Supplementary cementitious materials and mechanochemistry for sustainable concrete production

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ABSTRACT

Excavation and removal of instable clayey soils before construction works, e.g., in infrastructure, residential or commercial buildings etc., can generate vast amounts of waste clay deposits. Treatment of those clays to achieve suitable supplementary cementitious materials (SCMs) for use in concrete production can extensively contribute to a circular economy. Mechanical activation (MC) by ball milling has shown suitability to be an alternative and sustainable method to process clays and to obtain dehydroxylation at reduced temperatures and without the addition of chemicals. Furthermore, BM can induce amorphization, increased chemical reactivity and improved pozzolanic properties. Amorphization of crystalline phases can be achieved also for poorly reactive materials as air-cooled blast furnace slags (ACBFS), which can be further utilized as a precursor in sodium silicate alkali activated systems. This study shows how mechanical activation is promoting the reactivity of clay and ACBFS, and their potential to be used as replacement of cement in concrete production. Evaluation of the pozzolanic activity before and after treatment was performed for the treated clay, suggesting increased pozzolanic properties. While alkali activated systems based in mechanically treated ACBFS reached, after 28 days, comparable compressive strength values with the commonly used ground granulated blast furnace slag (GGBFS)

Keywords: sustainability, SCM, mechanical activation, clay, air-cooled slag

INTRODUCTION

The 17 sustainable developmental goals of the 2030 UN´s agenda [1] address awareness in fields as innovation, circularity, climate change, inclusivity and sustainable living. According to this agenda and to the Paris Agreement [2], by 2030 the European Cement Association (CEMBUREAU) aims to reduce with 30% the CO_2 emissions for cement and by 2050 to achieve zero net emissions. Several stages of the value chain of concrete production and constructions can be improved in order to achieve carbon neutrality. The "5C approach", elaborated in the latest Roadmap by the CEMBUREAU, encourages actions in this 5 areas: Clinker, Cement, Concrete, Construction and Carbonation [3]. Cement manufacturing includes primarily the clinker production, which is based in the extraction of the materials (e.g. limestone, clay and sand) and the following kiln-processing step. Production of Portland cement is contributing for approximately 8% of the overall anthropogenic CO_2 emissions and the calcination process delivers alone approximately 60-65%. The remaining part comes from the fuels used in the kiln-process, so approximately 35-40% [3]. This is the reason why clinker production gives various opportunities for CO_2 reduction.

A rapid and proven countermeasure to this issue is partial replacement of cement with supplementary cementitious materials (SCMs). SCMs are siliceous, aluminosiliceous or calcium aluminosiliceous materials in form of powders. These can be natural, e.g. clay, or by-products of other industries, e.g. slag, fly ash or tailings [4]. Ground granulated blast furnace slags (GGBFS) and fly ash are the two main SCMs utilized, but their forthcoming usage is unreliable due to the environmental concerns associated with the industries they are generated from. On the other hand, clay is a commonly occurring material but a pretreatment is required. Amorphized structures are fundamental for increased reactivity of these sources and preliminary heat treatment is often performed for this purpose. Kaolinitic clay is thermally treated at around 600-1000 °C to produce metakaolin, which is a well-established and highly reactive SCM. Not only kaolinitic clays but also mixed layer clays, after treatment, can have a great potential as SCM [5,6]. Thermal treatment of clays or natural pozzolans can contribute at some degree to the CO_2 emissions and requires high temperatures. However, studies have shown that clay can be activated by a cleaner technology without the need to use high temperatures [7]. Mechanical activation in a ball mill can induce amorphization of the structure increasing the pozzolanic reactivity of clays.

Another efficient solution to increase the sustainability of building materials is by replacing Portland Cement (PC) with alkali-activated materials (AAM). This solution implicate a full replacement of PC and the requirement to use strong alkalis, as e.g. sodium hydroxide or sodium silicate, for inducing the chemical reaction and hydration process [8–11]. For AAM production, the main precursor is GGBFS, which is obtained by the water-cooling process of the slag removed from the blast furnace. However, this quenching method requires large amounts of water and produces pollution. Another quenching method that can be utilized is the air-cooling, which on the other hand leads to a poorly reactive material characterized by reduced amorphized phases. Nonetheless, poorly reactive sources as ACBFS can be treated with mechanochemistry to increase their reactivity and utilize them as valid precursors in AAM [12].

This article summarizes opportunities and utilization potential of SCMs, including clay and ACBFS can have for the future. Utilization of mechanochemistry to increase reactivity of these materials is crucial for efficient utilization of these resources, which in their natural form have not a great performance.

MATERIALS

According to their behaviour during the hydration and hardening process, SCMs are divided in two categories: *hydraulic* and *pozzolanic*. Hydraulic SCMs have a similar behaviour to cement and harden due to an irreversible hydraulic reaction when combined with water. On the other hand, pozzolanic SCMs do not react when in contact with water. Blended cements, both with hydraulic and pozzolanic SCM, are characterized by metastable phases developed during hydration.

In this study, two different types of SCMs are used: clay (pozzolanic) and ACBFS (hydraulic). Both of the materials were mechanically treated before their solidification. The chemical composition is shown in Table 1.

Table 1. Chemical composition of ACBFS and clay

	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	LOI
ACBFS	31,3	11,9	31,1	1,67	0,639	13,7	0,515	-1,6
Clay	52,6	15,1	6,41	6,9	3,78	2,51	1,68	7,5

METHODS

Both materials were processed in a ball mill, using the same process parameters. The time of grinding (20 minutes), filling ratio (25 ball to powder ratio) and rotation speed (500 rpm). The ball mill was a Retsch equipment, type PM100.

Phase composition and amorphization rate were determined through the XRD analysis, using an X-ray diffractometer type Empyrean. The XRD samples were not pre-treated and back-loading sample holders was used to avoid preferred orientation of the particles. The main identified phases by Panalytical´s Highscore Plus equipped with a COD database, include kaolinite (Kln), muscovite (Ms), illite (Ilt), montmorillonite (Mnt), quartz (Qz), and calcite (Cal). In the untreated ACBFS crystalline phases as akermanite (A), melilite (Ml), and merwinite (Me), were identified. Decreased intensities and broaden peak areas were produced upon the application of mechanical activation process suggesting a partial destruction of A and Ml phases.

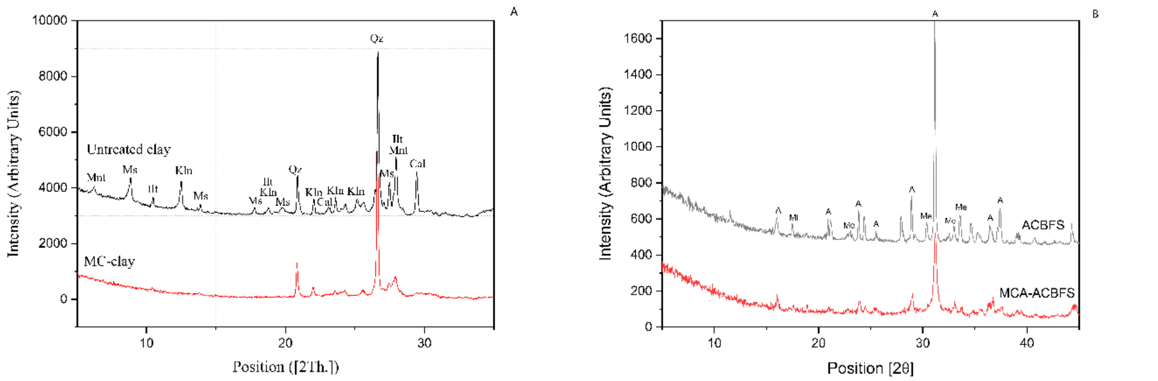

Figure 1. XRD pattern of a) clay and b) ACBFS, before and after mechanical treatment.

Pozzolanic activity was evaluated with the indirect method of Strength Activity index (SAI) through comparison of compressive strength tests, according to standard ASTM C 618 [13]. Compressive strength tests were done on mortar beams with dimensions 40*40*160 mm^3, prepared with the water to binder ratio (w/b) of 0.5 and the binder to sand ratio of 1:3. A Hobart mixer was used to prepare the mortar mixes and the mixing time was 5 minutes. Mortar beams were produced using cement as a binder and a mixture of 80 wt. % of cement and 20 wt. % of the processed clay and mine tailings. SAI was calculated as a percentage of the ratio between the compressive strength value of the control beam (containing only the PC) and the compressive strength value of the mortar beam prepared with 20 wt.% of cement replacement.

For AAM samples, activation was done with liquid sodium silicate (SS) provided by the PQ Corporation. The water to binder (W/B) ratio was 0.45 and the mass ratio of sand to slag was kept constant at 1:1. The SS had an alkali modulus AM (mass ratio SiO2/Na2O) of 2.2, with 34.37 wt. % of SiO2, 15.6 wt. % of Na2O and a solid content of 49.97 wt.%. The AM of the SS was adjusted to reach three different values of 1, 1.5 and 2.0, by addition of sodium hydroxide pellets (98% purity). The alkali activator was added as 10 wt. % of the binder content calculated as a solid material. The compressive strength was determined using a CTM test machine combined with the QuantumX MX440B, universal measuring amplifier. The test specimens had dimensions of 12x12x60 mm3 and 76 were cast into Teflon moulds without application of demolding oil.

RESULTS

After 7 days, compressive strength of mortar prepared with 20% replacement of untreated clay decreased slightly, suggesting the poor reactivity of the natural clay (Figure 2a). On the other hand, replacement by the mechanical treated (MC) clay has achieved higher values for the compressive strength. Similar trend was evidenced for the results of the compressive strength after 28 days. Further information and results about parameters of the MC process were reported earlier, assessing that mechanical activation can enhance the reactivity of natural clays [7]. According to the results from the compressive strength tests, strength activity index (SAI) after 7 and 28 days was calculated (Figure 2b). All samples have reached the minimum required index. However, mechanically treated samples had exceeded these values by 100%, suggesting an increased pozzolanic activity and improved mechanical properties.

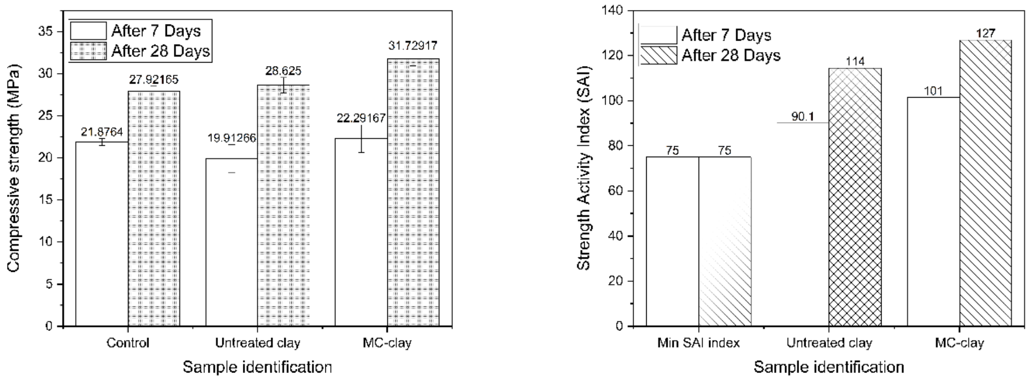

Figure 2.a) Compressive strength and b) SAI after 7 and 28 days of clay samples, before and after mechanical treatment.

All mortar samples made from ACBFS with alkali modulus 1.0 and solid solution of 10%, were characterized by an acceptable workability. MC-ACBFS based mortars activated with the SS having the alkali modulus of 1 showed 28-day compressive strength values comparable with the commonly used GGBFS [11,12]. Higher alkali modulus of the used SS activator decreased the compressive strength values after both 7 and 28 days.

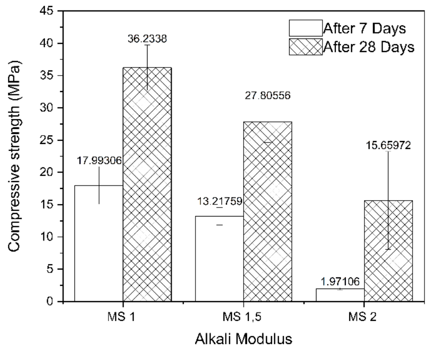

Figure 3. Compressive strength after 7 and 28 days of alkali activated ACBFS samples after mechanical activation, with different alkali modulus.

CONCLUSION

Mechanical activation in a ball mill is an environmentally friendly process enabling to increase the chemical reactivity and pozzolanic activity of clay.

An optimized mechanical activation process can enhance the reactivity of poorly reactive and crystalline air-cooled slag.

Mechanically treated clay showed enhanced mechanical properties when utilized as a cement replacement, while mechanically treated slag can be utilized as a precursor for production of alkali activated materials.

Compressive strength values measured after 7 and 28 days increased for the mortar samples prepared containing 20%wt% of MC-clay. SAI after 7 and 28 days overpassed the minimum required value of 75% for both MC-clays. MC-ACBFS reached after 28 days compressive strength values comparable to similar AAM systems prepared with GGBFS as a precursor.

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