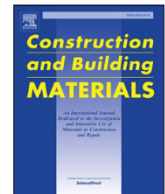




Contents lists available at ScienceDirect

## Construction and Building Materials

journal homepage: [www.elsevier.com/locate/conbuildmat](http://www.elsevier.com/locate/conbuildmat)

## Enhancement of the pozzolanic activity of natural clays by mechanochemical activation

Ilda Tole<sup>a,\*</sup>, Francesco Delogu<sup>b</sup>, Elsa Qoku<sup>c</sup>, Karin Habermehl-Cwirzen<sup>a</sup>, Andrzej Cwirzen<sup>a</sup><sup>a</sup> Building Materials, Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, 97187 Luleå, Sweden<sup>b</sup> Dipartimento di Ingegneria Meccanica, Chimica e dei Materiali, Università degli Studi di Cagliari, via Marengo 2, 09123 Cagliari, Italy<sup>c</sup> School of Civil and Environmental Engineering, Georgia Tech, 790 Atlantic Drive, Atlanta, GA 30332, Georgia

## ARTICLE INFO

## Keywords:

Grinding  
Blended Cement  
Pozzolan  
SCMs  
Clays

## ABSTRACT

Replacement of cement with supplementary cementitious materials (SCMs) is a proven method to reduce clinker in cement and contribute to decreased CO<sub>2</sub> emissions. Natural clays are commonly occurring materials that do not possess pozzolanic activity in their original state. Mechanochemical activation (MCA) can be an alternative and sustainable method to enhance their reactivity. In this study, the pozzolanic reactivity of three natural clays, originating from Sweden, was analyzed after the application of MCA in a planetary ball mill. Strength activity index (SAI), Frattini test, and conductivity test were used to evaluate the pozzolanic reactivity. All processed clays by MCA have achieved a SAI greater than 100%, while the Frattini test indicated an improved pozzolanic activity of samples containing a higher amount of clay minerals. The obtained results show that MCA could improve the pozzolanic reactivity, but the effect depends on the mineralogical composition and particle size of the clays.

## 1. Introduction

The recent IPCC report shows that the building and construction sectors can meet the goals of the Paris Agreement on greenhouse gas emission only by reducing the use of carbon building stock within 2050 [1]. Reducing the building sector's total emissions deeply involves EU in a global campaign to take on the challenge [2]. In such regard, the partial replacement of Portland Cement (PC) by secondary cementitious materials (SCMs) has been proposed as a rapid countermeasure [3–8]. Thus, the use of SCMs, as e.g. fly ash, slags, calcined clays, tailings, silica fume, etc., has been explored, while their availability and pozzolanic reactivity are key drivers for the selection [3,9].

A pozzolana is defined as a “siliceous and aluminous material which, in itself, possesses little or no cementitious property, but which will, in finely divided form and in the presence of moisture, react chemically with calcium hydroxide at room temperature to form compounds possessing cementitious properties” [10]. This generalized definition covers also waste or by-products such as fly ash (FA), rice husk ash (RHA) and silica fume (SF). The pozzolanic reaction forms additional C—S—H due to the consumption of calcium hydroxide, thus enhancing the mechanical properties and decreasing the pore size distribution of the cementitious matrix [11,12].

Within the framework of the partial replacement strategy mentioned above, clay can play an important role. The natural and commonly available material is characterized by a heterogeneous composition also due to the weathering conditions in its original deposits. This might be a challenge for their utilization. The main components are clay minerals such as kaolinite, illite, and montmorillonite with fine microstructure mixed with sediments and soils [13]. Several non-clay minerals can be found in natural deposits, i.e. quartz, calcite, mica, feldspars, etc. [14].

Thermal activation of pure minerals, as e.g. kaolinite or illite, is comprehensively documented and the calcined products are largely used as a SCM, even though they are high-priced due to the extensive utilization of the pure kaolin in other sectors, as e.g. refractories, paper and white ware industries [15]. Several studies showed that specific clay minerals could influence the required calcination temperature and the pozzolanic activity of the thermally treated clay [14,16,17]. Thermal treatments at 750–800 °C, i.e., above the dehydroxylation temperature of kaolinite, causes the layered structure to collapse and to form a typical amorphous structure (metakaolin) that exhibits enhanced pozzolanic activity. Among clay minerals, kaolinite requires lower temperatures to achieve dehydroxylation, while exhibiting a higher pozzolanic activity and it is followed by illite and muscovite. Thus, the thermal treatment should be adjusted according to the mineralogical composition.

\* Corresponding author.

E-mail address: [ilda.tole@ltu.se](mailto:ilda.tole@ltu.se) (I. Tole).<https://doi.org/10.1016/j.conbuildmat.2022.128739>

Received 22 April 2022; Received in revised form 5 July 2022; Accepted 6 August 2022

0950-0618/© 2022 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Extensive research has been performed to understand the potential of the short and long-term performances of SCMs [13,18–20] based on calcined clays [11,21].

Within this framework, mechanochemical activation (MCA) by ball milling (BM) can be an alternative and sustainable method to process clays and to obtain dehydroxylation at reduced temperatures without the addition of chemicals. Calcination is inconsistent when clays with different minerals are processed because each type of clay mineral is characterized by a different calcination temperature. Thus, the thermal treatment requires adjustment of the temperature according to the content of the clay minerals. MCA, on the other hand has shown to induce significant and non-selective changes to the microstructure of all types of clay minerals [22].

Mechanochemical activation can achieve remarkably high degrees of mixing on fine length scales, eventually inducing transitions between allotropic phases and an enhanced chemical reactivity [23–26]. In addition, mechanical stresses generated during impacts can break chemical bonds in molecules as well as covalent and ionic ones [23,27–29]. The structure of clay minerals reacts to damage and disordering processes induced by mechanical stresses. It is composed of repetitive layers of tetrahedral ( $\text{SiO}_4$ ) and octahedral ( $\text{Al}_2\text{O}_6$ ) sheets connected by hydrogen bonds [13]. Mechanochemical activation showed its ability to separate this layered structure and to create active sites, which can enhance the chemical reactivity of ground aluminosilicates [30–32].

The aim of this study was to determine the effect of MCA on the pozzolanic activity of three different natural clays, originating from different parts of Sweden. MCA is proposed as an alternative method to enhance the pozzolanic activity of natural clays. Compared to the thermal treatment, MCA is not selective on the mineralogical composition. However, the grindability of the system is dependent on the hardness and structural arrangement of the minerals. For this reason, it is important to optimize the process accordingly with its mineralogical composition. The optimization of the process was previously investigated and described [33]. Furthermore, the investigation and evaluation of the pozzolanic activity are done through different standardized tests aiming to provide consistent information on the process and its effects.

## 2. Materials and methods

### 2.1. Materials characterization

Experiments were performed on three different natural clays, collected in Sweden in the regions of Stockholm (S), Göteborg (G) and Malmö (M). The chemical compositions of these clays and of the used Portland cement (PC) are summarized in Table 1. After being oven-dried at 100 °C for 24 h, the clay samples were hand ground in a ceramic mortar with a pestle for 1 min. The ground clays were processed in a planetary ball mill, type Retsch PM 100. The volume of the stainless steel jar was 500 ml. Optimization of the used grinding parameters can be found elsewhere [34]. The present study used twelve stainless steel balls

with diameter of 20 mm and applied the following process parameters: ball to powder ratio (B/P) of 25, rotation speed 500 rpm, and grinding duration 20 min.

The Particle Size Distribution (PSD) was determined with a Dynamic Light Scattering (DLS), type Malvern Zetasizer, equipped with a back-scattering detector and with a detection range of 0.1–11000 nm. Ultrasonicated suspensions in distilled water were prepared from untreated and ground clays. The duration of the sonication was limited to one minute to avoid delamination of the particles [35]. The particle size distribution of the three natural clays is shown in Fig. 1.

### 2.2. Pozzolanic activity of blended cements

The pozzolanic activity was assessed using the following tests: (1) Strength Activity Index (SAI), (2) Frattini Test, and (3) Conductivity Test [36,37].

The Strength Activity Index (SAI) is one of the indirect methods to evaluate the pozzolanic activity through comparative compressive strength tests of mortars, following the ASTM C618 standard [38]. The used water-to-binder ratio (w/b) was 0.5 and the binder-to-sand ratio was 1:3. A Hobart N50 mixer was used to prepare mortar mixes, with the rotation speed of 280 rpm and the total mixing time of 5 min. Mortar beams were produced using 100 wt% of PC for the control-sample, and a mixture of 80 wt% of PC and 20 wt% of the respective clay for the remaining samples. Mix designs and sample identification are shown in Table 2. The *m* suffix corresponds to mortar samples, while the *g* suffix prior to the clay label (S, M, and G) corresponds to the ground/mechanochemically treated samples. After mixing, samples were kept in laboratory conditions and a plastic foil was used to cover the surface. Demolding was done 24 h after casting and the samples were cured in a water bath for 7 and 28 days. Compressive strength tests after 7 and 28 days were performed on all samples.

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 the 20 wt% replacement level, Eq. (1):

$$SAI = A/B \times 100\% \quad (1)$$

where A is the compressive strength of the beam with 20 wt% of PC replacement and B is the compressive strength of the control mortar sample containing 100 wt% of PC.

The Frattini test was performed according to the EN 196–5 [39]. The pozzolanic activities of PC, untreated clays and MCA clays were

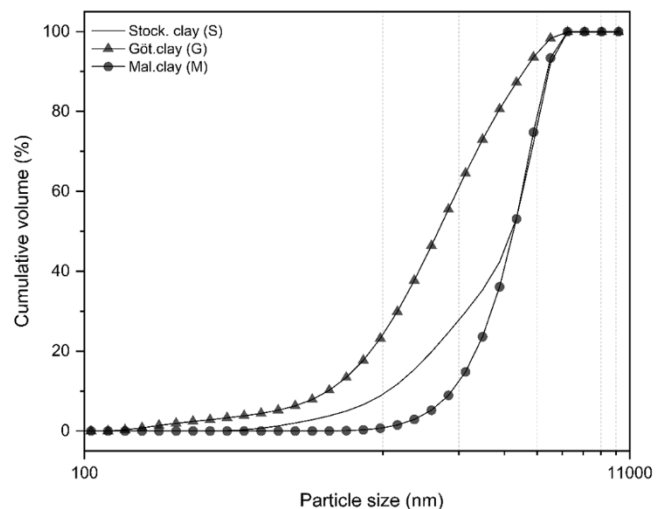


Fig. 1. Particle size distribution of the natural clays originating from Stockholm (S), Göteborg (G), and Malmö (M).

Table 1  
Chemical composition of the natural clays S, G, and M and PC.

	Stockholm clay (S)	Göteborg clay (G)	Malmö clay (M)	PC
CaO	6.41	2.18	16.4	63.3
SiO <sub>2</sub>	52.6	59	49.8	21.2
Al <sub>2</sub> O <sub>3</sub>	15.1	12	8.47	3.4
Fe <sub>2</sub> O <sub>3</sub>	6.9	4.5	3.86	4.1
MgO	2.51	1.5	1.84	2.2
MnO	0.0897	0.064	0.051	–
TiO <sub>2</sub>	0.696	0.607	0.511	–
P <sub>2</sub> O <sub>5</sub>	0.153	0.176	0.161	–
K <sub>2</sub> O	3.78	3.24	2.37	0.56
Na <sub>2</sub> O	1.68	2.66	0.879	0.18
SO <sub>3</sub>	–	–	–	2.7
L.O.I.	7.5	4.5	15.6	2.5

**Table 2**

Mix design of mortars prepared for the SAI test.

Sample identification	Cement (g)	Sand (g)	Clay (ID)	Clay (g)	Water (ml)
Control	450	1350	–	–	225
m-S	360	1350	S	90	225
m-gS	360	1350	gS	90	225
m-G	360	1350	G	90	225
m-gG	360	1350	gG	90	225
m-M	360	1350	M	90	225
m-gM	360	1350	gM	90	225

compared. The Frattini test assumes no other source of  $\text{Ca}^{2+}$  in the system [11,37]. Three samples were prepared for each composition. During the preparation of the PC sample, 100 ml of distillate water was mixed with 20 g of PC to form a suspension. Samples for the natural and ground clays were prepared by replacing 20 wt% of PC. The samples were cured in an oven at 40 °C for 8 days. Subsequently, the suspension was filtered in vacuum through a 2.7 µm nominal pore size filter paper and allowed to cool down at room temperature. The filtrated solution was used to determine concentrations of  $[\text{OH}^-]$  and  $[\text{Ca}^{2+}]$ . 50 ml of the filtrate solution were titrated with hydrochloric acid (HCl) 0.1 M, using methyl orange as indicator.  $[\text{Ca}^{2+}]$  ions were titrated with a solution of EDTA 0.3 M using Patton and Reeder's indicator. The concentration of hydroxyls and  $[\text{Ca}^{2+}]$  ions are plotted and show a concentration of CaO as a function of  $[\text{OH}^-]$  ions at 40 °C. Ion concentrations are expressed in millimols per litre [21,36,37].

The Conductivity Test was done according to the procedure described earlier by Tironi *et al.* [21]. For sample preparation, 2 g of clay were added to 20 ml of a saturated calcium hydroxide solution. Samples were kept under constant stirring at a temperature of 40 °C. Successively, changes of the electrical conductivity were measured at regular intervals, for a total of 3 h. The measurements were done with a digital multimeter, type Keysight 34465A.

### 2.3. Microstructural investigation

Paste specimens were prepared by mixing PC (80 wt%) with the ground or natural clays (20 wt%), utilizing a water to binder ratio (w/b) of 0.4. Dry materials were homogenised by hand for 1 min. After water addition, the mix was stirred for 2 min in a vacuum mixer, type Ecovac Bredent, at 390 rpm, and then sealed-cured in laboratory conditions until being tested. After 7 and 28 days, hydration was stopped by the solvent exchange method with isopropanol as a solvent. The paste samples were immersed in isopropanol for 7 days, the solvent was renewed twice, after 1 day and 3 days, following the procedure described elsewhere [19,40]. Successively, the samples were stored in a desiccator for 3 days. After stopping the hydration, samples were ground and analysed in XRD or impregnated in resin for the SEM-EDS analysis.

*X-ray Diffraction* (XRD) was used to evaluate changes in crystallinity due to the mechanochemical process, as well as to investigate the hydrated crystalline phases of pastes prepared with 20 wt% of clay as a replacement of PC. The used XRD diffractometer was Empyrean by PANalytical equipped with a PIXcel 3D detector. The samples were prepared in holders according to the backloading technique to reduce the effect of a preferred crystal orientation. Cu-K $\alpha$  radiation with a wavelength of 1.54060 Å was generated at 45 kV and 40 mA. The step size was 0.0260 [°2 $\theta$ ]. The X-ray profiles for phase identification and Rietveld semi-quantitative phase analysis were fitted using the X'Pert Highscore program version 4.8. PDF collection codes utilized to perform the X-ray phase analysis are included in Table 3.

OriginLab 2021 software was used for calculating the full width at half maximum (FWHM) and peak areas of the characteristic portlandite peak [001], utilizing a Gaussian fitting [22,41,42].

Paste samples for the SEM-EDS analysis were impregnated with resin 7 and 28 days after casting. The accelerating voltage of 15 kV and a low

**Table 3**

PDF collection codes used for the X-ray phase analysis.

Phases	Crystal structure	PDF collection codes
Quartz	Hexagonal	00–046-1045
Albite	Anorthic	00–041-1480
Microcline	Anorthic	00–019-0926
Orthoclase	Monoclinic	01–086-0437
Calcite	Rhombohedral	00–005-0586
Muscovite	Monoclinic	01–075-0948
Illite	Monoclinic	00–026-0911
Chlinochlore	Monoclinic	01–074-1137
Kaolinite	Monoclinic	01–075-0938
Cordierite	Orthorhombic	01–072-0172
Quintinite	Hexagonal	00–051-1528
C <sub>3</sub> S	Monoclinic	01–086-0402
C <sub>2</sub> S	Monoclinic	00–033-0302
C <sub>4</sub> AF	Orthorhombic	01–071-0667
Ettringite	Hexagonal	00–041-1451
Portlandite	Hexagonal	00–044-1481
Hemicarbonate	Rhombohedral	00–041-0221

vacuum mode were used. Ten images were taken for each sample at 4000x magnification. A minimum of 20 points for each image, and a minimum of 10 images per sample were analysed. The points were manually chosen according to the grey level scale and a point analysis using the EDS analyser was performed [19]. Manual point selection and sufficiently high magnification can limit a number of unintentional analyses of intermixed phases [43].

### 3. Results

#### 3.1. Characterization of the materials before and after mechanochemical activation

The phase composition of natural clays determined by the semi-quantitative Rietveld analysis is shown in Table 4. The XRD analysis performed on samples before and after MCA is shown in Fig. 2. MCA induces a significant change in the degree of crystallinity of all clays. Intensities and areas of the crystalline reflections of clay minerals such as kaolinite, illite and muscovite undergo a marked decrease, whereas the peaks of quartz were only moderately affected. The intensities of the calcite peaks tended to decrease, yet an extensive amorphization was not achieved. Microcline and albite peak intensities were decreasing but these phases did not reach a complete amorphization. Table 5..

The utilized materials in this study were not pure clay compounds, thus the presence of silt and sand were expected. Clay minerals are identified in soils as a fraction with the particle size finer than 4 µm [13]. Hence, PSD of natural and MCA clay samples was investigated and illustrated for the particle size range of 100–11000 nm (Fig. 3). The particle size distribution is affected by the mineralogical composition of clays. Before MCA, the G sample, which has a higher amount of albite

**Table 4**

Semi-quantitative XRD analysis of natural clays collected in Stockholm (S), Göteborg (G), and Malmö (M).

Phases	Content [wt. %]		
	Malmö Clay (M)	Göteborg Clay (G)	Stockholm clay (S)
Quartz	42.0	46.5	31.0
Albite	8.4	32.0	24.1
Microcline	4.7	11.3	10.3
Orthoclase	1.9	2.8	0.9
Calcite	30.2	–	8.6
Muscovite	0.4	0.1	1.2
Illite	10.1	4.8	12.9
Chlinochlore	1.0	Traces	7.7
Kaolinite	1.4	Traces	1.6
Cordierite	–	2.4	1.9
Quintinite	–	0.2	–



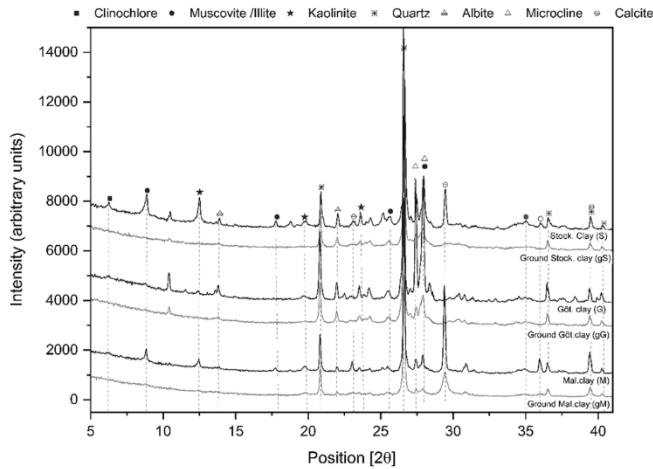


Fig. 2. XRD of natural and MCA Stockholm clay (respectively S and gS), Göteborg clay (G and gG) and Malmö clay (M and gM).

Table 5

Portlandite peaks area and full width at half maximum (FWHM) for PC, natural clays (S, G, M), and mechanochemically activated clays (gS, gG, gM).

Sample	Area	FWHM
PC	59.91	0.135
S	47.88	0.145
gS	31.29	0.116
G	65.07	0.123
gG	39.71	0.111
M	51.07	0.128
gM	30.36	0.119

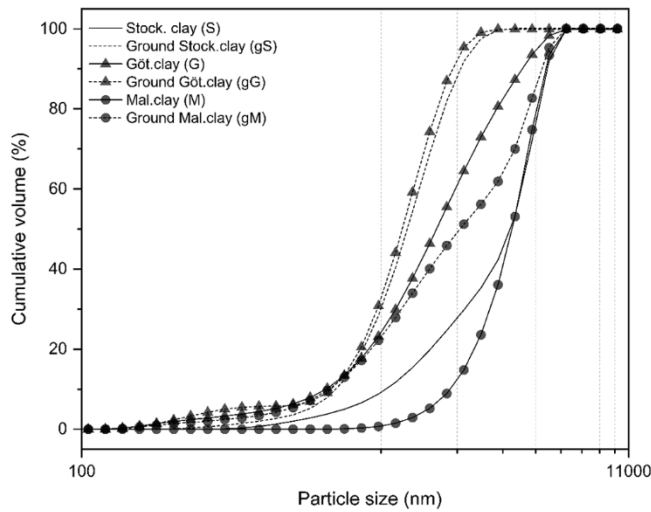


Fig. 3. Particle size distribution of natural and mechanochemical activated clays.

and quartz, exhibited finer particle size distribution than samples S and M. While, after application of MCA, all three samples showed a finer particle size distribution.

### 3.2. Pozzolanic activity

Compressive strength values of mortars were calculated as an average of three measurements, and the results are shown in Fig. 4. The reference mortar (Cntr), prepared with 100 wt% of PC, reached 21.9 MPa after 7 days and of 27.9 MPa after 28 days. Mortar samples

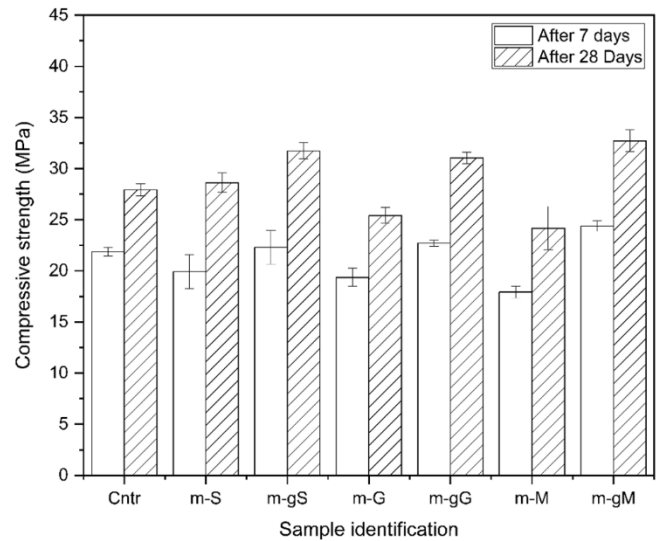


Fig. 4. Compressive strength values of mortar beams prepared with 100 wt% PC (Cntr), with 20 wt% replacement by natural clays (m-S, m-G, and m-M) and by MCA clays (m-gS, m-gG, and m-gM), after 7 and 28 days.

prepared with natural clay (m-S, m-G, and m-M) had a lower 7-day compressive strength than the control mortar. After 7 days, samples containing natural clay exhibited a reduction in the compressive strength by approximately by 9 % for m-S and m-G and 18 % for m-M. No significant changes were observed for the ground clays. m-G and m-M showed a reduction of the 28 days compressive strength, by 8 and 13 %, respectively, while m-S achieved similar values to the control group. An increase on the compressive strength value was evident for the ground clays, m-gS, m-gG and m-gM. A replacement of PC with 20 wt % of gS and gM enhanced the compressive strength by 20 %. Materials are considered to have pozzolanic reactivity when the SAI is greater than 75 % measured after 7 and 28 days of 20 wt% replacement level, ASTM C618 [38].

The calculated SAI values are summarized in Fig. 5. Both natural and MCA clays showed the SAI index higher than 75 % after 7 and 28 days. All mortar samples prepared with 20 wt% of the ground clay showed SAI values higher than 100 % for both 7 and 28 days, thus indicating an increase of the reactivity due to the applied MCA process. SAI is strongly dependent on the crystallinity of the clay minerals [21]. According to

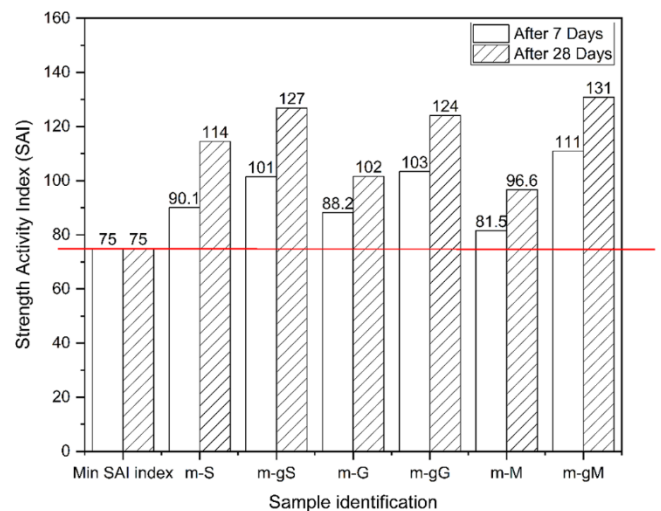


Fig. 5. Strength Activity Index (SAI) of mortar beams prepared with 20 wt% replacement of PC by natural clays (m-S, m-G, and m-M) and by ground clays (m-gS, m-gG, and m-gM), after 7 and 28 days.

ASTM C618, all samples can be considered reactive pozzolanic materials.

The *Frattini test* results are plotted together with the lime solubility curve, which represents the concentration of  $\text{Ca}^{2+}$  in an alkaline solution at 40 °C, Fig. 6. The lime solubility curve was evaluated for  $[\text{OH}^-]$  in the range between 45 mmol/l and 90 mmol/l and a theoretical concentration of  $[\text{CaO}]$  was calculated by Equation (2) [37,44]:

$$[\text{CaO}] = 350/([\text{OH}^-] - 15,0) \text{ mmol/l} \quad (2)$$

Materials with an evident pozzolanic reactivity are located below the lime solubility curve while PC and other non-pozzolanic materials are above this curve [21]. PC, used as a reference, did not show pozzolanic activity, and the mean value after the Frattini test was located on the solubility curve. In general, all natural clays (S, G and M) were located above the solubility line thus indicating weak or no pozzolanic reactivity.

After 8 days, mixes containing activated clays showed an increased pozzolanic reactivity, except for the gG clay. According to the standard, below the solubility line indicates that the analysed material is a pozzolan and that a significant amount of  $\text{Ca}^{2+}$  ions produced by the cement hydration, was consumed in the pozzolanic reaction. Hence, all studied natural untreated clays and the ground Göteborg clay (gG) cannot be classified as pozzolana. Tests performed after 28 days have shown that also the ground Göteborg (gG) clay lied below the solubility line, indicating enhanced pozzolanic activity.

The results of the *Conductivity Test* presented as a function of time for the ground clays are shown in Fig. 7. The electrical conductivity is expected to decrease with time due to the ongoing pozzolanic reaction [21]. In the first 30 to 40 min, the consumption of  $[\text{Ca}^{2+}]$  and  $[\text{OH}^-]$  led to a rapid decrease of the electrical conductivity for the ground clays. The rate of the lime consumption is dependent, among other factors, on the specific surface area of the material and it does not involve the cement hydration [45]. EC showed that the ground Stockholm clay (gS) is the most reactive pozzolan, followed by the ground Malmö clay (M), and least reactive being the Göteborg clay (gG).

### 3.3. Microstructure

XRD spectra of pastes containing 80 wt% of PC with 20 wt% of ground (gS, gG, gM) or natural (S, G, M) clays, after 28 days, are shown

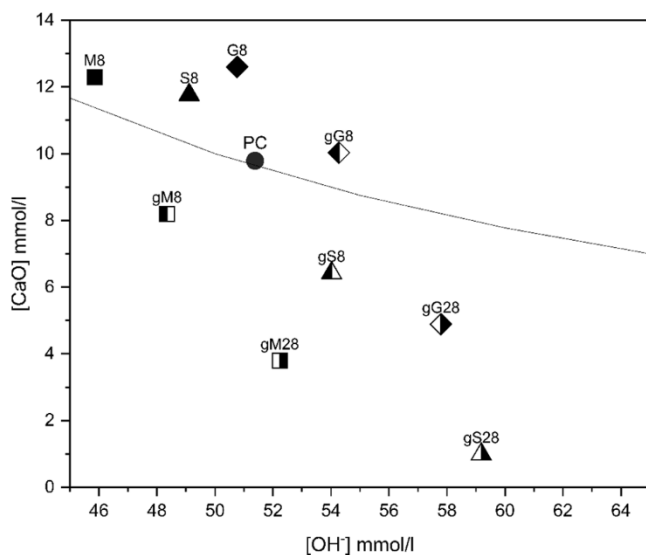


Fig. 6. Frattini test results for cement paste containing 20 wt% of different natural clays after 8 days (S8, G8, M8), ground clays after 8 days (gS8, gG8, gM8), and ground clays after 28 days (gS28, gG28, gM28) compared with a control sample of 100 wt% of Portland cement (PC).

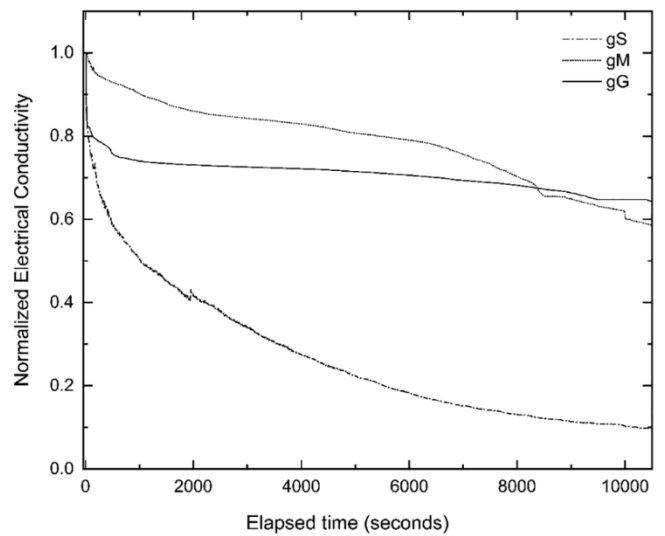


Fig. 7. Relationship of the electrical conductivity with time for ground Stockholm clay (gS), for the ground Malmö clay (gM), and for the ground Göteborg clay (gG).

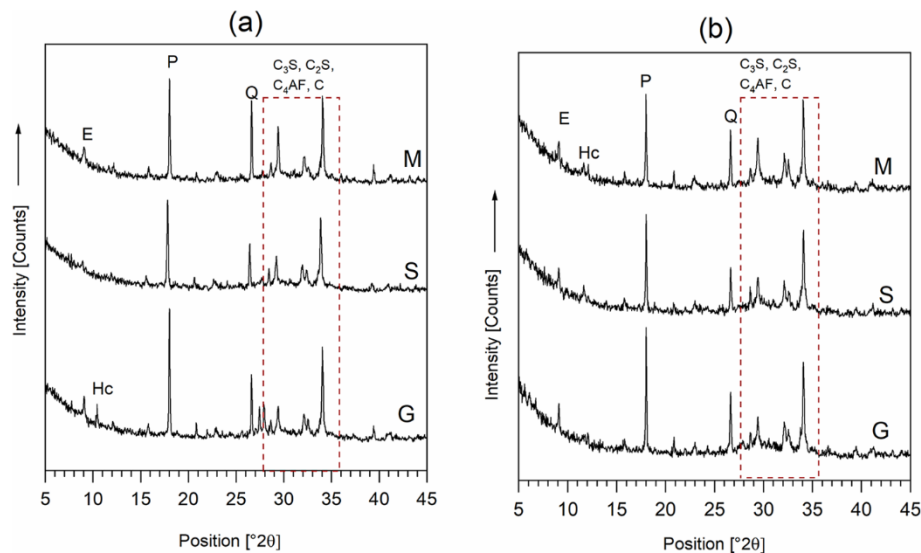
in Fig. 8. The intensity of the peaks corresponding to Portlandite (P) was higher for samples containing 20 wt% of Göteborg clay (G) compared to Stockholm and Malmö (S and M) clays.

Generally, all samples containing clays subjected to the mechano-chemical activation process (gS, gG, and gM) showed less intensive Portlandite peaks. Furthermore, the intensity of the main quartz peak located at  $26.6^\circ 2\theta$ , decreased for all pastes containing ground clays. Belite and alite peaks located at  $32.5^\circ 2\theta$ , were visible in all samples. AFm phases, such as hemihydrate was visible after 28 days, especially for the clays originating from Stockholm (S). Compared to the natural untreated clays, ettringite peak intensities were slightly higher for samples prepared with 20 wt% replacement of the ground clays gS and gM and almost unchanged for the gG clay.

The composition of the C—S—H after 28 days was determined according to the Rossen and Scrivener method [43]. SEM micrographs are shown in Fig. 9. An addition of 20 wt% of clay altered the phase composition of the C—S—H, which was determined by calculating average Si/Ca and Al/Ca ratios as shown in Fig. 10 and Fig. 11. The pozzolanic reaction has produced C—S—H with higher Si/Ca and Al/Ca ratios. After 7 days, changes in the Si/Ca and Al/Ca ratios were visible for all the samples, with higher values for the ground clays. After 28 days, it was possible to identify ratios corresponding to the AFm and AFt phases, for gS and gM.

### 4. Discussions

Crystallinity is an important factor governing the development of pozzolanic reactivity due to the different rates of the chemical reactions of the crystalline and amorphous phases [22]. The MCA was shown to increase the amorphization of clay minerals and resulted in SAI values being higher than 100 %. The addition of SCMs affects the hydration of PC. In the beginning, it is limited to the filler effect [34,35]. Later, the hydration of PC accelerates and is followed by the pozzolanic reactions [36]. The amount and fineness of SCMs are major factors affecting the kinetics of the hydration process [37]. In geology and sedimentology, the clay fraction is defined as having an average particle size smaller than  $4 \mu\text{m}$  [13]. These very fine particles can fill free spaces formed between cement and aggregate particles, leading to a denser microstructure and a higher compressive strength of the hydrated matrix, [39]. Even if not composed of pure clay fractions, the studied natural clays (S, G, and M) showed a size distribution with the average particle diameter  $< 8 \mu\text{m}$ , Fig. 3. Thus, the filler effect could have occurred in the



**Fig. 8.** Comparison of the phase composition for pastes prepared with 20 % replacement of cement by a) natural clays and b) ground clays at 28 days of hydration. Phase abbreviation used: E = ettringite, P = Portlandite, Hc = hemihydrate.

case of the untreated samples, which did not show any pozzolanic activity according to the Frattini test results, while reaching a value of 100 % for the SAI test. It could explain the behaviour of the gG sample, which exhibited a poor pozzolanic activity in the Frattini test but still reached higher values in the SAI (m-gG). Moreover, the natural clay from Göteborg (G) was characterized by a finer particle size distribution (Fig. 2).

#### 4.1. Comparison of test methods to assess the pozzolanic activity

It is quite common to compare test methods for the pozzolanic activity, due to the significant differences in the existing methods. The Frattini and the Conductivity tests were performed after 8 days of exposure to 40 °C, while the SAI is determined on samples cured at around 20 °C. Samples for SAI and Frattini tests contained 20 wt% of clay. No significant correlation was found for results obtained after 8 days for the Frattini test and 7 or 28 days for the SAI test (Fig. 12), which complies with earlier results by Tironi et al. [21]. However, when comparing the results of the two measurements after 28 days, Fig. 13, a correlation was observed complying this time with the study conducted by Donatello et al. [37].

The EC test is directly dependent on the nature, composition, and specific surface area of the analysed pozzolana since cement is not used for these measurements. The consumption of species leads to a drop of the electrical conductivity. A direct relationship between the EC of the untreated samples and their SAI complies with earlier results published by Tironi et al. [21], Fig. 14. At the same time, no correlation was found for the ground clays. An interesting result is gG samples behaving like an outlier. This effect might confirm the Frattini test after 8 days, which did not classify gG as a pozzolanic material. Hence, confirming that a high SAI determined for the gG was related to the small particle size and to the filling effect rather than due to the pozzolanic reactivity. The studied clays had different properties, which affected their interaction with the hydrating PC, i.e., content of clay minerals and calcite, particle size distribution, and specific surface area. The results obtained from these three methods indicated that clays originating from Stockholm (S) and Malmö (M) the MCA enhanced their pozzolanic reactivity. The particle size distribution influences more the SAI test, thus it is necessary to perform additional tests based on a direct method, i.e., the used Frattini test.

#### 4.2. Influence of clay composition

A number of earlier studies have indicated a dependency between the amorphization due to the calcination process, and the improved pozzolanic reactivity of kaolinitic and low-grade clays [16,46]. Yet, comprehensive studies on improved pozzolanic reactivity due to mechanochemical activation are missing. Among clay minerals, kaolinite is the one having a sheet layer composed by aluminates and silicates repeated in a 1:1 pattern. While subjected to the MCA process, kaolinite have shown extensive structural changes, increased surface area, and higher pozzolanic reactivity [17,30,47,48]. In the studied clays, the kaolinite content was low (1.6 for S and 1.4 for M), however the corresponding XRD peaks disappeared after 20 min of grinding, suggesting structural changes in the ground clays.

Illite particles can be amorphized by a high-energy grinding in a planetary ball mill within the early stage of grinding. Studies from Yang et al. [49] indicated that the application of MCA to illite decreased the specific surface area and the total pore volume after 2 h of grinding. The Stockholm clay (S), which had also a higher content of this mineral (12.9 wt%), showed a nearly completely disappearing illite peaks after 20 min of grinding, thus indicating an extensive amorphization. A similar effect was also observed in the Malmö clay, where the illite content was 10.1 wt%.

As the muscovite phase is concerned, processing of pure phase with MCA using a planetary ball mill decreased the crystallinity and increased the pozzolanic activity index to 94.36 %, Yao et al. [50]. In the present study, the content of muscovite was generally low, with the highest for clay originating from Stockholm, (S). XRD peaks related to Muscovite disappeared after 20 min of grinding.

The studied clay samples had a high content of these phases, identified as albite, microcline, and orthoclase. The MCA of feldspars in a planetary ball mill for 20 min, has shown a high amorphization rate and an increased final pozzolanic reactivity. The highest pozzolanic activity index was achieved by the microcline phase, followed by the albite phase [51]. In this study, the XRD intensity of peaks related to feldspars decreased. Similarly, the intensity of microcline and albite peaks decreased after grinding for 20 min but did not disappear completely. Thus, indicating only a partial amorphization. Albite possess a lower pozzolanic reactivity compared to the other feldspars. Furthermore, albite content was higher for G clay, explaining the lower reactivity of this ground clay (gG).

As the quartz phase is concerned, mechanochemical activation of the



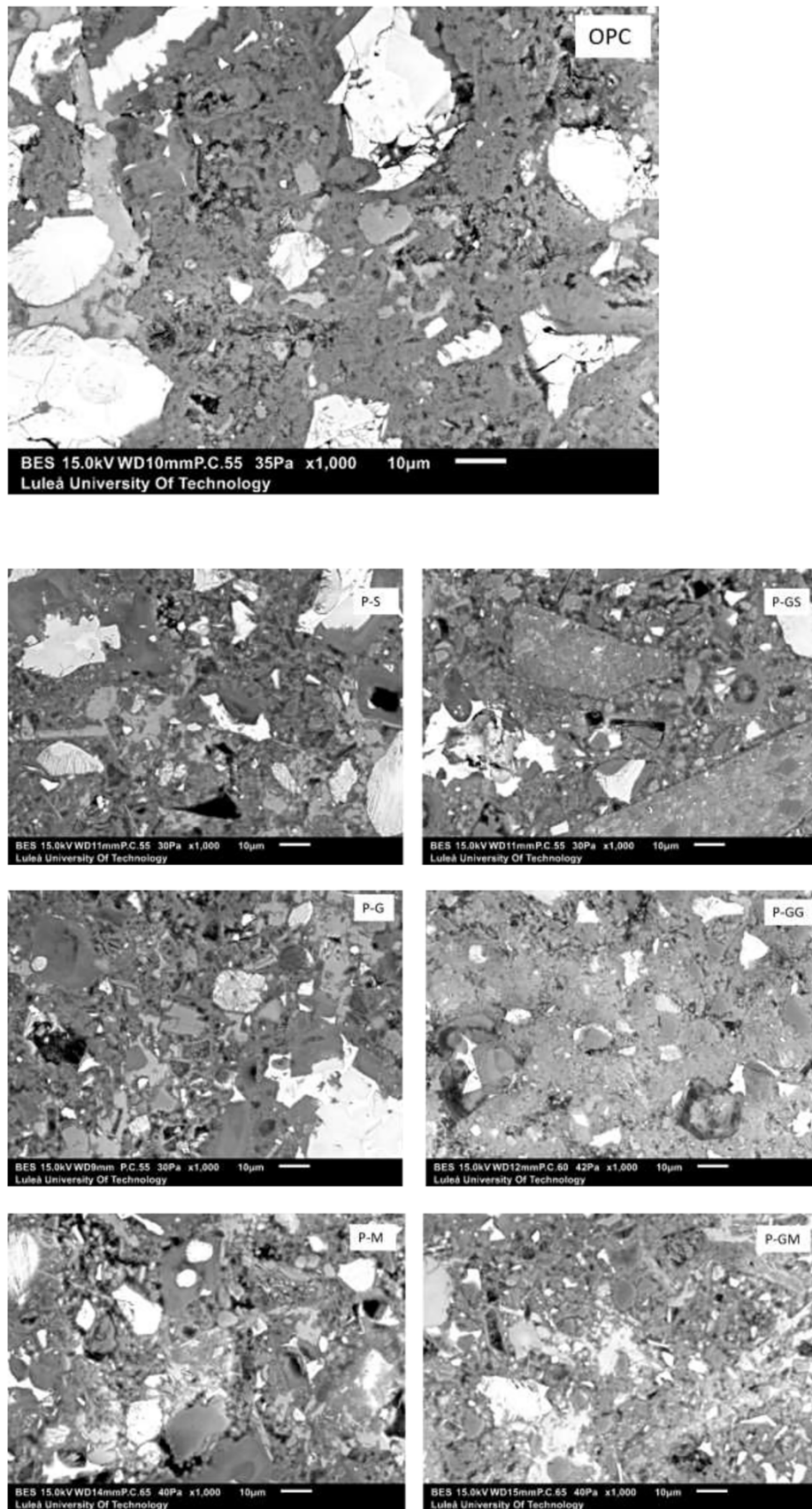
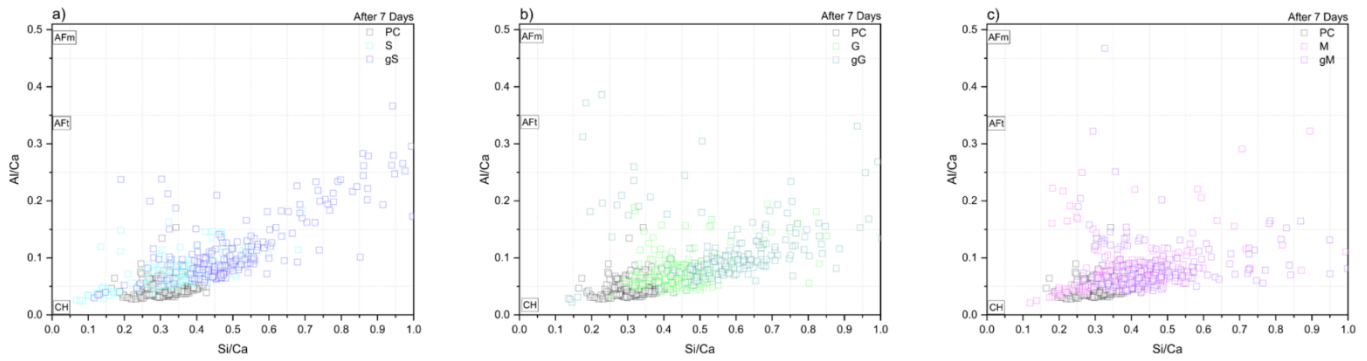
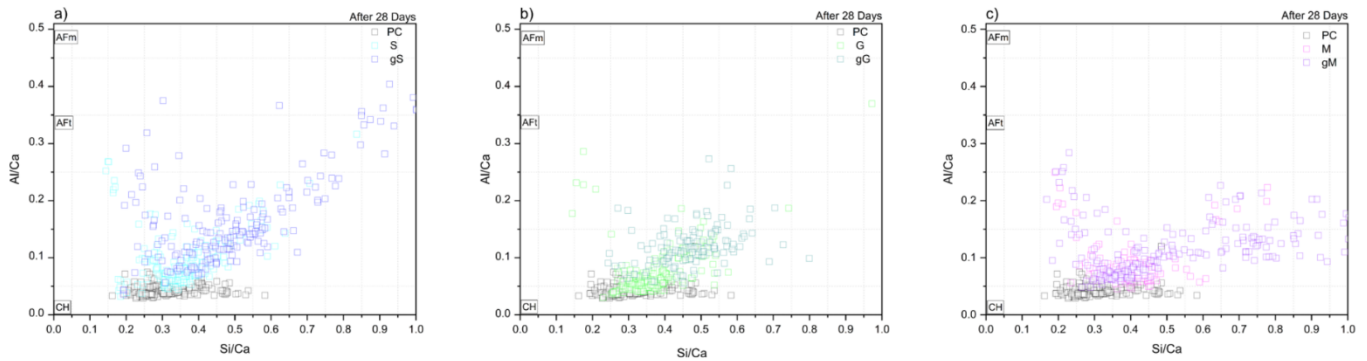


Fig. 9. SEM micrographs after 28 days, for reference OPC, natural and ground clay from Stockholm (S and gS), natural and ground clay from Göteborg (G and gG), and natural and ground clay from Malmö (M and gM).



**Fig. 10.** Relation between Al/Ca and Si/Ca element ratio analyzed by SEM-EDX point analyses after 7 days, for reference PC in relationship with a) natural and ground clay from Stockholm (S and gS), b) natural and ground clay from Göteborg (G and gG), and c) and natural and ground clay from Malmö (M and gM).



**Fig. 11.** Relation between Al/Ca and Si/Ca element ratio analyzed by SEM-EDX point analyses after 28 days, for reference PC in relationship with a) natural and ground clay from Stockholm (S and gS), b) natural and ground clay from Göteborg (G and gG), and c) and natural and ground clay from Malmö (M and gM).

latter phase, can induce changes in its surface, its crystalline structure, and its pozzolanic reactivity [27,52–55]. This is usually related to lattice distortions and the formation of active species [27]. In our study we observe a slight decrease of the main quartz peak ( $2\theta = 26.65^\circ$ ) after MCA as visualized in *in* Fig. 15. However, this decrease is minor and the main relevant XRD peaks of quartz are still present after MCA since quartz has a considerably higher hardness compared to the other minerals contained in these natural clays, and it requires different process parameters to achieve a complete amorphization [56]. Based on this data, we hypothesize that a small portion of the quartz may have been mechanochemically activated, characterized by active Si, which might have participated to the hydration process. While the crystalline quartz might have contributed only to the filler effect. This could explain why the gG showed still good results in the SAI testing, as the quartz content in the Göteborg clay (G) was higher compared to the other clays (46.5%). However, this hypothesis needs to be further verified and a more intensive study in this regard, should be carried out.

Calcite is a commonly occurring clay mineral, but it is not suitable for production of burnt brick clays, yet it can be utilized as SCMs. An extensive research has been done aiming to partially substitute cement with calcined clays and limestone, [6,18,57,58]. Calcium carbonate has the ability to react with alumina originating from the calcined kaolinite to produce additional AFm phases [59]. Calcareous clays with a calcite content between 15 and 25 wt% can form a reactive glass phase during calcination and the reactivity of some clay minerals, e.g., illite and smectite could be enhanced when calcite is present as raw material [60].

Zunino et al. [61] has shown that clays containing up to 10 wt% of calcite could be used as SCMs, after calcination. The Frattini test of two samples containing 8.6 wt% and 30.2 wt% calcite (S and M), has shown an enhanced pozzolanic reactivity for both. A study by Habert et al. [14] has indicated that compressive strength is more influenced by the

content of minerals rather than by their type. The mineral compositions of the studied clays are shown in Fig. 16.

Comparison of the results from Frattini and EC tests comply with the results from Habert et al. [14] because the S clay has a higher pozzolanic reactivity. However, according to SAI, the M clay seems to have a higher pozzolanic reactivity. The increased pozzolanic reactivity is not dependent only on the clay minerals content. As previously mentioned, the contribution of the filler effect might have influenced the SAI results. Furthermore, the other phases play an important role, especially in the strength development. Optimization of MCA parameters might be a solution for achieving a higher amorphization rate of other phases as feldspars and calcite, and consequently improve their pozzolanic activity.

#### 4.3. Hydrated phases

The product from the reaction of PC with water is calcium-silicate-hydrate (C—S—H), which constitutes the majority of the final volume of the paste [57]. The composition of C—S—H is strongly dependent on the degree of reaction of SCMs, and affected by the dissolution of the aluminate and silicate phases [62]. There are three main defects that contribute to changes in the Ca/Si in cement blended with calcined clays: 1) missing bridges in the silicate tetrahedra; 2) substitution of two protons by calcium ions, in the terminating unlinked silicate tetrahedra; 3) presence of calcium ions in the interlayer [57]. The MCA of kaolinite contributes to the rupture of the hydrogen bonds between the adjacent kaolinite layers [63]. The high-energy grinding can cause modifications of the crystal structure by the rupture of O—H, Al—OH, Al—O—Si and Si—O bonds [64]. Thus, the Si/Ca and Al/Ca ratio are expected to show an increase for the ground clays due to the structural changes of the silicate tetrahedra during MCA. On the other hand, small changes of Si/Ca and



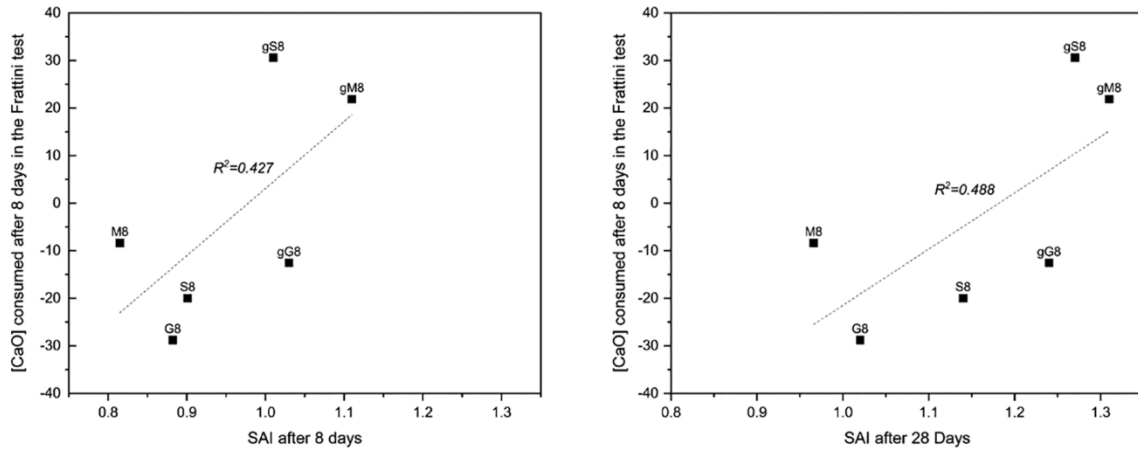


Fig. 12. Correlation between CaO consumed during the Frattini test and the SAI test respectively at a) after 8 and 7 days, and b) after 8 and 28 days.

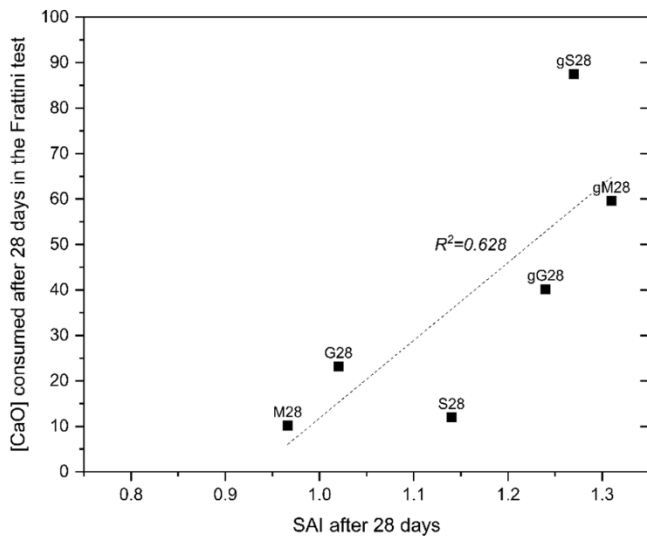


Fig. 13. Correlation between CaO consumed during the Frattini test both after 8 and 28 days.

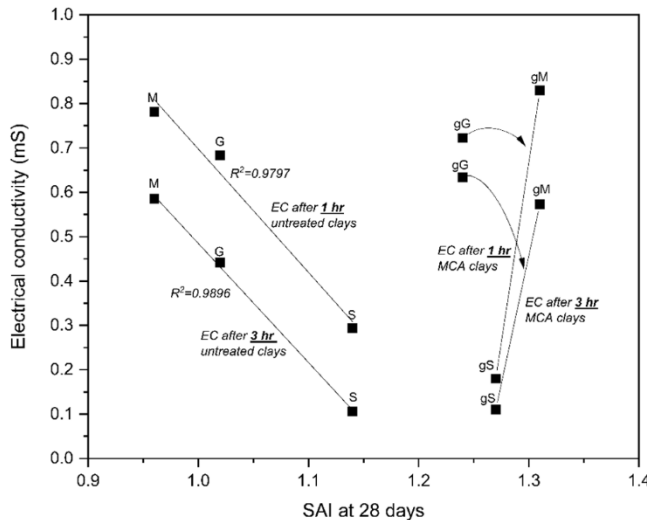


Fig. 14. Correlation between electrical conductivity measured at 1 and 3 h and the SAI test at 28 days.

Al/Ca in the blended cement pastes with natural clay (S, G, and M) are related to the increased content of Al and Ca originating from the aluminosilicates and calcite in clay. This phenomenon was visible for all ground samples, especially for gS and gM, as a confirmation once again to their improved pozzolanic activity, Fig. 17.

The gM clay has shown the highest increase in the Si/Ca, maintaining a relatively low Al/Ca compared with the other ground clays, due to its high calcite content. It is known that metakaolinite, during the pozzolanic reaction, reacts with portlandite, water and sulphate, to form C-A-S-H, AFt phases and ettringite. Addition of limestone can also induce the formation of AFm carbonate equivalent phases [57] as shown in Fig. 8. gS and gM contained the highest amount of clay minerals and calcite, thus promoting formation of AFm phases. Moreover, the formation of AFm carbonate equivalent phases was evident for gS and gM. The portlandite content was determined by estimation of the intensity of the XRD peaks and calculation of the peak areas of the characteristic peaks, Table 4. The lower portlandite content was detected for gS and gM, thus confirming Frattini and EC test results. Due to its lower pozzolanic activity, natural and MCA Göteborg clay (G and gG) did not show the same trends. FWHM values are lower for all the ground samples compared with the natural untreated clays. A significant change was observed for the S, followed by M, and finally by the G clay. The decrease of the FWHM and smaller area corresponding to the portlandite peak indicated that the reaction with the amorphous clay minerals has occurred [42].

## 5. Conclusions

Enhancement of the pozzolanic reactivity of three natural clays after application of the mechanochemical activation process (MCA) was investigated through SAI, Frattini and Conductivity tests. The hydration of pastes containing 20 wt% of MCA clays was preliminary studied using XRD and SEM-EDS. The results showed that MCA can improve the pozzolanic reactivity of natural clays. It is necessary to optimize the process parameters to achieve extensive amorphization of all the phases, which are characterized by different hardness and structural arrangement.

The following conclusions were formulated:

- Mechanochemical activation in a ball mill can enhance the pozzolanic reactivity of natural clays reaching SAI higher than 120 % after 28 days of hydration. The pozzolanic reactivity of MCA clays was also confirmed by the direct Frattini test method and the indirect Electrical conductivity test.
- Clays with a higher content of clay minerals and calcite, S and M, showed an improved pozzolanic activity after grinding for 20 min.

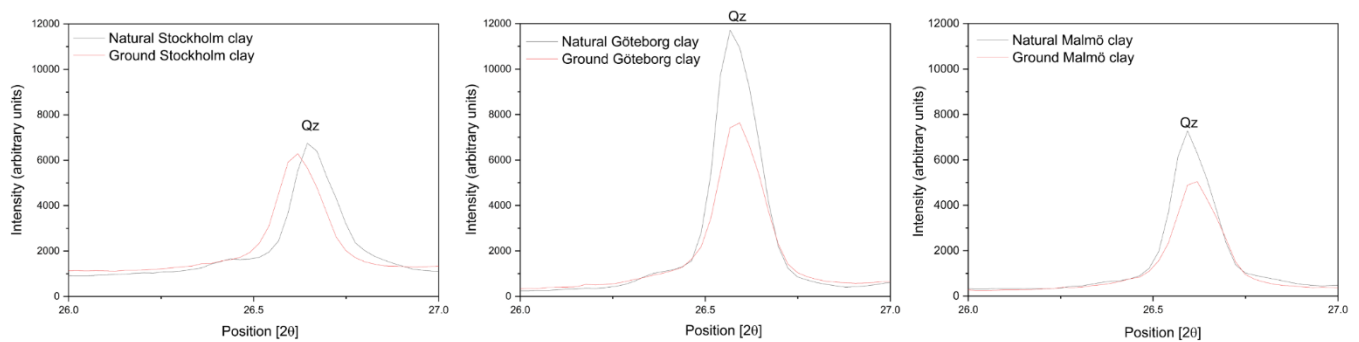


Fig. 15. XRD pattern of the main characteristic peak for quartz before and after grinding. The slight shift of the quartz peak in Fig. 15 (a) may relate to sample preparation effect.

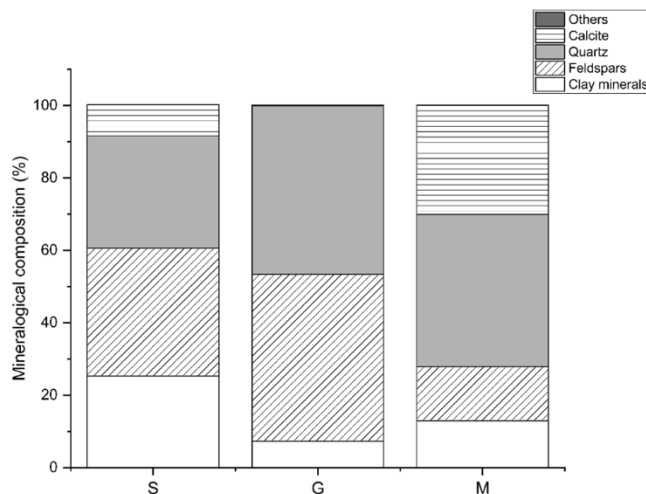


Fig. 16. Mineralogical composition of the natural clays, collected in Stockholm (S), Göteborg (G), and Malmö (M).

- Mechanochemical activated feldspars can also achieve extensive structural amorphization, indicating a contribution to the pozzolanic reactivity.
- Due to the nature of the clay fractions, characterized by a fine particle size distribution, SAI must be compared with direct methods such as the Frattini test to assess changes in the pozzolanic reactivity due to application of MCA.

#### Funding

This work was supported by the Swedish Research Council – FORMAS.

#### CRediT authorship contribution statement

**Ilda Tole:** Conceptualization, Methodology, Formal analysis, Writing – original draft. **Francesco Delogu:** Supervision, Writing – review & editing. **Elsa Qoku:** Visualization, Software, Validation, Writing – review & editing. **Karin Habermehl-Cwirzen:** Supervision, Writing – review & editing. **Andrzej Cwirzen:** Supervision, Funding acquisition, Writing – review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

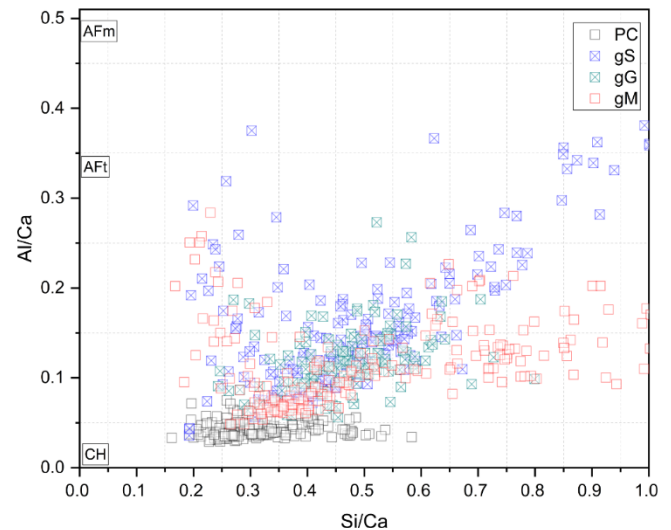


Fig. 17. Comparison of C—S—H composition by SEM-EDS for the ground clays and PC after 28 days.

#### References

- [1] IPCC, 2014: Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, R.K. Pachauri and L.A. Meyer (eds.)]. IPCC, Geneva, Switzerland, 151 pp.
- [2] BPIE (Buildings Performance Institute Europe) (2022). Roadmap to climate-proof buildings and construction – How to embed whole-life carbon in the EPBD. <https://www.bpie.eu/publication/roadmap-to-climate-proof-buildings-and-constructionhow-to-embed-whole-life-carbon-in-the-epbd/>.
- [3] B. Lothenbach, K. Scrivener, R.D. Hooton, Supplementary cementitious materials, *Cem. Concr. Res.* 41 (12) (2011) 1244–1256.
- [4] H.M. Owaid, R.B. Hamid, M.R. Taha, A review of sustainable supplementary cementitious materials as an alternative to all-Portland cement mortar and concrete, *Aust. J. Basic Appl. Sci.* 6 (9) (2012) 287–303.
- [5] K.L. Scrivener, Options for the future of cement, *Indian Concr. J* 88 (7) (2014) 11–21.
- [6] F. Zunino, K. Scrivener, The reaction between metakaolin and limestone and its effect in porosity refinement and mechanical properties, *Cem. Concr. Res.* 140 (2021) 106307.
- [7] M. Kasaniya, M.D.A. Thomas, E.G. Moffatt, Pozzolanic reactivity of natural pozzolans, ground glasses and coal bottom ashes and implication of their incorporation on the chloride permeability of concrete, *Cem. Concr. Res.* 139 (2021) 106259.
- [8] M. Schneider, The cement industry on the way to a low-carbon future, *Cem. Concr. Res.* 124 (2019) 105792.
- [9] M.C. Juenger, R. Siddique, Recent advances in understanding the role of supplementary cementitious materials in concrete, *Cem. Concr. Res.* 78 (2015) 71–80.
- [10] A.c.i., Committee, Cement and concrete terminology, The Institute (1978).
- [11] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Incorporation of calcined clays in mortars: porous structure and compressive strength, *Procedia Mater. Sci.* 1 (2012) 366–373.

- [12] B.B. Sabir, S. Wild, J. Bai, Metakaolin and calcined clays as pozzolans for concrete: a review, *Cem. Concr. Compos.* 23 (6) (2001) 441–454.
- [13] F. Bergaya, G. Lagaly, *Handbook of clay science*, Newnes, 2013.
- [14] G. Habert, N. Choupay, G. Escadeillas, D. Guillaume, J.M. Montel, Clay content of argillites: Influence on cement based mortars, *Appl. Clay Sci.* 43 (3–4) (2009) 322–330.
- [15] H.H. Murray, Traditional and new applications for kaolin, smectite, and palygorskite: a new overview, *Appl. Clay Sci.* 17 (2000) 207–221.
- [16] A. Alujas, R. Fernández, R. Quintana, K.L. Scrivener, F. Martirena, Pozzolanic reactivity of low grade kaolinitic clays: Influence of calcination temperature and impact of calcination products on OPC hydration, *Appl. Clay Sci.* 108 (2015) 94–101.
- [17] R. Fernandez, F. Martirena, K.L. Scrivener, The origin of the pozzolanic activity of calcined clay minerals: A comparison between kaolinite, illite and montmorillonite, *Cem. Concr. Res.* 41 (1) (2011) 113–122.
- [18] K. Scrivener, F. Martirena, S. Bishnoi, S. Maity, Calcined clay limestone cements (LC3), *Cem. Concr. Res.* 114 (2018) 49–56.
- [19] F. Avet, K. Scrivener, Investigation of the calcined kaolinite content on the hydration of Limestone Calcined Clay Cement (LC3), *Cem. Concr. Res.* 107 (2018) 124–135.
- [20] K.L. Scrivener, B. Lothenbach, N. De Belie, E. Gruyaert, J. Skibsted, R. Snellings, A. Vollpracht, TC 238-SCM: hydration and microstructure of concrete with SCMs, *Mater. Struct.* 48 (4) (2015) 835–862.
- [21] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Assessment of pozzolanic activity of different calcined clays, *Cem. Concr. Compos.* 37 (2013) 319–327.
- [22] B. Ilić, V. Radonjanin, M. Malešev, M. Zdujić, A. Mitrović, Effects of mechanical and thermal activation on pozzolanic activity of kaolin containing mica, *Appl. Clay Sci.* 123 (2016) 173–181.
- [23] F. Delogu, A combined experimental and numerical approach to the kinetics of mechanically induced phase transformations, *Acta Mater.* 56 (4) (2008) 905–912.
- [24] F. Delogu, Kinetics of allotropic phase transformation in cobalt powders undergoing mechanical processing, *Scr. Mater.* 58 (2) (2008) 126–129.
- [25] P. Baláz, *Mechanochemistry in minerals engineering*. In *Mechanochemistry in nanoscience and minerals engineering*, Springer, Berlin, Heidelberg, 2008, pp. 257–296.
- [26] F. Gomollón-Bel, Ten Chemical Innovations that will change our world: IUPAC identifies emerging technologies in Chemistry with potential to make our planet more sustainable, *Chem. Int.* 41 (2) (2019) 12–17.
- [27] F. Delogu, Mechanochemical behavior of surface radicals in ground quartz, *The Journal of Physical Chemistry C* 115 (43) (2011) 21230–21235.
- [28] M.K. Beyer, H. Clausen-Schaumann, Mechanochemistry: the mechanical activation of covalent bonds, *Chem. Rev.* 105 (8) (2005) 2921–2948.
- [29] C. Suryanarayana, Mechanical alloying and milling, *Prog. Mater. Sci.* 46 (1–2) (2001) 1–184.
- [30] R.L. Frost, É. Makó, J. Kristóf, E. Horváth, J.T. Klopogge, Mechanochemical treatment of kaolinite, *J. Colloid Interface Sci.* 239 (2) (2001) 458–466.
- [31] P. Baláz, M. Achimovičová, M. Baláz, P. Billik, Z. Cherkezova-Zheleva, J.M. Criado, F. Delogu, E. Dutková, E. Gaffet, F.J. Gotor, R. Kumar, I. Mitov, T. Rojac, M. Senna, A. Streletskii, K. Wieczorek-Ciurro, Hallmarks of mechanochemistry: from nanoparticles to technology, *Chem. Soc. Rev.* 42 (18) (2013) 7571.
- [32] O. Cocco, S. Garroni, S. Enzo, G. Pia, P. Meloni, F. Delogu, Ball milling of silica-based pyroclastic scoriae: measurement of mechanochemical reactivity by radical scavenging, *The Journal of Physical Chemistry C* 122 (5) (2018) 2773–2782.
- [33] I. Tole, K. Habermehl-Cwirzen, A. Cwirzen, Optimization of the Process Parameters Controlling the Degree of Amorphization during Mechanical Activation of Clay Using the Taguchi Method, *Multidisciplinary Digital Publishing Institute Proceedings* 34 (1) (2019) 15.
- [34] I. Tole, K. Habermehl-Cwirzen, M. Rajczakowska, A. Cwirzen, Activation of a raw clay by Mechanochemical process—effects of various parameters on the process efficiency and cementitious properties, *Materials* 11 (10) (2018) 1860.
- [35] A.L. Polí, T. Batista, C.C. Schmitt, F. Gessner, M.G. Neumann, Effect of sonication on the particle size of montmorillonite clays, *J. Colloid Interface Sci.* 325 (2) (2008) 386–390.
- [36] X. Li, R. Snellings, M. Antoni, N.M. Alderete, M. Ben Haha, S. Bishnoi, Ö. Cizer, M. Cyr, K. De Weert, Y. Dhandapani, J. Duchesne, J. Haufe, D. Hooton, M. Juenger, S. Kamali-Bernard, S. Kramar, M. Marroccoli, A.M. Joseph, A. Parashar, C. Patapy, J.L. Provis, S. Sabio, M. Santhanam, L. Steger, T. Sui, A. Telesca, A. Vollpracht, F. Vargas, B. Walkley, F. Winnefeld, G. Ye, M. Zajac, S. Zhang, K.L. Scrivener, Reactivity tests for supplementary cementitious materials: RILEM TC 267-TRM phase 1, *Mater. Struct.* 51 (6) (2018).
- [37] S. Donatello, M. Tyrer, C.R. Cheeseman, Comparison of test methods to assess pozzolanic activity, *Cem. Concr. Compos.* 32 (2) (2010) 121–127.
- [38] Astm c., 618, Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, *Annu. B. ASTM Stand.* (2014) 1–5.
- [39] Methods of testing cement—Part 5: Pozzolanicity test for pozzolanic cements 2011, (2011).
- [40] Y. Briki, F. Avet, M. Zajac, P. Bowen, M.B. Haha, K. Scrivener, Understanding of the factors slowing down metakaolin reaction in limestone calcined clay cement (LC3) at late ages, *Cem. Concr. Res.* 146 (2021) 106477.
- [41] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Potential use of Argentine kaolinitic clays as pozzolanic material, *Appl. Clay Sci.* 101 (2014) 468–476.
- [42] M. Wu, Y. Zhang, Y. Jia, W. She, G. Liu, Z. Yang, Y.u. Zhang, W. Zhang, W. Sun, Effects of sodium sulfate on the hydration and properties of lime-based low carbon cementitious materials, *J. Cleaner Prod.* 220 (2019) 677–687.
- [43] J.E. Rossen, K.L. Scrivener, Optimization of SEM-EDS to determine the C-A-S-H composition in matured cement paste samples, *Mater. Charact.* 123 (2017) 294–306.
- [44] European Standard EN 196-5:2011, Methods of testing cement - Pozzolanicity test for pozzolanic cement, (2011).
- [45] P. Hewlett, M. Liska (Eds.), *Lea's Chemistry of Cement and Concrete*, Butterworth-Heinemann, 2019.
- [46] S. Hollanders, R. Adriaens, J. Skibsted, Ö. Cizer, J. Elsen, Pozzolanic reactivity of pure calcined clays, *Appl. Clay Sci.* 132 (2016) 552–560.
- [47] C. Vizcayno, R.M. De Gutierrez, R. Castelló, E. Rodríguez, C.E. Guerrero, Pozzolan obtained by mechanochemical and thermal treatments of kaolin, *Appl. Clay Sci.* 49 (4) (2010) 405–413.
- [48] E.F. Aglietti, J.P. Lopez, E. Pereira, Mechanochemical effects in kaolinite grinding. II. Structural aspects, *Int. J. Miner. Process.* 16 (1–2) (1986) 135–146.
- [49] H. Yang, W. Yang, Y. Hu, C. Du, A. Tang, Effect of mechanochemical processing on illite particles, *Part. Part. Syst. Char.* 22 (3) (2005) 207–211.
- [50] G. Yao, H. Zang, J. Wang, P. Wu, J. Qiu, X. Lyu, Effect of mechanical activation on the pozzolanic activity of muscovite, *Clays Clay Miner.* 67 (3) (2019) 209–216.
- [51] G. Yao, Z. Wang, J. Yao, X. Cong, C. Anning, X. Lyu, Pozzolanic activity and hydration properties of feldspar after mechanical activation, *Powder Technol.* 383 (2021) 167–174.
- [52] K. Gobindlal, Z. Zujovic, P. Yadav, J. Sperry, C.C. Weber, The Mechanism of Surface-Radical Generation and Amorphization of Crystalline Quartz Sand upon Mechanochemical Grinding, *The Journal of Physical Chemistry C* 125 (38) (2021) 20877–20886.
- [53] P. Meloni, G. Carcangiu, F. Delogu, Specific surface area and chemical reactivity of quartz powders during mechanical processing, *Mater. Res. Bull.* 47 (1) (2012) 146–151.
- [54] S. Rescic, P. Plescia, P. Cossari, E. Tempesta, D. Capitani, N. Proietti, F. Frattini, A. M. Mecchi, Mechano-chemical activation: an ecological safety process in the production of materials to stone conservation, *Procedia Eng.* 21 (2011) 1061–1071.
- [55] K. Tkáčová, N. Stevulova, Change in structure and enthalpy of carbonates and quartz accompanying grinding in air and aqueous environments, *Powder Technol.* 52 (2) (1987) 161–166.
- [56] G. Yao, T. Cui, J. Zhang, J. Wang, X. Lyu, Effects of mechanical grinding on pozzolanic activity and hydration properties of quartz, *Adv. Powder Technol.* 31 (11) (2020) 4500–4509.
- [57] F. Avet, E. Boehm-Courjault, K. Scrivener, Investigation of CASH composition, morphology and density in Limestone Calcined Clay Cement (LC3), *Cem. Concr. Res.* 115 (2019) 70–79.
- [58] U.N. Environment, K.L. Scrivener, V.M. John, E.M. Gartner, Eco-efficient cements: Potential economically viable solutions for a low-CO<sub>2</sub> cement-based materials industry, *Cem. Concr. Res.* 114 (2018) 2–26.
- [59] M. Antoni, J. Rossen, F. Martirena, K. Scrivener, Cement substitution by a combination of metakaolin and limestone, *Cem. Concr. Res.* 42 (12) (2012) 1579–1589.
- [60] T. Danner, G. Norden, H. Justnes, in: *The Effect of Calcite in the Raw Clay on the Pozzolanic Activity of Calcined Illite and Smectite*, Springer, Singapore, 2020, pp. 131–138.
- [61] F. Zunino, E. Boehm-Courjault, K. Scrivener, The impact of calcite impurities in clays containing kaolinite on their reactivity in cement after calcination, *Mater. Struct.* 53 (2) (2020) 1–15.
- [62] J. Skibsted, R. Snellings, Reactivity of supplementary cementitious materials (SCMs) in cement blends, *Cem. Concr. Res.* 124 (2019) 105799.
- [63] R.L. Frost, É. Makó, J. Kristóf, E. Horváth, J.T. Klopogge, Modification of kaolinite surfaces by mechanochemical treatment, *Langmuir* 17 (16) (2001) 4731–4738.
- [64] I. Tole, K. Habermehl-Cwirzen, A. Cwirzen, Mechanochemical activation of natural clay minerals: an alternative to produce sustainable cementitious binders—review, *Mineral. Petrol.* 113 (4) (2019) 449–462.