Review Article

Reaction products, structure and properties of alkali-activated metakaolin cements incorporated with supplementary materials – a review

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\section*{ABSTRACT}

Incorporation of mineral blending and/or modifying additions which are single- or multi-component materials is one of the main trends in the development of both Portland clinker-based and non-clinker cements. There is an increasing scientific and industrial interest in alkali-activated binders as ecologically and technically promising inorganic materials. Progress in this area is also derived from advances in the technologies of production and processing of a wider range of mineral materials from natural and waste origins, and by constant expansion of the raw materials base of alkali-activated materials. This paper reviews (i) alkali-activated metakaolin-based cements incorporated with mineral supplementary materials from the point of view of the supplementary additions raw materials base, features of reaction products, structure, properties and formation process; (ii) a range and classification of mineral additions to alkali-activated metakaolin cements; (iii) the feasibilities of improving the structure and properties of mixed alkali-activated metakaolin cements.

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\section*{1. Introduction}

Alkali activation, which is an approach for the non-fired or low-temperature production of cements from various natural and technogenic aluminosilicate materials whose properties are comparable to those of Portland cement, has gained increasing appeal from the standpoints of theoretical research and practical development \cite{1,2}. Progress in this area has also been derived from a constant expansion of the raw materials base, the possibility of using a wide range of natural and waste alumino-silicate materials \cite{3-5}, and ways to improve the performance of alkali-activated materials (AAMs) through introduction of mineral additions and chemical additives including various fibres \cite{6-10}.

Over the last few decades, calcined clays and especially metakaolin (MK) have become a significant part of the raw materials base of AAMs and can be used both as a main...
aluminosilicate precursor of AAMs and as a supplementary component in blended activated systems. Since 2000, researchers have used MK from different parts of the world to synthesize alkali-activated systems, including Germany, France, UK, USA, Ukraine, Australia, China, Czech Republic, Colombia, Malaysia, Brazil, Iran, Cameroon, Tunisia, Nigeria and Jordan [10].

MK is generated by the calcination of kaolinite clay at temperatures ranging from 500 to 800 °C depending on the purity and crystallinity of the precursor clay [11–15]. The main components are silica (SiO₂, 44.4–73%) and alumina (Al₂O₃, 14.5–47.43%). The MK average particle size and specific surface area are in the range 1.20–38 μm and 2.16–22 m²/g, respectively [10]. According to most researchers the key to the reactivity of MK as compared to kaolinite is the strain in the bonding network induced by thermal dehydroxylation [1]. The main reaction product of secondary reaction taking place during reaction of MK with alkali components (potassium and/or sodium silicate, hydroxide) is an amorphous alkaline aluminosilicate hydrate (Mₓ(SiO₂)ₓ(Al₂O₃)ₓ·nH₂O) known as N-A-S-H gel [16]. The secondary reaction products are zeolites such as hydrosodalite, zeolite P, Na-chabazite, zeolite Y and faujasite [17].

The reaction, structure and properties of the resulting product are controlled by several factors, including the nature and composition of the aluminosilicate source material, the type and concentration of the alkaline activator and curing conditions [1,2,18–20]. The benefits of hardened metakaolin-based alkali-activated materials (MAAMs) can be good thermal [21], chemical [22], and mechanical properties [23]. The properties of AAMs can provide applications as construction materials, as host matrix in waste encapsulation, as a low-cost ceramic, and in fire protection of structures [1,2]. At the same time there can be shortcomings in the use of metakaolin-based alkali-activated cements (MAACs) such as the scarcity of kaolin clays, high alkali demand and high specific surface area of MK leading to a high water demand and consequently high shrinkage and cracking [24].

One of the main trends in the development of both Portland clinker-based and non-traditional cements is the incorporation of mineral blending and/or modifying additions which are single-, double- or ternary-component materials. The research and development of mixed cements is one of the most effective ways to control economic and ecological performance, the tailoring and design of reaction products assemblage, structure, technological and physico-technical properties, and their durability [25–32]. A great number of studies have shown the effectiveness of using various additives for MAACs. This is possible because alkali activation allows not only the production and technical efficiency of alkali-activated binder systems in matrices but also effective interaction between matrix with a wide range of mineral supplementary materials of various sources, compositions and structures.

Despite a diversity of modern inorganic binders (Fig. 1, [33]), there are common theoretical bases for blending and modifying binders. The structural and property formation process of blended cements regardless of the mechanism of mineral matrix hardening (hydration, acid–base or polycrystallization reactions) is complicated and multidimensional. It involves depending on a structural level of influence (macro-, micro-, nanostructure), physical and chemical interactions or both physical and chemical interactions between the starting materials. It is a generally accepted practice to call mineral additions that possess “cementitious ability” and may influence the reaction product composition as “active” and those that do not form reaction products with binding properties as “inert” or simply “fillers”. This distinction is obviously relative, because all types of mineral powders have some influence on the structure and properties of the blended binders. Therefore, they are not only active, but multifunctional, and in most cases mineral powders provide a simultaneous effect on the characteristics of the structure and the properties of the mixed cements. The differences include only the mechanism of influence on the binder gel composition, structure, and properties of the mixed binders. Therefore, the authors of this paper propose to consider “inert” mineral admixtures as “physically active”, and “reactive” as “chemically active” since the latter form hydration products with binding properties. “Physically active” materials do not form hydration products, but they do affect the physical structure and the properties of blended binders. “Physically and chemically active” materials demonstrate both properties [9]. This approach to classification of the activity of supplementary materials is also applied to MAAC.

At the same time the composition of starting materials, hardening mechanism, and reaction products assemblage of every group of binders determines the range of supplementary materials which are suitable and effective for its blending and/or modification. In this paper we intend to review:

- survey of mineral supplementary materials for MAACs;
- the features of reaction products, mechanism of hardening, structure and properties formation process of MAAC incorporated with “physical”, “chemical” and “physical and chemical” materials; and
- the feasibilities of improvement of mixed MAACs structure and properties.

2. Physically active materials

The physical activity of supplementary materials and their beneficial effect on the structure and properties of blended cementing systems is mainly based on the so-called “filler” effect – an increase of packing density, an improvement of pore structure (shape and size distribution of pores), and a decrease in total porosity, shrinkage and cracking by forming a crystalline skeleton. In addition, the changes in structure of the hardened pastes mixed with fillers can result in the appearance of a new structural element – a transitional zone between the mineral matrix and the filler particles which may have a different composition and structure compared to the matrix, thus contributing to the properties of the micro-composite material. Fillers may also have an effect on the hardening process by acting as nucleation sites for reaction products. The main influencing factors of physically active additions are specific surface area, particle size distribution, chemical and mineralogical composition and similarity to mineral matrix, porosity, strength, etc. [34–38].

The following physically active additions for MAACs are considered, classified by their chemical composition.

2.1. Si-based physically active materials

Chemical affinity to the MAAC matrix and high mechanical characteristics provide the positive effects of quartz on its properties [39,40]. Quartz in kaolin which is calcined to produce MK [1] and dissolved silica in activator [2] have been shown to have positive effects on the properties of MAACs. Autef [41], Kuenzel [37], Rashad [38], Buchwald [42], Wan [36] have reported on the strengthening effect of quartz sand on hardened MAAC. Rashad [38] found that quartz filler (grain size <32 μm)-MK activated blended systems displayed higher workability and higher compressive strength before and after exposure to elevated temperatures (Fig. 2). Kuenzel [37] reported increase in viscosity with an increase in sand content (Fig. 3) and a noticeable improvement in mechanical strength of MAAM blended with about 25 vol.% quartz sand (grain size <100 μm) and described this effect by the rule of mixtures. Sand particles also limited the linear shrinkage by forming a supportive network with a fixed void volume.

Concerning the influence of a quartz filler on the reaction rate and microstructural features, Autef [41] found that an increase in quartz sand content (grain size of 90 μm) mixed with MK dilutes the matrix resulting in a decreased geopolymerization/polycondensation reaction. Chemical and mechanical cohesion between the matrix and the sand particle was not observed. However, Wan [36], by energy dispersive X-ray (EDX) mapping in SEM images, indicated the formation of shell by several micrometres around quartz particles, which associates them to the geopolymeric gel as filler materials in MAACs. The XRD and NMR spectra of MAAMS with quartz sand confirmed both the presence of residual quartz sand particles and the dissolution and precipitation of reaction products on quartz particle surfaces. In MAAM synthesized with quartz sand of various size ranges (32–75 μm), the smaller the particle size, the higher is the particle surface involved in the formation of matrix, thus higher fractions of Q3(2Al) and Q4(1Al) are observed in their micro-structures.

2.2. Si,Al-based physically active materials

Gharzouni [43] studied low reactivity clay as an additive to MAAMs. It was stated that the associated minerals in Tunisian clay did not participate in the polycondensation reaction and remained simply agglomerated by the alkaline solution. The optimal properties were obtained for a substitution ratio of Tunisian clay to MK of 50% and a Si/K ratio of the alkaline solution of 0.50.
Hemra [44] reported that 30 wt% of cordierite improved thermal shock resistance of MAAM. After 15 cycles at 800 °C the retained compressive strength decreased from 24.9 to 19.8 MPa which was 20% less than original. The FT-IR spectra of geopolymer composites revealed the cordierite incorporated in the geopolymer structures.

Kaya [45], in investigating red mud as an addition to MAAC found that the iron species originating from red mud in activated blended systems is the key factor responsible for the structural and mechanical features observed. Iron species in the geopolymer system tend to re-precipitate as iron oxide hydroxide, removing OH⁻ ions from the solution and preventing the dissolution of raw materials in the geopolymer matrix to a great extent.

2.3. Ca-based physically active materials

One of the most used physically active supplementary materials both for blended Portland cements and non-clinker cements [46-49] is limestone and MAAC is not an exception.

According to a study by Yip [50], introduction of 20 wt% of calcite into MK, activated by sodium silicate solution (SiO₂/Na₂O ratio of 1.2–2) is found to improve the mechanical strength of the hardened AAM. The obtained result authors explained by contributions of the calcium and magnesium ions to an increase in contact area between the particles and the binder gel. However, the contribution of these ions to the polymerization process is not significant.

Cwirzen [51], in studying the system MK-limestone-NaOH, stated that the presence of limestone enhances the release of Al and Si ions from MK. The amount of leached Ca was generally low in all cases independent of the limestone/MK ratio. The dissolved concentration decreased with time, probably due to solution saturation effects and a reduction in solubility of Ca as the dissolved Si concentration increased. From the experimental data, it was concluded that a small amount of Ca released from LS at an early stage hinders the initial release of Al and Si from MK. However, the authors believe that the actual mechanism is more complex, and involves a complexation and reprecipitation/gel formation process rather than direct hindrance. Newly formed precipitates may be forming on the unreacted particle surfaces and creating some degree of hindrance, but this is likely to be a secondary effect. Later, when the dissolved Ca concentration is lower, the release of Al and Si increases. The main alkali-activation product in investigated pastes is a geopolymer gel with inclusions of unreacted MK, limestone particles, zeolite A, and AFm phases, while other zeolites such as faujasite-like and hydrosodalite phases were also identified at higher reaction temperatures (Fig. 4). The replacement of MK by 50% limestone increased the strength of hardened paste from 4 to 5 MPa (curing temperature 20 °C) and from 5 to 7 MPa (curing temperature 80 °C).

Aboulayt [52] found that height basic environment does not promote the dissolution of calcite, which acts as an inert filler in replacement of MK. Low amounts of Ca²⁺ ions in the initial mixture do not cause a variation of the activation energy.

Qian and Song [53] reported the addition of limestone up to 10% in MK activated by potassium hydroxide improved the mechanical properties and the workability of fresh MAAC paste. Authors suggest it can be attributed to the formation of a more compact structure and a better particle size distribution.

Allali [54] compared the alkali activator nature on the effect of calcareous sand on MAACs. The results suggested a partial surface dissolution of the CaCO₃ phases in the potassium silicate solution whereas no dissolution was observed for the Na-silicate solution. These different behaviours suggest differences in the mechanical properties, since the CaCO₃ can play the role of binder in potassium silicate solution. Contrary to sodium silicate solution, calcareous sand is partially dissolved in potassium silicate media allowing the formation of a Si–O–Ca bond, leading to better mechanical stress whatever the amount of calcareous sand addition.

Fig. 4 – X-ray diffractograms of 10 day-old pastes made using 5 M NaOH solution cured at 80 °C (MK, metakaolin; LS, limestone). Phases identified are: C, calcite; Z, zeolite A; J, faujasite-type zeolite; HS, hydrosodalite; A, AFm phase; M, muscovite; MI, mica; K, kaolinite; Q, quartz [51].
3. Physically and chemically active materials

Unlike physically active materials which usually have a crystalline structure, physically and chemically active supplements contain both crystalline and amorphous phases. From a composition point of view, they are usually high-, low- or calcium-free glassy aluminosilicates. The amorphous part is able to form its own reaction products as a result of alkali activation. The amount of binder gel in blended MAACs increases and changes and a blend of MK and additional aluminosilicates may be considered as a blend of AAMs precursors. Unreacted particles of glassy phase and crystalline mineral additions act as a physically active material. Hence the influence of physically and chemically active materials on MAACs is a combination of the effect of physically active additions on the macro- and microstructure structure level and the effect of the chemically active component on the nanostructural level of the hardened blended activated systems. To beneficial influences from the introduction of a physically active additive described in Section 2 is added the beneficial influence of a chemically active additive.

The effect of physically and chemically active materials is dependent on their composition (especially the presence of Ca, reactive Si and Al), glassy phase content, fineness, type and concentration of the alkali activator, and the curing conditions of activated blending materials.

Since Ca content in alkali-activated systems is one of the key factors influencing the properties of fresh and hardened paste, it is reasonable to separate physically and chemically active materials on Ca-containing and low/non-Ca mineral additions.

3.1. Ca-containing physically and chemically active materials

The combination of aluminosilicate-rich materials with more reactive calcium sources is an effective way to regulate Ca content and to control the reaction rate and reaction products, the micro- and nanostructure and properties of blended activated systems.

One of the most studied and representative Ca-containing physically and chemically active materials is blast furnace slag. Blending of non-calcium aluminosilicate MK and Ca-rich blast furnace slag is beneficial for the acceleration of the condensation reaction (and consequently setting and hardening) [55], porosity decrease [56], improvement of mechanical properties [57], better residual strength after high temperature exposure [58,59], and immobilization of heavy metal wastes [60–62]. Many researchers accept that such properties result from stable coexistence of complex and chemically different reaction products as the high Al-substituted calcium silicate hydrate (C-N-(A)-S-H)-type gel and the alkali aluminosilicate gel N-A-S-H [63,64]. However, acceleration of hardening affects on the rheological properties of MK-blast furnace slag blends. Kadlec [57] noted that increasing potassium silicate activated MK substitution by slag leads to significant reduction of viscosity.

The effect of blast furnace slag on the mechanical properties of alkali-activated MK and optimal blast furnace slag/MK ratio depend on alkali concentration and activator modulus in the case of sodium silicate, because precursors with different reactivities have differing alkali demand [65]. The N-A-S-H component formed at high alkalinity conditions is the main contributor to the mechanical strength, while at lower alkalinity, the presence of C-S-H gel formed from the activation of the blast furnace slag significantly contributes to the binder performance, which is highest in the case where the coexistence of C-S-H and N-A-S-H gels is reached [66]. The C-N-(A)-S-H is a mechanically strong gel composed by a combination of crystalline tobermorite-like structures and amorphous cross-linked products with a relatively high content of silicon in the form of Q^1, Q^2 and Q^3 sites that promote the densification of the microstructures [67–70]. The mechanism of effective coexistence of different binder gels is in C-A-S-H-gel filling the pores and voids in the geopolymer network like a microaggregate, as well as bridging the gaps between different reaction products and unreacted particles [66].

Bignozzi [71,72] showed an improvement in compressive strength and a decrease in porosity of alkali-activated MK incorporated with electric arc furnace and ladle slags.

Kamseu [73] proposed a strengthening mechanism of MAAC incorporated with ladle slag and nepheline syenite. The physical aspect includes the particle packing and homogenous phase distribution which is based on the dissolution of reacting grains and the formation of a shell of reaction products around these grains. The authors observed the formation of C-S-H and N-A-S-H gels (Fig. 5) capable of embedding the particles in continuous matrices with a poorly-identifiable interface transition between paste and aggregate. The formation of C-S-H, N-A-S-H and additional siliceous gels contributed to acting as new nucleating sites for the formation and consolidation of a strength-enhancing system. In terms of the chemistry occurring during the overall process, the action of aggregates in the inorganic polymer composites decreases the Na/Si ratio of N-S-A-H and N-S-H phases as well as Na/Al and thereby improves its chemico-physical equilibrium. The authors believe that a fine powder of nepheline
syenite can be used to remove poorly bounded aluminate oligomers [Al(OH)₄]⁻ in MAAC and this provides the possibility of improving the interface zone for the design of mortars and concretes with optimum performance.

3.2. Low and non-Ca physically and chemically active materials

As fly ash is one of the key precursors for AAMs many studies have considered the results of fly ash-MK mixing. Fly ashes are diverse in composition and that is why differences in reactivity of MK and fly ash caused by differences in composition (especially content of reactive Si and Al) lead to differences in rate of polycondensation reaction and may change the composition of N-A-S-H and its micro- and nanostructure. Yang [74] reported that the partial replacement of fly ash for MK decreases the average reactivity of the solid precursors, resulting in a prolongation of the polymerization stage. This promotes densification of the binding gels prior to hardening, and then a more compact N-A-S-H gel phase with lower Al/Si ratio is formed, leading to higher strength of the hardened pastes. Fernandez-Jiménez [75] observed an increase of mechanical strength of fly-ash-MK blends compared to materials containing only MK. The reason for this is because fly ash is responsible, in part, for an increase in the gel/zeolite ratio in the reaction products (the gel being the main source of the mechanical properties in the resulting material). At the same time, the gel that forms in the fly ash-MK matrices displays a larger percentage of Q¹(3Al) and Q¹(2Al units) and higher Si/Al ratio than the gel that develops in the materials containing only MK.

According to many authors the incorporation of fly ash into MK leads to an increase in fluidity of fresh paste, prolongation of setting times, lower porosity, improvement of mechanical characteristics [76–79], higher impact strength after 20 freeze–thaw cycles [76] and decreased drying shrinkage strain [73]. In studies by Bankowski [80] and Xu [81], fly ash-MK activated systems were found to be effective for immobilization of heavy metals.

According to Papa [82] fluidized bed combustion ash can be conveniently used as a partially reactive filler in combination with the MK powder. The composite material has good thermal performance and compressive strength (30 MPa) suitable for the building sector. Bottom ash and biomass fly ash were also studied as supplementary materials to MAAC [83,84].

Several studies have been conducted on activated zeolite-MK systems. Andrejkovičová [85,86] reported zeolite particles are responsible for the higher amount of crystalline phases which lead to formation of more compact and firm microstructure of blended MAAC relative to that of a reference sample. MAAC introduced with 50% zeolite are characterized by a denser microstructure. Elaborated material showed good adsorption capacities for Pb²⁺ and Cd²⁺.

Lin [87] used as supplementary material to MAAC thin-film transistor liquid-crystal display waste glass melted to 3000 cm²/g. The results showed that both initial and final setting times increased and compressive strength decreased as the replacement levels of MK increased.

MK has also been widely studied as a component of ternary activated systems with aluminosilicate materials of various origin and composition [88-97].

4. Chemically active materials

Materials which are alkali and water soluble, fully amorphous and/or have nanometre size can be considered as chemically active modifiers for MAACs. The reactivity of chemically active modifiers mostly influence structure at the nanoscale.

Chemically active additives for MAACs are also considered depending on their chemical composition.

4.1. Ca-based chemically active materials

In many studies lime, Ca(OH)₂, was incorporated as a Ca-source to MAAC. The alkali activation of lime-MK systems can lead to formation of both C-S-H/CASH and N-A-S-H and results in improvement of MAAC performance [98-101]. The alkalinity of the activator is the key factor influencing reaction development in these systems. Boonjaeng [102] studied the effect of NaOH concentration on reactions of lime-calcined clay mixtures. The strength of lime-MK mixtures of 0.4:1 with alkaline activation at low 0.01 and 0.1 M NaOH concentration was higher due to the formation of C-S-H (I) gel. At slightly higher 1M NaOH concentration, the strength was considerably reduced due to the reduction of C-S-H (I) gel phase. At moderate 3 and 5 M NaOH concentrations, C-S-H (I) gel disappeared while zeolitic products, N-A-S-H and N-C-S-H compounds were formed and strength improved to slightly less than those at the low NaOH concentration. At a high 10 M NaOH concentration, the zeolitic products disappeared and alkali aluminosilicate hydrate was formed, adversely affecting the strength. At low concentration of 1M NaOH, the pozzolanic reaction was dominant. The zeolitic reaction was dominant at medium NaOH concentration (1 M < NaOH < 5 M) and geopolymerization became dominant at high 5 M NaOH concentration.

Pacheco-Torgal [103] noted that the workability of the 10–16 M NaOH activated MK-based fresh mortars decreased with increasing NaOH concentration and increased with the content of calcium hydroxide and superplasticizer. Several studies found that addition of calcium hydroxide to MK shortens setting times [104,105] and have a positive effect on mechanical properties of MAAMs [100,104,105].

4.2. Si-based chemically active materials

Zhang used silica fume with 98% SiO₂ content as a means to compensate the shortage of silicon in MK [106]. Autef [41] found that the increase of amorphous silica in the mixture with MK favours the geopolymerization of MAAM and the amorphous silica was totally consumed during the reaction. Sarkar [107] reported that incorporation of 50% colloidal silica filler decreased the crystallinity of the MAAM matrix. The compressive strength of the blended activated system increased with 13 M NaOH as activator and decreased with sodium silicate activator.
4.3. **Al-based chemically active materials**

Sarkar [107] reported that $\alpha$-Al$_2$O$_3$ was effective for improving the mechanical characteristics of sodium hydroxide and sodium silicate-activated MAACs.

Tchakoute [108] stated that Al$_2$O$_3$ helps to improve the mechanical properties of the material by increasing the geopolymeric phase of the material which helps to imprison the unreacted/partially reacted crystalline phase of the starting material. The limits in dosage of Al$_2$O$_3$ addition for improvement of the hardened MAAC compressive strength for the studied materials were 20% and 40%, increasing compressive strength by 18.1% and 32.4%, respectively.

4.4. **Nano-sized chemically active materials**

The rapid development of nanotechnology has touched the field of AAMs [109–112]. Sumesh [112] reported that a particle size of nano-materials of more than 10 nm is effective in geopolymerization. The particle size of nano-materials used in alkali-activated binder systems is generally larger compared to that of cement based products. Moreover, nano-particle dispersion is influenced positively by alkaline solutions. The optimum content of nano-materials is 1–2% by the weight of binder materials for alkali-activated mortar and paste. The incorporation of nano-materials into AAMs leads to a reduction of Si/Al ratio which is essential for the development of high performance materials. The presence and type of superplasticizer also is important, because nanomaterials significantly reduce the fluidity of the modified pastes. A modified polycarboxylate based superplasticizer was found to be best for workability and strength among the different types studied.

Gao [113] found that MAAC activated with sodium silicate and hydroxide at a solid-to-liquid ratio 1.03 and incorporated with 1% nano-SiO$_2$ had high compressive and flexural strength, high bulk density and low porosity (Fig. 6). The authors believe that this was due to formation of more geopolymeric products in the presence of nano-SiO$_2$ and the filler effect of nano-particles. The reaction product was an amorphous hydrated aluminosilicate, dominated by Q$^4$Si (3Al) and Q$^4$Si (2Al) type 3D structures and modified MAAC contained more structural water and gels, which benefit structural development.

5. **Conclusion**

A review of recent studies in the field of incorporation of mineral supplementary materials into MAAMs was carried out from the point of view of supplementary mineral additions used, reaction product composition, structure, properties and formation process, and revealed:

- The incorporation of physically, physically and chemically, and chemically active mineral additions into inorganic matrices based on MAACs is an effective way to influence the composition, the macro-, micro-, and nano-structural levels and to design AAMs with required properties.

- There is a wide variety of raw materials that can be used as mineral supplementary materials for replacement of metakaolin in metakaolin-based alkali-activated binders up to 50% without loss of mechanical characteristics and providing performance improvement of mixed MAAMs.

- A broad range of characteristics of MAACs may be controlled by the combination of metakaolin with Ca, Si, Al-based mineral materials, notably: condensation reactions, workability, density, pore structure, mechanical characteristics, shrinkage, thermal behaviour at high and low temperatures, and immobilization ability of heavy metals and radionuclides.

The studies in the field of MAACs incorporated with various blending and modifying mineral materials have contributed to scientific developments, widened our understanding of what is feasible, and aided in the commercialization of AAMs. Since the reserves of kaolin clays are limited, the results obtained will be useful for the investigation of AAMs based on the more widely available polymineral calcined clays.

**Conflicts of interest**

The authors declare no conflicts of interest.
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