Advances in alkali-activation of clay minerals

Ahmed Z. Khalifa[a], Özlem Cizer[a], Yiannis Pontikes[b], Andrew Heath[c], Pascaline Patureau[d], Susan A. Bernal[e], Alastair T.M. Marsh[c,e,*]

[a] Department of Civil Engineering, KU Leuven, Kasteelpark Arenberg 40, 3001 Leuven, Belgium
[b] Department of Materials Engineering, KU Leuven, Kasteelpark Arenberg 44, 3001 Leuven, Belgium
[c] Department of Architecture and Civil Engineering, University of Bath, Bath, BA2 7AY, United Kingdom
[d] Department of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom
[e] School of Civil Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom

ABSTRACT

To future-proof alkali-activation technology, there is a need to look beyond well-established precursors such as fly ash and blast furnace slag, due to resource competition, geographical distribution and technical limitations. Clay minerals are abundant and diverse aluminosilicate resources available around the world. However, due to the mineralogical complexity amongst the most common 1:1 (kaolinite, halloysite) and 2:1 (montmorillonite, illite) clay minerals, and practical issues such as workability, their use has been more limited. Recent advances have improved understanding both of pre-activation treatments (thermal, mechanical, chemical), and of the factors influencing clay reactivity, phase assemblages and properties of final products. This opens new opportunities for the exploitation of these resources to produce sustainable cements. A one-size-fits-all approach for processing and activating clay minerals is not viable. Instead, activation routes need to be tailored according to the clay mineralogy to achieve the binder properties required for key applications.

1. Introduction

Alkali-activated materials (AAMs) have been a subject of much research over the past decades because of their potential to have a lower environmental impact, and higher durability, than Portland cement-based materials [1–3]. AAMs are one of the leading options in an emerging 'toolkit' of cements, alongside limestone calcined clay (LC3) and belite-ye'elimite-ferrite (BYF) cements, that can meet the demand for sustainable development of infrastructure and the built environment [4]. As well as these high volume uses, AAMs are highly versatile ceramic materials that also have applications including nuclear waste encapsulation [5,6], fire resistant coatings [7] and electronic materials [8].

Significant progress has been made in recent years in understanding the fundamental mechanisms of the activation process of AAMs [9–12], as well as more applied aspects such as appropriate testing procedures [10,13] and life cycle analysis [14]. A vast range of precursors has been investigated, such as construction and demolition waste [15–18], non-ferrous metallurgy slags [6,19–21], amongst others. However, the depth of understanding required for commercial adoption is so far limited to a very few precursors: fly ash from coal combustion, blast furnace slag (GGBS) from the iron making process, and metakaolin obtained from calcination of kaolinitic clays.

Although their viability as precursors has been proven, there is a growing move to look beyond these three resources [4,22]. Fly ash and GGBS will continue to be produced in large quantities into the 21st century [23,24], but changes in industrial production and geographical distribution mean they are not guaranteed to be universally available for mass-scale AAMs production. Utilisation rates of coal combustion by-products (including fly ash) are already as high as > 90% in Europe and Japan, although this is lower (< 15%) in other regions such as Middle East, Africa and Asia [25]. There is debate over whether these are more efficiently used as high volume replacement supplementary cementitious materials (SCMs) in blended Portland cement systems, rather than as precursors in AAMs [26,27]. Although the construction industry is still the biggest consumer of these resources, there are numerous other potential applications for fly ash such as catalysts for the recovery of metals [28,29], and emerging uses of GGBS such as carbon sequestration and soil remediation in farmland [30]. Sustainability credentials are eroded by the use of long distance transport when there are not production sites in close proximity to cement plants, for example, the importing of fly ash from China to the U.K. Questions also remain over how to fairly assign their environmental impacts as by-products of industrial processes, rather than simply as waste [31].

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* Corresponding author at: Department of Architecture and Civil Engineering, University of Bath, Bath BA2 7AY, United Kingdom.
  E-mail address: a.marsh@leeds.ac.uk (A.T.M. Marsh).

Metakaolin, the calcined form of kaolinite, has also been a popular precursor for AAMs – low-Ca AAMs made with metakaolin are often referred to as geopolymers. Metakaolin's advantages are its purity and consistent composition [32–34], as well as experience of its use as an SCM in blended cements [35–37]. However, scale-up is problematic for pure metakaolin, as high purity and commercially available kaolinite deposits are limited, and there is competition from other industries (e.g. paper, ceramics) for high purity kaolinite. Metakaolin based AAMs can also suffer from technical issues of poor workability [38] and high water demand [39,40] due to the plate-like morphology of this clay, high specific surface area, and high electrostatic charge density of particles [41], although these depend somewhat on the calcination method used. These materials are also prone to drying shrinkage deformations in common environmental conditions, due to a large amount of unbound water – this creates a risk of cracking [41,42]. Methods suggested to address these issues include tailoring the viscosity of the alkaline activating solution [38], modifying the metakaolin particle morphology via the calcination process [43], modifying design factors to tailor the pore structure in order to minimize capillary porosity, and/or controlling water loss during curing [41,42] – but, these are far from being fully resolved.

In addition, independently of the precursor used, greater rheological control will be needed if AAMs are to be compatible with emerging digital methods of construction, including additive manufacturing (e.g. 3D printing) [44]. These difficulties may be partly remedied by ongoing efforts to develop appropriate plasticity-modifying admixtures for AAMs [45], as those developed for Portland cement-based systems are often incompatible [22]. Nonetheless, from the perspectives of both scalability and technical performance, it is clear that a wider range of precursors is needed [22] to future-proof alkali-activation technology for a wide variety of applications.

Clay minerals, beyond just high purity kaolinite, are a diverse and abundant aluminosilicate resource that has the potential to supply scalable, widely available and adaptable precursors for cementitious materials in general [4], including AAM production [1]. There has been a recent focus on the use of lower purity clay resources for AAM production, as well as LC3 cements [27], and how to test their reactivity [46]. Many of the findings from research into clay minerals as SCMs in Portland cement-based systems (as well as other engineering fields) are transferrable to AAMs, particularly around reactivity and measurement thereof. But as will be elaborated in this review, much of the research is not 'system-agnostic', due to the different reaction pathways and pore solutions found in AAMs. Hence, specific research is required to understand and validate the use of clay minerals in AAMs.

For AAMs, as in the field of cements as a whole, significant research efforts are focussed on identifying correlations between the chemistry of mix formulations and formation of specific cementitious binding phases. The primary driver for this is to be able to design and manufacture materials with appropriate properties for different applications, at the lowest environmental impact. A major part of how to resolve this depends on the roles played by, and sources of, the key metals (particularly calcium, silicon, and aluminium) in gel phases. A combination

of thermodynamic modelling approaches and experimental observation have clarified the existing interrelationships between the chemistry of a system and the evolution of its phase assemblages - albeit mainly for alkali-activated slag cements [47]. In contrast, there is less understanding of the interdependency between the structural ordering and chemistry of sodium aluminosilicate hydrates (N-A-S-H) forming in low calcium systems; and by extension, less understanding of their physico-mechanical and durability properties as well. From studies on aluminosilicate based AAMs blended with different calcium sources (e.g. slag, limestone, high calcium fly ashes, Portland clinker) [48], there is a general consensus that this approach offers great opportunities to design materials with targeted properties, as well as desirable cost and environmental credentials. However, their phase assemblage evolution and performance are strongly dependent on the kinetics of dissolution, and hence availability of calcium, during the reaction. As a result, the behaviour of such blended systems cannot be easily predicted based on results obtained from activating each precursor individually. The majority of studies using calcined clays in hybrid cementitious systems are limited to utilisation of metakaolin. This brings great opportunity to explore production of other alkali-activated cementitious blends with different types of clay minerals. Detailed information about the topic of blended AAMs can be found elsewhere [49–52]. Whilst there remain many outstanding questions for such blended systems, it is deemed prudent (for the reasons of system complexity already described) to focus firstly on developing a full understanding of using clays in low-Ca AAMs. For this reason, this review will focus on low-Ca AAMs. Specifically: how clay chemistry influences mineral resources' reactivity, how mineralogical and other factors influence reaction pathways and phase assemblages, and the engineering opportunities and barriers that these systems present. This synthesis of knowledge is most immediately relevant to the manufacture of low-Ca alkali-activated systems, which already have existing applications [47]. But it is also hoped to be a bridge towards an improved, future understanding of how to produce more complex systems involving both clay minerals and calcium sources as precursors.

The starting point of this review is a brief overview of clay mineralogy, with a focus on the characteristics which influence reactivity and reaction pathways in AAMs. From the large range of clay minerals in existence, this review focuses on kaolinite, halloysite, montmorillonite and illite. These were selected to give insights from comparisons within, and between, 1:1 clay minerals (kaolinite, halloysite) and 2:1 clay minerals (montmorillonite, illite) (Fig. 1). Other clay minerals, a small number of which have been investigated in alkali activation, are too numerous to be reviewed here – descriptions of the variety of clay minerals and their mineralogy can be found elsewhere [53]. Given that kaolinite (and metakaolin) have been exhaustively studied [54,55], these are considered here largely as a reference point for other clay minerals. The most recent understanding on the alkali-activation process is briefly presented, as is relevant to clay minerals. From then, the activation of these clay minerals as individual precursors is evaluated, considering the influences of processing, activator composition as well as the clay minerals themselves. Given that clay resources are often low
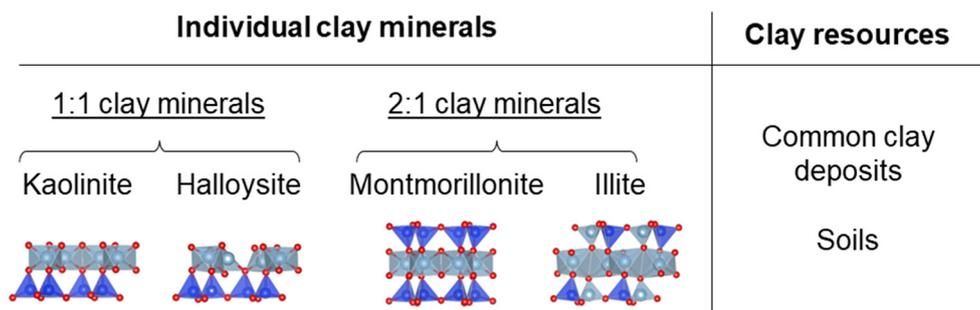
Fig. 1. Overview of clay resources reviewed in this article.

purity mixtures of clay minerals, analysis is then extended to studies of lower purity and/or mixed resources (common clay deposits, soils), before concluding with insights on the remaining opportunities and challenges for this field.

2. Clay minerals: Resources, compositions and mineralogy

2.1. Resources

Clay minerals are an abundant natural aluminosilicate resource: the clay phyllosilicates group (kaolinite, illite and smectite), together with the tectosilicates group (quartz, feldspar), make up approximately 90% of the earth's crust [56]. As a result, global reserves for all common industrial clays are extremely large [57], and so at least 6 GT/year could be produced [4].

"Common clays" define a variety of clay-containing deposits, having a wide range of mineralogical compositions [58]. As well as deposits, clay minerals are also present in soils. Soils are abundant in many parts of the world, as shown by their use in construction throughout human history [59]. Besides their natural abundance, they are also a waste stream - soils typically make up the single largest component of construction waste [60]. The mineralogy of soils can vary widely depending on location (Fig. 2). Clay minerals are also present in other waste streams, including mining wastes [61,62] and dredging wastes [63–65]. From these various sources, clay minerals are a diverse, abundant and widely available resource, and therefore have high potential as scalable precursors for cementitious materials production.

Of the clay minerals considered in this review, kaolinite, montmorillonite and illite have several large-scale industrial applications, including: paper, paints, ceramics (kaolinite); drilling fluids, landfill lining barriers (montmorillonite), and brickmaking (illite) [66]. As well as being found in abundant quantities in clay-containing deposits as previously described, these three are also the most common clay minerals found in soils. In contrast, halloysite does not currently have any large-scale industrial uses, though its nanostructure is making it a subject of much research interest in areas including nanocomposites, controlled release and pollution remediation [67]. However, it is found in a variety of deposits so can be abundant in some localised areas [68], and is often a major component of soils of volcanic origin in wet tropical and sub-tropical areas [69].

2.2. Compositions and structures

Clay minerals have a wide range of chemical compositions and mineralogical structures, caused by the highly variable influence of formation, weathering and transport conditions [71]. Clay minerals are formed by diagenesis from, or weathering of, other aluminosilicates (commonly feldspars) and are found in a variety of geological deposits - hydrothermal, residual or sedimentary [72]. Several factors control the chemical and physical properties of clays, including: the mineralogy of the layers; exchangeable interlayer cations; the type and quantity of associated minerals; presence of organic matter and soluble salts, and particle size distribution [53,58].

The specific structure of each clay mineral considered in this review will be given in Section 4 – a broad overview of generic structural features is given here. Clay minerals are phyllosilicates (layered silicates). Their crystallographic structure consists of regular repetition of two-dimensional tetrahedral and octahedral sheets forming layers. Tetrahedral sheets (Fig. 3) have the general formula T_2O_5: T is the cation, usually Si^{4+}, with each cation surrounded by four oxygens in a tetrahedral geometry. Each tetrahedron is linked to adjacent tetrahedra by three shared corners (the basal oxygen atoms, O_b) to form a hexagonal mesh pattern. The fourth corners (the tetrahedral apical oxygen atoms, O_a) form octahedra of formula MO_6, which together form an octahedral sheet (Fig. 4). M is either a divalent (Mg^{2+}, Fe^{2+}) or trivalent (Al^{3+}, Fe^{3+}) cation. For a divalent cation, the side-sharing

octahedra belong to a trioctahedral sheet, whereas for a trivalent cation, the sheet is called dioctahedral. The positioning of the octahedral anions O_o (most commonly OH^-, but can also be other anions such as F^- or Cl^-) in the octahedra can form either cis- or trans- types of octahedra. These features, and their effect on clay properties, will be described in detail in Section 4. Atomic substitutions in octahedral and tetrahedral sites determine the net layer charge on the unit cell, which can then influence several properties, such as swelling. In terms of which atoms can make these substitutions, cations such as Al^{3+} and Fe^{3+} can occur in either tetrahedral or octahedral sites, whereas larger cations such as Mg^{2+}, Ti^{4+}, Fe^{2+} and Mn^{2+} tend to occupy the octahedral sites [73].

The unit cells of clay minerals are formed by combinations of the octahedral and tetrahedral sheets. In 1:1 clay minerals, each layer is formed by one tetrahedral sheet and one octahedral sheet. In 2:1 clay minerals, each layer consists of one octahedral sheet sandwiched between two tetrahedral sheets. The arrangement and composition of the octahedral and tetrahedral sheets can vary, and this accounts for most of the differences in the physical and chemical properties [53,58,66,74].

Clay minerals do not have fixed stoichiometric compositions – instead, they are defined by their crystallography and layer charge. Depending on the clay mineral in question, they have loose ranges for chemical composition, depending on the type and extent of substitutions, as well as the identity of interlayer cations. A key point within the context of AAMs, is that they contain very low amounts of calcium. As previously stated, calcium is not known to be present in substitutions in the layer structure, but in some clay minerals (e.g. montmorillonite) can be present as exchangeable interlayer cations. Thus, the CaO content will typically never exceed a total of approximately 5 wt%, and can therefore be universally assumed to be low-Ca precursors (Fig. 5).

3. Fundamental aspects of alkali-activation for clay minerals

A short overview of the alkali-activation reaction process will be given specifically for clay minerals as low-calcium systems, along with reactivity-enhancing processes and other factors affecting their activation (Fig. 6). The precise mechanisms of alkali-activation are still not fully understood, although in recent decades there have been great advances in understanding some of the underlying processes [9–12].

3.1. Reaction process

There are two conditions for solid precursors to react, in both conventional Portland cement-based and AAM systems: there must be a sufficient thermodynamic driving force for the desired reaction, and the kinetics of dissolution must be fast enough [75]. In the case of alkali-activated systems, broadly speaking, any material which has a certain amount of silica and alumina in a reactive form – possessing either a high degree of disorder, or a crystal structure which is sufficiently soluble in an alkaline medium - can be used as a precursor. Dissolution of one or more aluminosilicate precursors in an alkaline solution of sufficiently high concentration is required to break the precursors down into aluminate and silicate oligomers [76]. The aluminate and silicate species in solution then undergo a nucleation and growth process. The reaction products formed are either crystalline zeolites [77] or an alkali aluminosilicate hydrate gel framework – these will be described in detail in the following section. In gel formation, a polycondensation step is involved [11]. Acid activation has been demonstrated to form poorly crystalline gel type products in several systems [78–80]. However, this review will only consider alkaline activation, as the majority of studies continue to use this method.

From the reaction steps described above, dissolution processes merit detailed attention, given the importance of dissolution as a critical reaction step and the variability in rates and mechanisms between clay minerals. These mechanisms will be described in detail in Section 4.
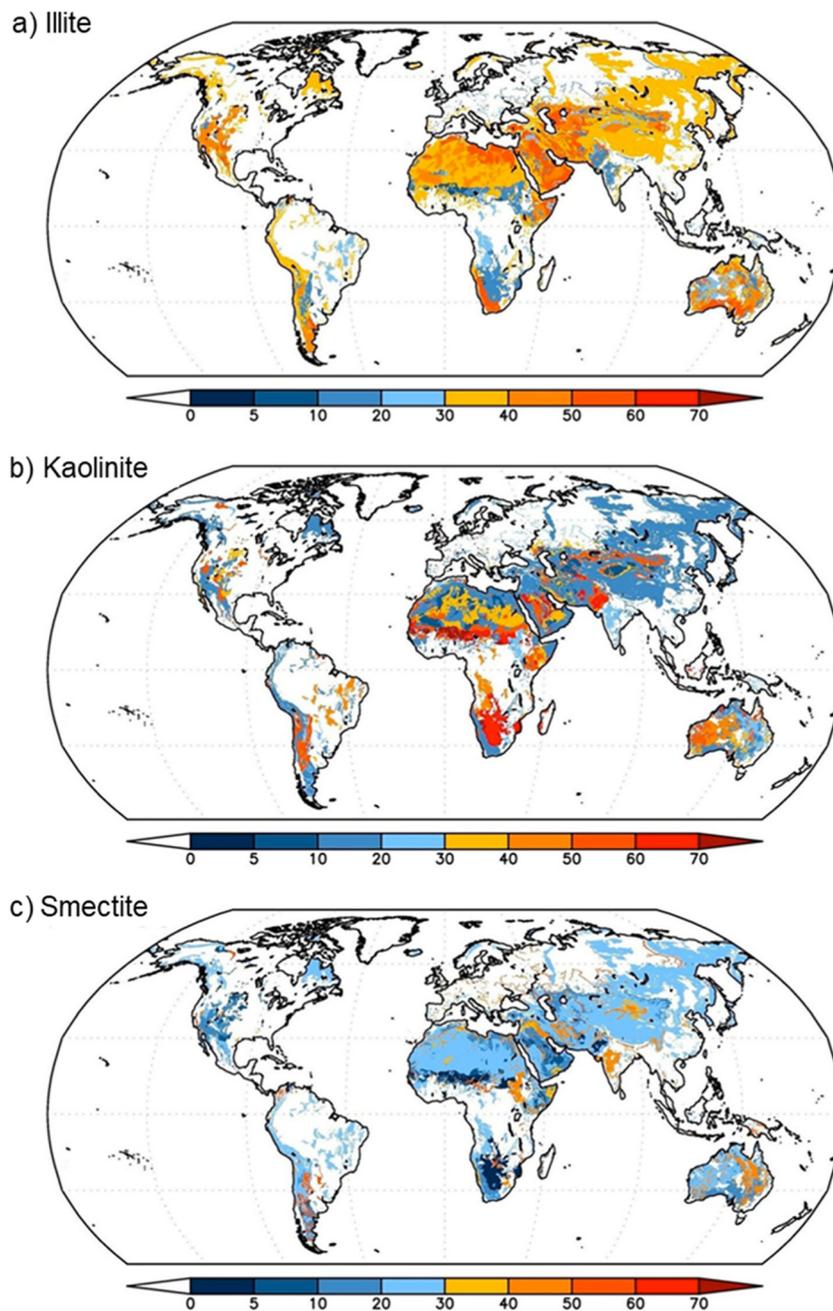
Fig. 2. Global distribution of the different clay minerals in soil. Adapted from Nickovic et al. [70].

Dissolution of aluminosilicates in general can be categorised as either congruent - if the dissolution ratio of Si:Al in the alkaline solution is similar to the Si:Al ratio in the solid raw material, or incongruent - if the dissolution ratio of Si:Al is not similar to the Si:Al ratio of the solid raw material. As discussed later, this has important implications for the nature of the phase assemblage formed. The dissolution behaviour of clay minerals is a well-studied area [81], but much of this knowledge cannot be readily transferred to the highly alkaline dissolution systems in alkali-activation. Much of previous research is limited to the range of pH 2–12, from studies on natural rock-forming and pedogenic processes [82] or barrier linings in deep geological storage of radioactive waste [83]. In contrast, alkali-activation of clay minerals typically requires alkaline solutions of $[OH] \geq 5$ M at the minimum [84], corresponding to pH $\geq$ 14. An optimal range has been empirically established as 8–12 M [85–89] albeit with less detailed description than in geological studies.

The reaction steps described above correspond to conventional 'two-part' synthesis, in which a solid aluminosilicate precursor is mixed with an alkaline activator in an aqueous solution. The majority of studies in AAMs have used this method. Recently, there has been a movement towards 'one-part' synthesis methods, in which a precursor is prepared such that only water needs to be added in the mixing procedure [90,91]. This is in response to the practical issues of mixing using large volumes of highly alkaline solutions – this is a promising route to make AAMs more usable for on-site fabrication but these procedures remain in their infancy.

3.2. Reaction products

The primary reaction products of alkali-activation of low-Ca precursors, such as clay minerals, are alkali aluminosilicates – these are classified as either crystalline zeolitic phases, or sodium aluminosilicate
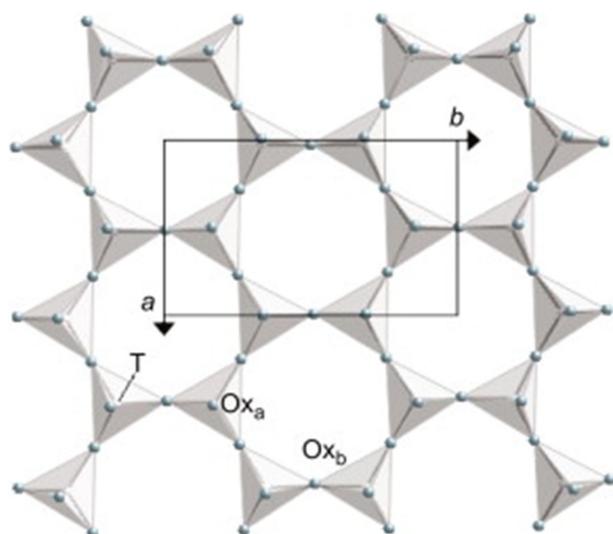
Fig. 3. Overhead diagram of the tetrahedral sheet. Ox_a = apical oxygen atoms; Ox_b = basal oxygen atoms; T = tetrahedral cations; a and b refer to unit cell parameters. Reprinted from Brigatti et al. [53].
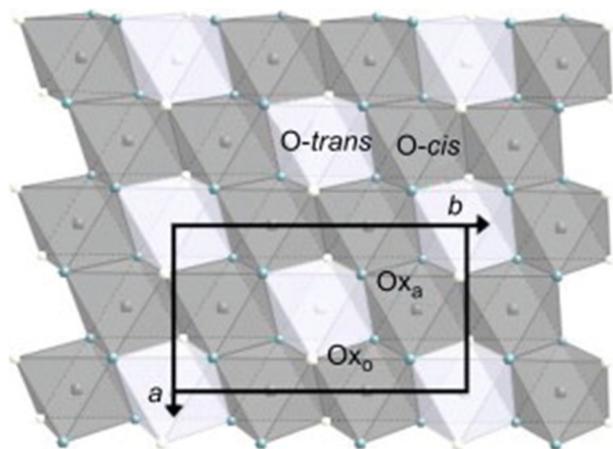
Fig. 4. Overhead diagram of the octahedral sheet. Ox_a = apical oxygen atoms; Ox_o = octahedral anions (typically OH). O-trans = trans-oriented octahedra; O-cis = cis-oriented octahedra; a and b refer to unit cell parameters. Reprinted from Brigatti et al. [53].

hydrates (N-A-S-H) gel frameworks. From here on, cement chemistry notation will be used to abbreviate chemical formulae: N = Na_2O; C = CaO; A = Al_2O_3; S = SiO_2; H = H_2O [92]. These gel frameworks are often abbreviated as N-A-S-H, although it is borne in mind that Na^+ and K^+ are the most common alkali metal cations present in the activating solution used for alkali-activated materials production. The N-A-S-H gel exhibits characteristics common to both amorphous and pseudo-zeolitic or proto-zeolitic structures [93]. Current models explain this as either a uniform intermediate amorphous-crystalline structure, or nanoscale alternating zones of crystalline and amorphous material (Fig. 7) [94,95]. Coined by Davidovits [96], the term geopolymer has been commonly used to describe low-Ca alkali-activated aluminosilicate binders [1,96], mainly those produced from metakaolin. Therefore, throughout the rest of this article, it is assumed that when the term geopolymer is used, it refers to a system whose main reaction product is a N-A-S-H type gel.

A key difference between zeolites and geopolymers is that zeolites have fixed stoichiometric compositions [97]. In contrast, geopolymers can have a continuous range of compositions due to the coexistence of a range of Q_4(mAl) tetrahedra in the disordered binder [33,98] – this is a
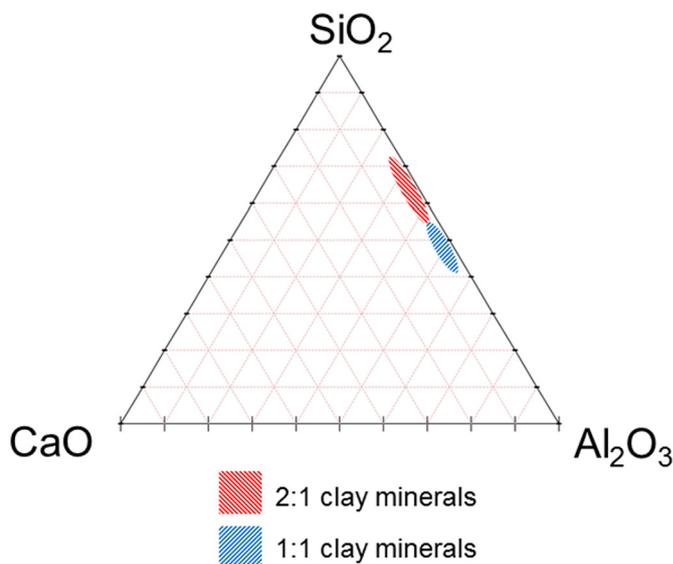
Fig. 5. Compositional diagram showing the approximate composition range of clay minerals, considering only CaO, SiO_2 and Al_2O_3.

consequence of different rates of reaction taking place upon activation. For zeolites, the stoichiometry of M, Al and Si depends on the exact zeolite phase. The composition of the aluminosilicate zeolites framework is $Al_xSi_{(2-x)}O_4$ (within the range of $0 \leq x \leq 2$), and includes sufficient framework cations M^+ required to balance the anionic charge in the framework arising from the inclusion of aluminium [99]. Similarly, for geopolymers, the charge balancing required for the presence of Al^{3+} atoms in the inorganic polymeric framework requires one alkali metal (M^+) cation for each Al atom [100,101]. Other cations such as Co^{2+}, Cu^{2+}, Fe^{2+}, Pt^{2+}, Cd^{2+}, Pb^{2+}, and Mg^{2+} can also act as charge-balancing cations - these can be inserted by exploiting the ion-exchange behaviour of the geopolymer, and can be used in the application of catalytic processes [102,103]. As the silicon proportion of a geopolymer framework increases, the proportion of Al linkages in the chains decreases - this induces strengthening of the framework [5]. It is claimed that geopolymers have been formed at Si:Al molar ratios of up to 600 – however, the industrial relevance of these high Si geopolymers is questionable as deformation behaviour was reported to become elastic at Si:Al > 48 [104]. In addition, a system containing too much silica may not fully react, resulting in lower strength beyond an optimal Si:Al ratio [98].

For construction and infrastructure materials development, a geopolymer is a desirable reaction product. Exact properties are determined by the microstructural features and service environment, but generally speaking geopolymers can achieve desirable properties of strength [98], thermal stability when exposed to high temperatures [105,106] and good durability against many aggressive environments [107,108]. Understanding the multi-scale structure of materials is key to explaining and predicting their performance in service conditions. In the case of geopolymers, this requires considering aspects of both amorphous gels and crystalline zeolites. In addition to their pseudo-zeolitic structure as discussed previously, beyond the molecular scale zeolites are often present alongside N-A-S-H gels in phase assemblages and can influence properties in ways that are not necessarily straightforward. For example, transformations from geopolymers to zeolites under hydrothermal conditions have the potential to either improve or worsen mechanical properties, depending on the volume of the zeolite fraction [109]. Hence, although it could be argued as slightly artificial to make a distinction between the two, both geopolymers and zeolites are relevant to understanding the behaviour of alkali-activated aluminosilicate binder systems including clays at different length scales, and so both will be considered in this review.

Clay resources		
Reactive surface area	Chemistry	
Degree of crystallinity	Mineralogy	

Processing of Clays

Thermal treatment	Mechanical treatment	Acid treatment
Calcination method	Type of milling	Length of treatment
Calcination temperature and heating rate	Energy of milling	Chemical species
	Milling environment	Concentration
Cooling rate and conditions		

Alkali activation

Type of alkali activator	Concentration of OH⁻
SiO_2/Na_2O, H_2O/Na_2O molar ratios	

Processing of wet mix

Mixing	Curing conditions	Shaping
Type of mixing	Temperature	Casting
Duration	Pressure	Extrusion
Time	Atmosphere	Pressing

Binder products

Phases formed	Extent of Transformation

Fig. 6. Influencing factors in the production of alkali-activated materials using clays.

Crystalline: Si:Al 1.4

Defective: Si:Al 1.5

Amorphous: Si:Al 1.5

Legend
H₂O
Si
Al
Na
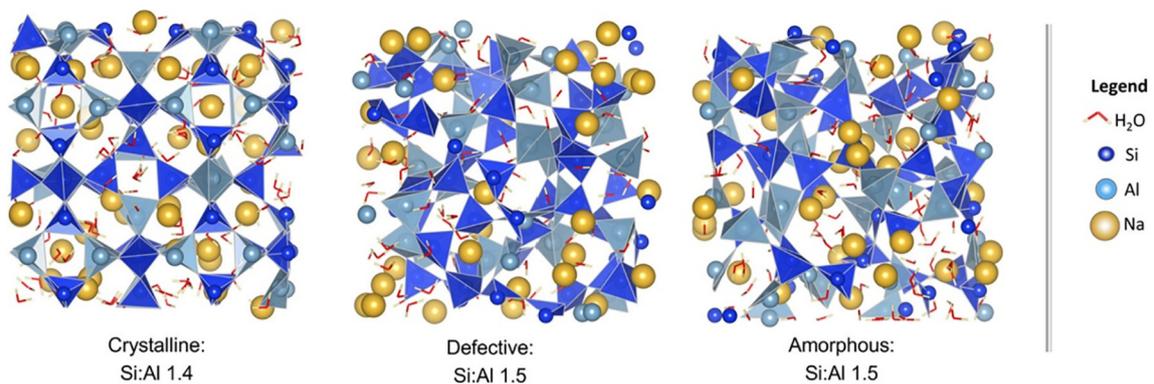
Fig. 7. Atomic structures for the intermediate (defective) model, alongside purely crystalline and amorphous models with similar Si:Al molar ratio. Shaded areas show the arrangement of Si and Al bonding tetrahedra. Reprinted from Lolli et al. [94].
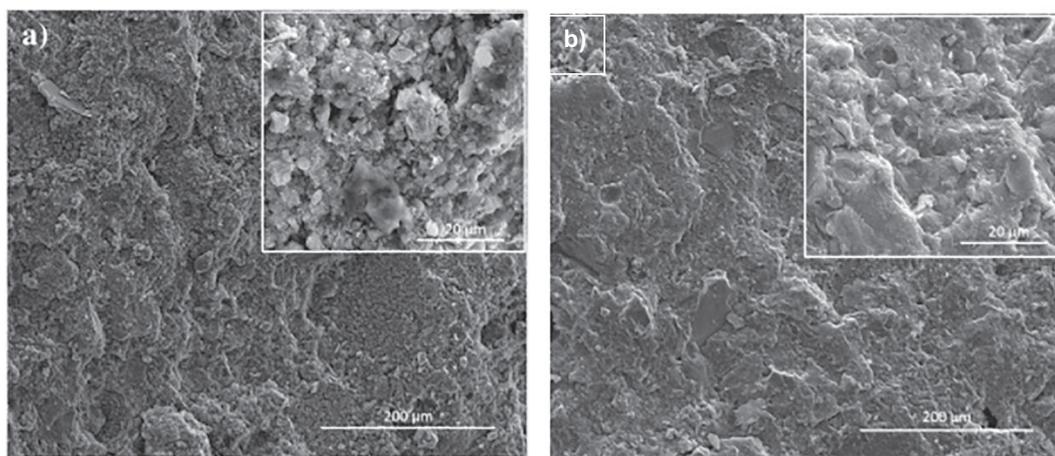
Fig. 8. Micrographs of alkali-activated clay sediments showing that activation with NaOH (a) resulted in a more porous, less dense microstructure than activation with (b) Na-silicate solution. Adapted from Ferone et al. [132].

3.3. Composition variables: Alkaline activator and aluminosilicate precursor

A wide range of aluminosilicate precursors and alkaline activators can be used to produce AAMs, making them highly versatile. In turn, many of the properties of the product phase assemblages are determined by aspects of chemical composition in both starting materials.

For the activating solution, the element, quantity and concentration of alkali metal cations is critical in determining both the type and the amount of product phases formed. A sufficiently high concentration of hydroxide anions is required to dissolve sufficient quantities of the precursor, whereas the metal cations are required for charge balancing in the product phase. In general, the dissolution rate of clay minerals increases with higher concentrations of the alkaline activators [54]. NaOH and KOH are commonly used as alkaline activators for clays, as well as for other precursors [38]. Although they perform the same function, there are some differences. The extent of dissolution is typically higher in NaOH solutions [89], but activation with KOH solution gives a faster rate of geopolymerisation [110] and typically yields higher compressive strength [89,111–113]. Higher strength was attributed to the larger K^+ ions' tendency to form larger silicate oligomers [89], which agree with rheological measurements [114]. The activating cation can also influence the degree of ordering of the framework gel and pore size distribution, which together affect resistance to acid attack [115]. There is a general tendency of NaOH to be more conducive to zeolite - rather than geopolymer - formation [116], but practical factors such as cost and viscosity also influence the choice of compound [38].

Activation with alternative alkali metal salts has been less widely explored for clays than for other precursors. GGBS can undergo dissolution at a much milder pH, and so near-neutral salts such as sodium carbonate and sodium sulphate can be used in activating solutions [117]. This approach is not transferrable to clay minerals, because of the higher pH required for dissolution. Nonetheless, other methods have been investigated to use alkali carbonates to replace alkali hydroxides. This has focussed on alkali fusion, whereby a clay mineral is calcined together with an alkali carbonate, and then water added. Whilst there is evidence to suggest that geopolymer phases could be formed by this process [118], the few existing studies in this area suggest that this route is more conducive to zeolite formation [118–120]. This partly arises from the fact that when fused in the range of 700–1000 °C, nepheline is the most common product, and so reactive aluminium and silicon is 'locked away' in a relatively inert phase. However, there is also evidence to suggest that an amorphous calcined product is formed from the process [119], which bears some similarity

to soda glass (at the high-Si end of the Na_2O-SiO_2 binary system). This differs from the ubiquitous soda-lime glass by its lack of calcium, and its resultant solubility gives it little commercial use [121]. Although little explored so far, this route might bear further success if approached from the perspective of producing a synthetic, soluble glass of tailored composition, rather than as an alternative route to standard calcination.

Another interesting alternative to the alkali hydroxide activating solution is to mix an alkali carbonate with an alkali earth hydroxide solution – the subsequent reactions produce an alkali hydroxide in-situ, as well as a carbonate salt of both metals [122,123]. So far this approach has only produced crystalline reaction products rather than gel phases, but if reactions can be controlled effectively, could provide a low-cost, safer alternative to aqueous alkali hydroxide activators.

For the overall system, the Si:Al molar ratio is a highly influential parameter in determining the phases formed, as well as influencing mechanical properties. When processing conditions conducive to geopolymer formation are used, geopolymers are typically formed for systems with Si:Al > 1.5 [124], whilst zeolites are typically formed for systems with Si:Al < 1.5. At intermediate ranges of Si:Al = 1–1.5, zeolites and geopolymers can form simultaneously [125–127]. Details on routes to intentionally co-form geopolymers and zeolites can be found elsewhere [128]. However, when processing conditions conducive to zeolite formation are used, zeolite species can form for a wide range of Si:Al molar ratio. The exact species of zeolites formed is influenced by the Si:Al ratio, with some species tending to form when Si:Al > 5, and others tending to form when Si:Al < 5 [97,129]. Higher Si:Al ratios also result in longer setting times [130].

The Si:Al molar ratio of the overall system refers to mobile Si and Al ions that are in the solution liquor and hence available to participate in phase formation. The Si:Al molar ratio of the aluminosilicate precursor may differ from the Si:Al molar ratio of the system as a whole – this depends both on the rates and congruency of dissolution for the precursor phases, as well as whether the activator contains soluble silicate. The differences in intrinsic Si:Al molar ratio between different clay minerals has important implications, and are discussed in Section 4. Activators containing additional soluble silica are commonly used in order to increase the soluble Si:Al ratio to be conducive to geopolymer formation - for example with metakaolin, which has a natural Si:Al ratio of 1. When $Na_2SiO_3 \cdot xH_2O$ solution is used, dissolution kinetics and water consumption are changed relative to NaOH, with a net result of reduced porosity and better mechanical strength (Fig. 8) [131,132]. Unsurprisingly, rheology is strongly affected too [133]. The speciation of the silicate oligomers themselves can influence final properties [38,134], as well as setting time [135]. The composition of the activator and precursor also has important practical implications in mix

design, given that the key molar ratios of Si:Al, M:Al and M:Si are related, and together affect workability and setting time. Together, these chemical ratios define the activator concentration and the liquid:solid ratio of the system. On a molecular level, higher liquid:solid ratios accelerate the dissolution and hydrolysis processes, but hinder polycondensation of N-A-S-H gel phases [136]. Zeolite formation is generally favoured by a saturated environment [77,137], and within this constraint, the liquid:solid ratio can determine the zeolite species formed [138]. On a micro-to-macro level, as for other cements, liquid:solid ratio influences the workability of the fresh mixture [139], as well as the drying shrinkage [41,42], porosity, and hence strength, of the hardened microstructure [140,141]. Another consideration in selecting an activator concentration is that efflorescence can occur if there is an excess of free alkali cations [142,143]. Mix design aspects have been investigated [52], but standardised methods for formulation of AAMs do not yet exist. This is a consequence of the large number of factors influencing properties at all scales, and lack of fundamental understanding about the existing connections between materials design, microstructural features and the final products' physical and mechanical properties.

3.4. Thermal treatment

Amongst the range of reactivity-enhancing treatments used for AAMs, thermal treatment is the most common route to increase the reactivity of clay minerals. Much has already been learnt in this area from the use of calcined clays as SCMs [144–147]. Thermal treatment involves heating the clay mineral to a specific temperature so that the octahedral layer undergoes dehydroxylation – this heating process is also known as calcination. The dehydroxylation process results in a reduction in the bonding coordination number of the Al atoms in the octahedral sheet, making them more reactive [148–150]. The exact nature of the structural transformation depends on many factors, including: heating rate, holding temperature and time, atmosphere (oxidizing or reducing) and cooling rate [151–153] - this is discussed specifically for each clay mineral in later sections. The temperature range for successful calcination of a given clay mineral must be high enough to achieve dehydroxylation, but not so high that recrystallisation occurs [145,154].

The most common calcination method used in research is the laboratory oven method, whereas rotary kiln, and to a lesser extent flash calcination, are used more widely in industry. The main effects of the calcination method are on the particle size and the specific surface area of the clays. The rotary kiln and furnace oven (also known as "soak") methods tend to increase the particle size and decrease the specific surface area, whereas these effects are not observed for flash calcination [43,155,156]. These phenomena are enhanced with increasing calcination temperature (Fig. 9) [151,157,158], with particle size increasing due to agglomeration, and specific area subsequently decreasing if sintering takes place at higher temperatures [159]. Since this coarsening effect decreases the available surface area for dissolution, the calcination temperature should be kept as low as possible. Two phenomena observed in flash calcination are the formation of metakaolin particles with spherical morphology, attributed to the rapid melting and subsequent cooling in a hot gas stream (Fig. 10), and lower densities than soak calcined metakaolins [63,160]. The choice of calcination method can result in different microstructures in the alkali-activated material, even when the calcined clays have similar composition and specific surface area [161]. An encouraging recent development is the use of modelling to optimise the flash calcination process [162]. The transformation also depends on precursor factors, including particle size [154,163,164], clay mineralogy [154,165,166], the degree of ordering [166], as well as the amount and type of associated minerals present [167]. Whilst the heating rate does affect calcination when comparing between different methods (i.e. soak and flash calcination), within soak calcination there is little evidence to suggest that the heating rate itself has any substantial effect [168]. Rather, it is advisable to consider how the heating of the material will be affected by its mass and distribution inside the furnace – in the case of large batches of material which are not spread thinly and subjected to short calcination times, it is plausible to suspect that the material may not be sufficiently heated throughout. Lastly, it seems to be an unstated assumption that once a clay mineral has been dehydroxylated, it stays dehydroxylated. In fact, rehydroxylation is possible under certain conditions (discussed in Section 4 for each clay mineral).

3.5. Mechanical treatment

Aside from thermal treatment, other treatments are also used to increase the reactivity of clay minerals [152], by increasing the thermodynamic driving force for dissolution through alteration of structure and bonding. Mechanical treatment is proposed as a viable alternative to thermal treatment for clays. The physics of milling processes are well-established [169], although there are still many challenges in understanding and predicting how these processes occur for a given material and set of milling conditions [170,171]. The exact changes undergone have a complex dependence on several factors, including material of the milling media, ball-to-powder ratio, milling atmosphere, milling speed and time [152,170]. Mechanical treatment has been shown to be able to achieve partial dehydroxylation [172–174], reduction of Al coordination [175,176] and amorphisation [177,178] in clay minerals, with similar but distinct effects to thermal treatment. The mechanism of dehydroxylation – formation of a water molecule via proton transfer between two hydroxyl groups - is suggested to be the same as in thermal dehydroxylation, caused in this context by localised heating generated during milling [177,179]. Remaining hydroxyl groups have a slightly lower dehydroxylation temperature after milling, attributed to a combination of increased structural disorder and possibly also decreased particle size [178]. The end result of mechanical treatment can be pozzolanic activity comparable to thermally treated clay [178]. Although milling is often used in the mineral industries to reduce particle size, it can cause agglomeration of clay particles and a reduction in specific surface area depending on the conditions used [180]. Detailed reviews on mechanical treatment of clay minerals can be found elsewhere [152,181].

3.6. Chemical treatment

Chemical treatments are used to amorphise the layer structure through partial dissolution [182], and can include both acid and alkali treatment [183]. A growing trend is the combination of different processes in sequence – such as acid treatment followed by calcination [184], or calcination followed by mechanical treatment [185]. With this proliferation of different techniques, there is a need to be wise in tailoring treatments to achieve desired changes for a given clay resource. For example, acid treatment of smectites results in preferential dissolution of the octahedral sheet through leaching of Al, increasing the Si:Al molar ratio of the clay mineral [182]. This compositional change could be undesirable in some instances, and so another treatment might be more appropriate. There is also a question of how scalable and cost-effective the range of treatment is, and how they might integrate into existing mineral processing infrastructure.

3.7. Curing variables

The optimal temperature and time of curing depends on the clay mineral, as well as the activation conditions. Highly reactive clay minerals such as metakaolin can form a geopolymer at room temperature [34,41,186], but in contrast, uncalcined kaolinite reacts most successfully in the range of 60–100 °C [187,188]. Curing temperature influences the rate of reaction [189], and also affects mechanical properties by influencing pore volume and size distribution [190]. For some
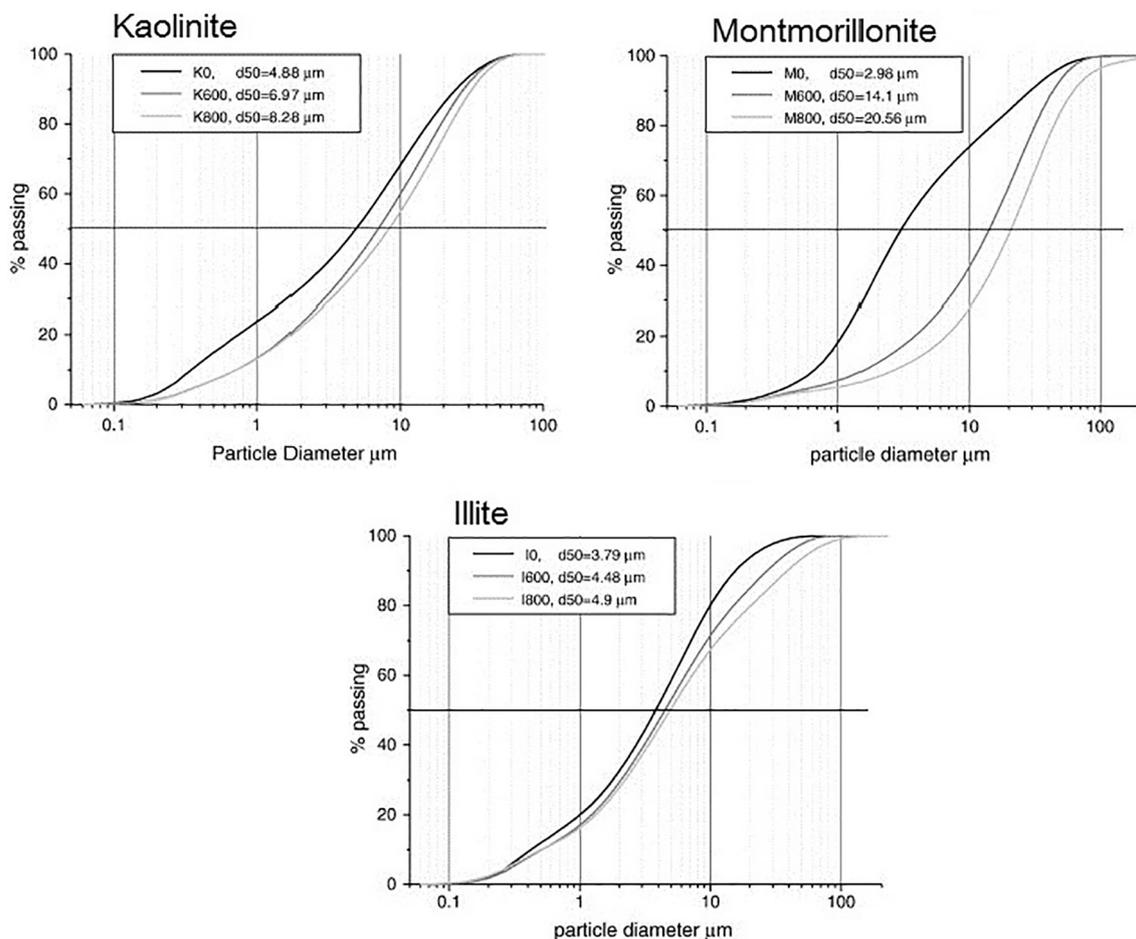
Fig. 9. Particle size distribution of clay minerals (series 0) and their products calcined at 600 °C (series 600) and 800 °C (series 800), for a) Kaolinite, b) Montmorillonite, and c) Illite. Adapted from Fernandez et al. [157].

compositions, extended curing times can result in a secondary transformation from a geopolymer into a zeolite [124]. Beside Si:Al and Na:Al molar ratios, the curing method plays a crucial role in the dimensional stability, mediated by the amount of ambient water present [136] – in air, drying shrinkage cracking can occur in dry or normal ambient environments [41,42]. For this reason, it is advised to avoid rapid drying during curing. For the ambient temperature curing of metakaolin AAMs, the extent of drying shrinkage was attributed to several factors including the ionic charge density of alkali cations (whether Na^+ or K^+), the total quantity of cations, and the relative number of AlO_4 sites in the gel structure [41]. Steam curing has been

found to accelerate geopolymer formation from kaolinite, by reducing the residual alkali content [191]. Pressure plays a role too by altering the solvent's dielectric constant and density, but the effects are specific to each system and also linked to temperature [192]. Higher pressures can result in the formation of finer zeolite particles [193].

4. Alkali-activation of individual clay minerals

To enable comparison of chemical and mineralogical influences on behaviours, the individual clay minerals have been grouped into the 1:1 clay minerals (kaolinite, halloysite) and 2:1 clay minerals
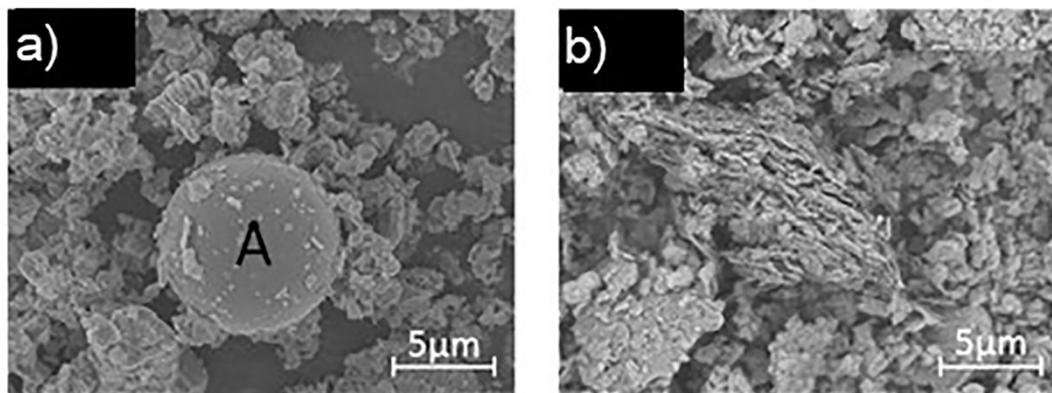
Fig. 10. Secondary electron images of metakaolins calcined by a) flash calcination, b) rotary kiln calcination. Adapted from San Nicolas et al. [43].
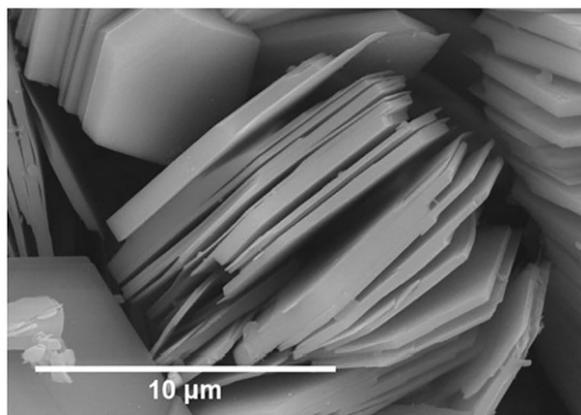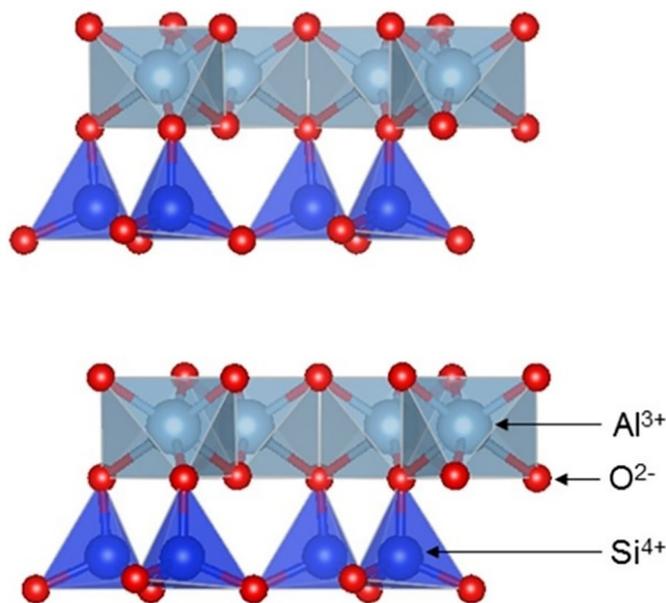
Fig. 11. Atomic diagram of kaolinite, showing two layers. Image generated in VESTA [194], using structural parameters from Bish [195]. Secondary electron image reproduced from the 'Images of Clay Archive' of the Mineralogical Society of Great Britain & Ireland and The Clay Minerals Society.

(montmorillonite, illite). A brief overview will be given for each clay mineral's structure, dissolution mechanisms, and the specific changes enacted by reactivity-enhancing treatments. This will be used to evaluate the reaction pathways and phase assemblages formed in alkali-activation.

4.1. 1:1 clay minerals

Kaolinite is the most common 1:1 clay mineral. It has the unit formula $Al_4Si_4O_{10}(OH)_8$, in which four sites of the octahedral sheet are occupied by Al^{3+} cations and two are vacant (Fig. 11). It can be formed by the dissolution of Al and Si by weathering of primary and secondary minerals [53,58,66,74]. Kaolinite tends to have very little atomic substitution and hence does not have a permanent layer charge. This means it has no interlayer cations, and exhibits non-swelling behaviour.

Halloysite has a 1:1 layer structure similar to kaolinite and can be found in two forms: one hydrated (halloysite-10 Å), $Al_2(OH)_4Si_2O_5\cdot2H_2O$, in which there is a layer of water molecules between the alumino-silicate layers, and one dehydrated (halloysite-7 Å), $Al_2(OH)_4Si_2O_5$ (Fig. 12). In contrast to the plate-like structure of kaolinite (Fig. 11), halloysite can have a range of morphologies (depending on its formation conditions). The dominant morphology of halloysite is
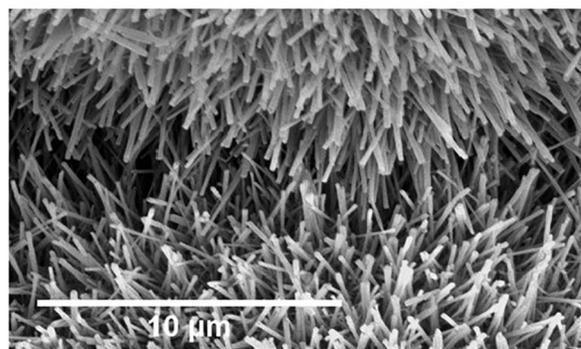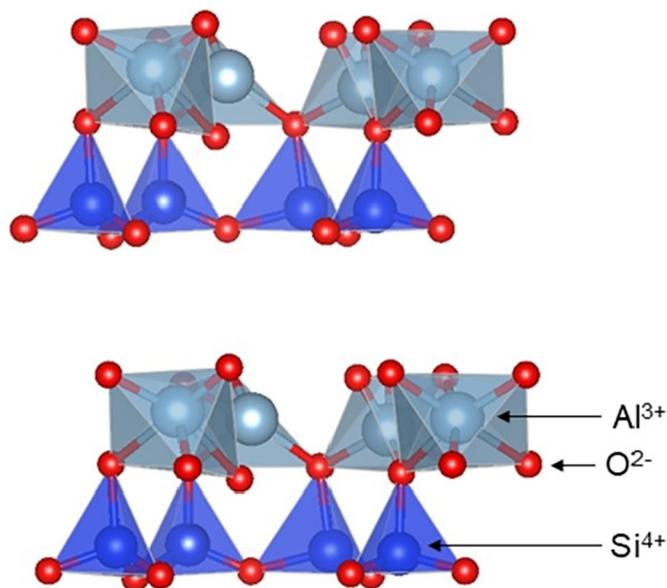
Fig. 12. Atomic diagram of dehydrated halloysite (halloysite-7A), showing two layers. Image generated in VESTA [194], using structural parameters from Zhang et al. [196]. Secondary electron mage of tubular halloysite reproduced from the 'Images of Clay Archive' of the Mineralogical Society of Great Britain & Ireland and The Clay Minerals Society.

tubular (Fig. 12), whereby a dimensional mismatch between the tetrahedral and octahedral sheets causes the sheets to roll up, enclosing additional water [53,58,69,73,74].

4.1.1. Dissolution mechanisms

Dissolution is approximately congruent for several phyllosilicate minerals [89], including kaolinite [197]. There are competing theories to describe the kinetics involved [81], but it is widely agreed that the dissolution rate of kaolinite as a whole is controlled by the dissolution of the layer edges [54,198,199]. Dissolution rate of kaolinite is highly dependent on pH above pH 10 [199].

Halloysite dissolution has received much less attention than kaolinite. It has been suggested that the tubular structure of halloysite allows attack from both the inside and outside of the tubes – thus giving it a higher dissolution rate than kaolinite, which has a stacked structure [200]. However, this remains a hypothesis as there has yet to be a direct comparative study between the two minerals in their pure form.

4.1.2. Thermal treatment

Kaolinite is the most commonly used clay mineral for alkali-activation, and also as an SCM in blended cements. Complete dehydroxylation of kaolinite occurs in the temperatures range of 650–700 °C [36,166,201]. As a result of dehydroxylation, several changes occur: the coordination of Al atoms in the octahedral sheet is reduced from 6-

fold to a distribution of 5-, 4- and sometimes 3-fold coordination [148–150]; delamination and buckling of the layers occur, caused by Al migration into vacant sites resulting from the loss of the hydroxyl groups [149,150]; and the available surface area decreases [158]. The Al sites in 5-fold coordination are the most reactive [202], although the proportion of Al sites in 5-fold coordination does not necessarily correlate with strength in an activated product [203]. The resulting structure is likely to be highly variable, rather than a repeating unit, with highly local variations in the distribution of Al atoms [150]. This dehydroxylated form is known as metakaolin - it is more reactive than kaolinite due to its strained, disordered structure, and reduced co-ordination of Al atoms.

The reactivity of metakaolin is inversely related to the degree of structural order (loosely referred to as 'crystallinity') of the starting kaolinite [166,204]. The underlying mechanisms for this are not yet clear, but differences in crystallinity have been shown to result in some differences in coordination changes in the dehydroxylation process [205]. Chemical activity increases with the amorphous content of a metakaolin [206].

It is rarely mentioned in the literature that dehydroxylation of kaolinite to form metakaolin is in fact reversible under certain conditions. Rocha and Klinowski [207] showed that after 6 days of hydrothermal treatment in an autoclave at 250 °C, metakaolin was effectively fully rehydrated. Aluminium sites were fully returned to AlO_6 coordination (Fig. 13), and crystalline order was restored as well (Fig. 13b).

Halloysite shares many structural similarities with kaolinite - it seems likely that similar coordination changes take place during the dehydroxylation of halloysite with a reduction in Al coordination number to 5 and 4 [67,208,209], but this has yet to be categorically shown. Dehydroxylation typically occurs in the range of 600–850 °C, a lower onset temperature than in kaolinite [67,209]. During dehydroxylation, there is a loss of long-range order and onset of disconnection between the octahedral and tetrahedral sheet [209]. However, the tubular morphology is maintained up until after dehydroxylation is fully complete, at ~1000 °C, brought on by formation of extremely fine scale gamma-Al_2O_3 [209].

4.1.3. Phase formation behaviour

Given the range of different routes that have been used in alkali-activation, studies will be evaluated in groups of similar reaction conditions, with kaolinite considered first. Activation of kaolinite, without additional silica supplied by a silicate-based activator (e.g. sodium silicate), tends to form hydrosodalite using hydrothermal synthesis [210–212] as well as in lower liquid:solid conditions than those typically used in hydrothermal syntheses [213]. Metakaolin can form a broader range of zeolitic phases including hydrosodalite, Zeolites A and X [212,214], or a geopolymer phase [186], depending on the processing conditions.

With the addition of soluble silica, both kaolinite [139,187] and metakaolin [34,212,215] tend towards forming geopolymers. However, if the additional silicate makes the system Si:Al = ~1.5, geopolymers and zeolites can co-form [127].

Si:Al molar ratio is an important factor in determining phase formation, but curing temperature and duration are highly influential too - these can cause different behaviours in systems with the same Si:Al molar ratio. In recent reviews of hydrothermal synthesis of zeolites from metakaolin, it was concluded that: for systems with Si:Al ≤ 5, the range of reaction products can include X zeolites, hydrosodalite or other Linde type A of zeolites (LTA); for systems with Si:Al ≥ 5, products can include zeolite β, zeolite Y, ZSM-5, ZDM-11 [97,129]. In several of these systems, the overall Si:Al molar ratio was conducive to geopolymer formation but a range of zeolites were formed instead, due to the curing conditions. The optimum conditions for zeolite synthesis are given as 70–200 °C for 16–120 h [97,129]. These involve higher temperatures and longer periods than those typically used for the synthesis of geopolymers. The metastable nature of geopolymers means that they can continue transforming into more stable zeolitic phases when cured at higher temperatures and/or longer periods than their optimal range [129]. This was observed for the silica-doped metakaolin systems of Lapides and Heller-Kallai [216], where curing for 72 h transformed the geopolymers into zeolites. Zhang et al. [186] agreed with this, showing that crystalline phases form preferentially over geopolymers in systems that have been subjected to high curing temperatures.

The concentration of the activating solution also has an influence. Both Johnson and Arshad, and Wang et al. [129,217], recommended a
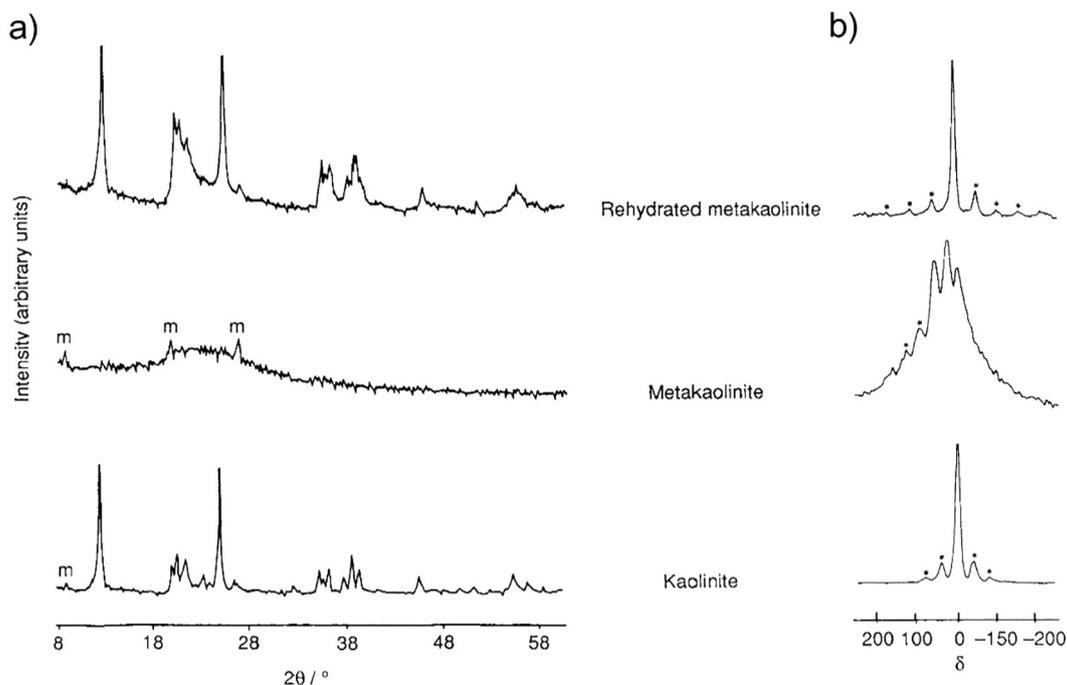
Fig. 13. Kaolinite, metakaolin (after heating for 1 h at 650 °C), and rehydrated metakaolin (after 6 days at 250 °C in an autoclave). a) X-ray diffraction patterns, b) ^{27}Al MAS-NMR spectrum. Adapted from Rocha and Klinowski [205].

NaOH concentration of < 3 M for tailored zeolite synthesis, as higher concentrations decrease the relative crystallinity. This zeolite perspective agrees with studies optimising the production of geopolymers - these typically use NaOH concentration of > 5 M [84], with an empirically determined optimal range for clays of 8–12 M [85–89]. In summary, even for relatively simple and well-understood minerals such as kaolinite and metakaolin, there can be a significant variety in product phases formed depending on the processing variables - specifically additional soluble silica and curing regime.

For halloysite, activation of uncalcined halloysite with NaOH solution resulted in some structural changes but no product phase [218], although this was likely due to the short synthesis time used of 1 h at only 50 °C. The use of treatments has been more successful - calcination between 550 and 800 °C, followed by activation with either sodium silicate, or a combined NaOH and sodium silicate solution formed a geopolymer in several studies [68,102,183,219,220]. In a more unusual formulation, lithium hydroxide and lithium silicate were used as activators for a similar calcined halloysite [221]. In this case, no geopolymer phases were formed, with zeolites formed instead, as anticipated from the lower reactivity and higher degree of silicate polymerization in lithium silicate solutions compared to sodium or potassium counterparts [221–223]. Another calcined halloysite was activated using sodium hydroxide only [224], but unfortunately, no characterisation was given.

There is a clear trend amongst the synthesis methods used for the 1:1 clay minerals - syntheses optimising zeolite production mostly use hydrothermal processes, which are rarely used in geopolymer production. There are two reasons for this. Firstly, considering reaction conditions, the effects of processing variables in hydrothermal synthesis are still not fully understood and it is not generally considered as an appropriate method for making amorphous phases such as geopolymers. Secondly, considering scalable processing, hydrothermal synthesis is appropriate for high purity reactions in small quantities [192] but is less appropriate for the manufacture of construction materials in bulk. Although the production of autoclaved aerated concrete is an established hydrothermal process, extending this to alkali-activation would bring major technical and safety challenges due to the high alkalinities involved. This principle also applies to the other clay minerals and clay-containing resources.

4.2. 2:1 clay minerals

2:1 clay minerals offer greater variety than their 1:1 relatives, and are classified using several factors: their permanent layer charge, which is caused by cationic substitution in the octahedral and/or the tetrahedral sheet; their interlayer cations, and their hydration ability [53]. This review will consider two of the most common 2:1 clay minerals – montmorillonite and illite.

4.2.1. Montmorillonite

Montmorillonite is the most commonly occurring mineral in the smectite group, with an approximate formula range of $(M_y^+ \cdot H_2O)(Al_{2-y}^{3+} Mg_y^{2+})Si_4^{4+}O_{10}(OH)_2$. It is defined as a dioctahedral smectite with little or no tetrahedral charge. The layer charge is generated mostly by the cationic substitution of Mg^{2+}, Fe^{2+} for Al^{3+} in the octahedral sheet or by the substitution in the tetrahedral sheets of Al^{3+} for Si^{4+}. This resultant negative layer charge is balanced by exchangeable interlayer cations (Fig. 14). A range of interlayer cations are possible, including Ca^{2+}, Na^+, Mg^{2+}, K^+ and Sr^{2+}, although Ca^{2+} and Na^+ are the most common. If the interlayer cation is predominantly Na^+, it is termed a Na-montmorillonite and likewise if it is predominantly Ca^{2+}, it is termed a Ca-montmorillonite [72]. The interlayer cations have the capacity to be become hydrated – the formation of diffuse double layers via osmosis results in swelling behaviour. The term bentonite has been avoided here, as it is a commercial name than can refer to a variety of smectite minerals, and has different meanings around the world [66].
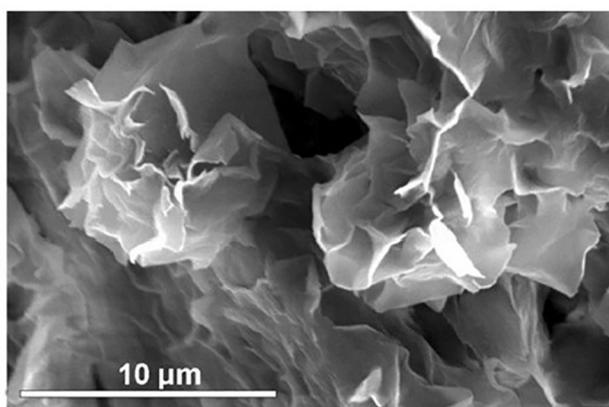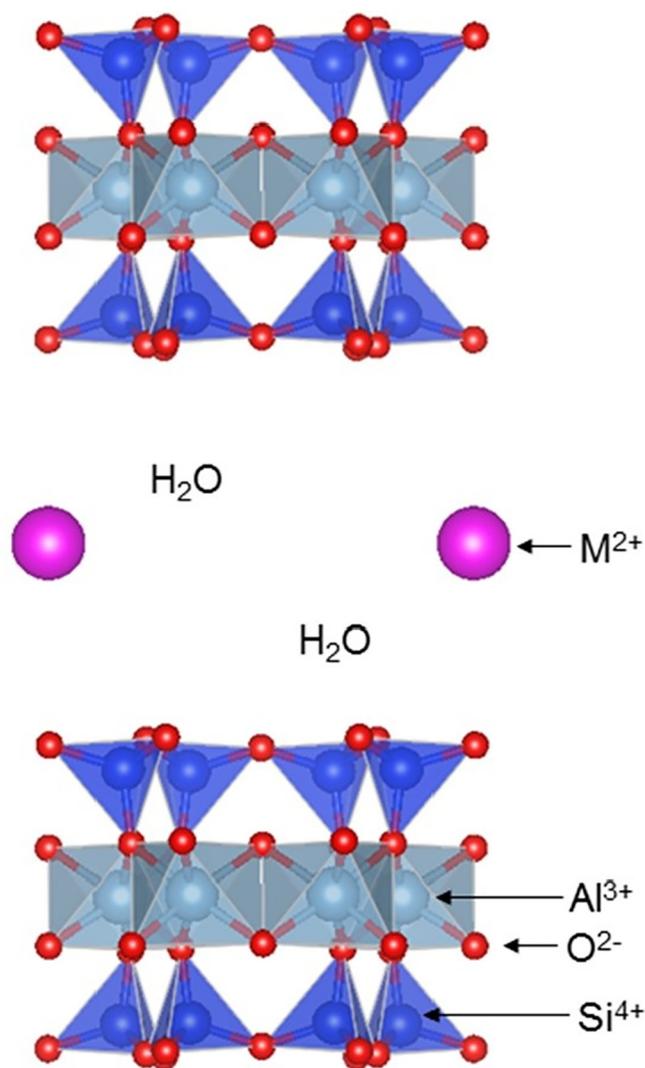
Fig. 14. Atomic diagram of montmorillonite, showing two layers. M = metallic interlayer cation. Image generated in VESTA [194], using structural parameters from Viani et al. [225]. Secondary electron image reproduced from the 'Images of Clay Archive' of the Mineralogical Society of Great Britain & Ireland and The Clay Minerals Society.

4.2.2. Illite

Illite is a commonly occurring dioctahedral clay mineral in the true mica group, with an approximate formula of $(K_{0.65})Al_2(Si_{3.35}Al_{0.65}) O_{10}(OH)_2$. A layer charge arises from substitution of Al^{3+} for Si^{4+} in
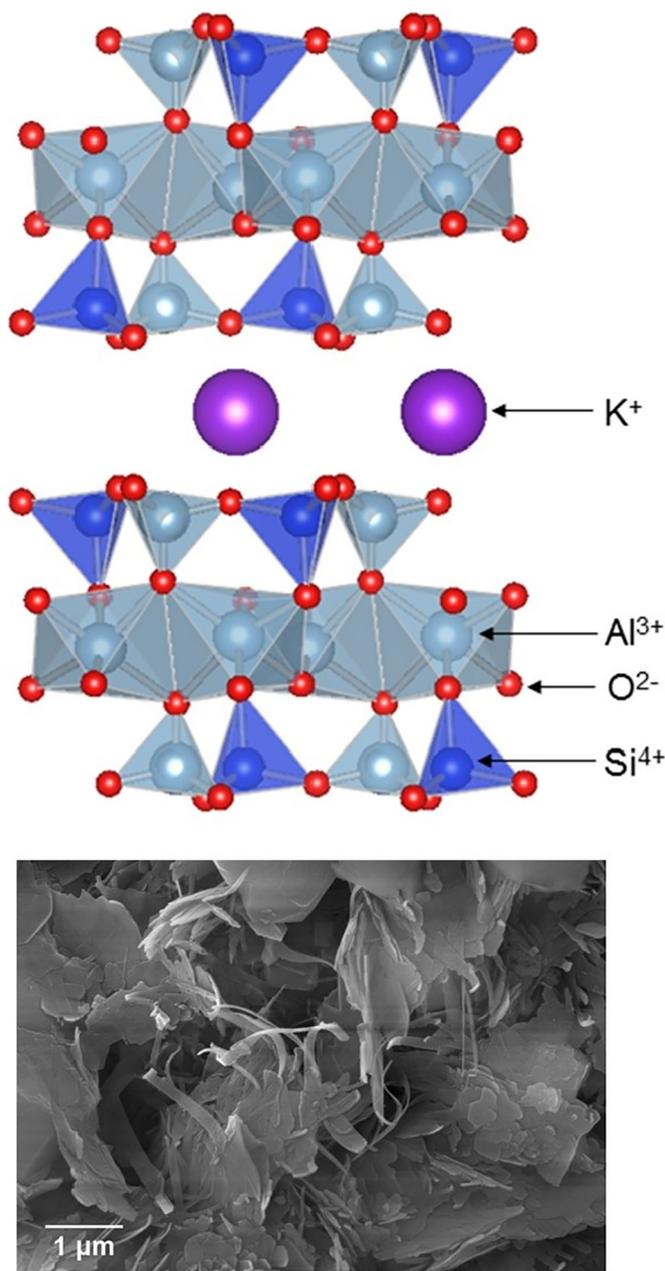
Fig. 15. Atomic diagram of illite, showing two layers. Image generated in VESTA [194], using structural parameters from Gualtieri [228]. Secondary electron image reproduced from the 'Images of Clay Archive' of the Mineralogical Society of Great Britain & Ireland and The Clay Minerals Society.

the tetrahedral sheet, as well as possible Mg^{2+} or Fe^{2+} substitution for Al^{3+} in the octahedral sheet (Fig. 15) [53,226]. The resultant negative layer charge is balanced by interlayer potassium ions – these are non-hydrated, due to how they are 'fixed' in the ditrigonal cavities on the surfaces of the tetrahedral sheet [53,227]. As a result of the non-hydrated nature of its interlayer cations, it is a non-swelling clay mineral, in contrast to some montmorillonites [58].

4.2.3. Dissolution mechanisms

Similar to the 1:1 clay minerals, dissolution of 2:1 clay minerals as a whole is limited by the dissolution rate of the layer edges [198,229,230]. For this reason, dissolution rate is dependent on the edge surface area available rather than the total surface area [230], in addition to the concentration of the alkali activator(s) [197].

The congruency of dissolution of 2:1 clay minerals is complex.

Montmorillonite in the natural state undergoes incongruent dissolution [231]. In the calcined state however, Garg and Skibsted [232] found that dissolution of montmorillonite was incongruent when calcined at 800 °C, but congruent when calcined at 900 °C. The authors suggested that at 800 °C, the montmorillonite contained a higher amount of amorphous aluminosilicate phase than at 900 °C, resulting in weaker Si-O-Si/Al bonds, and hence Si dissolved faster than Al. It is therefore wise not to make a general statement for dissolution of 2:1 clay minerals, given that congruency would seem to depend on the exact nature of bonding in a given clay mineral.

4.2.4. Thermal treatment

The thermal and chemical stability of 2:1 clay minerals is more variable than the 1:1 clay minerals, due to their greater variety in composition and structure. Additional influencing factors include the distribution of the octahedral cations over cis- and trans- sites, and the type of interlayer cations [233,234].

For montmorillonite, the overall principles of dehydroxylation are the same as for the 1:1 clay minerals - dehydroxylation brings a reduction in Al coordination from 6-fold to 5- and 4-fold [235,236]. It has been suggested that pozzolanic activity is linked to the extent of 5-coordinated Al [157] – however, in another case the highest activity was achieved when the extent of 4-coordinated Al was highest [235]. A possible obfuscating factor in attributing the precise causes for optimal reactivity is that depending upon the strength of magnetic field used, the signal for 5-fold Al can be difficult to observe [236,237].

Coordination and ordering generally plays a greater role in determining structure and properties in the 2:1 clay minerals than in the 1:1 clay minerals. Cis- and trans- sites describe different types of atomic position in the octahedral sheet (Fig. 16). In the cis-sites, OH^- groups are located on a shared edge of a triangular face on either the right or left side of the octahedron. In the trans-sites, OH^- groups are located on the top and bottom vertices of the octahedron. In the half-unit cell of a dioctahedral clay mineral, there are two cis-sites and one trans-site, of which only two are occupied. This gives the possibility of different structures depending on which sites are occupied (Fig. 17). If a sheet is cis-vacant (cv), one trans-site and one cis-site are occupied. If a sheet is trans-vacant (tv), both cis-sites are occupied [53]. Most montmorillonites consist of cv 2:1 layers and most illites consist of tv 2:1 layers, although the reverse can also be true [238,239].

During dehydroxylation, the mechanisms and resulting structural changes are different between the two sheet structures. The end result is that regardless of the initial sheet structure, the dehydroxylated structures of dioctahedral 2:1 layer silicates always have tv octahedral sheets [241]. This is not just an academic point of interest - this difference in
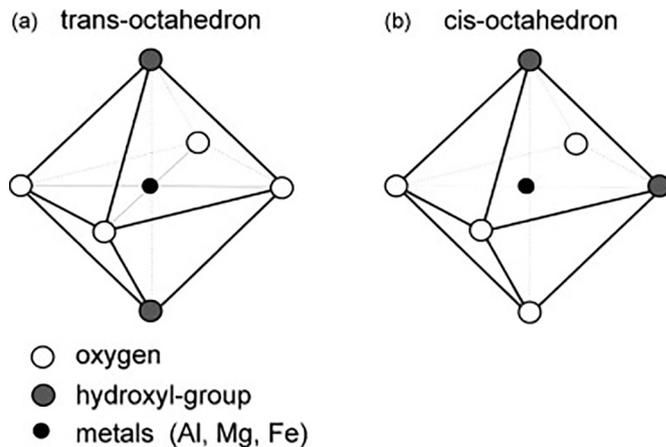
Fig. 16. Atomic diagrams of a) trans- and b) cis- configurations of octahedral sites, defined by the positions of the octahedral anion - usually a hydroxyl group. Reprinted from Wolters and Emmerich [240].
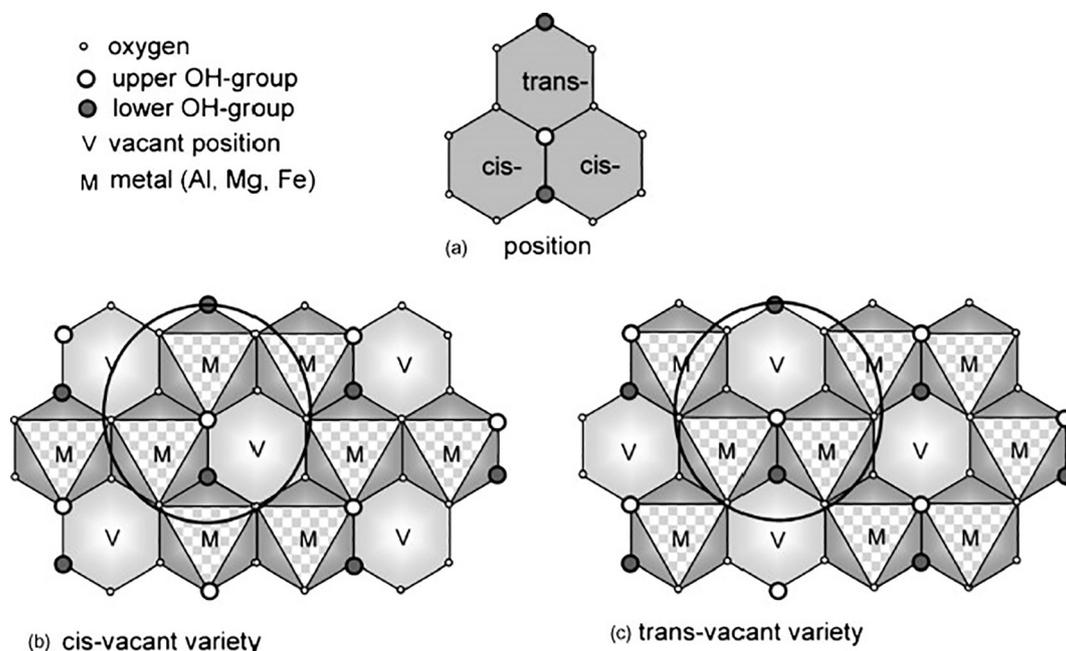
Fig. 17. Overhead diagrams of a) *trans-* and *cis-* configurations of octahedral sites; b) a cis-vacant sheet, in which both trans- sites are occupied; c) a trans-vacant sheet, in which both cis- sites are occupied. Reprinted from Wolters and Emmerich [240].

structural change is reflected in dehydroxylation temperature ranges: most cv 2:1 clay minerals dehydroxylate at > 600 °C, whereas tv clay minerals dehydroxylate at < 600 °C [233,240]. This temperature difference is usually large - the dehydroxylation temperature of a clay mineral with a cv sheet structure is typically higher by 150 °C to 200 °C than the same mineral with a tv sheet structure [239].

When 2:1 clay minerals have exchangeable interlayer cations (such as montmorillonite, but not illite), the dehydroxylation temperature is also dependent (albeit to a lesser extent than sheet structure) on the valency and ionic radius of the interlayer cations [234,242]. Regarding valency, divalent exchangeable cations (e.g. Ca^{2+}) in clay minerals bind more water, and bind more tightly, to the clay surface than the monovalent exchangeable cations (e.g. Na^+) in ambient temperature – therefore, higher dehydroxylation temperatures are needed to remove the additional water for divalent compared to monovalent interlayer cations [158]. Regarding ionic radius, dehydroxylation temperature increases for interlayer cations with a larger ionic radius, from 625 °C for Li-montmorillonite up to 685 °C for Sr-montmorillonite [234]. As for kaolinite, higher temperatures than the optimum calcination temperature cause formation of new phases, and a subsequent reduction in reactivity [166,235].

For illite, dehydroxylation also brings a reduction in coordination number from 6-fold to 5- and 4-fold [243,244]. This happens at lower temperatures for illite compared to montmorillonite [157]. There is variation in the extent of 5-fold coordination in dehydroxylated 2:1 minerals, with some exhibiting an appreciable proportion of Al in 5-fold bonding, and others exhibiting none [243]. The presence and identity of interlayer cations are suggested to influence this variation [245].

There is a crucial distinction between dehydroxylation and amorphisation: dehydroxylation is the loss of hydroxyl groups from the octahedral layer, whereas amorphisation is the increase in disorder of the layer structure such that crystalline order is no longer discernible. Amorphisation is desirable for increasing clay reactivity in AAMs; dehydroxylation can also result in amorphisation in some systems, but there is not a direct correlation between the two. This is a key difference between clay minerals. Unlike kaolinite, dioctahedral 2:1 clays retain their layer structure after dehydroxylation [154]. Although there is some loss of crystallinity, this retention of layer structure is possibly due to the fact that the Al atoms are 'trapped' between the less altered

tetrahedral silica layers [157]. This phenomenon was elegantly demonstrated for montmorillonite by Garg and Skibsted [235]. After 2 h of heating at 800 °C, the peak −96 ppm in the ^{29}Si CP/MAS NMR spectrum, corresponding to a Q_3 environment with a water/hydroxyl group neighbour, was reduced to negligible intensity (Fig. 18a) [211]. Aluminium coordination was changed from almost fully Al(VI) to Al(V) and Al(IV) (Fig. 18b). This demonstrated that complete dehydroxylation had taken place. In contrast, the montmorillonite X-ray diffraction reflections were reduced in intensity but still present, showing that there was still some degree of long-range order in the crystal structure, and hence was not fully X-ray amorphous (Fig. 18c). As previously mentioned, this is a notable difference between kaolinite and other clay minerals - whereas dehydroxylation and amorphisation occur simultaneously for kaolinite, dehydroxylation (and the associated reduction in coordination number of Al atoms) occurs without full amorphisation for montmorillonite and illite.

These Al coordination changes are reversible as they can undergo varying degrees of rehydroxylation, including under ambient conditions. Rehydroxylation can happen because the dehydroxylated clay structure is under stress from lattice distortions and from the cations in the hexagonal holes [234,241]. Dehydroxylated montmorillonite regained many of the hydroxyl groups by treatment under steam between 200 and 300 °C [241], and around 15% of hydroxyl groups after storage at 55% relative humidity for 16 days [246]. This phenomenon is of real importance to industrial processes - rehydroxylation will reduce reactivity, and hence storage and/or curing conditions should be carefully selected to prevent it.

4.2.5. Chemical treatment

Acid treatment is also used to increase reactivity and provides a useful comparison point for a broader consideration of alkaline dissolution of clay minerals. This process has been used most extensively for smectites, which causes dehydroxylation and dissolution of the octahedral sheet, and turns the tetrahedral sheet into a "*three-dimensional framework of protonated amorphous silica*" [182]. This increases reactivity by increasing the surface area, making the structure more disordered, and also increases the clay's Si:Al ratio through the dissolution of octahedral Al [247]. A higher proportion of substitutions in the octahedral layer has been associated with more extensive dissolution and
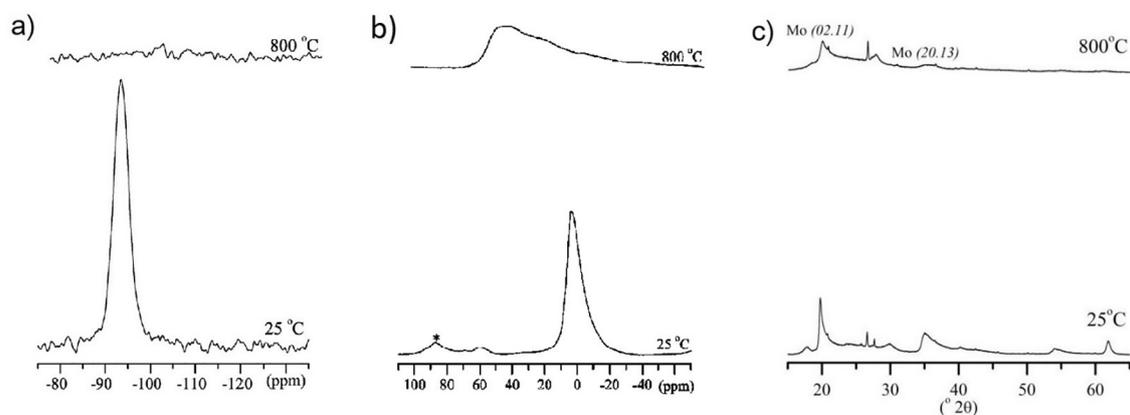
Fig. 18. Montmorillonite heated for 2 h at different temperatures. a) 29Si[1H] MAS NMR spectrum, b) 27Al MAS-NMR spectrum, c) X-ray diffraction pattern. Adapted from Garg and Skibsted [235].
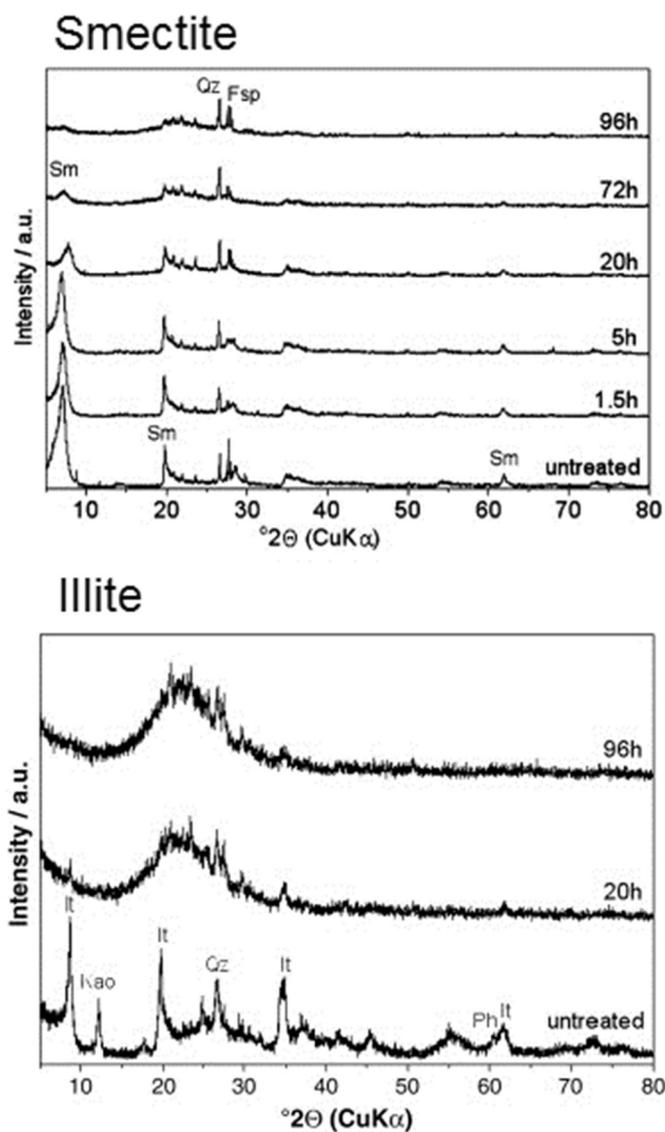
Fig. 19. X-ray diffraction patterns showing amorphisation of a) smectite, and b) illite after acid-washing in 5 M H_2SO_4 at 80 °C for up to 96 h. Adapted from Steudel et al. [249,250].

amorphisation [184,248]. The extent of this process depends on: the composition of the octahedral sheet; the strength of the acid treatment, and the length of time. Although the overall effects are the same, acid dissolution occurs via different mechanisms for montmorillonites and illite. Dissolution of the octahedral sheet occurs via layer edges for both, whereas in swelling clays (such as some montmorillonites) dissolution can occur via the interlayer faces too [249,250]. Since interlayer faces are accessible to protons in swelling layers, this increases the rate of dissolution [251]. As a result, acid dissolution is slower for illite [249]. Both montmorillonite and illite can be almost fully amorphised given a treatment of sufficient concentration and time (Fig. 19) [249,250]. Although there is no direct competition between the two processes, it is notable that this extent of amorphisation is greater than that achievable through thermal treatment.

4.2.6. Phase formation from alkali-activation of montmorillonite

For uncalcined montmorillonite, Ingles et al. [252] used NaOH and KOH as activators, but no aluminosilicate product phase was formed, and much of the activator was not consumed - likely due to the low curing temperature of 25 °C. Richardson et al. [253] activated a similar system, but using higher temperature curing at 105 °C. This resulted in a decrease in montmorillonite X-ray diffraction reflection intensity, and for microwave curing (a curing method rarely used due to difficulty of precise heating control), partial dehydration of the montmorillonite. No crystalline product phases were observed from X-ray diffraction analysis, but geopolymer formation cannot be excluded as no consideration of the formation of amorphous phases was made. Marsh et al. [254] activated both an acid-washed Ca-montmorillonite and an untreated Na-montmorillonite with NaOH solution, forming a geopolymer when the system molar ratio was Na:Al ≥ 1.

For calcined montmorillonite, phase formation (behaviour) is more highly dependent on the relative amounts of Al and Si in the system. Belviso et al. [184] reported probable geopolymer formation by 1 M NaOH hydrothermal alkali-activation of Na- and Ca-montmorillonites which were acid washed (80 °C for 48 h in 5 M HCl) and then calcined at 700 °C. However, when the samples were calcined without a preceding acid treatment, no reaction products were reported. This difference is likely due to the partial amorphisation and dissolution of the octahedral sheet as a result of the acid treatment, and the relatively low NaOH concentration used in synthesis.

When additional soluble silica is added, a geopolymer is formed. Prud'homme et al. [255] activated an uncalcined montmorillonite with KOH and K-silicate solution, and the later addition of silica fume as a foaming agent, forming a geopolymer. Seiffarth et al. [151] reported a geopolymer was formed from a silica-doped smectite clay calcined at various temperatures from 550 to 950 °C, but the lack of characterisation provided and simple inference from strength increase makes this

claim unsubstantiated. When Belviso et al. [184] adapted the calcination process to include a NaOH pre-fusion step at 700 °C, zeolites were much more readily formed.

In overview, uncalcined montmorillonite can form a geopolymer, provided that the activating solution is sufficiently highly concentrated and elevated temperature curing conditions are used. The same is also true for its calcined form, although zeolites can also be formed.

4.2.7. Phase formation from alkali-activation of illite

For un-calcined illite, reaction products are not generally formed. Richardson et al. [253] activated uncalcined illite with NaOH solution. No reaction products were formed for oven heating, but nepheline was formed when microwave heating was used. Sedmale et al. [256] mixed illite-rich clay with KOH solution, which underwent negligible changes, partly likely due to the very short curing time used. Marsh et al. [254] activated illite with NaOH without treatment. No product phase was formed, but secondary electron images showed that illite underwent some manner of alteration from the highly alkaline conditions. In contrast, Prud'homme et al. [255] activated uncalcined illite with KOH and K-silicate solution, and the addition of silica fume as a foaming agent, forming a geopolymer.

For calcined illite, the results are not always in broad agreement. Belviso et al. [184] showed that illite calcined at 700 °C underwent no obvious changes by 1 M NaOH hydrothermal alkali-activation, with the addition of a preceding acid treatment making no difference. Sperberga et al. [257] calcined (700–900 °C) illite with KOH solution, and Seiffarth et al. [151] activated a calcined (550–950 °C) illite clay with additional silica. In both cases, geopolymer formation was inferred simply from increased strength, without any phase characterisation - this is a very limited and fallible approach, and will be discussed further in Section 5.5. When Belviso et al. [184] used an additional NaOH fusion step as part of calcination, a sodalite was formed, and a variety of other sodalites were formed using various combinations of treatment processes.

In overview, the alkali-activation behaviour of illite is still largely unknown. From the small number of studies, it seems as though illite does have the capacity to react and form alkali aluminosilicate product phases under certain circumstances, but the range of conditions over which this is viable is not yet clear.

4.3. Comparison of individual clay studies

The question of most immediate interest is: which clay minerals have the potential to form a geopolymer? The existing evidence suggests that kaolinite, halloysite and montmorillonite can all form a geopolymer, provided the Si:Al molar ratio and activation conditions are sufficient. Whilst there is still a dearth of data for illite, what there is so far suggests that it is less reactive than its fellow 2:1 mineral montmorillonite, since it has not formed reaction products under the same conditions when montmorillonite has formed reaction products. Comparing clay minerals and the different treatments used (Table 1), there would seem to be some broad trends between the differing extents of treatments required to achieve sufficient reactivity for the different clay minerals.

Comparing the 1:1 and 2:1 clay minerals - one would expect differences in phase formation behaviour between them, due to the difference in Si:Al molar ratio which spans the 'tipping point' between zeolite formation (Si:Al < 1.5) and geopolymer formation (Si:Al > 1.5) [124]. From evaluation of the existing studies, it seems that less intensive reactivity-enhancing treatments are required to form a geopolymer from kaolinite and halloysite, but only given the use of additional soluble silicate. In contrast, it is possible to form a geopolymer from the 2:1 clay minerals without additional soluble silicate, but given their lower starting reactivity due to their layer structures, more severe reactivity-enhancing treatments are required.

Comparing within the 1:1 clay minerals - despite the smaller

number of studies on halloysite, it seems that halloysite is at least as conducive to geopolymer formation as kaolinite. There is some evidence to suggest that the more open structure of halloysite could make it more reactive than kaolinite, but this needs further investigation.

Comparing within the 2:1 clay minerals - geopolymers are formed more readily from montmorillonite than illite. Given their similarity in chemistry within the layers themselves, this difference could be partly attributed to smectites' capacity for swelling behaviour, giving a larger accessible area for dissolution in a wet mix. This mechanism applies for acidic dissolution [251], so it could offer an explanation for alkaline dissolution and subsequent reaction steps.

The majority of studies used calcined clays in alkali-activation. Calcined clays will likely be more highly used than uncalcined clays in AAMs due to their higher reactivity. This enables one to use lower molarity solutions and to cure at room temperature, eliminating the need for oven curing and hence making them suitable for casting on-site. In comparison, although the use of un-calcined clays has a lower embodied energy from avoiding calcination, their requirement for elevated temperature curing means they are restricted to off-site construction. However, it is still worthwhile to continue investigating both calcined and un-calcined clays: firstly, for different types of manufacturing as discussed, and secondly, to continue understanding the details of how mineralogy and chemistry influence reactivity and phase formation. In particular, the influences of crystallinity of the starting clay mineral and the influence of interlayer cation species still need to be fully elucidated.

From the comparison of studies by clay mineral and treatments used (Table 1), the most successful route to geopolymer formation is calcination followed by activation with additional soluble silica. Whilst acid washing and NaOH fusion do seem to increase reactivity, they do not necessarily make it more likely to form a geopolymer rather than a zeolite. This conclusion, that the use of soluble silica (and the associated expense, embodied impacts and workability issues) is a 'necessary evil' for some clay systems, supports previous recommendations for AAMs in general - that lower impact routes of alkali silicate production is a research priority [1,4,22]. On the other hand, the alternative routes described in Section 3.3 - in-situ hydroxide production and alkali fusion to produce a soluble glass precursor – offer enough promise to merit further investigation. Whilst the former method is particularly promising for kaolinite, it does not help the 2:1 clay minerals fulfil their potential – despite their Si:Al molar ratio precluding the need for additional soluble silica in an activator, their layer structure makes them less reactive than kaolinite, even when calcined. To overcome this issue, mechanical treatment may be the most promising route of investigation. Studies on montmorillonite indicate that not only can mechanical treatment achieve dehydroxylation, but it induces greater disorder in the layer structure than thermal treatment [258,259], and without the drawback of aluminium leaching suffered in chemical treatment. As for thermal treatment, the crystallinity of the starting clays influences how much energy of treatment is required to achieve a given extent of structural changes [174]. The environmental impacts have yet to be comprehensively compared, but mechanical treatment has the advantage of using similar machinery that is already used at scale in the cement industry [260].

5. Alkali-activation of common clays and soils

5.1. Nature and composition of common clays and soils

Common clay deposits and soils are both abundant sources of clay minerals. These are more widely available than the high purity deposits and refined products often used in laboratory studies - but also more complex and variable. Using kaolinite for example, primary residual is the most common type of deposit, but these are generally small and contain limited quantities of reserves [261]. Adopting lower purity resources is not a trivial step - there is evidence that both the exact

Table 1

Summary of reaction products for alkali-activation of individual clays in the studies reviewed, showing effects of different treatments and system additions. The default activation process in this context is with NaOH only.

Treatment	System additions	1:1 clay minerals		2:1 clay minerals	
		Kaolinite	Halloysite	Montmorillonite	Illite
None	None	Hydrosodalite [210–213])	None [218]	None [252,253] Geopolymer [254]	None [253,254,256]
None	Soluble silicate	Geopolymer [86,87,139,187,255]	–	Geopolymer [255]	Geopolymer [255]
Acid wash	None	–	–	Geopolymer [254]	–
Calcination	None	Hydrosodalite [214]		None [184]	None [184] Possible geopolymer [257]
		Various zeolites [186,212,214] Geopolymer + hydrosodalite [186]			
Acid wash + calcination	None	–	–	Geopolymer [184]	None [184]
Calcination + NaOH fusion	None	–	–	Various zeolites [184]	Sodalite [184]
Calcination	Soluble silicate	Geopolymer [34,215,216] Geopolymer + hydrosodalite [127]	Geopolymer [68,102,183,220] Zeolites [221]	Possible geopolymer [151]	Possible geopolymer [151]

nature of the clay mineral(s) and the presence of other minerals can affect product phase formation [262]. Thus, there is a need for research on a wider range of clay resources (including soils) than the small number of large deposits currently exploited in other industries. Understanding the influence of mineralogical aspects is key to unlocking their potential as scalable precursors. Given the scope of this review and the wide variety of other mineral phases found in clay resources, the majority of attention will be paid to the clay minerals in these resources, with only brief consideration given to the role of associated minerals and organic content.

Considering only the clay mineral content, there is significant variation in the types, amounts and exact nature of clay minerals in deposits and soils. Soils around the world contain clay minerals in different amounts [70,263], depending on climate, lithology and weathering history [66]. Within a single location, the distribution of clay minerals in the soil can vary with depth [264,265], due to varying extents of weathering [71]. In addition to differences in the amounts present, there can be large differences in the nature of the clay minerals, including particle size (Fig. 20), substitutions and crystallinity [71]. Crystallinity depends on geological formation routes - for example, kaolinite from a mixed hydrothermal and residual primary kaolin deposit in Cornwall, U.K. is well crystallised, whereas kaolinite from a sedimentary secondary deposit in Georgia, U.S.A. varies between extremely well crystallised and poorly crystallised [261,266]. A high degree of crystallinity is highly desirable for some industrial applications, such as paper coatings [267]. Conversely for AAMs, clay minerals with poorer crystallinity are generally more desirable, as they are typically more reactive. This is relevant to the different formation routes of clay minerals in different clay resources - some deposits may require less treatment, as their geological history has made them intrinsically more reactive [255].

5.2. Overview of types of systems

Clay resources vary in both the complexity of their clay mineralogy (i.e. how many different clay minerals are present), and in their purity (sometimes referred to as 'grade'). Whereas Section 4 evaluated comparatively pure, individual clay minerals, this section evaluates less pure, more complex common clays and soils (Fig. 21). Because these frequently contain more than one clay mineral, synthetic mixtures of the individual clays (complex, but relatively pure) have also been evaluated. These are helpful 'bridging studies' to understand the behaviour of natural systems containing multiple clay minerals. In the following sections, studies are grouped by the dominant clay in each clay resource.

5.3. Clay resources containing a single dominant clay mineral

For kaolinite-dominant resources, lateritic soils containing kaolinite as the sole clay mineral are a popular precursor. Lemougna et al. [88] and Diop and Grutzeck [85] activated uncalcined kaolinitic lateritic soils with NaOH, forming a hydrosodalite as the product phase.
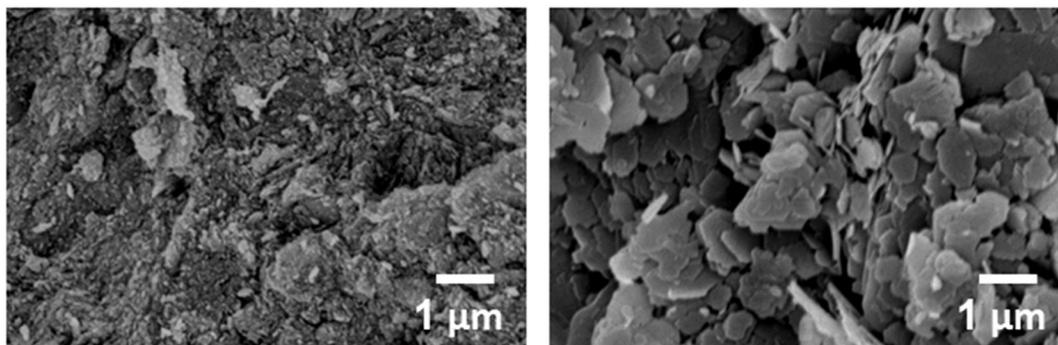
Fig. 20. Clay minerals can have different particle size depending on geological history. (Left) very fine kaolinite particles in a clay-rich soil from Bengaluru, India. (Right) larger kaolinite particles in a mixed hydrothermal and residual deposit in Cornwall, U.K. Adapted from Marsh et al. [268].
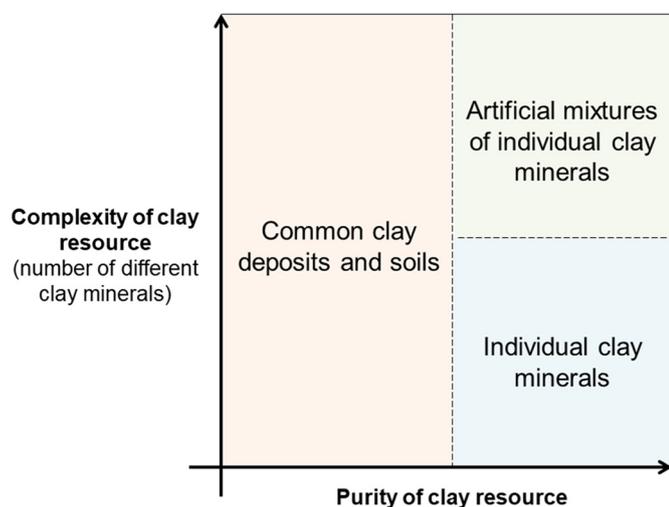
Fig. 21. Schematic diagram showing the variation in complexity and purity of clay resources.

Lemougna et al. [88] suggested a geopolymer phase may also have formed, but the characterisation evidence presented was not conclusive. In a similar study, Yousef et al. [269] identified the reaction products to be plagioclase feldspar and a geopolymer, but given the system, it is thought far more likely to be a hydrosodalite instead. Lassinantti Gualtieri et al. [270] activated a kaolinitic lateritic soil with NaOH and $Na_2SiO_3.xH_2O$ – this apparently had no effect on the uncalcined soil, but a geopolymer formed as the main reaction product for the calcined soil. Boutterin and Davidovits [271] activated a kaolinitic soil with NaOH, giving increased compressive strength. The authors attributed this to a zeolitic product, but no characterisation was given. Kaze et al. [68] used a halloysite deposit (in which halloysite was the only clay mineral), calcined at 600 °C and activated with sodium silicate solutions of varying moduli, forming a geopolymer. Samples calcined at 500 and 550 °C were not sufficiently reactive under the reaction conditions used. García-Lodeiro et al. [272] activated a calcined, low purity montmorillonite with NaOH, forming a geopolymer and a minor amount of faujasite. In an inversion of the common practice of including additional soluble silica for 1:1 clay minerals, sodium aluminate was added to lower the reactive $SiO_2:Al_2O_3$ molar ratio (measured to be 5.4). Additions of < 10% sodium aluminate increased the uptake of Al in the N-A-S-H gel, resulting in increased strength. Muñoz et al. [273] activated an uncalcined, synthetic montmorillonite-dominated soil (using clay and mining waste) with NaOH and Na-silicate – this seemed to form a geopolymer, although the relatively modest gains in strength suggested that much of the montmorillonite remained undissolved. The disappearance of the montmorillonite (001) peak was suggested to be due to layer exfoliation and destruction of stacking order. However, this would seem not to be a disappearance in fact, but rather a shift of the (001) peak to a smaller d-spacing. It seems likely that this is due to the exchange of Na^+ cations from the activating solution for the interlayer cations originally present - this is consistent with the observed reduction in the liquid limit. Notably, the use of mineral additives seemed to encourage geopolymerisation.

In summary, in resources containing a single dominant clay mineral, phase formation behaviour is generally in line with that expected from the individual clay minerals. This is line with a systematic study by Marsh et al. [268] – by comparing synthetic soils with their natural counterparts, it was found that whilst associated minerals could exert some influence on the extent of reaction, the clay mineralogy of the soils determined the phase assemblages formed.

5.4. Clay resources containing multiple clay minerals

For studies on resources containing multiple clay minerals, those containing two clay minerals will be reviewed first, followed by those containing three.

Kaolinite-illite is the most common binary combination encountered in the literature. Xu and van Deventer [89] activated an uncalcined, synthetic mixture of illite and kaolinite using NaOH and $Na_2SiO_3.xH_2O$. No chemical characterisation of the activated sample was given, but it did result in mechanical strength gain. Zibouche et al. [126] activated a calcined kaolinite-illite soil with NaOH and sodium silicate – this formed zeolites, geopolymers or both, depending on the amount of sodium silicate used in the NaOH activating solution. The illite did not fully react in the process. Essaidi et al. [274] studied two kaolinite-illite clays, one of which had lower kaolinite and higher illite content than the other. The soils were activated in the uncalcined and calcined states with KOH and K-silicate, forming geopolymers for all systems. Amongst the activated samples, the more illite-rich soil was the stronger of the two when calcined but weaker when uncalcined. However, the authors suggested this might be partly attributable to the surface defects in the kaolinite in the illite-rich soil, leading to more amorphous content after calcination. El Hafid and Hajjaji [275] calcined an illite-kaolinite clay sample at 700 °C and mixed it with NaOH solutions, producing the zeolites chabazite and natrolite. It was unclear what exact roles the kaolinite and the illite played in the development of these product phases. However, the formation of zeolites in this study is most likely due to the metakaolin supplying enough Al to solution, to give a lower Si:Al solution ratio that was more conducive to zeolite formation. Zhang et al. [200] calcined a mixed halloysite-kaolinite deposit (52.3 wt% kaolinite, 31 wt% halloysite) at 700 °C for 1 h and activated with sodium silicate solution - this formed a geopolymer. Several highly useful findings of this study came through comparison with activation of a kaolinite-only deposit (91 wt% kaolinite). The halloysite-kaolinite deposit had a higher extent of dissolution, a higher evolved heat of reaction and a smaller pore size distribution than the kaolinite-only deposit. This was attributed predominantly to the more open structure of the halloysite resulting in enhanced dissolution, but another possible contributing factor, the relative crystallinity of both deposits, was not analysed in the study. Richardson et al. [253] activated binary mixtures of kaolinite, montmorillonite and illite clays with aqueous NaOH solution, producing zeolites and/or nepheline - these had also formed during activation of the individual clays. However, no mention of geopolymers or amorphous phases was made, and the activated systems were not fully characterised. The use of microwave curing means there is limited comparability with other systems. Marsh et al. [276] also activated binary mixtures of kaolinite, montmorillonite and illite using aqueous NaOH, and conventional oven curing. The phases most often formed (hydrosodalite and geopolymer) were those expected from the behaviour of the individual clay minerals (Fig. 22). Comparing the identity and the amount of product phases formed against a 'rule of mixtures' model, kaolinite seemed to be the dominant mineral in terms of influencing product phase formation, montmorillonite was slightly more reactive, whilst illite was the least reactive.

There are fewer studies on resources containing three clay minerals. Richardson et al. [253] extended the previous study to a ternary mixture, which produced zeolites and nepheline. Similarly, Marsh et al. [276] extended the previously used methodology for binary systems to activate a ternary mixture, which produced a hydrosodalite and some evidence for a geopolymer too. Diop and Grutzeck [277] activated a raw clay containing kaolinite, montmorillonite and illite, although the relative quantities were not given. Activation of the uncalcined clay with NaOH formed a hydrosodalite. Dietel et al. [163] studied a different clay containing all three clay minerals, using thermal treatment and activation with KOH - a geopolymer was formed.

In overview, in common clays or soils containing multiple clay minerals, phase formation behaviour and clay mineral consumption is
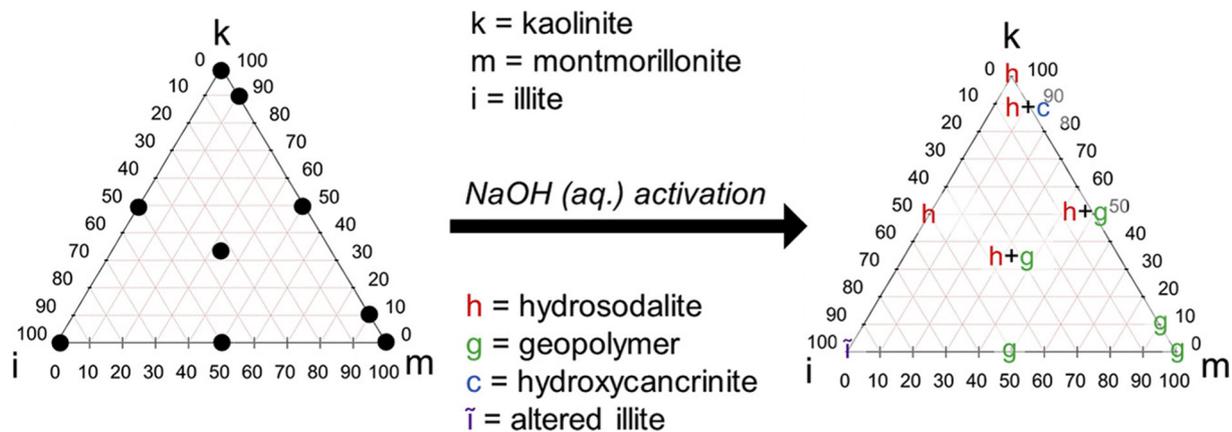
Fig. 22. The phases formed in alkali-activated mixtures of clay minerals were usually combinations of the same phases formed in alkali-activated individual clay minerals. Reprinted from Marsh et al. [276].

generally more complex than for a single clay mineral. However, no studies have observed radically different behaviour between clay resources containing single and multiple clay minerals.

5.5. Comparison of studies on clay resources

Compared with individual clays, there is greater complexity but also greater potential with using common clays and soils as precursors. The key challenge is to understand the effect of this complexity on phase formation behaviour and other material properties. A summary of basic details, including clay composition, of all the reviewed alkali-activation studies is given in Table 2. The clay minerals present, crystallinity of the clay minerals and purity of the resources are the main parameters of interest.

Clay resources containing more than one clay mineral provide additional challenges. Selecting an optimal calcination temperature is akin to figuratively sailing between the Scylla and Charybdis of incomplete dehydroxylation and recrystallization, both of which will result in sub-optimal reactivity. This is more difficult when different clay minerals dehydroxylate in different temperature ranges which do not necessarily overlap [145,166,278,279] (Fig. 23). Furthermore, as described previously, the rates and even congruency of dissolution can vary between clay minerals – this can provide a challenge to predicting the extent of dissolution and solution liquor composition from a given clay resource.

The purposeful use of clay minerals with naturally occurring low crystallinity, such as by Essaidi et al. [274] is a promising route in this field. It is encouraging that clay minerals from low crystallinity deposits could be better suited for alkali-activation than high crystallinity deposits, thereby avoiding competition with other industries (such as papermaking) for high value, high crystallinity deposits. For AAM precursors it is advantageous to have a higher purity clay, from a reaction perspective. This differs from clays as SCMs in blended cement, where higher purity clays can be less useful than low purity clays by inhibiting clinker reaction [280,281]. Another possible advantage of low purity clays arises from the ability of quartz to act as a grinding medium in mechanical activation, and hence reduce the milling times required to achieve amorphisation of the clay minerals [282].

In the testing of mechanical properties, there can be large differences between dry and saturated strength for AAMs (Fig. 24) [283]. Typically, only dry strength alone is tested, but if this is not also accompanied with increased saturated (or high humidity) strength and durability as required in standards, then use in construction will be severely limited. It is rarely mentioned that $Na_2SiO_3.xH_2O$ is an adhesive used to strengthen other materials, most commonly cardboard [284]. When increased dry strength is observed, there is a pitfall to assume this is wholly due to the formation of a product phase, whereas

it could be partly due to unreacted sodium silicate. There is also still limited understanding of the strength-giving mechanisms between geopolymers and aggregates [163,285,286]. This may be a key difference between 'pure' individual clays and common clays or soils with a high content of unreactive particles.

6. Concluding remarks and outlooks

Clay resources offer many opportunities for use in AAMs, but many challenges remain. There is a spectrum of reactivity between different clay minerals in their natural state, likely determined by a combination of layer structure, morphology and swelling ability. Reactivity can be enhanced through treatments, such as acid washing, mechanical treatment or calcination, as needed. Broadly speaking, the phase assemblages formed are primarily determined by the molar ratio of soluble Si:Al in the system, along with the curing conditions used. Although there is still uncertainty in intermediate compositions of Si:Al = ~1.5, conditions conducive to forming a geopolymer rather than a zeolite have been empirically established for Si:Al > 1.5.

Challenges remain in ensuring that clay minerals are processed in a way that brings out their full potential. For calcination, the optimal temperature range for dehydroxylation varies both between clay minerals, as well as within individual mineral categories – this depends on interlayer cations and structural order. This has practical implications for industrial processing - such variety presents greater challenges in optimising calcination when resources contain more than one clay mineral. Mechanical treatment merits further investigation, given its ability to bring about both structural disorder and dehydroxylation (to a limited extent) in montmorillonite, and potentially in other dioctahedral 2:1 clay minerals too – something which is not possible with thermal treatment alone. Although clay resources can be abundant, diverse precursors for AAM production, they need a tailored approach, based on chemistry, mineralogy and physical properties – a one-size-fits-all approach will not work. A thorough mineralogical understanding is needed to underpin the use of these resources all the way through the extraction to application cycle – for example, the capacity of calcined montmorillonites to partially re-hydroxylate under ambient conditions has practical implications for storage conditions. To enable a route to wider adoption, it would be beneficial to establish a common set of testing procedures for characterising resources, to include purity, crystallinity, particle size distribution and reactivity. Existing techniques from clay science can be adopted, particularly for comparing the structural order and crystalline nature of clay minerals [287]. An encouraging precedent is the recent development of testing procedures for SCMs, including calcined clays, in blended cements [46,280,288].

Although much progress has been made, there remain several scientific and engineering barriers to possible mass-scale commercial

Table 2
A summary of basic details of the alkali-activation studies reviewed (K = kaolinite, H = Halloysite, Mt. = montmorillonite, I = illite).

Study	Resource category	Clay mineral(s)	Treatments used	Alkali solution compound(s)	Phases formed
Barrer et al. (1968) [210]	Individual clay	K	None	NaOH	Hydrosodalite
Engelhardt et al. (1992) [211]	Individual clay	K	None	NaOH	Hydrosodalite
Heller-Keller and Lapides (2007) [212]	Individual clay	K	None	NaOH	Hydrosodalite
Marsh et al. (2018b) [213]	Individual clay	K	None	NaOH	Hydrosodalite
Barrer and Mainwaring (1972) [214]	Individual clay	K	Thermal	NaOH	Hydrosodalite; various zeolites
Heller-Keller and Lapides (2007) [212]	Individual clay	K	Thermal	NaOH	Hydrosodalite; Zeolite A; Zeolite X
Zhang et al. (2012b) [186]	Individual clay	K	Thermal	NaOH + Na$_2$SiO$_3$.xH$_2$O	Geopolymer + hydrosodalite
Heah et al. (2012) [139]	Individual clay	K	None	NaOH + Na$_2$SiO$_3$.xH$_2$O	Geopolymer
Heah et al. (2013) [86]	Individual clay	K	None	NaOH + Na$_2$SiO$_3$.xH$_2$O	Geopolymer
Rahier et al. (1996) [34]	Individual clay	K	Thermal	NaOH + Na$_2$SiO$_3$.xH$_2$O	Geopolymer
Lapides and Heller-Kallai (2007) [216]	Individual clay	K	Thermal	NaOH + Na$_2$SiO$_3$.xH$_2$O	Geopolymer
Zhang et al. (2013) [215]	Individual clay	K	Thermal	NaOH + Na$_2$SiO$_3$.xH$_2$O	Geopolymer
Rahier et al. (1997) [127]	Individual clay	K	Thermal	NaOH + Na$_2$SiO$_3$.xH$_2$O	Geopolymer + hydrosodalite
Wang et al. (2013) [218]	Individual clay	H	None	NaOH	None
MacKenzie et al. (2007) [183]	Individual clay	H	Thermal	NaOH + Na$_2$SiO$_3$.xH$_2$O	Geopolymer
O'Connor et al. (2010) [221]	Individual clay	H	Thermal	NaOH + Na$_2$SiO$_3$.xH$_2$O	Geopolymer
Tailby and MacKenzie (2010) [220]	Individual clay	H	Thermal	NaOH + Na$_2$SiO$_3$.xH$_2$O	Geopolymer
O'Connor and MacKenzie (2010) [221]	Individual clay	H	Thermal	NaOH + Li$_2$SiO$_3$.xH$_2$O	Zeolites
Zivica et al. (2014) [224]	Individual clay	H	Thermal	NaOH	Zeolites
Ingles et al. (1970) [252]	Individual clay	Mt	None	NaOH	None
Richardson et al. (1986) [253]	Individual clay	Mt	None	NaOH	None
Marsh et al. (2018a) [254]	Individual clay	Mt	None	NaOH	Geopolymer
Marsh et al. (2018a) [254]	Individual clay	Mt	Acid	NaOH	Geopolymer
Belviso et al. (2017) [184]	Individual clay	Mt	Acid	NaOH	Geopolymer
Belviso et al. (2017) [184]	Individual clay	Mt	Acid + thermal	NaOH	Geopolymer
Prud'homme et al. (2011) [255]	Individual clay	Mt	None	KOH + K$_2$SiO$_3$	Geopolymer
Seiffarth et al. (2013) [151]	Individual clay	Mt	Thermal	NaOH + Na$_2$SiO$_3$.xH$_2$O	Possible geopolymer
Belviso et al. (2017) [184]	Individual clay	Mt	Thermal + NaOH fusion	NaOH	Sodalite + zeolite + faujasite
Richardson et al. (1986) [253]	Individual clay	I	None	KOH	None
Sedmale et al. (2013) [256]	Individual clay	I	None	KOH	None
Marsh et al. (2018b) [213]	Individual clay	I	None	NaOH	None
Prud'homme et al. (2011) [255]	Individual clay	I	None	KOH + K$_2$SiO$_3$	Geopolymer
Belviso et al. (2017) [184]	Individual clay	I	Thermal	NaOH	None
Sperberga et al. (2011) [257]	Individual clay	I	Thermal	KOH	Possible geopolymer
Seiffarth et al. (2013) [151]	Individual clay	I	Thermal	NaOH + Na$_2$SiO$_3$.xH$_2$O	Possible geopolymer
Belviso et al. (2017) [184]	Individual clay	I	Thermal + NaOH fusion	NaOH + KOH	Sodalite
Boutterin and Davidovits (1988) [271]	Single clay soil	K	None	NaOH + KOH	Zeolite
Lemougna et al. (2014) [88]	Single clay soil	K	None	NaOH	Hydrosodalite
Lassinanti Gualtieri et al. (2015) [270]	Single clay soil	K	Thermal	NaOH + Na$_2$SiO$_3$.xH$_2$O	Geopolymer
Diop and Grutzeck (2008a) [85]	Single clay soil	K	None	NaOH	Hydrosodalite
Yousef et al. (2012) [269]	Single clay soil	K	None	NaOH	Hydrosodalite
García-Lodeiro et al. (2015) [272]	Single clay deposit	Mt	Thermal	NaOH + Na$_2$SiO$_3$.xH$_2$O	Geopolymer + faujasite
Munoz et al. (2015) [273]	Single clay soil	Mt	None	NaOH + Na$_2$SiO$_3$.xH$_2$O	Geopolymer
Kaze et al. (2018) [68]	Single clay deposit	H	Thermal	NaOH	Chabazite + natrolite
El Hafid and Hajjaji (2015) [275]	Multiple clay deposit	K + I	Thermal	NaOH + Na$_2$SiO$_3$.xH$_2$O	Geopolymer + faujasite
Zibouche et al. (2009) [126]	Multiple clay soil	K + I	Thermal	NaOH	Geopolymer
Essaidi et al. (2014) [274]	Multiple clay deposit	K + I	None	KOH + K$_2$SiO$_3$	Geopolymer
Essaidi et al. (2014) [274]	Multiple clay deposit	K + I	Thermal	KOH + K$_2$SiO$_3$	Geopolymer
Xu and Van Deventer (2000) [89]	Multiple clay mixture	K + I	None	NaOH + Na$_2$SiO$_3$.xH$_2$O	Possible geopolymer
Richardson et al. (1986) [253]	Multiple clay mixture	K + I	None	NaOH	Zeolites + Nepheline
Zhang et al. (2012c) [200]	Multiple clay deposit	K + H	Thermal	NaOH + Na$_2$SiO$_3$.xH$_2$O	Geopolymer
Richardson et al. (1986) [253]	Multiple clay mixture	K + Mt	None	NaOH	Zeolites
Richardson et al. (1986) [253]	Multiple clay mixture	Mt + I	None	NaOH	Nepheline

Table 2 (continued)

Study	Resource category	Clay mineral(s)	Treatments used	Alkali solution compound(s)	Phases formed
Richardson et al. (1986) [253]	Multiple clay mixture	K + Mt. + I	None	NaOH	Zeolites + Nepheline
Marsh et al. (2019) [276]	Multiple clay mixture	K + Mt	None	NaOH	Hydrosodalite + geopolymer (+ hydroxycancrinite)
Marsh et al. (2019) [276]	Multiple clay mixture	K + I	None	NaOH	Hydrosodalite
Marsh et al. (2019) [276]	Multiple clay mixture	Mt + I	None	NaOH	Geopolymer
Marsh et al. (2019) [276]	Multiple clay mixture	K + Mt. + I	None	NaOH	Hydrosodalite + geopolymer
Diop and Grutzeck (2008b) [277]	Multiple clay deposit	K + Mt. + I	None	NaOH	Hydrosodalite
Dietel et al. (2017) [163]	Multiple clay deposit	Mt + I + K	Thermal	KOH	Geopolymer

adoption. Understanding is limited to how restrictive the range of processing conditions is for forming a desired phase assemblage for a given clay resource. There is much scope for greater use of modelling for determining the physical and chemical changes resulting from the treatment of clays [162], the subsequent effects on their reactivity, and the alkali-activation reaction itself [93,131]. This will be aided by the expansion of thermodynamic databases to include AAMs [289]. This would be supported by experimentally investigating the influence of composition and characteristics in a more systematic manner, rather than the common 'proof of concept' route of optimising processing conditions for an individual resource. From a resource perspective, the scale of additional clay extraction required to meet even a fraction of global demand for cementitious materials through clay-based AAMs will be vast. Learning lessons from the past, mineral exploitation must be ethical, timely and efficient [290]. Given the barriers to the extraction of virgin resources, utilisation of clay resources in waste (e.g. from mining or construction excavation) offers a more accessible starting point.

There is much potential for developing alkali-activated systems that incorporate both clay minerals and a calcium source (e.g. blast furnace slag, limestone, quick lime or even clinker) in order to favour formation of a phase assemblage comparable to that of identified Portland and hybrid blended cements. This offers a solution to some of the cost, safety aspects and environmental impacts of alkaline activators typically used for low-Ca AAMs, which remain under scrutiny. Alkali-activated blended systems produced with clay minerals benefit from the existing research and understanding of Portland and hybrid blended cement systems, which can facilitate a faster commercial uptake. Given that such systems are complex even when using high purity metakaolin as a clay precursor [50,291], understanding the behaviour of the wider range of clay minerals in combination with calcium sources presents a further challenge and opportunity for research.

Beyond reaction pathways and phase assemblages, the practical aspects of using clay resources in alkali-activation - particularly workability, volume stability and mix design - remain under-investigated. This should be a priority area for further research. Another research priority is admixtures – it is well established that the current range of admixtures can exert a lesser degree of control for alkali-activated systems compared to Portland cement based systems [1]. In the specific case of clays, there are additional opportunities for desired fresh and hardened state properties to be 'designed in' to the precursor to some extent, rather than 'bolted on' through use of admixtures. Thus, it could be that admixtures can be made partly redundant (or at least to a greater extent than for Portland cement based systems). This tailored material design can be achieved through exploiting natural variation in material properties (such as Si:Al molar ratio, to determine the phase assemblages formed) as well as through processing (such as flash calcination, to reduce the particle aspect ratio and hence improve workability). With this knowledge, the ideal situation of being able to design cements for a diverse range of applications from a diverse range of local resources will be closer to reality. To this end, it is hoped that this research field moves further along the spectrum from materials discovery towards materials design and engineering.

Much progress has been made in understanding how clay minerals' chemistry and mineralogy can guide their effective use in the alkali-activation reaction. The next steps are to answer the remaining questions of how the abundant and diverse potential of clay resources can be best harnessed for sustainable, cost-effective production of AAMs, which have durable performance in different environments. This should centre on more widespread use of modelling to target specific processing effects and phase assemblages, and a more systematic approach to understanding the effects of compositional heterogeneity.
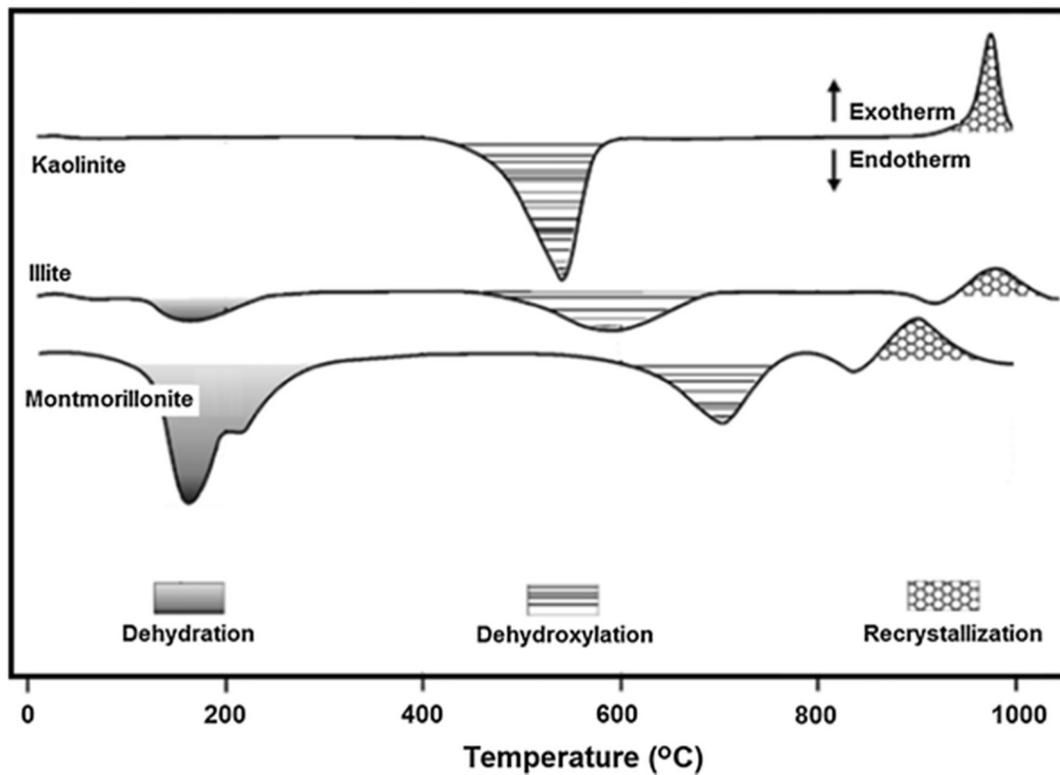
Fig. 23. The dehydroxylation temperature ranges of different clay minerals do not necessarily overlap. Reprinted from Snellings et al. [145].
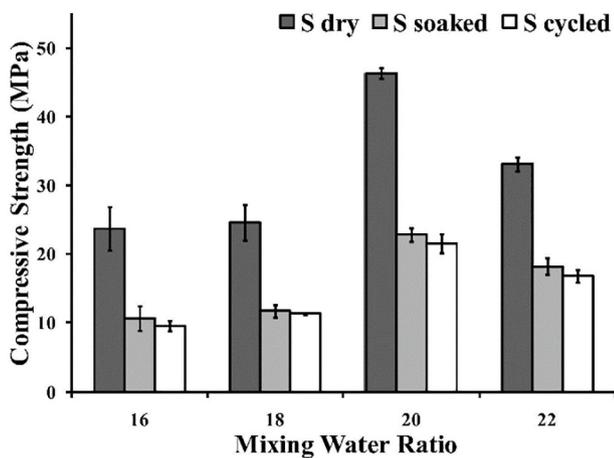
Fig. 24. Compressive strength of alkali-activated kaolinite samples measured in both dry and saturated (soaked) states. Adapted from Esaifan et al. [283].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

References

[1] J.L. Provis, Alkali-activated materials, Cem. Concr. Res. 114 (2018) 40–48, https://doi.org/10.1016/j.cemconres.2017.02.009.

[2] M.C.G. Juenger, F. Winnefeld, J.L. Provis, J.H. Ideker, Advances in alternative cementitious binders, Cem. Concr. Res. 41 (2011) 1232–1243, https://doi.org/10.1016/j.cemconres.2010.11.012.

[3] J.S.J. van Deventer, J.L. Provis, P. Duxson, D.G. Brice, Chemical research and climate change as drivers in the commercial adoption of alkali activated materials, Waste and Biomass Valorization 1 (2010) 145–155, https://doi.org/10.1007/s12649-010-9015-9.

[4] K.L. Scrivener, V.M. John, E.M. Gartner, Eco-efficient cements: potential economically viable solutions for a low-CO2 cement-based materials industry, Cem. Concr. Res. 114 (2018) 2–26, https://doi.org/10.1016/j.cemconres.2018.03.015.

[5] A. Fernández-Jiménez, A. Palomo, I. Sobrados, J. Sanz, The role played by the reactive alumina content in the alkaline activation of fly ashes, Microporous Mesoporous Mater. 91 (2006) 111–119, https://doi.org/10.1016/j.micromeso.2005.11.015.

[6] C. Shi, J. Qian, High performance cementing materials from industrial slags — a review, Resour. Conserv. Recycl. 29 (2000) 195–207, https://doi.org/10.1016/s0921-3449(99)00060-9.

[7] S.A. Bernal, P.V. Krivenko, J.L. Provis, F. Puertas, W.D.A. Rickard, C. Shi, A. van Riessen, Other potential applications for alkali-activated materials, in: J.L. Provis, J.S.J. van Deventer (Eds.), Alkali Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM, Springer Netherlands, Dordrecht, 2014, pp. 339–379, , https://doi.org/10.1007/978-94-007-7672-2_12.

[8] K.J.D. MacKenzie, Innovative applications of inorganic polymers (geopolymers), in: F. Pacheco-Torgal, J.A. Labrincha, C. Leonelli, A. Palomo, P. Chindaprasirt (Eds.), Handbook of Alkali-Activated Cements, Mortars and Concretes, Woodhead Publishing, Oxford, 2015, pp. 777–805, , https://doi.org/10.1533/9781782422884.5.777.

[9] I. Garcia-Lodeiro, A. Palomo, A. Fernández-Jiménez, An overview of the chemistry of alkali-activated cement-based binders, in: F. Pacheco-Torgal, J.A. Labrincha, C. Leonelli, A. Palomo, P. Chindaprasirt (Eds.), Handbook of Alkali-Activated Cements, Mortars and Concretes, Woodhead Publishing, Oxford, 2015, pp. 19–47, , https://doi.org/10.1533/9781782422884.1.19.

[10] J.L. Provis, A. Palomo, C. Shi, Advances in understanding alkali-activated materials, Cem. Concr. Res. 78 (2015) 110–125, https://doi.org/10.1016/j.cemconres.2015.04.013.

[11] P. Duxson, A. Fernández-Jiménez, J.L. Provis, G.C. Lukey, A. Palomo, J.S.J. van Deventer, Geopolymer technology: the current state of the art, J. Mater. Sci. 42 (2007) 2917–2933, https://doi.org/10.1007/s10853-006-0637-z.

[12] J.L. Provis, Geopolymers and other alkali activated materials: why, how, and

what? Mater. Struct. 47 (2014) 11–25, https://doi.org/10.1617/s11527-013-0211-5.

[13] K. Abora, I. Beleña, S.A. Bernal, A. Dunster, P.A. Nixon, J.L. Provis, A. Tagnit-Hamou, F. Winnefeld, Durability and testing – Chemical matrix degradation processes, in: J.L. Provis, J.S.J. van Deventer (Eds.), Alkali Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM, Springer Netherlands, Dordrecht, 2014, pp. 177–221, , https://doi.org/10.1007/978-94-007-7672-2_8.

[14] G. Habert, C. Ouellet-Plamondon, Recent update on the environmental impact of geopolymers, RILEM Technical Letters 1 (2016) 17, https://doi.org/10.21809/rilemtechlett.2016.6.

[15] A. Mehta, R. Siddique, An overview of geopolymers derived from industrial by-products, Constr. Build. Mater. 127 (2016) 183–198, https://doi.org/10.1016/j.conbuildmat.2016.09.136.

[16] J. Payá, J. Monzó, M.V. Borrachero, M.M. Tashima, Reuse of aluminosilicate industrial waste materials in the production of alkali-activated concrete binders, in: F. Pacheco-Torgal, J.A. Labrincha, C. Leonelli, A. Palomo, P. Chindaprasirt (Eds.), Handbook of Alkali-Activated Cements, Mortars and Concretes, Woodhead Publishing, Oxford, 2015, pp. 487–518, , https://doi.org/10.1533/9781782422884.4.487.

[17] N. Toniolo, A.R. Boccaccini, Fly ash-based geopolymers containing added silicate waste. A review, Ceram. Int. 43 (2017) 14545–14551, https://doi.org/10.1016/j.ceramint.2017.07.221.

[18] L. Zhang, Production of bricks from waste materials – a review, Constr. Build. Mater. 47 (2013) 643–655, https://doi.org/10.1016/j.conbuildmat.2013.05.043.

[19] M. Criado, X. Ke, J.L. Provis, S.A. Bernal, Alternative inorganic binders based on alkali-activated metallurgical slags, in: H. Savastano Júnior, J. Fiorelli, S.F. dos Santos (Eds.), Sustainable and Nonconventional Construction Materials Using Inorganic Bonded Fiber Composites, Woodhead Publishing, Oxford, 2017, pp. 185–220, , https://doi.org/10.1016/B978-0-08-102001-2.00008-5.

[20] S. Onisei, A.P. Douvalis, A. Malfliet, A. Peys, Y. Pontikes, Inorganic polymers made of fayalite slag: on the microstructure and behavior of Fe, J. Am. Ceram. Soc. 101 (2018) 2245–2257, https://doi.org/10.1111/jace.15420.

[21] A. Peys, C.E. White, D. Olds, H. Rahier, B. Blanpain, Y. Pontikes, Molecular structure of CaO–FeOx–SiO2 glassy slags and resultant inorganic polymer binders, J. Am. Ceram. Soc. 101 (2018) 5846–5857, https://doi.org/10.1111/jace.15880.

[22] J.L. Provis, Alkali-activation of calcined clays – past, present and future, in: F. Martirena, A. Favier, K. Scrivener (Eds.), Calcined Clays for Sustainable Concrete, Springer Netherlands, Dordrecht, 2018, pp. 372–376.

[23] M. Yellishetty, P.G. Ranjith, A. Tharumarajah, Iron ore and steel production trends and material flows in the world: is this really sustainable? Resour. Conserv. Recycl. 54 (2010) 1084–1094, https://doi.org/10.1016/j.resconrec.2010.03.003.

[24] IEA, World Energy Outlook 2018, International Energy Agency, 2018.

[25] C. Heidrich, H.-J. Feuerborn, A. Weir, Coal combustion products: a global perspective, 2013 World of Coal Ash ConferenceLexington, Kentucky, 2013.

[26] R.J. Flatt, N. Roussel, C.R. Cheeseman, Concrete: an eco material that needs to be improved, J. Eur. Ceram. Soc. 32 (2012) 2787–2798, https://doi.org/10.1016/j.jeurceramsoc.2011.11.012.

[27] K. Scrivener, F. Martirena, S. Bishnoi, S. Maity, Calcined clay limestone cements (LC3), Cem. Concr. Res. 114 (2018) 49–56, https://doi.org/10.1016/j.cemconres.2017.08.017.

[28] R.S. Blissett, N.A. Rowson, A review of the multi-component utilisation of coal fly ash, Fuel 97 (2012) 1–23, https://doi.org/10.1016/j.fuel.2012.03.024.

[29] Z.T. Yao, X.S. Ji, P.K. Sarker, J.H. Tang, L.Q. Ge, M.S. Xia, Y.Q. Xi, A comprehensive review on the applications of coal fly ash, Earth Sci. Rev. 141 (2015) 105–121, https://doi.org/10.1016/j.earscirev.2014.11.016.

[30] D.J. Beerling, J.R. Leake, S.P. Long, J.D. Scholes, J. Ton, P.N. Nelson, M. Bird, E. Kantzas, L.L. Taylor, B. Sarkar, M. Kelland, E. DeLucia, I. Kantola, C. Müller, G. Rau, J. Hansen, Farming with crops and rocks to address global climate, food and soil security, Nature Plants 4 (2018) 138–147, https://doi.org/10.1038/s41477-018-0108-y.

[31] G. Habert, J.B. d'Espinose de Lacaillerie, N. Roussel, An environmental evaluation of geopolymer based concrete production: reviewing current research trends, J. Clean. Prod. 19 (2011) 1229–1238, https://doi.org/10.1016/j.jclepro.2011.03.012.

[32] J. Davidovits, Geopolymer chemistry and applications, 3rd ed., Institut Géopolymère, Saint-Quentin, 2011.

[33] J.L. Provis, S.L. Yong, P. Duxson, Nanostructure/microstructure of metakaolin geopolymers, in: J.L. Provis, J.S.J. van Deventer (Eds.), Geopolymers, Woodhead Publishing, Cambridge, 2009, pp. 72–88, , https://doi.org/10.1533/9781845696382.1.72.

[34] H. Rahier, J. van Mele, M. Biesemans, J. Wastiels, X. Wu, Low-temperature synthesized aluminosilicate glasses, J. Mater. Sci. 31 (1996) 71–79, https://doi.org/10.1007/bf00355128.

[35] R. Fernandez Lopez, Calcined clayey soils as a potential replacement for cement in developing countries, School of Engineering, École Polytechnique Federale de Lausanne, 2009.

[36] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Assessment of pozzolanic activity of different calcined clays, Cem. Concr. Compos. 37 (2013) 319–327, https://doi.org/10.1016/j.cemconcomp.2013.01.002.

[37] K. Scrivener, Options for the future of cement, Indian Concrete Journal 88 (2014) 11–21.

[38] J.L. Provis, J.L. Provis, J.S.J. van Deventer (Eds.), Activating solution chemistry for geopolymers, Geopolymers, Woodhead Publishing, Cambridge, 2009, pp. 50–71, , https://doi.org/10.1533/9781845696382.1.50.

[39] C. Li, H. Sun, L. Li, A review: the comparison between alkali-activated slag (Si +Ca) and metakaolin (Si+Al) cements, Cem. Concr. Res. 40 (2010) 1341–1349,

https://doi.org/10.1016/j.cemconres.2010.03.020.

[40] J.L. Provis, P. Duxson, J.S.J. van Deventer, The role of particle technology in developing sustainable construction materials, Adv. Powder Technol. 21 (2010) 2–7, https://doi.org/10.1016/j.apt.2009.10.006.

[41] C. Kuenzel, L.J. Vandeperre, S. Donatello, A.R. Boccaccini, C. Cheeseman, Ambient temperature drying shrinkage and cracking in metakaolin-based geopolymers, J. Am. Ceram. Soc. 95 (2012) 3270–3277, https://doi.org/10.1111/j.1551-2916.2012.s.x.

[42] D.S. Perera, O. Uchida, E.R. Vance, K.S. Finnie, Influence of curing schedule on the integrity of geopolymers, J. Mater. Sci. 42 (2007) 3099–3106, https://doi.org/10.1007/s10853-006-0533-6.

[43] R. San Nicolas, M. Cyr, G. Escadeillas, Characteristics and applications of flash metakaolins, Appl. Clay Sci. 83–84 (2013) 253–262, https://doi.org/10.1016/j.clay.2013.08.036.

[44] N. Roussel, Rheological requirements for printable concretes, Cem. Concr. Res. 112 (2018) 76–85, https://doi.org/10.1016/j.cemconres.2018.04.005.

[45] Y. Alrefaei, Y.-S. Wang, J.-G. Dai, The effectiveness of different superplasticizers in ambient cured one-part alkali activated pastes, Cem. Concr. Compos. 97 (2019) 166–174, https://doi.org/10.1016/j.cemconcomp.2018.12.027.

[46] X. Li, R. Snellings, M. Antoni, N.M. Alderete, M. Ben Haha, S. Bishnoi, Ö. Cizer, M. Cyr, K. De Weerdt, Y. Dhandapani, J. Duchesne, J. Haufe, D. Hooton, M. Juenger, S. Kamali-Bernard, S. Kramar, M. Marroccoli, A.M. Joseph, A. Parashar, C. Patapy, J.L. Provis, S. Sabio, M. Santhanam, L. Steger, T. Sui, A. Telesca, A. Vollpracht, F. Vargas, B. Walkley, F. Winnefeld, G. Ye, M. Zajac, S. Zhang, K.L. Scrivener, Reactivity tests for supplementary cementitious materials: RILEM TC 267-TRM phase 1, Mater. Struct. 51 (2018) 151, https://doi.org/10.1617/s11527-018-1269-x.

[47] C. Shi, B. Qu, J.L. Provis, Recent progress in low-carbon binders, Cem. Concr. Res. 122 (2019) 227–250, https://doi.org/10.1016/j.cemconres.2019.05.009.

[48] J.L. Provis, S.A. Bernal, Binder chemistry – blended systems and intermediate Ca content, in: J.L. Provis, J.S.J. van Deventer (Eds.), Alkali Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM, Springer, Netherlands, Dordrecht, 2014, pp. 125–144, , https://doi.org/10.1007/978-94-007-7672-2_5.

[49] C.K. Yip, G.C. Lukey, J.S.J. van Deventer, The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation, Cem. Concr. Res. 35 (2005) 1688–1697, https://doi.org/10.1016/j.cemconres.2004.10.042.

[50] S.A. Bernal, J.L. Provis, V. Rose, R. Mejía de Gutierrez, Evolution of binder structure in sodium silicate-activated slag-metakaolin blends, Cem. Concr. Compos. 33 (2011) 46–54, https://doi.org/10.1016/j.cemconcomp.2010.09.004.

[51] I. Garcia-Lodeiro, A. Palomo, A. Fernández-Jiménez, D.E. Macphee, Compatibility studies between N-A-S-H and C-A-S-H gels. Study in the ternary diagram Na2O–CaO–Al2O3–SiO2–H2O, Cem. Concr. Res. 41 (2011) 923–931, https://doi.org/10.1016/j.cemconres.2011.05.006.

[52] N. Li, C. Shi, Q. Wang, Z. Zhang, Z. Ou, Composition design and performance of alkali-activated cements, Mater. Struct. 50 (2017) 997, https://doi.org/10.1617/s11527-017-1048-0.

[53] M.F. Brigatti, E. Galán, B.K.G. Theng, Structure and mineralogy of clay minerals, in: F. Bergaya, G. Lagaly (Eds.), Handbook of Clay Science, Elsevier, Oxford, 2013, pp. 21–81, , https://doi.org/10.1016/B978-0-08-098258-8.00002-X.

[54] Y.-M. Liew, C.-Y. Heah, A.B. Mohd Mustafa, H. Kamarudin, Structure and properties of clay-based geopolymer cements: a review, Prog. Mater. Sci. 83 (2016) 595–629, https://doi.org/10.1016/j.pmatsci.2016.08.002.

[55] Z.H. Zhang, H.J. Zhu, C.H. Zhou, H. Wang, Geopolymer from kaolin in China: an overview, Appl. Clay Sci. 119 (2016) 31–41, https://doi.org/10.1016/j.clay.2015.04.023.

[56] K. Norrish, J.G. Pickering, Clay minerals, Soils: An Australian viewpoint, CSIRO/Academic Press, Melbourne, 1983, pp. 281–308.

[57] U.S. Geological Survey, Mineral Commodity Summaries 2019, U.S. Geological Survey, Reston, Virginia, 2019.

[58] H.H. Murray, Applied Clay Mineralogy: Occurrences, Processing and Application of Kaolins, Bentonites, Palygorskite-Sepiolite, and Common Clays, Elsevier, Amsterdam, 2006.

[59] H. Houben, H. Guillaud, Earth construction: A comprehensive guide, Practical Action Publishing, Rugby, 1994.

[60] C. Llatas, A model for quantifying construction waste in projects according to the European waste list, Waste Manag. 31 (2011) 1261–1276, https://doi.org/10.1016/j.wasman.2011.01.023.

[61] M.A. Longhi, E.D. Rodríguez, S.A. Bernal, J.L. Provis, A.P. Kirchheim, Valorisation of a kaolin mining waste for the production of geopolymers, J. Clean. Prod. 115 (2016) 265–272, https://doi.org/10.1016/j.jclepro.2015.12.011.

[62] C. Dupuy, A. Gharzouni, N. Texier Mandoki, X. Bourbon, S. Rossignol, Alkali-activated materials based on Callovo-Oxfordian argillite: formation, structure and mechanical properties, Journal of Ceramic Science and Technology 9 (2018) 127–140, https://doi.org/10.4416/JCST2017-00086.

[63] R. Snellings, Ö. Cizer, L. Horckmans, P.T. Durdziński, P. Dierckx, P. Nielsen, K. van Balen, L. Vandewalle, Properties and pozzolanic reactivity of flash calcined dredging sediments, Appl. Clay Sci. 129 (2016) 35–39, https://doi.org/10.1016/j.clay.2016.04.019.

[64] R. Snellings, L. Horckmans, C. van Bunderen, L. Vandewalle, Ö. Cizer, Flash-calcined dredging sediment blended cements: effect on cement hydration and properties, Mater. Struct. 50 (2017) 521, https://doi.org/10.1617/s11527-017-1108-5.

[65] N. Belmokhtar, M. Ammari, J. Brigui, L. Ben allal, Comparison of the microstructure and the compressive strength of two geopolymers derived from Metakaolin and an industrial sludge, Constr. Build. Mater. 146 (2017) 621–629, https://doi.org/10.1016/j.conbuildmat.2017.04.127.

[66] G. Christidis, Advances in the characterization of Industrial Minerals,

Mineralogical Society of Great Britain & Ireland, London, 2011.

[67] P. Yuan, D. Tan, F. Annabi-Bergaya, Properties and applications of halloysite na- notubes: recent research advances and future prospects, Appl. Clay Sci. 112–113 (2015) 75–93, https://doi.org/10.1016/j.clay.2015.05.001.

[68] C.R. Kaze, H.K. Tchakoute, T.T. Mbakop, J.R. Mache, E. Kamseu, U.C. Melo, C. Leonelli, H. Rahier, Synthesis and properties of inorganic polymers (geopoly- mers) derived from Cameroon-meta-halloysite, Ceram. Int. 44 (2018) 18499–18508, https://doi.org/10.1016/j.ceramint.2018.07.070.

[69] E. Joussein, S. Petit, J. Churchman, B. Theng, D. Righi, B. Delvaux, Halloysite clay minerals – a review, Clay Miner. 40 (2005) 383–426, https://doi.org/10.1180/ 0009855054040180.

[70] S. Nickovic, A. Vukovic, M. Vujadinovic, V. Djurdjevic, G. Pejanovic, Technical note: high-resolution mineralogical database of dust-productive soils for atmo- spheric dust modeling, Atmos. Chem. Phys. 12 (2012) 845–855, https://doi.org/ 10.5194/acp-12-845-2012.

[71] A. Meunier, Clays, Springer-Verlag, Berlin Heidelberg, Berlin, Heidelberg, 2005.

[72] H.H. Murray, Applied clay mineralogy today and tomorrow, Clay Miner. 34 (1999) 39–49, https://doi.org/10.1180/000985599546055.

[73] D.G. Schulze, Clay minerals, in: D. Hillel, J.L. Hatfield (Eds.), Encyclopedia of Soils in the Environment, Elsevier, Oxford, 2005, pp. 246–254.

[74] R.J. Schaetzl, S. Anderson, Soils: Genesis and Geomorphology, Cambridge University Press, Cambridge; New York, 2005.

[75] E.M. Gartner, D.E. Macphee, A physico-chemical basis for novel cementitious binders, Cem. Concr. Res. 41 (2011) 736–749, https://doi.org/10.1016/j. cemconres.2011.03.006.

[76] L. Weng, K. Sagoe-Crentsil, Dissolution processes, hydrolysis and condensation reactions during geopolymer synthesis: part I—low Si/Al ratio systems, J. Mater. Sci. 42 (2007) 2997–3006, https://doi.org/10.1007/s10853-006-0820-2.

[77] C.S. Cundy, P.A. Cox, The hydrothermal synthesis of zeolites: precursors, inter- mediates and reaction mechanism, Microporous Mesoporous Mater. 82 (2005) 1–78, https://doi.org/10.1016/j.micromeso.2005.02.016.

[78] C.-M. Guo, K.-T. Wang, M.-Y. Liu, X.-H. Li, X.-M. Cui, Preparation and char- acterization of acid-based geopolymer using metakaolin and disused polishing li- quid, Ceram. Int. 42 (2016) 9287–9291, https://doi.org/10.1016/j.ceramint. 2016.02.073.

[79] L.-P. Liu, X.-M. Cui, Y. He, S.-D. Liu, S.-Y. Gong, The phase evolution of phosphoric acid-based geopolymers at elevated temperatures, Mater. Lett. 66 (2012) 10–12, https://doi.org/10.1016/j.matlet.2011.08.043.

[80] Y.-S. Wang, J.-G. Dai, Z. Ding, W.-T. Xu, Phosphate-based geopolymer: formation mechanism and thermal stability, Mater. Lett. 190 (2017) 209–212, https://doi. org/10.1016/j.matlet.2017.01.022.

[81] J. Cama, J. Ganor, Dissolution kinetics of clay minerals, in: C. Tournassat, C.I. Steefel, I.C. Bourg, F. Bergaya (Eds.), Natural and Engineered Clay Barriers, Elsevier, Oxford, 2015, pp. 101–153, , https://doi.org/10.1016/B978-0-08- 100027-4.00004-8.

[82] S.V. Golubev, A. Bauer, O.S. Pokrovsky, Effect of pH and organic ligands on the kinetics of smectite dissolution at 25 °C, Geochim. Cosmochim. Acta 70 (2006) 4436–4451, https://doi.org/10.1016/j.gca.2006.06.1557.

[83] V. Metz, K. Amram, J. Ganor, Stoichiometry of smectite dissolution reaction, Geochim. Cosmochim. Acta 69 (2005) 1755–1772, https://doi.org/10.1016/j.gca. 2004.09.027.

[84] J.L. Provis, P. Duxson, E. Kavalerova, P.V. Krivenko, Z. Pan, F. Puertas, J.S.J. van Deventer, Historical aspects and overview, in: J.L. Provis, J.S.J. van Deventer (Eds.), Alkali Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM, Springer Netherlands, Dordrecht, 2014, pp. 11–57, , https://doi.org/10.1007/ 978-94-007-7672-2_2.

[85] M.B. Diop, M.W. Grutzeck, Low temperature process to create brick, Constr. Build. Mater. 22 (2008) 1114–1121, https://doi.org/10.1016/j.conbuildmat.2007.03. 004.

[86] C.Y. Heah, H. Kamarudin, A.M. Mustafa Al Bakri, M. Bnhussain, M. Luqman, I. Khairul Nizar, C.M. Ruzaidi, Y.M. Liew, Kaolin-based geopolymers with various NaOH concentrations, Int. J. Miner. Metall. Mater. 20 (2013) 313–322, https:// doi.org/10.1007/s12613-013-0729-0.

[87] A.D. Hounsi, G. Lecomte-Nana, G. Djétéli, P. Blanchart, D. Alowanou, P. Kpelou, K. Napo, G. Tchangbédji, M. Praisler, How does Na, K alkali metal concentration change the early age structural characteristic of kaolin-based geopolymers, Ceram. Int. 40 (2014) 8953–8962, https://doi.org/10.1016/j.ceramint.2014.02.052.

[88] P.N. Lemougna, A.B. Madi, E. Kamseu, U.C. Melo, M.-P. Delplancke, H. Rahier, Influence of the processing temperature on the compressive strength of Na acti- vated lateritic soil for building applications, Constr. Build. Mater. 65 (2014) 60–66, https://doi.org/10.1016/j.conbuildmat.2014.04.100.

[89] H. Xu, J.S.J. van Deventer, The geopolymerisation of alumino-silicate minerals, Int. J. Miner. Process. 59 (2000) 247–266, https://doi.org/10.1016/s0301- 7516(99)00074-5.

[90] P. Duxson, J.L. Provis, Designing precursors for geopolymer cements, J. Am. Ceram. Soc. 91 (2008) 3864–3869, https://doi.org/10.1111/j.1551-2916.2008. 02787.x.

[91] T. Luukkonen, Z. Abdollahnejad, J. Yliniemi, P. Kinnunen, M. Illikainen, One-part alkali-activated materials: a review, Cem. Concr. Res. 103 (2018) 21–34, https:// doi.org/10.1016/j.cemconres.2017.10.001.

[92] H.F.W. Taylor, Cement Chemistry, 2nd ed., Thomas Telford, London, 1997.

[93] J.L. Provis, J.S.J. van Deventer, Geopolymerisation kinetics. 2. Reaction kinetic modelling, Chem. Eng. Sci. 62 (2007) 2318–2329, https://doi.org/10.1016/j.ces. 2007.01.028.

[94] F. Lolli, H. Manzano, J.L. Provis, M.C. Bignozzi, E. Masoero, Atomistic simulations of geopolymer models: the impact of disorder on structure and mechanics, ACS

[95] J.L. Provis, G.C. Lukey, J.S.J. van Deventer, Do geopolymers actually contain nanocrystalline zeolites? A reexamination of existing results, Chem. Mater. 17 (2005) 3075–3085, https://doi.org/10.1021/cm050230i.

[96] J. Davidovits, Geopolymers and geopolymeric materials, J. Therm. Anal. 35 (1989) 429–441, https://doi.org/10.1007/bf01904446.

[97] T. Abdullahi, Z. Harun, M.H.D. Othman, A review on sustainable synthesis of zeolite from kaolinite resources via hydrothermal process, Adv. Powder Technol. 28 (2017) 1827–1840, https://doi.org/10.1016/j.apt.2017.04.028.

[98] P. Duxson, J.L. Provis, G.C. Lukey, S.W. Mallicoat, W.M. Kriven, J.S.J. van Deventer, Understanding the relationship between geopolymer composition, mi- crostructure and mechanical properties, Colloids Surf. A Physicochem. Eng. Asp. 269 (2005) 47–58, https://doi.org/10.1016/j.colsurfa.2005.06.060.

[99] J.M. Newsam, The zeolite cage structure, Science 231 (1986) 1093–1099, https:// doi.org/10.1126/science.231.4742.1093.

[100] V.F.F. Barbosa, K.J.D. MacKenzie, C. Thaumaturgo, Synthesis and characterisation of materials based on inorganic polymers of alumina and silica: sodium polysialate polymers, Int. J. Inorg. Mater. 2 (2000) 309–317, https://doi.org/10.1016/s1466- 6049(00)00041-6.

[101] B. Walkley, G.J. Rees, R. San Nicolas, J.S.J. van Deventer, J.V. Hanna, J.L. Provis, New structural model of hydrous sodium aluminosilicate gels and the role of charge-balancing extra-framework Al, J. Phys. Chem. C 122 (2018) 5673–5685, https://doi.org/10.1021/acs.jpcc.8b00259.

[102] S.J. O'Connor, K.J.D. MacKenzie, M.E. Smith, J.V. Hanna, Ion exchange in the charge-balancing sites of aluminosilicate inorganic polymers, J. Mater. Chem. 20 (2010) 10234, , https://doi.org/10.1039/c0jm01254h.

[103] P. Sazama, O. Bortnovsky, J. Dědeček, Z. Tvarůžková, Z. Sobalík, Geopolymer based catalysts—new group of catalytic materials, Catal. Today 164 (2011) 92–99, https://doi.org/10.1016/j.cattod.2010.09.008.

[104] R.A. Fletcher, K.J.D. MacKenzie, C.L. Nicholson, S. Shimada, The composition range of aluminosilicate geopolymers, J. Eur. Ceram. Soc. 25 (2005) 1471–1477, https://doi.org/10.1016/j.jeurceramsoc.2004.06.001.

[105] J. Temuujin, W. Rickard, M. Lee, A. van Riessen, Preparation and thermal prop- erties of fire resistant metakaolin-based geopolymer-type coatings, J. Non-Cryst. Solids 357 (2011) 1399–1404, https://doi.org/10.1016/j.jnoncrysol.2010.09.063.

[106] A. Natali Murri, W.D.A. Rickard, M.C. Bignozzi, A. van Riessen, High temperature behaviour of ambient cured alkali-activated materials based on ladle slag, Cem. Concr. Res. 43 (2013) 51–61, https://doi.org/10.1016/j.cemconres.2012.09.011.

[107] S.A. Bernal, J.L. Provis, D.J. Green, Durability of alkali-activated materials: pro- gress and perspectives, J. Am. Ceram. Soc. 97 (2014) 997–1008, https://doi.org/ 10.1111/jace.12831.

[108] Z. Zhang, X. Yao, H. Zhu, Potential application of geopolymers as protection coatings for marine concrete III. Field experiment, Appl. Clay Sci. 49 (2010) 1–6, https://doi.org/10.1016/j.clay.2010.01.014.

[109] D. Koloušek, J. Brus, M. Urbanova, J. Andertova, V. Hulinsky, J. Vorel, Preparation, structure and hydrothermal stability of alternative (sodium silicate- free) geopolymers, J. Mater. Sci. 42 (2007) 9267–9275, https://doi.org/10.1007/ s10853-007-1910-5.

[110] X. Yao, Z. Zhang, H. Zhu, Y. Chen, Geopolymerization process of alkali–meta- kaolinite characterized by isothermal calorimetry, Thermochim. Acta 493 (2009) 49–54, https://doi.org/10.1016/j.tca.2009.04.002.

[111] D. Bondar, C.J. Lynsdale, N.B. Milestone, N. Hassani, A.A. Ramezanianpour, Effect of type, form, and dosage of activators on strength of alkali-activated natural pozzolans, Cem. Concr. Compos. 33 (2011) 251–260, https://doi.org/10.1016/j. cemconcomp.2010.10.021.

[112] N. Hu, D. Bernsmeier, G.H. Grathoff, L.N. Warr, The influence of alkali activator type, curing temperature and gibbsite on the geopolymerization of an inter- stratified illite-smectite rich clay from Friedland, Appl. Clay Sci. 135 (2017) 386–393, https://doi.org/10.1016/j.clay.2016.10.021.

[113] J.G.S. van Jaarsveld, J.S.J. van Deventer, Effect of the alkali metal activator on the properties of Fly ash-based geopolymers, Ind. Eng. Chem. Res. 38 (1999) 3932–3941, https://doi.org/10.1021/ie980804b.

[114] A. Poulesquen, F. Frizon, D. Lambertin, Rheological behavior of alkali-activated metakaolin during geopolymerization, J. Non-Cryst. Solids 357 (2011) 3565–3571, https://doi.org/10.1016/j.jnoncrysol.2011.07.013.

[115] T. Bakharev, Resistance of geopolymer materials to acid attack, Cem. Concr. Res. 35 (2005) 658–670, https://doi.org/10.1016/j.cemconres.2004.06.005.

[116] A. Fernández-Jiménez, A. Palomo, M. Criado, Alkali activated fly ash binders. A comparative study between sodium and potassium activators, Mater. Constr. 56 (2006) 51–65, https://doi.org/10.3989/mc.2006.v56.i281.92.

[117] S.A. Bernal, Advances in near-neutral salts activation of blast furnace slags, RILEM Technical Letters 1 (2016) 39–44, https://doi.org/10.21809/rilemtechlett.2016.8.

[118] M.X. Peng, Z.H. Wang, S.H. Shen, Q.G. Xiao, L.J. Li, Y.C. Tang, L.L. Hu, Alkali fusion of bentonite to synthesize one-part geopolymeric cements cured at elevated temperature by comparison with two-part ones, Constr. Build. Mater. 130 (2017) 103–112, https://doi.org/10.1016/j.conbuildmat.2016.11.010.

[119] M.X. Peng, Z.H. Wang, S.H. Shen, Q.G. Xiao, Synthesis, characterization and mechanisms of one-part geopolymeric cement by calcining low-quality kaolin with alkali, Mater. Struct. 48 (2015) 699–708, https://doi.org/10.1617/s11527-014- 0350-3.

[120] H. Ma, Q. Yao, Y. Fu, C. Ma, X. Dong, Synthesis of zeolite of type a from bentonite by alkali fusion activation using Na2CO3, Ind. Eng. Chem. Res. 49 (2010) 454–458, https://doi.org/10.1021/ie901205y.

[121] W. Vogel, Glass Chemistry, 2nd ed., Springer-Verlag, Berlin, 1994.

[122] M. Esaifan, H. Khoury, I. Aldabsheh, H. Rahier, M. Hourani, J. Wastiels, Hydrated

lime/potassium carbonate as alkaline activating mixture to produce kaolinitic clay based inorganic polymer, Appl. Clay Sci. 126 (2016) 278–286, https://doi.org/10.1016/j.clay.2016.03.026.

[123] F. Shaqour, M. Ismeik, M. Esaifan, Alkali activation of natural clay using a Ca(OH)2/Na2CO3 alkaline mixture, Clay Miner. 52 (2017) 485–496, https://doi.org/10.1180/claymin.2017.052.4.06.

[124] P. Duxson, S.W. Mallicoat, G.C. Lukey, W.M. Kriven, J.S.J. van Deventer, The effect of alkali and Si/Al ratio on the development of mechanical properties of metakaolin-based geopolymers, Colloids Surf. A Physicochem. Eng. Asp. 292 (2007) 8–20, https://doi.org/10.1016/j.colsurfa.2006.05.044.

[125] A. Buchwald, H.-D. Zellmann, C. Kaps, Condensation of aluminosilicate gels—-model system for geopolymer binders, J. Non-Cryst. Solids 357 (2011) 1376–1382, https://doi.org/10.1016/j.jnoncrysol.2010.12.036.

[126] F. Zibouche, H. Kerdjoudj, J.-B. d'Espinose de Lacaillerie, H. van Damme, Geopolymers from Algerian metakaolin. Influence of secondary minerals, Appl. Clay Sci. 43 (2009) 453–458, https://doi.org/10.1016/j.clay.2008.11.001.

[127] H. Rahier, W. Simons, B. Van Mele, M. Biesemans, Low-temperature synthesized aluminosilicate glasses: part III influence of the composition of the silicate solution on production, structure and properties, J. Mater. Sci. 32 (1997) 2237–2247, https://doi.org/10.1023/A:1018563914630.

[128] P. Rożek, M. Król, W. Mozgawa, Geopolymer-zeolite composites: a review, J. Clean. Prod. 230 (2019) 557–579, https://doi.org/10.1016/j.jclepro.2019.05.152.

[129] E.B.G. Johnson, S.E. Arshad, Hydrothermally synthesized zeolites based on kaolinite: a review, Appl. Clay Sci. 97–98 (2014) 215–221, https://doi.org/10.1016/j.clay.2014.06.005.

[130] P.D. Silva, K. Sagoe-Crenstil, V. Sirivivatnanon, Kinetics of geopolymerization: role of Al2O3 and SiO2, Cem. Concr. Res. 37 (2007) 512–518, https://doi.org/10.1016/j.cemconres.2007.01.003.

[131] L. Valentini, Modeling dissolution–precipitation kinetics of alkali-activated metakaolin, ACS Omega 3 (2018) 18100–18108, https://doi.org/10.1021/acsomega.8b02380.

[132] C. Ferone, B. Liguori, I. Capasso, F. Colangelo, R. Cioffi, E. Cappelletto, R. Di Maggio, Thermally treated clay sediments as geopolymer source material, Appl. Clay Sci. 107 (2015) 195–204, https://doi.org/10.1016/j.clay.2015.01.027.

[133] F. Puertas, C. Varga, M.M. Alonso, Rheology of alkali-activated slag pastes. Effect of the nature and concentration of the activating solution, Cem. Concr. Compos. 53 (2014) 279–288, https://doi.org/10.1016/j.cemconcomp.2014.07.012.

[134] P.S. Singh, M. Trigg, I. Burgar, T. Bastow, Geopolymer formation processes at room temperature studied by 29Si and 27Al MAS-NMR, Mater. Sci. Eng. A 396 (2005) 392–402, https://doi.org/10.1016/j.msea.2005.02.002.

[135] M. Arnoult, M. Perronnet, A. Autef, S. Rossignol, How to control the geopolymer setting time with the alkaline silicate solution, J. Non-Cryst. Solids 495 (2018) 59–66, https://doi.org/10.1016/j.jnoncrysol.2018.02.036.

[136] Z. Zuhua, Y. Xiao, Z. Huajun, C. Yue, Role of water in the synthesis of calcined kaolin-based geopolymer, Appl. Clay Sci. 43 (2009) 218–223, https://doi.org/10.1016/j.clay.2008.09.003.

[137] H. Yan, C. Xue-Min, M. Jin, L.-P. Liu, X.-D. Liu, J.-Y. Chen, The hydrothermal transformation of solid geopolymers into zeolites, Microporous Mesoporous Mater. 161 (2012) 187–192, https://doi.org/10.1016/j.micromeso.2012.05.039.

[138] M. Alkan, Ç. Hopa, Z. Yilmaz, H. Güler, The effect of alkali concentration and solid/liquid ratio on the hydrothermal synthesis of zeolite NaA from natural kaolinite, Microporous Mesoporous Mater. 86 (2005) 176–184, https://doi.org/10.1016/j.micromeso.2005.07.008.

[139] C.Y. Heah, H. Kamarudin, A.M. Mustafa Al Bakri, M. Bnhussain, M. Luqman, I. Khairul Nizar, C.M. Ruzaidi, Y.M. Liew, Study on solids-to-liquid and alkaline activator ratios on kaolin-based geopolymers, Constr. Build. Mater. 35 (2012) 912–922, https://doi.org/10.1016/j.conbuildmat.2012.04.102.

[140] R. Pouhet, M. Cyr, R. Bucher, Influence of the initial water content in flash calcined metakaolin-based geopolymer, Constr. Build. Mater. 201 (2019) 421–429, https://doi.org/10.1016/j.conbuildmat.2018.12.201.

[141] M. Steveson, K. Sagoe-Crentsil, Relationships between composition, structure and strength of inorganic polymers, J. Mater. Sci. 40 (2005) 2023–2036, https://doi.org/10.1007/s10853-005-1226-2.

[142] A. Allahverdi, E. Najafi Kani, K.M.A. Hossain, M. Lachemi, Methods to control efflorescence in alkali-activated cement-based materials, in: F. Pacheco-Torgal, J.A. Labrincha, C. Leonelli, A. Palomo, P. Chindaprasirt (Eds.), Handbook of Alkali-Activated Cements, Mortars and Concretes, Woodhead Publishing, Oxford, 2015, pp. 463–483, , https://doi.org/10.1533/9781782422884.3.463.

[143] M.A. Longhi, Z. Zhang, E.D. Rodríguez, A.P. Kirchheim, H. Wang, Efflorescence of alkali-activated cements (Geopolymers) and the impacts on material structures: a critical analysis, Frontiers in Materials 6 (2019) 89, https://doi.org/10.3389/fmats.2019.00089.

[144] B. Lothenbach, K. Scrivener, R.D. Hooton, Supplementary cementitious materials, Cem. Concr. Res. 41 (2011) 1244–1256, https://doi.org/10.1016/j.cemconres.2010.12.001.

[145] R. Snellings, G. Mertens, J. Elsen, Supplementary cementitious materials, Rev. Mineral. Geochem. 74 (2012) 211–278, https://doi.org/10.2138/rmg.2012.74.6.

[146] R. Snellings, Assessing, understanding and unlocking supplementary cementitious materials, RILEM Technical Letters 1 (2016) 50, https://doi.org/10.21809/rilemtechlett.2016.12.

[147] M.C.G. Juenger, R. Snellings, S.A. Bernal, Supplementary cementitious materials: new sources, characterization, and performance insights, Cem. Concr. Res. 122 (2019) 257–273, https://doi.org/10.1016/j.cemconres.2019.05.008.

[148] D. Massiot, P. Dion, J.F. Alcover, F. Bergaya, 27Al and 29Si MAS NMR study of kaolinite thermal decomposition by controlled rate thermal analysis, J. Am. Ceram. Soc. 78 (1995) 2940–2944, https://doi.org/10.1111/j.1151-2916.1995.tb09067.x.

[149] C.E. White, J.L. Provis, T. Proffen, D.P. Riley, J.S.J. van Deventer, Combining density functional theory (DFT) and pair distribution function (PDF) analysis to solve the structure of metastable materials: the case of metakaolin, Phys. Chem. Chem. Phys. 12 (2010) 3239, https://doi.org/10.1039/b922993k.

[150] S. Sperinck, P. Raiteri, N. Marks, K. Wright, Dehydroxylation of kaolinite to metakaolin - a molecular dynamics study, J. Mater. Chem. 21 (2011) 2118–2125, https://doi.org/10.1039/C0JM01748E.

[151] T. Seiffarth, M. Hohmann, K. Posern, C. Kaps, Effect of thermal pre-treatment conditions of common clays on the performance of clay-based geopolymeric binders, Appl. Clay Sci. 73 (2013) 35–41, https://doi.org/10.1016/j.clay.2012.09.010.

[152] L.N. Tchadjie, S.O. Ekolu, Enhancing the reactivity of aluminosilicate materials toward geopolymer synthesis, J. Mater. Sci. 53 (2018) 4709–4733, https://doi.org/10.1007/s10853-017-1907-7.

[153] A.Z. Khalifa, Y. Pontikes, J. Elsen, Ö. Cizer, Comparing the reactivity of different natural clays under thermal and alkali activation, RILEM Technical Letters 40 (2019) 74–80, https://doi.org/10.21809/rilemtechlett.2019.85.

[154] L. Heller-Kallai, Thermally modified clay minerals, in: F. Bergaya, G. Lagaly (Eds.), Handbook of Clay Science, Elsevier, Oxford, 2013, pp. 411–433, , https://doi.org/10.1016/B978-0-08-098258-8.00014-6.

[155] M. Claverie, F. Martin, J.P. Tardy, M. Cyr, P.d. Parseval, O. Grauby, C. Le Roux, Structural and chemical changes in kaolinite caused by flash calcination: formation of spherical particles, Appl. Clay Sci. 114 (2015) 247–255, https://doi.org/10.1016/j.clay.2015.05.031.

[156] A. Gharzouni, C. Dupuy, I. Sobrados, E. Joussein, N. Texier-Mandoki, X. Bourbon, S. Rossignol, The effect of furnace and flash heating on COx argillite for the synthesis of alkali-activated binders, J. Clean. Prod. 156 (2017) 670–678, https://doi.org/10.1016/j.jclepro.2017.04.056.

[157] R. Fernandez, F. Martirena, K.L. Scrivener, The origin of the pozzolanic activity of calcined clay minerals: a comparison between kaolinite, illite and montmorillonite, Cem. Concr. Res. 41 (2011) 113–122, https://doi.org/10.1016/j.cemconres.2010.09.013.

[158] C. He, E. Makovicky, B. Osback, Thermal stability and pozzolanic activity of calcined kaolin, Appl. Clay Sci. 9 (1994) 165–187, https://doi.org/10.1016/0169-1317(94)90018-3.

[159] B. Fabbri, S. Gualtieri, C. Leonardi, Modifications induced by the thermal treatment of kaolin and determination of reactivity of metakaolin, Appl. Clay Sci. 73 (2013) 2–10, https://doi.org/10.1016/j.clay.2012.09.019.

[160] D. Bridson, Properties of flash-calcined kaolinite, Clay Clay Miner. 33 (1985) 258–260, https://doi.org/10.1346/ccmn.1985.0330313.

[161] V. Medri, S. Fabbri, J. Dedecek, Z. Sobalik, Z. Tvaruzkova, A. Vaccari, Role of the morphology and the dehydroxylation of metakaolins on geopolymerization, Appl. Clay Sci. 50 (2010) 538–545, https://doi.org/10.1016/j.clay.2010.10.010.

[162] A. Teklay, C. Yin, L. Rosendahl, Flash calcination of kaolinite rich clay and impact of process conditions on the quality of the calcines: a way to reduce CO 2 footprint from cement industry, Appl. Energy 162 (2016) 1218–1224, https://doi.org/10.1016/j.apenergy.2015.04.127.

[163] J. Dietel, L.N. Warr, M. Bertmer, A. Steudel, G.H. Grathoff, K. Emmerich, The importance of specific surface area in the geopolymerization of heated illitic clay, Appl. Clay Sci. 139 (2017) 99–107, https://doi.org/10.1016/j.clay.2017.01.001.

[164] S. Louati, S. Baklouti, B. Samet, Acid based geopolymerization kinetics: effect of clay particle size, Appl. Clay Sci. 132–133 (2016) 571–578, https://doi.org/10.1016/j.clay.2016.08.007.

[165] A. Buchwald, M. Hohmann, K. Posern, E. Brendler, The suitability of thermally activated illite/smectite clay as raw material for geopolymer binders, Appl. Clay Sci. 46 (2009) 300–304, https://doi.org/10.1016/j.clay.2009.08.026.

[166] S. Hollanders, R. Adriaens, J. Skibsted, Ö. Cizer, J. Elsen, Pozzolanic reactivity of pure calcined clays, Appl. Clay Sci. 132–133 (2016) 552–560, https://doi.org/10.1016/j.clay.2016.08.003.

[167] S. Hollanders, Mineralogical study of the pozzolanic properties of calcined clays, Arenberg Doctoral School, KU Leuven, 2017.

[168] B.B. Kenne Diffo, A. Elimbi, M. Cyr, J. Dika Manga, H. Tchakoute Kouamo, Effect of the rate of calcination of kaolin on the properties of metakaolin-based geopolymers, Journal of Asian Ceramic Societies 3 (2015) 130–138, https://doi.org/10.1016/j.jascer.2014.12.003.

[169] C.F. Burmeister, A. Kwade, Process engineering with planetary ball mills, Chem. Soc. Rev. 42 (2013) 7660–7667, https://doi.org/10.1039/C3CS35455E.

[170] P. Baláž, M. Achimovičová, M. Baláž, P. Billik, Z. Cherkezova-Zheleva, J.M. Criado, F. Delogu, E. Dutková, E. Gaffet, F.J. Gotor, R. Kumar, I. Mitov, T. Rojac, M. Senna, A. Streletskii, K. Wieczorek-Ciurowa, Hallmarks of mechanochemistry: from nanoparticles to technology, Chem. Soc. Rev. 42 (2013) 7571–7637, https://doi.org/10.1039/C3CS35468G.

[171] D.L. Zhang, Processing of advanced materials using high-energy mechanical milling, Prog. Mater. Sci. 49 (2004) 537–560, https://doi.org/10.1016/S0079-6425(03)00034-3.

[172] R.L. Frost, É. Makó, J. Kristóf, E. Horváth, J.T. Kloprogge, Mechanochemical treatment of kaolinite, J. Colloid Interface Sci. 239 (2001) 458–466, https://doi.org/10.1006/jcis.2001.7591.

[173] R.L. Frost, É. Makó, J. Kristóf, J.T. Kloprogge, Modification of kaolinite surfaces through mechanochemical treatment—a mid-IR and near-IR spectroscopic study, Spectrochim. Acta A Mol. Biomol. Spectrosc. 58 (2002) 2849–2859, https://doi.org/10.1016/S1386-1425(02)00033-1.

[174] C. Vizcayno, R. Castelló, I. Ranz, B. Calvo, Some physico-chemical alterations caused by mechanochemical treatments in kaolinites of different structural order, Thermochim. Acta 428 (2005) 173–183, https://doi.org/10.1016/j.tca.2004.11.

012.

[175] R.M. Torres Sánchez, E.I. Basaldella, J.F. Marco, The effect of thermal and mechanical treatments on kaolinite: characterization by XPS and IEP measurements, J. Colloid Interface Sci. 215 (1999) 339–344, https://doi.org/10.1006/jcis.1999.6241.

[176] J. Temuujin, K. Okada, K.J.D. MacKenzie, T. Jadambaa, Characterization of porous silica prepared from mechanically amorphized kaolinite by selective leaching, Powder Technol. 121 (2001) 259–262, https://doi.org/10.1016/S0032-5910(01)00363-1.

[177] J.G. Miller, T.D. Oulton, Prototropy in Kaolinite during Percussive Grinding, Clays and Clay Minerals, 18 (1970), pp. 313–323, https://doi.org/10.1346/CCMN.1970.0180603.

[178] B. Ilić, V. Radonjanin, M. Malešev, M. Zdujić, A. Mitrović, Effects of mechanical and thermal activation on pozzolanic activity of kaolin containing mica, Appl. Clay Sci. 123 (2016) 173–181, https://doi.org/10.1016/j.clay.2016.01.029.

[179] R.L. Frost, E. Horváth, É. Makó, J. Kristóf, Modification of low- and high-defect kaolinite surfaces: implications for kaolinite mineral processing, J. Colloid Interface Sci. 270 (2004) 337–346, https://doi.org/10.1016/j.jcis.2003.10.034.

[180] E.F. Aglietti, J.M. Porto Lopez, E. Pereira, Mechanochemical effects in kaolinite grinding. I. Textural and physicochemical aspects, Int. J. Miner. Process. 16 (1986) 125–133, https://doi.org/10.1016/0301-7516(86)90079-7.

[181] I. Tole, K. Habermehl-Cwirzen, A. Cwirzen, Mechanochemical activation of natural clay minerals: an alternative to produce sustainable cementitious binders – review, Mineral. Petrol. 113 (2019) 449–462, https://doi.org/10.1007/s00710-019-00666-y.

[182] P. Komadel, Chemically modified smectites, Clay Miner. 38 (2003) 127–138, https://doi.org/10.1180/0009855033810083.

[183] K.J.D. MacKenzie, D.R.M. Brew, R.A. Fletcher, R. Vagana, Formation of aluminosilicate geopolymers from 1:1 layer-lattice minerals pre-treated by various methods: a comparative study, J. Mater. Sci. 42 (2007) 4667–4674, https://doi.org/10.1007/s10853-006-0173-x.

[184] C. Belviso, F. Cavalcante, G. Niceforo, A. Lettino, Sodalite, faujasite and A-type zeolite from 2:1dioctahedral and 2:1:1 trioctahedral clay minerals. A singular review of synthesis methods through laboratory trials at a low incubation temperature, Powder Technol. 320 (2017) 483–497, https://doi.org/10.1016/j.powtec.2017.07.039.

[185] C. Vizcayno, R.M.d. Gutiérrez, R. Castello, E. Rodriguez, C.E. Guerrero, Pozzolan obtained by mechanochemical and thermal treatments of kaolin, Appl. Clay Sci. 49 (2010) 405–413, https://doi.org/10.1016/j.clay.2009.09.008.

[186] Z. Zhang, H. Wang, J.L. Provis, F. Bullen, A. Reid, Y. Zhu, Quantitative kinetic and structural analysis of geopolymers. Part 1. The activation of metakaolin with sodium hydroxide, Thermochim. Acta 539 (2012) 23–33, https://doi.org/10.1016/j.tca.2012.03.021.

[187] A.D. Hounsi, G.L. Lecomte-Nana, G. Djétéli, P. Blanchart, Kaolin-based geopolymers: effect of mechanical activation and curing process, Constr. Build. Mater. 42 (2013) 105–113, https://doi.org/10.1016/j.conbuildmat.2012.12.069.

[188] F. Slaty, H. Khoury, H. Rahier, J. Wastiels, Durability of alkali activated cement produced from kaolinitic clay, Appl. Clay Sci. 104 (2015) 229–237, https://doi.org/10.1016/j.clay.2014.11.037.

[189] B.-H. Mo, H. Zhu, X.-M. Cui, Y. He, S.-Y. Gong, Effect of curing temperature on geopolymerization of metakaolin-based geopolymers, Appl. Clay Sci. 99 (2014) 144–148, https://doi.org/10.1016/j.clay.2014.06.024.

[190] P. Rovnaník, Effect of curing temperature on the development of hard structure of metakaolin-based geopolymer, Constr. Build. Mater. 24 (2010) 1176–1183, https://doi.org/10.1016/j.conbuildmat.2009.12.023.

[191] A. Hamaideh, K. Komnitsas, M. Esaifan, J.a.K. Al-Kafawein, H. Rahier, M. Alshaaer, Advantages of applying a steam curing cycle for the production of kaolinite-based geopolymers, Arab. J. Sci. Eng. 39 (2014) 7591–7597, https://doi.org/10.1007/s13369-014-1314-1.

[192] K. Byrappa, T. Adschiri, Hydrothermal technology for nanotechnology, Prog. Cryst. Growth Charact. Mater. 53 (2007) 117–166, https://doi.org/10.1016/j.pcrysgrow.2007.04.001.

[193] F. Tong, W. Ji, M. Li, C. Zeng, L. Zhang, Investigation of the crystallization of zeolite A from hydrogels aged under high pressure, CrystEngComm 16 (2014) 8563–8569, https://doi.org/10.1039/c4ce00688g.

[194] K. Momma, F. Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, J. Appl. Crystallogr. 44 (2011) 1272–1276, https://doi.org/10.1107/S0021889811038970.

[195] D.L. Bish, Rietveld refinement of the kaolinite structure at 1.5 K, Clay Clay Miner. 41 (1993) 738–744, https://doi.org/10.1346/ccmn.1993.0410613.

[196] H.L. Zhang, X.R. Lei, C.J. Yan, H.Q. Wang, G.Q. Xiao, J.R. Hao, D. Wang, X.M. Qiu, Analysis on crystal structure of 7Å-Halloysite, Adv. Mater. Res. 415–417 (2011) 2206–2214, https://doi.org/10.4028/www.scientific.net/AMR.415-417.2206.

[197] I. Aldabsheh, H. Khoury, J. Wastiels, H. Rahier, Dissolution behavior of Jordanian clay-rich materials in alkaline solutions for alkali activation purpose, Appl. Clay Sci. 115 (2015) 238–247, https://doi.org/10.1016/j.clay.2015.08.004.

[198] A. Bauer, G. Berger, Kaolinite and smectite dissolution rate in high molar KOH solutions at 35° and 80°C, Appl. Geochem. 13 (1998) 905–916, https://doi.org/10.1016/s0883-2927(98)00018-3.

[199] F.J. Huertas, L. Chou, R. Wollast, Mechanism of kaolinite dissolution at room temperature and pressure part II: kinetic study, Geochim. Cosmochim. Acta 63 (1999) 3261–3275, https://doi.org/10.1016/s0016-7037(99)00249-5.

[200] Z. Zhang, H. Wang, X. Yao, Y. Zhu, Effects of halloysite in kaolin on the formation and properties of geopolymers, Cem. Concr. Compos. 34 (2012) 709–715, https://doi.org/10.1016/j.cemconcomp.2012.02.003.

[201] I. Biljana, M. Aleksandra, M. Ljiljana, Thermal treatment of kaolin clay to obtain metakaolin, Hemijska industrija 64 (2010) 351–356, https://doi.org/10.2298/hemind100322014i.

[202] C. Ruiz-Santaquiteria, J. Skibsted, Identification of reactive sites in calcined kaolinite and montmorillonite from a combination of chemical methods and solid-state NMR spectroscopy, in: F. Martirena, A. Favier, K. Scrivener (Eds.), Calcined Clays for Sustainable Concrete, Springer Netherlands, Dordrecht, 2018, pp. 404–408.

[203] C. Kuenzel, T.P. Neville, S. Donatello, L. Vandeperre, A.R. Boccaccini, C.R. Cheeseman, Influence of metakaolin characteristics on the mechanical properties of geopolymers, Appl. Clay Sci. 83–84 (2013) 308–314, https://doi.org/10.1016/j.clay.2013.08.023.

[204] G. Kakali, T. Perraki, S. Tsivilis, E. Badogiannis, Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity, Appl. Clay Sci. 20 (2001) 73–80, https://doi.org/10.1016/s0169-1317(01)00040-0.

[205] J. Rocha, J. Klinowski, Solid-state NMR studies of the structure and reactivity of metakaolinite, Angew. Chem. Int. Ed. Engl. 29 (1990) 553–554, https://doi.org/10.1002/anie.199005531.

[206] A. Shvarzman, K. Kovler, G.S. Grader, G.E. Shter, The effect of dehydroxylation/amorphization degree on pozzolanic activity of kaolinite, Cem. Concr. Res. 33 (2003) 405–416, https://doi.org/10.1016/s0008-8846(02)00975-4.

[207] J. Rocha, J. Klinowski, The rehydration of metakaolinite to kaolinite, J. Chem. Soc. Chem. Commun. (1991) 582, https://doi.org/10.1039/c39910000582.

[208] M.E. Smith, G. Neal, M.B. Trigg, J. Drennan, Structural characterization of the thermal transformation of halloysite by solid state NMR, Appl. Magn. Reson. 4 (1993) 157–170, https://doi.org/10.1007/bf03162561.

[209] P. Yuan, D. Tan, F. Aannabi-Bergaya, W. Yan, M. Fan, D. Liu, H. He, Changes in structure, morphology, porosity, and surface activity of mesoporous halloysite nanotubes under heating, Clay Clay Miner. 60 (2012) 561–573, https://doi.org/10.1346/ccmn.2012.0600602.

[210] R.M. Barrer, J.F. Cole, H. Sticher, Chemistry of soil minerals. Part V. Low temperature hydrothermal transformations of kaolinite, Journal of the Chemical Society A: Inorganic, Physical, Theoretical (1968) 2475, https://doi.org/10.1039/j19680002475.

[211] G. Engelhardt, J. Felsche, P. Sieger, The hydrosodalite system Na6 + x[SiAlO4]6(OH)x.cntdot.nH2O: formation, phase composition, and de- and rehydration studied by 1H, 23Na, and 29Si MAS-NMR spectroscopy in tandem with thermal analysis, x-ray diffraction, and IR spectroscopy, J. Am. Chem. Soc. 114 (1992) 1173–1182, https://doi.org/10.1021/ja00030a008.

[212] L. Heller-Kallai, I. Lapides, Reactions of kaolinites and metakaolinites with NaOH—comparison of different samples (Part 1), Appl. Clay Sci. 35 (2007) 99–107, https://doi.org/10.1016/j.clay.2006.06.006.

[213] A. Marsh, A. Heath, P. Patureau, M. Evernden, P. Walker, A mild conditions synthesis route to produce hydrosodalite from kaolinite, compatible with extrusion processing, Microporous Mesoporous Mater. 264 (2018) 125–132, https://doi.org/10.1016/j.micromeso.2018.01.014.

[214] R.M. Barrer, D.E. Mainwaring, Chemistry of soil minerals. Part XIII. Reactions of metakaolinite with single and mixed bases, J. Chem. Soc. Dalton Trans. (1972) 2534–2546, https://doi.org/10.1039/dt9720002534.

[215] Z. Zhang, J.L. Provis, H. Wang, F. Bullen, A. Reid, Quantitative kinetic and structural analysis of geopolymers. Part 2. Thermodynamics of sodium silicate activation of metakaolin, Thermochim. Acta 565 (2013) 163–171, https://doi.org/10.1016/j.tca.2013.01.040.

[216] I. Lapides, L. Heller-Kallai, Reactions of metakaolinite with NaOH and colloidal silica — comparison of different samples (part 2), Appl. Clay Sci. 35 (2007) 94–98, https://doi.org/10.1016/j.clay.2006.06.007.

[217] Y. Wang, J. Chen, H. Wu, X. Lei, Controllable preparation of zeolite P1 from metakaolin-based geopolymers via a hydrothermal method, Clay Clay Miner. 65 (2017) 42–51, https://doi.org/10.1346/ccmn.2016.064048.

[218] Q. Wang, J. Zhang, A. Wang, Alkali activation of halloysite for adsorption and release of ofloxacin, Appl. Surf. Sci. 287 (2013) 54–61, https://doi.org/10.1016/j.apsusc.2013.09.057.

[219] M. Alzeer, K.J.D. MacKenzie, Synthesis and mechanical properties of new fibre-reinforced composites of inorganic polymers with natural wool fibres, J. Mater. Sci. 47 (2012) 6958–6965, https://doi.org/10.1007/s10853-012-6644-3.

[220] J. Tailby, K.J.D. MacKenzie, Structure and mechanical properties of aluminosilicate geopolymer composites with Portland cement and its constituent minerals, Cem. Concr. Res. 40 (2010) 787–794, https://doi.org/10.1016/j.cemconres.2009.12.003.

[221] S.J. O'Connor, K.J.D. MacKenzie, Synthesis, characterisation and thermal behaviour of lithium aluminosilicate inorganic polymers, J. Mater. Sci. 45 (2010) 3707–3713, https://doi.org/10.1007/s10853-010-4383-x.

[222] P.W.J.G. Wijnen, T.P.M. Beelen, J.W. de Haan, C.P.J. Rummens, L.J.M. van de Ven, R.A. van Santen, Silica gel dissolution in aqueous alkali metal hydroxides studied by 29Si NMR, J. Non-Cryst. Solids 109 (1989) 85–94, https://doi.org/10.1016/0022-3093(89)90446-8.

[223] S.D. Kinrade, D.L. Pole, Effect of alkali-metal cations on the chemistry of aqueous silicate solutions, Inorg. Chem. 31 (1992) 4558–4563, https://doi.org/10.1021/ic00048a023.

[224] V. Zivica, M.T. Palou, T.I.Ľ. Bágeľ, High strength metahalloysite based geopolymer, Compos. Part B 57 (2014) 155–165, https://doi.org/10.1016/j.compositesb.2013.09.034.

[225] A. Viani, A.F. Gualtieri, G. Artioli, The nature of disorder in montmorillonite by simulation of X-ray powder patterns, Am. Mineral. 87 (2002) 966–975, https://doi.org/10.2138/am-2002-0720.

[226] G.W. Brindley, G. Brown, Crystal Structures of Clay Minerals and Their X-ray Identification, 3rd ed., Mineralogical Society, London, 1980.

[227] K. Verburg, Hysteresis in the binary exchange of cations on 2:1 clay minerals: a critical review, Clay Clay Miner. 42 (1994) 207–220, https://doi.org/10.1346/ccmn.1994.0420211.

[228] A.F. Gualtieri, Accuracy of XRPD QPA using the combined Rietveld–RIR method, J. Appl. Crystallogr. 33 (2000) 267–278, https://doi.org/10.1107/s002188989901643x.

[229] S.J. Köhler, F. Dufaud, E.H. Oelkers, An experimental study of illite dissolution kinetics as a function of ph from 1.4 to 12.4 and temperature from 5 to 50°C, Geochim. Cosmochim. Acta 67 (2003) 3583–3594, https://doi.org/10.1016/s0016-7037(03)00163-7.

[230] S. Yokoyama, M. Kuroda, T. Sato, Atomic force microscopy study of montmorillonite dissolution under highly alkaline conditions, Clay Clay Miner. 53 (2005) 147–154, https://doi.org/10.1346/ccmn.2005.0530204.

[231] A. Bauer, B. Velde, Smectite transformation in high molar KOH solutions, Clay Miner. 34 (1999) 259–273, https://doi.org/10.1180/000985599546226.

[232] N. Garg, J. Skibsted, Heated montmorillonite: structure, reactivity, and dissolution, in: K. Scrivener, A. Favier (Eds.), Calcined Clays for Sustainable Concrete, Springer Netherlands, Dordrecht, 2015, pp. 117–124.

[233] K. Emmerich, F. Wolters, G. Kahr, G. Lagaly, Clay profiling: the classification of Montmorillonites, Clay Clay Miner. 57 (2009) 104–114, https://doi.org/10.1346/ccmn.2009.0570110.

[234] K. Emmerich, F.T. Madsen, G. Kahr, Dehydroxylation behavior of heat-treated and steam-treated homoionic Cis-vacant montmorillonites, Clay Clay Miner. 47 (1999) 591–604, https://doi.org/10.1346/CCMN.1999.0470506.

[235] N. Garg, J. Skibsted, Thermal activation of a pure montmorillonite clay and its reactivity in cementitious systems, J. Phys. Chem. C 118 (2014) 11464–11477, https://doi.org/10.1021/jp502529d.

[236] I.W.M. Brown, K.J.D. MacKenzie, R.H. Meinhold, The thermal reactions of montmorillonite studied by high-resolution solid-state 29Si and 27Al NMR, J. Mater. Sci. 22 (1987) 3265–3275, https://doi.org/10.1007/BF01161191.

[237] S. Stackhouse, P.V. Coveney, D.M. Benoit, Density-functional-theory-based study of the dehydroxylation behavior of aluminous dioctahedral 2:1 layer-type clay minerals, J. Phys. Chem. B 108 (2004) 9685–9694, https://doi.org/10.1021/jp037608p.

[238] S.I. Tsipursky, V.A. Drits, The distribution of octahedral cations in the 2:1 layers of dioctahedral smectites studied by oblique-texture electron diffraction, Clay Miner. 19 (1984) 177–193, https://doi.org/10.1180/claymin.1984.019.2.05.

[239] V.A. Drits, G. Besson, F. Muller, An improved model for structural transformations of heat-treated aluminous dioctahedral 2:1 layer silicates, Clay Clay Miner. 43 (1995) 718–731, https://doi.org/10.1346/CCMN.1995.0430608.

[240] F. Wolters, K. Emmerich, Thermal reactions of smectites—relation of dehydroxylation temperature to octahedral structure, Thermochim. Acta 462 (2007) 80–88, https://doi.org/10.1016/j.tca.2007.06.002.

[241] F. Muller, Structural transformation of 2:1 dioctahedral layer silicates during dehydroxylation-rehydroxylation reactions, Clay Clay Miner. 48 (2000) 572–585, https://doi.org/10.1346/ccmn.2000.0480510.

[242] A. Derkowski, A. Kuligiewicz, Rehydroxylation in smectites and other clay minerals observed in-situ with a modified thermogravimetric system, Appl. Clay Sci. 136 (2017) 219–229, https://doi.org/10.1016/j.clay.2016.11.030.

[243] D.L. Carroll, T.F. Kemp, T.J. Bastow, M.E. Smith, Solid-state NMR characterisation of the thermal transformation of a Hungarian white illite, Solid State Nucl. Magn. Reson. 28 (2005) 31–43, https://doi.org/10.1016/j.ssnmr.2005.04.001.

[244] N. Garg, J. Skibsted, Pozzolanic reactivity of a calcined interstratified illite/smectite (70/30) clay, Cem. Concr. Res. 79 (2016) 101–111, https://doi.org/10.1016/j.cemconres.2015.08.006.

[245] G.E. Roch, M.E. Smiths, S.R. Drachman, Solid state NMR characterization of the thermal transformation of an Illite-rich clay, Clay Clay Miner. 46 (1998) 694–704, https://doi.org/10.1346/ccmn.1998.0460610.

[246] K. Emmerich, Spontaneous rehydroxylation of a dehydroxylated Cis-vacant montmorillonite, Clay Clay Miner. 48 (2000) 405–408, https://doi.org/10.1346/ccmn.2000.0480312.

[247] P. Komadel, J. Madejová, Acid activation of clay minerals, in: F. Bergaya, G. Lagaly (Eds.), Handbook of Clay Science, Elsevier, Oxford, 2013, pp. 385–409, , https://doi.org/10.1016/b978-0-08-098258-8.00013-4.

[248] J. Madejová, J. Bujdák, M. Janek, P. Komadel, Comparative FT-IR study of structural modifications during acid treatment of dioctahedral smectites and hectorite, Spectrochim. Acta A Mol. Biomol. Spectrosc. 54 (1998) 1397–1406, https://doi.org/10.1016/s1386-1425(98)00040-7.

[249] A. Steudel, L.F. Batenburg, H.R. Fischer, P.G. Weidler, K. Emmerich, Alteration of non-swelling clay minerals and magadiite by acid activation, Appl. Clay Sci. 44 (2009) 95–104, https://doi.org/10.1016/j.clay.2009.02.001.

[250] A. Steudel, L.F. Batenburg, H.R. Fischer, P.G. Weidler, K. Emmerich, Alteration of swelling clay minerals by acid activation, Appl. Clay Sci. 44 (2009) 105–115, https://doi.org/10.1016/j.clay.2009.02.002.

[251] P. Komadel, J. Bujdák, J. Madejová, V. Šucha, F. Elsass, Effect of non-swelling layers on the dissolution of reduced-charge montmorillonite in hydrochloric acid, Clay Miner. 31 (1996) 333–345, https://doi.org/10.1180/claymin.1996.031.3.04.

[252] O.G. Ingles, Mechanisms of clay stabilization with inorganic acids and alkalis, Soil Research 8 (1970) 81, https://doi.org/10.1071/sr9700081.

[253] C.K. Richardson, R. Markuszewski, K.S. Durham, D.D. Bluhm, Effect of caustic and microwave treatment on clay minerals associated with coal, in: K.S. Vorres (Ed.), Mineral Matter and Ash in Coal, American Chemical Society, Washington, DC, 1986, pp. 513–523, , https://doi.org/10.1021/bk-1986-0301.ch038.

[254] A. Marsh, A. Heath, P. Patureau, M. Evernden, P. Walker, Alkali activation behaviour of un-calcined montmorillonite and illite clay minerals, Appl. Clay Sci. 166 (2018) 250–261, https://doi.org/10.1016/j.clay.2018.09.011.

[255] E. Prud'homme, P. Michaud, E. Joussein, C. Peyratout, A. Smith, S. Rossignol, In situ inorganic foams prepared from various clays at low temperature, Appl. Clay Sci. 51 (2011) 15–22, https://doi.org/10.1016/j.clay.2010.10.016.

[256] G. Sedmale, A. Korovkins, V. Seglins, L. Lindina, Application of chemical trated illite clay for development of ceramics products, IOP Conference Series: Materials Science and Engineering 47 (2013) 012056, , https://doi.org/10.1088/1757-899x/47/1/012056.

[257] I. Sperberga, G. Sedmale, G. Stinkulis, K. Zeila, D. Ulme, Comparative study of illite clay and illite-based geopolymer products, IOP Conference Series: Materials Science and Engineering 18 (2011) 222027, , https://doi.org/10.1088/1757-899x/18/22/222027.

[258] R. Borges, L.M. Dutra, A. Barison, F. Wypych, MAS NMR and EPR study of structural changes in talc and montmorillonite induced by grinding, Clay Miner. 51 (2016) 69–80, https://doi.org/10.1180/claymin.2016.051.1.06.

[259] M. Fernández, M.D. Alba, R.M. Torres Sánchez, Effects of thermal and mechanical treatments on montmorillonite homoionized with mono- and polyvalent cations: insight into the surface and structural changes, Colloids Surf. A Physicochem. Eng. Asp. 423 (2013) 1–10, https://doi.org/10.1016/j.colsurfa.2013.01.040.

[260] M. Schneider, Process technology for efficient and sustainable cement production, Cem. Concr. Res. 78 (2015) 14–23, https://doi.org/10.1016/j.cemconres.2015.05.014.

[261] H.H. Murray, W.D. Keller, Kaolins, kaolins, and kaolins, in: H.H. Murray, W.M. Bundy, C.C. Harvey (Eds.), Kaolin Genesis and Utilization, Clay Minerals Society, Boulder, 1993, pp. 1–24, , https://doi.org/10.1346/CMS-SP-1.1.

[262] A. Autef, E. Joussein, A. Poulesquen, G. Gasgnier, S. Pronier, I. Sobrados, J. Sanz, S. Rossignol, Influence of metakaolin purities on potassium geopolymer formulation: the existence of several networks, J. Colloid Interface Sci. 408 (2013) 43–53, https://doi.org/10.1016/j.jcis.2013.07.024.

[263] S.S. Abe, T. Masunaga, T. Honna, T. Wakatsuki, Comprehensive assessment of the clay mineralogical composition of lowland soils in West Africa, Soil Science and Plant Nutrition 52 (2006) 479–488, https://doi.org/10.1111/j.1747-0765.2006.00060.x.

[264] J.B. Dixon, S.B. Weed, Minerals in soil environments, 2nd ed., Soil Science Society of America, Madison, WI, 1989.

[265] F. Claret, A. Bauer, T. Schäfer, L. Griffault, B. Lanson, Experimental investigation of the interaction of clays with high-pH solutions: a case study from the Callovo-Oxfordian formation, Meuse-Haute Marne underground laboratory (France), Clay Clay Miner. 50 (2002) 633–646, https://doi.org/10.1346/000986002320679369.

[266] H.H. Murray, Correlation of paper-coating quality with degree of crystal perfection of kaolinite, Clay Clay Miner. 4 (1955) 31–40, https://doi.org/10.1346/ccmn.1955.0040105.

[267] H.H. Murray, S.C. Lyons, Correlation of paper-coating quality with degree of crystal perfection of kaolinite, Clay Clay Miner. 4 (1955) 31–40, https://doi.org/10.1346/CCMN.1955.0040105.

[268] A. Marsh, A. Heath, P. Patureau, P. Evernden, P. Walker, Influence of clay minerals and associated minerals in alkali activation of soils, Constr. Build. Mater. 229 (2019) 116816, , https://doi.org/10.1016/j.conbuildmat.2019.116816.

[269] R.I. Yousef, B. El-Eswed, M. Alshaaer, F. Khalili, H. Rahier, Degree of reactivity of two kaolinitic minerals in alkali solution using zeolitic tuff or silica sand filler, Ceram. Int. 38 (2012) 5061–5067, https://doi.org/10.1016/j.ceramint.2012.03.008.

[270] M. Lassinantti Gualtieri, M. Romagnoli, S. Pollastri, A.F. Gualtieri, Inorganic polymers from laterite using activation with phosphoric acid and alkaline sodium silicate solution: mechanical and microstructural properties, Cem. Concr. Res. 67 (2015) 259–270, https://doi.org/10.1016/j.cemconres.2014.08.010.

[271] C. Boutterin, J. Davidovits, Geopolymeric cross-linking (LTGS) and building materials, Geopolymer 88 (1988) 79–88.

[272] I. García-Lodeiro, N. Cherfa, F. Zibouche, A. Fernández-Jimenez, A. Palomo, The role of aluminium in alkali-activated bentonites, Mater. Struct. 48 (2015) 585–597, https://doi.org/10.1617/s11527-014-0447-8.

[273] J.F. Muñoz, T. Easton, J. Dahmen, Using alkali-activated natural aluminosilicate minerals to produce compressed masonry construction materials, Constr. Build. Mater. 95 (2015) 86–95, https://doi.org/10.1016/j.conbuildmat.2015.07.144.

[274] N. Essaidi, B. Samet, S. Baklouti, S. Rossignol, Feasibility of producing geopolymers from two different Tunisian clays before and after calcination at various temperatures, Appl. Clay Sci. 88–89 (2014) 221–227, https://doi.org/10.1016/j.clay.2013.12.006.

[275] K. El Hafid, M. Hajjaji, Effects of the experimental factors on the microstructure and the properties of cured alkali-activated heated clay, Appl. Clay Sci. 116–117 (2015) 202–210, https://doi.org/10.1016/j.clay.2015.03.015.

[276] A. Marsh, A. Heath, P. Patureau, M. Evernden, P. Walker, Phase formation behaviour in alkali activation of clay mixtures, Appl. Clay Sci. 175 (2019) 10–21, https://doi.org/10.1016/j.clay.2019.03.037.

[277] M.B. Diop, M.W. Grutzeck, Sodium silicate activated clay brick, Bull. Eng. Geol. Environ. 67 (2008) 499–505, https://doi.org/10.1007/s10064-008-0160-3.

[278] G. Habert, N. Choupay, G. Escadeillas, D. Guillaume, J.M. Montel, Clay content of argillites: influence on cement based mortars, Appl. Clay Sci. 43 (2009) 322–330, https://doi.org/10.1016/j.clay.2008.09.009.

[279] S.C. Taylor-Lange, E.L. Lamon, K.A. Riding, M.C.G. Juenger, Calcined kaolinite–bentonite clay blends as supplementary cementitious materials, Appl. Clay Sci. 108 (2015) 84–93, https://doi.org/10.1016/j.clay.2015.01.025.

[280] F. Avet, R. Snellings, A. Alujas Diaz, M. Ben Haha, K. Scrivener, Development of a new rapid, relevant and reliable (R3) test method to evaluate the pozzolanic reactivity of calcined kaolinitic clays, Cem. Concr. Res. 85 (2016) 1–11, https://doi.org/10.1016/j.cemconres.2016.02.015.

[281] F. Avet, K. Scrivener, Investigation of the calcined kaolinite content on the

hydration of limestone calcined clay cement (LC3), Cem. Concr. Res. 107 (2018) 124–135, https://doi.org/10.1016/j.cemconres.2018.02.016.

[282] É. Makó, R.L. Frost, J. Kristóf, E. Horváth, The effect of quartz content on the mechanochemical activation of kaolinite, J. Colloid Interface Sci. 244 (2001) 359–364, https://doi.org/10.1006/jcis.2001.7953.

[283] M. Esaifan, H. Rahier, A. Barhoum, H. Khoury, M. Hourani, J. Wastiels, Development of inorganic polymer by alkali-activation of untreated kaolinitic clay: reaction stoichiometry, strength and dimensional stability, Constr. Build. Mater. 91 (2015) 251–259, https://doi.org/10.1016/j.conbuildmat.2015.04.034.

[284] M. Fawer, M. Concannon, W. Rieber, Life cycle inventories for the production of sodium silicates, Int. J. Life Cycle Assess. 4 (1999) 207–212, https://doi.org/10.1007/bf02979498.

[285] W.K.W. Lee, J.S.J. van Deventer, The interface between natural siliceous aggregates and geopolymers, Cem. Concr. Res. 34 (2004) 195–206, https://doi.org/10.1016/s0008-8846(03)00250-3.

[286] F. Pacheco-Torgal, J. Castro-Gomes, S. Jalali, Investigations about the effect of aggregates on strength and microstructure of geopolymeric mine waste mud binders, Cem. Concr. Res. 37 (2007) 933–941, https://doi.org/10.1016/j.cemconres.2007.02.006.

[287] S. Guggenheim, D.C. Bain, F. Bergaya, M.F. Brigatti, V.A. Drits, D.D. Eberl, M.L.L. Formoso, E. Galán, R.J. Merriman, D.R. Peacor, H. Stanjek, T. Watanabe,

Report of the association Internationale pour l'Etude des Argiles (AIPEA) Nomenclature Committee for 2001: order, disorder and crystallinity in phyllosilicates and the use of the 'Crystallinity Index', Clay Miner. 37 (2002) 389–393, https://doi.org/10.1180/0009855023720043.

[288] E.C. Arvaniti, M.C.G. Juenger, S.A. Bernal, J. Duchesne, L. Courard, S. Leroy, J.L. Provis, A. Klemm, N. De Belie, Determination of particle size, surface area, and shape of supplementary cementitious materials by different techniques, Mater. Struct. 48 (2015) 3687–3701, https://doi.org/10.1617/s11527-014-0431-3.

[289] B. Lothenbach, D.A. Kulik, T. Matschei, M. Balonis, L. Baquerizo, B. Dilnesa, G.D. Miron, R.J. Myers, Cemdata18: a chemical thermodynamic database for hydrated Portland cements and alkali-activated materials, Cem. Concr. Res. 115 (2019) 472–506, https://doi.org/10.1016/j.cemconres.2018.04.018.

[290] S.H. Ali, D. Giurco, N. Arndt, E. Nickless, G. Brown, A. Demetriades, R. Durrheim, M.A. Enriquez, J. Kinnaird, A. Littleboy, L.D. Meinert, R. Oberhänsli, J. Salem, R. Schodde, G. Schneider, O. Vidal, N. Yakovleva, Mineral supply for sustainable development requires resource governance, Nature 543 (2017) 367, https://doi.org/10.1038/nature21359.

[291] C.K. Yip, G.C. Lukey, J.L. Provis, J.S.J. van Deventer, Effect of calcium silicate sources on geopolymerisation, Cem. Concr. Res. 38 (2008) 554–564, https://doi.org/10.1016/j.cemconres.2007.11.001.