFm, hydrotalcite
Raw material CO_2 (g/g) primary phase [36]	$C_3S = 0.578$	$CA = 0.279$	$C_4A_3\bar{S} = 0.216$ $C_2S = 0.511$	Activator $NS = 0.361$	0
Clinkering temperature	~1450 °C	>1450 °C	1250 °C	Fly ash/slag: N/A Metakaolin: 800 °C	N/A
Grinding energy (kWh/t)	30 [144]	>30 [9]	~20 [145]	Slag: 50 [146]	Slag: 50 [146]
Advantages	—Long history —Standard compositions	—Rapid strength —Sulfate resistant —No alkali–silica reaction —Abrasion resistant	—Low CO_2 —Low energy —Rapid strength —Shrinkage compensating	—Low CO_2 —Low heat of reaction —Heat and acid resistant	—Low heat of hydration —Durable in aggressive environments
Disadvantages	—High energy —High CO_2 —Limited early strength —Poor in aggressive environments	—Strength loss on conversion of metastable to stable hydrates	—Durability unproven —Sometimes expansive	—Sometimes slow strength gain —Caustic activating solution —Challenging rheology —Durability unproven	—Slow strength gain

m* = metastable.

as raw material, thermodynamic modeling of phase formation, and long-term durability characterization.

Alkali-activated binders offer the possibility of making binders almost entirely from waste materials. However, the effects of raw material composition on the reaction kinetics and reaction product development are still incompletely understood, hindering the ability to model and predict phase and property development. Characterizing the binders has been particularly challenging because the raw materials and the gel products are amorphous to poorly-crystalline. In spite of this, many advances have been made in binder development, resulting in the ability to generate good strength gain at room temperature and implement the material in large-scale structures.

Supersulfated cements also have the advantage of being made almost entirely from waste materials, coupled with low heat production and good durability in aggressive environments such as seawater. They are seeing a resurgence as the European Union has re-established specifications for their use and characterization. While they suffer from poor early strength development, with adequate curing they can reach the same strength as Portland cement concrete by 28 days and have excellent durability.

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