

Final Disposal of Ashes from Sunflower Husk in Cementitious Mortars

L. Señas

*Civil Engineer, Professor, Department of Engineering
Universidad Nacional del Sur. Bahía Blanca, Argentina
E-mail: lsenas@uns.edu.ar
Tel: 54-291-4595103 ext. 3225*

C. Priano

*Civil Engineer, Department of Engineering
Universidad Nacional del Sur. Bahía Blanca, Argentina
E-mail: cpriano@uns.edu.ar*

S. Marfil

*Geologist, Professor, Department of Geology, Universidad Nacional del Sur
Researcher at CIC Province of Buenos Aires – INGEOSUR, Bahía Blanca, Argentina
E-mail: smarfil@uns.edu.ar
Tel: 54-291-4595101 ext. 3021; Fax: 54-291-4595148*

P. Maiza

*Geologist, Department of Geology, Universidad Nacional del Sur
CONICET-INGEOSUR. Bahía Blanca, Argentina.
E-mail: pmaiza@uns.edu.ar*

J. Valea

*Civil Engineer, Professor, Department of Engineering
Universidad Nacional del Sur. Bahía Blanca, Argentina
E-mail: jfvalea@uns.edu.ar*

Abstract

This paper presents the study of the behavior of cementitious mortars with incorporated ashes produced during the incineration process of sunflower husk in boiler. For ash characterization, the chemical composition of majority and minority elements was determined by Inductively Coupled Plasma Mass Spectroscopy (ICP), the crystalline structure by X-ray diffraction (XRD), and the optical properties by petrographic microscopy. Two different groups of mortars were elaborated. In one of them fluidity of the mixture was maintained constant throughout the study, and in the other, the w/c ratio. Proportions of incorporated ashes were 5 %, 10 % and 15 % compared with the weight of the cement used. As the rate of incorporated ashes increased, the fluidity of the mixture and the setting time changed compared with those of the control mortar. The flexural strength and the compressive strength were determined at the age of 7 and 28 days. Both parameters decreased compared with those of the control as the percentage of incorporated ashes

increased. A petrographic study of thin sections of the mortars was conducted using a petrographic microscope. No textural or compositional changes were observed at microscopic level in the different mixtures studied.

Keywords: Mortar, ash, sunflower husk

1. Introduction

The reuse of different types of mineral waste from agro-industrial sectors has gained particular interest in recent years due to the characteristics shown by the cementitious matrixes when added to the mixture [Talero et al, 2009]. These additions may be either blast furnace slag or pozzolanic additions. They are called “active” since despite their lack of hydraulic activity or cementitious properties, they have chemical constituents that in the presence of water at room temperature combine with calcium hydroxide generated during portland cement hydration to form hydrated compounds similar to the substances formed during that process [Malhotra and Mehta, 1996].

Several lines of research have been undertaken to identify new natural or artificial mineral additions for portland cements. Rice husk illustrates a good example of natural additions, whose ashes generated as a product during the process of fueling of boiler, or during the drying of grains in the rice industry, may be added to a cementitious matrix. Due to its high silica content, rice husk produces a pozzolanic effect by which the husk can replace part of the cement content, and also provides a series of beneficial effects such as controlling hydration heat, higher capacity, lower permeability, higher compressive strength and higher resistance to chlorides-ion penetration [Zhang et al, 1996].

Fossil fuels (coal, natural gas and petroleum) represent the most important source for energy in the modern world. They account for 75 % to 85 % of the total energy worldwide. Since they are non-renewable energy sources and their reserves are limited, alternative sources such as bio fuels are currently being used. They are of biological origin and obtained from organic residues.

Sunflower seeds are hulled before they enter the industrial process of oil extraction. Thus, the husk becomes an agricultural waste, which needs to be used. In the last decade, the average production of sunflower in Argentina was 4 million tons, and considering that 20 % of the seed constitutes the hull, 800.000 tons of sunflower husk per year are obtained. The specific bulk density accounts for 100 kg/m³, therefore, such amount of seed hull represents 8 million m³/year [Capurro, 2003a].

Using seed hulls as biomass fuel for boilers to produce steam is a possible alternative use; it reduces environmental contamination since during biomass combustion the amount of CO₂ released to the atmosphere is equivalent to the CO₂ absorbed from the atmosphere by the organic material during plant growth, therefore a neutral balance of the emissions to the environment is obtained [Fatih Demirbas et al, 2009]. Steam production of this type of boilers by burning the total amount of the hull extracted duplicates the necessity of the factory. Only if there are two oil extractions of similar capacities, for example sunflower and soy, an adequate thermal balance can be achieved [Capurro, 2003a].

Most of the boilers used present a special design to allow complete combustion. Biofuels can be used as sole fuel or in combination with carbon, gas or fuel-oil. Boilers must have a large special furnace, specially designed to burn cellulose fuel. They must also have a bottom part to allow collection of flying ashes, which need to be taken out from the furnace. Three per cent of the total biomass burnt becomes ash, which needs to be taken out periodically.

Little information is available on the impact produced by ashes, since most of the literature focuses on the performance and durability assessment of materials [Klich et al, 1999; Señas et al, 2004], and provides an alert to possible contamination of upper soil layers and groundwater caused by infiltration [Domínguez and Ullman, 1996].

Part of the ashes can be used as natural fertilizer [Penichet Cortiza et al, 2008; Capurro, 2003b] due to its high nutrient content. However, ash surplus cannot be accumulated in landfill because of its

detrimental effect on the environment and storing the ash surplus would imply a high investment. Ashes can also be used by brick manufacturers, cleaning products, etc. The factories should be located near the place where ashes are originated since their low specific gravity makes freight more expensive. Also, factories producing ashes must have a production control to eliminate any possibility of environmental contamination.

The present paper illustrates an experimental study on the effects of incorporating ashes from sunflower hull incineration, on the behavior of cementitious mortars. The aim of the study is to stabilise the surplus material by including it in a cementitious matrix, assessing the quality of the mortar and determining the application conditions to optimise their final disposal.

2. Materials and Methods

Mortars were elaborated with normal portland cement from a factory located in the province of Buenos Aires (Argentina) according to an argentine standard [IRAM 50000, 2010], demineralised water and normalised sand, graded as shown in Table 1, composed of at least 90% of quartz. Granulometry is illustrated in Table 1.

Table 1: Sand granulometry

sieve N°	10	12	18	35	100	170
% retained	0	5	33	67	88	98
accumulated						

The ash added to cementitious mortars is a light-grey pulvurent material, which is obtained from calcination of the sunflower husk in boilers at 600 °C. Size distribution of the particles ranges from 10 µm to 200 µm.

To characterise the ash, its chemical composition, crystalline structure and optical properties were studied.

Chemical analyses were conducted by Inductively Coupled Plasma Mass Spectroscopy (ICP). Samples were scanned by Rigaku D-Max III C X-ray diffractometer with Cu K α radiation and monochromator, at 35 Kv -15 mA. Petrographic studies were carried out using an Olympus BH-2 petrocalographic microscope.

Six types of mortars were elaborated. Table 2 shows mortar dosages.

Table 2: Dosages of elaborated mortars

	Mortar	Cement (g)	Water (g)	Sand (g)	Ashes (g)
Group I	C	500	250	1500	---
	I-5	500	250	1500	25
	I-10	500	250	1500	50
Group II	II-5	500	298	1500	25
	II-10	500	358	1500	50
	II-15	500	380	1500	75

Mortars from Group I presented three dosages and a constant w/c (relationship ratio between the water weight and the cement weight). Mortar C (control) does not include ashes. To the other two mixtures were added 5 % and 10 % of ashes in relation to the weight of the used cement; they were named I-5 and I-10, respectively.

Mortars from Group II were elaborated maintaining the mixture fluidity constant. In this case, cement content was not modified, but the amount of water of each paste was increased to keep the consistency with respect to the reference mortar. In this second group, three different dosages were

studied, II-5, II-10 and II-15, with 5 %, 10 % and 15 % of incorporated ash according to the weight of the cement used.

The mortars were elaborated using a standardised mechanical mixer and following the methodology described in ASTM C305-65 [1965]. Before molding the test specimens, the consistency of each of the mixtures was determined using a flow table [ASTM C230-65T, 1965].

Prismatic bars (40x40x160 mm) were made to determine the flexural strength and compressive strength [ASTM C348-63T, 1963; ASTM C349-64, 1964]. Six prisms were done from each paste. Three bars were analysed at the age of 7 days and the other three at the age of 28 days.

Once the samples were demolded they were kept at room temperature and submerged in water at 20 °C until testing date. Hardening was performed independently for each test specimen set.

It is important to analyse the characteristics of the cementitious paste and those of the interface zone of the mortars with and without ashes to determine if there are differences between them. To this end, a petrographic study on thin sections of the samples was conducted.

3. Results

3.1. Ash Characterization

3.1.1. Chemical Analysis

The chemical composition of major and trace elements was analysed.

Major elements: Material is mainly composed of K_2O (36.64 %), with subordinated amounts of CaO (13.69 %), MgO (8.84 %) and P_2O_5 (4.49 %) and scarce silica (2.33 %). Total C and total S contents account for 8.11 % and 4.45 %, respectively. Weight loss determined by ignition accounts for 24.56 %. Contents of Al_2O_3 , Fe_2O_3 and Na_2O are less than 1 %.

Trace elements: Table 3 illustrates trace elements expressed in ppm. The content of the remaining elements is not significant.

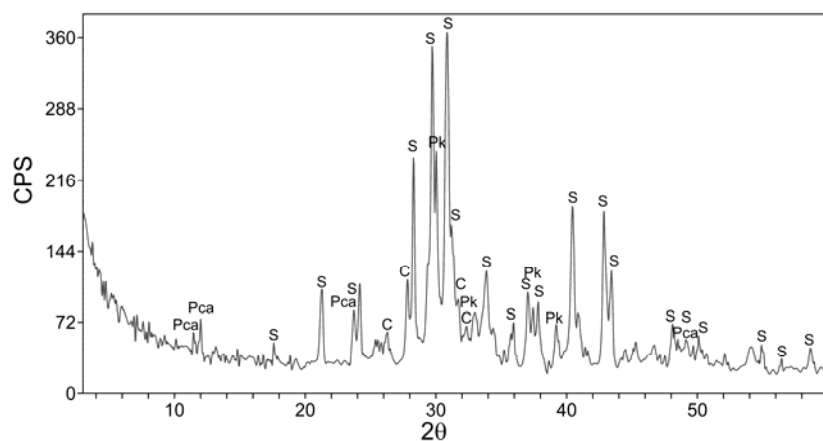
Table 3: Trace elements expressed in ppm

Cu	Zn	Ba	Rb	Sr
290	360	369	155	571

3.1.2. X-Ray Diffraction (XRD)

The ash is mainly composed of potassium sulphate (K_2SO_4) (S), with subordinate amounts of hydrated calcium acid phosphate ($CaHPO_4 \cdot 2H_2O$) (Pca); potassium carbonate and hydrated sodium ($CO_3KNax6H_2O$) (C) and potassium phosphate ($K_5P_3O_{10}$) (PK). Figure 1 show the diagram obtained.

Figure 1: X-ray diffraction of ash



3.1.3. Polarization Microscopy

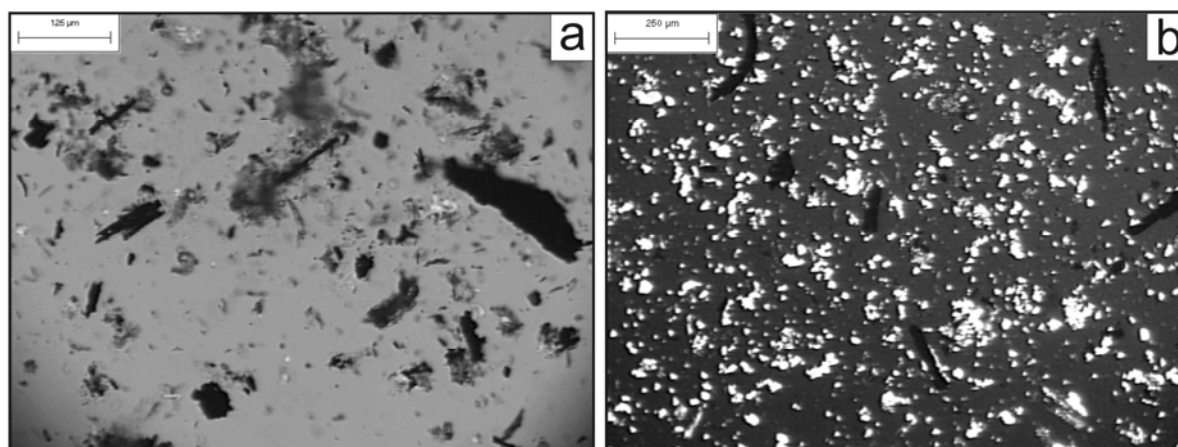
Three clearly distinguishable materials were identified at microscopic level: a) carbonous materials; b) highly birefringent crystalline material; c) low birefringence crystalline material.

Carbonous materials. Viewed by transmitted light, are characterised by being opaque. It is only possible to observe elongated fibrous forms, sometimes porous, of vegetal material rests. This type of material constitutes the largest forms, reaching 0.5 mm, though the average size is 0.1 mm. (Figure 2a). This material was not identified by XRD, since it is amorphous and/or cryptocrystalline.

Highly birefringent crystalline material. The average size of this type of material is 40 μm . These are particles with undefined, granular and irregular form with higher interference color than those from the second order. Due to their optical properties, they are attributed to carbonates and phosphates. They constitute the majority of the birefringent particles observed in Figure 2b (with crossed nicols).

Low birefringence crystalline material. In general they are similar to carbonates and phosphates because of their form. However their birefringence is lower than 0.009 (first order). They are attributed to sulphates. Figure 2b shows scarce material of low birefringence.

Figure 2: Optical microscopy of ashes a: carbonous material (with parallel light). b: crystalline material (with crossed nicols). High birefringence particles correspond to potassium carbonates and phosphates, while very low birefringence particles are attributed to potassium sulphates



3.2. Characterization of Mortars

3.2.1. Fresh State Properties

Table 4 shows the degree of fluidity of each of the mixtures.

Table 4: Degree of fluidity of mixtures

	Group I			Group II		
Mortar	C	I-5	I-10	II-5	II-10	II-15
Fluidity degree	1,84	---	---	1,79	1,86	1,84

The first group shows more rigid mixtures, with constant amount of water as the rate of incorporated ashes increased. The degree of fluidity could never be determined due to the characteristics of the mortar obtained. When a 15 % of ashes was added, compared to the weight of the cement, the obtained material showed null docility, which prevented the bar molding. Therefore, a second group was elaborated in which, the amount of cement and fluidity was kept constant. When the amount of incorporated ashes was increased, the volume of mixture water had to be increased, as well (column 4, Table 2). Table 4 shows that in the second group, fluidity is similar in all pastes.

The presence of ashes in any of the percentages used markedly delayed the start and end of the setting time in comparison with those of the reference mortar. Once the hardening process started, it continued normally. In the control mortar and in samples with ash addition the setting time finished after 3 h 45 min and 8 h 15 min, respectively.

3.2.2. Hardened State Properties

Table 5 shows the results of weight per volume unit (WVU) of each of the mortars.

Table 5: Weight per volume unit of the mortars

	Group I			Group II		
Mortar	C	I-5	I-10	II-5	II-10	II-15
WVU (g/cm ³)	2,273	2,261	2,148	2,270	2,199	2,148

The unit weight of the mortars decreased as the percentage of incorporated ash increased.

Table 6 shows the results of the tests for determining the cracking module by flexion and compressive strength at the age of 7 and 28 days in accordance with ASTM C348-63T and ASTM C349-64 respectively. Figure 3 and 4 show the comparison of the results of the resistances in the different mortars.

Table 6: Results of the flexural and compressive strength tests

Mortar	Flexural strength (MPa)		Compressive strength (MPa)	
	7 days	28 days	7 days	28 days
C	3,2	5,0	30,3	37,8
I-5	3,0	3,8	22,8	26,9
I-10	2,6	3,1	13,8	16,4
II-5	2,9	3,7	17,3	21,3
II-10	2,3	3,2	12,8	17,9
II-15	2,4	3,0	8,9	14,6

Figure 3: Compressive strength at the age of 7 and 28 days

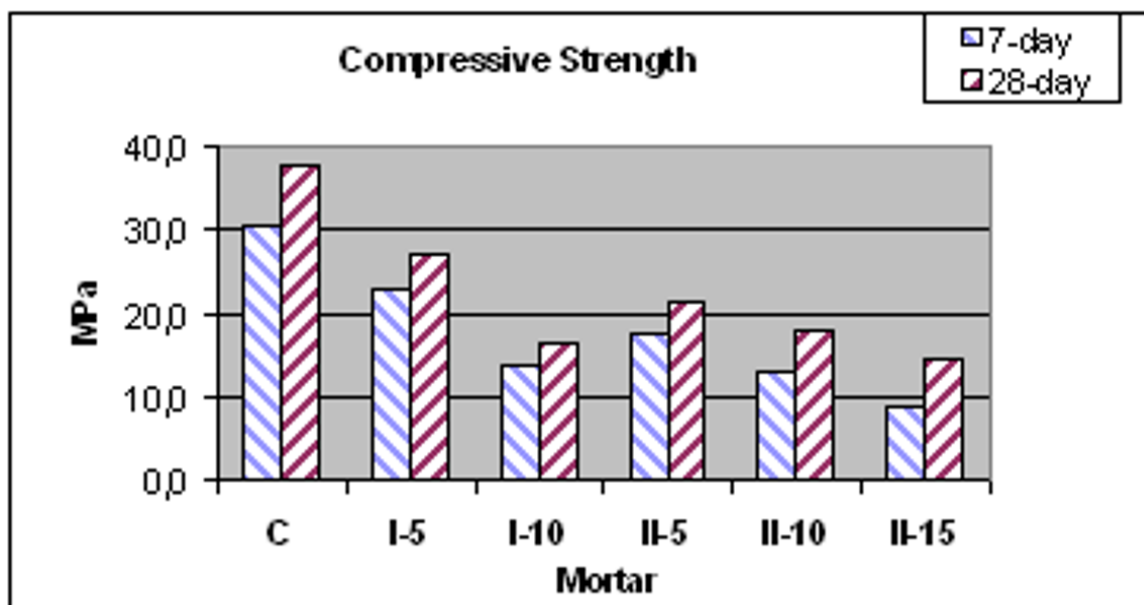
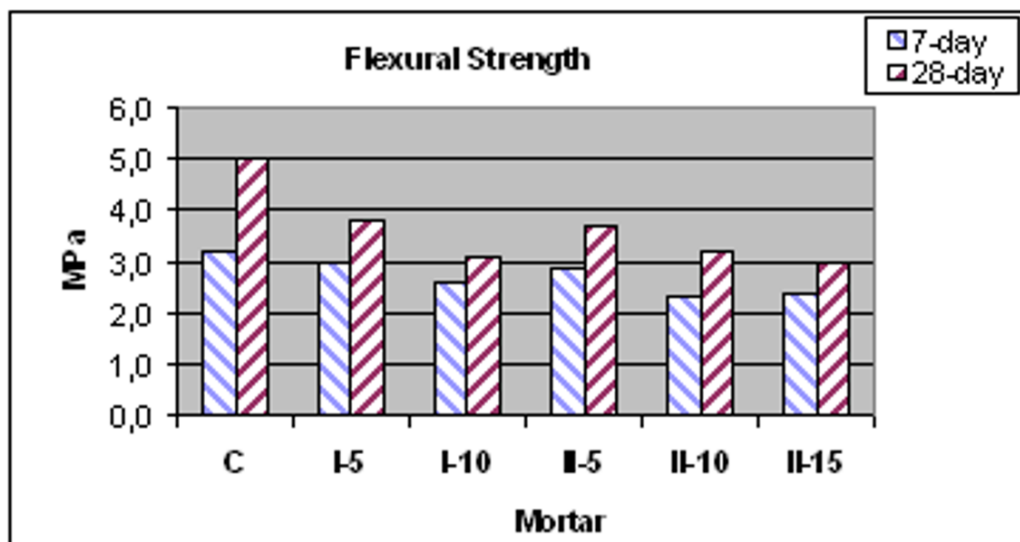


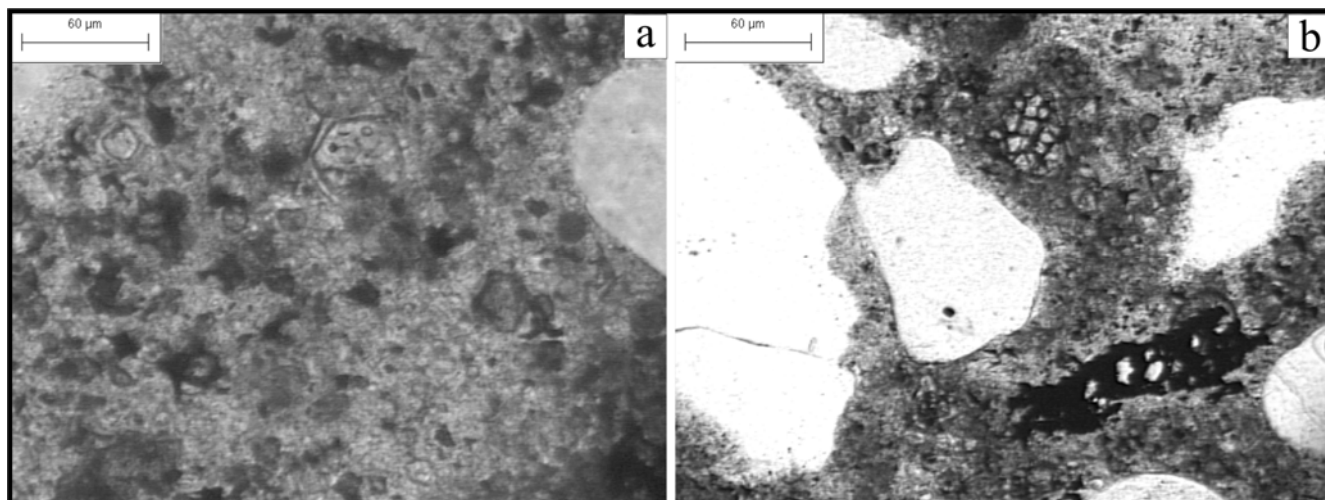
Figure 4: Flexural strength at the age of 7 and 28 days

In all the mortars with ashes incorporated, the flexural and compressive strength reduce their values compared to the control. This phenomenon is observed for all percentage of incorporation, confirming that for an increasing rate of incorporated ashes, higher is the reduction in the resistance value.

3.2.3. Polarization Microscopy

Analysis was conducted on thin sections of each of the mortars from group I: Control, I-5 and I-10 and from group II: II-5, II-10 and II-15. Observations were done using parallel light (with no nicol analyzer) at different scales to observe the texture of the mortar (x100) and the microscopic characteristics of the paste (x500). The purpose of the analysis is to determine possible differences between the mortars with ashes and the control sample. Special emphasis was put on the contact zones between aggregate-mortar, fisuration, reaction process, porosity, to analyse the effect produced by the ash presence at microscopic level. The fine aggregate, mainly composed of quartz, is a natural sand of homogeneous size with good rounded shape. Figure 5a illustrates control test mortars. Figure 5b shows the characteristics of the mortar from group II with 15 % of ashes.

Figure 5: Optical microscopy of mortars with parallel light a: morphology of the control paste. b: texture of the mortar with 15 % of ashes from sunflower husk (Group II)



Accidental air content is higher in the control mortar than in the mixtures with incorporated ash. The development of reaction processes or microfissuration was not observed in any case. Aggregate-mortar contact zones are clearly defined. Ash incorporation does not affect textural nor morphological characteristics of the mortar. When carefully observed, the paste is darker due to carbonous material from the residue of sunflower husk that was not fully burnt.

4. Conclusions

- Ash is mainly composed of potassium sulfate (K_2SO_4), with subordinate amounts of hydrated calcium acid phosphate ($CaHPO_4 \cdot 2H_2O$), hydrated potassium and sodium carbonate ($CO_3KNa_6H_2O$) and potassium phosphate ($K_5P_3O_{10}$)
- K_2O predominates in the chemical composition with subordinate amounts of CaO , MgO , P_2O_5 , SiO_2 , C and S . Loss due to ignition accounts for 24.56 %.
- Cu ; Zn ; Ba ; Rb and Sr were identified in amounts ranging from 155 to 571 ppm.
- As the amount of incorporated ashes increases, the mixture becomes more rigid, fluidity decreases and the material becomes difficult to handle.
- The presence of ashes delays the start and end of the setting time compared to those of the control sample. Once the hardening period is started the process continues normally.
- No textural or compositional changes were observed at microscopic level in the different mortars.
- The flexural and compressive strength of the mortars with incorporated ashes decrease compared to those of the control mortar. The compressive strength decreases as the amount of incorporated ashes increases, ranging from 43% to 61%, in the samples at 28 days. Therefore, it should not be included in cementitious matrixes to be used in structural elements.

Acknowledgement

The authors thank Universidad Nacional del Sur, Comisión de Investigaciones Científicas de la Provincia de Buenos Aires and Consejo Nacional de Investigaciones Científicas y Técnicas for the support provided to carry out the present research work.

References

- [1] ASTM C230-65T, 1965. "Flow table for use in tests of hydraulic cement". *American Society for Testing and Materials*, pp. 233-237.
- [2] ASTM C305-65, 1965. "Mechanical mixing of hydraulic cement pastes and mortars of plastic consistency". *American Society for Testing and Materials*, pp. 315-318.
- [3] ASTM C348-63T, 1963. "Flexural strength of hydraulic cement mortars". *American Society for Testing and Materials*, pp. 323-331.
- [4] ASTM C349-64, 1964. "Compressive strength of hydraulic cement mortars (using portions of prisms broken in flexure)". *American Society for Testing and Materials*, pp. 332-335.
- [5] Capurro, C., 2003a. "Cáscara de girasol. Buscando opciones para su utilización". Parte 1. *Revista A&G* 52, Tomo XIII, N° 3, pp. 396-402.
- [6] Capurro, C., 2003b. "Cáscara de girasol. Buscando opciones para su utilización". Parte 2. *Revista A&G* 53, Tomo XIII, N° 4, pp. 554-558.
- [7] Domínguez, E. and Ullman, R., 1996. "Ecological bricks made with clays and steel dust pollutants". *Applied Clay Science* 11, pp. 237-249.

- [8] Fatih Demirbas, M., Balat, M. and Balat, H., 2009. "Potential contribution of biomass to the sustainable energy development". *Energy Conversion and Management* 50 issue 7, pp. 1746-1760.
- [9] IRAM 50000, 2010. "Cemento. Cemento para uso general. Composición, características, evaluación de la conformidad y condiciones de recepción". *Instituto Argentino de Normalización y Certificación*.
- [10] Klich, I., Batchelor, B., Wilding, L. and Drees, L., 1999. "Mineralogical alterations that affect the durability and metals containment of aged solidified and stabilized wastes". *Cement and Concrete Research* 29, pp. 1433-1440.
- [11] Malhotra, V. and Mehta, P., 1996. "Pozzolanic and cementitious materials". 1st edn. Gordon & Breach Publishers, Amsterdam.
- [12] Penichet Cortiza, M., Guerra Garcés, M. and Carballo García, P., 2008. "El girasol. Sus posibilidades económico-productivas en el desarrollo agropecuario". *Observatorio de la Economía Latinoamericana* 95, pp. 1-13.
- [13] Señas, L., Valea, J., Maiza, P. and Marfil, S., 2004. "Morteros cementicios con polvos de acería, Su impacto ambiental". *Revista Materia* (Brasil) 9, N° 1, pp. 55-59.
- [14] Talero, R., Pedradas, C., Delgado, A. and Rahhal, V., 2009. "Valorización de residuos agroindustriales incinerados como adición puzolánica. Estudio comparativo con el humo de sílice español". *Materiales de Construcción* 59, N° 296, pp. 53-89.
- [15] Zhang, M., Lastra, R. and Malhotra, V., 1996. "Rice-husk ash paste and concrete: some aspects of hydration and the microstructure of the interfacial zone between the aggregate and paste". *Cement and Concrete Research* 26, N° 6, pp. 963-977.