



## Fly ash from a Mexican mineral coal I: Mineralogical and chemical characterization

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### ABSTRACT

The properties of coal fly ash are strongly dependent on the geological origin and the combustion process of the coal. It is important to characterize regional fly ash in detail to ascertain its potential uses as raw material in the production of high value products. The physicochemical properties of fly ash coming from the "Jose Lopez Portillo" coal-fired power plant, Coahuila, Mexico (MFA), are presented in this work. A detailed study of trace elements, the chemical composition of the amorphous phase, thermal stability and the leaching of contaminant elements under different conditions are included. MFA is composed of mullite, quartz, calcite, magnetite and an amorphous phase. This material contains mainly silica (59.6%), alumina (22.8%) and magnetite (5.6%). Its amorphous phase (78.3%) has a high silica (49.4%) and alumina (14.4%) content. According to its mineralogical and chemical composition, MFA is potentially useful as a raw material for making cement, silica, and alumina, as well as low silica/alumina ratio zeolites. Deleterious elements could be removed during the zeolitization process or with an additional acid treatment. Because of its morphological properties and structural and thermal stability, MFA can be used in thermal isolation and refractory materials and as a support for heterogeneous catalysts.

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### 1. Introduction

Several studies have reported the danger that arises during the handling and disposal of fly ash obtained as a byproduct of mineral coal combustion. The relevant conclusions from these studies [1] were as follows: (1) the management of fly ash produced by coal-fired power plants is considered a major problem in many parts of the world, (2) fly ash should be used as much as possible to reduce the environmental inventory, (3) better understanding is needed about the mobilization of potentially hazardous chemical elements from ash residue and the environmental impact of their disposal and use, and (4) new, efficient applications of fly ash as a raw material are needed. To discover the potential applications of fly ash, it must be characterized completely [2], as different conditions during incineration give rise to different coal fly ash properties [3]. These components of coal fly ash that differ in morphology and texture give the ash different chemical compositions [4].

Even though trace metals are present as a relatively small fraction in fly ash, they are of special interest due to their cumulative

build-up, long life, and high toxicity to humans, plants, and animals. Because trace elements existing in fly ash can leach out and contaminate soil, as well as surface and groundwater, their study has become important for environmental protection [1]. Fly ashes from several countries were studied, including those from Spain, Italy, the Netherlands [5,6], Greece [7], Turkey [8], England [9–11], Russia [12], China [13], the United States [4,14,15] and Argentina [16].

Fly ashes have been applied in composite cements [17,18], as a support for catalysts [19], as raw material for the recovery of highly valued metals [20,21], in concrete [22], in silica extraction [23], and in low Si/Al zeolite synthesis [24]. According to our own results, zeolitization of MFA results in faujasite X, analcime, and P and W zeolites [25].

The main reserve of mineral coal in Mexico is located in the state of Coahuila. Currently, 11.2 million tons of mineral coal are extracted per year for use in the iron and steel industry, but it is mainly used to produce electricity in the two coal-fired power plants "Jose Lopez Portillo" and carbon II [26]. The "Jose Lopez Portillo" coal-fired power plant burns 15,000 tons of a mixture of coals (80% long flame sub-bituminous and 20% bituminous coal) daily to produce 1,200,000 kW/h of electricity and around 2700 tons/day of solid residues. To use this coal for producing energy, it is conveyed from an external stack and ground to a very fine powder.

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The pulverized coal is then mixed with preheated air and driven by a forced-draught fan. This hot air–fuel mixture is forced at high pressure into the boiler where it rapidly ignites. Exhaust gas from the boiler is drawn by the induced draft fan through an electrostatic precipitator and is then vented through the chimney stack. Near 80% of the solid residues (fly ash) is recovered in the electrostatic precipitators. The main destination of this recovered material is an open landfill.

In this work, MFA coming from the “Jose Lopez Portillo” coal-fired power plant, located 24 km south of Piedras Negras, Coahuila, Mexico, was characterized in detail to evaluate its potential as a raw material in the production of high value products, increasing the productive chain of coal. Special emphasis was placed on determining the mineralogical components, the chemical composition of the amorphous phase, the thermal stability of the crystalline phase, the content of trace elements, and the degree of leaching under acidic conditions. Comparing the properties of MFA with those reported for other fly ashes, it could be presumed that MFA is potentially useful for producing high value products.

## 2. Experimental

### 2.1. Materials and chemical reagents

The MFA was obtained from the “Jose Lopez Portillo” coal-fired power plant located in Coahuila, Mexico. A composite sample of 700 kg of fly ash was randomly taken from a landfill and re-sampled by the quarter method using Johnson equipment [27]. A sample of 40 kg was obtained and subsequently kept in hermetically sealed bottles until analysis or use as a raw material to obtain derivative products. All reagents used were analytical grade and obtained from Merck.

### 2.2. Characterization of fly ash

Mercury and moisture content were analyzed in MFA as it was sampled. A representative sample of about 500 g was previously dried at 60 °C overnight and used to determine the major, minor, and trace elements, in addition to the other parameters described below. The results were averaged and presented as MFA properties.

#### 2.2.1. Chemical characterization

The mercury content in the fly ash was determined without drying using an AMA 254 LECO analyzer. Mercury values were corrected for moisture content. Major, minor and trace element concentrations were determined after acid treatment using a special two-step method devised for the analysis of trace elements in coal and combustion wastes by inductively coupled plasma mass spectrometry (ICP–MS) and inductively coupled plasma atomic emission spectrometry (ICP–AES) [28]. First, volatile metals were extracted with HNO<sub>3</sub> in closed Teflon perfluoroalkoxy reactors at 90 °C for 6 h. The solid residue isolated by centrifugation was dissolved in a solution of HF:HNO<sub>3</sub>:HClO<sub>4</sub>. The resultant solution was dried and re-dissolved in HNO<sub>3</sub>. The fly ash international reference material NBS 1633b, obtained from the National Institute of Standards & Technology, USA, was also digested to verify the accuracy of our analytical methods. The silica content was determined directly in solid samples by X-ray fluorescence. Other elements were analyzed by ICP–MS and ICP–AES in the resultant aqueous acid digestion solution using the analytical conditions developed by Querol et al. [28] and Tait and Ault [29]. Finally, the carbon and sulfur content were determined using a LECO CS244 elemental analyzer.

#### 2.2.2. Mineralogical characterization

The MFA sample was homogenized and then dried for 6 h at 105 °C. MFA mineralogical characterization was determined by X-ray diffraction (XRD) using a Bruker D5500 powder diffractometer with a graphite monochromator, NaI(Tl) detector, and Cu K $\alpha$  radiation. Quantitative XRD analysis was performed according to the Reference Intensity Method (RIM) described by Chung [30,31]. Scans were performed between 2 $\theta$  values of 10–70° with a step size of 0.028°, and CaF<sub>2</sub> was used as an internal standard. Samples composed of 0.75 g of MFA and 0.25 g of CaF<sub>2</sub> were prepared and analyzed by XRD. The 2-theta peaks on 3.35 for quartz, 4.05 for cristobalite, 3.39 for mullite, 3.03 for calcite and 3.15 for fluorite were selected, and their corresponding areas were measured. The content of crystalline and amorphous phases was calculated according to the following equations:

$$\text{Dilution factor, \%} = \frac{100}{\text{MFA in sample}}$$

$$\text{Crystalline phase, \%} = \left[ \frac{A_{\text{Phase}} \times \text{fluorite, \%}}{A_{\text{Fluorite}} \times K_{\text{phase}}} \right] \times \text{dilution factor}$$

$$\text{Amorphous phase, \%} = 100 - \sum \text{crystalline phases}$$

where  $A_{\text{Phase}}$  and  $A_{\text{Fluorite}}$  are the areas of the chosen peaks of the corresponding phases and the internal reference, respectively;  $K_{\text{phase}}$  is the proportionality constant defined according to the method proposed by Klug and Alexander [32] using peak area.

#### 2.2.3. Physical properties

The moisture content was determined by the weight difference between room temperature and 105 °C, and the volatile material (LOI) content was determined by the weight difference between 105 and 1075 °C. In both cases, the maximum temperature was held constant for 4 h. The particle size distributions of MFA were determined by laser diffraction particle size analysis (Malvern MASTERSIZER/E<sup>®</sup>) using ethanol as the dispersant. To measure specific area and pore volume, samples were degassed at 300 °C in Quantachrome Autosorb-1 equipment and analyses were carried out at –196 °C. The specific area was calculated with a multipoint BET equation and the pore volume was calculated from the maximum adsorption amount of nitrogen at  $P/P_0 \approx 0.99$ .

### 2.3. Morphological analysis

The morphology of different crystalline phases identified by XRD was inferred by combining the results obtained by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX). Samples were coated with graphite and analyzed with a JEOL JSM-8440 Scanning Microscope.

#### 2.3.1. Glass composition

Chemical composition of the amorphous phase, commonly called glass matrix was obtained from the chemical mass balance using the chemical and mineralogical data of MFA. The proportion of crystalline and amorphous phases was determined by XRD, based on the area of the selected peak. The glass content was then obtained by subtracting the volatile materials (LOI) from the total amorphous phase. The content of bulk oxides of MFA was determined by chemical analysis. Total oxides in the amorphous phase were determined by subtracting the sum of the oxides contained in the crystalline phases from the bulk oxide content. The total metallic oxide in the glass was obtained by dividing 100 times the oxide in the amorphous material by the glass content obtained from the mineralogical composition.

**Table 1**  
Chemical composition of MFA and comparison with other fly ashes.

%	MFA	C.I. <sup>a</sup>	NBS 1633b certified	NBS 1633b	European [5]	UKQAA [34]	Puertollano Spain [5]
Al <sub>2</sub> O <sub>3</sub>	22.82	0.0068	28.4	26.75	17.6–35.6	24–32	27.4
CaO	3.11	0.0032	2.1	2.04	0.5–11.8	1.8–5.3	0.8
Fe <sub>2</sub> O <sub>3</sub>	5.57	0.0017	11.1	10.96	2.6–16.0	7–15	7.3
K <sub>2</sub> O	1.28	0.0007	2.3	2.32	0.4–4.0	2.3–4.5	2.4
MgO	0.87	0.0002	0.8	0.76	0.8–3.8	1.2–2.1	1.0
SiO <sub>2</sub>	59.6	0.0606	49.2	49.24	41.1–59.6	48–52	58.6
Na <sub>2</sub> O	0.45	0.0003	0.3	0.27	0.1–1.2	0.8–1.8	0.3
SO <sub>3</sub>	0.4	0.0002	0.5	0.51	0.1–8.6	0.3–1.7	0.2
TiO <sub>2</sub>	0.94	0.0003	1.3	0.34	0.5–2.6	0.9–1.1	0.7
P <sub>2</sub> O <sub>5</sub>	0.04	0.00005	0.5	0.54	0.1–1.7	ND	0.1
Carbon	5	0.0046	ND	ND	0.6–7.6	ND	0.7
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	2.61	–	1.73	1.84	1.2–2.8	1.6–2.2	2.1
Pozzolanic reactivity	88.00	–	88.8	86.9	74.5–93.3	79–99	93.3

Concentrations are in weight %.

<sup>a</sup> Confidence interval (95%).

### 2.3.2. Thermal stability

The thermal stability was determined by gravimetric and differential thermal analysis (TGA and DTA) using Pyris Diamond TG/DTA equipment. The sample was heated under an air atmosphere from room temperature to 1200 °C at a rate of 10 °C min<sup>-1</sup>. To explain the energy and mass changes observed as a consequence of this heating, different samples were heated for 4 h at 60, 105, 450, 750, 1075 and 1200 °C. They were then analyzed by XRD and the phase content was calculated as a function of the area of the measured peaks.

### 2.3.3. Leaching test

To determine the potential mobility of trace elements from MFA, the European Union leaching test (EN 12457) [33] was applied. The leaching test was performed at a liquid/solid ratio of 10 L/kg with a stirring time of 24 h and deionized water as the leachant. A blank sample was prepared in addition using deionized water. At the end of the leaching process, the samples were filtered, and the content of major and trace elements in the leachates were determined by means of ICP–AES and ICP–MS. To promote trace pollutant leaching without changing the nature of the MFA, the leachant was acidified with 5 milliequivalents of acetic (CH<sub>3</sub>COOH) or oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>). The conductivity and pH were monitored during these tests.

## 3. Results and discussion

### 3.1. Characterization of fly ash

#### 3.1.1. Chemical characterization

The chemical composition of the MFA was put further into context by comparing with other thoroughly studied fly ashes, such as European [5] and English fly ashes (UKQAA) [34]. Additionally, Puertollano Spanish fly ash has been specifically used for comparative purposes as it has proven to be one of the most successful fly ashes in regard to silica extraction [23] and further zeolitization [24]. The composition of MFA and a fly ash certified standard (NBS 1633b), as well as European and English fly ash data, are shown in Table 1. The experimental values obtained for the NBS 1633b fly ash were used as a reference to check the accuracy of the analytical and digestion methods applied in this study. The obtained results were very similar to the certified composition. On average, analysis of the main oxides in the reference material resulted in values that were 97.6% of the certified values. This result testified to the reliability of this method in determining the composition of the MFA.

As in the case for European fly ash, MFA consisted mainly of silica (59.6%), alumina (22.8%) and iron oxides (5.6%). According to

the classification of the American Society for Testing and Materials (ASTM C618-92a [35]), the MFA investigated in this study could be classified as a class F fly ash. Furthermore, MFA has pozzolanic properties and is characterized by a total SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> content of 88% and a total SO<sub>3</sub> content of 0.4%. The losses in weight observed when MFA was heated at high temperature were attributed to the oxidation of carbon (5%) and sulfur (0.4% as SO<sub>3</sub>) compounds in MFA.

MFA was found to have the highest SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio (2.6) and pozzolanic activity of the characterized fly ashes. It contained low K<sub>2</sub>O (1.3%), Na<sub>2</sub>O (0.4%), TiO<sub>2</sub> (0.9%), and P<sub>2</sub>O<sub>5</sub> (0.04%) levels compared with European fly ash. MFA also had similar properties to fly ashes reported as raw materials used to synthesize zeolites [36] and geopolymers [6], and for silica extraction [24,37].

Trace element concentrations of MFA are shown in Table 2. The mercury content of MFA, corrected for moisture, was 0.195 ppm. Additionally, it was worth noting that MFA had lower concentrations of a number of trace elements, namely Pb, Zn, Sb, Ge, As, and Cr, than the Puertollano fly ash, chosen from several European fly ashes as a raw material to obtain silica [5] and to synthesize zeolites. Due to the relatively low levels of leachable trace elements, MFA could be directly converted into zeolite. MFA could have additional advantages in that the resultant zeolites could be used for specialized purposes, such as water treatment and acid catalysis.

In addition to the elements reported for European fly ash, other elements were analyzed in MFA to have preliminary information about two important aspects: (a) its potential usefulness as a source of rare earths and other transition metals used in petroleum refining catalysts and in many modern technological devices; and (b) the environmental risk posed by the presence of contaminant heavy metals in the MFA exposed to the action of rain and air. The additional detected metals were reported in ppm: Cs (5), Mn (153), Tl (5), Sc (14), Ga (39), Y (29), Zr (236), Nb (26), Sn (5), La (40), Ce (79), Pr (10), Nd (37), Sm (5), Eu (1), Gd (6), Tb (1), Dy (6), Ho (1), Er (3), Yb (4), Hf (5), Ta (7), W (5), and Bi (1).

#### 3.1.2. Mineralogical properties

The proportionality constants calculated according to the method proposed by Klug and Alexander [32] were 1.75, 0.15 and 1.5 for quartz, mullite and calcite, respectively. The dilution factor was calculated from the experimental composition of the samples prepared as described in Section 2.2.2. The obtained values were between 1.3340 and 1.3362 for the MFA studied. Areas of the chosen peaks were measured, and the content of the MFA phases was calculated. The obtained results are summarized in Table 3.

Some of the major phases present in the fly ashes were aluminosilicate glass, mullite (Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub>), quartz (SiO<sub>2</sub>), calcite

**Table 2**  
Comparative analysis of trace elements in MFA.

Element	MFA	C.I. <sup>a</sup>	NBS 1633b certified	NBS 1633b	European [5]	UKQAA [34]	Puertollano Spain [5]
As	40	0.1316	136	127	22–162	4–109	140
B	157	1.0730	–	89	24–534	5–310	534
Ba	589	0.2540	709	800	311–3134	<1–36,000	460
Be	5	0.0067	–	14	3–34	–	14
Cd	0.9	0.0038	0.8	1.4	1–6	<1–4	5
Co	13	0.0137	50	50	20–112	2–115	31
Cr	44	0.0916	198	199	47–281	97–192	108
Cu	46	0.0349	113	121	39–254	119–474	75
Ge	12	0.0170	–	17	1–61	–	61
Hg	0.2	0.0002	0.14	0.1	<0.01–1.4	–	1.3
Li	99	0.0998	–	183	36–377	–	185
Mo	11	0.0233	–	21	5–22	3–81	11
Ni	22	0.0409	121	119	49–377	108–583	96
Pb	46	0.0271	68	71	40–175	<1–976	1075
Rb	52	0.0657	140	138	22–202	–	139
Sb	4	0.0033	6	6	1–120	1–325	120
Se	6	0.0780	10	10	3–30	4–162	7
Sn	5	0.0042	6	8	4–15	933–1847	10
Sr	302	0.1584	1041	1101	131–4406	–	131
Th	25	0.0164	26	28	17–65	–	30
U	9	0.0034	9	8	5–29	–	15
V	116	0.0610	296	283	154–514	292–1339	202
Zn	94	0.1218	210	208	70–924	148–918	924

<sup>a</sup>Confidence interval (95%); concentration of trace elements given in ppm.

**Table 3**  
Mineralogical composition of MFA and others fly ashes.

	Quartz (au)	Mullite (au)	Calcite (au)	Fluorite (au)	Quartz (%)	Mullite (%)	Calcite (%)	Amorphous (%)
MFA-1	16	1.98	0.92	36	8.5	12.3	0.6	78.7
MFA-2	18	1.91	0.74	28	12.3	15.3	0.6	71.8
MFA-3	19	1.68	0.45	48	7.6	7.9	0.2	84.3
C.I. <sup>a</sup>	0.06	0.01	0.01	0.36	0.09	0.13	0.01	0.23
MFA <sup>b</sup>	–	–	–	–	9.47	11.83	0.47	78.27
European [5]	–	–	–	–	1.7–12.5	0.3–40.4	<0.3–0.6	48–89
UK [38]	–	–	–	–	1.5–10.8	1.2–8.3	–	74–90
Puertollano [5]	–	–	–	–	10.4	20.7	<0.3	65

<sup>a</sup> Confidence interval (95%).

<sup>b</sup> Average; area units (au).

(CaCO<sub>3</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>). The background hump between 10 and 40° in the X-ray spectrum provided additional evidence of the presence of an amorphous phase. The very few differences observed in the mineralogical composition might be attributed to the heterogeneity of the components in the mixture. The MFA composition was considered as the average obtained from the analysis of quartz (9.5%), mullite (11.8%), calcite (0.5%) and the amorphous material (78.3%). A comparison with European and English fly ash is also included in Table 3. MFA was found to be one of the fly ashes with the highest amorphous material and lowest quartz and mullite contents. These are two important characteristics that point to high MFA reactivity in direct conversion processes, such as alumina and silica extraction and zeolite synthesis, among others. MFA has properties similar to United Kingdom fly ashes, used as a cement component in concrete [38], so MFA could be useful in the production of concrete.

### 3.1.3. Physical characterization

The characterized MFA was a dark gray powder consisting of spheres, grains, crystals and agglomerated particles. Due to coal burning, the gray color changed to a slight reddish color from heat treatment under the LOI conditions. Nevertheless, all of the MFA physical parameters were between the ranges reported for different European fly ashes [5], but there were important differences in moisture content (7.75%) and LOI value (4.45%) with respect to the fly ash (Puertollano) chosen as a reference in this study (0.1 and 1.1%, respectively, Table 4). The source of the fly ash samples could explain these differences in moisture content. While MFA was sampled from an open landfill, European fly ashes were directly collected in electrostatic precipitators. Furthermore, LOI was higher in MFA than in Puertollano fly ash because of the higher carbon (5.0 vs. 0.7%) and calcite content (0.47 vs. <0.3%).

The MFA samples studied revealed very similar particle size distribution, apparent density, specific surface area, and LOI values. On

**Table 4**  
Physical properties of MFA and comparison with others.

	Perc 10	Perc 50	Perc 90	$d_a$ (g cm <sup>-3</sup> )	BETSA (m <sup>2</sup> g <sup>-1</sup> )	Moisture (%)	LOI (%)
MFA-1	6.59	50.08	140.35	0.880	4.73	6.86	4.39
MFA-2	12.18	60.05	175.92	0.882	–	8.36	4.37
MFA-3	10.36	53.64	161.84	0.869	–	8.04	4.60
Puertollano [5]	4.7	26.2	123.8	0.7	2.7	0.1	1.1
European [5]	2.3–14	11.8–82	43.8–332	0.5–1.1	1.3–12.4	0.01–2.4	1.1–8.1

Apparent density ( $d_a$ ); LOI: at 1050 °C for Puertollano and the other fly ashes and 1075 °C for MFA; BET specific surface area (BETSA); Percentiles (Perc)

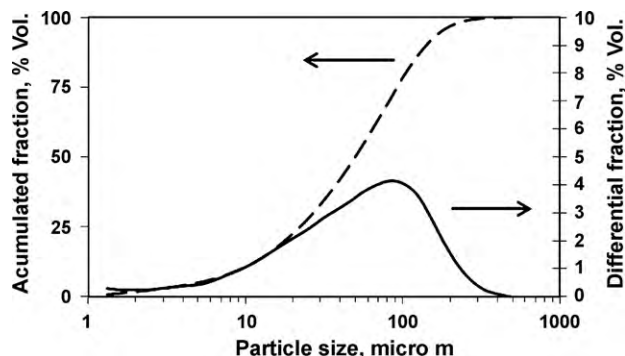


Fig. 1. Particle size distribution of MFA and the accumulated fraction.

average, 9.7% of the particles had a size less than 10  $\mu\text{m}$  and 10% of the material had a size greater than 160  $\mu\text{m}$ , with the 50th percentile particle size at 55  $\mu\text{m}$ . All of the studied MFA samples had a Gaussian asymmetric monomodal distribution, as shown for a composite sample in Fig. 1.

The small particle size of the fly ashes, including MFA, was another advantageous factor for the reactivity of the materials in transformation processes. However, there was a large problem in handling them during conditioning, storage or disposal of the fly ash because of its low apparent density and the fraction of the ash with a particle size less than 10  $\mu\text{m}$  ( $\text{PM}_{10}$ ). In MFA, 9.7% of the total particles were  $\text{PM}_{10}$  particles, considered breathable and potentially dangerous to human health.

#### 3.1.4. Morphological analysis

As was discussed before, MFA was a mixture of unburned organic materials and different inorganic phases. MFA was mainly composed of spherical hollow particles (cenospheres and pleurospheres), as shown in Fig. 2A. Other particles with different shape, size and texture were identified by SEM and analyzed by EDX. Porous particles with high carbon content were identified as unburned coal, as shown in Fig. 2B. Additionally, irregular agglomerations immersed in an amorphous matrix, shown in Fig. 2C, were also found and had a high calcium and low sulfur content (Fig. 3A). These characteristics led us to conclude that these irregular agglomerations corresponded to calcite ( $\text{CaCO}_3$ ).

The high iron content detected by the EDX analysis (Fig. 3B) on the rough surface of the pseudospheres, shown in Fig. 2D, suggested that these particles corresponded to the magnetite detected by XRD. This assumption was in agreement with the ferrospheres con-

taining magnetite reported previously [39]. Phases with high and low alumina content were also identified. Needles with high alumina and low silica content (Fig. 3C) were found either as isolated particles or covering the vitreous MFA spheres (Fig. 2E). Similar particles were reported in the literature as mullite [40]. Low alumina and high silica content was detected in the shell of these spheres (Fig. 2A) indicating that this material was mainly composed of an amorphous phase. Quartz was also found as irregular particles (Fig. 2F) containing only silicon and oxygen (Fig. 3D).

#### 3.1.5. Glass composition

The high content of amorphous phase found in MFA (78.3%) made it potentially reactive in direct conversion processes. To evaluate its usefulness in processes such as alumina and silica extraction and zeolite synthesis, the chemical composition of the amorphous phase, commonly called glass, was calculated, and the obtained values were compared with data reported for European fly ashes [5]. The results showed that MFA was constituted mainly by silica, alumina, iron and calcium oxides (Table 5). It had similar silica and alumina content in the glass to the Puertollano fly ash chosen as one of the best for the extraction of silica and used to synthesize zeolites [5].

#### 3.1.6. Thermal stability

Results obtained from TGA and DTA are shown in Fig. 4. TGA showed three important changes. The first was a loss of weight between room temperature and 100  $^{\circ}\text{C}$  related to the loss of humidity. Then from 100 to 450  $^{\circ}\text{C}$ , hydration water was lost. Between 450 and 700  $^{\circ}\text{C}$ , there was a further loss of weight attributed mainly to the decomposition of  $\text{CaCO}_3$  and the burning of residual coal present in the fly ash. These results led us to conclude that MFA was thermally stable at temperatures around 900  $^{\circ}\text{C}$  and could be directly used in processes carried out at or below this temperature. Differential thermal analysis showed an additional change above 900  $^{\circ}\text{C}$ . This energy changed without a loss of mass, which pointed to structural changes in MFA.

To elucidate the processes occurring above 900  $^{\circ}\text{C}$ , different samples were thermally treated at 750, 1075 and 1200  $^{\circ}\text{C}$  for 4 h. They were then analyzed by XRD, and the phase contents were calculated as a function of the area of the peaks. It was found that the XRD pattern of the sample treated at 750  $^{\circ}\text{C}$ , taken as a reference, was very close to that found for the 105  $^{\circ}\text{C}$  fly ash. As was concluded from DTA and TGA, the X-ray analysis showed that the crystalline components of MFA had no important changes at temperatures near 750  $^{\circ}\text{C}$ . However, higher temperatures promoted a structural rearrangement leading to the

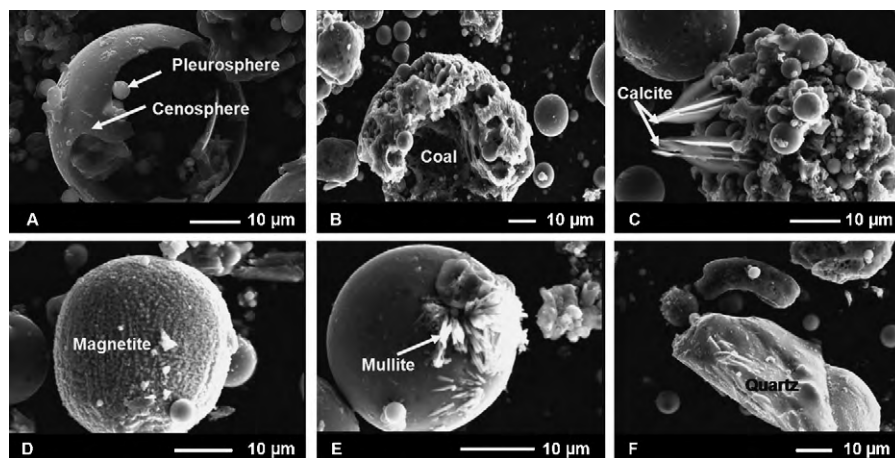
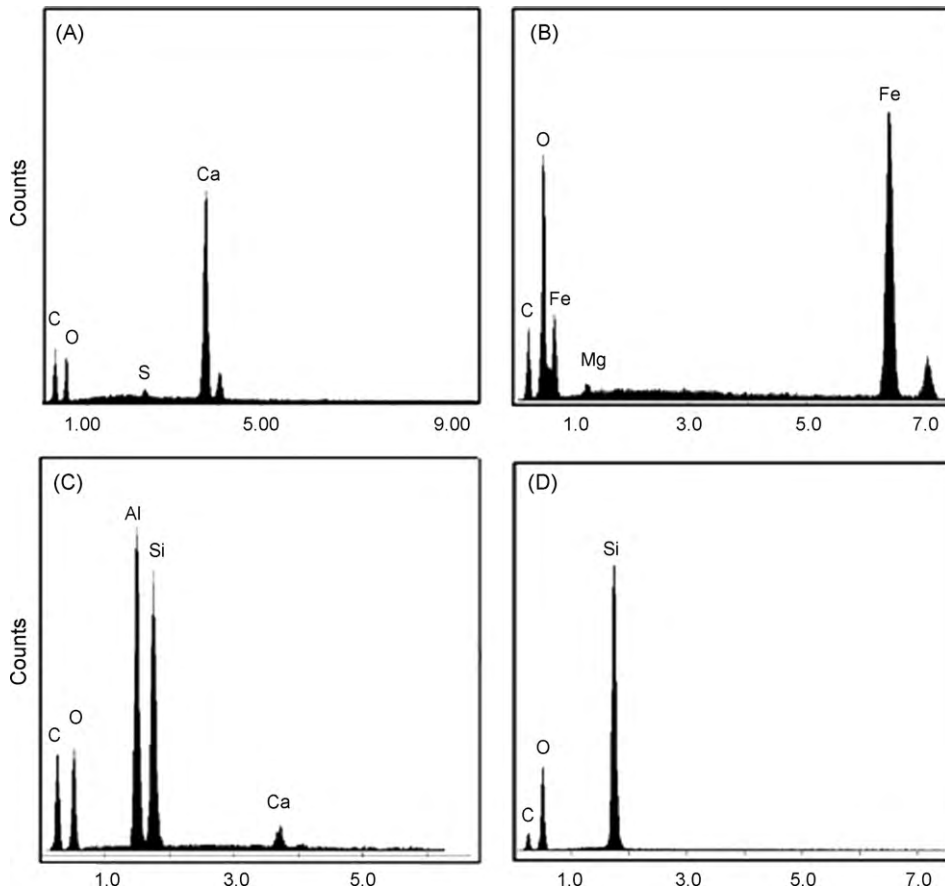


Fig. 2. Morphology of the main MFA phases. Pleurospheres and cenospheres (A), unburned material (B), calcite (C), magnetite (D), mullite growing on the glass sphere (E) and quartz particles (F).



**Fig. 3.** EDX chemical analysis determined in inorganic phases with different shapes and textures included in MFA. Calcite (A), magnetite (B), mullite (C) and quartz (D).

formation of albite ( $\text{Si}_3\text{O}_8\text{AlNa}$ ) and cristobalite ( $\text{SiO}_2$ ), as shown in Fig. 5.

The X-ray spectra from 1075 and 1200 °C were similar, so it could be assumed that the material treated at temperatures of 1075 °C <  $T$  < 1200 °C were stable and that MFA treated at these temperatures could be applicable in high-temperature processes, such as ceramics manufacturing.

### 3.2. MFA leaching trials

The use of three leaching agents provided information on the leaching potential in different environments. Moreover, acetic and oxalic acids behave as chelating agents, as they have a strong affinity for heavy metals. Hence, results on leaching might give an estimation of the fraction of heavy metals that could be environmentally available for leaching. The water leaching (Table 6) trial brought to light the mobility of those elements existing as soluble

salts, such as  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ , and the few elements occurring as their oxyanionic species under alkaline conditions, specifically Mo, Se, V and W. These metals displayed high extractable proportions, up to 36% of the total content of the heavy metals (Fig. 6). The significant mobility was in line with other studies that identified the above elements as a matter of concern in terms of leaching [41–45]. It was worth noting that all of the elements depicted in Table 6 were released into water within the typical range of leaching of 23 different pulverized coal combustion fly ashes from different European countries [5].

A variety of transition and rare earth elements were leached close to or below the detection limit with water, but the overall leaching was increased under more aggressive conditions. Metal dissolution was enhanced under acidic conditions provided by acetic and oxalic solutions, which promoted the leaching of the aforementioned elements and increased their water extractable fractions by 5% and 10%, respectively. However, according to the

**Table 5**

Chemical glass composition based on 100 g of MFA.

%	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{Fe}_2\text{O}_3$	$\text{K}_2\text{O}$	$\text{MgO}$	$\text{Na}_2\text{O}$	$\text{SO}_3$	$\text{TiO}_2$	$\text{P}_2\text{O}_5$
Quartz <sup>a</sup>	9.5	0.0	0.0							
Mullite <sup>a</sup>	3.3	8.5	0.0							
Calcite <sup>a</sup>	0.0	0.0	0.2							
$\sum$ Oxide in crystalline phases <sup>a</sup>	12.8	8.5	0.2							
Oxide Bulk content <sup>b</sup>	59.6	22.8	3.1	5.6	1.3	0.9	0.4	0.4	0.9	0.04
Oxide in amorphous phase	46.8	14.3	2.9	5.6	1.3	0.9	0.4	0.4	0.9	0.04
Oxide in glass	63.3	19.4	4.0	7.5	1.7	1.2	0.6	0.5	1.3	0.05
European [5] <sup>c</sup>	46–65.5	5.4–29.1	0.6–24	4.1–13.8	–	–	–	<1.4	–	–
Puertollano [5] <sup>c</sup>	65.5	19.4	1.2	7.6	3.8	–	0.5	0.3	–	–

<sup>a</sup> Data are obtained by XRD.

<sup>b</sup> Data obtained by chemical analysis

<sup>c</sup> Oxide in glass.

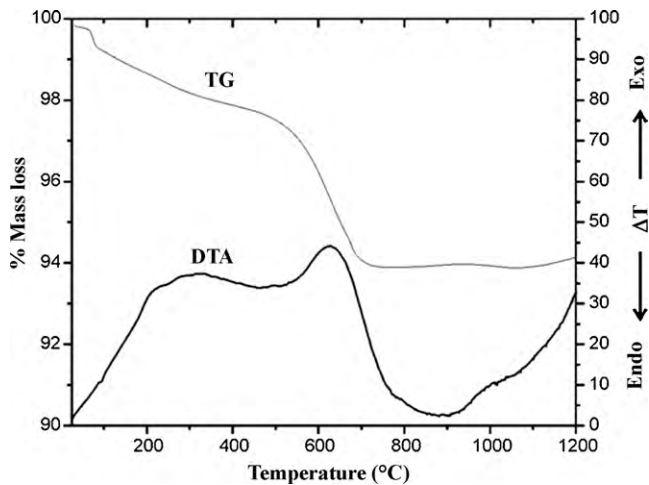


Fig. 4. Differential and gravimetric thermal analyses of MFA.

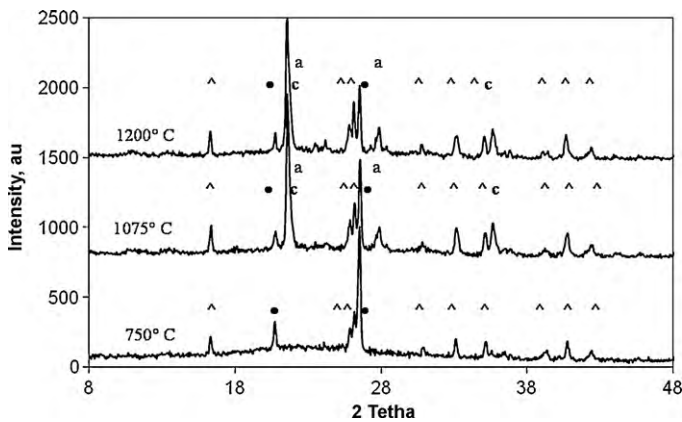


Fig. 5. Thermal stability of MFA and its dependence on temperature. Mullite ( $\Delta$ ), quartz ( $\bullet$ ), cristobalite (c), and albite (a).

data in Table 6, these deleterious releases did not result in a significant impact.

In comparison to water leaching, acetic acid media removed considerably higher Ca concentrations. This observation was consistent with the presence of calcite, given that, aside from anhydrite (also soluble in water), carbonate minerals are soluble in acetate solutions [46]. This solubility accounted for the large amount of released Ca, which exceeded 10 g/kg. Bearing in mind the Ca content in the MFA, such a leachable content indicated that around half the calcium in fly ash occurs as sulfate and carbonate species.

Oxyanionic metalloids, however, were not particularly sensitive to the acetic acid leaching. The release of these species remained constant or even decreased slightly in the case of V, Mo and W (Fig. 6) because their mobility typically only increased under alkaline conditions. Their leaching did not seem to be related to calcium sulfate, which pointed to these species occurring as oxyanionic phases (presumably with Ca), rather than forming solid solutions with  $\text{SO}_4^{2-}$  in calcium sulfate lattices or bound to calcite surfaces, as suggested by Cornelis et al. [45].

More extreme leaching conditions were imposed by oxalic acid, as its two carboxylic groups endowed the leachant with a stronger dissolving ability with respect to the one-carboxylic acid-containing acetic acid. Consequently, dissolution of certain components of the aluminosilicate glassy matrix, such as Si, Al or Ti, was achieved, although the water extractable proportions remained very low (<2%). The sharp increase in Fe and Mn leaching was attributed to the fact that oxalate solutions can extract those elements bound to amorphous and poorly crystalline hydroxides. With the available data it was not possible to elucidate the status of trace metals, but it was reasonable to assume that Ni, Cr, Cu and Zn, which have affinity for Fe hydroxides, were incorporated with this fraction. Thus, oxalic acid could partly release the metal content bound to this fraction, accounting for the higher observed leaching, but values were not significantly in regards to environmental concerns.

It was worth noting that Ca leaching decreased when fly ash was leached with an oxalic solution, but this observation did not mean that calcite and/or gypsum were not removed. Rather, high calcium content in solution induced secondary precipitation reactions in the presence of this reagent, as calcium oxalates are highly insoluble. The lower Sr and Cd leaching could also be linked to this process.

Among the oxyanionic metalloids, only V leaching was considerably increased in oxalic media when compared with water leaching. Nevertheless, it was worth mentioning that V releases were still lower than those reported for co-firing of fly ash with petroleum coke, even at relatively low proportions [47].

Such conditions may not resemble a conventional scenario, but were useful in providing key indications on (1) the leaching potential in landfills (the present fate of MFA is an open landfill site) or other situations in which the acid neutralization capacity is lost and (2) the available fraction in a medium-long time frame because the long-term evolution of pH in fly ash tends to increase in acidity [48]. It could be stated that, although a number of metals and metalloids in MFA could be partially leached with water under typical field conditions, the observed releases were not of critical concern. Moreover, if it was assumed that acid leaching provided a reasonable estimation of the metal availability in a medium time frame, the release of elements of environmental concern should not be a hindrance to most value-added applications of this fly ash.

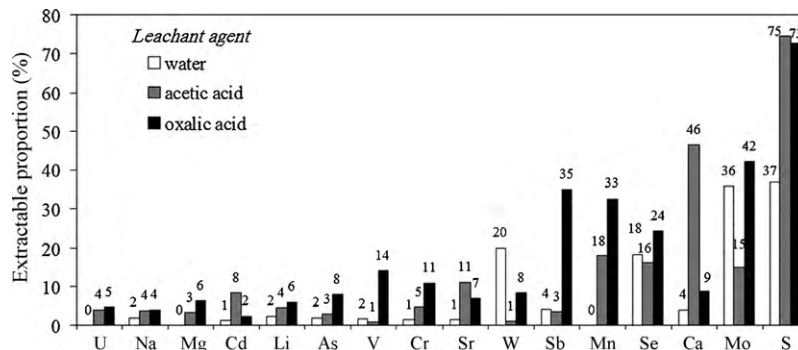


Fig. 6. Extractable proportions of mobile elements in different leaching media.

**Table 6**  
Leachable concentrations of a number of elements in different leaching media.

	Conductivity	pH	Al	Si	S	Na	Mg	K	Ca	Fe	Li	Be	B	Sc	Ti
Water	496	8.8	39	33	586	65	0.8	60	877	<1	2	<0.01	28	<0.01	0.01
C.I. <sup>a</sup>			1.7E-02	3.1E-02	6.3E-01	9.7E-02	1.5E-03	1.1E-01	5.6E-04	-	3.9E-03	-	5.5E-07	9.4E-06	2.5E-04
Acetic acid	3739	4.7	397	1118	1186	124	167	129	10,325	23	4	0.1	91	0.4	0.9
Oxalic acid	1209	4.1	2947	4606	1156	129	333	183	1934	1103	6	0.2	95	0.8	42
		V	Cr	Mn	Co	Ni	Cu	Zn	As	Se	Rb	Sr	Y	Zr	Nb
Water	2	2	0.6	0.01	<0.01	0.01	0.01	0.1	0.7	1.1	0.1	4	<0.01	<0.01	<0.01
C.I. <sup>a</sup>			5.6E-04	2.4E-05	-	1.2E-04	8.4E-05	8.8E-04	9.5E-04	1.1E-03	2.3E-04	2.8E-03	1.4E-06	5.0E-06	2.3E-06
Acetic acid	0.9	0.9	2	27	0.3	0.7	0.6	5	1.1	1	0.3	34	1.3	0.04	<0.01
Oxalic acid	17	17	5	50	0.5	0.9	2	7	3	2	0.5	21	0.01	0.2	0.1
		Mo	Cd	Sn	Sb	Cs	Ba	Hf	Ta	W	Tl	Pb	Bi	Th	U
Water	4	4	0.01	<0.01	0.2	0.01	0.6	<0.01	<0.01	1	<0.01	<0.01	<0.01	<0.01	<0.01
C.I. <sup>a</sup>			2.7E-05	-	1.4E-04	7.5E-06	7.8E-04	-	-	1.7E-03	-	-	-	2.1E-07	2.5E-06
Acetic acid	2	2	0.1	0.02	0.1	0.02	3	0.02	0.02	0.05	0.06	0.06	0.01	0.02	0.3
Oxalic acid	5	5	0.02	0.2	1.4	0.03	5	0.03	0.4	0.4	0.1	<0.01	0.01	0.01	0.4

<sup>a</sup>Confidence interval (95%). Leaching in water was analyzed by triplicate; values are given in ppm, except for conductivity (mS cm<sup>-1</sup>)

Bearing in mind that North Coahuila produces almost 100% of all Mexican mineral coal, the discussed fly ash could be regarded as a strongly representative sample. Therefore, the above statements could be roughly attributable to Mexican coal fly ash in general.

#### 4. Conclusions

The MFA properties determined in this work could be regarded as representative of all coal fly ash produced in Mexico because it was taken from the region where mineral coal is concentrated. Because of its morphological properties and structural and thermal stability, MFA could be used in thermal isolation materials, refractory products and as a solid support for high-temperature heterogeneous catalysts. MFA has high pozzolanic reactivity and is potentially useful as a raw material to make cement. The chemical and mineralogical composition of MFA led us to conclude that it was suitable for the synthesis of low Si/Al ratio zeolites and for obtaining other silica and alumina compounds. Nevertheless, MFA contained some potentially deleterious elements that could be removed during the zeolitization process or with an additional acid treatment. It is recommended to carry out a detailed research to evaluate the potential recovering of transition metals from MFA and the mobility of the contaminant heavy metals in MFA disposed of in open landfills toward underground water.

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