Industrial Crops and Products 103 (2017) 39–50

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Rice straw ash: A potential pozzolanic supplementary material for cementing systems

Josefa Roselló [a], Lourdes Soriano [b], M. Pilar Santamarina [a], Jorge L. Akasaki [c], José Monzó [b], Jordi Payá [b,*]

[a] Departamento de Ecosistemas Agroforestales, Universitat Politècnica de València, Spain
[b] Instituto de Ciencia y Tecnología del Hormigón ICITECH, Universitat Politècnica de València, Spain
[c] Departamento de Engenharia Civil, Universidade Estadual Paulista Campus Ilha Solteira, Brazil

ARTICLE INFO

Article history:
Received 11 October 2016
Received in revised form 9 March 2017
Accepted 21 March 2017

Keywords:
Rice straw ash
FESEM
Spodogram
Chemical composition
Amorphous silica
Pozzolanic reactivity

ABSTRACT

Biomass waste from rice straw has many management problems, including field firing causing severe air pollution and natural organic decomposition resulting in methane emission. The conversion of this waste to ashes may offer the possibility of reusing them in cementing systems. For the first time ashes from different parts of the rice plant (*Oryza sativa*) were characterised from the chemical composition point of view: rice leaf ash (RLA), rice leaf sheath ash (RlsA) and rice stem ash (RsA). Microscopic studies on ashes revealed heterogeneity in the distribution of chemical elements in the remaining cellular structure (spodograms). The highest concentration of SiO_2 was found in dumbbell-shaped phytoliths (%SiO_2 > 78%). In the global chemical composition of ashes, SiO_2 was also the main oxide present. According to Vassilev's classification of chemical composition, RLA belongs to the K-MA zone (medium acid), RlsA to the K-zone (low acid) and RsA to the S-zone (high acid). Calcination temperatures ≥550 °C completely removed organic matter from the straw and ashes underwent significant sinterisation by calcining at 650 °C due to the presence of potassium chloride. Here, ashes from global straw (rice straw ash, RSA) are characterised (via X-ray diffraction, Fourier transform infrared spectroscopy and thermogravimetry) and tested from a reactivity point of view (reaction towards calcium hydroxide) in order to assess the possibility for its reuse in cementing systems. Results from pastes made by mixing RSA and calcium hydroxide showed that the pozzolanic reactivity of the ashes is important (hydrated lime fixation of 82% for 7 days and 87% for 28 days in RSA:hydrated lime paste) and cementing C—S—H gel is formed after 7 and 28 days at room temperature. Compressive strength development of Portland cement mortars with 10% and 25% replacements by RSA yielded 107% and 98% of the strength of control mortar after 28 days of curing. Frattini test confirmed the pozzolanicity of the RSA blended cements. These reactivity results are very promising in terms of the potential reuse of ashes in cementing systems.

1. Introduction

Agricultural wastes are commonly assessed as biomass sources for energy purposes. They can be classified in three groups: energy crops, food production wastes and agricultural wastes (Titiloye et al., 2013). Agricultural wastes are usually composed of straws (leaves and stems) and fruit-shells. Some industrially derived agricultural wastes also include bagasse, cobs, seeds, pods and husks. Huge amounts of these wastes are available and the selection and appropriate treatments of them could provide building and infrastructure materials.

One of the most important challenges related to the production of building materials is focused on their environmental impact (ecological footprint, carbon footprint), mainly on the production of

Abbreviations: AWA, agricultural waste ashes; BLA, Bamboo leaf ash; CH, calcium hydroxide (hydrated lime); C—S—H, calcium silicate hydrate gel; DTG, derivative thermogravimetric curves; EDS, energy dispersive X-ray spectroscopy; FESEM, field emission scanning electron microscopy; FTIR, Fourier transform infrared spectroscopy; OM, optical microscopy; RHA, rice husk ash; RLA, rice leaf ash; RlsA, rice leaf sheath ash; RsA, rice stem ash; RSA, rice straw ash; SCM, supplementary cementing material; SLA, sugarcane leaf ash; TG, thermogravimetry; XRD, X-ray powder diffraction.

* Corresponding author.
E-mail addresses: jrosello@upvnet.upv.es (J. Roselló), lousomar@upvnet.upv.es (L. Soriano), mpsantam@eaf.upv.es (M.P. Santamarina), akasaki@dec.feis.unesp.br (J.L. Akasaki), jmmonzo@cst.upv.es (J. Monzó), jjpaya@cst.upv.es (J. Payá).

http://dx.doi.org/10.1016/j.indcrop.2017.03.030
0926-6690/

inorganic binders, such as ordinary Portland cement OPC (Barceló et al., 2014). It is well known than the production of OPC is a very intensive process both in terms of energy and raw materials. About 5% of total worldwide anthropogenic CO_2 emissions are generated from the manufacture of OPC-based cement products (Worrell et al., 2001). Cement production has rapidly increased over the last few decades and reached annual production of 4.3 billion tonnes in 2014 (CEMBUREAU, 2014). Since 1990, the blending compositions of cements have changed significantly (Schneider et al., 2011), which has involved a reduction in clinker content (also named the Clinker factor, CF). The CF value in 2003 was 0.85, whereas in 2010 it was 0.77; the prediction for 2050 is for it to be 0.71 (WBCSD, 2009). This reduction in CF was due to the use of supplementary cementing materials (SCMs). Traditionally (Siddique and Khan, 2011), wastes from industrial activities are blended with Portland cement clinker: ground granulated blast furnace slag, coal fly ash and silica fumes. The first ash from agricultural biomass used in cement or concrete was rice husk ash (RHA) (Mehta, 1983). Utilisation of ashes will contribute to the sustainability of biomass for power generation. Valorisation of bottom ashes, fly ashes and fluidised bed ashes can be carried out by bulk optimisation options: fertiliser and soil amendment, component of building materials or, in the case of carbon-rich ashes, reuse as fuel (Pels and Sarabèr, 2011).

Over the last few decades, greater interest on the development of new SCM derived from agricultural wastes (biomass) is observed in the scientific literature; although the commercialisation of agricultural waste ashes (AWA) and its application in building materials is still scarce (Aprianti et al., 2015). Moreover, in the last years interest has increased regarding the reuse of some biomass-derived ashes in geopolymers (alkali activated materials) to partially replace the inorganic precursor (Moraes et al., 2016) or totally replace the sodium silicate in the alkaline activator (Bouzón et al., 2014). In both cases, reactive silica in the ashes plays an important role for the development of high-performance geopolymers.

The main basis for the valorisation of these AWA lies in the fact that they contain high amounts of silica. This silica is a basic component required for a pozzolanic reaction. This reaction consists of the acid-base reaction between calcium hydroxide (portlandite, when produced from hydration of Portland cement) and silicon oxide (silica):

$$Ca(OH)_2 + SiO_2 \rightarrow \text{C—S—H(gel)}$$

The chemical reaction yields calcium silicate hydrate gel (C—S—H), which has cementing properties. When a SCM presents this behaviour, it is termed a pozzolan and it presents pozzolanic properties. The presence of silica in ash is a necessary factor for a pozzolanic reaction, although it is not the only required factor: a small size of ash particle (high specific surface area) and amorphous state (not crystalline phase) are also required. In some cases, amorphous alumina is also involved in the pozzolanic process.

Over the last few years, interest has increased regarding the study the valorisation of AWA (Vassilev et al., 2013; Pels and Sarabèr, 2011), specifically on the addition of AWA to cements (blended Portland cements, alkali-activated cements) and concrete for the following reasons: (a) biomass is produced worldwide in huge amounts and frequently its management is very complicated; (b) valorisation as livestock food, fertiliser, cellulosic-based derived materials (fibres, boards) are not always available or are not economically viable; (c) energetic valorisation of biomass gained interest as a substitute for fossil fuels since it is technically viable worldwide; (d) the transformation of biomass into AWA is an CO_2 neutral process because the carbon released to the atmosphere during combustion was recently fixed by photosynthesis; (e) the ashes could show pozzolanic properties and be then valorised in building materials and (f) the construction industry has the capacity to take in these ashes due to its large requirements in terms of raw materials.

Recently, some advances in the application of new AWA in cementing systems were reported, including: ashes from banana leafs (*Musa* sp., Kanning et al., 2014), switchgrass (*Panicum virgatum*) (Wang et al., 2014), elephant grass (*Pennisetum purpureum*, Cordeiro and Sales, 2015), bamboo leaf (*Bambusa* sp., Frías et al., 2012), sugarcane straw (*Saccharum officinarum*, Moraes et al., 2015), barley straw (*Hordeum vulgare*, Cobreros et al., 2015) and plane tree (*Platanus* sp., Binici et al., 2008).

Rice straw is an agricultural waste that has some management problems: field firing causes severe air pollution and natural organic decomposition favours methane emission (Yuan et al., 2014). This last process has a potent environmental effect in terms of greenhouse gas emission, as the global warming potential of methane is much higher than that of CO_2: 25-times more for a 100-year horizon and 72-times more for 20-year horizon (IPCC, 2007). Thus, it is crucial to valorise this waste as rice production accounts for 5–10% of worldwide methane emissions. Huge amounts of rice straw are produced worldwide, considering that 1–1.5 kg of straw is generated for every 1 kg of paddy rice (Binod et al., 2010). The worldwide production of rice straw was 731 million tonnes in 2008 (Abdel-Rahman et al., 2015) and Asia was the major producer, generating 620 million tonnes of the straw (IRRI, 2016). However, scarce research exists on the characterisation of ashes from rice straw ash (RSA) and their potential applications. An interesting approach for obtaining pure silica from rice straw by a sono-assisted sulphuric acid process was reported (Rehman et al., 2013) and Abou-Sekkina et al. (2010) studied three samples of RSA from Egypt and concluded that the silica content was 65% by mass and that no crystalline phases were identified. Ataie et al. (2015) prepared ashes from rice straw and wheat straw after previous treatment with hydrochloric acid and further calcination at 650 °C and 500 °C.

It is well-known that silicon is an element absorbed by the roots of plants in the form of silicic acid, which is transported through the vascular system and deposited in the form of opal or hydrated amorphous silica ($SiO_2 \cdot nH_2O$). This silica compound is deposited in: (a) the cellular walls; (b) the interior of the cells (lumen); (c) epidermal appendages (trichomes) and (d) the intercellular spaces in stems and leaves (Prychid et al., 2003). This precipitation process of silica is irreversible (Epstein, 1999): in the three first cases a silica particle replicates the shape of the cellular structure, while for the fourth case no relationship between silica deposit shape and the intercellular space is obtained.

Monocot plants accumulate silica (>3 mg of Si per g of dried matter), mainly plants belonging to Poaceae family: rice (*Oryza sativa*) and sugarcane (*Saccharum officinarum*) (Ma and Yamaji, 2006). Epidermal tissues in Poaceae species present particular characteristics that are used in taxonomy. Some taxonomic classifications are based on these cellular dispositions: siliceous cells (phytoliths), suberous cells and trichomes. Phytoliths are solid deposits in which silica is the main component. Their size (typically 10–20 μm) and their shape vary significantly depending on the plant. The following main morphotypes are described: dumbbells, saddle and cross; also intermediate shapes can be found (Wilding and Drees, 1971; Piperno, 2006).

In the rice plant, the silica is highly concentrated in the husk (more than 20% by mass of dried husk). Leaves (formed by leaf blades and leaf sheaths) also are silica-rich parts and contain 13% and 12% silica, respectively. Finally, roots store less silica (2%) (Anala and Nambisan, 2015).

The goal of this paper is to characterise different parts of the rice plant (*Oryza sativa*) by means of the identification and analysis of