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Recycling of Waste Paper Sludge in Cements: Characterization and Behavior of New Eco-Efficient Matrices

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1. Introduction

The pulp and paper industry, in Europe, generates 11 million tons of solid waste each year (Monte et al., 2009). Paper waste covers a diverse range of non-hazardous waste streams, prominent among which are different types of sludge, boiler ash, combustion furnace ash and organic and inorganic rejects. Manufacturing processes to produce new paper from the deinking of recycled paper account for 70% of these waste products.

Following its reception, sorting and storage, the recycled paper is transformed into an aqueous suspension of fibers, while inappropriate materials are eliminated in different cleaning processes. Following this initial treatment, the resultant paper sludge is subjected to deinking in a froth flotation process, which produces waste known as de-inked sludge. This waste sludge is fundamentally composed of water, fiber, ink and a mineral load. In addition, various paper manufacturing processes have water treatment plants that generate sludges with high humidity contents.

The deinked paper sludge and the sludge from the water treatment process have a high humidity content ($\approx 50\%$), and are roughly composed of organic material with their origin in paper fibers ($\approx 25\%$) and mineral loads such as calcium carbonate, kaolin, talc and titanium oxide ($\approx 25\%$). A similar composition highlights the wealth of energetic and mineral resources saturating the paper sludge. Thus, the most advanced techniques for the use of paper sludge are intended to take full advantage of the saturated biomass and the recovery of the mineral constituents in the inorganic fraction.

The most common options for the processing of paper industry sludge range from their exploitation for agricultural purposes, composting, or use as a primary material in the manufacture of ceramics and cement (Moo-Young & Zimmie, 1997; Ahmadi & Al-Khaja, 2001; Lima & Dal Molin, 2005; Conesa et al., 2008), to energy recovery in biomass boilers or fluidized bed systems. Thus, the Dutch CDEM process (International Patent, 2006) represents a pioneering recovery system, where the paper sludge is treated at temperatures of around 730°C , in a fluidized bed combustion system, so as to activate the latent

pozzolanic properties of its mineral content. The CDEM process was industrialized after the pioneering work of research groups led by Prof. Pera (Pera & Amrouz, 1998), which demonstrated that controlled calcination of the deinked sludge produces a highly reactive pozzolanic material, within a temperature range of between 700 and 750°C.

On the basis of the scientific knowledge presented earlier, a team of Spanish researchers led by Dr. Frías, has been conducting in-depth research over the past decade into the scientific, technological and environmental aspects of obtaining active admixtures from the calcination of paper sludge and its behavior in cement and mortar.

2. Waste paper sludge and its activated products

2.1 Nature of the raw waste and activation process

The characteristic composition of this industrial waste is a mixture of organic material (non-recovered cellulose) and inorganic materials (principally, kaolinite and limestone), normally used as loadings in the manufacture of paper.

An example of the chemical and mineralogical composition of this type of waste is presented in Table 1. The characterization of this dry material is provided by the Spanish paper manufacturer Holmen Paper Madrid, S.L, which uses 100% recycled paper as the raw material. X-Ray Fluorescence (XRF) confirms that the principal oxides are CaO, SiO₂ and Al₂O₃, the sum of which exceeds 43% of the total mass. The high Loss on Ignition (LOI) in these waste products, at around 54%, should be underlined, due to the presence of organic material, kaolinite dehydroxylation and the decarbonation process of calcite. These values, for guidance only, vary in accordance with the type of paper, its origin, the percentage of recycled paper used as primary material, the loadings, and the type of process etc. With respect to its mineralogical composition, it is worth highlighting the presence of cellulose residue (about 32%, determined according to the results of XRF and XRD), as well as the presence of calcite and kaolinite content in a ratio of 3.3 (Frías et al., 2010). This value is above those in other research works that report ratios of under 2, even for samples from the same paper manufacturing process (Pera & Amrouz, 1998; Frías et al., 2008a). The variation in the composition of this industrial waste is therefore confirmed.

<i>Chemical composition by XRF (%)</i>										
CaO	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	SO ₃	TiO ₂	Na ₂ O	K ₂ O	P ₂ O ₃	LOI
25.43	10.79	6.82	0.86	0.46	0.33	0.28	0.13	0.24	0.13	54.34
<i>Mineralogical composition (%)</i>										
Organic material	By XRD									
	Calcite	Kaolinite	Phyllosilicates (talc, mica) and quartz							
32.34	45.27	13.67	8.72							

Table 1. Composition of the raw paper sludge

In the same way as with other clayey materials, this waste has to be subjected to a process of thermal activation to provide it with pozzolanic properties. As it is not a pure natural

kaolinite, research into its thermal activation has centered on the range of temperatures between 500 and 800°C, with retention times in the furnace of between 2 and 5 hours (Frías et al., 2008b; Rodríguez et al., 2009). All of this has the purpose of establishing optimal conditions that will guarantee total elimination of the organic material, an appropriate transformation of the kaolinite into MK, as well as a minimum content of free lime, which relates to aspects of volumetric instability.

2.2 Properties of the activated products

Knowledge of the chemical, physical, mineralogical and pozzolanic properties that determine the behavior of Portland cements prepared with activated wastes in the form of active additions represents a key point for the evaluation of their viability.

2.2.1 Physical properties

Laser diffraction granulometry confirms the presence of particle sizes of less than 90 micrometers. The distribution density curves show 2 maximums located at 40 and 4 micrometers. The BET surface area varies between 7 and 8 m²/g, for original activated sludge, a much higher value than that found for a cement type I 42.5 R (<1 m²/g), reaching values of around 12-13 m²/g for activated paper sludge that is ground down to particle sizes of less than 45 micrometers (Ferreiro, 2010).

The different coloration between the raw paper sludge and the activated product is also worth mentioning (Fig.1). Whereas the former presents a grayish coloring due to the deinking process, the latter shows a white color.



Fig. 1. Appearance of the sludges before (left) and after calcination (right)

Determination of the colorimetric variables (Fig. 2) show values for the coordinate of luminosity (L*)(or whiteness index) of between 75% and 94%. It may be seen that the luminosity value increases with the conditions of activation (higher temperature and a longer retention time). The increase in luminosity is directly related to different processes that take place in that temperature interval (presence of organic residues, inks, degree of



Fig. 2. Luminosity values (%) versus activation conditions

transformation of the kaolinite into metakaolinite and degree of calcite decarbonation). This parameter is of greater importance when using these activated products as pozzolans in the manufacture of commercial cements, especially in white cements, the minimum required value of which is 85% (RC-08).

2.2.2 Chemical composition

In a similar way to the processes described for basic paper sludges, the products yielded by thermal activation are formed principally of silica (20-30%), lime (34-45%), alumina (13-20%) and magnesia (2-3.5%). The remaining oxides are present in amounts of less than 1%. The chemical values increase with the intensity of the activation conditions, as a consequence of the reduction in loss on calcination. These results are in accordance with those obtained by Bai (Bai et al., 2003), but differ from those indicated by Toya (Toya et al. 2006).

2.2.3 Mineralogical and morphological composition

The mineralogical composition of the activated sludge from the most labile (500°C for 2 hours) to the most drastic (800°C for 2 hours) conditions reflects the changes undergone in the different minerals due to heating. The paper sludge calcined at 500°C for 2 hours is composed of talc, kaolinite, illite, dolomite, calcite and quartz. As the temperature increases (550°C/2 hours), the kaolinite is transformed into metakaolinite. This compound is detected by SEM, as it is not a crystalline material (Fig. 3). The talc and quartz remain unaltered in the range of temperatures under study. In contrast, the dolomite is transformed at 550°C/2 hours and the calcite disappears at 800°C/2 hours, as a result of the decarbonation of those minerals. The illite undergoes a transformation process at 800°C/2 hours. The appearance of portlandite is notable at 650°C/5 hours or more as a consequence of the exposure of the paper sludge to environmental humidity, while the formation of dicalcium silicate (bredigite) is detected at 800°C or more.

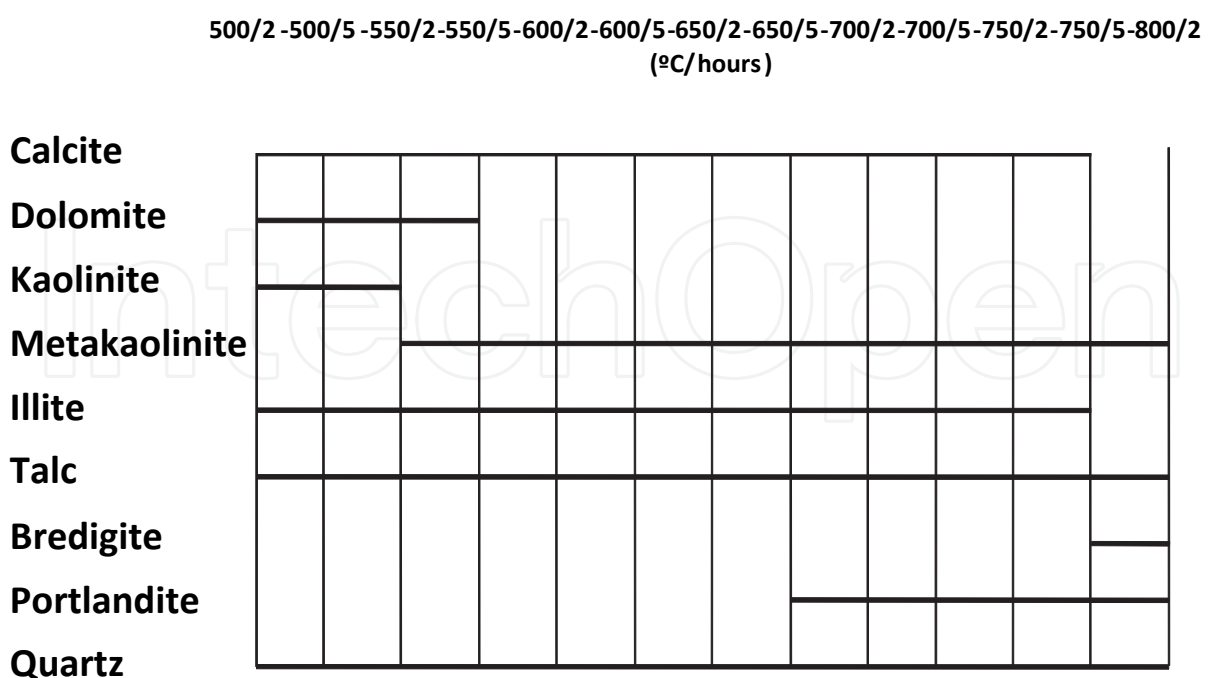


Fig. 3. Stability fields of the different materials identified in the interval 500°C/2h and 800°C/2h

Morphologically, the formation of aggregates takes place with the increase in heat through the coldest to the warmest stages, which entails an increase in the specific surface of the materials and means that they become absorbent. Fig. 4 (left) shows the situation of the crystals at 500°C/2 hours, whereas Fig. 4 right illustrates the great number of aggregates present in the activated paper sludge, corresponding above all to metakaolinite and portlandite, at 800°C, after 2 hours.

2.2.4 Pozzolanic properties

The fundamental property for a material or an industrial waste product to be used as an active admixture in the manufacture of commercial blended cements is its pozzolanic nature. A rapid method of supplying information in the short term is through the use of an accelerated chemical method in the pozzolan/lime system (Frías et al., 2008c).

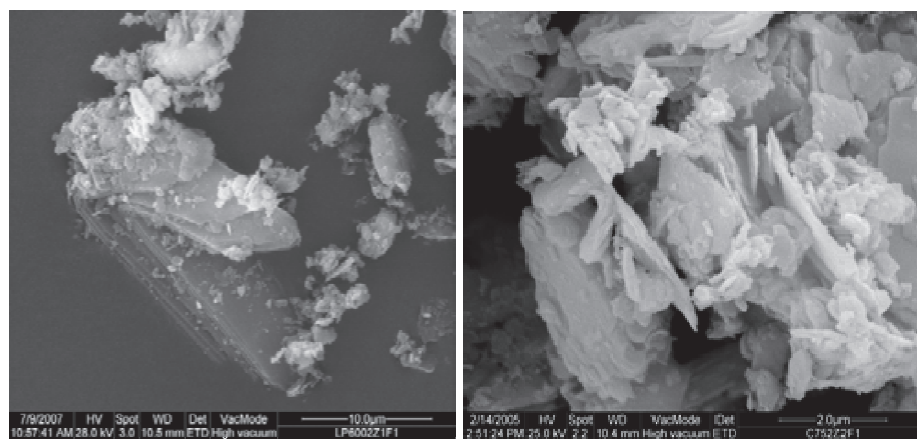


Fig. 4. Left) Large crystals of kaolinite, talc and calcite. Right) Aggregates of metakaolinite and portlandite

The results obtained for the different types of paper sludge, which are activated at temperatures of between 500 and 800°C after two furnace retention times of 2 and 5 hours (Fig. 5), reveal good pozzolanic activity in all cases. No appreciable differences have been found between periods of 2 and 5 hours. With regard to the activation temperature, it is clearly observed that lime consumption drops at temperatures of 700°C. This phenomenon may be attributed, on the one hand, to morphological changes in the metakaolinite in the form of more compact aggregates and less specific surface area and; on the other hand, to the initiation of the decarbonation process of the calcite that is present in the waste, liberating free CaO in dissolution, which overlaps with the pozzolanic reaction itself.

A comparative study of these results with pozzolans, normally included in the standards currently in force, shows that the activity of this activated waste is similar to that obtained for pure metakaolin (MK), and very close to silica fume (SF) (Frías et al., 2008d).

As a consequence of the above, together with the mineralogical and morphological observations, it is recommended that the activation of this type of paper sludge should be at temperatures of between 650 and 700°C for 2 hours, so as to ensure high pozzolanic activity, to reduce energy costs and to minimize the generation of CO₂ associated with the calcite decarbonation process. Higher temperatures generate high contents of quicklime, whereas lower temperatures reveal the presence of kaolinite that is not transformed into metakaolinite.

At present, in view of the current global crisis, the preparation of commercial cements with more than one pozzolan (Types II/M, IV and V) acquires great importance from the economic and energetic point of view. For this reason, the pozzolanic behavior of this activated waste is analyzed when mixed with fly ash (1:1 by weight), as this is one of the most widely-used pozzolans in the world (Sanjuan, 2007).

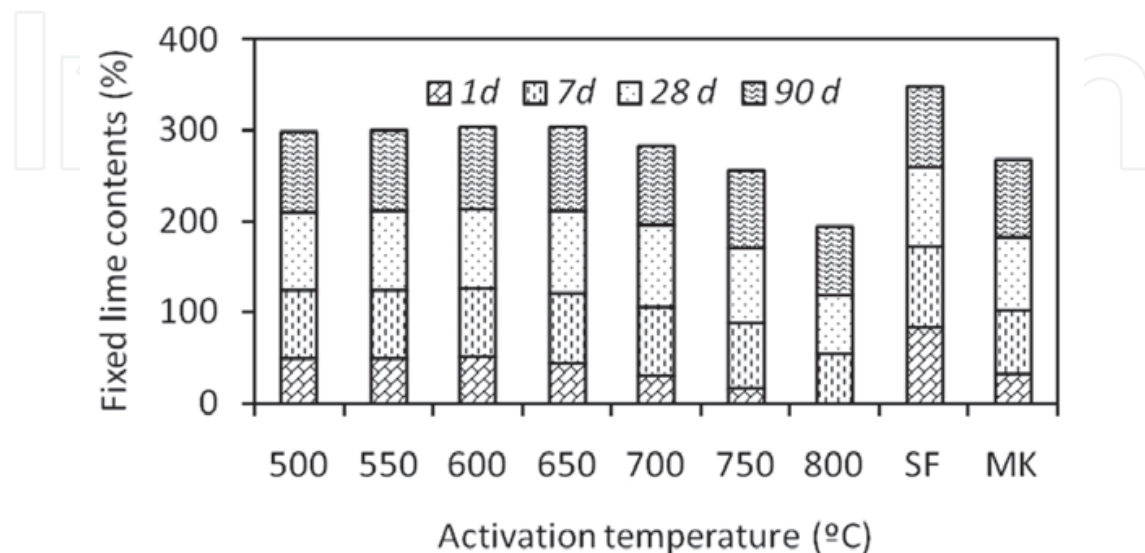


Fig. 5. Evolution of fixed lime (%) versus reaction time

Fig. 6 summarizes the evolution of pozzolanic activity for the activated sludge-fly ash systems $\text{Ca}(\text{OH})_2$, for the first 90 days of the reaction. The figure shows an analysis of two waste paper sludges activated in different ways: a laboratory scale production (LPS) obtained under optimal conditions and secondly, an industrial scale production (IPS) at temperatures of over 700°C , which is commercialized and patented (Patent, 1996).

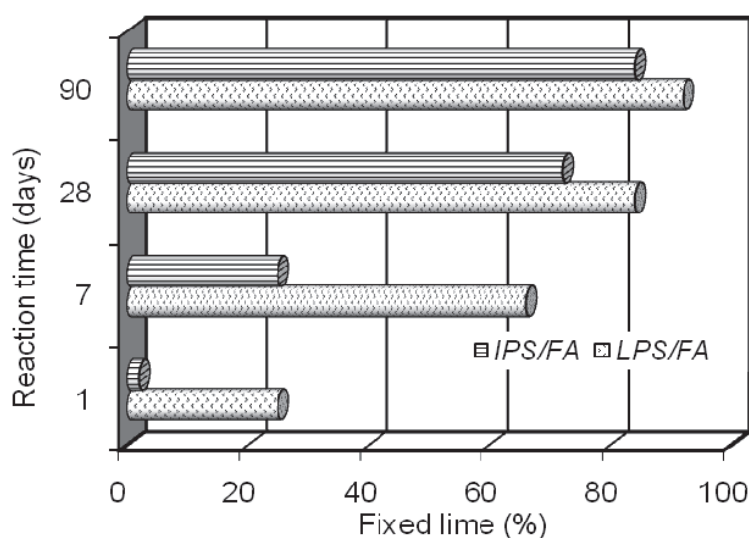


Fig. 6. Evolution of fixed lime in pozzolanic activated sludge mixtures /FA

The results show that the pozzolan mixtures under analysis behave in different ways. As the fly ash is the same in both cases, these differences in pozzolanic activity are directly related

to the activation conditions of the paper sludge. This fact may be explained as the consequence of the sludge activation temperature that is higher at an industrial scale than it is at a laboratory scale. Moreover, other parameters may be involved such as the morphology of metakaolinite, the different origins of the paper sludge and the kaolinite/calcite ratio.

After a reaction time of 28 days, the pozzolanic behavior of both mixtures was very similar and evened out at reaction times of over 90 days, due to the slower speed of the pozzolanic reaction of the fly ash (Sánchez de Rojas et al., 1993 and 1996). It is worth highlighting that in the ISP/FA mixture, a significant jump in lime consumption takes place between day 7 and day 28 of the reaction time. This fact may be due to the fly ash acting as an activator of the pozzolanic reaction between the activated sludge and the surrounding lime, as additional quicklime is available from the industrial sludge.

3. The behavior of binary and ternary blended cement prepared with thermally activated paper sludge

3.1 Scientific aspects

3.1.1 Reaction kinetics in binary cements with the addition of 10% activated sludge

In general, the kinetics of pozzolanic reactions depends on various chemical, physical and mineralogical factors. In a study of the influence of the activation conditions on the hydrated phases, percentages of 10 and 20% cement were replaced in this study, which gave similar results. For example, the mineralogical behavior is described here over the reaction time in prismatic specimens (1x1x6 cm) of paste cement prepared with the addition of 10% paper sludge calcined at 700°C/2h.

XRD and SEM/EDX techniques were used to perform the kinetic study of the reaction, so as to semi-quantify the formation of hydrated phases and the development of their morphologies with the reaction time. The XRD results are provided in Table 2, where the appearance of allite, portlandite, calcite, calcium aluminate hydrates (C₄AH₁₃), and LDH compounds (or compounds of double oxides, at times referred to as hydrotalcite-type compounds) were detected; the last three materials being the most stable over longer periods.

Cement with 10% activated sludge	1 day	7 days	28 days	180 days	360 days
Allite (%)	21	10	9	4	1
Portlandite (%)	38	37	41	32	27
C ₄ AH ₁₃ (%)	6	13	5	7	8
LDH compounds (%)	2	1	19	15	9
Calcite (%)	33	40	27	41	55

Table 2. Semiquantitative mineralogical composition by XRD of cement pastes with the addition of 10% activated sludge

Morphologically, layers of allite surrounded by CSH gels are much more easily identified by SEM/EDX (Fig. 7a), although they go undetected by XRD, given their amorphous nature. The CSH aggregates are arranged in bundles of short fibers, together with the LDH

compounds (Fig. 7b) and the same situation reoccurs throughout the test period. Chemical composition by EDX analysis after curing for one year is shown in Table 3.

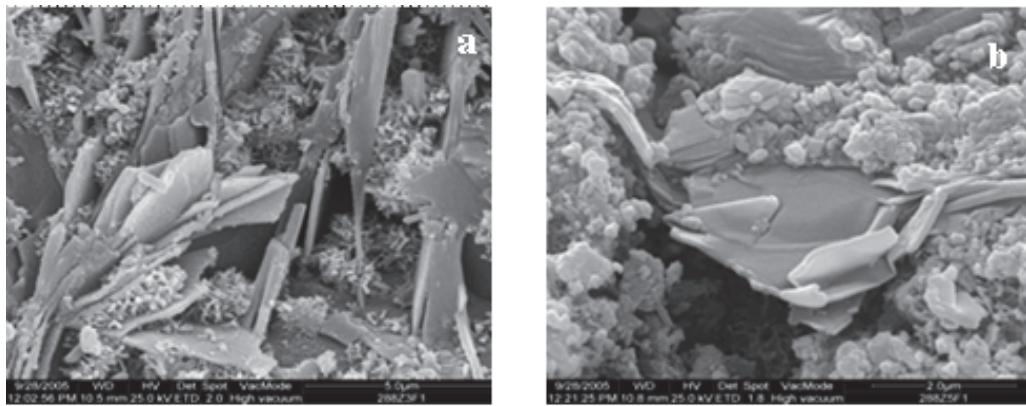


Fig. 7. a) Aggregates of gels and allite layers; b) CSH gels and LDH compounds

Oxides (%)	C-S-H Gel	Allite	Portlandite	LDH Compounds
Al ₂ O ₃	6.27±0.38	2.87±0.36	-	7.70±0.58
SiO ₂	29.45±1.52	29.87±1.46	-	22.66±1.04
CaO	64.28±0.95	67.26±0.74	100	69.64±1.36
CaO/SiO ₂	2.18	2.25	-	3.07
CaO/Al ₂ O ₃	10.25	23.44	-	9.04
SiO ₂ /Al ₂ O ₃	4.70	10.41	-	2.94

Table 3. EDX chemical analysis in the cement with the addition of 10% calcined sludge.

3.1.2 Reaction kinetics in ternary cements prepared with 21% pozzolan mixture

In the case of paper sludge, the pioneering studies (Pera et al., 1998 and 2003) established that the formation of their hydrated phases depended on the relative quantities of metakaolinite and calcium carbonate present in the calcined sludge. Any variant that is introduced into the system will have a direct influence on the kinetic reaction. This is the case of the pozzolan mixtures where the influence of the calcined sludge in the reaction will be conditional upon the competitiveness of the other reaction with the surrounding lime. The absence of scientific works in this area means that these aspects are not extensively applied to the technical properties of cement matrices, principally with regard to their durability.

The study of these scientific aspects is based on ternary cements, prepared with the substitution of different percentages of Portland cement (6%, 21%, 35% and 50%), which gave similar results. The description therefore centered on the samples in which 21% of the Portland cement was replaced by a mixture of pozzolans, activated sludge and fly ash at a ratio of 1:1 by weight. The result of this system was the same for the OPC/activated sludge system, except for the presence of mullite from the fly ash and type II CSH gels, according to the Taylor classification (Taylor, 1997), with Ca/Si ratios of between 1.5 and 2.5 (Fig. 8).

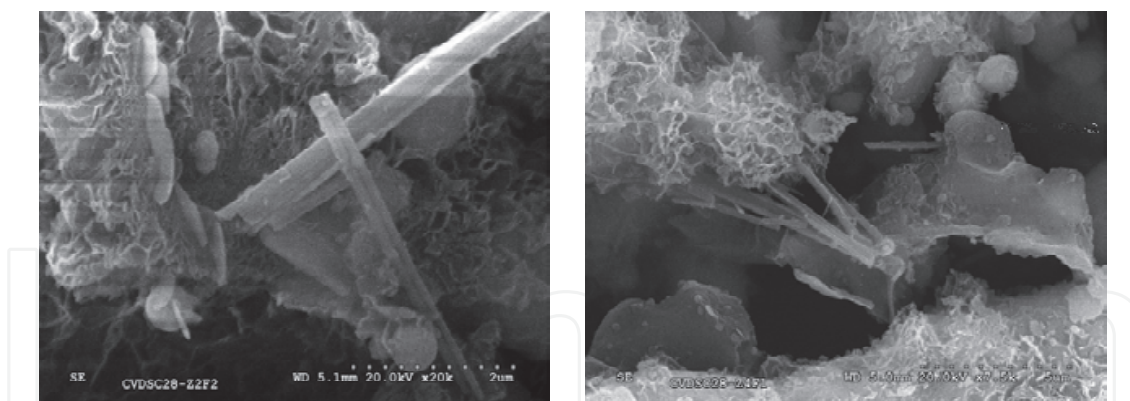


Fig. 8. Left) Formation of gels and layers on amorphous forms. Right) Bundles of CSH gel (II) fibers.

3.2 Technical aspects of blended cements

3.2.1 Properties of binary cements in fresh and hardened states prepared with thermally activated paper sludges

The fresh state of any base cement material may be defined as the period between the initial cement hydration process and its setting. During this period the mixtures show a plastic behavior. A study of a base cement mixture during its plastic state and its properties are of special interest, in order to ensure appropriate preparation and transport and the on-site laying of mortars and concretes. Once the cement has set, the material shows a certain capacity to withstand mechanical stress.

The binary mixtures were studied on the basis of the reference cement pastes and mortars prepared with proportions (0%, 10% and 20% of the Portland cement (CEM I 52,5N) replaced by paper sludge activated at 700°C for 2 hours. The mortars were prepared at a water/binder ratio of 0.5 and at a binder/sand ratio equal to 1/3. Table 4 presents the main characteristics of the blended cements in their fresh state.

Percentage in weight of CEM I 52.5N Portland cement substituted by calcined paper sludge	Ratio of water consistency/ binder	Initial setting time (minutes)	Final setting time (minutes)	Expansion by Le Chatelier needles (mm)
100/0	0.29	145	255	< 0.5
90/10	0.32	120	170	< 0.5
80/20	0.37	60	130	< 0.5

Table 4. Fresh state properties of binary blended cements prepared with paper sludge calcined at 700°C

The incorporation of thermally activated paper sludge under optimal conditions produces a parabolic increase in water demand for normal consistency. The greater specific surface of the thermally activated paper sludges, together with the distribution of finer sized particles, complicates the fluidity of the paste. Greater quantities of water are required with these additions to wet the cement surface.

These paper wastes accelerate setting times, especially when they replace percentages of over 10% of Portland cement (Vegas et al., 2006; Frías et al., 2008e). This phenomenon may

be attributed to the joint presence of metakaolinite and calcium carbonate. Ambroise and colleagues (Ambroise et al., 1994) demonstrated that MK produces an accelerator effect on the hydration of C_3S when the ratio $C_3S:MK$ is below 1.40; or in other words, when up to 30% of clinker is replaced by MK.

The expansion results reveal that the inclusion of activated paper sludge does not influence the variation in the volume of cement pastes. In fact, the values of the test are well below the limit of 10 mm established in the UNE-EN 197-1 for common cements.

Fig. 9 illustrates the evolution of relative compressive strength determined for standardized mortars with partial additions of 0%, 10% and 20% of thermally activated paper sludge. Up until 14 days of curing, an increase is observed in the relative compressive strength, as the incorporation of calcined paper sludge is increased. The acceleration of cement hydration and the pozzolanic reaction constitute the principal effects that explain the evolution of these strengths. The relative maximum is achieved after 7 days of curing. Likewise, replacement of 20% of the cement by calcined sludge provides greater relative compressive strength during the first fortnight of curing. This discussion coincides with the findings of other authors (Wild et al., 1996) when studying this mechanical property in cement mortars or concretes prepared with pure metakaoline. The lower the content of metakaolinite in the added sludge (10%), the further the values of relative compressive strength will fall for curing periods of over 14 days. The pioneering studies of Pera (Pera & Ambroise, 2003) demonstrated that the most influential parameter in pozzolanic activity at 28 days is the quantity of metakaolinite present in the sludges, regardless of other parameters, such as specific surface area, numbers of particles under 10 micrometers or the average diameter of the distribution of particle sizes.

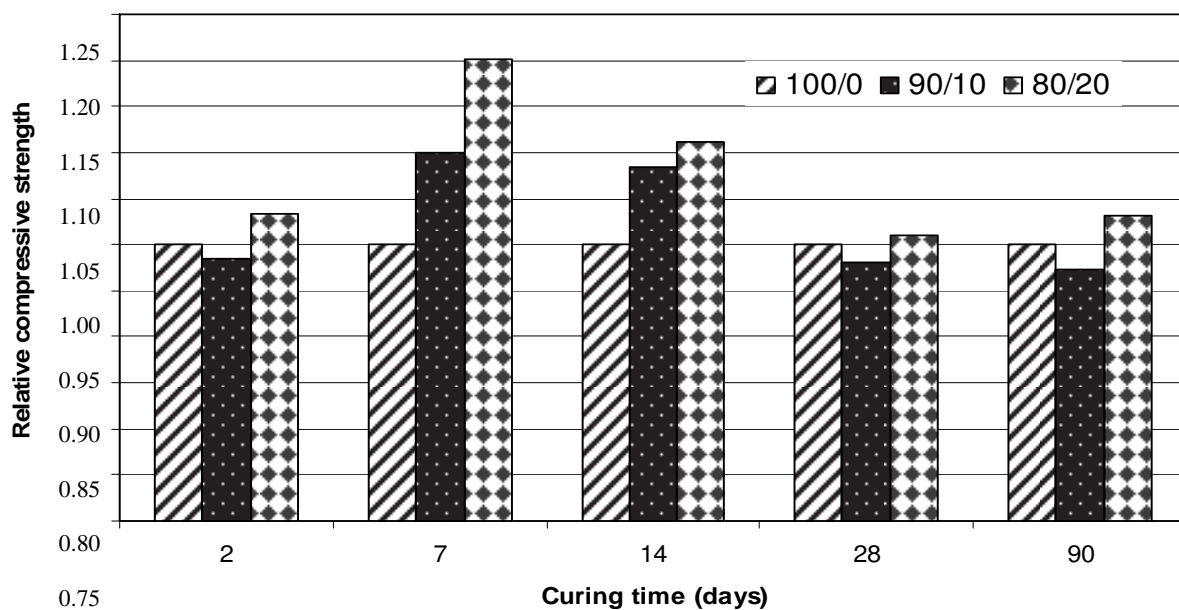


Fig. 9. Relative compressive strength of blended cements with paper sludge calcined at 700°C

Table 5 presents other physico-mechanical properties of binary blended cements with paper sludge calcined at 700°C.

Percentage in weight of CEM I 52.5N Portland Cement replaced by calcined paper sludge	Modulus of longitudinal deformation (GPa)	Total retraction at 28 days (%)	Creep deformation after one year of constant load (%)
100/0	34.8	0.04	0.114
90/10	33.0	0.09	0.120
80/20	34.9	0.12	0.093

Table 5. Modulus of longitudinal deformation, retraction and creep of binary cement mixtures prepared with paper sludge calcined at 700°C

In general terms, it may be concluded that the inclusion of paper sludge calcined at 700°C, up to a percentage of 20%, hardly modifies the value of the elastic modulus at 28 days of curing. There are few bibliographic references that cover the influence of pozzolanic additions on this mechanical parameter. Qian (Qian & Li., 2001) establishes that the partial replacement of cement by metakaolin, in percentages of up to 15%, produces an increase in the concrete’s elastic modulus. These mineral additions show a certain refinement in the porous network of the base cement material; above all, for amounts replaced of 20%. This greater densification means that the fines contribute to a greater extent to the modulus of deformation.

Drying shrinkage increases with the percentage inclusion of paper sludge calcined at 700°C. After 28 days of drying, cement shrinkage with 20% thermally activated paper sludge triples that shown in the reference cement sample. Greater contraction shown by those mortars that incorporate thermally activated paper sludge may be explained on the basis of phenomenon such as:

- Nucleation of hydration products on the particles of this mineral additions, accelerating the hydration of cement, and therefore, increasing the drying of the product.
- Pozzolanic reaction between the metakaolinite and the calcium hydroxide, either from the calcined sludge, or from hydration of the cement clinker. This reaction requires greater water consumption, accelerating drying of the mixture.
- Increase in capillary pressure, as a consequence of a greater refinement of the distribution of pore size. The greatest relative refinement is observed at 14 days of curing.

The inclusion of 20% thermally activated paper sludge reduces creep deformation by approximately 20% of the deformation observed in the reference mortar sample, after one year subject to a pressure state of 40% of the respective compressive strengths. In a similar way to the explanations of other mechanical characteristics, this reduction may be attributed to a denser pore structure, a stronger cement matrix, and greater adherence between the cement paste and the fines (Brooks & Megat, 2001). As a more refined porous network is created, the movement of free water is prevented, which is responsible for the initial creep. Likewise, the pozzolanic activity contributes to the consumption of water, and therefore, to reductions in early creep.

3.2.2 Properties of ternary blended cements prepared with thermally activated paper sludge and fly ash

The characteristics of the ternary mixtures were determined in standardized pastes and mortars prepared with Portland cement (CEM I 52.5N), thermally activated paper sludge calcined at 700°C and fly ash. Table 6 presents the percentage mixture of each agglomerate.

Percentages in weight OPC replaced by calcined paper sludge	CEM I 52.5N (% in weight)	Paper sludge calcined at 700°C (% in weight)	Fly ash (% in weight)
100/0	100	0	0
94/6	94	3	3
79/21	79	10.5	10.5
65/35	65	17.5	17.5
50/50	50	25	25

Table 6. Proportions of ternary cement mixtures with activated paper sludge

Table 7 presents the principal characteristics of the ternary cement mixtures under study in their fresh state.

Percentage in weight of OPC replaced by calcined paper sludge and fly ash	Ratio water consistency /binder	Initial setting time (minutes)	Final setting time (minutes)	Expansion Le Chatelier needles (mm)
100/0	0.28	155	270	0.7
94/6	0.29	140	225	0.3
79/21	0.31	105	165	0.5
65/35	0.34	90	165	0.4
50/50	0.41	35	70	0.2

Table 7. Fresh state properties of ternary cement mixtures prepared with paper sludge calcined at 700°C and fly ash

In a similar way to the description of the study of binary mixtures, the thermally activated paper sludge calcined at 700°C appears to control water demand for water consistency, although this result is less apparent in binary mixtures due to the presence of fly ash. This latter mineral addition requires less water content as a consequence of its spherical morphology, thereby minimizing the surface/volume ratio of the particle (Li & Wu, 2005). Likewise, the joint presence of paper sludge calcined at 700°C and fly ash accelerates the setting times, though there is no evidence of a significant effect on the expansion of cement pastes.

Fig. 10 illustrates the evolution of relative compressive strength determined from standardized cement mortars with partial additions of 0%, 6%, 21%, 35% and 50% of the mineral additions under study. The ternary cements 79/21, 65/35 and 50/50, with a thermally activated paper sludge content of over 10% in weight, display lower mechanical strength than the reference cement sample, although the decrease in their strength is lower than the total percentage of cement that is replaced. At 90 days, a recovery of

mechanical resistance is observed in the ternary cements as a consequence of the activity developed by the fly ash.

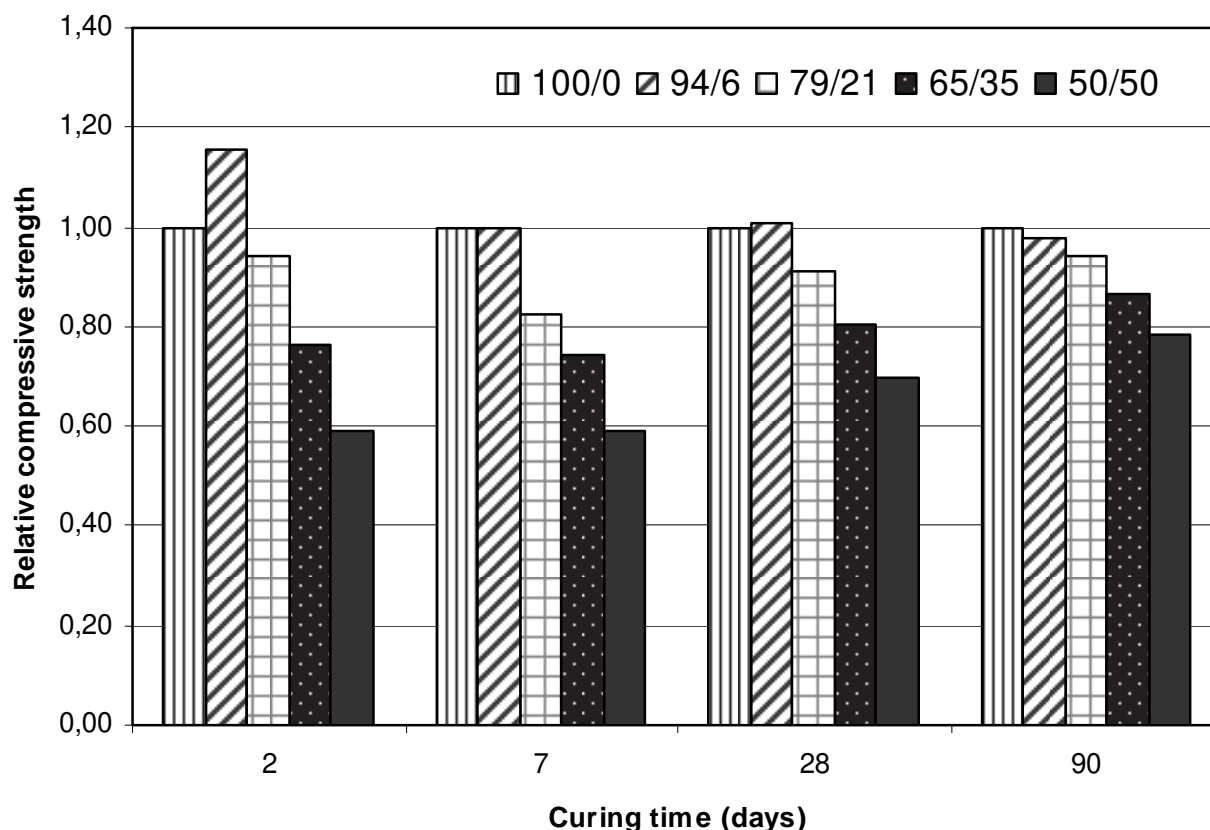


Fig. 10. Relative compressive strength in relation to ternary cement mixtures with paper sludge calcined at 700°C and fly ash

3.2.3 Durability aspects

Durability is understood as a capacity that maintains a structure or element safely in service for at least a specific period of time, which is referred to as its useful life, in the environment where it will be sited, even when the surrounding conditions (physical, chemical and biological) are unfavorable. In short, the condition demanded from the construction materials and components is that they should perform the function for which they were intended, throughout a certain period of time.

This section discusses the behavior of binary mixtures prepared with thermally activated paper sludge when exposed to weathering action. The durability of the ternary mixtures is at present under study, for which reason it can not be included in this chapter. Among the various degradation mechanisms, two types of aggressive attack are covered: one of a physical nature where extreme temperatures and water intervene, the second of a chemical type in the presence of sulfates.

3.2.3.1 Behavior in the face of freezing/thawing cycles

Binary cement mortars that include 10% and 20% thermally activated paper sludge present, respectively, two and three times more strength faced with freezing/thawing

actions than the standard reference mortar (Fig. 11). As the exposure cycles progress, the increase in total porosity is less for those cements that incorporate thermally activated paper sludge. The higher the percentage substitution of cement by calcined paper sludge, the denser the mortar microstructure throughout a higher number of freezing/thawing cycles. Moreover, the greater the replacement percentage of thermally activated paper sludge, the slower the loss of compressive strength in the mortars exposed to freezing/thawing cycles (Vegas et al., 2009).

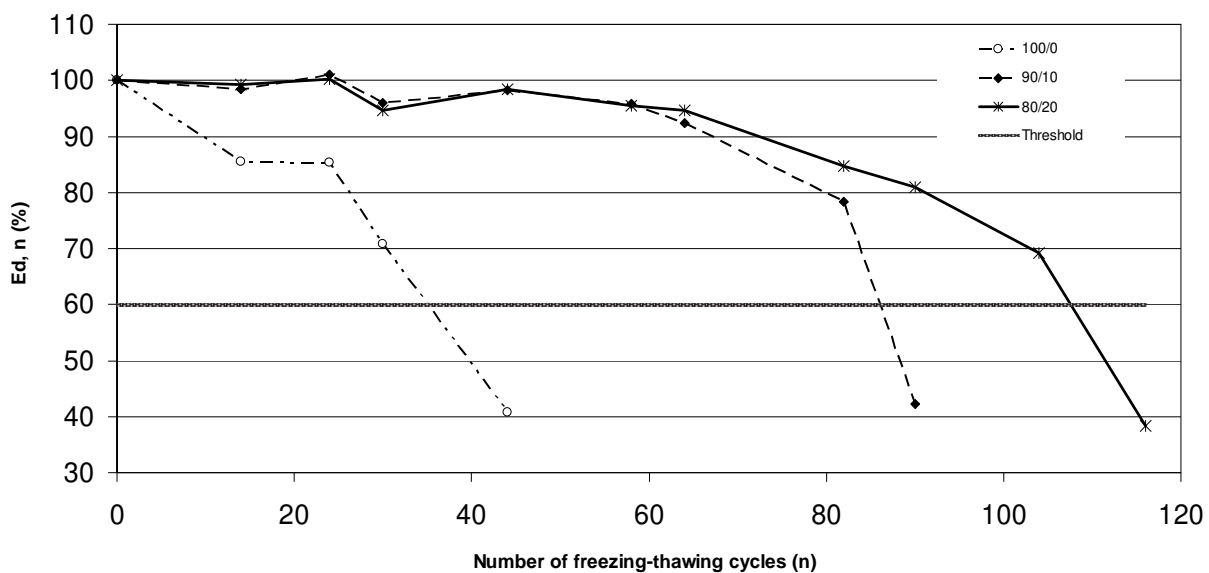


Fig. 11. Evolution of the dynamic modulus of binary cement mixtures with paper sludge activated at 700°C subjected to freezing/thawing cycles

3.2.3.2 Resistance to sulfates

It is well known that sulfates constitute one of the most aggressive agents against cement based materials, and cause different deterioration mechanisms as a consequence of the direct reaction between sulfate ions and the alumina phases in the cement, giving rise to ettringite, a highly expansive compound. The cements prepared with pozzolans of a siliceous-aluminous nature (fly ash and metakaolinite) can be more susceptible to sulfate attacks, owing to the incorporation of the reactive alumina of the pozzolan (Taylor, 1997; Siddique, 2008). The bibliographic data found on the behavior of normal Portland cements prepared with calcined paper sludge highlights the lower strength in the face of sulfate attacks (external and internal source) with respect to the reference cement sample. Thus, in accordance with the research into cement/calcined sludge/gypsum mortars by Vegas (Vegas, 2009) that is in agreement with the American standard (ASTM C 452-95), the following considerations are proposed:

- The reference cement (CEM I 52.5N) may be categorized by a high resistance to sulfates, given that $\Delta L_{28 \text{ days}} \leq 0.054\%$ and $\Delta L_{14 \text{ days}} \leq 0.040\%$.
- Binary mixtures with percentages of thermally activated paper sludge above 10% may be classified as having low resistance to sulfates presenting a $\Delta L_{28 \text{ days}} \geq 0.073\%$.
- Observing the increase in length at 7 days, and in accordance with the physical requirements of the ASTM C 845-04 standard, binary cements with 10% and 20% in

volume of activated paper sludge may be classified as hydraulic cements, given that the values $\Delta L_{7\text{days}}$ are greater than 0.04% and less than 0.10%.

5. Conclusions

The paper industry that uses 100% recycled paper as a primary material generates waste paper sludge which, by its nature, constitutes an inestimable source of kaolin, with the subsequent environmental benefits.

Controlled calcination of waste (500-800°C) supplies an alternative approach to obtain recycled metakaolin, a highly pozzolanic material for the manufacture of commercial cements.

The products obtained in this way present a high pozzolanic behavior, comparable to a natural metakaolin, which is very close to silica fume; temperatures of between 650-700°C and 2 hours of retention time in the furnace are established as the most efficient laboratory conditions to obtain these pozzolans. It is likewise worth highlighting their high pozzolanic compatibility with fly ash.

The cement pastes prepared with 10% sludge calcined at 700°C/2h generate LDH compounds and CSH gels as stable products. The incorporation of a second pozzolan (fly ash) into the blended cement system does not modify the reaction kinetics, for which reason it is worth highlighting the compatibility between both pozzolans.

In the manufacture of binary cements, and in a similar way to the regulations for silica fume, it is recommended that the percentage should be limited to around 10% clinker for paper sludge calcined at 700°C. A compromise has to be reached between the positive effect on the mechanical properties and the determining factors associated with the reduction in setting times, loss of workability and excessive total drying shrinkage.

In the manufacture of ternary cements that contain sludge calcined at 700°C and fly ash, the percentage of clinker replaced by the addition of these minerals should not exceed 21%, in order to guarantee the maximum pozzolanic effect (synergy between the two industrial by-products), while ensuring that the workability of the mixture is not adversely affected.

The results of this research have clearly shown the scientific and technical viability of including thermally activated waste paper sludges as active admixtures in the manufacture of binary and ternary cements.

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