

Co-calcination of Bauxite Residue with Low-grade Kaolin in Pursuit of an Economic and High-quality Supplementary Cementitious Material

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Abstract

The cement industry roadmap towards decarbonization by 2050 highlights the need for alternative supplementary cementitious materials (SCMs). The use of industrial residues and by-products as SCMs is an established strategy to enhance the circularity and lower the environmental footprint of cement production. In the alumina industry bauxite residue (BR) represents the major by-product for which commercialized valorization pathways are scarce. Previous work showed that BR could be transformed into a robust and high-quality SCM after co-calcination with kaolinite. This thermal treatment of blends of BR and pure kaolinite at 700-750 °C delivered SCMs of acceptable reactivity that contributed to strength development, for a wide range of BR sources. Unfortunately, pure kaolinite is considered expensive from the cement industry's perspective. This paper presents new results to significantly improve the economic feasibility of the co-calcination process with focus on its upscaling. Instead of pure kaolinite, low-grade kaolins with 40 wt% of kaolinite were used. Co-calcined blends of 50 wt% BR and 50 wt% of low-grade kaolin delivered adequate reactivity as SCM and showed a contribution to strength development similar to when the kaolin was calcined without the addition of BR. A cement with strengths complying to the 42.5 N strength class specifications (EN 197-1) could be obtained at a cement replacement level of 30 wt% by co-calcined product (70 wt% of CEM I 52.5 N). Modelling the calcination process offers promising perspectives for industrial implementation.

Keywords: Bauxite residue (Red mud), Supplementary cementitious material, Co-calcination, Kaolin.

1. Introduction

The cement industry is searching for alternative supplementary cementitious materials (SCMs). The currently used by-products are being phased-out due to expected changes in their respective industries: blast furnace slag from iron production and fly ashes from coal combustion. An increased demand for SCMs – due to the climate neutrality roadmaps of the cement sector itself – renders this decreased availability even more pressing [1]. Enter bauxite residue (BR), the high-volume by-product from the alumina industry which can be part of the solution [2]. The use as SCM has been investigated previously, although when used directly a set of issues arise, limiting the potential percentage of cement clinker that can be replaced (or the potential amount of BR that can be valorized). A minor contribution to strength development and detrimental effect on setting kinetics and workability are the most reported issues [3-5]. However, when turned into a slag by melting [6,7] or after co-calcination with kaolinite [5,8] the properties as SCM are superior and more robust.

The co-calcination of BR and pure kaolinite can lower the free sodium in the calcined product, mitigating completely the severe acceleration of cement hydration and excessive rapid setting

observed when using calcined BRs as SCM with a higher initial free sodium content [8]. The flow of mortars is also made more robust for the same reason. The reactivity as SCM and the contribution to strength development could be controlled using the kaolinite content of the blend before calcination; a blend with 20 wt% of kaolinite (80 wt% BR) delivered the desired reactivity and strength profile [8], independently from the origin of the BR investigated.

Unfortunately, pure kaolinite is an expensive resource; the lab-grade material was only used for proof-of-concept purposes. To have real application potential, the process needs to be possible using the low-grade kaolinitic clays which are currently already starting to be sourced for cement production [9]. The present paper targets the study of co-calcination of BR with kaolinitic clay containing 40 wt% of kaolinite. The process is modelled in more detailed to obtain a pre-feasibility and assess further the application potential of the co-calcination process.

2. Materials and Methods

BR from Mytilineos was used, of which more detailed characteristics can be found in previous work [8]. As a brief summary of the most important characteristics, the major elements in the chemical composition (X-ray fluorescence, XRF) and major phases in the composition (X-ray diffraction, XRD) presented previously is repeated in Table 1. The cancrinite phase, including XRD amorphous cancrinite, or the de-silication products in general, was shown to be the most important phase for the reactivity of the BR.

Table 1. Chemical and phase composition of the Mytilineos BR obtained in previous work by XRF and XRD [8].

| Element (as oxide) | wt% | Phase | wt% |
|--------------------------------|------|------------------------------|------|
| Fe ₂ O ₃ | 39.6 | Goethite | 5.4 |
| Al ₂ O ₃ | 21.5 | Hematite | 32.4 |
| SiO ₂ | 8.8 | Gibbsite | 3.2 |
| Na ₂ O | 3.6 | Bayerite | 1.0 |
| CaO | 8.0 | Böhmite | 1.6 |
| TiO ₂ | 5.6 | Diaspore | 11.5 |
| L.O.I. | 9 | Quartz | 0.5 |
| | | Anatase | 0.4 |
| | | Perovskite | 1.5 |
| | | Calcite | 4.7 |
| | | Cancrinite | 12.3 |
| | | Hydrogarnet | 12.9 |
| | | Kaolinite | 2.5 |
| | | Amorphous Fe/Al-(hydr)oxides | 4.7 |
| | | Amorphous cancrinite | 5.4 |

Two kaolinitic clays with 40 wt% of kaolinite were studied. The Soka GA (Soka, France) and the Amberger 40 wt% (Amberger Kaolinwerke, Quarzwerke Gruppe, Germany) were used. The blends for calcination were designed starting from the 20 wt% kaolinite as optimum from previous work: a blend with 50 wt% of a kaolin with 40 wt% of kaolinite also delivers 20 wt% kaolinite in the final blend. Hence, the investigated blends contain 50 wt% of BR and 50 wt% of kaolin: Myt50/K(GA) and Myt50/K(A4), containing the Soka GA and the Amberger 40 wt%, respectively. These samples are compared with a blend Myt80/K containing 80 wt% of BR and 20 wt% of pure kaolinite. The blends are calcined in a box furnace at 750 °C, using a 1-hour dwell time and heating and cooling rates of 3 °C/min.

A measure of the free sodium was obtained from batch leaching tests according to EN 12457-2 with subsequent ICP-OES analysis. The reactivity as SCM of the calcined materials was

investigated using the cumulative heat release in the R³ test (ASTM C1897). Compressive strength of mortars was determined using a replacement of 30 wt% of CEM I 52.5 N from Holcim. Mixing and testing was carried out according to EN 196-1, with curing at > 95% RH (not under water).

3. Results and Discussion

The co-calcination process showed to be effective in reducing the free sodium content of the BR when carried out using pure kaolinite [5, 8]. The sodium concentrations after the batch leaching test in Table 2 suggest that the reduction in free sodium is also stimulated using low-grade kaolinitic clay. Even more, due to the decreased BR content of the blend, resulting in a higher kaolinite/BR ratio, the free sodium content of the calcined material Myt50/K(GA) was lower than that of Myt80/K.

Table 2. Sodium concentration measured in the batch leaching test, a measure for the free sodium.

| | Raw Myt | Myt100 | Myt80/K | Myt50/K(GA) |
|-----------------------------------|---------|--------|---------|-------------|
| Free sodium (mg/kg dry matter BR) | 1350 | 2170 | 1220 | 748 |

The reactivity of the calcined BR-kaolin blends are compared to the calcined clays without BR addition in Figure 1. The reactivity was lower than the clays, as expected. However, the reactivity just reached the target reactivity of 200-250 J/g and can be considered as an SCM with moderate reactivity; it is only slightly lower than when 20 wt% of pure kaolinite was used. The small difference can be attributed to the lower BR content of the Myt50/K(A4) and Myt50/K(GA) and the higher content of non-reactive phases from the low-grade kaolinitic clay. The de-silication product in the BR, sodalite or cancrinite, was shown to be the reactive component in the BR to contribute to the cement hydration reactions [8].

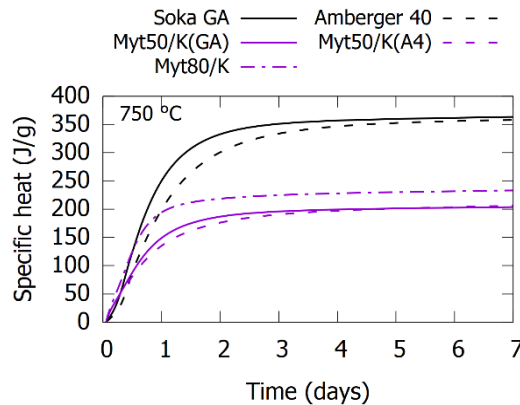


Figure 1. Heat release in the R3 test of the calcined materials.

The compressive strength is shown in Figure 2. The strength of the Myt50/K(GA) and Myt50/K(A4) was slightly lower than that of Myt80/K, especially at 2 and 7 days. This lower strength was due to the lower BR content (or higher inert content of the clay), resulting in less de-silication product to contribute to the hydration reactions at early age. The de-silication products was shown very important for the contribution to strength development at early age, even more than can be suggested from the reactivity data [8]. Due to the involvement of the de-silication product, the strength was comparable to mortars with calcined clay without blending with BR. In other words, calcined clay which is currently sourced for cement production provided the same

compressive strength in standard mortars as the calcined blends of calcined clay and BR. The compressive strength can overall be considered as comfortably fitting the 42.5 N strength class in EN 197-1, which is one of the most used cements.

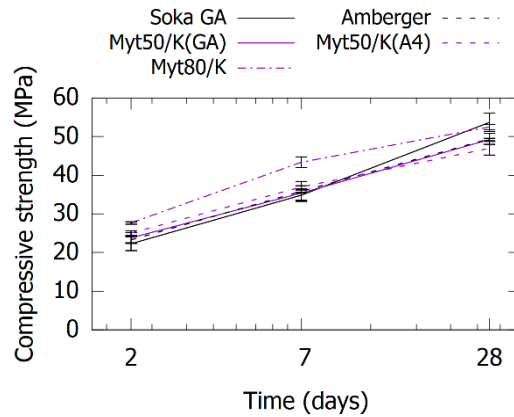


Figure 2. Compressive strength of mortars at 2, 7 and 28 days.

Desirable technical performance as SCM was met with co-calcined BR, even when using economically more interesting low-purity kaolinitic clay. The potential for industrial implementation is evaluated in more detail by setting up a process flow diagram (Figure 3). Using the diagram, a more thorough assessment of the necessary unit processes, equipment, energy requirements, etc. can be made, enabling more accurate estimations of the costs and environmental impacts of the process. Figure 3 shows the process from BR to SCM from left to right. The BR is mixed with the kaolinitic clay before the calcination process, good quality mixing is needed so the kaolinite can capture the free alkalis contained in the BR. The actual co-calcination occurs in the middle of Figure 3. A multiple hearth furnace – well-known for the burning of lime – was selected as one of the furnace types with most potential for the calcination of BR. Other possibilities are for instance a rotary furnace or flash calciner. The SCM product exits at the bottom of the furnace and can be blended with cement (at the site or transported to a cement plant). Only one other output needs to be taken care of: the dust and fumes from the calciner.

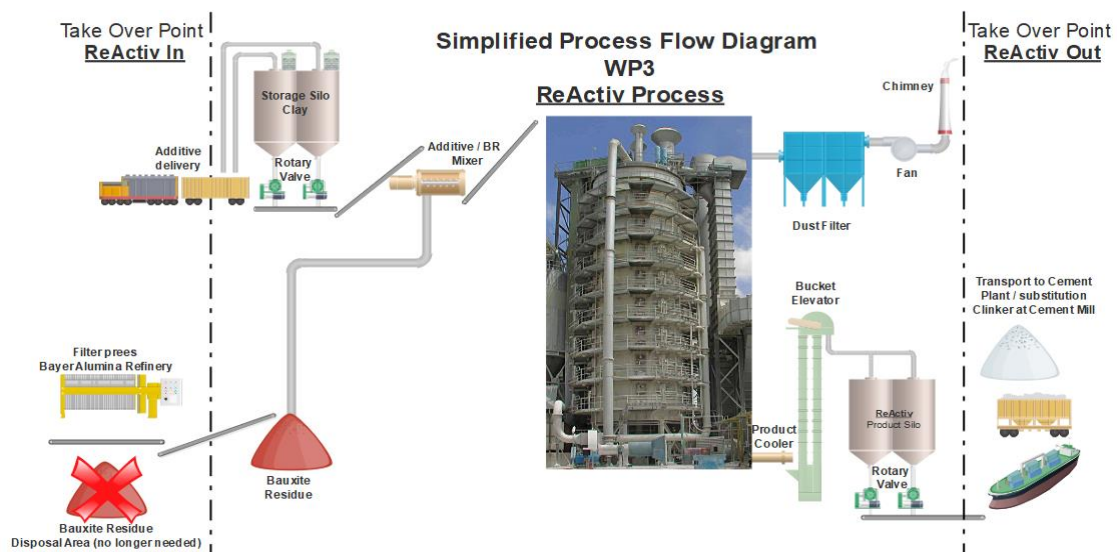


Figure 3. Flowsheet of the co-calcination process with illustrations of the unit processes. The process flow diagram for the co-calcination of BR with kaolinitic clay is simple. Moreover, both the alumina and cement industries have the necessary expertise to operate a calcination plant

due to similar processes in these industries. Hence, the process flow diagram does not reveal any hurdles towards the implementation of the co-calcination process. Future work will focus on calculating the economic and environmental costs of the process in comparison with the status-quo scenario of BR landfilling and cements without calcined BR.

4. Conclusions

The cement sector and alumina sector are both demanding the valorization of bauxite residue (BR) as supplementary cementitious material (SCM). To deliver a high-quality and robust SCM further processing of the BR is necessary. The co-calcination process of BR and low-grade kaolinitic clay was able to produce a SCM with moderate reactivity and low free sodium content. The compressive strength of standard mortars with 30 wt% replacement of CEM I was similar for the co-calcined BR as for the calcined clay reference samples. The economically optimized SCM – with low-grade kaolinitic clay instead of pure kaolinite – thus meeting the desired technical requirements. Modelling the process and laying out the details in a process flow diagram did not reveal weak-spots that might mitigate industrial implementation. The co-calcination process of BR with kaolinitic clays has potential to provide the SCMs of tomorrow's cement industry.

5. References

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