

Beyond kaolinite content: untangling the influence of other clay properties on the reactivity of calcined clays

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ABSTRACT

Vast quantities of clays are available worldwide for the production of supplementary cementitious materials. However, they have a drawback – their variation in mineralogy and purity. The correlation between kaolinite content and reactivity is well-established for kaolinitic clays. However, a detailed understanding remains incomplete for other mineralogical factors that could also influence reactivity. This study investigated over twenty different kaolinitic, montmorillonitic and mixed clays from various locations and geological origins. Mineralogical and chemical composition were measured via standard characterization techniques. Clays were calcined in a laboratory static furnace; some industrially-calcined clays were also sourced. Chemical reactivity was measured using 7-day cumulative heat via the R3 method (ASTM C1897-20). The influence on early age hydration of blended Portland cements (30 wt.% replacement) was investigated via isothermal calorimetry. A calcined high-purity montmorillonitic clay had equivalent reactivity to a 50% metakaolin calcined clay. In mixed mineralogy clays, Fe-based associated minerals contributed to higher specific surface area; this in turn accelerated hydration kinetics in blended cements containing those calcined clays, leading to under-sulphation. These findings highlight that mixed clays, found in many world regions, have potential beyond what their kaolinite content alone suggests – however, they do present additional challenges around characterization and blend formulation. Whilst kaolinite content can be a useful ‘rule of thumb’ in screening clays, it cannot be solely relied upon as an accurate predictor of reactivity and other key parameters to formulate a blend composition.

KEYWORDS: *associated minerals; blended cements; calcined clays; chemical reactivity; kaolinite*

1. Introduction

To exploit diverse clay resources from a variety of locations for the large scale adoption of calcined clay cement, several research challenges remain. These include understanding how different mineralogical factors affect the reactivity of calcined clays and how to effectively design formulations of calcined clay blended cements. Alongside kaolinite, many different types of clay minerals can be present in clays. 2:1 clay minerals have a layer structure consisting of an octahedral sheet sandwiched between two tetrahedral sheets. This layer structure gives 2:1 clay minerals lower intrinsic reactivity than kaolinite (Fernandez et

al., 2011), yet they can still make a modest contribution to reactivity. ‘Associated minerals’ refer to all other minerals in a clay which are not classified as clay minerals. Whilst associated minerals are largely (but not exclusively) unreactive, they can strongly influence the physico-chemical properties of clays (e.g. specific surface area, adsorption capacity), which could then influence workability and early age hydration kinetics of calcined clay cements. In the United Kingdom (U.K.) and in southern areas of the United States of America (U.S.A.), there are substantial resources of 2:1 clay deposits and mixed mineralogy clays. The mineralogical composition of these clays deviates significantly from the ‘classic’ kaolinitic clays on which the majority of research has been carried out. Kaolinite content has been a highly effective predictor of performance for some kaolinitic clays (Avet and Scrivener, 2018). But to facilitate the adoption of the low purity and/or mixed mineral clays of the U.K. and southern U.S.A., they need to be assessed on their reactivity potential, rather than solely on their kaolinite content. It is imperative to relook at the composition-processing-performance relationships for clays based on reactivity alone, as calcined clays with similar reactivity could present challenges during blend formulation (Zunino et al., 2022). This study uses data for a range of clays from the U.K. and U.S.A. to highlight how mineralogical factors beyond kaolinite can influence calcined clays’ reactivity, as well as the reaction kinetics and blend formulation of calcined clay blended cements.

2. Materials and Methodology

Six clays were chosen from 22 sourced clays (11 from the U.K. and 11 from the U.S.A), and classified into three categories, based on their mineralogy. Kaolinitic clays contained kaolinite as the sole clay mineral (“Kn” prefix); mixed clays contained ≥ 2 clay minerals (e.g. MixedClay_B contained kaolinite and chlorite) or a high proportion of Fe-rich associated minerals (e.g. MixedClayA contained 29 wt.% goethite) (“MixedClay” prefix), and montmorillonitic clays contained montmorillonite as the sole clay mineral (“Mnt” prefix). Table 1 lists the kaolinite content obtained using TGA, and montmorillonite content using Quantitative XRD with a 10% ZnO internal standard. The clays were calcined for 1 hour in a static furnace at the calcination temperatures listed in Table 1, or industrially calcined. Specific surface area (SSA) of calcined clays were measured via the BET method for N₂ sorption isotherms, degassed at 135°C for ≥ 5 h.

Table 1: Summary of source clays and calcination temperatures. SSA values are for post-calcination.

Reactivity groups	Clay notation	Kaolinite (wt.%)	Montmorillonite (wt.%)	Calcination temperature (°C)	SSA (m ² g ⁻¹)	d ₅₀ (µm)
Group A	Kn_A	50%	-	Flash calcined industrially	13.9	24.2
	MixedClay_A	48%	-	Flash calcined industrially	60.9	8.1
	Mnt_A	-	78%	820 °C	47.9	14.1
Group B	Kn_B	26%	-	800 °C	4.8	82.9
	MixedClay_B	29%	-	800 °C	21.0	8.0
	Mnt_B	-	61%	820 °C	5.6	47.6

Reactivity of the calcined clays was measured via the R3 test cumulative heat method (ASTM, 2020), using a TAM Air isothermal calorimeter. Blended cement pastes were prepared with a 52.5R ordinary Portland cement from Heidelberg cement, using a 30 wt.% replacement ratio. Reaction kinetics of the blended cements were measured at 20°C for 9 g of paste, using a TAM Air isothermal calorimeter.

3. Results and Discussion

3.1 Influence of 2:1 clay minerals and associated minerals on reactivity

Data for the calcined clays are plotted in two groups, based on their similar range of R3 cumulative heat (Table 1): 400-550 J / g of SCM for Group A (Fig.1A,C) and 300-350 J / g of SCM for Group B (Fig.1B,D). All these calcined clays were classified as ‘moderately reactive’ (>190 J / g of SCM, 90% confidence limit) as per Londono-Zuluaga et al. (2022). Despite their lack of meta-kaolinite, Mnt_A and Mnt_B exhibit similar 7 day reactivity to the two calcined kaolinitic clays Kn_A and Kn_B, albeit these latter two have a

lower clay mineral content. A distinct difference between these calcined clays' cumulative heat curves is the kinetics of heat evolution, shown in the profile of the cumulative heat curves – Mnt_A and Mnt_B react more slowly, and exhibit non-negligible heat flow at 7 days. Fig.1B presents the cumulative heat curves from the R3 test for the Group B calcined clays. Despite the as-received clays containing similar proportions of montmorillonite, Mnt_A has a noticeably higher 7 day cumulative heat (502 J/g of SCM) than Mnt_B (358 J/g of SCM). This difference is partly attributed to the siliceous associated mineral opal-CT in Mnt_A, as previously observed in similar montmorillonitic clays (He et al., 1996). These examples show how 2:1 clay minerals and associated minerals can make non-negligible contributions to reactivity, which is especially relevant for moderately reactive calcined clays.

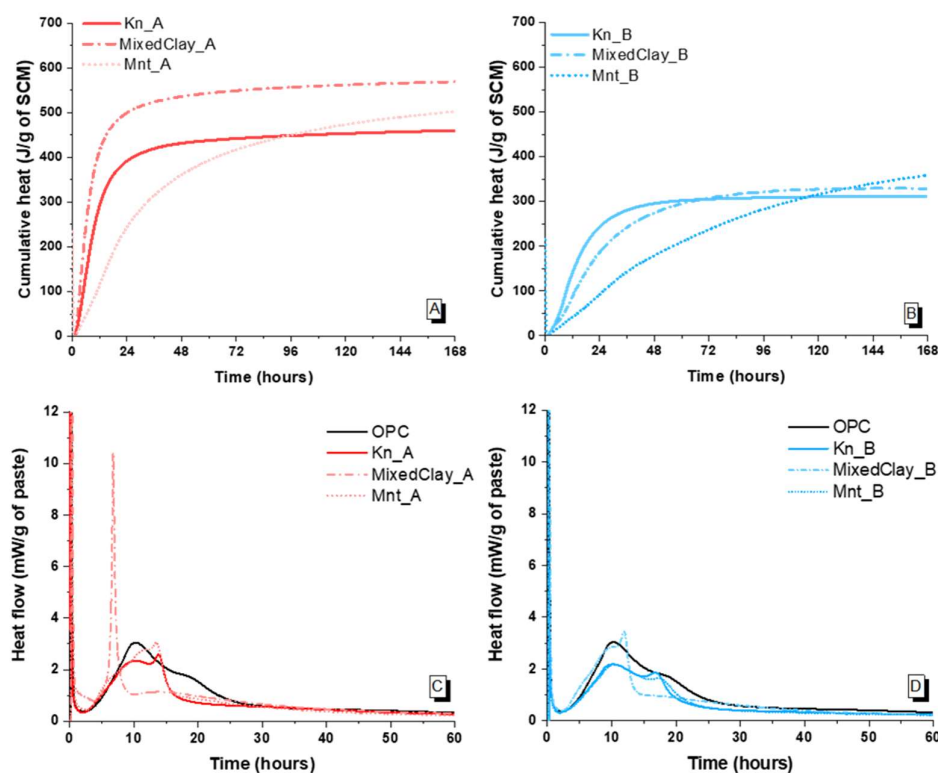


Figure 1: A, B) R3 cumulative heat for calcined clays; C, D) heat flow for calcined clay blended cements.

3.2 Influence of specific surface area on reaction kinetics

Kn_A and MixedClay_A had very different specific surface areas (13.9 and 60.9 m²/g, respectively), but similar kaolinite content (50 and 48 wt.%, respectively) in their un-calcined clays. Despite having similar reactivity (Fig.1A), the reaction kinetics of their calcined clay blended cements are markedly different (Fig. 1C). The high intensity and early onset of the aluminate peak centred at ~8 hours in MixedClay_A was attributed to enhanced heterogeneous nucleation of aluminate phases on extremely fine particles, consistent with its high specific surface area. This was likely to involve the meta-kaolinite themselves – given the MixedClay_A has a lateritic origin, the meta-kaolinite particles are very fine and likely to be highly disordered. A similar earlier onset and higher intensity of aluminate peak for a calcined clay with higher specific surface area was attributed by Tironi et al. (2014) to more extensive structural disorder of kaolinite in the un-calcined clay. Another possible contribution to enhanced nucleation came from extremely fine particles of hematite, which made up 24 wt.% of MixedClay_A. The comparison between Kn_A and MixedClay_A demonstrates the influence that the nature of the meta-kaolinite in a calcined clay (beyond meta-kaolinite content alone), and its associated minerals, can have on reaction kinetics in calcined clay blended cements. Beyond this direct comparison of Kn_A and MixedClay_A, for a range of calcined kaolinitic clays, mixed clays and 2:1 clays, Fig.2 shows that the aluminate peak tends to occur earlier in clays with higher specific surface area.

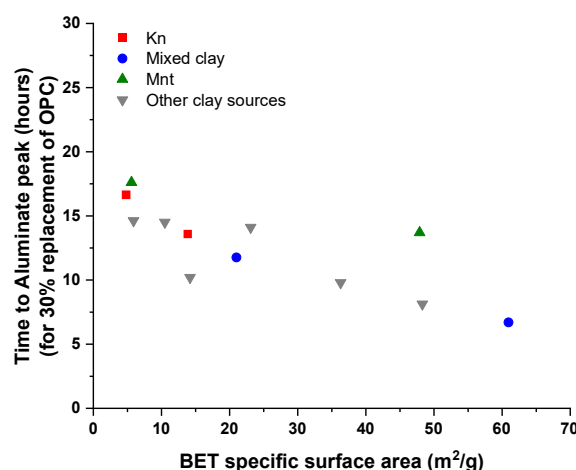


Figure 2: Time to aluminate peak in calcined clay cements as a function of calcined clays' BET surface area

4. Conclusions

Comparing calcined clays with similar reactivity, there was substantial variation in the reaction kinetics in the R3 test and also in the hydration kinetics of calcined clay cements, both of which influence the formulation of binders. Given that specific surface area can be strongly influenced both by the type of clay minerals and associated minerals present in a clay, it is important to understand the various possible mineralogical contributions to sulphate depletion before designing a blend formulation. On a practical basis, it is advisable to measure the specific surface area of a given calcined clay to optimise sulphate adjustments. Whilst kaolinite content may remain the single most important attribute in many kaolinitic clays, this study highlights that the content of 2:1 clay minerals and specific surface area are significant factors affecting reactivity and reaction kinetics for clay resources with non-kaolinitic or mixed clay mineralogy.

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