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Pozzolanic Reaction of a Biomass Waste as Mineral Addition to Cement Based Materials: Studies by Nuclear Magnetic Resonance (NMR)

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Abstract

Non-fossil alternative fuels from biomass (agro-industrial, forestry and fodder plants) focus on getting cleaner, cheaper and more environmentally friendly energy sources directly related to the sustainable development of future societies. The resulting ash produced from the biomass calcination is a viable alternative for use as supplementary cementing materials in the construction industry. This study explores the scientific knowledge of calcium-silicate hydrate (C-S-H) gel formation during pozzolanic reaction between the biomass ash and calcium hydroxide through nuclear magnetic resonance technique with two different types of elephant grass ash that have different microstructure. The ash with the highest initial percentage of Q⁴ and Q³ units was found to react most actively and give rise to gels with the greatest inter-tetrahedral connectivity. In contrast, ash with higher content of total SiO₂, exhibited lower reactivity and the C-S-H gel formed is characterised by low inter-tetrahedral connectivity from the earliest ages. Evaluation of C-S-H gel by nuclear magnetic resonance (NMR), as main hydrated phase for the engineering properties, revealed the potential of this tool to determine the effectiveness of this type of grass as raw material in cementing matrices through the evolution of the microstructure of the gel C-S-H formed.

Keywords: biomass ash, pozzolan, nuclear magnetic resonance spectroscopy, C-S-H gel, microstructure

1 Introduction

In the wakeup of the worldwide economic crisis, recycling industrial waste as an active addition or admixture in cement or concrete composites has aroused a good deal of attention in the scientific community, given the potential for economic and environmental benefits and energy savings (Juenger and Siddique 2015; Sánchez de Rojas *et al.* 2014).

Agro-industrial waste is considered a major environmental problem due to the vast volumes generated, which are stockpiled or incinerated under uncontrolled conditions in landfills. This can be potentialized by the slow degradability and generation of other by-products,

which may be toxic, cumulative or difficult to decompose (IPEA 2012).

According to FAO (2014), demand for food will grow by 70% by 2050, primarily in Asia, Africa and Latin America. This will call for more sustainable food production and good management of the concomitant waste. One possible alternative is to convert the waste into a new product for manufacturing eco-efficient cement matrices (Nozahic and Amziane 2012; Aldahdooh *et al.* 2014). That is the case of the usage of mineral additions, proposed by Payá *et al.* (2001), which, besides reducing the content of cement clinker and CO₂ emission, provides improvement in the mechanical performance of the blended material. The power plants can play an important role in the conversion process, because they can use agricultural wastes, *i.e.* sugar cane bagasse (Frías *et al.* 2011; Moraes *et al.* 2016), bamboo (Frías *et al.* 2012), as alternative biomass to fossil fuels in the generation of cleaner and more sustainable energy (Moraes *et al.* 2016; Abbasi and Abbasi 2010).

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In this direction, Brazil (State of Bahia) has pioneered the cultivation of a fast-growing crop, elephant grass, as a source of biomass for a steam power plant, whose sole source of energy is a mix of different varieties of this plant, generating about 4–5% of ash, which are stockpiled in landfills. Preliminary laboratory studies from Nakanishi et al. (2014), have shown that value can be derived from this ash, in light of its substantial pozzolanicity (after activation at 700 °C), with calcium-silicate hydrate gel (C-S-H) as the sole hydrated phase identified during the pozzolanic reaction. However, given the high potassium oxide content in this ash, it must be processed to reduce the concentration of K₂O.

Including supplementary cementitious materials (SCM) as pozzolans in hydrated cement composite results in the formation of *secondary* C-S-H, as reported by Frías et al. (2015), which, due to the pozzolanic reaction, has a lower Ca/Si ratio (about 1.0) than the primary product coming from cement particles.

This study aimed primarily to conduct a first analysis of C-S-H gel by NMR with focus on the calcium silicate hydrate microstructural development and polymerisation in elephant grass ash/Ca(OH)₂ composite. The nuclear magnetic resonance (NMR) is one of the powerful techniques to provide information about the microstructural characteristics of the C-S-H amorphous gel (Wieker et al. 1982; Moon et al. 2016).

The microstructure of the matrices with the ashes was assessed comparing with a traditional pozzolan, silica fume. An additional purpose is the effective contribution for reusing this agro-industrial waste and avoiding its disposal, which is related to the priority aiming of the Global Circular Economy.

2 Materials and Method

2.1 Materials

The Cameroon and Napier varieties of elephant grass were chosen for the present study as current options normally considered for biomass production. The plant matter was crushed 150 days after harvesting and dried at 60 °C for 72 h. The material was then subjected to control heating in an electrical furnace, in which the temperature was ramped to 400 °C at 10 °C/min, held at that temperature for 20 min, ramped to 700 °C and held for a further 60 min. Both varieties of elephant grass (Cameroon or EGC and Napier or EGN) yielded 4–5% ash under these conditions. Mineralogically speaking, the ash comprised primarily cristobalite and quartz, with traces of sylvite (KCl) as crystalline materials (Nakanishi et al. 2014). After heating, the ash was ground in a ball mill for 30 min and analysed for fineness with laser diffraction granulometry following the procedure describe by Frías et al. (Frías et al. 1991). The D₅₀ value (D₅₀=median particle

size; i.e., 50% of the material is finer than D₅₀) for EGC and EGN was 25.5 and 49 µm respectively. The different particle size distribution for the two distinct ashes was not equalized during their preparation due to the adoption of the same grinding procedure.

According to John et al. (2003), this kind of ash can present high K₂O contents in its composition (above 20%). This fact precludes its direct use in cement, where the potassium would induce the alkali-aggregate reaction and concomitant degradation of the cement matrices (Lima et al. 2011). For this reason, the ash previously was treated with a 3.3% (v/v) hydrochloric acid (HCl) solution and heated at 90 °C for 1 h, which reduced the K content by about 70%. ELKEM 920D commercial silica fume (SF) with a D₅₀ of 11 µm was used as reference, since it is well known that it is a very reactive pozzolanic material because of its extreme fineness and very high amorphous silicon dioxide content (Siddique 2011; Khan and Siddique 2011). The lime used to prepare the pozzolan/calcium hydroxide pastes was an analytical grade calcium hydroxide (purity of at least 95%). One-to-one (by weight) pozzolan—Ca(OH)₂ blends were prepared with a water: binder ratio of 1.0. The pastes were stored in a saturated environment at 22 ± 2 °C for 7 or 60 days, after which the hydration reaction was interrupted by immersion of the samples in isopropyl alcohol and drying in an electric oven at 60 °C during 1 h.

2.2 Instrumental Techniques

Both types of elephant grass ash and the silica fume were characterised on a PANalytical Axios X-ray fluorescence (XRF) spectrometer. The starting materials and the 7- and 60-day samples of both ashes and the silica fume were analysed on a Bruker AV-400 (9.4 T) MAS NMR spectrometer (Rheinstetten, Germany) with the following settings for the ²⁹Si MAS NMR experiments: ν_R = 5 kHz; pulse width = 3 µs; relaxation delay = 20 s. Typically, 3000 scans were run and the ²⁹Si chemical shifts were determined relative to tetramethylsilane.

3 Results and Discussion

3.1 Elephant Grass Ash Characterization

Table 1 gives the XRF findings for the chemical composition of the EGN and EGC elephant grass ash and the commercial silica fume (SF).

The analyses showed that the chemical composition of the two ashes differed, even though both derived from elephant grass.

From the XRD analysis (Fig. 1), it can be seen that before HCl treatment the main crystalline compound in both elephant grass is sylvite. EGC also have a relatively high amount of calcinite and in minor proportion gypsum, anhydrite and potassium sulphate and nitrate. EGN

Table 1 Chemical composition of the pozzolans.

Oxide (%)	SF	EGN before HCl treatment	EGN after HCl treatment	EGC before HCl treatment	EGC after HCl treatment
SiO ₂	84.5	43.30	80.0	22.4	49.4
Al ₂ O ₃	0.97	1.05	0.44	0.28	0.47
Fe ₂ O ₃	2.62	1.13	0.77	0.321	0.83
CaO	2.93	5.47	1.85	3.98	10.10
Na ₂ O	0.15	0.25	0.11	0.07	–
K ₂ O	1.04	21.10	7.05	53.9	8.60
MgO	0.60	6.25	1.11	3.94	4.22
SO ₃	–	2.01	0.65	2.3	0.47
P ₂ O ₅	–	2.41	0.56	4.06	9.91
Cl	–	7.40	0.95	8.44	0.46
LOI	7.53	9.01	6.31	n.d.	14.6

SF silica fume, EGC Cameroon elephant grass, n.d. non determined, EGN Napier elephant grass, LOI/ loss on ignition at 1000 °C.

shows a broad background indicating the presence of an amorphous compound with sodium magnesium phosphate; cristobalite and potassium sulphates are minor

compounds. After HCl treatment, quartz is the main crystalline phase present in EGC ash. For EGN ash, quartz (SiO₂), cristobalite (SiO₂) and small amount of sylvite (KCl) were detected.

Some differences in the oxide contents and in the loss on ignition of the two varieties of elephant grass were found. The differences may have been due to a number of factors. Among them, the type of soil, the fertilization performed and the genus of elephant grass.

The HCl used to reduce the potassium content also have extracted other soluble salts as calcium sulphates, clorures, etc. Additionally it was observed, that the content decrease of K, provided an increase in other components such as SiO₂ content.

After the treatment with HCl, the greatest differences were found in the calcium and phosphorus oxide contents, probably, differences in the chemical structural of the compounds reacted the different way during the treatment.

The loss on ignition was greater in the sample EGC, which had a lower SiO₂ content, possibly signifying

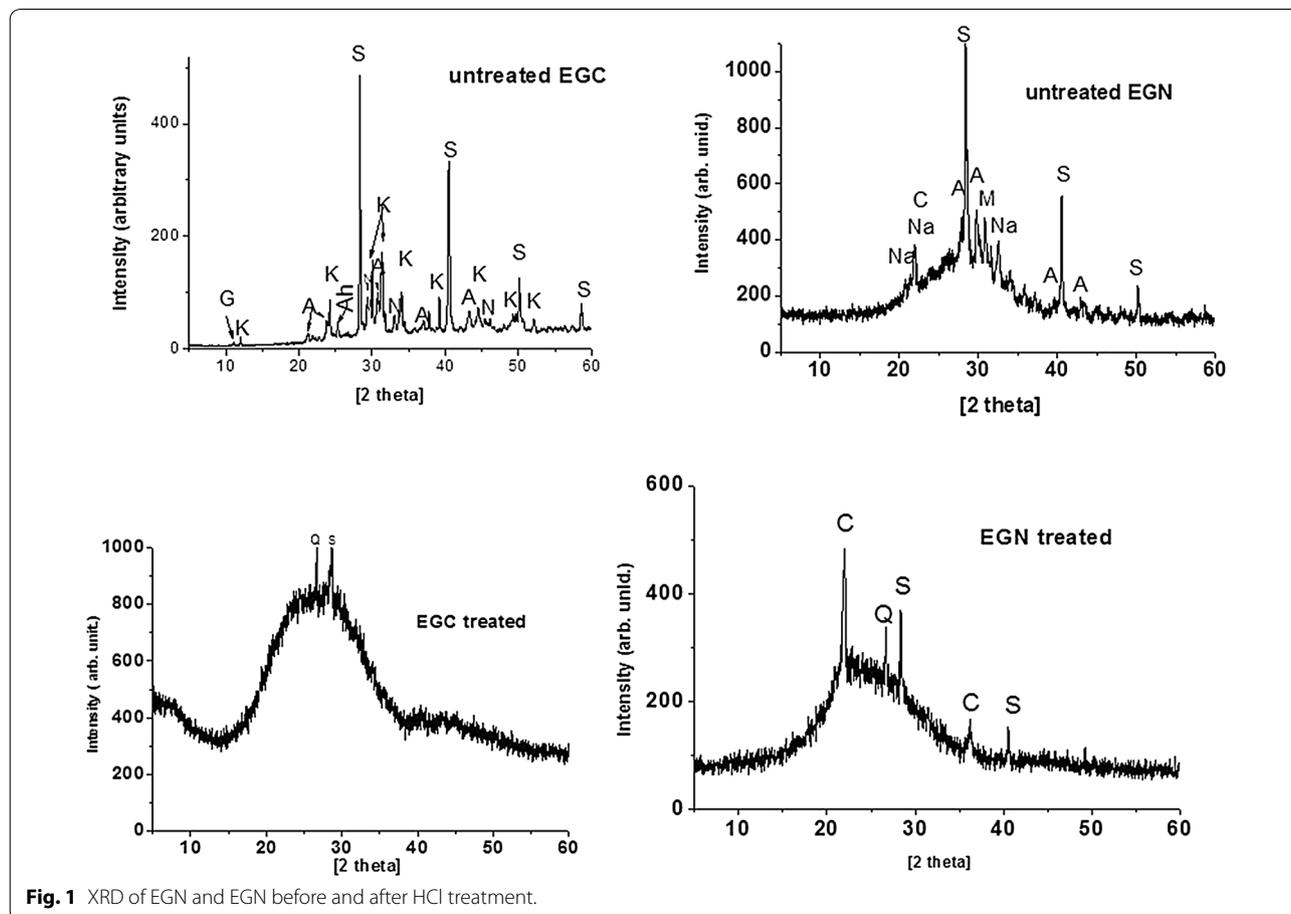


Fig. 1 XRD of EGN and EGN before and after HCl treatment.

a higher percentage of organic matter (traces of unburned particles), i.e., presence of carbon.

3.2 C-S-H Gel Characterization by NMR

Figure 2 shows the ^{29}Si MAS NMR spectra for the starting materials.

The wide signals on all the spectra denoted the presence of amorphous compounds while the spectra of the initial samples are different for the three materials. The proportion of silicon associated with each Q_n unit was determined by deconvoluting the spectra and measuring the peak areas with Origin (version 7.5) software (Table 2).

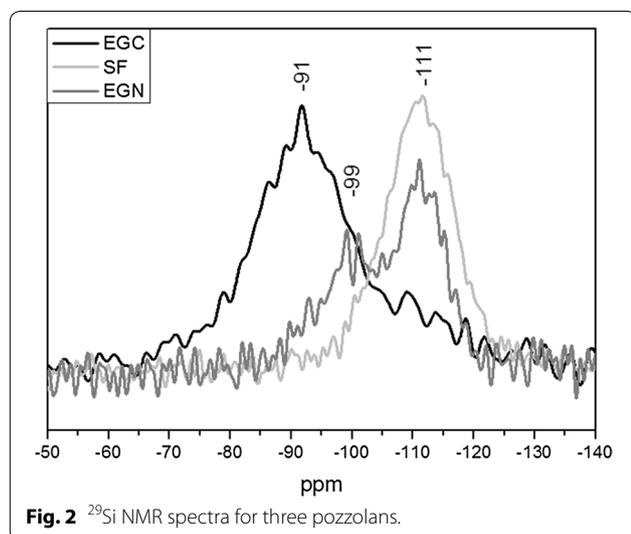


Fig. 2 ^{29}Si NMR spectra for three pozzolans.

The EGC ash spectrum contained a wide signal whose deconvolution revealed the presence of a big signal at -91 ppm attributed to Q^3 (2Al) from the amorphous phase identified by XRD (Smith and Blackwell 1983; Laridjani et al. 1999; Fyfe et al. 1983, 1986; Urbanova et al. 2013; Lagerblad et al. 2013). Additionally the deconvoluted spectrum shows another small signal at -111 ppm. The spectrum for silica fume also contained a wide signal with a maximum at -111 ppm, attributed to quartz.

Deconvolution of the spectrum for the EGN ash yielded three resonances: the most intense (-111 ppm) was associated with the Q^4 units in quartz, the middle intensity (-100 ppm) with Q^3 from $\text{Si}(\text{OSi})_3\text{OH}$ units and the less intense (-93 ppm) with Q^3 (2Al) units.

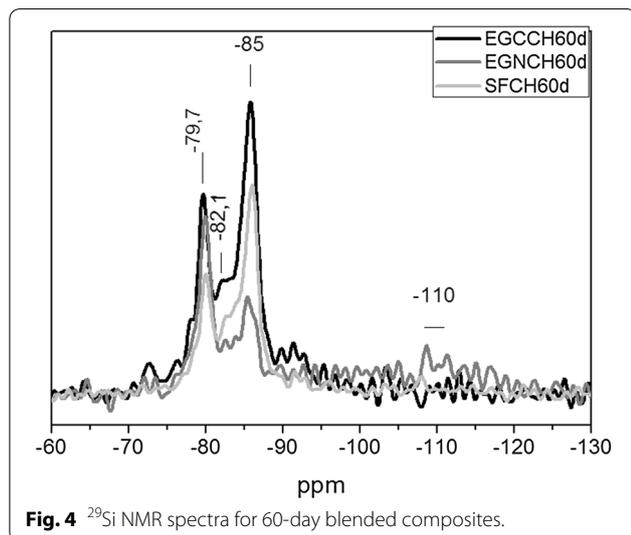
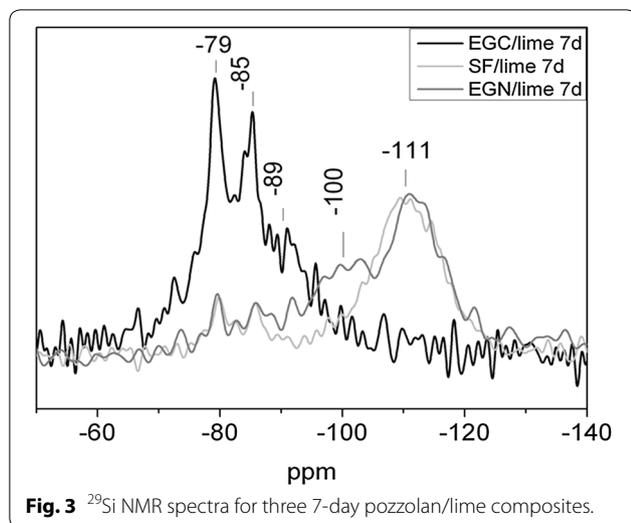
A significant change was observed in the spectrum for the 7-day EGC/lime paste (Fig. 3). The signals generated by the Q^4 units in the unreacted ash nearly disappeared, while two new narrow resonances, peaking at -79 and -85 ppm, were respectively attributed to Q^1 and Q^2 units. The spectra for the EGN/lime and SF/lime pastes exhibited minor changes: primarily the presence of low intensity resonances attributed to the aforementioned Q^1 and Q^2 units. These findings were indicative of higher initial reactivity in the EGC/lime paste, which was consistent with the fixed lime values determined with thermogravimetric methods in an earlier study from Nakanishi et al. (2014). See Fig. 3 and Table 2 for the results of signal deconvolution.

A comparison of these spectra to the spectra for the starting materials (Fig. 2) showed that the highest reactivity was recorded for the sample with the lowest Si content as well as minor number of Q^4 units.

Table 2 Results of deconvoluting ^{29}Si NMR spectra for blended composites (%).

	Initial			7 days			60 days		
	EGC (%)	EGN (%)	SF (%)	EGC/lime (%)	EGN/lime (%)	SF/lime (%)	EGC/lime (%)	EGN/lime (%)	SF/lime (%)
Q^3 (2Al) (-93 ppm)									
Q^3 (-100 ppm)		31.8				5.9		15.7	
Q^3 (-103 ppm)					40				
Q^4 (-111 ppm)	15.8	58.6	100	10.0	41.8	77.9		16.6	
Q^3 (-90 ppm)	84.2	9.5		30.6	2.9	2.7		6.3	
Q^2 (-82.3 ppm)				11.6	1.4	1.7	38.9	6.4	40.8
Q^{2p} (-83.2 ppm)									
Q^2 (1Al) (-85.3 ppm)									
Q^{2b} (-85.8 ppm)				13.0	8.5	5.5	43.7	23.4	42.5
Q^1 (-79 ppm)				15.7	5.3	6.2	17.4	31.4	16.7
Q^1 (-75.2 ppm)				19.0					
\bar{n}				2.1	1.6	1.5	1.8	1.5	1.8
PA				37	9.6	16	100	64	100

Obs. the highest band in each column is showed in italics.



After 60 days, the spectra for the EGC/lime and SF/lime pastes contained none of the initial signals. Moreover, although all treatments exhibited two narrow resonances at -85 and -79.7 ppm, the relationship between the intensities of the two signals was different (Fig. 4).

The spectrum for the EGN/lime paste, in turn, exhibited a resonance at -110 ppm associated with Q^4 units, an indication that it had not reacted completely after 60 days.

The signals present denoted Q^1 unit formation (-79.7 ppm), more in the paste containing EGN ash, while most of the resonance on the spectra for the other two pozzolans was attributed to the presence of Q^2 units (-85 ppm). The spectra for all the pastes

contained a shoulder of varying intensity at -82.1 ppm, associated with Q^2 (1Al) units.

With a view to monitoring silica fume reactivity, Le Saoût et al. (2006) calculated the mean tetrahedra connectivity for SiO_4 (\bar{n}) in C-S-H gel and the pozzolanic activity of the material (PA_{SF}) as follows:

$$\bar{n} = \left[Q^1 + 2Q^2 + 3Q^3 \right] / \left[Q^1 + Q^2 + Q^3 \right]$$

$$\text{PA}_{\text{SF}} = \left[Q_{\text{SF}}^4(t=0) - Q_{\text{SF}}^4(t) \right] / Q_{\text{SF}}^4(t=0)$$

When the values for elephant grass ash were entered into these equations, the connectivity figures ranged from 2.4 to 1.8 for EGC, with almost no changes for SF and EGN.

The PA value of the samples is 100% after 60 days of hydration for EGC and SF, but only 64% for EGN (Table 2). These results agree with Nakanishi et al. (2014) where less pozzolanic reactivity was observed for EGN. Additionally, in the previous paper it was also indicated that weight loss of the samples, in the interval $100\text{--}300$ °C, after 60-days of reaction was 46% for EGC; 34% for SF and 26% for EGN with less C-S-H formation for the last sample. In the same way the loss weight from portlandite was higher for EGN (26% against 8 and 7 for EGC and SF respectively), due to less pozzolanic reaction.

The composition, structure and morphology of the C-S-H gels forming in cements with supplementary cementitious materials (SCM) as additions are known to differ from the same properties in the gel resulting from ordinary cement hydration (Hjorth et al. 1988; Groves and Rodger 1989; Dai et al. 2014). SCM additions, three-dimensional silicon compounds consisting essentially of Q^4 units, are fragmented during gel formation. At the same time, the C-S-H gel induced by cement hydration is the result of the condensation of Q^0 and Q^1 units. Consequently, the nature of the two gels differs. Sáez del Bosque et al. (2013, 2014) reported that the presence of nanosilica in cement generated jennite-type C-S-H gels, which were more polymerised when the gel was the hydration product of plain cement.

The percentage variations in the Q^n units in the three materials studied are shown on the bar graph in Fig. 5.

Initially, ash EGC exhibited a high percentage of Q^3 units, whose content is reduced to zero after 60 days. Q^4 units were detected in 60-day EGN pastes, confirming that the pozzolanic reaction was slower in this ash. The initial material had practically no Q^3 and Q^1 units, which would explain the lower connectivity in both the 7- and 60-day pastes, with value of 1.4. The finer grain size in ash EGC than in EGN, would also have favoured

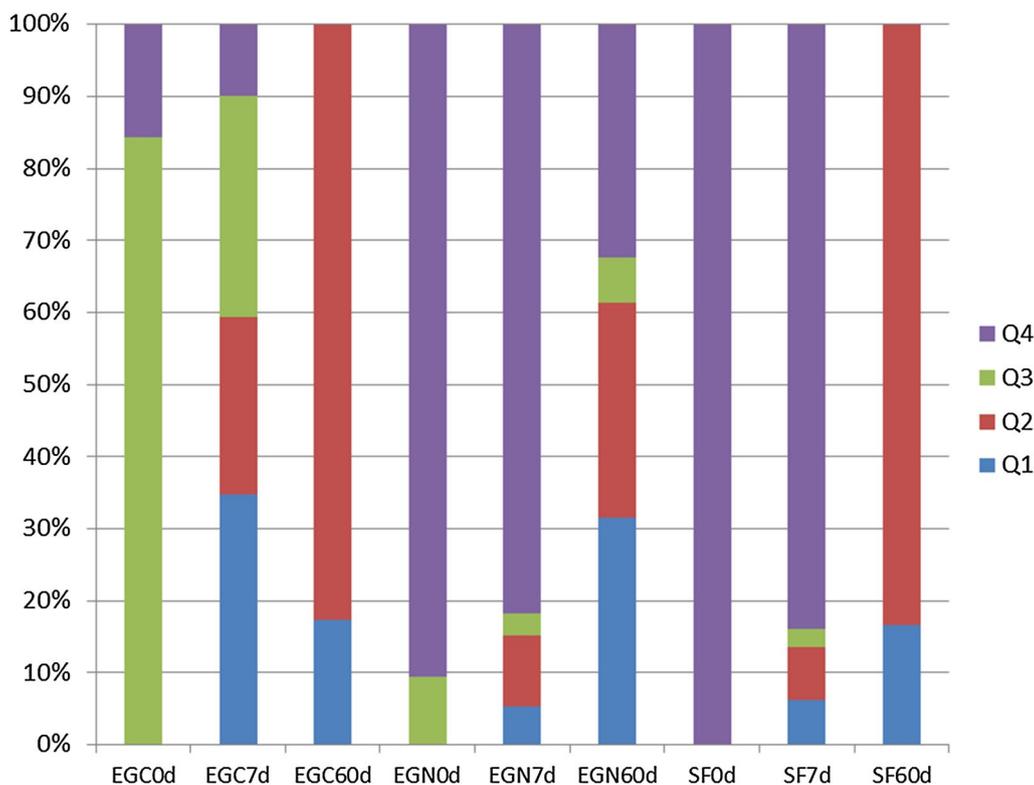


Fig. 5 Percentage of Q^n units in the starting materials and 7- and 60-day composites.

its greater reactivity. The two ashes were therefore observed to form C-S-H gels with different structures.

In the case of SE, the pozzolanic reaction was slow in the first 7 days, when a high percentage of Q^4 units were observed. Those units disappeared in the 60-day samples, however, and the Q^2 units rose.

Pozzolanic activity reached 100% in the 60-day EGC/lime and SF/lime pastes, whereas the value for EGN/lime paste was 64% at that age. Although 7-day reactivity was half in silica fume (16) than in EGC (37) paste, their 60-day values were similar.

Three pozzolans with different pozzolanicities were therefore obtained: one with high initial and final reactivity (EGC) which, at older ages, gave rise to highly polymerised gels; another with low initial but high final reactivity (EGS); and a third with low initial and final reactivity (EGN), which generated more weakly polymerised gels. These findings are consistent with the fixed lime values determined by Nakanishi et al. (2014), with accelerated chemical testing, where the reaction rate was observed to be: $EGC > SF > EGN$. The inference is that the pozzolanic reaction depends less on the total SiO_2 content than on the amount of reactive silica present, in this case associated with a higher Q^3 and a

lower Q^4 unit content. It has also to be considered that particle size of GEN is higher than for EGC.

Further to the findings observed and the variations in C-S-H gel structures with the variety of elephant grass used, future research might address the effect of structural change on the mechanical properties and durability of new eco-efficient cements manufactured with the type of ash studied here.

4 Conclusions

The use of elephant grass plants is a viable and sustainable solution for the production of cleaner and cheaper energy, but presents an environmental problem due to the large amount of ash generated. If disposed improperly in landfills, the ashes will cause environmental impact; instead of being clean production, they will result in environmental problems such as soil contamination. These may have an engineering application as pozzolanic material in the manufacture of low- CO_2 cements. In this paper the evolution of the pozzolanic reaction of two different types of elephant grass ashes are analyzed by ^{29}Si NMR technique, through the evolution of gel C-S-H formed. Initially the possible chemical compatibility of the two matrices is studied and determined that

both elephant grass ashes, Cameroon Elephant grass and Napier Elephant Grass, are a silica-rich (SiO_2) material and also contains varying amounts of calcium, potassium and phosphorus oxides, which makes them compatible with the nature of the cement.

Despite its lower silica content, EGC was the most reactive paste, with 7- and 60-day pozzolanic activity values of 37 and 100%, respectively. That greater activity, related to an abundance of Q^3 , prompted the formation of gels with high inter-tetrahedral connectivity.

In contrast, the EGN ash, with more total SiO_2 , exhibited lower reactivity than the EGC ash, with 60-day pozzolanic activity value of 64% and C-S-H gels characterised by low inter-tetrahedral connectivity from the earliest ages.

Considering the silica fume as reference pozzolan, the EGC shows a better pozzolanic behavior at all ages analyzed; while the EGN does not improve it at any ages.

From the ^{29}Si NMR results presented it can be possible to conclude that the high initial pozzolanic activity is due to the presence of Q^3 units in the ash. However, the presence of Q^4 promotes pozzolanic activity at longer ages, confirming again the usefulness of the NMR technique in the study of the pozzolanic reaction of this type of ashes, in order to select the most suitable ash from the engineering point of view.

Authors' contributions

SMR, MR and HS Jr. designed the project. EYN developed the samples preparation and characterization by XRD and XRF. SMR characterized the samples by NMR. All authors contributed to the analyses of the results and the writing of the manuscript. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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