ENGINEERING PROPERTIES OF CEMENT MORTARS CONTAINING THERMALLY ACTIVATED PAPER SLUDGE

*I. Vegas[1], J. Urreta[1], M. Frías[2], O. Rodríguez[2], S. Ferreiro[2], B. Nebreda[2], R. García[3], R. Vigil[3]

[1] LABEIN-Tecnalia, Derio, Spain
[2]Eduardo Torroja Institute (CSIC), Madrid, Spain.
[3]Universidad Autónoma de Madrid, Spain

ABSTRACT:

In recent times, a rapid development in the production of less energy intensive cements and concretes with high performance (resistance and durability) has occurred. This has been accomplished by the use of industrial wastes or by-products (fly ash, slag, silica fume, rice husk) with considerable pozzolanic activity. The use of those secondary materials results in improvements in durability and strength enhancement. Recent studies are focusing on thermally activated clays as potential sources for pozzolanic materials.

This research work presents and discusses the pozzolanic potential of thermally-treated paper sludge on technical behaviour of new cementing matrixes, mainly on the engineering properties. Metakaolinite and calcite in activated paper sludge (APC) have influence on physical-mechanical properties of blended cements containing this mineral admixture. This contribution discusses the main effects of thermally activated paper sludge on cement based matrixes. This alternative admixture leads to:

- Acceleration in setting times of cements
- Demand of more water
- Enhancement in compressive strengths with replacement greater than 10%
- Increase in drying shrinkage of cement based materials

* Corresponding author: Iñigo VEGAS
Email: ijvegas@labein.es

1 INTRODUCTION

In Spain, the paper industry recycles large amounts of waste paper in the new paper production process. The rate of use of recovered waste paper for making new paper is estimated over 76% in Spain, well over the European average established in 50% (CEPI, 2003). During the paper recycling process, ink is removed from old paper in a process called de-inking. As consequence of the recycled paper de-inking process, over 219.047 tons of paper sludge are yearly generated (ASPAPEL, 2007). In this context, Spanish paper industry is working on reducing their wastes, as well as on finding alternative ways to use them in other applications. Concerning the paper de-inking sludge, different possibilities of valorisation are being studied and developed by the Spanish paper mills. During the boom of the building sector, a great deal of this waste has been managed in the ceramic industry. Nevertheless, at present, the paper sector is looking for other ways of managing the paper de-inking sludge. In this sense, some Spanish paper manufacturers are analysing the Dutch approach followed by the CDEM process (Pèra and al, 2001b). In 2001, a joint venture by 4 paper producers, called CDEM, started the construction of an industrial unit in Arnhem, transforming 200.000 tons per year of paper sludge waste into 50.000 tons of a mineral mix called "Topcrete" with high pozzolanic properties, and producing "green" electricity in the process.

On the other hand, the cement industry, in line with new sustainable development policies, has been using in last decades, different industrial by-products (fly ash, silica fume and blast furnace slag) as active additions in the manufacturing of blended cements. This practice is mainly due to the need to reconcile inherent environmental aspects in clinker production (reduction of impacts associated with CO_2 emissions and exploitation of natural resources) with purely financial aspects and the market (Horton, 2001). Furthermore, the use of additions provides other benefits of scientific, technical and economic nature such as the improvement in the mechanical performance and durability of cement, as well as the reduction of energy consumptions associated with the clinkerization process (Frías et al., 2005; Frías and Sánchez de Rojas, 2005; and Pèra et al., 2003).

In this context, research works are now being aimed at obtaining active additions from industrial by-products (Lorenzo et al., 2003 and Cheerarot and Jatirapitakkul, 2004) other than those traditionally used in the cement industry. In this sense, one of the most recent topics deals with the study of active additions from thermal activation of de-inking paper sludge. Pèra et al. (Pèra et al., 2001a; Pèra and Amrouz, 1998 and Pèra and Ambroise, 1998) are responsible for the pioneering works. This research team found that de-inking paper sludge calcined in the range between 700ºC and 750 ºC produces a highly reactive metakaolin (MK).

At present, Spanish researchers (Frías et al., 2004; Rodríguez et al., 2005; Vegas et al., 2006 and Vigil et al., 2007; and Frías et al., 2008), on the basis of the aforementioned scientific knowledge, are going deeper into the scientific and engineering aspects concerning performance of blended cements containing thermally activated paper sludge.

This work aims to present and discuss engineering properties of blended cements containing thermally activated paper de-inking sludge.

2 MATERIALS AND EXPERIMENTAL PROCEDURE

2.1 Materials

The waste raw material used in the present research was paper de-inking sludge from the paper mill "Holmen Paper Madrid Peninsular, S.L". This company exclusively uses 100% recycled paper as raw material in the production of new paper. The chemical characterisation was determined with X-ray fluorescence (XRF), using a Phillips PW 2404 sequential XRF spectrometer. Table 1 shows the chemical composition of the raw paper sludge. Characterisation reveals high lime, silica and alumina contents, whose oxide total content exceeds 47% by weight. The high loss on ignition due to the presence of calcite and organic matter is also worth mentioning.

Table 1: Characteristics of the initial sludge

CHEMICAL COMPOSITION (% in mass)	
CaO	19.82
SiO_2	18.01
Al_2O_3	10.14
MgO	2.58
Fe_2O_3	0.55
SO_3	0.33
Na_2O	0.25
TiO_2	0.26
K_2O	0.21
P_2O_5	0.10
Loss on ignition	47.62

The organic matter value was calculated by calcination of the raw paper sludge at the temperature of 500ºC giving a value of 32.10%.

The mineralogical composition of the sludge was studied with X-ray diffraction techniques (XRD) by using the unoriented powder method, while the oriented aggregate method was used to identify the constituent phyllosilicates. The components were quantified with the reflection powers method (Schultz, 1964; Barahona, 1964; and Brindley, 1980). The areas for the phyllosilicates (4.45 -4.50 ?), quartz (4.26 ?) and calcite (3.04 ?) were measured on the unoriented powder traces, while the areas for the other phyllosilicates: talc (9.40 ?), kaolinite (7.15 ?), and mica (9.95 – 10.01 ?) (Brindley, 1980) were taken from the oriented aggregate patterns. Conventional mathematical software was used to fit the peaks to a Gaussian curve and subtract the baseline, thereby determining their areas. Figure 1 and Table 2 show the X Ray Difraction (XRD) pattern of the dried de-inking paper sludge.

Figure 1: XRD pattern of the raw paper sludge

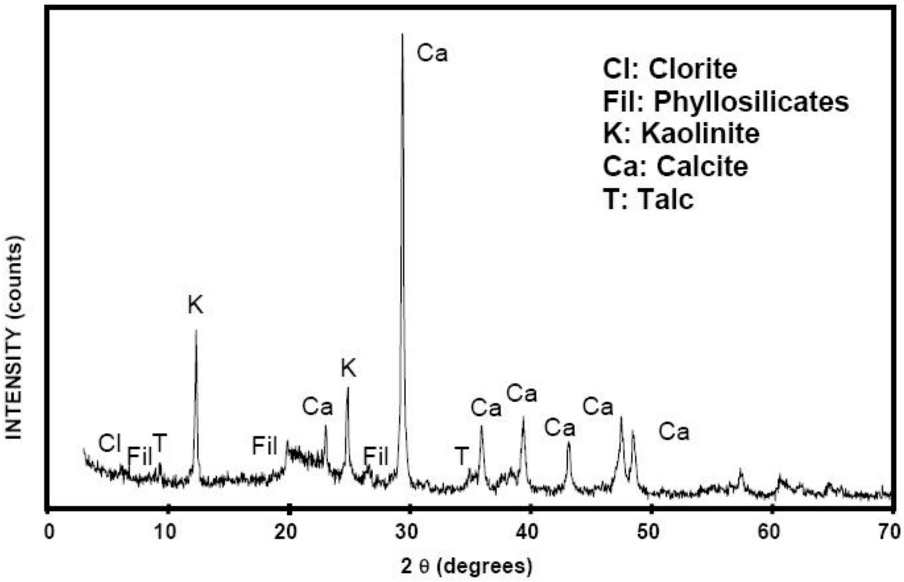


Table 2: Mineralogical composition of the dried de-inking paper sludge

MINERAL	CONTENT (% by weight)
Organic matter	32.10
Calcite	35.30
Kaolinite	20.83
Talc	6.85
Quartz	1.71
Minority components (chlorite, micas,…)	1.71

On the other hand, ordinary Portland cement (OPC) CEM I 52,5 N was used in this research. The chemical composition and physical properties of the OPC are given in Table 3.

2.2 Thermal activation of paper de-inking sludge

The dry paper sludge was calcined in a laboratory electric furnace. The heating rate was 20 ºC/min. Based on previous studies by Frías et al (2008), and taking into account economic and energetic aspects, activation conditions, at lab scale, were established in the range from 650ºC to 700ºC. After the thermal treatment, the calcined product was ground and sieved to obtain particles below 45 µm.

Table 3: Chemical and mineralogical composition of the CEM I 52,5 N.

CHEMICAL COMPOSITION (% in mass)	
Total CaO	62.44
SiO_2	19.70
Al_2O_3	5.62
Fe_2O_3	3.08
MgO	1.21
SO_3	3.29
K_2O	0.89
Na_2O	0.27
TiO_2	0.24
P_2O_5	0.11
Loss on ignition	2.72
MINERALOGICAL COMPOSITION (% in mass)	
C_3S	67.4
C_2S	8.6
C_3A	9.28
C_4AF	9.97
PHYSICAL PROPERTIES	
Specific surface area (g/cm^2)	4010
Density (g/cm^3)	2.93
Specific gravity (kg/dm^3)	3.1

2.3 Chemical and mineralogical characterisation of the thermally activated material.

Chemical characterization of the thermally activated paper sludge is shown in Table 4.

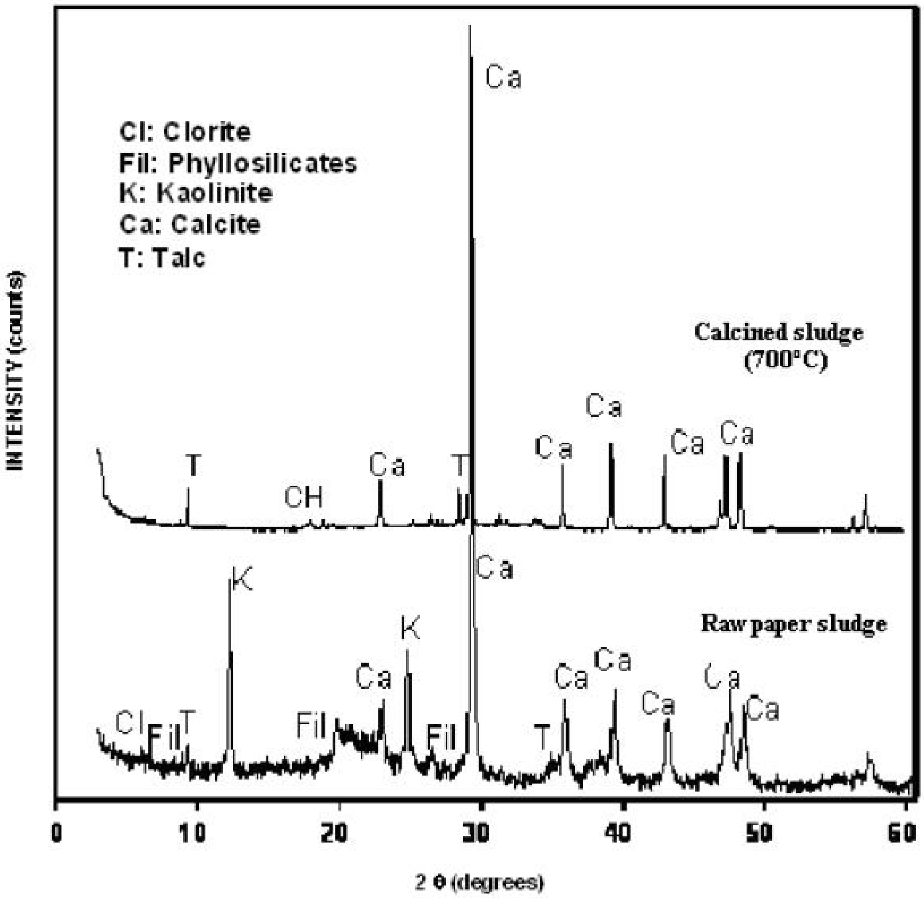
Table 4: Chemical composition of the calcined paper sludge

CHEMICAL COMPOSITION (% in mass)	
CaO	31.40
SiO_2	30.20
Al_2O_3	18.00
Fe_2O_3	0.70
SO_3	0.27
MgO	3.70
K_2O	0.32
Na_2O	0.21
TiO_2	0.35
P_2O_5	0.19
Loss on ignition	14.53

As with the raw paper sludge, calcined paper sludge is mainly composed of silica and calcium oxides in very similar proportions (30-35%), followed by alumina (ranging from 15% to 20%) and magnesium oxide (in proportions below 5%). The remaining oxides do not exceed 1%.

Figure 2 presents the XRD patterns of the calcined paper sludge. It can be observed that the kaolinite is totally transformed into MK and the decomposition process of talc, calcite and chlorite begins (Vigil et al., 2007).

Figure 2: XRD pattern of the calcined paper sludge



The specific gravity of the calcined paper sludge, calculated with a Le Chatelier volumeter according to the standard UNE 80103-86, was 2.67 gr/ cm^3 . The specific surface area, obtained from the values of particle size distribution and density, was 9.6 cm^2/g**.** The specific gravity of calcined paper sludge is lower than that for the cement. Specific surface area is higher than that of the cement.

2.4 Engineering properties of cement mortars containing the thermally activated paper sludge: experimental procedures.

Cement pastes and standardised mortars blended with 0%, 10%, 20% calcined paper sludge were prepared for assessing their engineering properties.

The setting times of the blended cements were determined in accordance to UNE EN 193-3.

Mechanical properties were assessed by testing cement mortars. The mix design for all mortars is given in Table 5. Binder:sand ratio was 1:3 for all mortars and water:binder ratio was 1:2 for all mortars. Standardised siliceous sand was used. 40x40x40 mm prisms were cast for testing the compression strength in accordance with UNE-EN 196-1. Specimens were cured in water till the testing age. The evolution of compressive strength versus time allows us to verify the pozzolanic activity of calcined paper sludge. The workability of fresh cement mortars was determined by means of flow test, measuring the diameter of the cement mortar with a yardstick.

Table 5. Mix design for cement mortar specimens blended with calcined de-inking paper sludge

Nomenclature	Water (kg)	CEM I 52,5 N (kg)	Standarized sand (kg)	Calcined sludge (kg)
BC-0%	0.225	0.450	1.350	--
BC-10%	0.225	0.405	1.350	0.045
BC-20%	0.225	0.360	1.350	0.090

The drying shrinkage test was accomplished in accordance with the standard ASTM C 596 using 25 by 25 by 285-mm bars. Four specimens were casted for each batch of mortar.

3 RESULTS AND DISCUSSION

3.1 Setting time and slump

Setting times are shown in the Tables6. Calcined paper sludge provides an accelerating effect on setting times of blended cements. This phenomenon can be attributed to the presence of both MK and calcium carbonate in calcined paper sludge. Previous studies on MK blended cements (Ambroise et al, 1994) showed that MK has accelerating effect on the hydration of C_3S up to replacement levels of 30%. Furthermore, the presence of calcium carbonate accelerates setting of cements as reported in several works (Vuk et al, 2001; Heikal et al, 2000; and Péra and Amrouz, 1998). This mineral, acting as filler, provides larger nucleation points facilitating hydration of cement. Likewise, the presence of calcium carbonate leads to reactions with aluminate to form hydrated carboaluminates.

Table 6. Setting times for the different blended cements

Nomenclature	Water content (cm^3)	Initial set (min)	Final set (min)
BC-0%	147	145	255
BC-10%	161	120	170
BC-20%	184	60	130

Table 7 presents the relationship between the calcined paper sludge content and the slump value in fresh cement mortars. The slump progressively decreases with increasing calcined paper sludge content. This mineral admixture is finer than ordinary Portland cement and it demands more water. When increasing the content of calcined paper sludge, higher interparticle attractions are produced. This is consistent with the study on rheology accomplished by Banfill and Frías (Banfill et al, 2007).

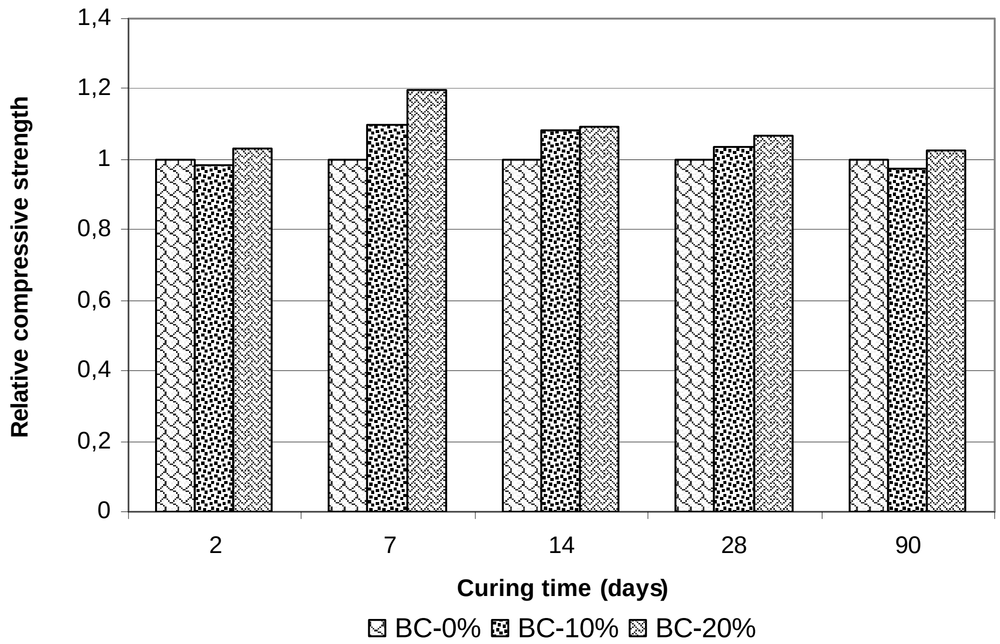
Table 7. Slump of the different blended cements

Nomenclature	Slump (mm)	% Reduction
BC-0%	188.75	---
BC-10%	141.5	25.03
BC-20%	117.75	37.62

3.2 Compressive strength

Results for compressive strengths are shown in Figure 3. At early ages (2 days), BC-10% and BC 20% exhibit compressive strengths similar to the control cement (BC-0%). In this interval, the replacement of cement prevails over the pozzolanic effect. This is in line with other contributions (Vegas et al, 2006). After 7 days, BC-10% and BC-20% give higher compressive strengths than the control cement. The presence of MK contributes to the hydration reaction producing additional C-S-H gel, and, consequently, leading to enhancement in strength. Furthermore, this mineral admixture acts as filler reducing the porosity of the bulk cement matrix. It results in a more densified matrix. These results are in agreement with the data obtained from the pozzolan activity test. Pèra and Ambroise (1998) and Péra and Amrouz (1998), using 20% replacement levels replacement percentages, obtained compressive strength values 10% higher than the commercial Portland cement used for comparison.

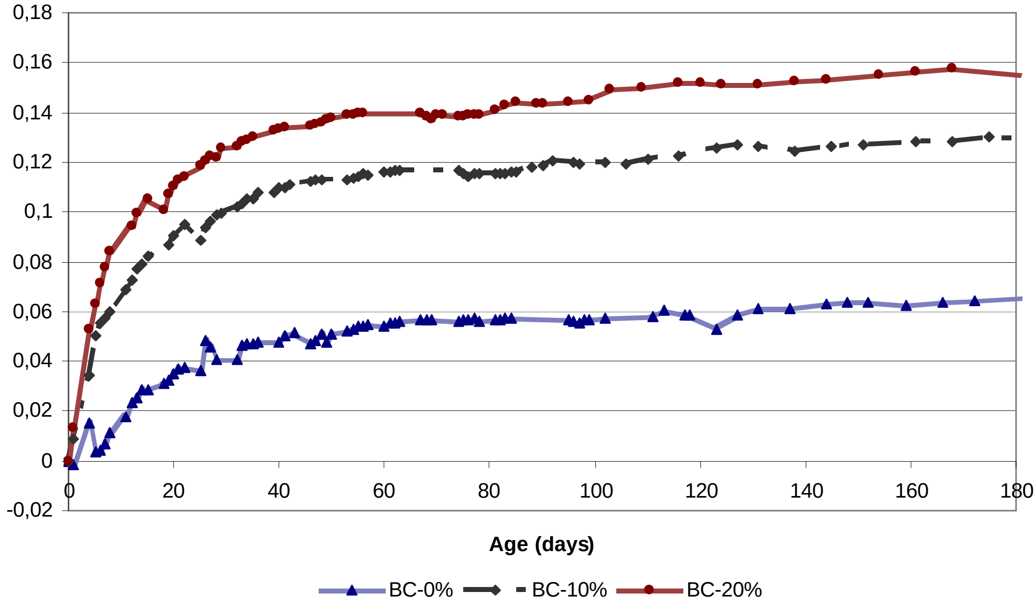
Figure 3: Relative compressive strength evolution for blended cement mortars



3.3 Drying shrinkage

The results of drying shrinkage of the mortar bars are shown in Figure 4.

Figure 4: Drying shrinkage of cement mortars containing calcined paper sludge



The incorporation of 10% and 20% thermally activated paper sludge significantly increases the drying shrinkage of mortar: up to 2,5 times more than the shrinkage exhibited by the ordinary portland cement used as control.

The effect of calcined paper sludge on total shrinkage of cement mortars can be the consequence of the following phenomena: (i) heterogeneous nucleation of hydrates on the surface of calcined paper sludge particles (specially, calcite particles), accelerating cement hydration and, consequently, increasing shrinkage, (ii) pozzolanic reaction of MK with CH produced by cement and, (iii) increase of capillary tension, due to the refinement of pore size distribution, leading to an increase in autogenous shrinkage.

4 CONCLUSIONS

The main conclusions of this research work can be drawn as follows:

- Incorporation up to 20% calcined paper sludge into cement paste modifies initial setting time by accelerating the process just to 60 minutes. Workability is reduced when using calcined paper sludge
- The partial replacement of cement by calcined paper sludge enhances compressive strengths slightly after 7 days of curing.

- The incorporation of 10% and 20% thermally activated paper sludge leads to increase in the drying shrinkage of mortar 2 and 2.5 times more that shown by the ordinary portland cement used as control.

5 ACKNOWLEDGMENTS

This research work has been funded through a Research project (CTM2006-12551-C01/02) of the Spanish Ministry of Education and Science. Thanks to Holmen Paper Madrid company and IECA for its contribution to this research.

6 REFERENCES

Ambroise, J. Maximilien, S. and Pera, J. (1994) "Properties of Metakaolin Blended Cements". *Advanced Cement Based Materials*, No. 1, pp. 161-168.

ASPAPEL (2007). "Diagnosis of the generation and management of solid wastes on spanish paper industry". *Aspapel, and Spanish Industry Ministry*. pp. 15.

Barahona, E. (1964) "Arcillas de ladrillería de la provincia de Granada. Evaluación de algunos ensayos en materias primas". *Phd., University of Granada*.

Banfill, P., Frías, M. (2007) "Rheology and conduction calorimetry of cement modified with calcined paper sludge". *Cement and Concrete Research*, No. 37, pp. 184–190

Brindley, G.W. (1980) "Order-Disorder in Clay Minerals Structure. Cristal Structures of Clays Minerals and their X-Ray identification", *Mineralogical Society Monograph* Vol. 5, pp.. 496. - G.W. Bridley and G. Brown (Eds.).

CEPI. (2003). "Confederation of European Paper Industries and the International Confederation of Paper and Board Converters in Europe: Towards a Thematic Strategy on Prevention and Recycling of Waste Paper and board manufacturing and converting industry's position".

Cheerarot, R. and Jatirapitakkul, C. (2004) "A study of disposed fly ash from landfill to replace Portland cement". *Waste Management*, No. 24, pp. 701-709.

Frías, M. and Sánchez de Rojas, M.I. (2005). "Influence of metastable hydrated phases on the pore size distribution and degree of hydration of MK-blended cements cured at 60ºC". *Cement and Concrete Research*. No.35, pp. 1292-1298.

Frías, M., Sánchez de Rojas, M.I., Menéndez, I., Cristina, C., and García de Lomas, M. (2005). "Propiedades de la escoria Si-Mn como material puzolánico en la fabricación de cementos Pórtland". *Matereriales de Construcción*., Vol.55, nº 280, pp. 1-9.

Frías, M., Sánchez de Rojas, M.I., and Rivera, J. (2004) "Influence of calcining conditions on pozzolanic activity and reaction kinetics in paper sludge-calcium hydroxide mixes". *8th CANMET/ACI International Conference on fly ash, silica fume, slag and natural pozzolans in concrete*. pp. 879-892. Ed. V.M. Malhotra.

Frías, M., Rodríguez, O., Vegas, I., García, R. (2008). "Influence of activation temperature on reaction kinetics in recycled clay waste–calcium hydroxide systems". *Journal of American Ceramic Society,* DOI: 10.1111/j.1551-2916.2008.02807.x.

Heikal, M., El-Didamony, H., Morsy, M.S. (2000). "Limestone-filled pozzolanic cement". *Cement and Concrete research,* No. 30, pp. 1827, 1834.

Horton, R. (2001). "Factor Ten Emision Reductions: The Key to Sustainable Development and Economic Prosperity for the Cement and Concrete Industry". *3rd CANMET/ACI International Symposium on Sustainable Development of Cement and Concrete*, Vol.1, pp.1-14. Ed. V.M. Malhotra, ACI SP-202, San Francisco, U.S.A.

Lorenzo, Mª.P., Goñi, S., and Guerrero, A. (2003). "Role of aluminous component of fly ash on the durability of Portland cement-fly ash pastes in marine environment". *Waste Management*, No. 23, pp. 785-792.

Pèra, J. and Ambroise, J. (1998). "Calcined paper sludge: an interesting admixture for the cement industry". *Proceedings of the Sidney Diamond Symposium-Materials Science of Concrete*, pp. 467-479. Ed. M. Cohen et al.

Pèra, J. and Amrouz, A. (1998). "Development of highly reactive metakaolin from paper sludge". *Advanced Cement Based Materials,* No.7, pp. 49-56.

Pèra, J., Ambroise, J., and Chabannet, M. (2001a). "Transformation of wastes into complementary cementing materials". *7th International Conference on fly ash, silica fume, slag and natural pozzolans in concrete*, Vol. II, pp. 459-475. Ed. V.M. Malhotra, ACI SP-26, Chennai, India

Pèra, J., Ambroise, J., Biermann, J., and Voogt, N., (2001b). "Use of Thermally Converted Paper Residue as a Building Material". *Proceedings of the Third Canmet7Aci International symposium of Sustainable Development of Cement and Concrete*, pp. 11-124.

Pèra, J. and Ambroise, J. (2003). "Pozzolanic properties of calcined paper sludge". *Proceedings of the 11th International Congress on the Chemistry of Cement*, pp. 1351-1360.

Rodríguez, O., Frías, M., Sánchez de Rojas, M.I. and Menéndez, I. (2005). "Viabilidad de la incorporación de lodos de papel al cemento como adición puzolánica". *VI Congreso Nacional de Materiales Compuestos,* Vol 1, pp. 917-923. UPV (Ed.), Valencia, España.

Sabir, B.B. (1997) "Mechanical properties and frost resistance of silica fume concrete". *Cement and Concrete Composites,* No. 19, pp. 285-204.

San José, J.T., Vegas, I., Meyer, F. (2006) "Structural analysis of FRP". *Construction and Building Materials,* No. 20, pp. 971, 981.

Schultz, L.G. (1964). "Quantitative interpretation of the mineralogical composition from X-ray and Chemical data for the Pierre Shale, 391C". U. S. Geol. Surv. Prof. Pap.

Vegas, I., Frías, M., Urreta. J., San José J.T. (2006). “Obtaining a pozzolanic addition from the controlled calcination of paper mill sludge. Performance in cement matrices”. *Materiales de construcción*, Vol. 56, No.283, pp. 49-60.

Villar Cociña, E., Frías, M., Valencia, E., and Sánchez de Rojas, M.I. (2005). “Validación de un modelo cinético-difusivo para caracterizar la cinética de reacción puzolánica en sistemas ceniza de paja de caña-arcilla-cal”. *Materiales de. Construcción*, Vol.55, No 278, pp. 29-40.

Vuk, T., Tinta, V., Gabrovsek, R., Kaucic, V. (2001). “The effects of limestone addition, clínker type and fínense on properties of Pórtland cement”. *Cement and concrete Research*, No. 31, pp. 135-139.

ASTM C 596-07, Standard Test Method for Drying Shrinkage of Mortar Containing Hydraulic Cement

UNE-EN 196-1:2005, Methods of testing cements. Part 1: Determination of strength

UNE-EN 196-2:1996, Methods of testing cements. Part 2: Chemical testing of cement

UNE-EN 196-3:2005, Methods of testing cements. Part 3: Determination of setting time and soundness

UNE-EN 197-1:2000 / A1:2005, Cement. Part 1: Composition, specifications and conformity criteria for common cements.

UNE 80103-1986: Métodos de ensayo de cementos. Ensayos físicos. Determinación de la densidad real mediante el volumenómetro de Le Chatelier