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Mineralogical and chemical evolution of hydrated phases in the pozzolanic reaction of calcined paper sludge

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ABSTRACT

Calcined residual paper sludge can be reused and valorized in a safe an environmental way by the construction industry. The highly reactive metakaolin produced by calcination of the paper sludge exhibits good pozzolanic properties and permits its incorporation in cement systems. The pozzolanic reaction of metakaolin in $Ca(OH)_2$-saturated solution at 40 °C is reported in this study as a function of time, up to 1 year. The stability of hydrates phases has been evaluated according to the evolving aqueous conditions. Analytical determinations of the solid phase show early formation of C–S–H phases and a later precipitation of laminar minerals, hydrotalcite and strätlingite, at the expense of the C–S–H phases. The thermodynamic calculations confirm the experimental observations.

1. Introduction

The amount of domestic and industrial waste generated worldwide increases alarmingly and, in most cases (especially in developing countries) the only disposal method employed is landfilling, which itself consumes relatively large areas. On the other hand, a large demand placed on building construction due to increasing population has caused a chronic regional shortage of building materials. Utilization of waste materials for construction shall not only solve waste problems, but also provide a new resource for construction purposes [1].

Significant residual waste streams from pulp and paper mills. In general, solid wastes from pulp production and paper mill operations are humid and contain some organic compounds in the form of wood or recycled paper fibers, chlorinated organic compounds and pathogens, significant amounts of ash and trace quantities of heavy metals. Sludge compositions, however, vary widely throughout the industry and are dependent on the type of operations carried out at the mill. Presently, the wastes can be reused and valorized in a safe and environmental way, so landfill must strongly being reduced as their final destination [2].

Pèra and Amrouz [3] originally demonstrated that calcined paper sludge at 700–800 °C could be used in the concrete industry due to its transformation to a highly reactive MK (metakaolin $Al_2O_3{\cdot}SiO_2$), which exhibit good pozzolanic properties, similar in many respects to those of Portland or blended cement systems. The mechanism of hydration of MK in the lime–water system and the properties of MK as addition to cement has also been reported [3–5].

In the course of the present study, the hydration reaction of MK, obtained by calcination of paper sludge at 650 °C during 2 h, with a $Ca(OH)_2$ saturated solution at 40 °C has been investigated over time, up to 1 year. The $Ca(OH)_2$ solution simulates portlandite (CH) conditions of an ordinary Portland cement (OPC). Since the $Ca(OH)_2$ solution is just a simplification of the real system, the products formed will probably be different from those that could be obtained in cement paste.

A previous study evaluated three calcination temperatures at 600, 650 and 700 °C and 2, 5 h of residence in furnace for a similar art paper sludge in order to achieve the better pozzolanic properties [6]. Calcination at 650 °C and 2 h of residence in furnace were considered the optimum conditions since high specific surface area, complete lack of organic fibers and low or null decarbonation of calcite are achieved.

At lower temperatures, in the range 450–600 °C, the Si–O network in MK remains largely intact while the structure of Al–O network is reorganized [7,8]. At higher temperatures, in the range 700–800 °C, the minerals of the paper sludge (limestone, kaolinite and talc) are converted to amorphous CAS ($CaO–Al_2O_3–SiO_2$) and talc. On heating at 900 °C, the CAS is converted to gehlenite (C_2A_2S) and anorthite (CA_2S_2) [9].

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Thermodynamic studies provide a guide to phase formation and the nature of phase assemblages obtained under equilibrium conditions; considerable success has also been obtained in representing metastable but long-lived states. An equilibrium phase distribution diagram of the $CaO–Al_2O_3–SiO_2–H_2O$ system includes many of the hydrates encountered in MK–CH blends. The hydrates formed in this system in the range of temperatures 20–60 °C evolve with time as a function of the chemical conditions. The metastable phases C_4AH_{13} and strätlingite (C_2ASH_8) forms early in the pozzolanic reaction, but they can transform into more stable phases like hydrogarnet (C_3AH_6) and gehlenite at long term [10,11]. Additionally, the system contains an important metastable but persistent phase, tobermorite-type C–S–H gel [12]. The stability relations of the more crystalline hydrates in cement systems and their thermodynamic properties are reported by several authors [13–16].

The chemical reaction between cement and the hydration water generates an exothermic reaction that produces heat. The hydration heat of mortars and concretes can be reduced by means of the pozzolanic additions that partially substitute cement. Other authors, e.g. [17–19], that evaluate the pozzolanic activity of calcined kaolin have worked at constant curing temperatures in the range 35–60 °C. In this paper, the study of the pozzolanic reaction of MK in $Ca(OH)_2$-saturated solution at 40 °C is reported as a function of time. This curing temperature was previously established by Frías et al. [20]. The objective of this research is focused to determine the nature of hydrated phases in the system paper sludge/$Ca(OH)_2$, in order to give utility to the waste and explain the behavior of cements with this kind of additions. The stability of hydrates phases has been evaluated according to the evolving aqueous conditions, which is a novelty with respect to previous studies. The findings are used to derive a phase model to predict steady-state assemblages for paper sludge MK/CH blends. Major uncertainties derive from the carbonate-dominant minerals accompanying MK after calcination of paper sludge because they are a source of Ca^{2+} that could hinder the Ca^{2+} spent in the aqueous medium through the pozzolanic reaction and because they buffer the pH of the reaction.

2. Materials and methods

The industrial waste provided by the paper manufacturer Holmen Paper Madrid, used in this study, consists essentially of a mixture of organic matter (32 wt.%) and inorganic compounds, such as limestone (45%), quartz (3%), phyllosilicates 6% and kaolinite 14%. This mineralogical composition was calculated based on the oxides composition determined by X-ray fluorescence (XRF) and the mineralogical quantification performed by X-ray diffraction (XRD). The raw paper sludge does not present pozzolanic properties, but once calcined at 700 °C during 2 h, exhibits high pozzolanic activity, similar to silica fume at 28 days (which is another bulk inert waste, by-product of electrothermal ferrosilicon production, suitable for cement making), as a consequence of the kaolinite (K) transformation into MK [21]. The pozzolanic activity expected after calcinations at 650 °C during 2 h may be lesser. Although not all of the calcined product can be considered as MK, it controls the reactivity through the pozzolanic reaction. The content of secondary phases present with the MK may influence properties of the composites [22].

Temperatures of calcination in the range 700–800 °C and time of permanence in the furnace for 2 and 5 h were evaluated in a previous study using the same paper sludge [23]. However, in order to improve the energy efficiency, lower temperatures of calcination in the range 500–700 °C have been performed under a wider scope of the a new project. The results offered in this study are limited to 650 °C and 2 h, since the better mineralogical properties and good pozzolanic activity are achieved under these conditions.

One gram of calcined paper sludge grounded, pestle and sieved below 45 μm was placed in 75 ml of a $Ca(OH)_2$-saturated solution, hermetically sealed in a polyethylene container and wet-cured at 40 °C for independent periods of 6 h, 1, 7, 28, 90 and 360 days (a set of six different experiments performed in duplicate).

At the end of the reaction time, the hydrated solid sample was filtered, washed with ethanol and heated at 105 °C for 24 h in order to stop the hydration reaction. Then, the mineralogy was studied by XRD and scanning electron microscopy (SEM) to identify the products of the pozzolanic reaction.

XRF measurements were taken using a PHILIPS PW 1404/00/01 spectrometer with a Rh anode, working from 0° to 47.6° 2θ, operating at 80 mA and 100 kV. X-ray powder diffraction patterns were obtained using a Siemens D-5000 diffractometer with a Cu anode, operating at 30 mA and 40 kV, using divergence and reception slits of 2 mm and 0.6 mm respectively. The characterization of bulk samples was carried out by XRD using the random powder method operating from 3° to 65° 2θ at a rate of 2°/min, and the nature of phyllosilicates was determined in the <2 μm fraction using the oriented slides method operating from 2° to 40° 2θ at a scanning rate of 1°/min [24]. The SEM equipment was a FEI INSPECT microscope with an energy dispersive X-ray analyzer (EDX).

Immediately after solid–liquid separation, a fraction of the aqueous solution was used for pH measurement and titration of aqueous Ca^{2+} and OH^- with ethylenediaminetetraacetic acid (EDTA) and diluted HCl, respectively. The pozzolanic activity is inferred by the amount of aqueous $Ca(OH)_2$ consumed in the reaction. The measurements were normalized with respect to a reference blank solution saturated in $Ca(OH)_2$. In these conditions, $Ca^{2+}_{(aq)}$ = 17.45 mM and pH = 11.96 at 40 °C, and $Ca^{2+}_{(aq)}$ = 19. 17 mM and pH = 12.47 at 25 °C (measurements optimized with the geochemical code PHREEQC [25] due to the large uncertainties of experimental analyses at these conditions of pH and temperature; the pH is not determined in laboratory conditions at 40 °C). The aqueous species of interest (Na, K, Mg, Ca, Al and Si) were determined by inductively coupled plasma mass spectrometry (ICP-MS) with an Elan 6000 Perkin–Elmer Sciex analyzer.

Analyses by Fourier transform infrared spectroscopy (FTIR) were performed in order to confirm the mineralogical changes observed by XRD and SEM–EDX. The IR spectral analyses were performed using a spectrometer ATI Mattson Genesis Series FTIR-TM.

To study the state of equilibrium of the system, the activities of aqueous species were calculated by geochemical modeling, entering the concentrations of aqueous species and pH measured in solution. In order to predict the stability of reaction products as a function of time, the saturation indices of minerals able to dissolve/precipitate in the system were calculated with PHREEQC and the thermodynamic database LLNL (Lawrence Livermore National Laboratory). Crystalline hydrates minerals not included in LLNL were added from the database THERMODDEM [26]: hydrotalcite [$Mg_4Al_2(OH)_{12}(CO_3):2H_2O$], strätlingite [$Ca_2Al_2SiO_2(OH)_{10}:2.5H_2O$], C–S–H phases with Ca/Si ratios 0.8, 1.2 and 1.6 ($Ca_{0.8}SiO_{2.8}:1.54H_2O$, $Ca_{1.2}SiO_{3.2}:2.06H_2O$ and $Ca_{1.60}SiO_{3.6}:2.58H_2O$), C_3AH_6 [$Ca_3Al_2(OH)_{12}$] and C_4AH_{13} ($Ca_4Al_2O_7:13H_2O$). Calcite ($CaCO_3$) and portlandite [$Ca(OH)_2$], although present in LLNL were inserted from the NAPSI database [27] due to a higher refinement in the thermodynamic data. The dissolution reactions of minerals acquired from THERMODDEM were properly adapted to fit the same aqueous species format as in LLNL (SiO_2 instead of H_4SiO_4). Electrochemical charge in solution was balanced with pH. The aqueous carbonate, not determined in solution, was equilibrated with calcite.

3. Results

3.1. Initial characterization of the calcined paper sludge

The quantification of minerals in the calcined paper sludge was performed by XRD. Calcite is the main constituent in the mineral assemblage that could be quantified by XRD (98 wt.%), but additional accessory minerals were also detected (talc, illite, dolomite and quartz), although the quantification of their peaks are below 1%. Since this method only allows the quantification of crystalline minerals, it can be assumed that all the organic matter was lost on ignition at 650 °C for 2 h in furnace, and silicates, mostly kaolinite, were converted into MK. Illite and quartz, quantified previously in the original paper sludge in higher concentrations, are poorly crystalline after calcination since their concentrations decrease and their peaks decrease in the X-ray diffractogram, therefore, the resulting amorphous phases have been considered as part of MK. Consequently, a simple mass balance from the original composition, discarding the mass lost at high temperature, leads to a composition: calcite 66 wt.%, MK 33 wt.% and accessory minerals (mostly quartz) 1 wt.%.

3.2. Aqueous chemistry

The consumption of $Ca^{2+}_{(aq)}$ in the solution is associated with the pozzolanic reaction. It is considered that MK reacts with $Ca^{2+}_{(aq)}$ in the alkaline medium to form mainly C–S–H phases. Calcium aluminate silicate hydrates (C–A–S–H) are frequently found as metastable phases. Their stabilities decrease with the increasing temperature of the reaction, and in some cases C–A–S–H gels appear to be precursors for zeolites formation [12]. As the reaction evolves, the pH decreases and the system achieves a stationary state in a period of time normally comprehended within the range 7–28 days. The pH and the aqueous Ca^{2+} concentration (determined by EDTA titration) were measured in laboratory immediately after each time programmed, when the hydration reaction ceased. However, the reaction proceeds at a constant temperature of 40 °C and measurement taken in laboratory are determined at room temperature (assumed at 25 °C but possibly higher since the solution slowly decreases its temperature when is retired of the oven, from 40 °C to room temperature). Aqueous Ca^{2+} is again quantitatively determined, as other relevant ions, by ICP-MS at a constant room temperature. Differences in both measurements of Ca^{2+} may show the temperature dependency at high pH conditions (Fig. 1). Since the ICP-MS measurements are considered more accurate (the range of error is only 1–2%), chemical speciation determined by this method was inserted in PHREEQC in order to optimize the pH measurements at a constant temperature of 25 °C. Not much difference is found for Ca^{2+} determined by both methods, except for the first measurement taken after 6 h of reaction, which differ in more than 3 mM units. The pozzolanic reaction is observed to achieve a steady state after 28 days when Ca^{2+} remains almost constant in solution. The pH theoretically calculated decreases one order of magnitude from 12.4 to 11.4 in the same period and then maintains in the range 11.4–11.3. This agrees with the Ca^{2+} determinations and confirms that the availability of $Ca^{2+}_{(aq)}$ controls the reaction. The pH measured in laboratory does not show the cease of the hydration reaction and differ strongly with the calculated pH in the measurement taken after 7 days of reaction.

In addition to the solid characterization, aqueous silica and alumina provide complementary information on the reactions of aluminosilicate phases. Aqueous silica increases in solution until 28 days of reaction and then decreases (Fig. 2). However, the range of concentration remains below 0.1 mM at any time, which is very low compared to the presumed silica content that react from MK and other accessory minerals to transform into C–S–H and related secondary minerals. These data suggest a rapid process of nucleation of C–S–H phases on the reactive surface of MK, with low release of silica to the solution. On the other side, aqueous alumina increases in solution for the first 7 days of reaction and remains almost constant in the range 1.3–1.5 mM at longer time. The evolution of aqueous alumina over time and high concentration in solution suggests a strong degradation of the primary minerals but also difficulty of aqueous alumina (dominated by the species AlO_2^- in the alkaline medium) to be incorporated into the secondary minerals formed. Although, not many studies regarding the pozzolanic reaction of MK include specific analyses of the aqueous solutions, the solid characterization reveals lack or poor crystallization of C–A–H phases and larger formation of C–A–S–H phases [19].

Aqueous Na^+ and K^+ increase their concentration with time indicating the dissolution of phyllosilicates, considered as the only mineral phases containing these elements in the calcined paper sludge (Fig. 3). Any soluble salt that could be present in the initial solid sample is excluded due to the correction performed with the reference blank solutions. The evolution of these two ions in solution suggests the continuous dissolution of phyllosilicates in the alkaline medium. Previous studies demonstrated that supposedly 'inert' aggregate minerals, such as muscovite and feldspar, may become reactive towards cement [28]. In MK–cement mixtures, much of the alkali liberated (mostly K^+) is probably incorporated

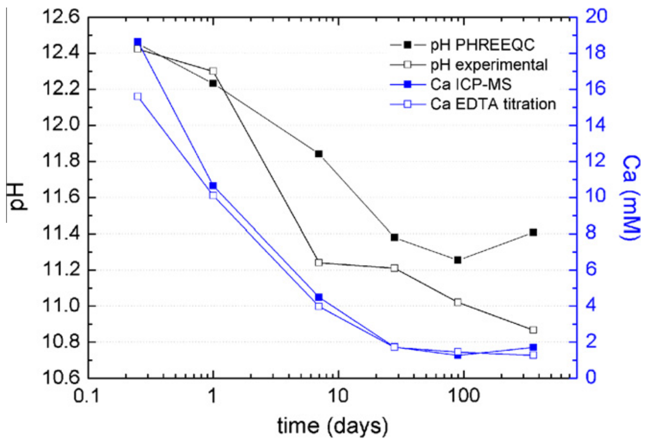

Fig. 1. Calculated $Ca^{2+}_{(aq)}$ and pH based on the experimental aqueous determinations.

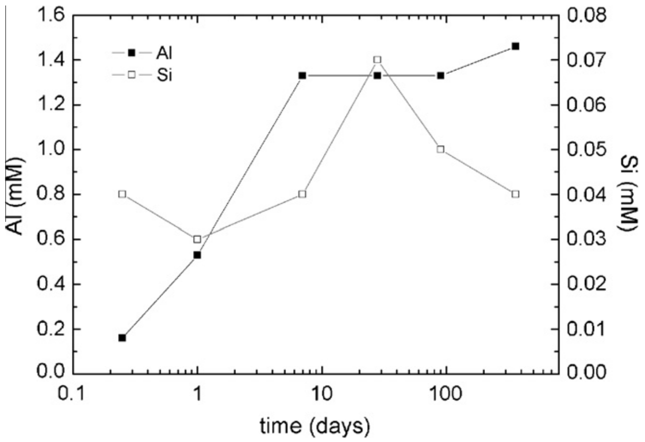

Fig. 2. Aqueous Al and Si determined in solution by ICP-MS as a function of time.

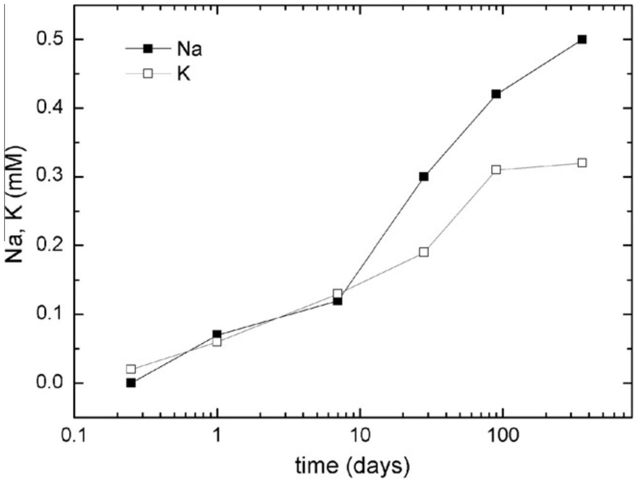

Fig. 3. Aqueous Na and K determined in solution by ICP-MS as a function of time.

into cement solids but the overall effectiveness of MK in decreasing the alkali contents of cement pore fluid is reduced. However, alkali release may also be beneficial: MK may release sufficient alkali to enhance slag hydration in slag–$Ca(OH)_2$–MK blends.

Aqueous Mg, although determined by ICP-MS, does not show relevant information since its concentration remains below the μM scale at any time.

The analysis of carbonates has been neglected in this study. It is assumed that the high content in calcite and some dolomite present in the initial sample may have their influence on the solution chemistry, basically, buffering the pH and partially balancing the positive charge in solution. However, also the exposure of solution to the atmosphere, unavoidable during manipulation of samples, would lead to the partial carbonation of solution.

3.3. XRD

Identification (Fig. 4) and semi-quantification of XRD peaks (Table 1) on activated solid samples that reacted for 1, 7, 28, 90 and 360 days permits the observation of mineralogical transformations involved in the alkali-activated reaction as a function of time. Calcite is still present because is stable up to temperatures of around 800 °C. Amorphous minerals, such as C–S–H and MK, do not appear in the diffractogram because of their low order structures.

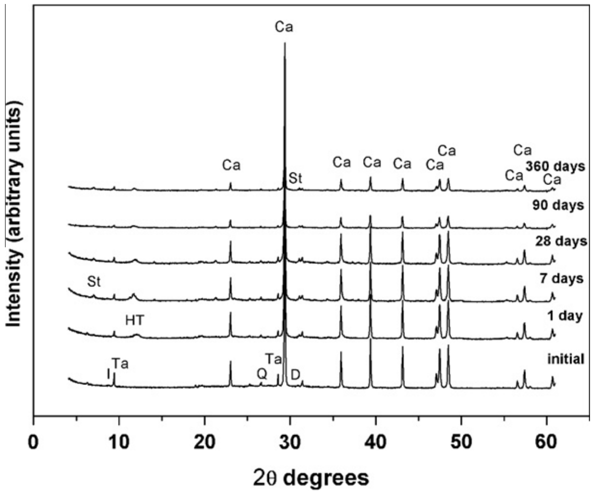

Fig. 4. Identification and evolution of crystalline mineral phases by XRD as a function of time. St = strätlingite; I = illite; Ta = talc; HT = hydrotalcite; Q = quartz; D = dolomite; Ca = calcite.

Table 1
Semi-quantification of crystalline minerals (wt.%) obtained by XRD.

Mineral	Initial	1 Day	7 Days	28 Days	90 Days	360 Days
Talc	1	Traces	Traces	Traces	1	Traces
Hydrotalcite	0	4	3	3	4	7
Strätlingite	0	0	1	1	2	2
Quartz	Traces	Traces	Traces	Traces	Traces	Traces
Illite	Traces	Traces	Traces	Traces	Traces	Traces
Dolomite	0	Traces	Traces	Traces	Traces	Traces
Calcite	98	95	95	95	92	90

Hydrotalcite is identified early in pozzolanic reaction (after only 1 day) and increases its concentration with the evolving time. Hydrotalcites have a variable composition of the general formula $Mg_{1-x}(Al,\ Fe)_x(OH)_2{\cdot}[A^{n-}]_{x/n}{\cdot}mH_2O$, and a structure composed of positively charged brucite-like layers intercalated with anions $[A^{n-}]$ and water molecules. The structure can accommodate a number of cations, interlayer anions such as OH^-, Cl^-, CO_3^{2-} and SO_4^{2-} and varying amount of water [29]. In this study, hydrotalcite mainly accommodates CO_3^{2-} anions in the interlayer due to the excess of carbonates in the aqueous medium.

Strätlingite also forms early (after 7 days of reaction) and increases as a function of the reaction time. Other than hydrotalcite and strätlingite no new-formed crystalline phases have been clearly identified by XRD. Some traces of quartz, illite, talc and dolomite present in the paper sludge before the thermal activation could be semi-quantified by XRD, but the dominant mineral phase detected is calcite.

3.4. SEM

Amorphous C–S–H phases, hydrotalcite and strätlingite are the main hydration products observed by SEM–EDX. The CaO/SiO_2 ratio determined for C–S–H gels varies within the range 1.6–2.5 (Table 2), that correspond to type-II C–S–H according to the Taylor classification [30]. The structural order increases with the increasing Ca/Si ratio, and therefore, the evolving time of reaction. At any time the C–S–H gels exhibit rounded shape of flaky aspect (Fig 5a) but at longer time they appear along with intergrowth thin layers of hydrotalcite (Fig 5b) and strätlingite. Hydrotalcite and strätlingite always exhibit laminar aspect but are found in a wide range of sizes.

3.5. FTIR

Structural aspects of the main minerals involved in the pozzolanic reaction can be observed by FTIR (Fig. 6). Wavelengths corresponding to tension vibration in water (ν(O–H)) at 3443 cm^{-1} and deformation (δ(H–O–H)) at 1632 cm^{-1} are observed along with structural OH vibrations of illite and talc, and hydration water of C–S–H gels, strätlingite and OH–OH vibrations in hydrotalcite-type compounds. The increase in intensity and sharpness of these bands confirm the increase of the reaction products as a function of the reaction time [31–34].

The carbonate group, either from calcite or dolomite, is identified by the bands at 2515, 1795, 1435, 875 and 714 cm^{-1}. Si–O(Si) vibrations in tetrahedral sites are identified for talc at 1050 and 1018 cm^{-1} and for quartz at 1172, 1150 and 1084 cm^{-1}. The band at 914 cm^{-1} is characteristic of the vibration Al–O–H associated to illite. Bands near 800 cm^{-1} correspond to Al–O vibrations in tetrahedral sites in illite and MK. Bands at 1080 and 1150 cm^{-1} are attributed to amorphous silica in MK [35–37].

Table 2
Chemical compositions of C–S–H gels determined as a function of the reaction time (based on 10 EDX analyses performed on different aggregates).

Oxides (wt.%)	C–S–H gel				
	1 Day	7 Days	28 Days	90 Days	360 Days
Al_2O_3	21.87 ± 0.47	18.15 ± 0.36	19.55 ± 0.28	15.12 ± 0.79	17.50 ± 0.28
SiO_2	30.05 ± 0.84	27.97 ± 0.58	26.57 ± 0.87	24.13 ± 1.06	23.70 ± 0.87
CaO	48.08 ± 1.12	53.88 ± 1.30	53.88 ± 0.56	60.25 ± 0.96	58.79 ± 1.18
CaO/SiO_2	1.6	1.92	2.02	2.49	2.48

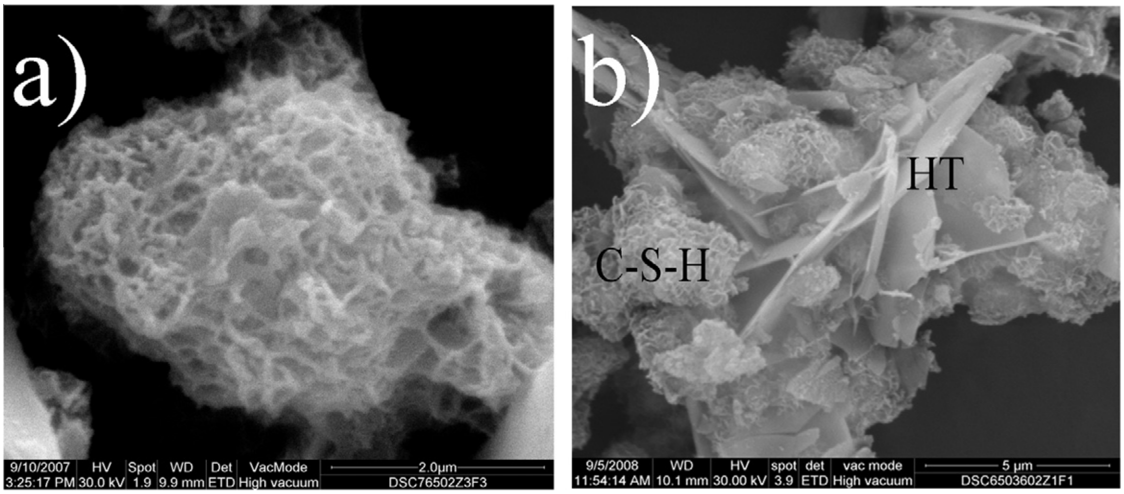

Fig. 5. (a) Early C–S–H gel (low Ca/Si ratio) formed after 7 days of reaction and (b) hydrotalcite (HT) and well-formed C–S–H (high Ca/Si ratio) after 360 days.

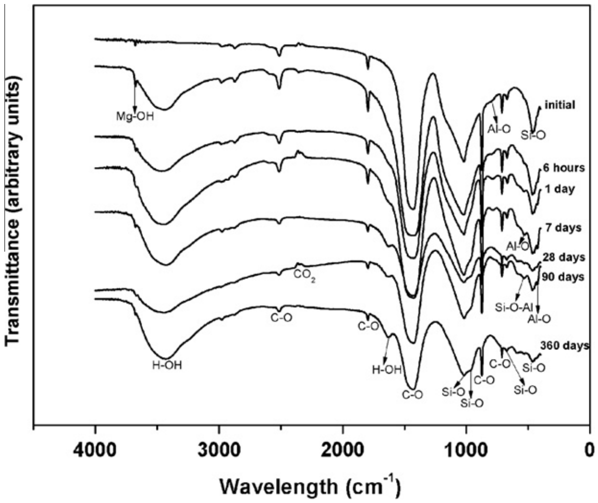

Fig. 6. FTIR spectra of the activated initial sample and evolution as a function of the reaction time.

The band at 463 cm^{-1} corresponds to the Si–O(Si) vibration in tetrahedral sites and can be attributed to talc, quartz and MK [38,39]. This band decreases intensity with the evolving time indicating the consumption of MK in the pozzolanic reaction. In addition, it can be observed a shift of the band to higher wavelengths (467 cm^{-1}), characteristic of the v^4 Si–O vibration in tetrahedral sites of C–S–H phases.

A new band at 423 cm^{-1} is observed with the increasing time, attributed to Al–O vibrations in octahedral sites and associated to calcium aluminates hydrates and/or strätlingite [32].

3.6. Thermodynamic modeling

Saturation indices show the tendency of equilibrium for the minerals of interest to precipitate or dissolve under the experimental conditions used. The saturation indices are calculated with PHREEQC from the activities of species determined in solution by ICP-MS and the equilibrium constants of the dissolution reactions for the minerals evaluated. A positive saturation index (SI) indicates the tendency of a mineral to precipitate (aqueous solution oversaturated with respect to the mineral) while a negative value of the SI indicates the trend of a mineral to dissolve (aqueous solution undersaturated with respect to the mineral). SI for portlandite decreases from zero at the starting time to negative values indicating that the mineral is at equilibrium in the initial $Ca(OH)_2$ saturated solution and the later consumption of aqueous Ca^{2+} during the pozzolanic reaction (Fig. 7). Hydrotalcite and strätlingite are clearly favoured to precipitate, which agree the experimental observations. Hydrotalcite is very sensitive to the aqueous concentration of Mg^{2+}, but the analytical measurements performed by ICP-MS showed concentrations below the μM scale. In order to normalize the Mg^{2+} concentration, a fixed 1×10^{-3} μM was established at any time. Calcium aluminates hydrates are far too unsaturated to precipitate under these conditions and agree the high concentrations of Al determined in solution. C–S–H phases, however, are predicted to be more stable with the increasing Ca/Si ratio at short term (6 h, 1 day), and they decrease their stability with the increasing Ca/Si ratio at long term (7, 28, 90 and 360 days). This is related with the Ca^{2+} concentration that remains in solution. At short term, when the $Ca^{2+}_{(aq)}$ concentration is high, C–S–H gels with higher Ca/Si ratios are thermodynamically favoured, but normally gels with lower Ca/Si form faster due to kinetic considerations. As the reaction evolves, the Ca^{2+} availability decreases in the aqueous medium and C–S–H gels with lower Ca/Si are

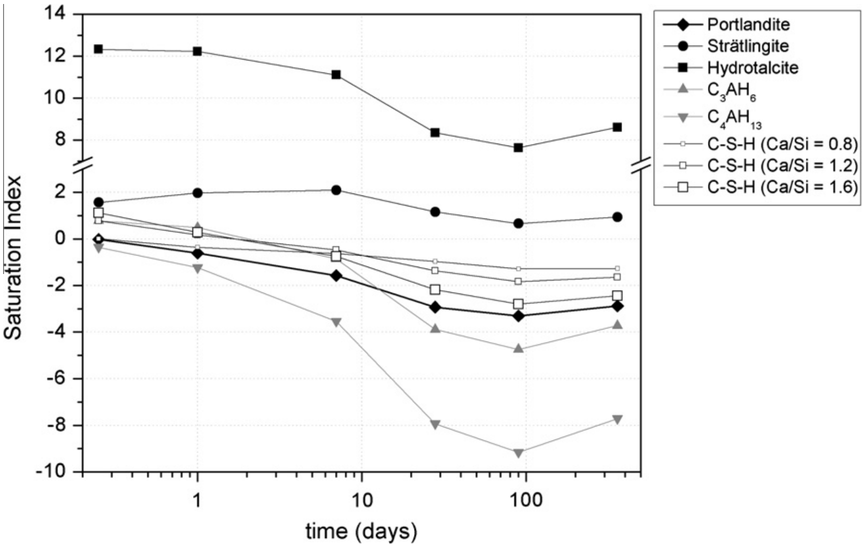

Fig. 7. Saturation indices calculated with PHREEQC as a function of time for the potential mineral phases involved in the pozzolanic reaction.

thermodynamically favoured. However, the inclusion of Ca^{2+} in an already formed C–S–H gel is preferred if kinetics are also considered. Although the thermodynamic analysis do not predict the precipitation of C–S–H, the three phases considered are near equilibrium and favoured over portlandite (and even more over calcium aluminate hydrates), therefore, their precipitation are presumed due to kinetic factors.

In addition, the chemical stability of the experimental solutions in the system OH-hydrotalcite $[Mg_4Al_2(OH)_{14}{\cdot}3H_2O]$–strätlingite $[Ca_2Al_2SiO_2(OH)_{10}{\cdot}3H_2O]$–C–S–H (Ca/Si = 0.83) $[Ca_{0.83}SiO_2(OH)_{1.66}{\cdot}0.5H_2O]$ was evaluated according to their mineral stability fields. The chemical reactions considered are:

$$\mathrm{R1}: M_4AH_{10} + HSiO_3^- + 3H_2O + 2Ca^{2+} \rightleftharpoons C_2ASH_8 + 3H^+ + 4\mathrm{Brucite}$$

$$\mathrm{R2}: M_4AH_{10} + 0.83Ca^{2+} + HSiO_3^- \rightleftharpoons CSH_{0.83} + 2\mathrm{Gibbsite} + 4\mathrm{Brucite} + 0.66H^+ + 1.74H_2O$$

$$\mathrm{R3}: C_2ASH_8 + 2.34H^+ \rightleftharpoons CSH_{0.83} + 1.17Ca^{2+} + 2\mathrm{Gibbsite} + 4.84H_20$$

The thermodynamic standard properties required to calculate the equilibrium constants for each reaction (ΔG^0 [J/mol], ΔH^0 [J/mol], S^0 [J/mol K] and V^0 [cm^3/mol]) were selected from the database "cemdata2007" [29], completed recently for cement phases. The reactions were considered at 40 °C and the equilibrium constants were calculated with the program SUPCRT92 [40] making use of the Maier–Kelly coefficients: a [J/mol K], b [J/mol K^2] and c [J K/mol] given in cemdata2007; where $C_p^0 = a + bT + cT^{-2}$, obtaining:

$$\log K_{R1} = -29.586; \quad \log K_{R2} = -9.526; \quad \log K_{R3} = 24.034$$

The activities of aqueous species were calculated previously with PHREEQC. The thermodynamic modeling shows that aqueous activities evolve with time within the stability field of the C–S–H phase, approaching the stability field of OH-hydrotalcite (Fig. 8). This means that C–S–H is the most thermodynamically stable phase out of these three under the experimental conditions; however, as the reaction evolves with time, the system approaches the stability field of hydrotalcite, which is consequently favoured over strätlingite (far from the local equilibrium). The model supports the experimental observations regarding the formation of C–S–H and possibly hydrotalcite. Kinetic considerations have been neglected in this study due to the lack of validated data, but are highly expected to be involved in the reactivity.

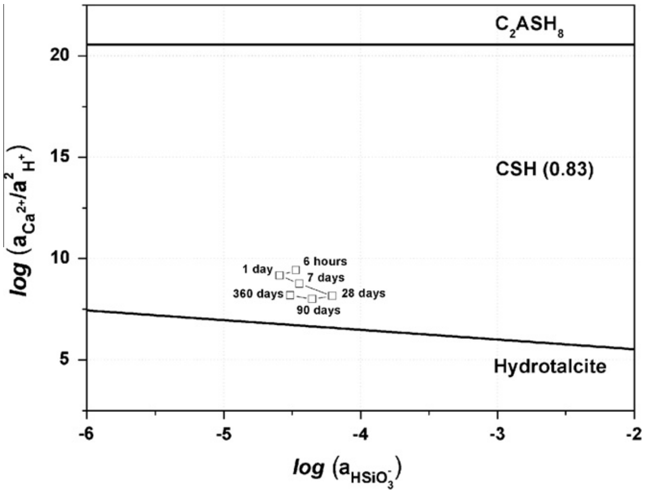

Fig. 8. Stability fields diagram for the system OH–hydrotalcite–strätlingite–C–S–H (Ca/Si = 0.83) at 40 °C and aqueous activities evolution with time.

Although CO_3-hydrotalcite, whose thermodynamic standard properties are also given in cemdata2007, is closer in composition to the mineral phase determined in this study, OH-hydrotalcite was preferred in order to avoid carbonates in the equilibrium reaction. OH-hydrotalcite shows more stability than CO_3-hydrotalcite under conditions typical for Portland cements.

4. Discussion

The quantification of amorphous C–S–H and C–A–S–H phases (not possible by XRD) can be estimated if it is considered that these phases, in addition to strätlingite and hydrotalcite, exclusively form in the reaction of MK with the aqueous $Ca(OH)_2$, and assuming that calcite is not involved in the pozzolanic reaction. The experimental results show that calcite dissolution could be involved in the formation of hydrotalcite but its contribution is neglected in the calculation. Therefore, 0.66 g of calcite present in the initial calcined sample (1 g) corresponds to the 95% of crystalline mineral phases semi-quantified by XRD after 1, 7 and 28 days of reaction with the $Ca(OH)_2$ solution, and 92%, 90% after 90 and 360 days, respectively. The amount of the secondary crystalline minerals formed, hydrotalcite and strätlingite, can be inversely calculated from the crystalline weight%. The amount of MK initially present in the calcined sample (0.33 g) is assumed to reacts totally. If the calculated amounts of strätlingite and hydrotalcite are discount, the amount of amorphous phases (C–S–H and C–A–S–H) is inferred (Table 3). The formation of C–A–H phases is neglected.

The analytical determinations in the aqueous solutions showed high concentrations of Al and low concentrations of Si that can be related to their incorporation into the solid phases. It might be presumed that precipitation of C–S–H is favoured over C–A–S–H but the EDX analyses reveal that C–S–H phases contain a remaining amount of Al, present in the initial MK and retained in the reaction products due to the fast rate of reaction at early time.

Although mechanical properties have not been evaluated in this study, the formation of strätlingite is considered beneficial due to its relatively high strength in cement matrices [41]. Ding et al. [42] showed the role of alkali ions in strätlingite formation. They postulated a mechanism where strätlingite forms from microsilica and calcium aluminates hydrates. The reaction is accelerated by increasing amount of alkali ions acting as catalysts that activate the microsilica surfaces. Silicate anions then react with hydrated calcium aluminates to produce strätlingite. In agreement with this argument, the increasing concentrations of Na^+ and K^+ in solution observed in the present study could indicate that the alkaline ions mediate in the pozzolanic reaction without incorporation into the new-formed cement phases. The calcium aluminates hydrates, however, were not detected as metastables phases in this study. Consequently, the reaction should proceed by catalytic activation of alkaline ions on reactive aluminum silicates surfaces and the resulting absorption of calcium hydrates.

The stability analysis shows that C–S–H phases are thermodynamically stable over strätlingite and hydrotalcite, but very near the stability field of hydrotalcite. Although C–S–H gels with high Ca/Si ratio and Al in the composition were detected experimentally by SEM–EDX, a more stable tobermorite-type phase was preferred for the calculation as it can be considered precursor of evolved C–S–H phases with higher Ca/Si ratio. The calculation is in agreement with the estimated quantification performed in Table 3 that shows increase of hydrotalcite with the reaction time at the expense of C–S–H (or C–A–S–H). This, again, confirms the SEM observations. At short time (7 days), the morphology of the aggregates are reticular or honey-combed structures, but at long time (90–360 days) it is observed intergrowth of laminar minerals (identified as hydrotalcite and strätlingite) precipitating from the C–S–H structures.

The mineralogical and thermodynamic studies show that paper sludge exhibit good pozzolanic properties to be incorporated into cement matrices once calcinated at 650 °C for 2 h, but mechanical experiments must be carried out in order to confirm that the studied paper sludge improves the quality of the construction materials. The later experiments have been performed with similar materials confirming the good behavior of calcined paper sludge for construction purposes [43,44].

Table 3
Quantification of non-reactive and secondary mineral estimated in the pozzolanic reaction.

% Mineral	1 Day	7 Days	28 Days	90 Days	360 Days
Calcite	66	66	66	66	66
Hydrotalcite	3	2	2	3	5
Strätlingite	0	1	1	1	2
C–S–H + C–A–S–H	30	30	30	29	26
Others	<1	<1	<1	<1	<1

5. Conclusions

Residual paper sludge generated by the paper industry can be reused by the construction industry after calcination. The conditions evaluated in this study, 650 °C and 2 h of residence in furnace, show that the formed MK exhibits good pozzolanic properties and reacts rapidly with a saturated $Ca(OH)_2$ solution that simulates conditions of Portland cement. C–S–H and C–A–S–H phases precipitate early and evolve to increase the Ca/Si ratio. In addition, hydrotalcite and strätlingite precipitate as hydration products, nucleating from the C–S–H gels. The thermodynamic stability of the reaction products was evaluated as a function of the reaction time confirming the experimental observations. Uncertainties regarding the role of carbonates were neglected in this study but do not seem to play an important role except for an additional source of Ca^{2+} and the pH buffering.

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