

## Co-Calcination of BR with Kaolin for Economic Production of SCM. Industrial Pilot Results

Foteini Kratouna<sup>1</sup>, Panagiotis Davris<sup>2</sup>, Efthymios Balomenos<sup>3,4</sup>, Dimitrios Kotsanis<sup>5</sup>,  
Arne Peys<sup>6</sup>, Pipat Termkhajornkit<sup>7</sup>, Frédérique Ferey<sup>8</sup> and Philippe Benard<sup>9</sup>

1. Engineer, Research and Sustainable Development Activity

2. Manager, Research and Sustainable Development Activity

3. Senior Consultant, Research and Sustainable Development Activity

Metlen Energy and Metals, Aluminium of Greece Plant, Agios Nikolaos, Greece

4. Assistant Professor

5. Researcher, XRD Specialist

NTUA, Laboratory of Metallurgy, TESMET group, Athens, Greece

6. Researcher, Materials and Chemistry

VITO, Mol, Belgium

7, 8. Specialist, Cement Manufacturing Department

9. R&D Project Manager, Cement Manufacturing Department

Holcim Innovation Center, Saint Quentin Fallavier, France

Corresponding author: efthymios.balomenos-external@metlengroup.com

<https://doi.org/10.71659/icsoba2024-br013>

### Abstract

Adequate supplementary cementitious materials (SCMs) with an interesting influence on the strength of cement mortars can be obtained by co-calcining bauxite residue (BR) with kaolin clay. The process has proven its technical feasibility in lab scale for a variety of BRs and different grades of kaolin clays, under the EC funded ReActiv project and has been presented in ICSOBA 2022. In the present paper the co-calcination of BR with kaolin clay in an industrial pilot plant is reported. Using a 6 m long indirect heated rotary kiln located at METLEN, several tons of BR have been mixed with clay in a 70 %-30 % weight mix range and calcined at temperatures between 700–800 °C, in the length of the kiln. Heat of hydration obtained by R3 test using calorimetry at VITO confirms the activity of the calcined material, while further laboratory testing at Holcim validates its potential as a new SCM material that can replace part of the clinker used in cement formulations.

**Keywords:** Bauxite Residue, Supplementary cementitious materials, SCM, Calcined Clay, Cement.

### 1. Introduction

The EC funded ReActiv collaborative project aims at producing Supplementary Cementitious Materials (SCMs) from Bauxite Residue. SCMs are materials that exhibit pozzolanic and/or hydraulic properties and can therefore be used in cement composition as a partial substitute to Portland cement clinker and/or in concrete as an active addition [1]. They can be natural materials (limestone, pozzolans, etc.) or by-products from other industrial processes (blast-furnace slag, fly ash, silica fume, calcined clay etc.). As clinker production is a CO<sub>2</sub> intensive process (due to the calcination of limestone), partial substitution of clinker with SCMs is one of the main decarbonization strategies of the cement industry [2,3].

Calcination has been shown to be especially useful for boosting the reactivity of clays, leading to the potential for high clinker replacement levels such as in the case of limestone calcined clay (LC3) cements [4], where kaolin minerals are transformed into reactive metakaolin. Similarly, but not as extensive as for clay, the reactivity of BR can be improved using a calcination process.

As shown in previous publications [5, 6, 7] calcined BR exhibits low pozzolanic activity (~100 J/g after 7 days acc. R<sup>3</sup> heat release test) and might result in severe setting acceleration, but when mixed with kaolin and calcined to temperatures 650–800 °C, it can produce a reactive material without detrimental effects on the workability, potentially suitable for substitution of Portland cement clinker as supplementary cementitious material. Laboratory scale investigations performed at VITO on this technology on a variety of BRs has shown that, following the calcination step, the reactivity of the mixed material can be attributed to both the newly formed metakaolin phase from the kaolinite and to the calcined desilication products (DSPs) from the BR. Due to the high reactivity of the DSP phases, the kaolin clay used for co-calcination does not have to be high purity. Furthermore, the reaction of the DSP phases occurs very fast, providing already a positive effect on the early strength (2–7 days), which is rather unique for SCMs. On the other hand, the metakaolin phase captures the free sodium contained in the BR, eliminating the issues with severe setting acceleration.

In the current work, the first industrial pilot scale test of this technology is presented, along with lab-scale evaluation of the produced SCM in concrete formulation. Co-calcination of 5 tonnes of BR with kaolinite took place in the alumina refinery of METLEN in Greece and the produced SCM was evaluated at the Holcim Innovation center in France.

## 2. Co-Calcination Pilot Trials

### 2.1 Materials

The materials used in the pilot trials were filterpressed bauxite residue from METLEN’s alumina refinery and kaolin clay with ~80 % kaolinite provided by HOLCIM. The chemical composition of both materials is presented in Table 1 (XRF analysis). The XRD patterns of the bauxite residue and kaolin samples are shown in Figures 1 and 2, and their mineralogical compositions are given in Tables 2 and 3 respectively.

**Table 1. XRF analysis of bauxite residue and kaolin samples.**

Material	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	CaO %	SiO <sub>2</sub> %	TiO <sub>2</sub> %	Na <sub>2</sub> O %	LOI %
Bauxite Residue	20.27	40.71	9.17	8.29	5.00	4.00	9.29
Kaolin	36.35	1.07	0.07	47.72	0.45	ND	12.48

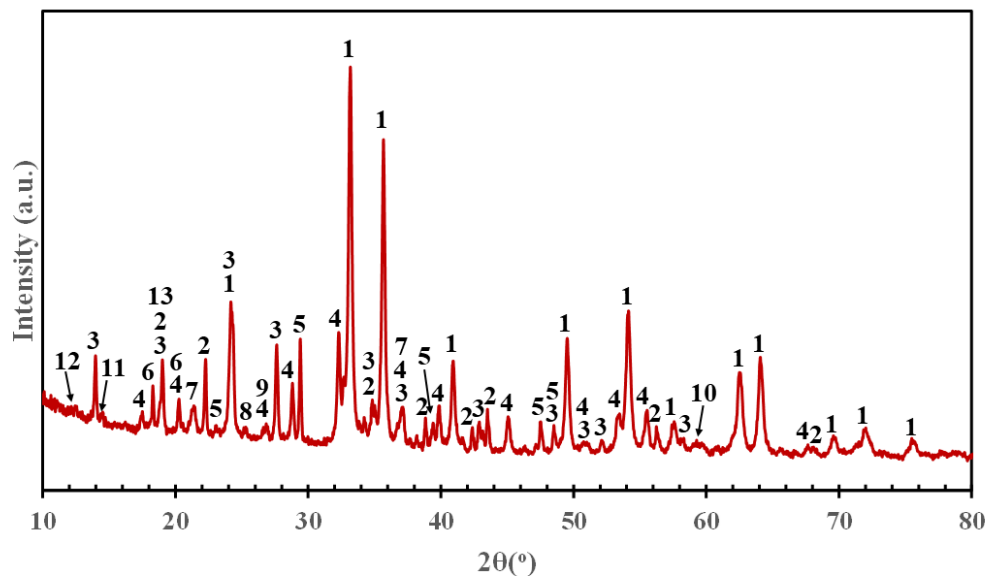


Figure 1. XRD pattern of BR sample.

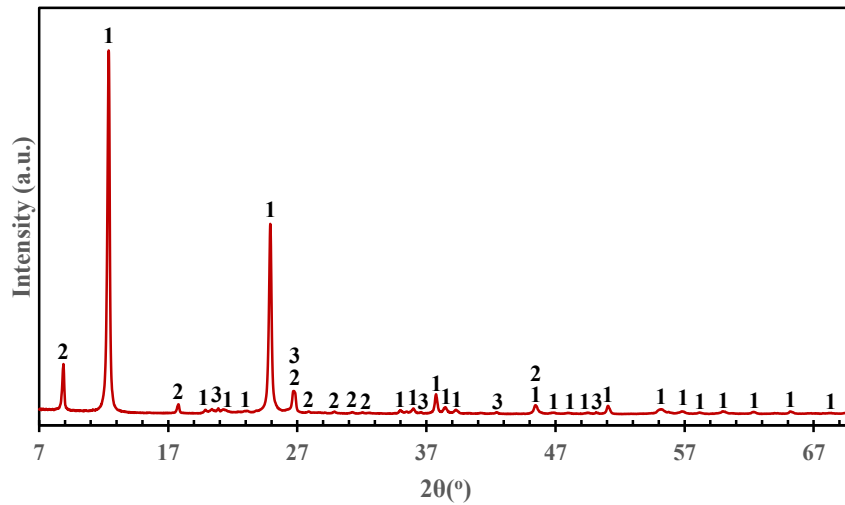


Figure 2. XRD pattern of Kaolin sample.

Table 2. Mineralogical composition and quantitative analysis of the BR sample (Fig. 1).

Code	Mineral	%	Code	Mineral	%
1	Hematite	31.29	8	Anatase	0.56
2	Diaspore	15.06	9	Quartz	0.45
3	Cancrinite	13.27	10	Perovskite	4.75
4	Si-Katoite	11.90	11	Boehmite	0.34
5	Calcite	4.32	12	Chamosite	1.26
6	Gibbsite	2.80	13	Bayerite	1.36
7	Al-Goethite	3.96	Amorphous content		8.68

Table 3. Mineralogical composition and quantitative analysis of the kaolin sample (Fig. 2).

Code	Mineral	%
1	Kaolinite	74.28
2	Muscovite	19.08
3	Quartz	6.65

## 2.2 Pilot Unit and Process

METLEN’s pyro pilot plant operates an indirect fired rotary kiln, produced by CEMTEC. The kiln tube is 6 m long, made of stainless steel and is heated by 5 natural gas burners, positioned on its exterior. Material is fed in the tube through a feeding screw, which in turn is fed from a double helix mixer. The rotary kiln temperature is controlled through 5 thermocouples which regulate the burners into 3 temperature zones. The rotation of the kiln is controlled independently, ranging from 0.1 to 0.9 rpm.

The optimum set of conditions imposed on the kiln were those corresponding to the achievement of complete transformation of the kaolinite to amorphous kaolin or metakaolin, as derived in previous testing with the kaolin clay in the specific pilot furnace.

The process followed in the trials consisted of weighing BR and kaolin to achieve a mix (adjusted for respective moisture) of 75 wt.% BR and 25 wt.% of kaolin and feeding them in the kiln mixer, in batches of 250 kg. The kiln was preheated at 750–800 °C for 80 min, following which the material feeding started at an average rate of 60 kg/h. Temperature was set to 800 °C and was recorded in each trial along with trial time and kiln rotation speed.

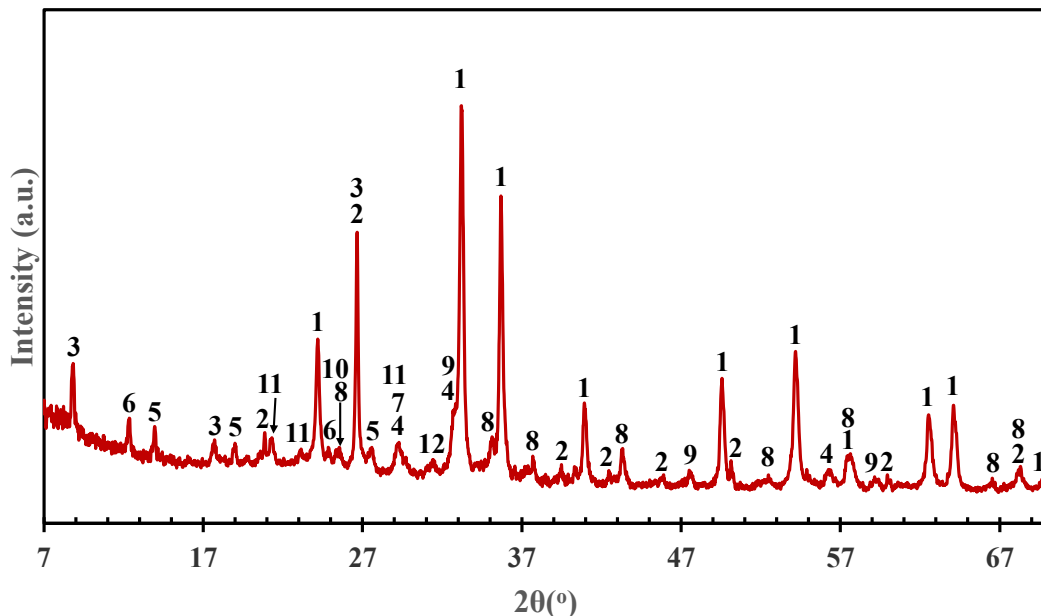
The material was collected from the bottom of the kiln and weighed and sampled for chemical and mineralogical analysis. In total more than 5 tons of calcined material were produced in 20 production batches.

### 2.3 Results

Table 4 presents the parameters of one specific co-calcination trial performed at METLEN. XRD analysis of related sample is presented in Figure 3 and Table 5. As seen the main kaolinite peaks at 12.5 and 25 degrees in the co-calcined material are completely or nearly absent in the samples examined, indicating that the material reached temperatures of at least 700 °C. The quantitative analysis of the XRD pattern in Table 5, reveals 32 % of amorphous material. When comparing the XRF analysis and the XRD quantitative analysis in Figure 4, large deviations are found for the alumina and silica content, indicating the 32 % amorphous content is mostly aluminosilicates coming from the transformation of kaolinite but also from decomposed DSP phases and amorphous content in BR.

**Table 4. XRF analysis of co – calcined Bauxite residue - kaolin mixture sample.**

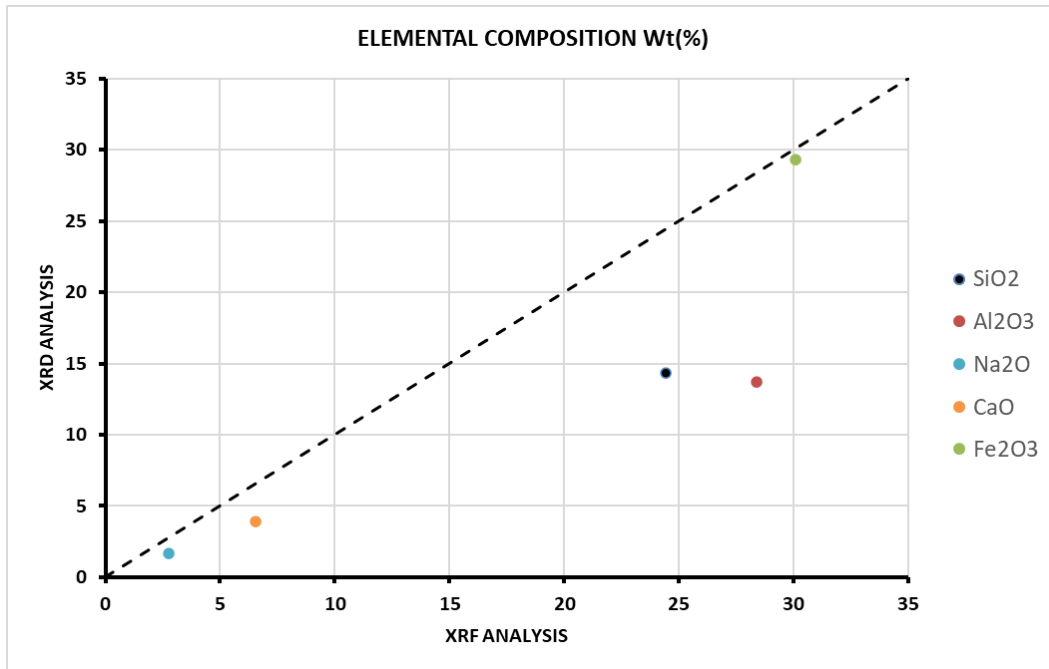
Material	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	CaO %	SiO <sub>2</sub> %	TiO <sub>2</sub> %	Na <sub>2</sub> O %	LOI %
Calcined mixture	28.38	30.11	6.53	24.43	3.81	2.74	1.53



**Figure 3. XRD pattern of co-calcined sample.**

**Table 5. Mineralogical composition, quantitative analysis of the co-calcined sample (Fig. 3)**

Code	Mineral	%	Code	Mineral	%
1	Hematite	27.83	8	Corundum	7.73
2	Quartz	4.56	9	Perovskite	3.32
3	Muscovite	7.13	10	Anatase	0.06
4	Ti-Andradite	4.95	11	Nepheline	3.01
5	Cancrinite	5.53	12	Gehlenite	1.33
6	Kaolinite	3.01	Amorphous Content		32.05
7	Calcite	0.29			



**Figure 4. Comparison of XRF and XRD Quantitative analysis of co-calcined sample.**

As the co-calcination process in the pilot was carried out in daily batches of ~250 kg of feed material, instead of a continuous operation, it was not possible to reach a steady state in the furnace and achieve complete and uniform conversion of kaolinite in all the processed material batches. Figure 5 shows the variations of the kaolinite transformation in different pilot samples.

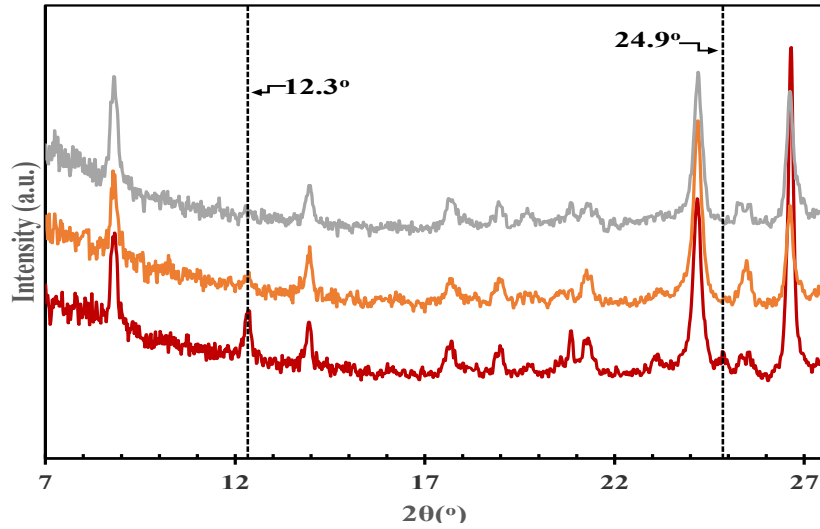


Figure 5. Variation of XRD patterns of kaolinite in co-calcined samples.

### 3. SCM Testing

#### 3.1 R3 Calorimetry

The reactivity of the co-calcined pilot product was measured using the R3 heat release test (ASTM 1897-20). In Figure 6, the reactivity of the pilot product is compared with the reactivity of the relevant laboratory results, using the same material mixture but performing the co-calcination in static-bed laboratory furnace. The observed difference is partially related to the incomplete conversion of kaolinite shown in section 2.3. However, other formulations that were evaluated positively with a beneficial effect on strength in previous work [7], showed a similar heat release as the result of the pilot here. According to [8], the specific heat at 7 days of the co-calcined BR-clay R3 test, shown in Figure 6, is like those of good quality fly ash but less than those of slag.

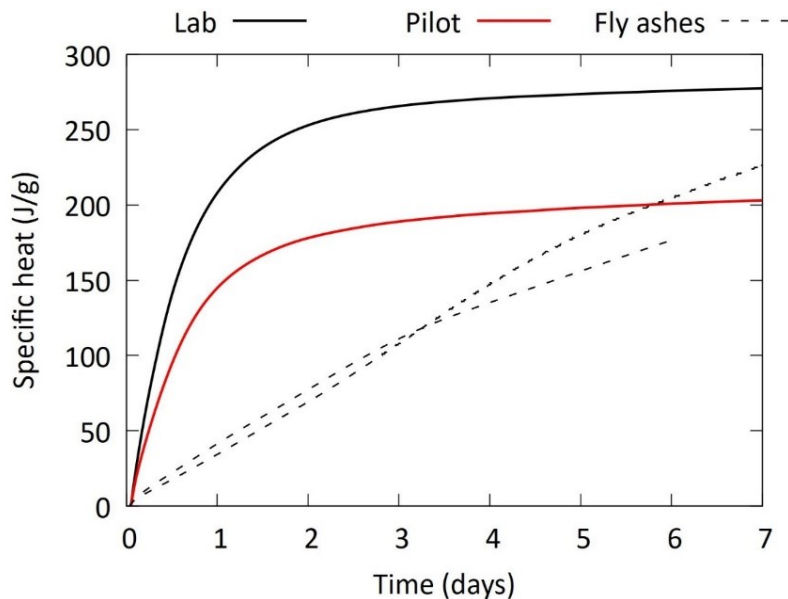


Figure 6. Cumulative heat from R3 test of co-calcined BR in VITO lab and METLEN pilot. Specific heat release of typical fly ash is provided for comparison.

In the broader perspective of contemporary and other upcoming SCMs, co-calcined BR can be classified as a SCM with moderate reactivity at later age (7-day heat value) and fast reaction kinetics (already large fraction of total heat after only 1 day) [7]. The contribution to hydration reactions could thus be expected to be similar as fly ashes on the long term but might contribute to the early hydration reactions to a larger extent than granulated blast furnace slag.

### 3.2 Mortar Tests

The co-calcined BR-clay was ground until D50 is between 15 to 20  $\mu\text{m}$ . The physical properties of the ground co-calcined BR-clay are in Table 6.

Then the cement mix containing 70 % CEM I 52.5N and 30 % of the co-calcined BR and clay was prepared for mortar test and benchmarked with cements with 70 % of CEM I 52.5N and 30 % of siliceous inert as well as 100 % CEM I 52.5N. Water demand for a standard consistency and setting time were measured according to the standard EN 196-3. The compressive strengths were measured according to the standard EN 196-1 at 1, 2, 7 and 28 days.

**Table 6. The physical properties of the ground co-calcined BR-clay.**

Density	( $\text{g}/\text{cm}^3$ )	3.25
Particle Size	D10 ( $\mu\text{m}$ )	2.4
	D50 ( $\mu\text{m}$ )	15.4
	D90 ( $\mu\text{m}$ )	192.4

Table 7 shows the water demand and setting time. The water demand of the cement with 70 % CEM I + 30 % Co calcined BR-clay is significantly higher than other cements. It implies that a use of superplasticizer in cement application is required to decrease the water/cement ratio. The initial setting time of all cements in this table respects the standard EN 197-1.

**Table 7. The water demand and setting time.**

	<b>70 % CEM I + 30 % Co-calcined BR-Clay</b>	<b>70 % CEM I + 30 % siliceous inert</b>	<b>100 % CEM I 52.5 N</b>
Water Demand (%)	38	30	29
Initial Setting Time (min)	224	188	134
Final Setting Time (min)	292	306	223

Figure 7 shows the compressive strength as a function of time. A comparison between the mortars containing the co-calcined BR-clay and those containing the siliceous inert gives information about when and how much the co-calcined BR-clay gives the contribution to the compressive strength. On the other hand, a comparison with the mortar that contains 100 % CEM I 52.5 N gives Strength Activity Index (SAI) as shown in Table 8. Figure 7 shows that the co-calcined BR-clay gives contribution on compressive strength even at 1 day. Furthermore, the gain on strength continues from 1 day to 28 days.

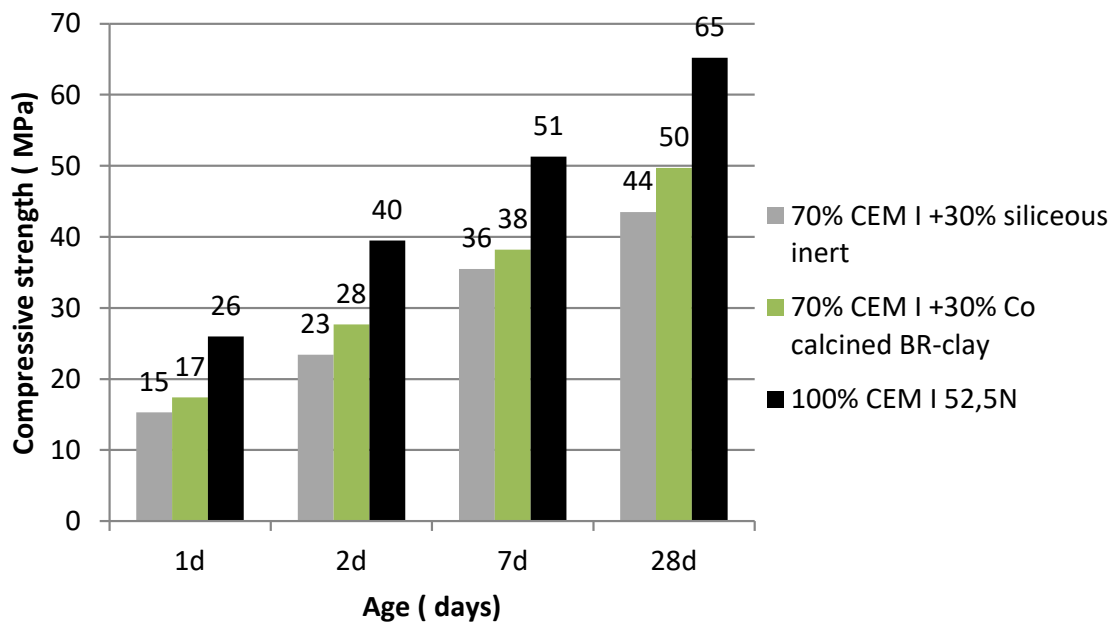


Figure 7. Compressive strength as a function of time.

Table 8. Strength Activity Index (SAI)

1 day	67
2 days	70
7 days	74
28 days	76

The blended cement containing 30 wt.% of the co-calcined BR-clay could be potentially applied for cement applications of class 42.5 R according to EN 197-1.

#### 4. Conclusions

BR can be co-calcined with kaolin clay to produce an SCM for green cement production. The produced co-calcined material has ~30 wt.% amorphous aluminosilicates, originating from both kaolin and BR.

The specific heat at 7 days from the co-calcined BR-clay R3 test is like those of good quality fly ash but less than those of slag. From the values of total heat after 7 days the reactivity is lower than granulated blast furnace slag, but fast reaction kinetics are observed with high heat release after 1 day.

The blended cement containing 30 wt.% of the co-calcined BR-clay could be potentially applied for cement applications of class 42.5 R according to EN 197-1. The contribution to strength development of the co-calcined BR is already observed from the 1-day strength and increases further as a function of time.

The technology needed for the co-calcination is well within the know-how of the alumina refinery, thus providing a potentially viable in-house BR valorisation technology.

## 5. Acknowledgments

The research leading to these results has been performed within the ReActiv project and received funding from the European Community's Horizon 2020 Programme (H2020/2014-2020) under grant agreement no. 958208.

## 6. References

1. Daman K. Panesar, Supplementary cementing materials, in *Developments in the Formulation and Reinforcement of Concrete* (Editor Sidney Mindess), Woodhead Publishing Series in Civil and Structural Engineering, (2019) Pages 55-85, ISBN 9780081026168.
2. CEMBUREAU, Use Of Secondary Raw Materials in the EU Cement Industry <https://cembureau.eu/media/kj3no0w3/230123-cembureau-qa-secondary-materials.pdf> (Accessed 19/04/2024).
3. GCCA, 2021. Concrete future – The GCCA 2050 cement and concrete industry roadmap for net zero concrete, <https://gccassociation.org/concretefuture/wp-content/uploads/2022/10/GCCA-Concrete-Future-Roadmap-Document-AW-2022.pdf>, (Accessed 19/04/2024).
4. Karen Scrivener et al., Calcined clay limestone cements (LC3). *Cem. Concr. Res.* 114, (2018), 49–56. doi:10.1016/j.cemconres.2017.08.017
5. Arne Peys and Ruben Snellings, Co-calcination of bauxite residue with kaolinite to enhance its performance as supplementary cementitious material, *TRAVAUX 50, Proceedings of the 39th International ICSOBA Conference, 2021, 22–24*
6. 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*, Volume 9, (2022), doi.org/10.3389/fmats.2022.913151
7. Arne Peys et al., Co-calcination of bauxite residue with low-grade kaolin in pursuit of an economic and high-quality supplementary cementitious material, *TRAVAUX 51 Proceedings of the 40th International ICSOBA Conference, 2022, 709–711*.
8. Diana Londono-Zuluaga et al., Report of RILEM TC 267-TRM phase 3: validation of the R3 reactivity test across a wide range of materials, *Materials and Structures, Volume 55*, article 142, (2022), <https://doi.org/10.1617/s11527-022-01947-3>