

Thermal activation of flexographic wastewater sludge and its influence on Portland cement hydration

Maximiliano Iván Delletesse

mdelletesse@fio.unicen.edu.ar

Universidad Nacional del Centro de la Provincia de Buenos Aires

Research Article

Keywords: flexographic wastewater sludge, thermal activation, calcined sludge, cement hydration, isothermal calorimetry, pozzolanic reactivity

Posted Date: September 4th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10360612/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Thermal activation of flexographic wastewater sludge and its influence on Portland cement hydration

Maximiliano Iván Delletesse

Universidad Nacional del Centro de la Provincia de Buenos Aires (UNICEN),
CIFICEN, UNICEN-CICPBA-CONICET, Olavarría, Buenos Aires, Argentina.

mdelletesse@fio.unicen.edu.ar

<https://orcid.org/0000-0001-5472-9938>

Abstract

Sludge generated during the coagulation–flocculation treatment of flexographic printing wastewater is a heterogeneous industrial residue with a high organic content. This study investigated the effect of thermal treatment on its structural evolution, apparent pozzolanic reactivity, and interaction with Portland cement hydration. Sludge dried at 100 °C and calcined at 550 °C was characterized by XRF, XRD, FTIR, and SEM, while structural changes were monitored over the 500–800 °C range. Calcination promoted organic matter removal and the progressive dehydroxylation of kaolinite, leading to the formation of an amorphous metakaolinite-like phase. Reactivity was evaluated using an accelerated lime-consumption test and the Frattini method. Although the material calcined at 700 °C showed greater lime consumption than that treated at 550 °C, all cement blends yielded negative Frattini results. This behavior was attributed to the release of Ca^{2+} and OH^- from the residue, which maintained high ionic concentrations in solution and obscured any limited pozzolanic consumption. The influence of the calcined sludge on cement hydration was further assessed by isothermal conduction calorimetry and FTIR. The residue modified hydration kinetics and, at 10% replacement, increased heat release during the acceleration period without substantially altering the main hydration products. Therefore, the calcined sludge was not inert, but its interaction with Portland cement was governed mainly by physical and ionic effects rather than by effective pozzolanic activity. These results demonstrate that the thermal behavior and cement interaction of hybrid industrial residues cannot be interpreted solely using conventional pozzolanicity criteria.

Keywords: flexographic wastewater sludge; thermal activation; calcined sludge; cement hydration; isothermal calorimetry; pozzolanic reactivity.

1. Introduction

The management of industrial sludge has progressively shifted from a disposal-based approach toward strategies focused on valorization and circular use of residual materials. This transition is particularly relevant in sectors that generate complex semisolid residues with high organic load and limited biodegradability, where conventional disposal routes such as landfilling or incineration entail both environmental and economic burdens. In this context, construction materials have attracted growing interest as potential receiving matrices because they can incorporate industrial by-products while reducing the consumption of virgin raw materials [1–3].

Among these residues, sludge generated during wastewater treatment in the printing industry represents a particularly challenging stream. Flexographic and related printing processes use water-based inks, varnishes, adhesives and auxiliaries that produce wastewaters with high organic load, strong coloration and significant temporal variability [4]. Their treatment is further complicated by the presence of dispersants, emulsifiers and high-molecular-weight organic compounds that keep particles in suspension and hinder natural settling [5–7]. For this reason, coagulation-flocculation is commonly used as a primary treatment step, allowing the separation of a clarified liquid phase

and a sludge phase that concentrates most of the suspended solids, organic matter and recalcitrant compounds [8,9]. Although effective for wastewater clarification, this process transfers the contamination problem to a semisolid residue whose subsequent management remains unresolved. From the viewpoint of reuse, sludge from the printing and paper sectors has been explored as a possible component in cementitious systems. Previous studies have reported the incorporation of paper sludge, deinking sludge and related ashes into cement- and concrete-based matrices, either in untreated form or after thermal processing [10–16]. In many of these materials, the coexistence of silica-, alumina- and calcium-bearing phases makes thermal activation an attractive route, since calcination can simultaneously remove organic matter and transform kaolinitic fractions into amorphous aluminosilicate phases with potential pozzolanic reactivity. This strategy has been successfully discussed for paper-industry residues and other calcined wastes, with typical activation windows ranging from 500 to 800 °C depending on the mineralogical composition and treatment time [17–21].

The interest in this approach is also supported by the broader role of thermally activated aluminosilicate additions in blended cement systems. Reactive mineral additions may contribute through both physical and chemical mechanisms: they can modify early hydration through dilution, filler and heterogeneous nucleation effects, while also reacting with portlandite to form additional hydration products when sufficient amorphous silica and alumina are available [22–25]. However, the existence of an amorphous phase after calcination does not by itself guarantee effective pozzolanic behavior. The actual performance of a residue in cementitious systems depends on its full chemical and mineralogical constitution, the presence of inert or interfering phases, its own ionic contribution in solution, and the balance between physical and chemical effects once incorporated into the binder.

This point is especially relevant for sludge generated from coagulation-flocculation of flexographic effluents. Unlike many of the paper sludges previously reported, this type of residue is formed from a complex mixture of inks, adhesives, fillers and treatment chemicals [4,8]. As a result, it cannot be regarded as a simple kaolinitic precursor. Instead, it should be considered a hybrid waste in which mineral phases coexist with a high volatile fraction and potentially calcium-rich components. Such complexity limits the direct extrapolation of results reported for recycled paper sludge or conventional calcined clays. Therefore, assessing this type of waste only in terms of “pozzolanic” or “non-pozzolanic” behavior may be insufficient; its interaction with Portland cement hydration must also be examined.

Under these conditions, a relevant research question is whether thermal treatment of this sludge leads to a meaningful improvement in its cementitious reactivity, or whether the material mainly behaves as a complex addition with limited chemical contribution but measurable effects on the hydration process. Addressing this question is necessary not only to evaluate the technical feasibility of its reuse, but also to define realistic boundaries for its valorization in cement-based systems.

Accordingly, this study aimed to investigate the thermal transformation of sludge generated during the coagulation–flocculation treatment of flexographic printing wastewater and to determine how these changes influence its interaction with Portland cement. The structural evolution of the residue over the 500–800 °C range was analyzed by XRD and FTIR, while its apparent reactivity was evaluated through accelerated lime-consumption and Frattini tests. In addition, isothermal conduction calorimetry and FTIR were used to assess the effect of the selected calcined sludge on cement hydration. Particular attention was given to distinguishing true pozzolanic behavior from physical and ionic effects arising from the complex composition of the residue.

2. Materials and Methods

The sludge used in this study was obtained from the coagulation-flocculation treatment of wastewater from a printing industry located in Buenos Aires Province, Argentina. A representative sample (5 L) was collected from the sedimentation tank and immediately conditioned in the

laboratory. The material was dried at 100 °C (M100) and subsequently subjected to thermal treatment at 550 °C (M550) and 700 °C (M700) in order to remove organic compounds and promote structural transformations. After treatment, the samples were ground and sieved to a particle size below 45 µm.

The cement used was a commercial Portland cement supplied by a local producer. Its chemical composition was typical of this type of material, including gypsum as a setting regulator and limestone as a minor constituent.

The physicochemical characterization of the dried and calcined materials was performed using a multi-technique approach. Chemical composition was determined by X-ray fluorescence (XRF). Mineralogical phases were identified by X-ray diffraction (XRD) using Cu K α radiation over the 5–70° (2 θ) range, with a step size of 0.02° and a scanning rate of 2°/min. Infrared spectra (FTIR) were obtained using the KBr pellet method in the 400–4000 cm⁻¹ range. Morphological characterization was carried out by scanning electron microscopy (SEM). Phase identification was performed using the JCPDS database and specific literature on clay minerals [26].

To evaluate the structural changes induced by thermal treatment, the sludge was calcined in a muffle furnace over the 500–800 °C range, following a stepwise treatment with 50 °C increments every 2 h, and intermediate samples were withdrawn for mineralogical characterization [27]. The resulting samples were analyzed by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR), allowing the evolution of mineral phases to be identified. For thermal monitoring, the samples calcined between 500 and 800 °C were obtained under the same residence time and analyzed by FTIR under identical instrumental and sample preparation conditions. The evolution of metakaolinite associated with thermal treatment was assessed by FTIR through analysis of the band centered at approximately 1083 cm⁻¹. The relative area of this band was determined after baseline correction in the 1317–843 cm⁻¹ spectral region.

Pozzolanic activity was evaluated by means of an accelerated chemical test following the method reported by Frias et al. [28], based on the reaction of the material with a saturated Ca(OH)₂ solution at 40 °C and different contact times. Lime consumption was expressed as fixed lime, calculated from the difference between the CaO concentration in the initial saturated solution and that measured in the solution in contact with the sample at the end of each period. In addition, electrical conductivity was monitored as a complementary parameter to assess the evolution of ionic species in solution.

Based on the results of the accelerated test, M550 was selected for evaluation by the Frattini test (UNE-EN 196-5:2011) on cement blends with different replacement levels. In order to distinguish the effect of any potential pozzolanic reaction from the residue's own ionic contribution, an independent contact test was also carried out by exposing M550 to distilled water at 40 °C for 7 days, after which Ca²⁺ and OH⁻ concentrations were determined.

Blended cements were prepared by partially replacing Portland cement with M550 at 5%, 10%, and 20% by mass (CM5, CM10, and CM20). The hydration process was analyzed by isothermal conduction calorimetry at 20 °C using 20 g of cementitious material and a water-to-binder ratio of 0.5. The paste was manually mixed for 30 s, sealed, and immediately introduced into the calorimeter. Heat flow and cumulative heat were recorded for 48 h. The calorimetric curves were analyzed in terms of heat flow and cumulative heat normalized per unit mass of cementitious material. The intervals corresponding to the dormant period and the acceleration period were defined from slope changes and the position of the main maximum of the exothermic signal.

The evolution of hydration products was studied by FTIR in pastes cured for 2, 7, 28, and 90 days. Hydration was stopped by grinding in the presence of acetone in order to prevent further reactions and remove free water. The dry powders were stored in sealed containers until analysis.

3. Results

3.1. Characterization of the dried sludge

The composition of the dried sludge (M100) reveals a markedly heterogeneous residue in which a predominant volatile fraction (LOI $\approx$ 68%) coexists with an inorganic fraction mainly composed of

CaO, TiO₂, SiO₂, and Al₂O₃ (Table 1). This result indicates that the material does not behave as a simple mineral clay, but rather as a complex matrix derived from the coagulation-flocculation process, in which mineral phases are combined with organic and volatile compounds that may influence both its subsequent thermal treatment and its interaction with cementitious systems.

%	M100	M550
LOI	68.12	31.72
TiO₂	7.31	16.23
CaO	10.27	21.6
SiO₂	5.79	12.1
Al₂O₃	5.69	11.91
Cl	1.42	1.99
P₂O₅	0.62	2.00
SO₃	0.28	0.55
Fe₂O₃	0.23	0.53
K₂O	0.16	0.37
CuO	0.12	0.29
MgO	ND	0.15
ZrO₂	ND	0.02
ZnO	ND	0.01
SrO	ND	0.01
Na₂O	ND	0.59

Table 1. Chemical composition of M100 and M550. ND: not detected.

From a mineralogical standpoint, the XRD pattern of M100 reveals the presence of calcite (CaCO₃), kaolinite (Al₂Si₂O₅(OH)₄), rutile (TiO₂), and quartz (SiO₂), thus indicating a heterogeneous system in which carbonate, clay, and siliceous phases coexist (Figure 1). Kaolinite is clearly identified by its characteristic basal reflection, associated with its 1:1 layered structure composed of silica tetrahedral sheets and aluminum octahedral sheets [29,30]. This structure confers a high specific surface area and a potentially reactive behavior under thermal treatment.

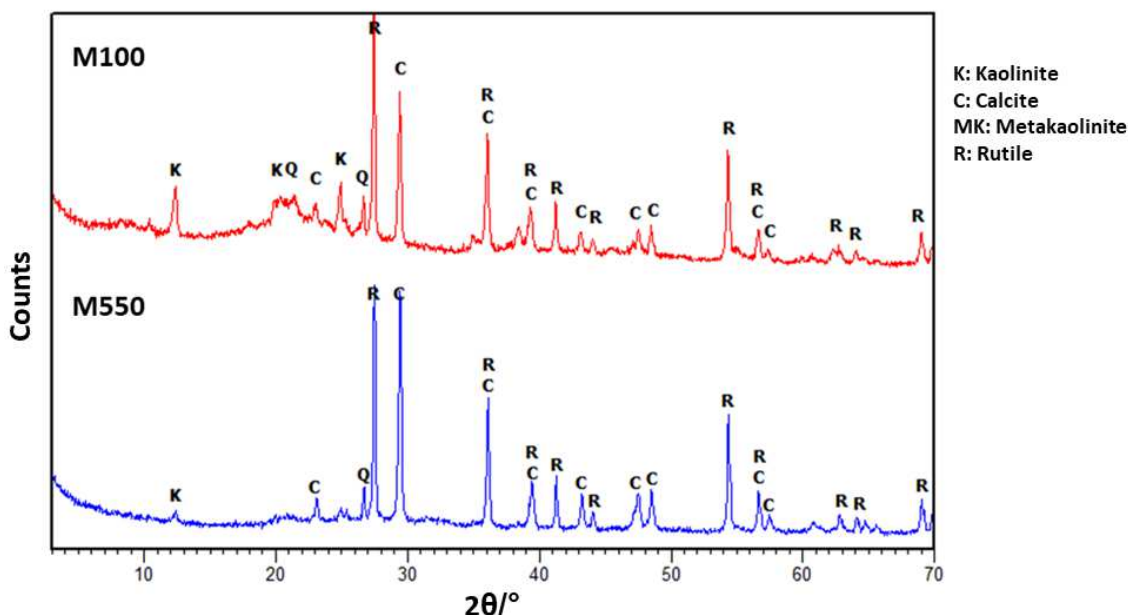


Figure 1. XRD patterns of M samples dried at 100 °C and calcined at 550 °C.

Analysis of the diffractogram allowed semi-quantification of the different phases based on the main reflection of each detected component. By applying rational analysis based on chemical composition (Table 1) and considering the mineral species identified by XRD, the following composition (% w/w) was estimated for M100: 18.33% calcite, 7.31% rutile, 14.41% kaolinite, 2.44% quartz, and 57.51% volatile solids.

SEM characterization highlights the heterogeneous nature of the material in terms of both particle size and particle shape (Figure 2). At higher magnification, lamellar structures characteristic of clay minerals can be observed, in agreement with the kaolinite identified by XRD. These lamellae appear partially disordered, probably as a consequence of interaction with the aqueous medium during formation, which may disrupt the typically stacked structures [31].

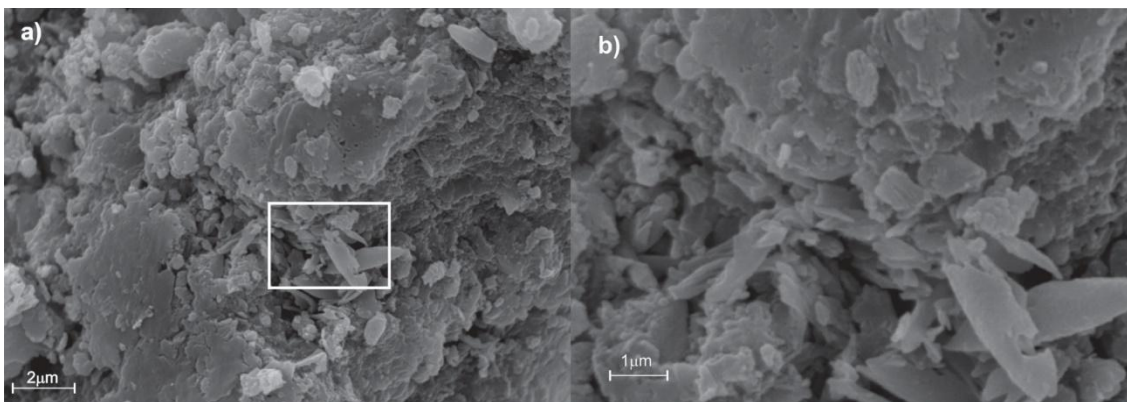


Figure 2. SEM micrographs of M100: (a) general view at 6000×; (b) selected area from Fig. 2a at 18000×.

FTIR analysis (Figure 3) further supported the presence of the kaolinitic fraction detected by XRD through the characteristic bands associated with OH and Al–OH groups, consistent with those reported for this mineral [26,30,32]. Vibrations associated with bonds present in organic compounds contained in M100 but not identified by XRD were also observed, such as CH₂, C=O,

C=C, and COOC groups [33]. The characteristic bands of rutile (674 and 560 cm^{-1}) and quartz (1144 and 1085 cm^{-1}) partially overlap with absorptions assigned to kaolinite.

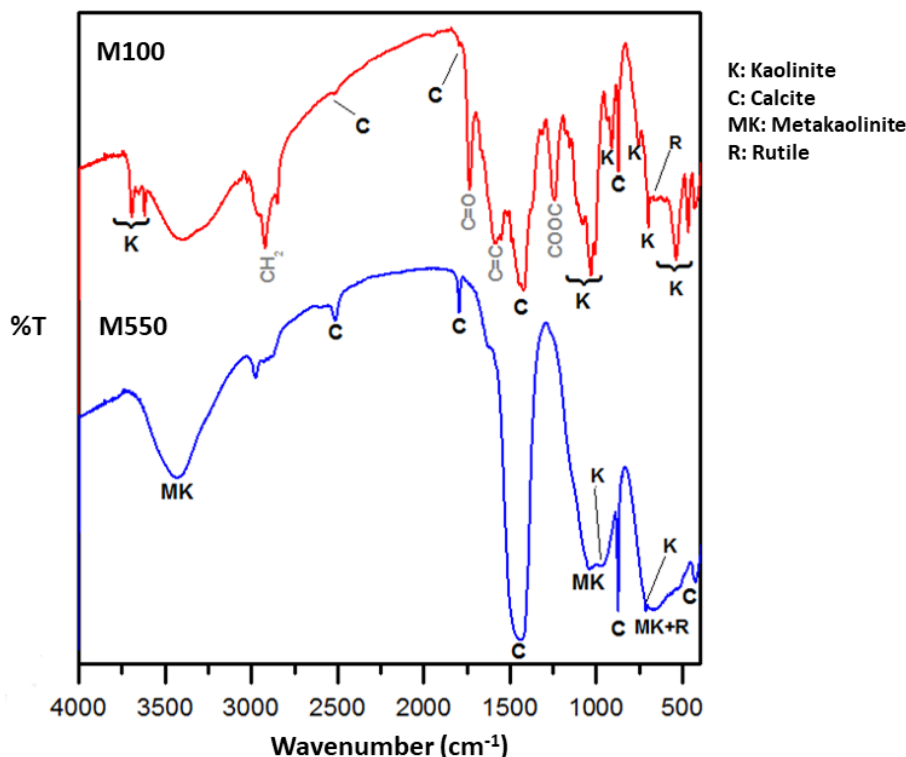


Figure 3. FTIR spectra of M samples dried at 100 °C and calcined at 550 °C.

The dried sludge therefore contains a high organic fraction together with a well-defined mineral phase assemblage, providing an adequate structural basis for modification through thermal treatment.

3.2. Transformation by calcination

Thermal treatment of the sludge at 550 °C produces significant transformations in both its chemical composition and mineralogical structure. The reduction in LOI from values close to 68% in M100 to approximately 32% in M550 (Table 1) confirms the removal of organic matter and the release of volatile compounds, together with dehydroxylation and partial decarbonation processes. This treatment leads to a relative enrichment in inorganic oxides (CaO , SiO_2 , Al_2O_3 , and TiO_2), accompanied by improved detectability of minor elements, attributable to changes in the material matrix.

At the structural level, calcination induces dehydroxylation of kaolinite and loss of its crystalline order, in agreement with the formation of an amorphous metakaolinite-like phase. This transformation is supported by the decrease in the characteristic kaolinite reflections in XRD and the disappearance of structural OH bands in FTIR (Figure 3) [30,34]. At the same time, attenuation of the signals associated with organic compounds confirms that thermal treatment simultaneously affects both the reactive mineral fraction and the organic fraction of the residue.

Calcination causes a profound transformation of the sludge, characterized by removal of organic matter, dehydroxylation of kaolinite, and generation of an amorphous metakaolinite-like phase. These structural changes are decisive for the subsequent behavior of the material, particularly in its interaction with cementitious systems.

3.3. Selection of calcination temperature

Selection of the calcination temperature was based on monitoring the kaolinitic fraction within a complex residual matrix. In the 500–800 °C range, XRD showed the progressive disappearance of the characteristic kaolinite reflections, whereas other crystalline phases present in the residue, such as rutile and calcite, remained relatively stable. This indicates that the main structural transformation induced by thermal treatment is concentrated in the clay fraction, although it occurs within a compositionally more complex system than a conventional kaolinitic raw material.

At temperatures close to 600 °C, the appearance of an intermediate aluminosilicate spinel-like phase, considered a precursor to mullite, was detected [35]. The intensity of this phase increased with temperature, reaching greater development toward 800 °C. This behavior may be associated with the structural reorganization of metakaolin at higher temperatures, in which denser and more ordered arrangements are formed, in contrast with the amorphous nature of the initial metakaolinite [36].

Structural evolution was analyzed in greater detail by FTIR through quantification of the area of the characteristic metakaolin band centered at 1083 cm^{-1} . Figure 4 shows the evolution of this corrected area as a function of treatment temperature. A progressive increase is observed up to approximately 700 °C, attributable to the increase in the amorphous fraction associated with metakaolinite. At higher temperatures, a decrease in band area is recorded, which may be related to partial transformation of this phase into more ordered structures such as spinel.

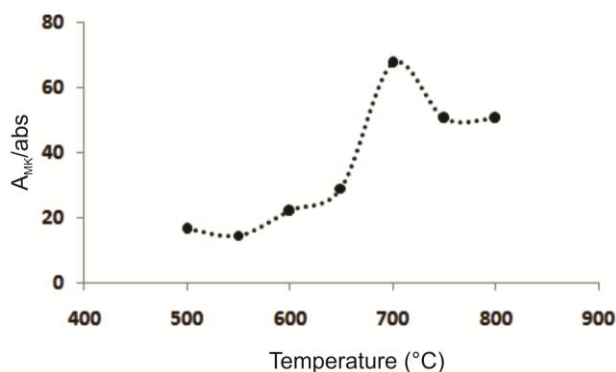


Figure 4. Thermal evolution of the FTIR band centered at 1083 cm^{-1} .

Based on these results, 550 and 700 °C were selected as representative conditions for evaluating material reactivity. The former corresponds to the minimum temperature at which substantial elimination of the organic fraction and dehydroxylation of kaolinite are observed, whereas the latter represents a condition of greater amorphous phase development. Comparison between both temperatures allows assessment of whether the structural improvement induced by calcination is effectively translated into a relevant increase in the pozzolanic activity of the residue.

3.4. Evaluation of pozzolanicity

The pozzolanic activity of the calcined material was evaluated by means of an accelerated chemical test and the standardized Frattini test in order to assess its ability to react with $\text{Ca}(\text{OH})_2$ and form cementitious compounds under controlled conditions.

The results of the accelerated test (Figure 5) show that the reference materials (commercial metakaolin, ground glass, and silica fume) exhibit high reactivity from early ages, reaching fixed-lime values above 85%, in agreement with literature reports [27]. In contrast, the calcined sludges displayed markedly different behavior. Sample M550 showed fixed-lime values between 55 and 66%, whereas M700 reached slightly higher values (78–82%), consistent with its higher degree of structural transformation. However, in neither case was the level of reactivity characteristic of the reference pozzolans attained.

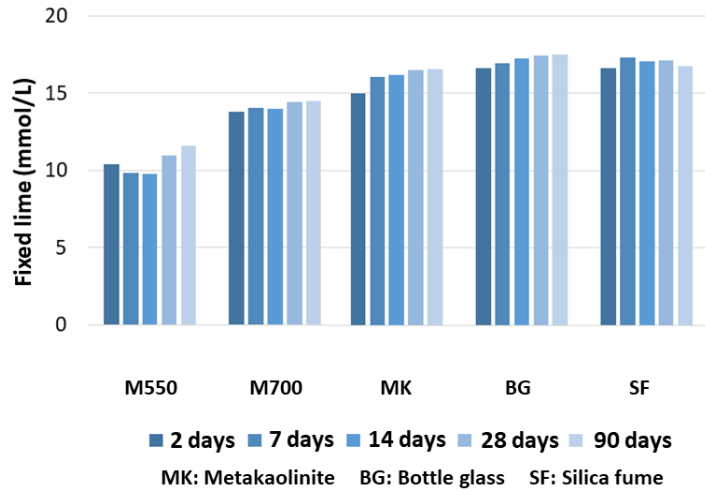


Figure 5. Evolution of pozzolanic activity.

Monitoring of electrical conductivity (Figure 6) provides further insight into these results. M550 initially produced a significant increase in the concentration of ionic species in solution, even higher than that observed for the reference materials, followed by a progressive decrease at later ages. This behavior suggests the coexistence of ion-release and ion-consumption processes in the system. In contrast, M700 showed a more balanced behavior in which calcium consumption was more evident, although still lower than that observed for conventional pozzolans. These results indicate limited reactivity of the calcined materials toward lime solution.

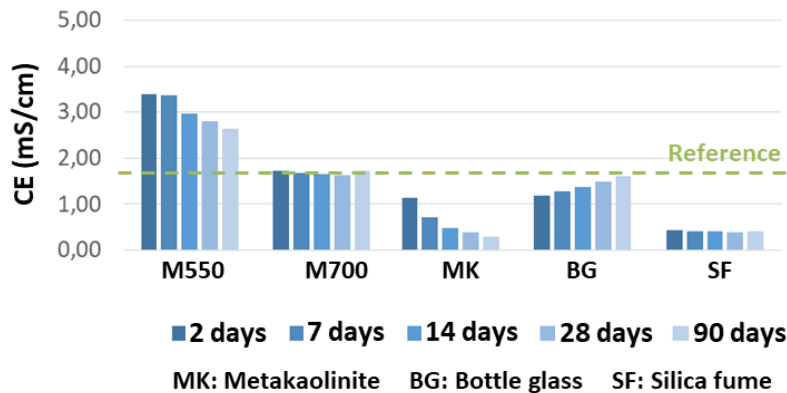


Figure 6. Evolution of electrical conductivity in an accelerated chemical test (40 °C).

The pozzolanic behavior of M550 was then analyzed by the standardized Frattini test on cement blends containing 5, 10, and 20% replacement levels (Figure 7). This sample was selected because it represents the minimum thermal activation condition at which elimination of the organic fraction and transformation of kaolinite into an amorphous phase are achieved. In all cases, the points corresponding to the blended cements are located above the CaO solubility curve, indicating a negative pozzolanicity result according to the standard criterion (UNE-EN 196-5:2011). This behavior contrasts with that expected for pozzolanic materials, in which reaction with $\text{Ca}(\text{OH})_2$ leads to a decrease in Ca^{2+} concentration in solution.

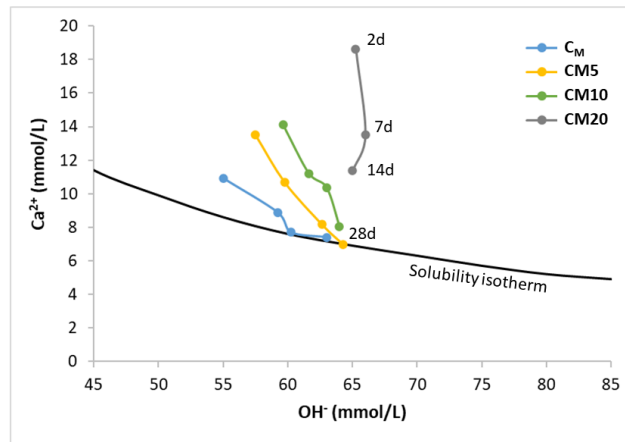


Figure 7. Frattini tests for blended cements.

However, incorporation of the sludge led to a significant increase in Ca^{2+} concentration relative to the reference cement, even when the dilution effect is taken into account. This increase became more pronounced as the replacement level rose and was accompanied by an increase in the initial OH^- concentration, thus evidencing an intrinsic ionic contribution from the material. This behavior was confirmed by an independent test in which sample M550, when placed in contact with distilled water, released significant concentrations of Ca^{2+} and OH^- , confirming its ability to modify solution chemistry.

In this context, although thermal transformation of the material leads to formation of a potentially reactive amorphous metakaolinite-like phase, its contribution is not sufficient to offset the effect of calcium input to the system. As a result, Ca^{2+} concentration in solution remains high and the experimental points stay above the solubility curve, preventing classification of the material as pozzolanic according to the Frattini test. This type of behavior has been reported for calcium-bearing industrial residues, in which Ca^{2+} release may mask incipient reaction processes [37].

Despite the structural modification of the material, the calcined sludge did not exhibit effective pozzolanic behavior. Its limited $\text{Ca}(\text{OH})_2$ consumption capacity, together with its intrinsic ionic contribution, conditions its performance in cementitious systems and differentiates it from the behavior expected for supplementary cementitious materials.

3.5. Hydration of blended cements

The influence of calcined sludge incorporation (M550) on cement hydration was evaluated by isothermal calorimetry and FTIR spectroscopy in pastes with different replacement levels (CM5, CM10, and CM20).

The calorimetric curves (Figure 8a) show that incorporation of M550 modifies the hydration kinetics of the system, producing a delay and extension of the dormant period relative to the reference cement (Table 2). This behavior may be attributed to the lower initial reactivity of the replacement material and to the time required for its interaction with the aqueous medium. However, for intermediate replacement levels (CM10), the dormant period was shorter than in CM5 and CM20, suggesting stronger interaction between the incorporated material and the initial hydration products.

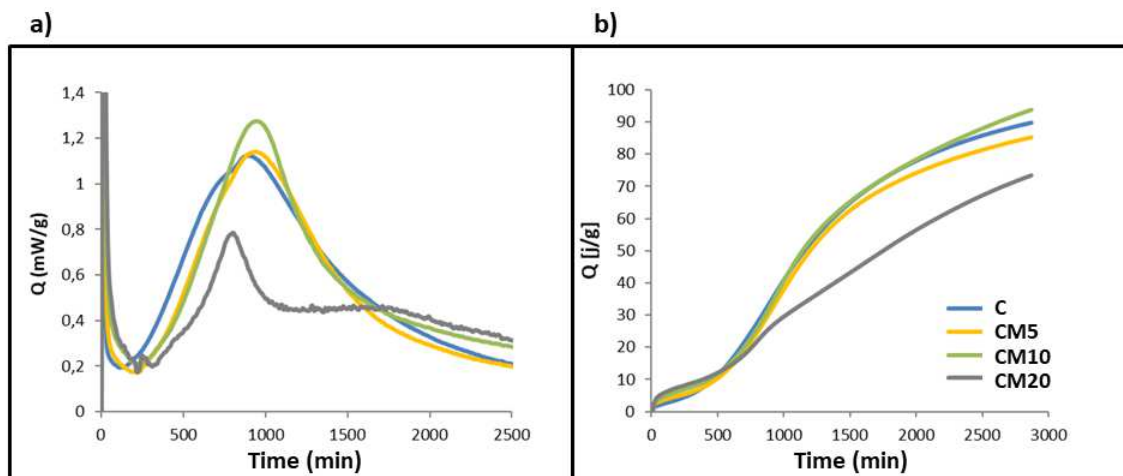


Figure 8. Calorimetric tests for the reference cement and CMi blends: a) calorimetric curves; b) cumulative heat curves.

Sample	Dormant period			Acceleration period				Total heat	
	t_i (h)	t_f (h)	Δt (h)	t_i (h)	t_f (h)	Δt (h)	V (mW/g.h)	Q_T (J/g)	Q_{CM}/Q_C (%)
C	0.75	2.38	1.63	2.38	14.78	12.4	0.0761	89.80	--
CM5	0.82	3.90	3.08	3.90	15.72	11.82	0.0778	85.23	94.91
CM10	1.65	3.77	2.12	3.77	15.72	11.95	0.0872	93.80	104.5
CM20	1.93	5.65	3.72	5.65	13.32	7.67	0.0565	73.43	81.77

Table 2. Analysis of the dormant period, acceleration period, and total heat. t_i : initial time; t_f : final time.

During the acceleration period, CM5 and CM10 exhibited reaction rates comparable to that of the reference cement, even reaching higher heat-flow intensities, particularly in CM10. This behavior suggests a stimulation effect on hydration reactions, possibly associated with the presence of additional surfaces acting as nucleation sites. However, at higher replacement levels (CM20), this effect was reduced, and splitting of the calorimetric curves was observed, indicating a modification of the hydration mechanism.

Analysis of cumulative heat release (Figure 8b) shows that CM10 reached values higher than those of the reference cement, whereas CM5 and CM20 exhibited lower heat release, mainly attributable to the dilution effect. These findings indicate that the effect of calcined sludge incorporation depends on the replacement level, with 10% being the condition that maximizes system interaction without negatively affecting the overall kinetics.

The mineralogical evolution during hydration was analyzed by FTIR (Figure 9), and the characteristic bands of the main cement hydration products were identified: $\text{Ca}(\text{OH})_2$ (3643 cm^{-1}), C-S-H (975 cm^{-1}), and ettringite (1123 cm^{-1}) [37–39]. In the blended cements, these bands evolved similarly to those of the reference cement, indicating that sludge incorporation does not substantially alter the hydration products formed.

Nevertheless, subtle differences were observed in the intensity of some bands. In particular, the signal corresponding to $\text{Ca}(\text{OH})_2$ was slightly stronger in the blended systems, which is consistent with the Frattini results, where a Ca^{2+} contribution from the material was evidenced. In addition, higher intensity of carbonate-related bands was detected at intermediate ages, attributable to surface carbonation processes.

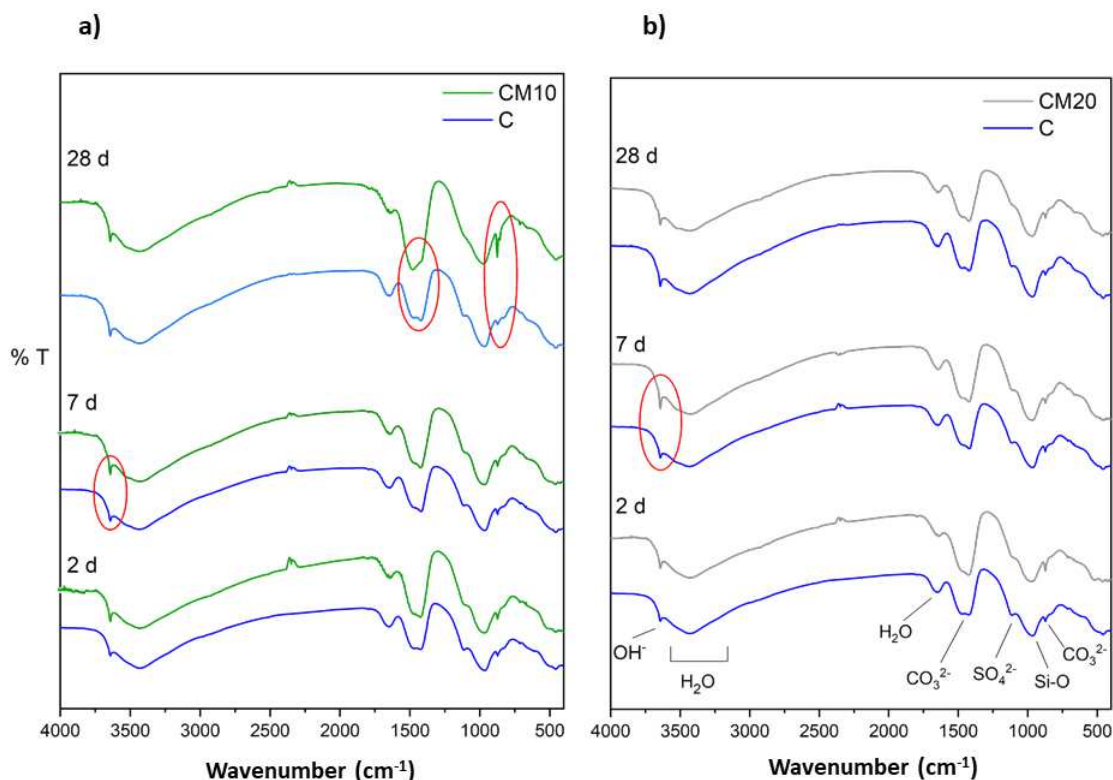


Figure 9. FTIR spectra of cement hydration at different ages: a) CM10 and C; b) CM20 and C.

Monitoring of the band associated with $\text{Ca}(\text{OH})_2$ showed an initial increase in this phase followed by a progressive decrease with age, particularly in CM20. This behavior suggests partial consumption of $\text{Ca}(\text{OH})_2$ during hydration, compatible with the presence of a reactive amorphous phase in the material. However, this consumption is limited and does not translate into effective pozzolanic behavior, in agreement with the previously obtained results.

Isothermal calorimetry and FTIR results show that incorporation of M550 modifies the hydration kinetics of the cementitious system without substantially altering the nature of the products formed. The variations observed in the induction period and heat-flow intensity, together with the limited portlandite consumption, suggest a combined interaction dominated by physical effects (dilution and nucleation) and, to a lesser extent, by a restricted chemical contribution. In this sense, the material cannot be considered inert, but neither does it behave as an effective pozzolanic addition. Rather, it exhibits an intermediate behavior that supports interpretation of its incorporation into cementitious matrices in terms of compatibility and hydration-process modification, rather than as a significant reactive contribution.

4. Conclusions

The sludge obtained from the coagulation-flocculation treatment of flexographic printing wastewater showed a markedly heterogeneous composition, characterized by a high volatile fraction and the coexistence of kaolinite, calcite, quartz and rutile. Calcination of the residue, particularly at 550 and 700 °C, promoted the removal of organic matter and the structural transformation of the kaolinitic fraction into an amorphous metakaolinite-like phase, confirming that thermal treatment effectively modifies the residue and increases its potential reactivity.

However, the results demonstrate that this structural transformation does not translate into effective pozzolanic behavior. Although the calcined materials interacted with lime solution and M700 showed higher reactivity than M550 in the accelerated test, the Frattini test performed on M550 yielded negative results for all replacement levels. This behavior was associated with the intrinsic ionic contribution of the residue, particularly its release of Ca^{2+} and OH^- , which maintained high calcium concentrations in solution and masked any limited pozzolanic consumption that may have occurred.

The hydration study further showed that the selected calcined sludge cannot be regarded as an inert filler, since it modified the hydration kinetics of blended cement systems. In particular, the 10% replacement level promoted a higher heat release during the acceleration period, while FTIR confirmed that the main hydration products remained similar to those of the reference cement. Nevertheless, the limited consumption of portlandite and the absence of positive Frattini results indicate that the residue does not behave as an effective supplementary cementitious material.

Overall, the results show that thermal treatment substantially modifies the structure and reactivity of flexographic wastewater sludge, but these changes do not lead to effective pozzolanic behavior. The residue nevertheless alters the kinetics of Portland cement hydration, mainly through physical and ionic effects. These findings demonstrate the importance of combining thermal, structural, and calorimetric analyses when evaluating heterogeneous industrial residues, since conventional pozzolanicity tests alone may not fully describe their interaction with cementitious systems.

CRedit authorship contribution statement

Maximiliano Iván Delletesse: Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Visualization, Writing – original draft, Writing – review & editing.

Funding

This work was supported by institutional funds from CIFICEN — Centro de Investigaciones en Física e Ingeniería del Centro de la Provincia de Buenos Aires, UNICEN-CICPBA-CONICET. No specific grant number was assigned to this work.

Declaration of competing interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work, the author used generative AI to support formatting review. After using this tool, the author reviewed and edited the content as needed and takes full responsibility for the content of the published article.

5. References

1. Geissdoerfer M, Savaget P, Bocken NMP, Hultink EJ. The Circular Economy – A new sustainability paradigm? *J Clean Prod.* 2017;143:757–68. <https://doi.org/10.1016/j.jclepro.2016.12.048>
2. Kishore K, Gupta N. Application of domestic & industrial waste materials in concrete: A review. *Mater Today Proc.* 2020;26:2926–31. <https://doi.org/10.1016/j.matpr.2020.02.604>

3. Valero Delgado A, Usón Gil S. Ecología industrial: cerrando el ciclo de materiales. Primera. Zaragoza, España: Prensas Universitarias de Zaragoza; 2011.
4. Vitale P, Ramos PB, Colasurdo V, Dellellesse MI, Barreto GP. Degradation of printing ink effluent and industrial predesign by UV/H₂O₂ treatment: A kinetic study. *Clean Waste Syst.* 2023;5:100106. <https://doi.org/10.1016/j.clwas.2023.100106>
5. Noonpui S, Thiravetyan P, Nakbanpote W, Netpradit S. Color removal from water-based ink wastewater by bagasse fly ash, sawdust fly ash and activated carbon. *Chem Eng J.* 2010;162:503–8. <https://doi.org/10.1016/j.cej.2010.05.051>
6. Papadopoulos KP, Argyriou R, Economou CN, Charalampous N, Dailianis S, Tatoulis TI, et al. Treatment of printing ink wastewater using electrocoagulation. *J Environ Manage.* 2019;237:442–8. <https://doi.org/10.1016/j.jenvman.2019.02.080>
7. Xiang-Juan M, Hui-Long X. Treatment of water-based printing ink wastewater by Fenton process combined with coagulation. *J Hazard Mater.* 2009;162:386–90.
8. Dellellesse MI, Pompei MC, Eyler GN, Nesprías RK. Ecology treatment of a real industrial effluent with chitosan: Characterization and design of coagulation-flocculation process. *Afinidad J Chem Eng Theor Appl Chem [Internet].* 2023 [cited 2026 Apr 22];80. <https://doi.org/10.55815/422668>
9. Imen F, Lamia K, Asma T, Neacute Ji G, Radhouane G. Optimization of coagulation-flocculation process for printing ink industrial wastewater treatment using response surface methodology. *Afr J Biotechnol.* 2013;12:4819–26. <https://doi.org/10.5897/AJB12.1900>
10. Chen M, Zheng Y, Zhou X, Li L, Wang S, Zhao P, et al. Recycling of paper sludge powder for achieving sustainable and energy-saving building materials. *Constr Build Mater.* 2019;229:116874. <https://doi.org/10.1016/j.conbuildmat.2019.116874>
11. De Azevedo AR, Alexandre J, Xavier GDC, Pedroti LG. Recycling paper industry effluent sludge for use in mortars: A sustainability perspective. *J Clean Prod.* 2018;192:335–46.
12. Fauzi MA, Sulaiman H, Ridzuan ARM, Azmi AN. The effect of recycled aggregate concrete incorporating waste paper sludge ash as partial replacement of cement. Penang, Malaysia; 2016 [cited 2026 Apr 22]. p. 030007. <https://doi.org/10.1063/1.4965063>
13. Logeswaran V, Ramakrishna DrG. Waste Paper Sludge Ash - State of art. *Int J Innov Technol Explor Eng.* 2019;8:2333–8. <https://doi.org/10.35940/ijitee.I8572.078919>
14. Vegas I, Frías M, Urreta J, San José JT. Obtaining a pozzolanic addition from the controlled calcination of paper mill sludge. Performance in cement matrices. *Mater Constr.* 2006;56:49–60. <https://doi.org/10.3989/mc.2006.v56.i283.8>
15. Yan S, Sagoe-Crentsil K, Shapiro G. Properties of cement mortar incorporating de-inking waste-water from waste paper recycling. *Constr Build Mater.* 2012;29:51–5. <https://doi.org/10.1016/j.conbuildmat.2011.09.012>

16. Yan S, Sagoe-Crentsil K, Shapiro G. Reuse of de-inking sludge from wastepaper recycling in cement mortar products. *J Environ Manage.* 2011;92:2085–90.
<https://doi.org/10.1016/j.jenvman.2011.03.028>
17. Frías M, Vegas I, García R, Vigil de la Villa R. Nuevos materiales ecoeficientes a partir de residuos de la industria papelera como adiciones activas para la fabricación de cementos portland. Madrid: Universidad Autónoma de Madrid; 2011.
18. Frías M, García R, Vigil R, Ferreiro S. Calcination of art paper sludge waste for the use as a supplementary cementing material. *Appl Clay Sci.* 2008;42:189–93.
19. Jwaida Z, Dulaimi A, Alyhya W, Algretawee H, Al-Busaltan S. Recycling and utilization of paper sludge ash -current status review and future perspectives. *Sustain Mater Technol.* 2024;40:e00960. <https://doi.org/10.1016/j.susmat.2024.e00960>
20. Sabador E, Frías M, Sánchez De Rojas MI, Vigil R, García R, San José JT. Characterization and transformation of an industrial by-product (coated paper sludge) into a pozzolanic material. *Mater Constr.* 2007;57:45–59. <https://doi.org/10.3989/mc.2007.v57.i285.38>
21. Vigil De La Villa R, Frías M, Sánchez De Rojas MI, Vegas I, García R. Mineralogical and morphological changes of calcined paper sludge at different temperatures and retention in furnace. *Appl Clay Sci.* 2007;36:279–86. <https://doi.org/10.1016/j.clay.2006.10.001>
22. De Weerdt K, Haha MB, Le Saout G, Kjellsen KO, Justnes H, Lothenbach B. Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash. *Cem Concr Res.* 2011;41:279–91. <https://doi.org/10.1016/j.cemconres.2010.11.014>
23. Hewlett PC, Liska M. *Lea's Chemistry of Cement and Concrete.* Oxford, United Kingdom: Butterworth-Heinemann; 2019.
24. Jhatial AA, Nováková I, Gjerløw E. A Review on Emerging Cementitious Materials, Reactivity Evaluation and Treatment Methods. *Buildings.* 2023;13:526.
<https://doi.org/10.3390/buildings13020526>
25. Lothenbach B, Scrivener K, Hooton RD. Supplementary cementitious materials. *Cem Concr Res.* 2011;41:1244–56. <https://doi.org/10.1016/j.cemconres.2010.12.001>
26. Wilson M. *A handbook of determinative methods in clay mineralogy.* New York: Blackie & Son Ltd.; 1987.
27. Frías M, Vegas I, La Villa RVD, Garcia R. Recycling of Waste Paper Sludge in Cements: Characterization and Behavior of New Eco-Efficient Matrices. In: Kumar S, editor. *Integr Waste Manag - Vol II* [Internet]. InTech; 2011 [cited 2026 Apr 22].
<https://doi.org/10.5772/20850>
28. Frías M, De Rojas MIS, Cabrera J. The effect that the pozzolanic reaction of metakaolin has on the heat evolution in metakaolin-cement mortars. *Cem Concr Res.* 2000;30:209–16.
[https://doi.org/10.1016/S0008-8846\(99\)00231-8](https://doi.org/10.1016/S0008-8846(99)00231-8)
29. Balan E, Lazzeri M, Mauri F. Infrared spectrum of hydrous minerals from first-principle calculations. *PsiK Newsl - Sci Highlight Mon.* 2006;75:143–50.

30. Bich Ch, Ambroise J, Péra J. Influence of degree of dehydroxylation on the pozzolanic activity of metakaolin. *Appl Clay Sci.* 2009;44:194–200. <https://doi.org/10.1016/j.clay.2009.01.014>
31. Bustamante Rúa MO, Rojas Reyes NR, Quitian Chila GR. Fine material effect on kaolin suspensions rheology. *DYNA.* 2016;83:105–11. <https://doi.org/10.15446/dyna.v83n195.48855>
32. Pansu M, Gautheyrou J. *Handbook of Soil Analysis* [Internet]. Berlin, Heidelberg: Springer Berlin Heidelberg; 2006 [cited 2026 Apr 22]. <https://doi.org/10.1007/978-3-540-31211-6>
33. Dutra R, Takahashi M, Diniz M. Nova metodologia para identificação de componentes em tintas comerciais. *Polímeros.* 2002;12:273–9.
34. Shvarzman A, Kovler K, Grader GS, Shter GE. The effect of dehydroxylation/amorphization degree on pozzolanic activity of kaolinite. *Cem Concr Res.* 2003;33:405–16. [https://doi.org/10.1016/S0008-8846\(02\)00975-4](https://doi.org/10.1016/S0008-8846(02)00975-4)
35. Padmaja P, Anilkumar GM, Mukundan P, Aruldas G, Warriar KGK. Characterisation of stoichiometric sol–gel mullite by fourier transform infrared spectroscopy. *Int J Inorg Mater.* 2001;3:693–8. [https://doi.org/10.1016/S1466-6049\(01\)00189-1](https://doi.org/10.1016/S1466-6049(01)00189-1)
36. Brindley GW, Nakahira M. The Kaolinite-Mullite Reaction Series: II, Metakaolin. *J Am Ceram Soc.* 1959;42:314–8. <https://doi.org/10.1111/j.1151-2916.1959.tb14315.x>
37. Kramar S, Ducman V. Evaluation of Ash Pozzolanic Activity by Means of the Strength Activity Index Test, Frattini Test and DTA/TG Analysis. *Teh Vjesn - Tech Gaz* [Internet]. 2018 [cited 2026 Apr 23];25. <https://doi.org/10.17559/TV-20171203193229>
38. Lin K-L, Wu H-H, Shie J-L, Hwang C-L, An Cheng. Recycling waste brick from construction and demolition of buildings as pozzolanic materials. *Waste Manag Res J Sustain Circ Econ.* 2010;28:653–9. <https://doi.org/10.1177/0734242X09358735>
39. Yu P, Kirkpatrick RJ, Poe B, McMillan PF, Cong X. Structure of Calcium Silicate Hydrate (C-S-H): Near-, Mid-, and Far-Infrared Spectroscopy. *J Am Ceram Soc.* 2004;82:742–8.