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Compressive Strength and Leaching Behavior of Mortars Using Cement and Wood Ash

Gabriele Fava[1]*, Tarun R. Naik[2], Giacomo Moriconi[1].

1. *Department of Materials, Environmental Sciences and Urban Planning (SIMAU). Università Politecnica delle Marche. Ancona, ITALY. . E-mail: *<g.fava@univpm.it> and <g.moriconi@univpm. it>.*
2. *Emeritus Professor, Formerly Research Professor and Academic Program Director UWM Center for By-Products Utilization, University of Wisconsin-Milwaukee; P. O. Box 784, Milwaukee, WI, USA. Tel: +414-395-6191..E-mail: <tarun@uwm.edu>.*

ABSTRACT

This study investigated the use of soft-wood ash as cement replacement for mortars production. The aim was to provide an opportunity for a by-product, that is increasingly being produced in Italy since biomass combustion is considered of importance for energy production. Biomass is able to substitute a part of conventional fuels and can also become essential for a cost-effective production of local energy. Measurements of the workability, compressive strength, water absorption rate, and leachate properties (pH, salinity and Calcium ion release) of mortars specimen at different cement substitution levels and ages were evaluated. The results obtained reveal definitive possibilities for virgin wood ash (pines and poplar) reuse. It requires further confirmation, on a longer span of time and of other types of mechanical properties and environmental tests.

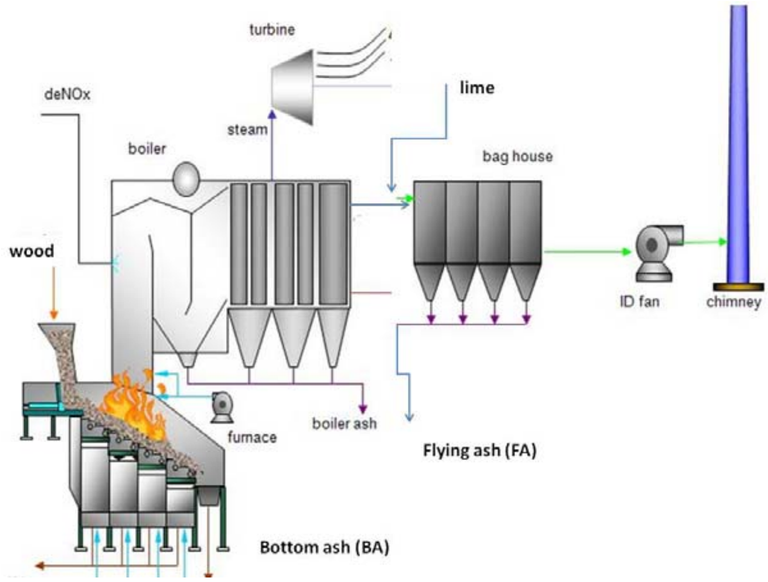
Keywords. *Coniferous wood ash, recycling, mortars, leaching, compressive strength*

INTRODUCTION

Utilization of agricultural residues and woody biomass is becoming an important issue either for the sustainability of agricultural industries or in satisfying the societal and environmental expectations, as well as governmental regulations. The high heating value of around 20 MJ/Kg of wood is considered of importance for energy production. It is increasing in popularity since it can substitute a significant part of conventional fuels and may also become a cost-effective way for local energy production. In Italy, however, the growing diffusion of power plants fueled by biomass requires the legal disposal of the ash produced (typically fly ash and bottom ash). According to the Legislative Decree N° 152 of 3rd April 2006 and its successive changes, wood is now considered a biomass fuel, covered by Title I and II of Part Five of the Decree 152/2006, where in particular Part II, Section 4, dictates the rules and related conditions for biomass ash disposal. Fly ash from biomass co-firing with coal have already been used as a component of ordinary portland cement (OPC) but much research has not been conducted on the wood ash alone (WA) (Maciejewska, A.et al, 2006; Berra, M. et al. 2009). The hydration behavior of OPC in the presence of WA by-products must be assessed as suitable for mechanical properties and environmental impact (Dwivedi V, et al.. 2006; Elinwa, A.U Mahmood ,Y.A, 2002). The Italian law protocol, designed to assess the environmental hazard for biomass ash reuse (Italian Decree 1997), is based on a leaching test to be performed, both on the ash as such or in the form of its reuse (such as in concrete), in the range of pH of the leaching, which is presumed to be proper to the field work of the form recovered in different environmental exposure conditions (Ceren Bakisgan.et al. 2009; Hieu T, et al. 20010). In the present research, a leaching protocol was applied to the cement-based specimens containing WA as supplementary cementitious material that might be used as a binder replacement for use in concrete production. The effects of the ash content were evaluated through comparison of: (i) time development of compressive strength; (ii) ions leaching release as a function of time; and, (iii) as a relationship between compressive strength and leaching. As part of the experimental research carried out for this purpose, the chemical and physical characteristics were analyzed for the biomass ashes from agro-industries and forestry, basically virgin wood chips, sawdust and virgin wood saw dust (pines and poplar). Tests were carried out also on mortars containing different amounts of ash for the evaluation of their water absorption, as well as their effects on the leaching properties.

Materials

Ordinary Portland Cement, CEM II/A-L 42.5R, and WA were used in preparing the mortar mixtures. WA was obtained from a thermal power station of about 14 MWe cogeneration, located in the Piemonte region (Italy). It supplies electricity to the national grid during winter and provides hot water for home heating purposes. The woody materials consumption is around 150,000 to 180,000 Mt per year, depending on the type and characteristics of the biomass. The thermal energy produced is recovered by means of steam production in a heat recovery boiler. Downstream the energy of the steam is transformed into electrical energy in a steam turbine. The combustion chamber type is "moving grid", which is inclined by about 40° and has a combustion surface area of of 64.2 m2, with a potential of 43750 kW and a production of 55 t/h of superheated steam at a temperature of about 450 °C, at a pressure of 55 bar. Combustion is controlled by adjusting both primary and secondary combustion air and flue gas recirculation that is taken out by cyclone separators. The combustion is regulated at temperatures >850 °C, ensuring an oxygen in the flue gas> 6% and residence times > 2 seconds. Ash recovered are of two types: - Bottom ash (BA), from the bottom of the grid, which are sent to special bins for the storage and disposal; and, Fly ash (FA) collected by the pollution control equipment, cyclone separators and bag filters with the addition of quick lime, as shown in Scheme 1.



Scheme 1.

DENOX system for reducing nitrogen oxides emissions has been deactivated since, at present, these emissions are below the Italian law limits. BA and FA samples were collected weekly during a three month period for chemical and physical characterization. The WA collected had gray color with a specific gravity of 1.90 g/cm^3. The main oxides content of WA as analyzed by EDXA is reported in Table 1 and Fig. 1. The mineralogical characterization was determined by X-ray diffraction (XRD) spectroscopy and reported in Fig. 2. Morphological properties were obtained by SEM-EDS Analysis (Fig. 3 and 4), because of their relevance in understanding hardening performance. A SEM examination revealed that the inorganic portion of the ash sample consisted predominantly of spongy irregular particles, mainly Potassium and Calcium with fractions of Sulfur and Chlorine. X-ray diffraction analysis shows the presence of Arcanite (Potassium Sulphate) Sylvite (Calcium Chloride) and Anhydride (Calcium Sulphate).

Table 1. *Main Oxides Composition from EDXA Analysis of WA*

Units	Mg	Al	Si	P	S	Cl	K	Ca	Fe
%	3.7	9.2	28.3	2.1	3.2	1.9	10.5	31.1	7.8

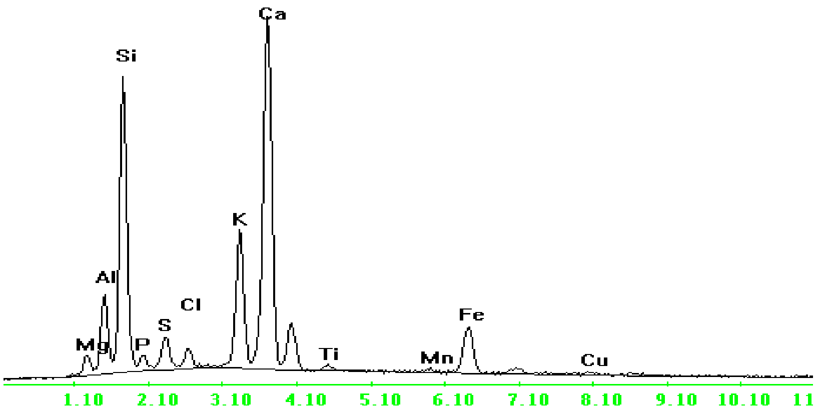


Figure 1. EDXA characterization of WA

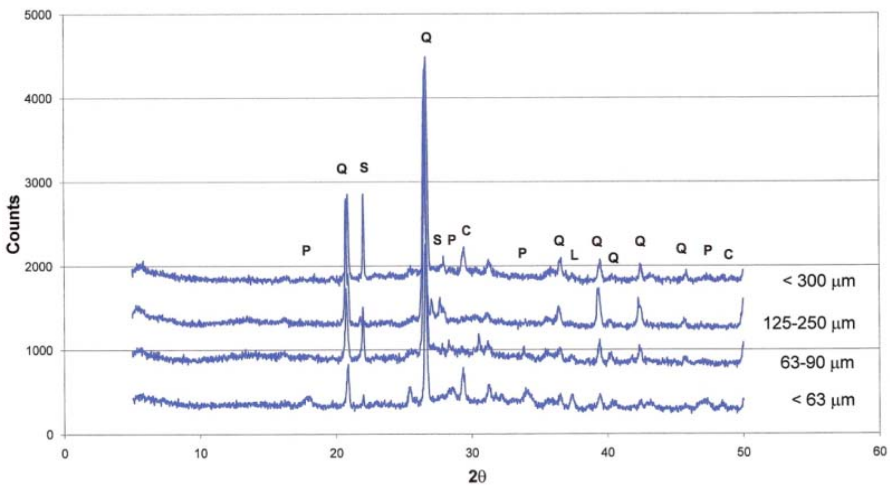


Figure 2. XRD pattern for WA

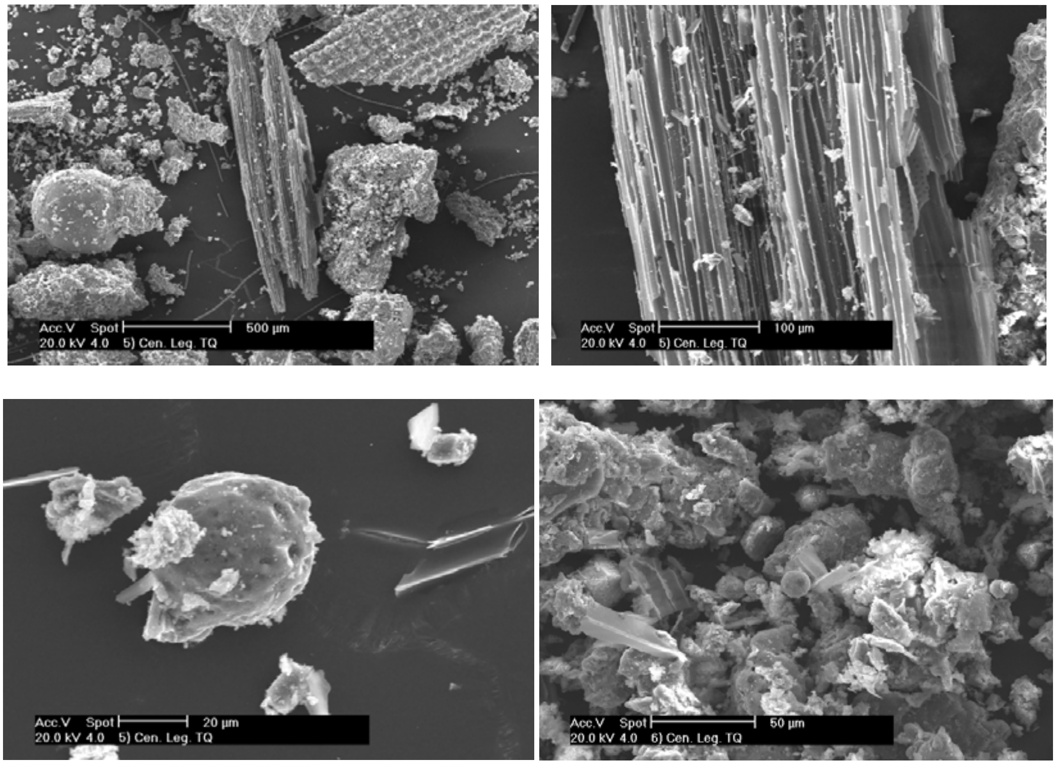


Figure 3, 4. Scanning electron micrograph of WA particles.

Specimens Preparation and Procedure

The test specimens used in this study were 4 x 4 x 16 cm prismatic samples. The WA was added to the mortar mixture as a partial replacement of the cement at three levels: 10%, 20%, and 30% by weight. A set of five specimen with water to cementitious materials ratio (w/l) of 0.4 were prepared for each level of cement substitution; and, also, adding another set of five specimen prepared with a constant 0.4 water to cement ratio (w/c). The workability of the mortar was measured according to UNI EN 1015-3 by the flow table test procedure for fresh mortars by measuring the increase of the grout diameter. For each mixture, the specimens were made and maintained in the sealed steel prismatic moulds to allow maturation in the presence of relative humidity (100%) and temperature (26 deg. C), as constant as possible. After curing for 3, 7, 28, and 90 days they were demolded and an average of three specimens were used to measure the compressive strength at each test age, while the leaching release was measured using the tank procedure following the Italian dynamic leaching test procedure (Legislative Decree, February, 5, 1998). This procedure deals with Italian regulations for reuse of non-toxic materials as by-products. Examples of similar international standard test include the ISO 6961:82, or the ASTM C1220. According to the extraction protocols, a specimen is placed in contact with a precise amount of deionized water for the predetermined extent of time. The solid to liquid ratio, expressed as the ratio of volume of solid to volume of the leachant, is 1:5. The volume of leaching solution is renewed for each specimen testing to drive the leaching process. At each renewing sequence, the fluid is collected for analysis. The renewing sequence was: 2, 8, 24, 48, 72, 102, 168, and 384 hours. The leachant was freshly distilled water with pH of around 6.3 and electrical conductivity of around 3 µS/cm, at room temperature of 20 °C ± 4°C. Because of the physical integrity of the sample matrix (which was maintained during the test), the specimen/leachant properties affect how much material can be leached out, as a function of time. In particular, the surface reactivity of the sample, more than the extraction force of the leachant, provides the concentrations of the contaminants in the water and the kinetic information about the dissolution process.

RESULTS AND DISCUSSION

Measurements of the mortar workability, compressive strength, and leachate properties (pH, electrical conductivity, and Calcium ion release) were used for the evaluation of the effect of cement substitution with WA and its suitability as a cementitious material. The effect of cement replacement by WA (Table 2) on the workability are reported in Table 3, while the compressive strength is reported in Tables 4 & 5 and reassumed following the Equation 1 after Carino-Knudsen.

$$f_c = f_{\max} \frac{k(t - t_0)}{1 + k(t - t_0)} \qquad (1)$$

Table 2 Mixture proportions of mortars (g)

WA %	*Water*	*CEM II/A-L 32,5R*	*Ash*	*Sand*
Cont.	*225*	*450*	*-*	*1350*
10%	*225*	*405*	*45*	*1350*
20%	*225*	*360*	*90*	*1350*
30%	*225*	*315*	*135*	*1350*

Table 3. Workability of specimen

WA %	*w/c*	*Average Diameter (cm)*	*w/l*	*Av.age Diameter (cm)*
0	0.4	16	0.4	16
10	0.4	12	0.4	15
20	0.4	11	0.4	14
30	0.4	10	0.4	12

Table 4 Compressive strength development (MPa)

w/c=0.4

Age, days	Control	10 %	20 %	30 %
3	28.0	26.4	26.6	23.3
7	32.5	35.0	32.3	25.6
28	38.4	38.8	41.7	36.0
90	39.0	40.0	41.2	36.7

w/l=0.4

Age, days	Control	10 %	20 %	30 %
3	28.0	22.0	17.8	14.6
7	32.5	27.3	21.1	17.6
28	38.4	30.5	27.9	25.2
90	39.0	31.0	28.1	26.0

Table 5 Equation 1: Carino-Knudsen (MPa) parameters

w/c=0.4

Sample Water/ash%	k (d-1)	fmax (MPa)
40/0	0.78	39.4
36/10	0.65	41.1
32/20	0.48	43.5
28/30	0.41	38.2

w/l=0.4

Sample Water/ash%	k (d-1)	fmax (MPa)
40/0	0.78	39.4
40/10	0.47	29.0
40/20	0.35	26.7
40/30	0.33	27.6

It is clear from these data that there is a significant impact of the effect WA content on the mechanical properties of the mortar. The compressive strength increased with increasing the WA content for the water to cement material ratio (*w/c*) equal to 0.4 for 10% and 20% WA content but decreased reaching a WA content of 30. The compressive strength decreased with increasing the WA content for the water to cementitious material ratio (*w/l*) equal to 0.4. The percent decrease in the compressive strength was 26, 32 and 30 for WA replacement of 10%, 20%, and 30%, respectively. This decrease with the increase of WA content may be attributed to both to the decreasing amount of cement used; and, to the absence of pozzolanic effect by the WA used. Observing the results obtained for the specimen obtained with a constant water to cement ratio (w/c) equal to 0.4, with those results obtained at constant w/l ratio one can possibly attribute the increase of the observed compressive strength to a filling effect of the ash or to a kinetic effect due to the high pH value observed during the leaching tests. The compressive strength development evaluated following the Carino-Knudsen relationship shows a clear effect, as reported on Table 5, with kinetics K values decreasing from 17% to 40% for a 10% of cement substitution or from 47% to 58% for the higher cement substitution of 30%. A relationship between water and cement content (Equation 2, Fig. 5) is found as:

Compressive Strength (MPa) = 89.15 – 83.88*w/c -0.21*Cement. **(2)**

(R-squared = 96,2 %)

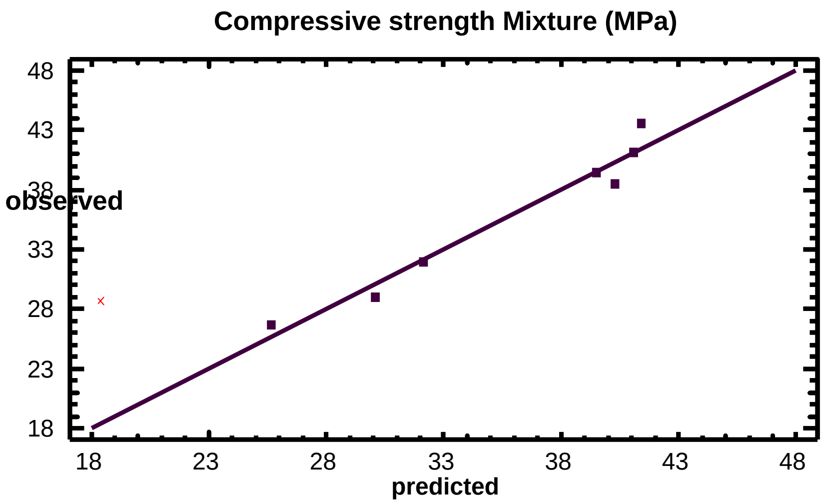


Figure 5: Effect of WA replacement on strength (see equation 2)

Leaching tests

The cumulated release of total ions as measured by electrical conductivity and Calcium ions are plotted as a function of time and related to specific surface area (meq/m^2) of the test specimens (Fig. 6).

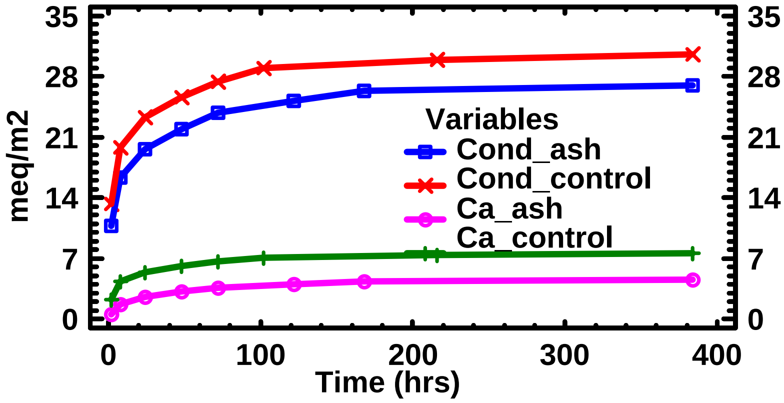


Figure 6 – Cumulative conductivity and Calcium release vs. time for control and WA mixture mortars (meq/m^2)

The leachates, alkaline throughout the testing period with very high pH values, always greater than 12, indicate that the interstitial pore fluid in contact with hydrated cementitious materials is highly buffered by the presence of alkaline ions. The resistance to the leaching is an important factor for the evaluation of the immobilized matrices (durability), because water would be the primary liquid available for the potential dispersion for any metal ions in the environment. As indicated in Fig. 6, Calcium ions leaching have a reverse release trend with respect to the total ions (electrical conductivity). The overall cations release involves mainly Ca^{2+} and K+ that are the elements that are found in higher concentrations in the pore water analysis. This was somewhat expected since, among other things, the major product of OPC hydration include portlandite ($Ca(OH)_2$), however, if the ratio of total soluble cations (conductivity measurements) is compared with Calcium release (Ca, chromatographic measurements), a change in pore water characteristics, as a results of cement replacement, appears as shown in Fig. 7.

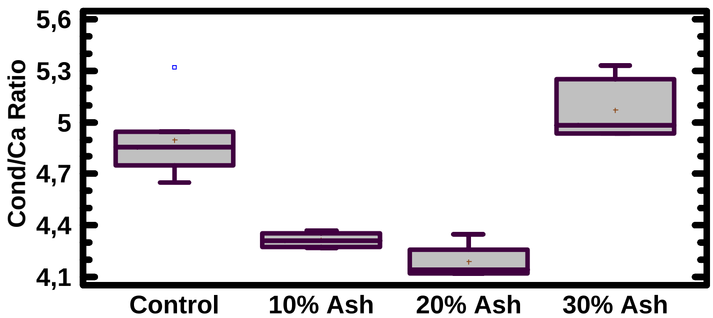


Figure 7 – Conductivity to Calcium ratio vs. control and WA mixture mortars.

CONCLUSIONS

The virgin wood ash (pines and poplar) is examined in this study. It is characterized by high amounts of potassium and calcium ions (11% and 31%) differing from many other biomass fly ash and bottom ash composition found in the literature (Naik and Kraus, 2003). The workability of the mortars mixtures, as measured by the flow test, decreased after 10 to 30% of cement replacement by WA. The compressive strength also decreased with increasing WA as a partial replacement of cement, for constant w/l ratio; however, it increased up to the 20% of cement replacement keeping constant the water to cement ratio (w/c), even though workability was reduced. The chemical properties of the pore solution given by the leaching tests are characterized by high concentration of Calcium and Potassium ions. Particularly the Calcium ion leached by WA specimens with respect to the control indicates a notable alteration of the pore water chemistry. This change has been attributed either to the particular composition of the WA examined or to the cement hydration delay as indicated by the K kinetics values obtained from Carino-Knudsen equation.

In conclusion, it is believed that with additional studies in the area, WA can be put to good use and diverted from landfill.

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