

Co-calcination to produce a synergistic blend of bauxite residue and low-grade kaolinitic clay for use as a supplementary cementitious material

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ABSTRACT

New sources of reactive supplementary cementitious materials (SCMs) are essential to help the cement industry to further lower CO₂ emissions. A co-calcination process in which bauxite residue (BR) is mixed with kaolinitic clay before calcination can deliver such SCM. The main novelty of the work discussed here is that acceptable reactivity as a SCM can be reached when co-calcining the BR with clays having only 40 wt% of kaolinite. The use of such low-grade kaolinitic clay greater increases the process economics and therefore likely increases overall feasibility. A high inherent reactivity of the desilication products present in the BR is the cause of this ability of using low-grade kaolinitic clays. Cement mortars were made with 30 wt% replacement of CEM I, which showed adequate strength at 28 days and increased strength in comparison with calcined clays or other SCMs in the literature at early age (2–7 days). A wide process temperature window with relatively constant reactivity was observed, but a range of 700–750 °C is recommended for process stability. In addition, a life-cycle assessment underlines that at these conditions a sufficiently low embodied CO₂ relative to Portland clinker production is obtained.

1. Introduction

Supplementary cementitious materials (SCMs) constitute one of the key solutions to decarbonise the cement industry [1]. Replacement of Portland clinker by SCMs is considered to be the most impactful technology after carbon capture and storage/utilisation, while it is more easily implemented in a short timeframe [2]. Current use of SCMs is estimated at about 1 Gt/y worldwide (4.2 Gt of cement, global clinker factor average 0.71, SCM ≤ 25 % of cement [3]). The annual production of high quality SCMs has to increase markedly to accommodate their increased demand to accommodate higher clinker replacements. Unfortunately, parallel decarbonisation roadmaps of the energy and steel

sectors indicate a diminishing supply of nowadays' widely used SCMs [4,5]. With coal fired power stations shutting down – especially in the EU – and forecasted increasing recycling and introduction of hydrogen technologies in the steel sector, the availability of pulverised coal combustion fly ashes and ground granulated blast furnace slag will decline as the move towards net zero gathers momentum. New SCMs not only have to be step in to achieve carbon reduction, but also to compensate the losses of fly ash and blast furnace slag.

A large body of research and innovation has targeted the utilisation of calcined clays and limestone as SCMs of the future (LC³ cements) [6]. Due to potential clinker replacements up to 50 wt% substantial CO₂ savings can be made. This technology is especially suited where natural

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clay resources are abundant and alternative industrial by-products are scarce. However, in industrialised countries the capacity of cement to absorb industrial by-products and residues and maintaining the circular nature of cement would be beneficial over sourcing virgin clay. In these cases, utilisation of mineral waste streams can provide a circular and low environmental impact solution. An extensive list of materials has been studied and each waste stream requires a tailored beneficiation treatment to obtain a good quality SCM [7]. Examples of such mineral wastes with promising technical properties (and available volume) are dredging sediments and BR, which after a calcination treatment can provide a substantial contribution to the strength development of cement [8,9].

Some 97–98 % of the 170 Mt of BR generated annually was reported to be landfilled [10]. These BR storage facilities represent a large liability for alumina producers and neighbouring communities. The need for finding valorisation options is high and the use as a cementitious material was identified by the International Aluminium Institute (IAI) as the most promising route [11]. The direct use of BR as SCM does permit substantial clinker replacements in most studies [12,13]. Some specific cases present no substantial strength loss with up to 30 wt% clinker replacement [14], while loss in workability and undesirable acceleration of setting was observed when using > 10 wt% BR. This was related to the free alkali content of the BR [14,15]. Vitrification of BR results in a high reactivity as SCM (~400 J/g after 7 days in R3 test) [16,17], clear contribution to strength development and potentially up to 50 wt% clinker replacements when used in combination with limestone (Giels et al. under review). Avoiding the use of lime and carbon additions and lowering the processing temperature would benefit the sustainability of the process, yet reducing the temperature of treatment, i.e. calcining the BR at 600–800 °C, does not significantly benefit the reactivity as a SCM nor solve the free alkali problems when no other constituents are blended before calcination [18,19].

The co-calcination process was developed to overcome the incompatibility issues of BR and cement. In this process, kaolinite and BR are calcined together. During calcination, the soluble sodium level is lowered substantially [13] as a result of its reaction with the metakaolin phase [9,20]. This avoids severe acceleration and fast setting of a mortar or concrete mixture. The co-calcination process was found to be a generic solution for the broad range of BR types examined in this study, enabling a clinker replacement of 30 wt% whilst still providing > 50 MPa after 28 days in standard mortars [9]. This behaviour was reached with a blend of 20 wt% kaolinite and 80 wt% of BR. The early strength (2 and 7 days) was significantly improved in comparison with other blended cements having 30 wt% clinker replacement. This was attributed to the highly reactive desilication products (DSP, which includes minerals such as sodalite and cancrinite) in the BR that contribute to strength development at early ages [9]. These DSP are formed in the Bayer process due to the reaction of NaOH with clay phases in bauxite and are thus sodium aluminosilicates. The initial experimental work was carried out using high-purity kaolinite, which is an expensive resource. For developing an economically feasible process, lower grades of kaolinitic clay should be applied, similar to those used in LC³ cements. Before further upscaling, a better view should be obtained on the process itself and its robustness in terms of temperature and duration of calcination. Additionally, the process flowsheet and necessary equipment need to be defined for a proper evaluation of the feasibility.

This work seeks to determine the optimal co-calcination process to produce SCMs from BR and kaolinitic clay. The synergetic reactions between the two during co-calcination are optimised from a techno-economic perspective, while assessing the embodied CO₂ of the calcined material as well. Enhancing the economic feasibility of co-calcination is undertaken by testing blends of BR and low-grade kaolinitic clay (down to 40 wt% purity). A secondary effect of this study was unravelling the inherent reactivity of the de-silication product in the BR, underlining its importance for the use of BR as SCM. The large discussion section in this paper targets to put the technology from the

perspective of the alumina and cement industries.

2. Materials and methods

2.1. Experimental

The experiments in this paper are focused on BR from Metlen Energy & Metals' Agios Nikolaos plant (designated "Myt" in the naming of samples). The chemical composition by X-ray fluorescence (XRF), phase composition from X-ray diffraction (XRD), and particle size distribution (PSD) from laser diffraction are reported in Table 1. This table contains the relevant characteristics of the BR for this paper obtained in previous work [9]. All other experiments described in the continuation of the paper are original. The cancrinite will also be referred to in the continuation of the paper as desilication products (DSP). DSP are silicate minerals - general composition sodium aluminium hydro silicate - which form during the Bayer process due to the "reactive silica" compounds, such as kaolinite, present in the bauxite and are removed with the BR. Often, these are present in the hydroxylated crystal form sodalite or cancrinite (Na₈Al₆Si₆O₂₄(OH)₂ or Na₆Ca₂Al₆Si₆O₂₄(OH)₄). The raw data was gathered from previous work [9], where also the characterisation methodology was developed and explained in detail. High-purity kaolinite was obtained from VWR. Low-grade kaolinitic clay was supplied by Soka (Soka CL containing 75 wt% kaolinite + 18 wt% muscovite/illite + 7 wt% quartz, Soka GA - 40 wt% kaolinite + 60 wt% quartz) and Amberger Kaolinwerke (Amberger 40 - 40 wt% kaolinite + 36 wt% feldspar + 22 wt% quartz + 2 wt% muscovite/illite). The phase compositions were determined using XRD according to the same procedure as described later for the calcined materials.

Calcination was carried out in a Nabertherm box furnace in 250 g batches in alumina crucibles. The reported temperatures are calculated temperatures at the sample location based on calibration experiments using a thermocouple. The calcination temperature was 750 °C and dwell time 1 h unless otherwise mentioned in the results section. The heating and cooling rate was 3 °C/min. The raw blends of BR and clay investigated in this paper are listed in Table 2; mixing was carried out manually using dried materials until no colour difference was observed, afterwards at least 10 revolutions were carried out in a closed container. No milling after calcination was required, as shown in previous work [9].

X-ray diffraction measurements were carried out on a PANalytical Empyrean equipped with a Co tube. HighScore X'Pert Plus and the PDF-4 database was used for qualitative analysis, although only relevant selected phases were considered. These structures are reported in the supplementary information of a previous paper [9]. Quantitative phase analysis was carried out using Rietveld refinement in HighScore X'Pert Plus and Profex in parallel to check the robustness of the results towards the quantification strategy. The amorphous content is calculated using the external standard method, the external standard was measured less

Table 1
Characteristics of the BR obtained in previous work [9].

| XRF (wt%) | | XRD (wt%) | | Percentiles (µm) | |
|--------------------------------|------|-------------|------|------------------|------|
| Fe ₂ O ₃ | 39.6 | Hematite | 32.4 | d ₉₀ | 12.0 |
| Al ₂ O ₃ | 21.5 | Goethite | 5.4 | d ₅₀ | 2.9 |
| SiO ₂ | 8.8 | Gibbsite | 3.2 | d ₁₀ | 0.5 |
| CaO | 8.0 | Bayerite | 1.0 | | |
| TiO ₂ | 5.6 | Boehmite | 1.6 | | |
| Na ₂ O | 3.6 | Diaspore | 11.5 | | |
| LOI (TGA) | 9.0 | Quartz | 0.5 | | |
| | | Anatase | 0.4 | | |
| | | Perovskite | 1.5 | | |
| | | Calcite | 4.7 | | |
| | | Cancrinite | 12.3 | | |
| | | Hydrogarnet | 12.9 | | |
| | | Kaolinite | 2.5 | | |
| | | Amorphous | 10.1 | | |

Table 2

Raw blends for co-calcination to produce SCMs.

| Sample name | Type of clay | BR content (wt%) |
|-------------|---------------------------------------|------------------|
| Myt100 | / | 100 |
| Myt90/K | Kaolinite VWR (99 wt% kaolinite) | 90 |
| Myt80/K | Kaolinite VWR (99 wt% kaolinite) | 80 |
| Myt70/K | Kaolinite VWR (99 wt% kaolinite) | 70 |
| Myt75/K(CL) | Kaolin Soka CL (75 wt% kaolinite) | 75 |
| Myt50/K(GA) | Kaolin Soka GA (40 wt% kaolinite) | 50 |
| Myt50/K(A4) | Kaolin Amberger 40 (40 wt% kaolinite) | 50 |

than 10 days before/after the sample measurements.

The reactivity of the calcined materials was measured using the R3 test (ASTM C1897-20), in an isothermal calorimeter (TAM Air) for 7 days at 40 °C. Mortars were made and tested according to EN 196-1. Unless otherwise mentioned, Portland cement (PC), CEM I 52.5 N from Holcim Saint-Pierre-la-Cour, France, was replaced at 30 wt% with calcined material. The mortar mixtures tested in this study are listed in Table 3 (all mixtures included 1350 g of CEN sand and 225 g of demi-water). Superplasticiser Master Glenium 51 (PCE, 35 wt% active content) was added until the mortar flow, measured according to EN 1015-3, reached the same value as the reference PC without calcined material. An amount of 2–4 g of superplasticiser per kg cement was needed for achieving this flow. Curing was carried out in a high humidity climate chamber (> 95 % RH). The strength was tested on 2 prisms of 4 × 4 × 16 cm (i.e. 4 compressive strength tests) at 2, 7, and 28 days after mixing.

Table 3

Mix-proportions of the mortars using the mixture name as presented in the results and discussion section.

| Mixture name | Portland cement (g) | SCM (g) | Type of SCM (see also Table 2) |
|-------------------------|---------------------|---------|--|
| CEM I | 450 | 0 | None |
| Myt100 | 315 | 135 | Myt100 calcined at 750 °C with 1 h dwell time |
| Myt90/K Myt90/K-30 % | 315 | 135 | Myt90/K calcined at 750 °C with 1 h dwell time |
| Myt80/K Myt80/K-30 % | 315 | 135 | Myt80/K calcined at 750 °C with 1 h dwell time |
| Myt70/K | 315 | 135 | Myt80/K calcined at 750 °C with 1 h dwell time |
| Myt90/K-40 % | 270 | 180 | Myt90/K calcined at 750 °C with 1 h dwell time |
| Myt80/K-40 % | 270 | 180 | Myt80/K calcined at 750 °C with 1 h dwell time |
| 650 °C – 20 min | 315 | 135 | Myt80/K calcined at 650 °C with 20 min dwell time |
| 650 °C – 60 min | 315 | 135 | Myt80/K calcined at 650 °C with 1 hour dwell time |
| 700 °C – 20 min | 315 | 135 | Myt80/K calcined at 700 °C with 20 min dwell time |
| 700 °C – 60 min | 315 | 135 | Myt80/K calcined at 700 °C with 1 hour dwell time |
| 750 °C – 20 min | 315 | 135 | Myt80/K calcined at 750 °C with 20 min dwell time |
| 750 °C – 60 min | 315 | 135 | Myt80/K calcined at 750 °C with 1 h dwell time |
| Myt75/K(CL) | 315 | 135 | Myt75/K(CL) calcined at 750 °C with 1 h dwell time |
| Myt50/K(GA) | 315 | 135 | Myt50/K(GA) calcined at 750 °C with 1 h dwell time |
| Myt50/K(A4) | 315 | 135 | Myt50/K(A4) calcined at 750 °C with 1 h dwell time |
| Soka GA | 315 | 135 | Soka GA clay (without BR) calcined at 750 °C with 1 h dwell time |
| Amberger 40 | 315 | 135 | Amberger 40 clay (without BR) calcined at 750 °C with 1 h dwell time |

2.2. Life cycle assessment (LCA)

Process flowsheet

A potential industrial scale flowsheet of the co-calcination process is provided in Fig. 1, where the process from BR and kaolinitic clay to SCM goes from left to right. The scheme is simple and apart from powder handling and storage, the calciner is the only major equipment. To this end, a multiple hearth furnace was selected. This was chosen over the rotary furnace for its capacity of treating fine dusty materials and has an estimated thermal energy requirement of 987 MJ/t of calcined product [21]. The MHF was chosen over the flash calciner because it was theorised that sufficient dwell time is necessary to ensure the uptake of alkalis in the metakaolin phase [9].

System boundaries

A cradle-to-gate analysis was conducted, including processes within raw material extraction and preparation, co-calcination of kaolin with BR, and transportation. The system boundaries of the co-calcination of BR include unit processes, such as the milling of kaolin clay, mixing of kaolin clay with BR, the pre-heating of combustion air, raw mix calcination, and subsequent cooling, as illustrated in Fig. 1. The functional unit is 1 kg of co-calcined BR at the factory gate. Production is modelled as occurring in Europe. The evaluation did not consider activities related to machinery and equipment production and maintenance.

Inventory analysis and modelling approach

The analysis was carried out using the Activity Browser software [22], in conjunction with data from the ecoinvent database v3.9.1 [23] covering the kaolin production, electricity, and heat production. Direct inputs were considered focusing on material flows and energy requirements for the co-calcination unit process. Our baseline model represented the co-calcination of BR at 700 °C for 60 min of dwell time. A sensitivity analysis was conducted changing the dwell time from 60 min to 20 min. The shift in energy demand between these two dwell times is caused by differences in radiative energy losses, leading to ~ 10 % reduction in energy requirements when transitioning from the 60 min to the 20 min dwell time scenario. In the present study, BR was allocated using a cut-off approach, i.e. the impacts of its production were attributed to its primary (upstream) producer, i.e., the alumina industry.

Impact assessment

The ReCiPe 2016 method at midpoint level ('hierarchist' approach) was adopted for the life cycle impact assessment, focusing on climate change impact.

3. Results

The objective of the co-calcination treatment is to provide (1) a reactive SCM (≥ 200 J/g in the R3 test) that (2) does not provide severe acceleration or workability issues (no flash setting due to high soluble sodium content) and (3) contributes substantially to the strength development enabling a clinker replacement of ≥ 30 wt% (4) in an economically and environmentally effective way (using economically favourable constituents and processes). The avoidance of severe acceleration and workability issues was shown to be inherent to the co-calcination process in previous work [9]. The results shown in the sections below target the production of a reactive SCM with substantial strength contribution in an economic (using low-grade kaolinitic clay) and environmentally sound (shown using LCA) process.

3.1. Verification of the required kaolinite content

The cumulative heat during the R3 test on Metlen BR co-calcined with pure kaolinite is shown in Fig. 2. A substantial fraction of the heat is evolved during the first day after mixing. The results are well-aligned with the data from previous work [9], where blends with the same ratios were made using BRs from three other producers. Presently used SCMs such as coal fly ashes deliver a heat after 7 days of 200–250

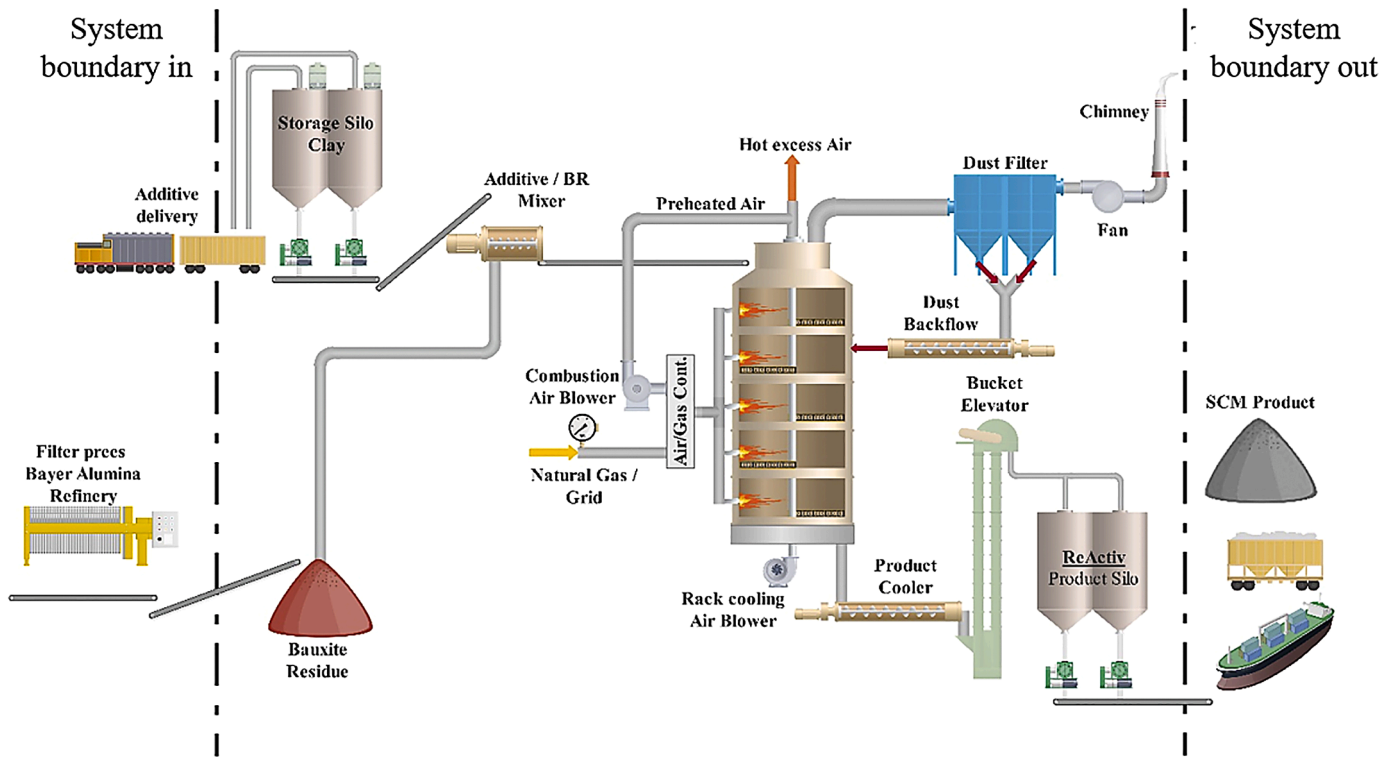


Fig. 1. Process flow sheet for co-calcination of BR, modified from Konlechner et al. [21].

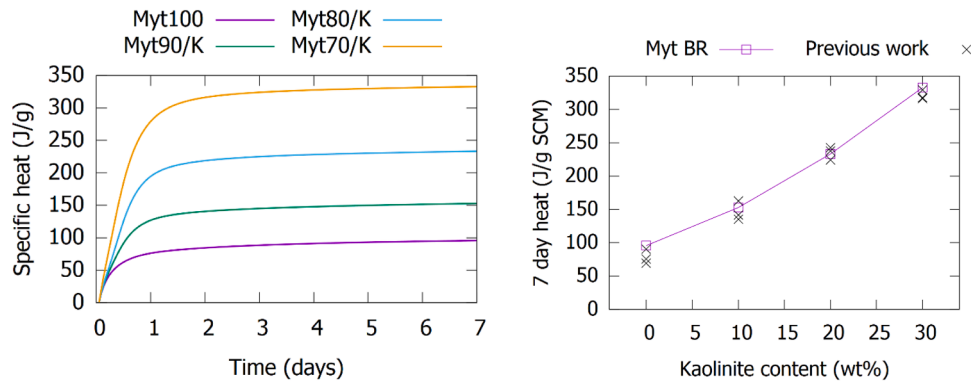


Fig. 2. Heat released during the R3 reactivity test of the co-calcined BR using 0–30 wt% of kaolinite in the raw mix for calcination.

J/g in the R3 test [24] or in a more broad set of samples 160–360 J/g [25], suggesting that 20 wt% of kaolinite (Myt80/K) would be a suitable content from the perspective of pozzolanic reactivity as its heat is situated in the middle of this range.

The compressive strength of mortars with 30 wt% replacement of PC (CEM I) for co-calcined material is shown in Fig. 3. The relative strength (strength divided by strength of the Portland cement reference sample) is shown on the secondary y-axis and indicated with grey squares. The strength after 2 days is independent of the kaolinite content and about 77 % of the reference PC sample, which is high compared to literature values that not often show strength reductions lower than the replacement ratio at 2 days, even for blast furnace slag [26–28]. This is most likely caused by the alkali content of the co-calcined BR or by an extended filler effect due to its fineness. After 7 days of curing, the strength values start to diverge among the samples with different kaolinite contents, although even the lowest values still represent a relative strength of 82 %. This is caused by the substantial reactivity of the SCMs at early age, shown in the R3 test. Previous work showed that

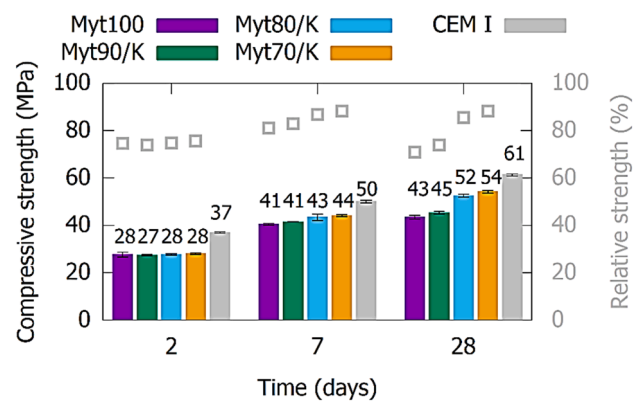


Fig. 3. Compressive strength in absolute values and relative to the reference PC (CEM I) of the mortars with 30 wt% PC replacement with co-calcined BR using 0–30 wt% of kaolinite in the raw mix for calcination.

the desilication products, cancrinite and sodalite, are causing this significant early age strength enhancement [9]. More notable differences are observed after 28 days and the increase in strength between 7 and 28 days are correlated with the initial kaolinite content of the blend. This suggests that the later age strength increase is mostly caused by the pozzolanic reaction of the metakaolin phase. The cements comprising 30 wt% of Myt80/K and Myt70/K can comfortably qualify as 42.5 R cements according to EN 197-1, while for Myt90/K, this is less definitive leaving less room for variation during production. The cements including Myt90/K and Myt100 should rather be seen as 32.5 R cements.

Increased replacement of PC (from 30 to 40 wt%) was explored using the Myt80/K and Myt90/K SCMs. The compressive strengths in Fig. 4 show, as expected, a further decrease of the compressive strengths with increasing replacement of PC at all ages. The replacement of PC by 40 wt% Myt90/K could still deliver a 32.5 R cement with comfortable safety margins. The difference between the requirements for 42.5 R cement and the strength profile of the mortars with 40 wt% Myt80/K becomes smaller, but if produced in a sufficiently robust process, the strength levels of 24 MPa at 2 days (> 20 MPa) and 48 MPa at 28 days (> 42.5 MPa) could be assessed as sufficient. However, as the remainder of the study focussed on lower-purity kaolinitic clays which is expected to cause loss in contribution to strength development, a larger margin is considered necessary and the cement with 30 wt% of Myt80/K is selected as optimal for continued developments.

The repeatability of the compressive strength was assessed based on 16 compressive strength values per testing age. At four different times over a year, two EN196-1 standard mortar mixtures were made to have sufficient prisms for testing. The 16 results per testing age were used for computing the box-plots shown in Fig. 5. The box-plots are narrow, showing a high repeatability of the tests. The single test results ranged from minimum 25.3 to maximum 31.6 MPa at 2 days, 41.1 to 45.8 MPa (outlier 39.8 MPa) at 7 days, and 48.0 to 55.8 MPa at 28 days. The results between the first and third quartile could all be rounded off to 28–30 MPa at 2 days, 43–44 MPa at 7 days, and 52–54 MPa.

3.2. Technical optimisation of the calcination process

Fig. 6 shows the cumulative heat from R3 test in isothermal calorimetry after 7 days as a function of calcination temperature (650–850 °C) and dwell time (20–60 min). Only minor variations are observed. Overall, a slightly higher reactivity is expected and observed for shorter calcination times; an adverse effect is only observed at 650 °C. This can be explained by the incomplete conversion of kaolinite to metakaolin. The latter is shown in the quantified phase composition in Fig. 7, where the sample calcined at 650 °C for 20 min is the only one with residual kaolinite. Future work might be needed to clarify whether the sample

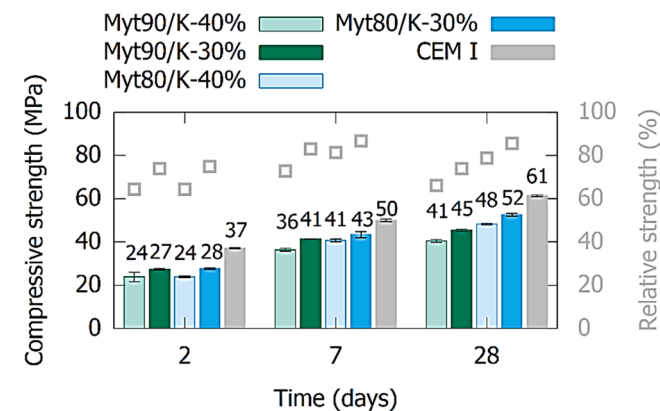


Fig. 4. Compressive strength in absolute values and relative to the reference PC (CEM I) of the mortars with 30–40 wt% PC replacement with co-calcined BR using 10–20 wt% of kaolinite in the raw mix for calcination.

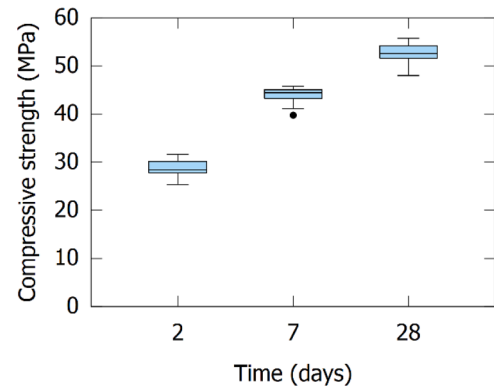


Fig. 5. Box-plots illustrating the statistical analysis on the compressive strength of the mortars with 30 wt% PC replacement with co-calcined BR using 20 wt% of kaolinite in the raw mix for calcination.

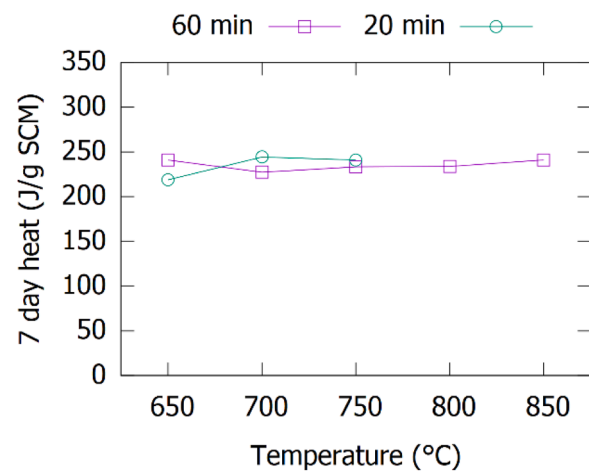


Fig. 6. Heat after 7 days in the R3 reactivity test of the co-calcined BR using 20 wt% of kaolinite in the raw mix for calcination as a function of time and temperature maintained in the calcination process.

size influences the kinetics of kaolinite conversion. The remainder of the phase composition is largely constant, which is in line with the unchanging reactivity. No additional high temperature phases were detected < 800 °C. Work by Danner et al. [13] shows that high temperature phases start forming from 800 °C and more extensively from 1000 °C onwards, lowering substantially the reactivity as SCM. Calcite started to decompose at 750 °C, but a dwell time of 1 hour was needed to have a significant effect on its content. No free lime or other additional crystalline Ca-containing phase was detected, so the Ca was also incorporated in the amorphous phase.

The compressive strength shown in Fig. 8 is equally unaffected by the calcination process parameters investigated. Only 750 °C and 60 min seems to be statistically significantly different from a visual comparison of the 28 days average strength and standard deviations. In view of the variability discussed previously based on Fig. 5, this difference is un-substantial despite the statistical significance in the current series of experiments. In other words, calcination at 700 °C might be slightly better than at 750 °C, but only marginal gains are to be expected. On the other hand, when calcining at 650 °C, temperature control and control of the residence time is crucial due to the potential incomplete conversion of kaolinite when going slightly lower and shorter.

A crucial factor to consider when choosing the optimal process parameters is their impact on the CO₂ footprint. An LCA study was conducted to investigate the impacts on climate change of calcination technology with respect to dwell time variations. The findings in Fig. 9

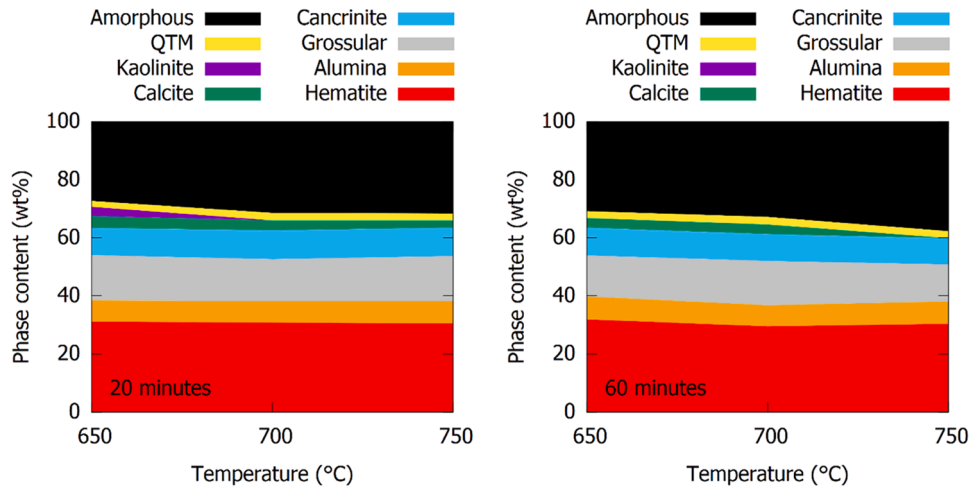


Fig. 7. Phase composition from Rietveld refinement after XRD measurements of the co-calcined BR using 20 wt% of kaolinite in the raw mix for calcination as a function of time and temperature maintained in the calcination process. QTM is a collection of minor phases (quartz, titanium-containing phases, and muscovite).

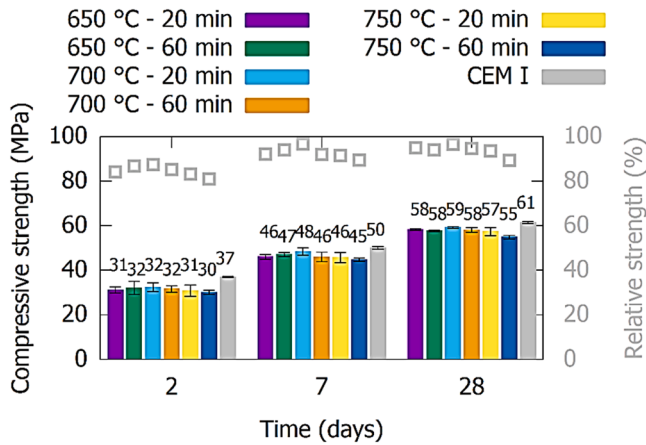


Fig. 8. Compressive strength in absolute values and relative to the reference PC (CEM I) test of mortars with 30 wt% PC replacement with co-calcined BR using 20 wt% of kaolinite in the raw mix for calcination as a function of time and temperature maintained in the calcination process.

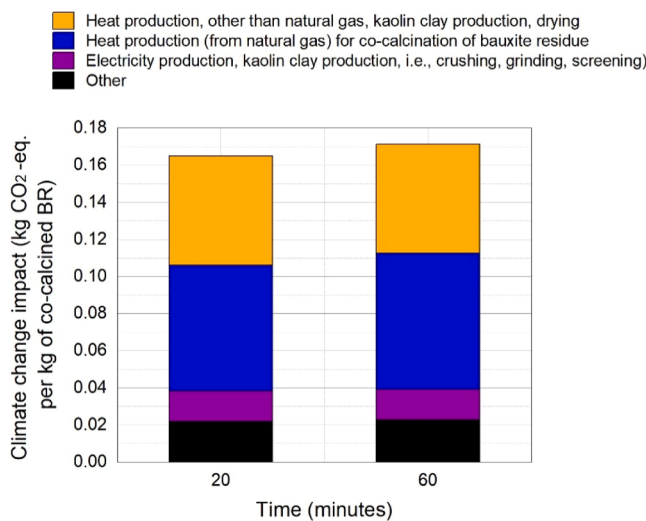


Fig. 9. Climate change impacts of co-calcination process for dwell times (20-min and 60-min).

indicated that the dwell time has a minor effect on the overall climate change impact of the process. Dwell time variations from 60-minute to 20-minute, resulted in a decrease of < 5 % in climate change impact (i. e., 0.17 kg CO₂ eq. for 60-minute dwell time and 0.16 kg CO₂ eq. for 20-minute dwell time). The analysis of shortening dwell time by 33 % revealed a slight decrease in the impact contribution from the energy demands i.e., heat production from natural gas reduced from 0.073 kg CO₂ eq. to 0.068 kg CO₂ eq. from 60 min to 20 min, respectively. Due to the large contribution of heating up the raw materials, the heat as a function of dwell time cannot simply be calculated using a linear equation.

In view of the large impact of plant location (e.g. through climate or fuel mix availability) and plant design (e.g. heat recuperation) on the variability on the influence of temperature, the impact of temperature was not included in the scenario analyses. This will need a detailed study when a specific location and company make plans for a co-calcination plant. Next to the footprint of the calcination process itself, an additional 0.075 kg CO₂ eq. per kg of co-calcined BR was caused by the energy demands (i.e., heat and electricity production) associated with kaolin clay production, assuming pure kaolinite. The production of lower grade kaolinitic clay is expected to have a lower footprint as the electricity and heat are mostly associated with the purification of the kaolinitic clay, but data is lacking to provide a sufficiently accurate calculation. In absolute values the results are in line with other literature on calcination processes [29] and underline the CO₂ emissions reduction that can be established by replacing PC with co-calcined BR.

Within the investigated range, the calcination parameters are unlikely to have a substantial impact on the climate change impact, although this will depend on the final plant design and needs to be reconsidered at that stage. However, when raising the temperature beyond 750 °C, the CaCO₃ contained in many BRs will decompose providing unnecessary extra CO₂ emissions, as mentioned in the discussion of Fig. 7. A calcination temperature of 700–750 °C is thus proposed as the optimal temperature. In view of comparing the embodied CO₂ at the application level, the final environmental impact of the material will have to be calculated at concrete scale and consider the potential strength classes of concrete that can be reached using the co-calcined BR (similar to [30]). The development and optimisation of concrete mixtures is necessary to enable such a study.

3.3. Use of low-grade kaolinitic clays

Industrial implementation depends on the economic feasibility of the proposed co-calcination process. The use of costly, high-purity kaolinite

poses an issue from an economic perspective. Use of lower grade kaolinitic clays as a key requisite for industrial implementation was already proposed in Section 2 and Table 2 provides purities of selected commercially available sources. A kaolin with 75 wt% kaolinite (Soka CL) and 2 kaolinitic clays with 40 wt% kaolinite (Soka GA and Amberger 40) are used in this study. Blends are made with BR targeting 20 wt% of kaolinite in the blend (e.g. 50 wt% of clay with 40 wt% of kaolinite = 20 wt% of kaolinite in the blend). The reactivity of the co-calcined blends is shown in Fig. 10. Independence of the reactivity with calcination temperature over the 650–800 °C range is observed for all samples, similar to when pure kaolinite is used. The co-calcined samples based on kaolinitic clay Soka CL (K(CL)) provide a slightly higher reactivity than expected from the kaolinite content when comparing to the samples with pure kaolinite (Myt80/K-750 °C). This can be explained by the presence of muscovite/illite in the Soka CL clay which can also provide a slight contribution to the reactivity. The reactivity of the samples based on Soka GA (K(GA)) is slightly lower than the samples with pure kaolinite. The Soka GA only has quartz as phase next to kaolinite. Due the lower content of BR (50 wt% instead of 80 wt% in the pure system), there is also less DSP that contributes to the reactivity. Fig. 10 also shows that the reactivity was independent from the source of the kaolinitic clay if the same purity is obtained. The Soka GA and Amberger 40 provide the same reactivity after calcination and also the co-calcined 50–50 mixtures with BR provide the same reactivity for the two different clay sources. The reactivity of the co-calcined materials is substantially lower than the reactivity of the calcined clays. The reactivity of the calcined kaolinitic clays in this paper is in line with results obtained for the same purity in the reported literature [31].

A quantitative relation between the phase composition of the blend before calcination and the measured reactivity is observed. The heat after 7 days in the R3 test can be calculated by:

$$h = 9.3 \times K + 6.0 \times D$$

With *h* for heat, *K* for the wt% of kaolinite in the blend and *D* for the wt% of DSP in the blend before calcination. This relation also matches well with the known reactivity of the pure calcined kaolinite used in this study [9] and implies that the DSP has a very high inherent reactivity as well of about 600 J/g. The DSP phase present in the BR used in this study is cancrinite, with general chemical formula $\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_4$. The reaction of cancrinite can therefore provide Si, Al, and to a lesser extent Ca to the system and stimulate further strength development. The high specific heat release and fast heat release therefore explains and underlines the benefits of DSP for the early age strength and by extension the benefit of co-calcining clays with BR. The equation was obtained when leaving out the data of Soka CL where the muscovite/illite was present. More data with varying contents of 2:1 clays should be obtained before a complete quantitative relation could be constructed taking into account these clays. The quality of the regression is visualised in Fig. 11. This also takes into account the samples with varying amounts of pure kaolinite from Section 3.1. The outlier is the sample

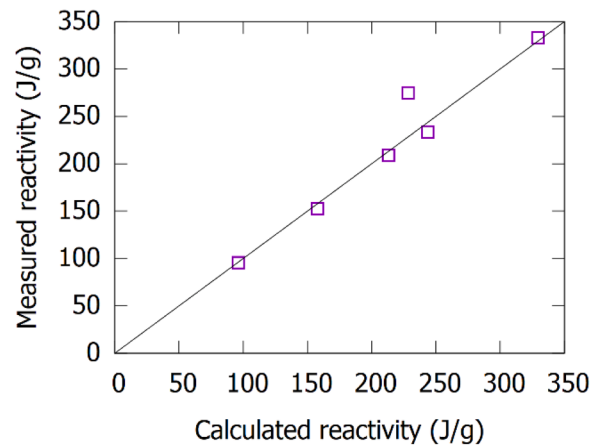


Fig. 11. Heat after 7 days in the R3 test compared to the calculated using equation 1. The line is a visual aid showing a 1:1 correlation.

based on Soka CL due to the presence of other clay minerals.

The compressive strength of mortars using 30 wt% replacement of PC was determined for the co-calcined blends with BR and low-grade kaolinitic clay, using calcined kaolinitic clay (without BR) as an additional reference. The strengths in Fig. 12 show results based on Mytilineos BR co-calcined with pure kaolinite (Myt80/K), Soka CL (Myt75/K (CL)), Soka GA (Myt50/K(GA)), and Amberger 40 (Myt50/K(A4)) taking calcined Soka GA and calcined Amberger 40 as reference SCMs. Lowering the kaolinite content in the clay used for co-calcination to 40

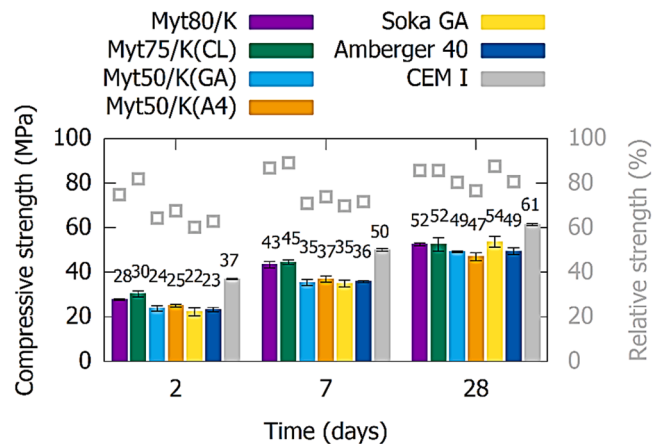


Fig. 12. Compressive strength in absolute values and relative to the reference PC (CEM I) test of mortars with 30 wt% PC replacement with the co-calcined BR using low-grade kaolinitic clay in the raw mix for calcination.

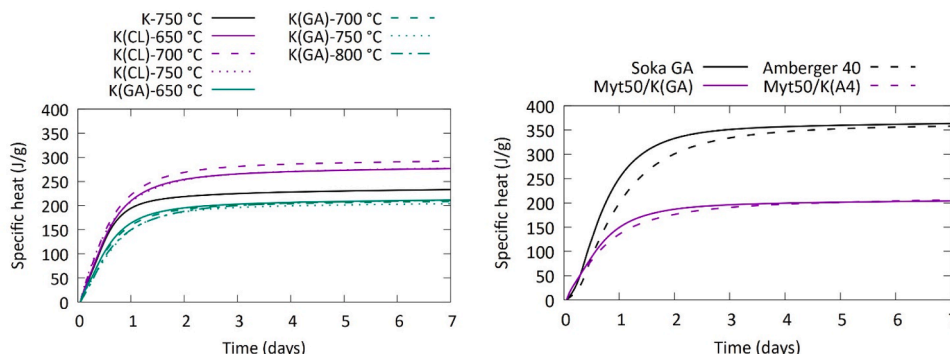


Fig. 10. Heat during R3 reactivity test of the co-calcined BR using low-grade kaolinitic clay in the raw mix for calcination.

wt% lowers the strength of the mortars with 30 wt% replacement at all ages, although most substantially at early age. The effect is not visible for the Soka CL, but due to its higher reactivity this could be expected. The co-calcined BRs with 40 wt% kaolinite clays still provide a good strength development for 42.5 N cements. Interestingly, the strength development is very close to the strength development of the calcined clay without BR, despite the substantially higher reactivity of the latter. Comparing Myt50/K(GA) with Soka GA and Myt50/K(A4) with Amberger 40, the early strength (2 days) is slightly increased and the late strength (28 days) is slightly decreased. This is most probably attributed to the acceleration of PC hydration due to the alkalis in the BR, or to a lesser extent to an increased filler effect due to the fineness of BR, but further work using detailed studies of the hydrate phase assemblage should clarify the extent of these effects.

The repeatability of the strength development of mortar bars with co-calcined blended cements with Soka GA with 40 wt% of kaolinite was investigated using 12 compressive strength tests for each age in Fig. 13. The single result points ranged from 20.9 to 25.6 MPa at 2 days, 33.3 to 38.3 MPa at 7 days, and 45.0 to 50.7 MPa at 28 days with two outliers of 36.9 and 39.1 MPa. These outliers were caused by using the material for mortar flow testing for the compressive strengths and could therefore be discarded from the analyses. This is not carried out here to highlight this sensitivity, which needs to be considered in future implementation of the cement as well. The 25 and 75 percentiles of the box-plots were 23–25 MPa at 2 days, 35–37 MPa at 7 days, and 47–49 MPa at 28 days.

4. Discussion

4.1. Industrial implementation of the calcination process

Whilst considerable work has been undertaken at the laboratory scale to optimise production of the co-calcined SCM, much additional work is still required to scale up the manufacture of the product on the industrial scale. Key areas for consideration include optimisation of calcination and processing conditions which could be different for different feedstocks or locations of the processing plant.

In terms of feedstock, one must take into account the variation of both the BR and kaolinite feed. The composition and characteristics of the BR depend strongly on the bauxite ore mixture processed in the alumina plant. The bauxite mix could well change as relative costs of different bauxites change and there may be seasonal changes, for example freezing conditions meaning that some moist bauxites cannot be used. Laboratory research so far indicates that there is little influence on the final product properties by varying the BR feeds investigated to

date. Kaolins are very common mineral resources and commercially mined in Australia, Brazil, China, Germany, India, Malaysia, Russia, Spain, Thailand, Ukraine, United States and Vietnam, all countries which also have alumina refineries producing BR. The impurities present in the kaolins could also influence the performance of the co-calcined material so this needs to be reviewed.

In terms of location of the processing plants: these could be located next to the alumina refinery or source of BR; or located at the cement plants or at regional hubs strategically located for supply of raw materials and the cement plants. The main difference between the three options is the issue of transporting the BR which as an industrial waste would require special handling, and the issue of retrofitting available equipment for the calcination. The high moisture content of many BRs would also add to the transport cost. However, the alumina industry is currently looking at pelletisation of BR prior to transporting in order to mitigate these transport issues and make the BR easier to handle. In the following section a discussion is made between these two options.

4.1.1. Calcination at the alumina plant

The alumina industry has over a century of experience in converting the aluminium hydroxide produced by the Bayer process to various types of aluminium oxide. Annually some 210 Mt/y of aluminium hydroxide is produced (data for 2022 [32]), of this, some 195 Mt are converted to aluminium oxide for conversion to aluminium metal using an electrolytic process (termed smelter grade alumina-SGA) [33,34]. Approximately 15 Mt of aluminium hydroxide are used in various forms or converted to ‘specialty’ aluminium oxide for specific end applications. SGA was traditionally manufactured in rotary kilns to convert the aluminium hydroxide, present as gibbsite, to a product with an α -Al₂O₃ content of typically 85–95 % and a specific surface area of < 5 m²/g (this product is termed flouly alumina). These rotary kilns were typically 120 m long with a diameter of 4 m, they had a maximum temperature of 1200 °C and controlled to give a residence time of 3 h. The residence time was controlled by the angle of inclination of the kiln, kiln length and diameter, speed of rotation of the kiln and the introduction of small walls or dams in the kiln. The larger rotary kilns had a capacity of 1400 t/d and had an energy requirement of typically 4100 kJ/kg of alumina and up to 6000 kJ/kg of alumina for small rotary kilns. During the late 1960s, the use of stationary kilns was introduced and this trend accelerated after the oil crisis of 1972 driven by the need to save energy, as well as the requirement to reduce fluoride emissions during smelting the aluminium oxide to give aluminium. The residence time at temperature was reduced to minutes in fluidised bed calciners and to seconds in gas suspension or flash calciners. The alumina produced was very different in nature and termed sandy alumina. In these flash calciners, the aluminium hydroxide was passed through a high temperature zone (1200 °C) for a few seconds. The resulting product had a significantly lower alpha-alumina content (5–10 %) but a much higher surface area 60–80 m²/g. This method is now the normal method of producing aluminium oxide for aluminium metal production and production rates are up to 4500 t/d. The latest fluid flash calciners are much more energy efficient than the former rotary kilns with an energy input of 2730 kJ/kg of SGA. Whilst oil was initially the main fuel used, almost all production now utilises gas, and in order to reduce carbon dioxide emissions, trials are now in progress using hydrogen as the energy source for alumina kilns as well as electrically heated kilns using green electricity sources.

In the manufacture of specialty aluminas requiring high alpha-alumina for applications such as ceramics, refractories, polishing, abrasives, catalyst supports, lithium battery separators etc. rotary kilns are still used although for very high purity, very high α -Al₂O₃ grades, tunnel kilns, pendulum kilns or box kilns are used. Intermediate α -Al₂O₃ grades, with surface areas of 10–20 m²/g, can be produced using modified flash calciners.

An additional area where the alumina industry uses kilns is in the manufacture of very high surface area aluminas for use in catalysts, air drying agents, adsorbent of impurities for contaminants such as arsenic

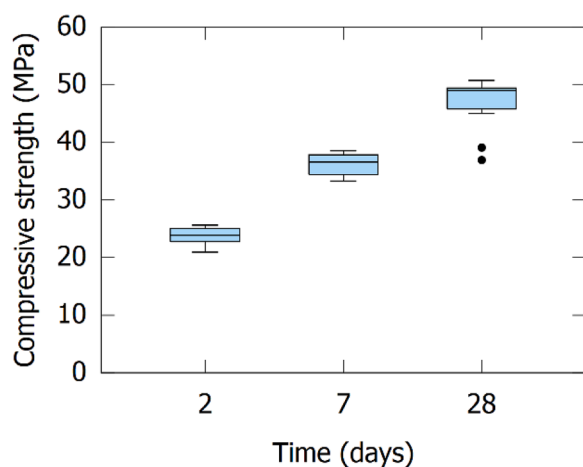


Fig. 13. Box-plots illustrating the statistical analysis on the compressive strength of the mortars with 30 wt% PC replacement with co-calcined BR using 50 wt% of low-grade kaolinitic clay in the raw mix for calcination.

and fluoride from drinking water, adsorbents in polyethylene manufacture etc. These products require the formation of carefully controlled phases and surface areas up to 300 m²/g. Various transition aluminas, such as gamma-alumina, chi-alumina, delta-alumina, theta-alumina and kappa-alumina are formed under the carefully controlled calcination conditions ranging between 600 °C in small rotary kilns to 1100 °C in flash activators.

The alumina manufacturing industry has consequently had many decades of experience in calcining materials to tailor make specific phases and surface areas to give the optimum material characteristics for different applications. Similar control of properties will be necessary in the co-calcination of BR and kaolin to obtain the necessary phases and degree of activity. Scaling up from laboratory scale to a full-scale production unit, however, presents particularly challenges in achieving similar heating rates, and heat flow rates through solids. Invariably, pilot scale trials will be necessary. With respect to the range of calcination temperature used in the trials, 650 to 850 °C, and the dwell times, 20 to 60 min, these should be readily achievable in rotary kilns.

So, calcination of BR and kaolinite at the alumina plant could well be an option, as know-how relating to calcination exists and where available inactive rotary kilns could be repurposed towards this process. The main advantage of course is the avoidance of BR transport from its production site. In this scenario the calcination is integrated in the alumina refinery as a method to produce a valuable new by-product and eliminate/reduce BR generation.

4.1.2. Calcination at the cement plant or regional SCM hub

Performing the calcination at the side of the cement producer (or a third party producing SCM) means that BR transport and handling comes into play, yet on the other hand the experience of a cement producer in calcination processes, material cooling and grinding and finally in cement / SCM chemistry is important. Furthermore, many cement plants have already begun researching the process of clay calcination (kaolin) for producing SCMs and securing kaolin deposits; some cement production sites already manufacture SCMs from clay [6]. The use of underused/inactive cement kilns as new clay calcination plants is being examined. If the cement industry moves in this direction, adding BR to their clay calcination operations can become a method of reducing use of virgin raw materials, similarly to the current established practice of substituting 1–3 % of clinker raw meal with BR [11]. Of course, the level of substitution in this case would be 20 times higher thus allowing for significant utilisation of BR. In this scenario, control of the process passes to the side of the cement industry, which has the established value chain and know-how for both the raw material (kaolin) and the product (SCM).

In either location scenario if existing equipment is not available, a new furnace is needed, the option of the multiple hearth furnace, sometimes called a Herreschoff furnace – is an excellent one for providing a long soaking time at a specific temperature and handling dusty materials [21]. The dwell time can be achieved by increasing the number of hearths and/or reducing the rotation speed. However, the capital costs for multiple hearth furnaces tend to be higher than rotary kilns for the same throughput. Additionally, in either scenario further research is needed in drying the BR and mixing it with kaolin prior to feeding it to the calcination furnace. Mixing to the necessary degree of homogeneity in a laboratory presents few problems but achieving an acceptable degree of mixing at large tonnages is more challenging. For dry materials, equipment such as ribbon blenders, Y-cone blenders etc. are normally adequate but the BR as produced could have a moisture content as high as 25 % if produced using a filter press or even 40 % if a dry mud stacking route or mechanical working route is used [10]. Drying the BR would add considerably to the cost, so using a rotary kiln to dry, mix and then calcine at different stages as it passes through the kiln could be one option. Researching alternative drying methods such as use of microwave radiation could be another option. However, the problem of drying the BR could prove crucial to the economics of the

operation, especially if this BR needs to be transported to the co-calcination site. Moving the moist BR will result in significant additional costs, while moving a dry BR would result in severe handling problems due to dusting.

In the end, the choice of location and equipment for producing the new SCM is something that would need a detailed feasibility study to weigh the various options in BR transporting and drying, retrofitting existing equipment or investing in new and finally establishing the appropriate symbiosis conditions between the cement and alumina industries.

4.1.3. Co-calcined BR in the wider perspective of emerging and future SCMs

The need for alternative SCMs to substitute or supplement the use of blast furnace slag and coal fly ash was discussed in the introduction. Although the previous sections proposed co-calcined bauxite residue as an alternative SCM, this subsection aims to discuss the available literature on competing technologies and compare them to the developed material. Table 4 provides an overview of such potential SCMs of the future, mentioning their heat release in the R3 test (data from Snellings et al. [7]) and specific quality characteristics (from Peys et al. [35] and Snellings et al. [7]). The subdivision in present, emerging, and future SCMs by Snellings et al. [7] is maintained. The co-calcined BR is only one of many optional SCMs of the future, which all have their own benefits, drawbacks, and local availability. It is this local availability together with the specific needs of specific concrete products that will decide whether BR and co-calcined BR is used in cement. The high strength at early age might be the unique selling point with respect to other SCMs, although further research is needed to clarify that the cause of the early strength (alkali-containing phases) does not lead to detrimental effects in the long term. Durability testing and optimization is thus an important next step in the development of the technology.

5. Conclusions

The paper investigates the potential of BR co-calcined with kaolinitic clay to produce a SCM and enable a replacement of PC of 30 wt%. The process conditions were investigated to further optimise the sustainability and implementation potential of the co-calcination process. The furnace temperature and dwell time were shown to have a limited effect on the reactivity of the SCM and strength of mortars replacing 30 wt% of PC by the SCM. In view of process robustness and minimisation of CO₂ emissions the temperature of calcination should be 700–750 °C. The effect of dwell time on environmental impact does not seem substantial when varying between 20 min and 60 min, although the CO₂ emissions could be slightly lowered by implementing shorter dwell times.

The decrease in purity of the kaolinitic clay could lead to a decrease in reactivity, but by modifying the BR-clay blend towards 50 wt% BR and 50 wt% clay, adequate reactivity can be obtained when using a clay with 40 wt% kaolinite. The inherent reactivity of the BR's DSP was estimated at about 600 J/g and BRs with varying contents of DSP could thus provide substantial differences in reactivity. The compressive strength of mortars including 30 wt% PC replacement with co-calcined BR is equivalent to that of mortars including 30 wt% of the respective calcined clay without BR, with slightly higher 2 days strengths and slightly lower 28 days strengths.

The alumina and cement industry both have substantial expertise on calcination processes. Both industries have been developing furnace technologies to optimise their processes. The knowledge is therefore present, but also old furnaces are standing still in some factories that could be used for calcination after adequate maintenance. This would reduce substantially the capital costs related to introducing a BR co-calcination line. The unique early strength associated with the co-calcined BR and expertise of the involved sectors make the technology a promising option for delivering the SCMs of the future.

Table 4
Overview of SCMs using the structure and information from Snellings et al. [7].

| Present, emerging, or future | SCM | Industry of origin | Heat release R3 test (J/g SCM) | Specific characteristics |
|------------------------------|---|---|--------------------------------|---|
| Present | Inert filler | Undefined | 0–100 | No pozzolanic or latent hydraulic reaction, but can enhance the hydration of PC or other SCMs or enhance the packing/workability of a concrete. Replacement of clinker of 5–15 wt% of commonly used. |
| | Coal fly ashes | Energy production | 150–350 | Pozzolanic reaction at late age can enhance the strength at > 28 days and durability* of mortars and concrete. Replacement of clinker of 20–30 wt% of commonly used. |
| | Natural pozzolans | Virgin | 120–380 | Pozzolanic reaction at late age can enhance the strength at > 28 days and durability* of mortars and concrete. Replacement of clinker of 20–30 wt% of commonly used. |
| | Blast furnace slags | Iron production | 350–520 | Latent hydraulic reaction enables the replacement of a large fraction of clinker, commonly 30–60 wt%. Substantial enhancement of durability observed.* |
| | Silica fume | Silicon or ferrosilicon production | 450–650 | The ultrafine nature can increase substantially the strength and durability, but also decrease workability. Replacement of clinker of 10–20 wt% of commonly used. |
| Emerging | Biomass ash | Energy production and/or waste treatment | 75–150 | Depending on source. Herbaceous biomass ashes are silica rich and have pozzolanic potential as SCM. Woody or agricultural ashes are alkali/calcium-rich and might be more suited for (alkali-)activation or as SCM after washing. |
| | Concrete recycling fines | Demolition | 50–150 | High water demand and limited pozzolanic activity. Thermal or carbonation treatment can improve both. |
| | Ceramic waste | Ceramic production or post-consumer | 75–250 | Pozzolanic activity can be present if ceramics are liquid-phase sintered and thereby comprise an amorphous silicate phase. |
| | Recycled glass | Post-consumer glass | 150–250 | Pozzolanic activity due to the amorphous nature of the glass (but dependent on the type of glass and its composition). |
| | Low-grade calcined clay | Virgin | 200–600 | High pozzolanic reactivity and synergy with limestone, enabling high replacement levels. Replacement of clinker of 30 wt% with additional replacement of 10–15 wt% with limestone often used. |
| Future | High-grade calcined clay | Virgin | 600–990 | Extremely high pozzolanic reactivity and synergy with limestone. Replacement level is more limited by the detrimental effect on workability. |
| | Steel slags | Steel production | 50–250 | Crystalline calcium silicates have insufficient reactivity to contribute to cement hydration. Modification at high temperature or through carbonation increases reactivity. |
| | MSWI ashes (Municipal Solid Waste Incineration ashes) | Waste treatment | 100–250 | Mineral fraction of the ashes can contain pozzolanic reactive phases (depending on waste collection policy of the country). Heavy metals and soluble salts can be present. |
| | Fayalitic slags | Non-ferrous metal or ferronickel production | 50–320 | Depending on composition and quenching can contain pozzolanic reactivity. Content of heavy metals might delay hydration (next to the environmental leaching). |
| | Bauxite residue | Alumina production | 50–150 | Insufficient reactivity as SCM. Alkalis can accelerate hydration, in most cases too extensive. Content and leachability of heavy metals needs to be checked. |
| | Vitrified BR | Alumina production | 350–450 | Converted bauxite residue into slag, which contains a reactive amorphous phase. This enables high replacement of clinker (30 wt%) and a synergy with limestone. |
| | Co-calcined BR | Alumina production | 180–300 | Addition of kaolinitic clay increases pozzolanic reactivity sufficiently and causes only mild acceleration of the cement hydration, resulting in high early strengths with minor workability issues. |

* excluding resistance to carbonation, which usually decreases with SCM addition due to Portlandite consumption.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

All co-authors report financial support was provided by European Commission. AP, RS has patent pending to VITO. Co-authors are active in the industry producing the material under study - EB, PD. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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