Co-calcination of Bauxite Residue with Kaolinite to Enhance its Performance as Supplementary Cementitious Material

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Abstract

The cement industry is one of the world's largest users of mineral waste streams and is continuously searching for alternative resources to reduce its environmental impact. With a global cement production of around 4 Gt/year and global bauxite residue (BR) generation of approximately 160 Mt/year, the cement industry is an often targeted market for BR valorization. The use of industrial residues as supplementary cementitious material (SCM) – a material partially replacing the CO_2 intensive clinker in Portland cement – is one of the key solutions to decrease the CO_2 emissions of the cement industry on the short term. The use of BR as SCM can thus be a solution for both the alumina industry and cement industry. Unfortunately, the performance of BR as SCM is poor without additional treatments. Calcination (i.e. thermal treatment at 600 – 900 °C) has been shown to enhance the reactivity of BR and the contribution of BR to compressive strength of cement mortars to some extent. The results of this work show that co-calcination of a blend of BR and kaolinite drastically boosts the reactivity and performance as SCM of the calcined BR-containing product. The calcination of a mixture of 70 wt% BR and 30 wt% kaolinite produces a reactive SCM. When this SCM is blended with Portland cement (30 wt% SCM) in mortar samples, the strength after 7 and 28 days is 85-90% of that of the reference sample, outperforming conventional SCMs such as coal combustion fly ashes.

Keywords: Bauxite residue, Red mud, Cement, Supplementary cementitious material, Calcination.

1. Introduction

The utilization instead of storage of bauxite residue (BR) allows for a reduction in resource depletion by keeping materials in beneficial use for longer. In addition, it would reduce costs and liability of the alumina producers associated with the BR storage facilities. The incentive can even become economically favorable if good quality products can be engineered from BR and introduced on a high volume market. The cement industry is identified as one of the key markets for the high volume use of BR [1]. With a global production of 4 Gt cement/year [2] and 160 Mt BR/year [1] (volumes in 2020), cement could easily absorb BR production volumes. The development of cementitious products from BR is the crucial step forward. Transformation is also required from the perspective of the cement sector. Supplementary cementitious materials (SCMs) are required to further decrease the CO_2 emissions of the cement industry while current SCM resources are in short supply [3].

The performance of BR as an SCM is a matter of dispute in the scientific literature. There is a consensus that high substitution levels of cement for untreated BR (> 20 wt%) are not technically feasible, however, for low replacement levels (< 20 wt%) the reported findings disagree: the contribution of BR to strength development ranges from worse than inert filler to no decrease in strength in comparison with the pure cement [4-7]. The cement hydration is accelerated and workability (flow) decreased by the introduction of BR in the cement blend [4-6, 8]. The reactivity of an SCM measured by the R3 test provides an indication of the amount of hydration products

that can be formed by the reaction of the SCM and therefore the strength development the SCM can cause and the impact on the durability it might have [9]. The reactivity of BR is only slightly higher than that of inert fillers, but this can be slightly increased by calcination if the calcination temperature is below 800 °C [10, 11]. A high quality BR-containing SCM was obtained by Danner et al [4] using co-calcination after blending with kaolinite. This co-calcination process increased the reactivity drastically and reduced the soluble Na content, with positive effects on long-term strength development of the blended cement.

This proceedings paper presents the results of an experimental study on co-calcination of BR and kaolinite for the production of an SCM. The process is applied to BRs from different alumina producers to assess whether the variability in SCM quality in literature might be caused by the characteristics of the different BRs used in the references. The reactivity, soluble Na content and compressive strength development are investigated on calcined and co-calcined BRs.

2.   Materials and Methods

BRs from 3 different alumina plants were used to study the effect of variability in BR characteristics on their performance as SCM. All 3 samples are received in the state as they would be sent to their respective storage area. The samples are dried before the start of the experiments. The chemical composition in Table 1 was determined using ED-XRF on glass beads. The composition is presented as oxides with the elements in the expected main oxidation state. The chemical compositions were similar for all 3 received samples. The samples are predominantly iron-rich. A significant amount of alumina and silica are present at similar levels among the different BRs. Minor elements were Na, Ti and Ca. Approximately 10 wt% of loss on ignition (LOI) was measured for the BRs, mostly related to the hydroxide and hydrate phases, but also due to the potential presence of calcite.

Table 1. Chemical composition of the BRs determined using XRF. All values are in wt%.

BR sample	Fe_2O_3	Al_2O_3	SiO_2	Na_2O	TiO_2	CaO	Others	LOI
Alum (Alum)	47	18	9	5	4	4	2	11
Rio Tinto (Rio)	49	18	10	5	5	2	2	9
Aughinish Alumina (AAL)	49	16	8	4	7	4	2	10

Particle size distribution (PSD) analysis was done after dispersing the BRs in isopropanol using ultrasound. Measurements were made using a Horiba LA-350 laser diffractometer. The distributions in Figure 1 show that the 3 BRs have similar PSDs. The d_{50} was 3-4 µm. Batch leaching tests were carried out on the calcined samples to determine the soluble Na content. The samples were mixed with demineralized water at a liquid/solid ratio of 10 and shaken for 24 hours. After 24 hours, the leachate was collected and the Na concentration was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES).
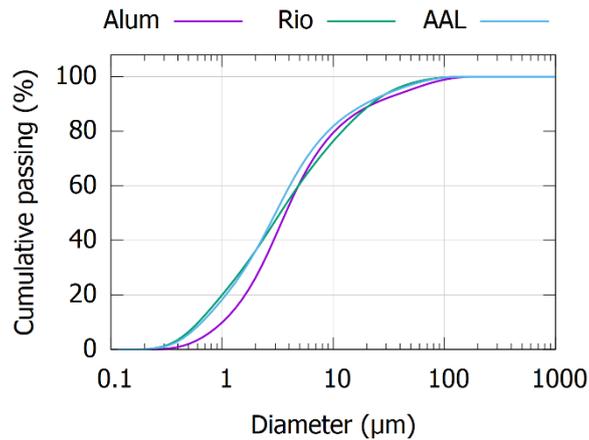
Figure 1. Particle size distributions of the BRs.

The BRs were blended with Bole White from VWR, which is a high purity kaolin (> 95 wt% kaolinite). The dried BR was blended with kaolin (K) in a weight ratio of 70:30 (BR:K). Calcination was carried out on the BR-K blends and the BR itself, using a dwell time of 1 hour at 750 °C and heating and cooling rates of 5 °C/min. The resulting 6 samples were named using an abbreviation of the BR origin, the BR content in wt% and "/K", indicating the addition of kaolinite: i.e. Alum100, Alum70/K, Rio100, Rio70/K, AAL100, AAL70/K. When referring to calcined samples with kaolinite in general BR70/K is used, while BR100 refers to the calcined BRs without kaolinite.

The reactivity of the samples was assessed according to the R3 heat release test (ASTM C1879-20). The sample was mixed with water, $Ca(OH)_2$ and minor quantities of K_2SO_4, KOH and $CaCO_3$ to simulate the Portland cement reaction environment. The heat released by the reaction of sample was determined using an isothermal calorimeter at a curing temperature 40 °C for 7 days. Mortars were made, conforming to EN 196-1:2016 using as binder 70 wt% CEM I 52.5 N (Lafarge-Holcim) and 30 wt% calcined sample. Superplasticizer Master Glenium 51 (BASF, PCE type) was used to compensate for the decreased mortar slump flow by the addition of the calcined samples. Mortar slump was measured according to EN 196-1:2016 and the amount of superplasticizer needed to reach the flow of the CEM I 52.5 N reference sample is provided in Table 2. The compressive strength was measured at 2, 7 and 28 days on 4 specimens per mixture for each age.

Table 2. Superplasticizer dosage required to obtain the same mortar slump flow as the reference.

Calcined sample	Superplasticizer need (ml/kg binder)
Alum100	8.88
Rio100	4.44
AAL100	2.22
Alum70/K	4.44
Rio70/K	4.44
AAL70/K	4.00

3.   Results and Discussion

The calcined samples were characterized using PSD analysis and batch leaching tests. The PSDs in Figure 2 showed a limited influence of the calcination procedure. The particle sizes were similar to those of the raw BRs in Figure 1. No coarsening was observed during the thermal

treatment at 750 °C. A comparison between the BR100 and BR70/K samples showed that the addition of kaolin had a minor coarsening influence on the PSD. The soluble Na levels shown in Table 3 varied from BR to BR and were significantly decreased by the addition of kaolin. Even though the total Na-content determined by XRF in Table 1 showed similar contents for the 3 BRs, the soluble Na in the calcined Alum100 was almost the double of that in the other calcined BRs (Rio100, AAL100). This can explain the observed increased need for superplasticizer shown in Table 2.
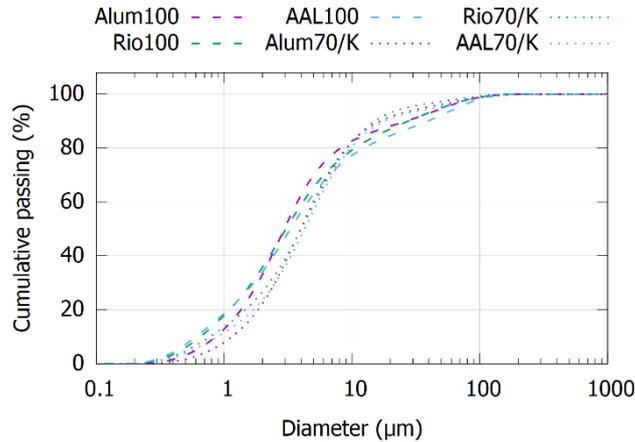

Figure 2. Particle size distributions of the calcined samples.

Table 3. Soluble Na content determined using batch leaching tests.

Sample	Na (mg/kg dry matter)
Alum BR	4540
Rio BR	5100
AAL BR	1780
Alum100	4140
Rio100	2490
AAL100	2340
Alum70/K	1350
Rio70/K	752
AAL70/K	612

The heat release measured by the R3 calorimetry test in Figure 3 enables to compare the reactivity of the calcined samples and the raw BRs. The BR100 samples showed that calcination of the BRs slightly increased the reactivity. The heat release after 7 days of the BR100 samples was however still lower than that of coal fly ashes, which is used as a reference in the Figure 3, and the reactivity as SCM is thus classified as "low". There were only minor differences in reactivity between the BRs. The addition of kaolin drastically increased the reactivity. The heat release at 7 days was more than 300 J/g and the BR70/K samples can be considered as moderately-highly reactive. In addition to a higher total heat release at 7 days than coal fly ashes, the heat in the R3 tests on the BR70/K samples is released much earlier. The fast heat release suggests that the contribution to compressive strength development might be observed from an early age.
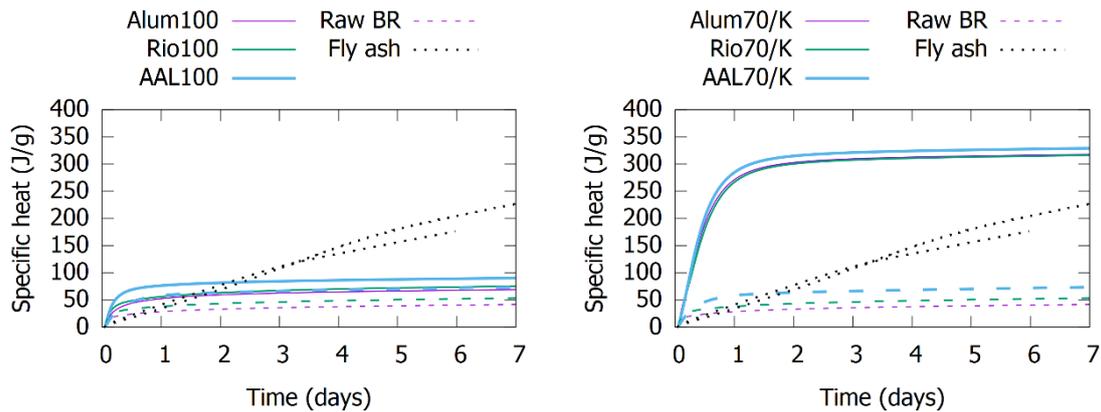
Figure 3. Heat from the R3 heat release test in the isothermal calorimeter. The heat release is normalized to the mass of sample and reported as specific heat. The result of coal fly ashes from Snellings et al. [12] is added as reference.

The compressive strength at 2, 7 and 28 days of mortars including the calcined samples as SCM is shown in Figure 4. The drastic increase in reactivity by the introduction of kaolinite translated into a significant increase of the 7 and 28 days compressive strength. The BR100 samples showed 7 days strengths of 34-39 MPa and 28 days strengths of 40-41 MPa, while the BR70/K samples reached 43-45 and 51-55 MPa, respectively. The 2 days strength was not significantly affected. The 2 days strength was relatively high for a 30 wt% replacement. This can be explained by the soluble Na in the calcined samples, which increases the rate of cement hydration by increasing the alkalinity. The extreme content of soluble Na in the Alum100 (Table 3) resulted in a higher compressive strength at 2 days. The other samples all have similar 2 days strengths: 26-27 MPa.
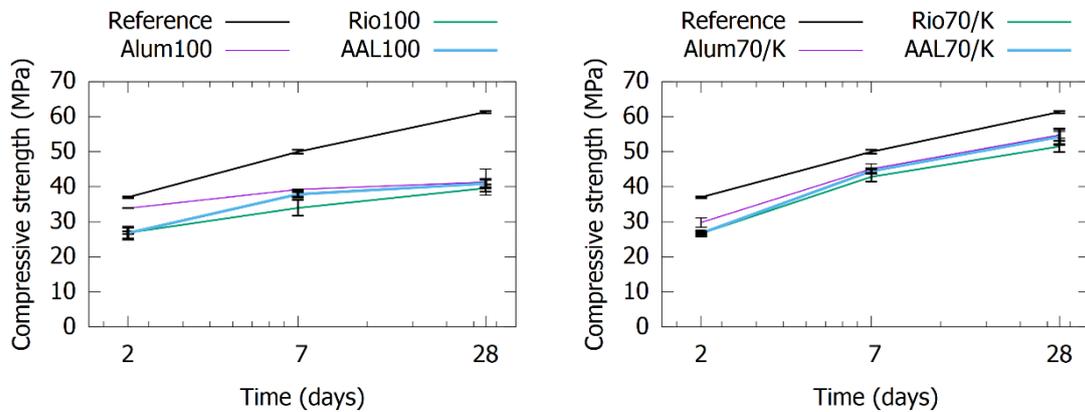

Figure 4. Compressive strength evolution of mortars using a 30 wt% replacement of the CEM I for the calcined samples.

4. Conclusions

The use of bauxite residue (BR) as supplementary cementitious material (SCM) would enable a high-volume utilization of BR and a reduction of the CO_2 emissions of the cement industry. Current state-of-the-art does not present BR as a reactive SCM that can substitute clinker to a significant extent; a pretreatment process has to be designed. A co-calcination process was developed in which BR is calcined in the presence of 30 wt% of kaolinite. This process was validated for 3 BRs from different suppliers. The addition of calcined BR as SCM led to an increased rate of cement hydration due to the soluble Na. In the case of the Alum BR, this resulted in a drastic decrease in workability, but also a faster compressive strength development. The

soluble Na is decreased with the addition of kaolinite and co-calcination. This enabled the technical issues with the Alum BR to be overcome, and for all BR70/K samples a satisfactory strength development was observed, caused by the high pozzolanic reactivity of the co-calcined kaolinite and BR.

5. Acknowledgements

6. References

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