

Strength Development of Blended Cements Containing Co-Calcined Bauxite with Kaolinitic Clay

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Abstract

The co-calcination of bauxite residue (BR) with kaolinitic clay for use as a supplementary cementitious material (SCM) has shown to be a promising processing route to enable the incorporation of more than 20 wt.% of BR in cement formulations. Previous research showed that, among several other improvements, the co-calcination process leads to a reduction in the content of soluble alkali, enhancing workability and maintaining the mechanical performance of mortars up to day 28. Building upon previous results, this work focuses on the strength development of blended cement mortars containing co-calcined BR 28, 56 and 90 days after mixing. Two different SCMs are included in the investigation: one produced using high-purity kaolin and another one produced under the same conditions but using a clay containing 40 wt.% kaolin, which is more advantageous from an economic perspective. The cement replacement ratio with SCM is 30 wt.%, but further replacement of cement with other mineral admixtures, e.g., blast furnace slag, limestone filler, and set regulator, is also explored. The results of this work show that the strength development of mortars containing co-calcined BR with kaolin continues up to day 90. Moreover, it is demonstrated that the use of lower grade kaolin to produce the SCM does not impair mechanical properties when the BR:kaolin weight ratio is maintained.

Keywords: Bauxite Residue, Co-calcination, Cement replacement, Supplementary Cementitious Materials, Late strength.

1. Introduction

One of the challenges in the use of bauxite residue (BR) as a supplementary cementitious material (SCM) is the abundance of soluble Na_2O in the residue. This often leads to the worsening of mortar and concrete properties, e.g., lower final strength and reduced workability [1], although higher early strength can be obtained due to the acceleration of early cement hydration by the soluble Na_2O . Both positive early-age and negative late-age effects of alkalis on the strength of cementitious systems are widely reported, although the mechanisms behind the latter remain under debate [2].

The deterioration of the strength development in systems containing BR is not a rule, but has been sporadically reported in literature. The absence of further strength gain as a function of time beyond 7 days was observed in blended cement mortars containing 30 wt% of calcined BR [3], while strength loss occurred from day 28 in mortars containing 10 wt.% of cement replacement with untreated BR [4]. On the other hand, several studies report continuous strength increase until later ages, e.g., 90 days, even when using untreated BR [5] or combinations of untreated BR with conventional SCMs such as silica fume [6]. Linking the patterns observed in strength development in the literature with the content of soluble Na_2O in the respective BR is not always easy, since data on soluble Na_2O is often not reported.

Aiming at making BR a more suitable resource for use as an SCM, several pretreatments have been developed to decrease the content of soluble Na_2O in BR [5, 7]. The co-calcination of BR with kaolinitic clay is one of such promising technologies [3, 5], as it also results in an SCM that

has moderate-to-high reactivity. This higher reactivity enables cement substitution rates of up to 30 wt.% with co-calcined BR, which translates into the incorporation of 15–27 wt.% of bauxite residue in the cement formulation [8, 9]. The technically optimized BR incorporation rate will depend on intrinsic characteristics of the BR, i.e., content of the reactive desilication product (sodalite, cancrinite), and on the content and purity of the kaolinic clay source used in the co-calcination process. Previous research showed that performance requirements can be fulfilled with lower-grade kaolinic clays [8], which naturally increases the potential of the technology towards industrial implementation.

Although previous results showed that no strength decrease with age is observed up to day 28 in mortars containing co-calcined BR [3], the assessment of the strength development beyond the first 28 days is required to evaluate if long term deterioration of the compressive strength will occur. This will be investigated here. In addition, the use of other SCMs in combination with co-calcined BR in blended cement formulations could further increase cement replacement, as long as there is no harm to performance. Here, the effect of the incorporation of 10 wt.% blast furnace slag on the strength development is investigated, as well as 5 wt.% limestone, and the addition of extra sulphate carrier (2 wt.% of anhydrite). Mortar mixes containing co-calcined BR with clays with different kaolin grades are produced and the strength development is characterized between 28 and 90 days.

2. Materials and Methods

2.1 Starting Materials

The BR used was supplied by the MYTILINEOS alumina plant, in Greece. The Portland cement used was a CEM I 52.5N provided by Holcim. Their chemical composition is shown in Table 1. The total Na₂O content in the BR is 3.6 wt.%, part of which, i.e., 0.135 wt.%, is readily soluble. The latter was taken as the sodium concentration in the leachate after a batch leaching test (EN 12457-2) but might not represent the total soluble Na₂O in the BR given that the EN 12457-2 is a one-stage leaching test.

Table 1. Chemical composition of BR and CEM I, measured by X-ray fluorescence (XRF).

%	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	LOI
BR (MYT) [3]	3.6	< 1	21.5	8.8	< 0,6	0.2	8.0	5.6	39.6	9.0
CEM I 52.5N	< 0,7	1.3	6.0	20.3	0.6	0.7	60.9	0.2	2.8	1.6

Two kaolinitic clays were used in the co-calcination with BR: a pure kaolin Bole white from VWR containing 99 wt.% kaolinite (henceforth named K) and a lower-grade kaolin from Amberger Kaolinwerke (henceforth named K(A4)). The K(A4) clay contained 40 wt% kaolinite, 36 wt% feldspar, 22 wt% quartz, and 2 wt% muscovite/illite, as determined by X-ray diffraction (XRD). Reagent grade CaSO₄ (anhydrite) was used as the sulphate carrier (set regulator) and reagent grade CaCO₃ (calcite) as limestone filler. The blast furnace slag is from Ecocem.

2.2 SCM Production

The dried BR and the respective clay (K or K(A4)) were mixed by hand and calcined to produce the SCMs used in this study. Calcination was done in a Nabertherm box furnace at 750 °C and a dwell time of 1 hour, using a heating and cooling rate of 3 °C/min [3]. Milling was not performed on the co-calcined products, since the particle size of the input materials was fine enough and no coarsening took place after calcination, as shown in previous work [3]. The raw blends used are shown in Table 2. The BR:clay mass ratios varied in order to keep the kaolinite content in the raw blends constant (20 wt%).

Table 4. Sodium concentrations measured in the leachates of 28-day mortars subject to batch leaching tests (EN 12457-2).

Mortar code	Na ($\mu\text{g/L}$)
MYT80/K	120 000
MYT50/K(A4)	76 000

The higher content of soluble Na_2O in the SCM can be beneficial in ternary blends containing slag because the slag reaction can be enhanced by higher alkalinity. Such chemical activation strategy has been applied to fly ash using raw BR [12]. Here, a positive effect of slag activation on strength seems to be observed only in the ternary mix containing extra sulfate (MYT80/K A2 S10). Contrary to what was expected based on this reasoning, in the mortars without extra sulfate (MYT80/K S10 and MYT50/K(A4) S10), higher strength was observed for the lower alkalinity mix (MYT50/K(A4) S10). This suggests that the effect of alkali activation is more complex than anticipated and might be related to the content of the sulphate carrier, although further investigations are needed to assess this hypothesis.

Based on the results of this study, looking at soluble Na_2O can help explain the late-age strength development of mixes containing BR. Nevertheless, more detailed investigations of hydration and microstructure are needed to clarify what is behind the mortar-level observations reported here, especially when it comes to the ternary mixes and the reactions with the set regulator.

4. Conclusions

This study assessed the strength development of mortars containing co-calcined BR with kaolinitic clay for up to 90 days. In addition to co-calcined BR, the blended cement formulations also incorporate anhydrite, limestone filler or slag, resulting in cement replacement ratios between 30 wt.% and 42 wt.%. The results showed that no strength deterioration occurred within the studied timeframe. The addition of extra sulphate carrier was beneficial both in the binary blends and in ternary blends containing slag. In the latter, the extra sulphate addition compensated for the slow reaction of the slag at early age. Moreover, despite the lower reactivity of the SCM produced from lower grade clay, those mortars reached higher late-age strength. This can be explained based on the content of soluble Na_2O in the SCM, which is dependent BR:clay ratio in the raw blend.

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6. References

1. Ruben Snellings, Prannoy Suraneni, and Jørgen Skibsted, Future and emerging supplementary cementitious materials, *Cement and Concrete Research*, 2023, vol. 171, 107199.
2. Mai Zhang et al., Understanding the negative effects of alkalis on long-term strength of Portland cement, *Cement and Concrete Research*, 2023, vol. 174, 107348.
3. Arne Peys, Tobias Hertel, and Ruben Snellings, Co-calcination of bauxite residue with kaolinite in pursuit of a robust and high-quality supplementary cementitious material, *Frontiers in Materials* 2022, vol. 9, 913151.

4. Jose Marcos Ortega et al., Effects of red mud addition in the microstructure, durability and mechanical performance of cement mortars, *Applied Sciences*, 2019, vol. 9, no. 5, 984.
5. Tobias Danner and Harald Justnes, Bauxite residue as supplementary cementitious material – Efforts to reduce the amount of soluble sodium, *Nordic Concrete Research* 2020, vol. 62, no. 1, 1–20.
6. Marko Cecez and Merima Sahinagic-Isovic, Fresh and hardened concrete properties containing red mud and silica fume, *Gradevinar*, 2023, vol. 75, no. 05, 439–449.
7. Tobias Danner, Malin Sletnes, and Harald Justnes, Alkali-reduced Bauxite Residue as Novel SCM, *Nordic Concrete Research*, 2020, vol. 63, no. 2, 1–20.
8. Arne Peys et al., Co-calcination of bauxite residue with low-grade kaolin in pursuit of an economic and high-quality supplementary cementitious material, *Proceedings of 40th International ICSOBA Conference*, Athens, Greece, 10–14 October 2022, *TRAVAUX* 50, 357–362.
9. Arne Peys et al., Co-calcination to produce a synergistic blend of bauxite residue and low-grade kaolinitic clay for use as a supplementary cementitious material, *Cement* (submitted).
10. Natalia Pires Martins et al., Hydration of ternary blended cements comprising co-calcined bauxite residue and kaolinitic clay, *Proceedings of 16th ICCG*, Bangkok, Thailand, 18–22 September 2023, Vol. I, 377–380.
11. Natalia Pires Martins and Arne Peys, Co-calcined bauxite residue with kaolinitic clay in blended cements: synergy with limestone?, *Proceedings of 19th International NOCMAT Conference*, Joao Pessoa, Brazil, 6-8 November 2023.
12. Marcelo Montini et al., Cementitious activity evaluation of bauxite residue and fly ash combination on Portland blended cement, *Proceedings of 37th International ICSOBA Conference and XXV Conference Aluminium of Siberia*, Krasnoyarsk, Russia, 16–20 September, 2019, *TRAVAUX* 48, 491–496.