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Materiali innovativi per uno sviluppo sostenibile: dal laboratorio alle applicazioni

Vegetal biomass ashes as alternative activator in alkaline activated binders: characterization and feasibility study

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INTRODUCTION

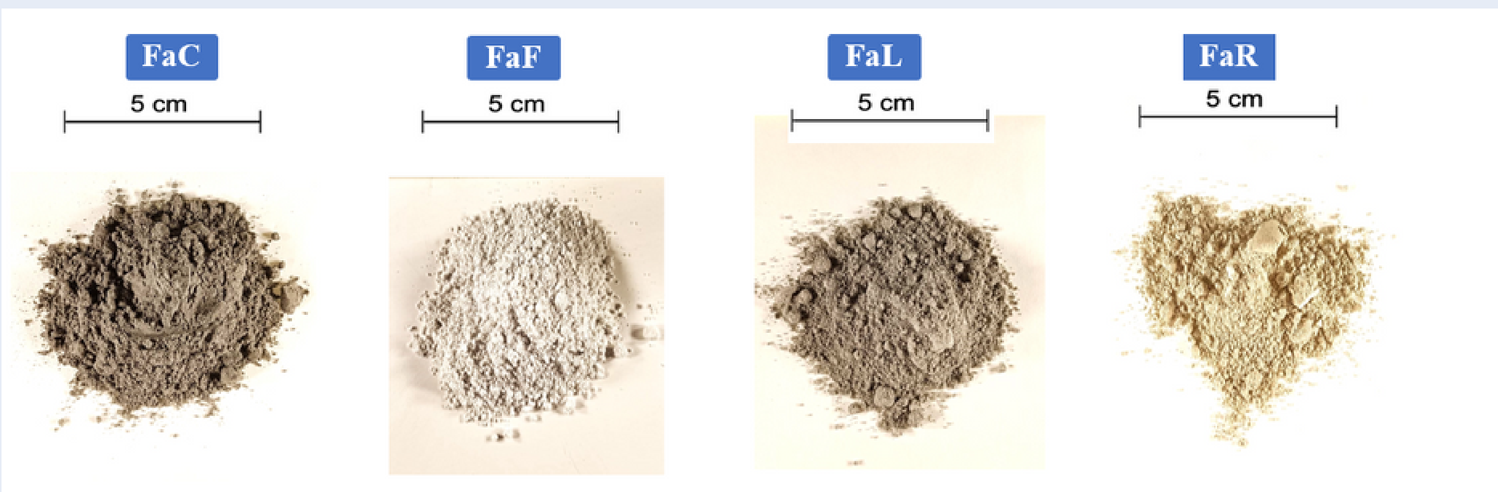
One of the main obstacles to industrial scale up of Alkaline Activate Binders (AABs) consists in the difficulty of handling high hazardous and corrosive alkaline activating solutions for their preparation. Furthermore, the use of very expensive alkaline activating solutions (i.e. Na and K silicates) produced by the conventional chemical industry, badly affects the economic and environmental feasibility of AABs. In the perspective of reducing the environmental impact of AABs, it is useful to find alternative alkaline activators, as well as to implement new strategies for reducing the amount of activating solution during the preparation. Therefore, to reduce the environmental impact of inorganic polymers, it is beneficial to reduce the amount of activating solution, to find another way to produce the solution or to search an alternative activator. Recent studies suggest that biomass ashes can be evaluated as interesting alternative activators owing to their high calcium, potassium and silicon content (*Vassilev et al 2013, Mobili et al 2020*). Furthermore, the production of biomass ash, estimated at around 500 million tonnes per year worldwide (*Alonso et al 2019*) creates the need to explore sustainable applications according to the circular economy strategy.

OBJECTIVE

In this perspective, this study aims to investigate the potential of various types of vegetal biomass ashes through chemical and mineralogical characterisation to evaluate their suitability as alternative activators in the formulation of AABs and, at the same time, to reduce the landfills disposal, economic costs and environmental impact of this industrial waste in accordance with the principles of the Circular Economy.

MATERIALS AND METHODS

In this study, eight samples of vegetal biomass ashes, consisting of four fly ashes and four bottom ashes from different cogeneration plants producing electricity through the combustion of agro-forestry residues, were characterised from the chemical and mineralogical point of view to evaluate their suitability as alternative activators in the formulation of AABs using the following techniques: scanning electron microscopy with EDS microanalysis (SEM-EDS) for the morphological, microstructural and microchemical analysis, X-ray fluorescence (XRF) and inductively coupled plasma-mass spectrometry,(ICP-MS) for the chemical characterization, X-ray diffraction (XRD) for determination of mineralogical content, Fourier-Transformed IR spectroscopy (FTIR) for the identification of functional groups and chemical bonds.



- **Fly ashes** recovered from the chimney filter of an industrial system.
- **Bottom ashes** that accumulates inside the burner of the combustion chamber composed of slag and unburnt materials.

PRELIMINARY RESULTS

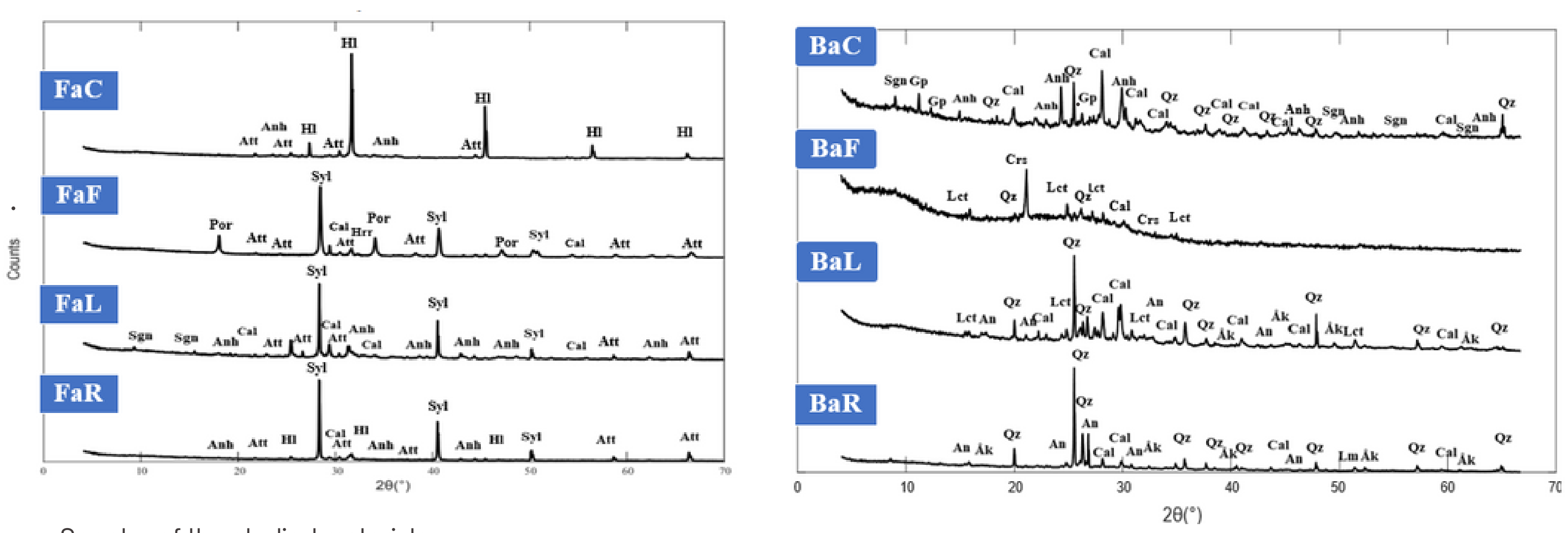
Chemical analysis of the fly ashes using X-ray fluorescence shows significant amounts of K_2O from a minimumof 16.05 wt% to the 19.8 wt% for three of the examined samples,with the exception of the 'FaC' sample, which has 31.78 wt% of Na_2O and only 0.68 wt% of K_2O . CaO percentages are significant with an averageof 14.51 wt%. Mineralogical analyses show the occurrence of crystalline phases based on potassium, sodium and calciumin accordance with chemical analyses. Many of these phases (i.e. aphthitalite, sylvite,syngenite, halite portlandite) are soluble in water and therefore able to produce a high alkalinity solution in a very simple way without the use of a complex chemical process typical of alkaline solutions produced by the chemical industry,in accordance with studies carried out by (*Liodakis et al., 2005*). From a morphological and microstructural point of view, fly ashes are very homogeneous, due to the characteristics of the source plants, which capture this type of ash through filters or cyclones able to select the fly ashes from a grain size point of view. At the microchemical level, they have abundance of K, Ca, Mg in accordance with mineralogical and chemical analyses. Therefore, due to the composition revealed by the investigations carried out, vegetal biomass fly ashes could serve as a solid activator of precursors in the 'One-Part Binders' technology, but can also serve as a liquid activator in the 'Two-Part Binders' technology for sustainable production of AABs (*Palomo et al., 2021*).
The analysis on bottom ashes shows high SiO_2 and CaO contents, ranging from 30.01 wt% to 58.31 wt% and from 9.31 wt% to 35.77 wt%, respectively, and relatively low concentrations of AlO_2 (from 5.17 to 8.18 wt%). X-ray diffraction analyses show the occurrence of peaks corresponding to crystalline phases such as Ca, K-sulfates and silicates (i.e. syngenite, quartz, cristobalite, anortite and akermanite) and humps about 8 °2ϑ and from ~ 20 to 30° 2ϑ, indicating the occurrence amorphous material. From a microstructural and morphological point of view, the bottom ashes are very heterogeneous, showing the presence of several phases based on Si, Al, Ca in agreement with chemical and mineralogical analysis. Owing to the presence of extensive amorphous phase, as well as their high silica and calcium content, the investigated vegetal biomass bottom ashes appear to have considerable potential also as precursor for the production of AABs.

- ***Chemical analysis (X-ray fluorescence)***

XRF FLY ASHES (w%)	LOI	Na_2O	MgO	AlO_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	FeO
FaC	62,07	31,78	0,81	0,54	1,59	0,62	0,68	1,46	0,25	0,02	0,18	0
FaF	53,13	5,51	0,04	0,11	2,26	1,53	16,05	21,28	0	0,01	0,08	0
FaL	27,71	4,14	6,72	2,05	6,91	2,82	19,7	28,26	0,12	0,17	1,39	0
FaR	50,45	10,7	2,86	1,3	4,85	1,88	19,8	7,12	0,05	0,07	0,92	0

XRF BOTTOM ASHES (w%)	LOI	Na_2O	MgO	AlO_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	FeO
BaC	12,26	5,62	5,09	5,17	31,72	2,06	5,29	23,87	3,98	0,26	4,68	0
BaF	5,3	1,19	1,84	5,47	58,31	0,86	13,93	9,31	0,3	0,14	2,63	0
BaL	8,34	0,8	6,86	5,94	30,01	1,34	6,57	35,77	0,4	0,18	3,8	0
BaR	3,08	1,13	5,68	8,18	43,79	1,82	6,83	23,64	0,6	0,2	5,06	0

- ***Mineralogical analysis (X-ray diffraction)***

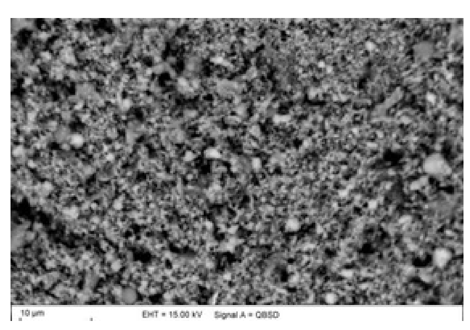


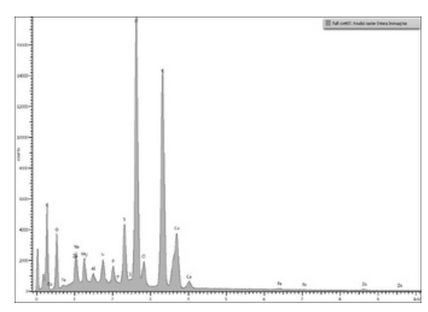
- Spectra of the studied materials.

Rigth: Fly ashes - Portlandite * **Por**, $Ca(OH)_2$, Aphthitalite **Att**, $(K,Na)_3Na(SO_4)_2$, Sylvite* **Syl**, KCl, Calcite* **Cal**, $CaCO_3$, Hatrurite **Hrr**, Ca_3SiO_5, Halite* **Hl**, NaCl, Anhydrite* **Anh**, $CaSO_4$ Syngenite* **Sgn**, $K_2Ca(SO_4)_2\cdot(H_2O)$.
Left: Bottom ashes - Leucite* **Lct ,** $KAlSi_2O_6$, Quartz* **Qz** SiO_2, ,Cristobalite*Crs, $\mathbf{SiO_2}$, Calcite* **Ca**, $CaCO_3$, Anhydrite* **Anh**, $CaSO_4$, Gypsum* **Gp**, $CaSO_4\cdot2(H_2O)$, Syngenite* **Sgn**, $K_2Ca(SO_4)_2\cdot(H_2O)$ Anorthite* **An**, $CaAl_2Si_2O_8$, Åkermanite* **Åk**, $Ca_2MgSi_2O_7$, Lime* **Lm**, CaO.

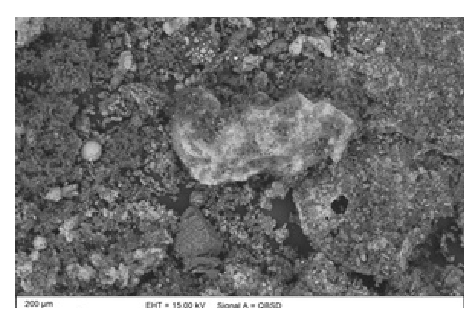
- ***Morphological, microstructural and microchemical analysis (SEM-EDS)***

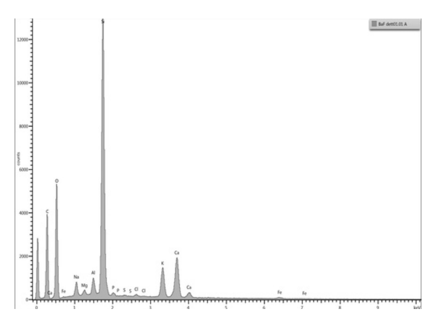
Fly ashes





Bottom ashes





CONCLUDING REMARKS

Preliminary investigations of vegetal biomassashes show the occurrence of elements and minerals which can be evaluated both as solid precursors or as a source for generating solid or liquid alkaline activators.
Future inspection will focus on the investigation of the presence of eventual dangerous elements in the investigated materials and on several tests to verify the possibility of preparing AABs through this waste material.

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