Quantitative determination of phases in the alkali activation of fly ash. Part I. Potential ash reactivity


Eduardo Torroja Institute (CSIC), c/Serrano Galvache, nº 4, 28080 Madrid, Spain
Department of Inorganic Chemistry, University of Málaga, Campus s/n, 29071 Málaga, Spain

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Abstract

The various (vitreous and crystalline) components of two type F fly ashes are quantified in this paper using three techniques: chemical analysis with selective solutions, X-ray powder diffraction combined with the Rietveld method and nuclear magnetic resonance. The findings confirm the suitability of the techniques to pursue the objectives while providing further insight into the chemical composition of the vitreous phase of the ash as well as an understanding of the thermal history of these materials. Finally, the paper corroborates the grounds established in prior research for regarding the glassy constituents of an ash to be instrumental in the control of its alkali reactivity during the manufacture of ‘alkaline cements’.

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Keywords: Fly ash; NMR-MAS; Rietveld

1. Introduction

Fly ash is a by-product of coal-fired steam power plants. With the growing demand for energy, more and more ash is being generated (production is expected to reach 800 Mton by 2010). As only a small portion (30–40%) is used at present, the rest has to be disposed of, with the concomitant problems of space, risk of air pollution, leaching and ensuing pollution of inland and marine water. The use of this by-product in the construction industry has been and continues to be the subject of many research studies [1,2]. Important progress is being made in the search for further ways to recycle fly ash, such as the development of new types of binders known as ‘alkaline cements’, which take their name from the industrial process involved in their manufacture [3,4].

The alkali activation of fly ash (AAFA) is a distinctive procedure in which this grey powder (FA) is mixed with alkaline activators (alkaline solutions) and then cured at a certain temperature to produce a solid material. The glassy constituent of the fly ash transforms into a compact cement in the process. Previous studies [5–7] have shown that the main reaction product formed in AAFA is an amorphous alumino-silicate gel. Until very recently, this X-ray amorphous material has been difficult to characterise. Today, however, the evidence shows that it is a ‘zeolite precursor’: a short-range order material with a three-dimensional structure, in which the Si is found in a variety of environments, but predominantly as Q4(3Al) and Q4(2Al). Palomo et al. [5,8,9] reported finding an Al-rich phase (meta-stable/intermediate phase) after short curing times. This phase evolves with curing time to a more stable Si-rich phase (zeolite precursor). Indeed, it might be hypothesised that the final stage of fly ash alkali activation—in the very long term—may be crystallisation into zeolite.

The same authors recently published a paper establishing the fundamentals governing the reactivity of type F fly ashes as potential alkaline binders [10]. They reported that one of the main parameters in the control of the alkali activation process is the composition of the vitreous phase in the fly ash. In the light of those findings, the primary objective pursued in the present analysis (which, given its length,
is published in two parts), consisted of identifying and quantifying the proportion of glassy constituent and crystalline phases in the fly ashes from two different thermal power plants (part I), and identifying and quantifying the reaction products of these ashes after alkali activation (part II). Both analytical and instrumental techniques were used: Selective chemical treatments [11, 12], Rietveld X-ray powder diffraction (XRPD) [13,14] and $^{29}$Si and $^{27}$Al MAS NMR.

2. Experimental methods

Characterisation of raw materials. Two different type F fly ashes, identified as L and M, were used in this study. Table 1 gives the chemical composition and amount of reactive silica, in percent, found with analyses conducted to Spanish standards UNE 80-215-88 and UNE 80-225-93. Table 2 shows the particle size distribution of each fly ash in terms of the percentage of powder retained in different size sieves.

Selective chemical treatment with 1% HF. After characterisation, the ashes were treated with a 1% HF solution. This type of chemical treatment dissolves the vitreous phase of the ash, but not the crystalline phases (mullite, quartz, hematite, etc.). The procedure described by D.M. Roy [12] was followed: 1 g of ash was added to 100 ml of 1% HF in a plastic beaker, stirred for 6 h at ambient temperature and then filtered. The filter paper containing the insoluble residue was then washed to a neutral pH, placed in a platinum crucible and oven-dried for 1–2 h at 100 °C. Thereafter, it was calcined at 1000 °C and the vitreous phase was determined by subtracting the final from the initial mass. Ash L was subjected to a second HF treatment to verify the effectiveness of the method.

Techniques. Both the initial ash and the residue obtained after the 1% HF treatment were characterised mineralogically and microstructurally using XRPD (Rietveld quantitative analysis) and $^{27}$Al and $^{29}$Si MAS (Magic Angle Spinning) NMR.

2.1. XRPD

Sample preparation. Standard $\alpha$-Al$_2$O$_3$ was synthesised as follows: 6 g of $\gamma$-Al$_2$O$_3$ (99.997% from Alfa) was ground in an agate ball mill at 200 rpm for 30 min. The resulting powder was placed in a Pt crucible and heated at 1200 °C for 4 h. The oxide was allowed to cool to 150 °C over ~ 5 h and ground at room temperature in an agate mortar for 5 min. The sample was subjected to a second thermal treatment at 1300 °C for 6 h and then cooled as above. This standard was then ground in an agate mortar for 5 min and sieved (< 35 μm) prior to weighing. Each of the mixtures used for analysis was carefully ground in an agate mortar for 10 min, adding acetone to facilitate particle dispersion, and then heated at 60 °C. Around 30% (wt) of corundum was added, with the exact quantity recorded for each measurement. The samples were gently loaded (vertically) onto an aluminium X-ray sample holder.

X-ray data collection. Laboratory XRPD measurements were performed for all mixtures on a Siemens D5000 automated diffractometer with Cu K$_{\alpha1,2}$ radiation (1.5418 Å) and a secondary curved graphite monochromator. The readings were taken in vertical Bragg-Brentano ($\theta/2\theta$) geometry (flat reflection mode) between 18 and 70° ($2\theta$) at 0.03° steps, measuring 15 s per step. The samples were rotated at 15 rpm during acquisition to improve powder averaging, which is essential to have accurate intensities and hence good phase analysis. The D5000 diffractometer optic consisted of a system of primary Soller foils between the X-ray tube and the 2-mm fixed aperture slit. One 2-mm scattered-radiation slit was placed downstream of the sample, followed by a system of secondary Soller slits and a 0.2-mm detector slit. The X-ray tube operated at 40 kV and 30 mA.

X-ray data analysis. Rietveld refinement was used on the powder patterns [15], applying GSAS software [16] with a pseudo-Voigt function [17] and including a correction for asymmetry due to axial divergence [18]. The crystal structures used to interpret the powder patterns were taken from the Inorganic Crystal Structure Database (ICSD). The collection codes for each structure were: corundum 73725; $\alpha$-quartz 63532; mullite 66263; maghemite 87119; calcium oxide 61550; calcite 80869; aphthitalite 26018 and albite 68193. Neither the positional nor the thermal vibration parameters were refined. The parameters optimised were: background coefficients, cell parameters, zero-shift error, peak shape parameters (including anisotropic terms if needed), and phase fractions.

$^{29}$Si and $^{27}$Al MAS NMR spectroscopic characterisation was conducted with a Bruker apparatus, model MSL-400. The resonance frequencies used in this study were 79.5 and 104.3 MHz and the spinning rates were 4 and 12 kHz. The measurements were made at ambient temperature with

Table 1

<table>
<thead>
<tr>
<th>Oxide%</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>SO$_3$</th>
<th>Reactive SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA L$^a$</td>
<td>51.51</td>
<td>27.47</td>
<td>7.23</td>
<td>4.39</td>
<td>1.86</td>
<td>0.70</td>
<td>3.46</td>
<td>0.15</td>
<td>42.17</td>
</tr>
<tr>
<td>FA M$^b$</td>
<td>59.89</td>
<td>27.67</td>
<td>3.02</td>
<td>3.45</td>
<td>1.22</td>
<td>0.94</td>
<td>1.01</td>
<td>0.51</td>
<td>45.07</td>
</tr>
</tbody>
</table>

$^a$ Loss on ignition = 1.89 and insoluble residue = 0.40.

$^b$ Loss on ignition = 2.09 and insoluble residue = 0.20.
tetramethylsilane (TMS) and Al(H2O)63+ as external standards. The error in the chemical shift values was estimated to be lower than 1 ppm. Magnetic materials were removed from the samples prior to NMR spectra recording by exposing the sample to a strong magnetic field.

3. Results

Table 3 shows the insoluble residue content, in percent, found after treating the ash samples with 1% HF as described in the preceding section; the (soluble) vitreous phase content was computed by subtracting the mass of the residue from the initial mass of the material. The results for sample LHF2(R) were obtained by re-calculating the values found for sample LHF2 (second treatment) with respect to original ash L. A comparison of the values for samples LHF(R) and MHF shows that ash L has of the order of 25% more glassy phase than ash M.

Rietveld XRPD phase quantification was conducted on these same samples, both for the initial ash and the insoluble residue obtained after HF treatment, to determine the phases present and compare these results to the findings from chemical analysis. The vitreous constituent was quantified by mixing all samples with (approximately) 30% wt of corundum (Al2O3) as described above. Rietveld quantitative analysis of the amorphous content relates the overall amorphous/vitreous content, A (wt%), to the overestimation, in Rietveld refinement, of an internal crystalline standard, Al2O3. Assuming a standard with no amorphous phases, A is obtained from Eq. (1)

\[
A = \frac{1 - \left(\frac{W_S}{R_S}\right)}{100 - W_S} \times 10^4\% 
\]

where \(W_S\) (%) is the concentration by weight of the internal standard and \(R_S\) (wt%) its Rietveld-quantified concentration.

Fig. 1(a) and (b) contains the Rietveld plots for initial fly ashes L and M, respectively, which show that both ashes present a pattern (halo) typical of vitreous/amorphous materials at 2θ angles of between 20 and 30°. The signals corresponding to the crystalline phases found in the material—quartz, mullite and Fe2O3 in the form of maghemite—can also be seen in these diffractograms.

When the ash is treated with 1% HF, most of the halo associated with its glassy constituent disappears (see Fig. 2, traces (a) and (b), for ash L (LHF) and M (MHF), respectively). At the same time, these diffractograms evidence an increase in the intensity of the peaks associated with the crystalline phases, compared to the traces in Fig. 1.

The Rietveld plots for ashes M and L in Fig. 2 show that after the acid treatment the halo disappears almost completely from the former, whereas a significant portion of the vitreous phase of ash L remains undissolved (Fig. 2(a)—LHF). This is why the ash L HF-insoluble residue was subjected to a second treatment under identical conditions. The diffractogram in Fig. 3 shows the pattern for the insoluble residue obtained after this second treatment (sample LHF2).

Table 4 shows the results of Rietveld quantification of the diffractograms in Figs. 1–3. The values given in the table for the vitreous phase are higher for both ashes L and M than the results found with the chemical treatment procedure (Table 3). Nonetheless, these values, like the data in Table 3, show a higher glassy content in ash L than in ash M. It may likewise be deduced from these results that ash M has twice the mullite content and a third more quartz than ash L. The rather obvious inference of these findings is that the differences between vitreous and crystalline phase content of ashes M and L are the chief explanation for the differences in their reactivity in alkaline media, and therefore in the cementitious properties of the resulting product. In short, these results indicate that while the ashes are very similar in terms of both their physical and chemical properties (see Tables 1 and 2), their considerable mineralogical differences have a visible impact on their reactivity.

LHF and MHF, which have a clearly higher mullite content than the initial ash, were examined to ascertain
whether Rietveld refinement revealed differences in the degree of crystallinity of that phase that might be indicative of different crystallisation temperatures or Si/Al ratios in its chemical composition.

Table 5 lists the values of parameters \(a\), \(b\) and \(c\) and unit cell volume \((V)\) for mullite in both samples. The significance of these data merits some discussion, although the following is by no means intended as an in-depth structural review of mullite, a complex issue falling outside the bounds of the present study. Based on the papers by Cameron [19], Okada [20] and Fisher [21] (who sustain that parameters \(a\) and \(b\) change linearly with composition and the value of parameter \(c\) depends on the initial formation temperature), the mullite in both types of ash may be said to present orthorhombic polymorphism, inasmuch as parameters \(a\) and \(b\) are similar to one another and a doublet is found on their respective diffractograms at \(2\theta\) position = 26.2°.

With respect to the formation temperature, according to Okada [20], parameter \(c\) for mullite crystals formed at a temperature below 1200 °C is approximately 0.0005 nm smaller than for mullite crystals with the same composition but formed at temperatures of over 1200 °C. Assuming the mullite composition to be the same in ashes M and L, the parameter \(c\) values found in the present analysis (see Table 5) might suggest that ash L was formed at a higher
temperature than ash M. This would substantiate the findings reported here, to the effect that ash L has a higher vitreous phase content than ash M.

Finally, Fig. 4 contains the MAS NMR spectra for $^{29}\text{Si}$ and $^{27}\text{Al}$ in the initial ashes and the insoluble residues obtained after treating the samples with HF solution as described in the section on experimental procedure.

Generally speaking, the wide signals on the silicon spectra for the ashes (L and M) are indicative of matrix heterogeneity in terms of the distribution of the Si atoms. Table 6 gives the spectral deconvolution values obtained assuming constant bandwidth. These results show that the wide signal corresponds to the envelope of a series of signals. Hence, according to the literature, the peaks detected at $-84$, $-94$, $-98$ and $-103$ ppm correspond primarily to the vitreous phase content of the ash [5]; the peak appearing at around $-87/88$ ppm corresponds to the crystalline mullite present in the ash [22,23]; and finally, the peaks at values of over $-108$ ppm are attributed to the presence of different crystalline phases of quartz [$Q^4 (0\text{Al})$ signals] [24].

A large portion of the $^{29}\text{Si}$ NMR spectra for the initial ashes is missing in the spectra for the HF-insoluble residues.
(see Fig. 4); and indeed, the part that has disappeared is the area associated with the vitreous phase of the ash. The most reactive environments in the ash are usually the ones around Si atoms surrounded by 2, 3 or even 4 aluminia; these environments correspond to the signals appearing on the spectrum between $-84$ and $-103$ ppm. The signals located at values higher than $-108$ ppm, on the contrary, which are associated with the free silica component (such as quartz), show a visible increase in intensity. This serves as further confirmation that the acid treatment with 1% HF primarily affects the glassy constituent of the ash, and not the crystalline phases.

The results given in Fig. 4(b) for the $^{27}$Al MAS NMR spectra show that both initial ashes (L and M) present two wide components: one centred at $+51.6$ ppm, associated with tetrahedral aluminium ($\text{Al}_T$), and another smaller signal at around $+1$ ppm associated with octahedral aluminium ($\text{Al}_O$). The octahedral component is attributed to the aluminium in the mullite present in the ash. This greater intensity of this peak in ash M than ash L is particularly visible in the $^{27}$Al spectra for the HF-insoluble residues (samples LHF and MHF). The immediate deduction from these spectra is that the $\text{Al}_T/\text{Al}_O$ ratio is higher for ash L than ash M, corroborating the XRD findings, which showed that the latter had a higher mullite content.

### 4. Discussion

A previous paper [10] showed that the vitreous phase content of a fly ash is one of the factors determining its reactivity in alkaline media and therefore in the manufacture of alkaline cement. The results of the present study not only

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**Table 4**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Characteristics</th>
<th>Quantification by Rietveld XRD (% by mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Vitreous</td>
</tr>
<tr>
<td>L</td>
<td>Raw material</td>
<td>80.6</td>
</tr>
<tr>
<td>L HF$^b$</td>
<td>First HF treatment (IR = 35.1%)</td>
<td>41.8</td>
</tr>
<tr>
<td>L HF2</td>
<td>Second HF treatment (IR = 24.12%)</td>
<td>22.7</td>
</tr>
<tr>
<td>LHF2(R)</td>
<td>Re-calculation</td>
<td>5.47</td>
</tr>
<tr>
<td>M</td>
<td>Raw material</td>
<td>65.7</td>
</tr>
<tr>
<td>M HF$^b$</td>
<td>First HF treatment (IR = 45.72)</td>
<td>28.7</td>
</tr>
</tbody>
</table>

$^a$ CaO was also identified in this sample.

$^b$ IR = 1% HF-insoluble residue.

$^c$ Albite was also identified in this sample.

$^d$ Albite: 2.5% and CaO: 0.4%—were also identified in this sample.
confirm prior research, but also evidence the effectiveness of the methodology used to determine and quantify the vitreous constituents of fly ash.

The data obtained with the various techniques for the insoluble residue had to be reformulated with Eqs. (2) and (3) for comparison to the data for the initial ash:

\[ V_T(\%) = SR_{HF} + V_R \]  
\[ V_R = \frac{V_{XRPD} \times IR_{HF}}{100} \]  

where \( V_T \) is the percentage of total vitreous phase in the ash; \( SR_{HF} \) is the soluble residue (in 1% HF = dissolved vitreous phase) (see Table 3); \( V_R \) is the residual vitreous phase = (vitreous phase not dissolved after 1% HF treatment); \( V_{XRPD} \) is the % of any phase quantified by XRPD Rietveld analysis (see Table 4); \( IR_{HF} \) = 1% HF-insoluble residue (see Table 3).

Table 5

<table>
<thead>
<tr>
<th>Sample</th>
<th>( a(\text{Å}) )</th>
<th>( b(\text{Å}) )</th>
<th>( c(\text{Å}) )</th>
<th>( V(\text{Å}^3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHF</td>
<td>7.5749(6)</td>
<td>7.6971(6)</td>
<td>2.8886(2)</td>
<td>168.42(2)</td>
</tr>
<tr>
<td>MHF</td>
<td>7.5610(8)</td>
<td>7.6978(8)</td>
<td>2.8883(2)</td>
<td>168.11(3)</td>
</tr>
</tbody>
</table>

The data in Table 7 also indicate that the quantity of vitreous phase found with the chemical treatment are of the order of 10–15% lower than the results obtained with the Rietveld technique. This is interpreted as being due to the fact that the 1% HF treatment does not fully dissolve the entire glassy constituent of the ash and that a poorly crystallised (not XRD-detectable) fraction of mullite or quartz remains insoluble after the treatment.

Finally, the results obtained in this study also serve to determine the SiO\(_2\) and Al\(_2\)O\(_3\) content in the vitreous phase and therefore deduce the quantities of these compounds available to form the alkaline silico-aluminate gel that is the main product of the alkali activation reaction [5]. The values in Table 8 were found using Eqs. (4) and (5)

\[ [\text{SiO}_2]_{\text{vitreous}} = [\text{SiO}_2]_{\text{Total}} \text{ (see Table 1)} - [\text{SiO}_2]_{\text{quartz}} - [\text{SiO}_2]_{\text{Mullite}} \]  
\[ [\text{Al}_2\text{O}_3]_{\text{vitreous}} = [\text{Al}_2\text{O}_3]_{\text{Total}} - [\text{Al}_2\text{O}_3]_{\text{Mullite}} \]
In the case of ash M, the sum of SiO$_2$ dissolved in the vitreous phase (54.16%) is almost the same as the value determined by chemical treatment with 1% HF (54.28%, see Table 3). In the case of ash L, there is a small difference, as discussed above, which may be due to the existence of poorly-crystallised and therefore more amorphous phases that are nonetheless unaltered by the acid treatment.

Another finding of note in Table 8 is the low vitreous aluminium content in ash M, a factor that will prove to limit the reactivity of this ash.

The number of resonances appearing in the NMR spectra, in turn, is identical to the number of physically non-equivalent nuclei per unit cell. Initially, wide spectra are obtained for both types of ash. The presence of Q$^n$(nAl) units (where n=0,1,2,3,4) may be deduced from signal deconvolution. When the samples are treated with 1% HF (samples LHF and MHF, see Fig. 4), the Si atoms surrounded by the largest number of Al are the first to be attacked. Normalising as per Eq. (2) yields the percentages of the different units dissolved, which are shown in Table 9. These findings indicate that structural units Q$^4$(4Al), Q$^4$(3Al) and Q$^4$(2Al) (signals $K_{88}$, $K_{94}$, $K_{98}$ ppm) are most readily dissolved, whereas the signals associated with the units Q$^4$(1Al) and Q$^4$(0Al) are much less soluble in the HF medium.

Another interesting finding (observed in the 29Si MAS NMR spectra for the 1% HF-insoluble residue) is the greater intensity of the signals appearing in chemical shifts of over $K_{108}$ ppm (associated with quartz-type phases) compared to the mullite signals (from $K_{87}$ to $K_{94}$ ppm). Such higher signal intensity does not necessarily denote a greater amount of quartz than mullite in these samples, and indeed, as the Rietveld XRD quantification showed, the mullite content is higher than the quartz content in both. Rather, this finding may be a reflection of the fact is that in NMR spectra the number of resonances is equal to the number of physically

| Table 6 | Results of $^{29}$Si MAS NMR spectral deconvolution for the fly ashes |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Chemical shift (error ± 1 ppm) | 84 | −88 | −94 | −98 | −103 | −108 | −113 | −118 |
| L | Pos. (ppm) | −84.0 | −88.3 | −93.6 | −98.6 | −103.4 | −108 | −115 |
| | Width | 7.15 | 7.15 | 7.15 | 7.15 | 7.15 | 7.15 | 7.15 |
| | Integration (%) | 5.32 | 11.0 | 16.98 | 20.66 | 19.46 | 20.9 | 5.61 |
| LHF | Pos. (ppm) | −88.5 | −93.0 | −97.5 | −102.8 | −108.6 | −114.5 |
| | Width | 7.48 | 7.78 | 7.78 | 7.78 | 7.78 | 7.78 |
| | Integration (%) | 9.34 | 10.39 | 12.24 | 33.76 | 23.53 | 10.74 |
| M | Pos. (ppm) | −89 | −95.2 | −99.4 | −104 | −109 | −116 |
| | Width | 8.52 | 8.52 | 8.52 | 8.52 | 8.52 | 8.52 |
| | Integration (%) | 14.25 | 7.76 | 9.15 | 17.58 | 34.17 | 16.84 |
| MHF | Pos. (ppm) | −86 | −89.7 | −94.6 | −99.10 | −103.2 | −108.2 | −113.2 | −118.5 |
| | Integration (%) | 10.51 | 11.21 | 9.19 | 7.08 | 12.31 | 31.50 | 13.91 | 4.29 |

| Table 7 | Total vitreous ($V_T$) and crystalline ($V_{XRD}$) phase content in the ashes |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Method | Phase | Sample |
| | | L | LHF | LHF2 | M | MHF |
| Chemical treatment | Vitreous phase | 64.94 | 76.18 | | | |
| XRPD Rietveld quantification | Vitreous phase | 80.6 | 79.57 | 81.35 | 65.7 | 67.40 |
| Quartz | 6.3 | 5.75 | 6.05 | 10.8 | 10.51 |
| Mullite | 11.7 | 13.37 | 11.57 | 22.6 | 20.6 |

In the case of ash M, the sum of SiO$_2$+Al$_2$O$_3$ dissolved in the vitreous phase (54.16%) is almost the same as the value determined by chemical treatment with 1% HF (54.28%, see Table 3). In the case of ash L, there is a small difference, as discussed above, which may be due to the existence of poorly-crystallised and therefore more amorphous phases that are nonetheless unaltered by the acid treatment. Another finding of note in Table 8 is the low vitreous aluminium content in ash M, a factor that will prove to limit the reactivity of this ash.

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| Table 8 | Oxide content in the fly ashes |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Fly ash | SiO$_2$ | Al$_2$O$_3$ | SiO$_2$/Al$_2$O$_3$ | SiO$_2$+Al$_2$O$_3$ |
| L | Total | 51.51 | 27.47 | 1.87 | 78.98 |
| | Vitreous phase | 40.53 | 20.45 | 1.98 | 60.98 |
| M | Total | 59.89 | 27.67 | 2.16 | 87.56 |
| | Vitreous phase | 40.05 | 14.11 | 2.84 | 54.16 |

These calculations were performed assuming that all the mullite present in the system is orthorhombic.
non-equivalent nuclei per unit cell present in the system, whereas signal intensity provides an indication of the total number of nuclei in that position. For this reason, the signals for Si atoms in environments rich in Al (Q^4(4Al)), such as in the case of mullite, are less intense.

According to findings reported by Gomes and Francois [23], mullite generates an NMR signal at around $K_{87}$ ppm that corresponds to tetrahedral SiO$_4$ surrounded by three tetrahedral AlO$_4$ and one polyhedral AlO$_6$. At the same time, this phase generates other signals at $K_{90}$ and $K_{94}$ ppm that correspond, respectively, to one or two SiO$_4$ substituting for a tetrahedral AlO$_4$. Consequently, the intensity changes in these signals must be attributed to the extent to which the Si and Al atoms combine in the mullite.

The $^{27}$Al MAS NMR spectra of the ashes, in turn, essentially comprise two resonances: one at around 53/54 ppm and the other at $+2/-2$ ppm. The strong resonance at 53/54 ppm is indicative of the existence of a majority of AlO$_4$ as opposed to AlO$_6$ units. In other words, it evidences the existence of –Si–O–Al– bonds. The greater quantity of octahedral aluminium in ash M than ash L, in turn, is seen more clearly when the $^{27}$Al MAS NMR spectra for the HF-insoluble residues are compared. These spectra seem to suggest that the AlO$_4$ content increases after the chemical treatment, when in fact it is the quantity of Al$_T$ that declines, since it is partially dissolved by the HF solution. These samples (LHF M, see Fig. 4) have another resonance at around 43/44 ppm, attributed to the tetrahedral aluminium units in the mullite. This signal is much sharper on the MHF than the LHF trace, because the former has a higher mullite content. It has been shown [19–21] that the higher the calcination temperature, the higher the Si content in mullite, which is tantamount to saying that its Al$_T$ content rises while its AlO$_4$ content drops.

In the light of these observations it is reasonable to assume that ash M was produced at a lower calcination temperature than ash L, providing further support for the hypothesis that ash M has a lower vitreous phase content and the mullite in ash M has a higher AlO$_4$ content.

5. Conclusions

- The three techniques used in the study—chemical analysis with selective HF acid solution, Rietveld X-ray powder diffraction quantification and nuclear magnetic resonance—can be regarded as being highly effective in characterising and quantifying the phases present in fly ash.
- Thanks to the complementary nature of these techniques, the information they generate can be used (in addition to obtaining a fairly accurate quantification of the vitreous phase content of fly ash), to deduce information on the thermal history of an ash and the SiO$_2$ and Al$_2$O$_3$ content present in its vitreous phase.
- A way to measure the Al$_2$O$_3$ content of the vitreous phase of an ash has been described. The role played by this oxide is essential in the correct establishment of the chemical reactions taking place in the alkali activation processes.

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