



## Fly ash from a Mexican mineral coal. II. Source of W zeolite and its effectiveness in arsenic (V) adsorption

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### ABSTRACT

Coal-fired plants in Coahuila (Mexico) produce highly reactive fly ash (MFA), which is used in a one-step process as a raw material in producing zeolite. We explored two routes in the synthesis of zeolite: (a) direct MFA zeolitization, which resulted in the formation of W zeolite with KOH and analcime with NaOH and (b) a MFA fusion route, which resulted in the formation of zeolite W or chabazite with KOH and zeolite X or P with NaOH. No residual crystalline phases were present. When LiOH was employed, ABW zeolite with quartz and mullite were obtained. For both zeolitization routes, the nature of the alkali (KOH, NaOH, LiOH), the alkali/MFA ratio (0.23–1.46), and the crystallization temperature and time (90–175 °C; 8–24 h) were evaluated. Additionally, the effect of temperature and time on MFA fusion was studied. W zeolite was obtained by both zeolitization methods. The direct route is preferred because it is a straightforward method using soft reaction conditions that results in a high yield of low cost zeolites with large crystal agglomerates. It was demonstrated that aluminum modified W zeolite has the ability to remove 99% of the arsenic (V) from an aqueous solution of Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O originally containing 740 ppb.

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### 1. Introduction

More than two million tons of fly ash (MFA) are produced every year in Coahuila (a northern state of Mexico) by "Jose Lopez Portillo" and Carbon II coal-fired plants owned by the Mexican state power company (CFE). Currently, MFA has no bulk applications and is therefore not commercialized. It is collected by cyclones, electric precipitators, and/or bag filters from the gas flowing at the burner top and ends up in an open landfill. Mineralogical and chemical characterization has shown that MFA has one of the highest reported silica (59.6%) and amorphous phase (78%) contents of others studied fly ashes [1]. As a result, it has a high reactivity in alkaline medium and without any additional treatment could be used to produce synthetic zeolites.

To the best of the authors' knowledge, there are no previous reports on the use of MFA or any other Mexican fly ash as a raw material for zeolite synthesis. However, other efforts have been made to develop methodologies for zeolite synthesis from different types of fly ash with special emphasis on the experimental conditions needed to obtain high cation exchange capacity (CEC) zeolites

[2]. The disadvantage of using a common class F fly ash as the source of silica and alumina for producing zeolites, however, is its low reactivity [3]. To enhance the zeolitization, an alkaline fusion process is recommended when using this type of fly ash [4]. Fly ash from several origins has been characterized and used as raw materials for zeolite synthesis by direct conversion, alkaline fusion, and SiO<sub>2</sub> extraction. Also, syntheses of zeolites in high yields (49–54%) were obtained from fly ash using conventional alkaline activation [5].

Based on reported information, the parameters involved in the synthesis of zeolites from fly ash (source of silica and alumina, mineralizing agent, mineralizing agent/fly ash ratio, presence of organic an inorganic additives, and crystallization conditions) were identified [6] and the factors and levels to be studied in the MFA zeolitization were established.

The main natural zeolites found in Mexico are mordenite, erionite, and clinoptilolite [7]. While the use of natural zeolites has advantages such as high availability in the country and low price (approximately 43 USD per metric tonnes) [8], disadvantages in commercial applications exist due to the lack of variety of zeolites available in the country, the heterogeneity of the mineral, and the low percentage of zeolite in bulk. As a result, a high amount of material or severe operating conditions are required to obtain a desired product. The natural zeolites normally include another crystalline phases and a significant amount of an amorphous phase [9]. In addition, further treatment is often necessary

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to attain the expected performance or to dispose of the aged materials.

Synthetic zeolites overcome the disadvantages of natural zeolite; however, typical zeolite synthesis requires the use of expensive chemical reagents, resulting in high product prices. Thus, the recycling of industrial waste is considered as having no commercial value, and MFA offers a potential alternative to produce a wide variety of low cost zeolites following the requirement of each industry. Alternative zeolites production route could have also positive environmental and economical impacts in Mexico. Due to the high level of mining activity in Mexico, the aqueous effluents from their processes contain critical levels of heavy metals, and Mexico has one of the highest arsenic contents in its drinking water [10]. Low cost zeolites could be an effective alternative to contribute to solve these problems. Although, in Mexico synthetic zeolites are used for petroleum refining, the petrochemical industry, and the chemical industry, they are not produced locally.

While the zeolitization of MFA would only minimally contribute in solving the problem of fly ash disposal, it could have a significant impact in facing the environmental challenges related to the removal of heavy metals and organic compounds from waste and drinking water.

According to the literature, the potassic zeolites could be an alternative to solving such environmental problems. The synthetic W zeolite ( $K_{10.3}[Si_{21.7}Al_{10.3}O_{64}] \cdot 20H_2O$ ) closely resembles natural merlinoite [11]. Like others zeolites, merlinoite can be found in nature [12], but to overcome the disadvantages of natural zeolites it can be synthesized from different silica and alumina sources. Strohmaier and Robson [13] reported the synthesis of W zeolite from alumina, colloidal silica, and potassium hydroxide by a hydrothermal method at 150 °C for 48 h. Crystallization of merlinoite and chabazite from KOH aluminum-silicate gels can be controlled by  $K^+$  ion concentration [14]. Thoma and Nenoff [15] reported a method for obtaining W zeolite by using organometallic silicon and aluminum precursors with and without the addition of organocations. Colella et al. [16] used natural glass to synthesize merlinoite-type zeolites.

MFA and its high valued products are worth investigation in light of the needs of Mexican agriculture and the chemical industry and the amount of hazardous metals and other environmental xenobiotic in the country's soil, water, and air. The great potential of the fly ash in agricultural production has been documented [17]. The incorporation of fly ash in the formulation of value-added construction materials is one of the alternative uses to reduce the potential environmental risks that contributed to the fly ash landfills [18]. The synthesis of geopolymers can be done by using fly ash as the main starting material, zeolite or bentonite as supplementary materials, and NaOH and CaO together as activators [19]. In addition, zeolites can be prepared from different fly ashes in the laboratory and pilot plant scales, which have several potential applications because of their cation exchange capacity (CEC). CEC values from 160 to 260 meq.  $100 g^{-1}$  for NaP1, herschelite, KM, linde F and K-chabazite have been demonstrated for the majority of the cations investigated [20]. The removal of heavy metals from aqueous solutions has been investigated with zeolites A and X obtained from fly ash [21]. High silica fly ash has been used as a source of silicon to synthesize Na-A, -X and -Y zeolites through alkali fusion followed by hydrothermal treatment at 100 °C for 12 h. Resultant materials have shown very high cation-exchange capability [22]. These and other zeolites are broadly used in the petroleum refining, petrochemical, and chemical industry. In addition, zeolites have many applications such as for ion exchange, molecular sieves, and adsorbents of organic and anionic species.

Converting fly ash into zeolites not only facilitates the disposal problem but also converts a waste material into a marketable commodity [23]. Furthermore, arsenic contamination in water,

especially groundwater, has been recognized as a major problem of catastrophic proportions. Also, the toxic nature of arsenic and the related health hazards have been reported for many years. Because of the recognition that arsenic at low concentrations in drinking water causes severe health effects, arsenic removal technologies have become increasingly important. Thus, the current regulation of the drinking water standard is becoming more stringent and requires arsenic content at only a few parts per billion [24].

In this study, the effect of the nature of the alkali (KOH, NaOH, LiOH), the direct method alkali/MFA ratio (0.23–0.5), the crystallization temperature and time (120–175 °C; 8–24 h), and the stirring speed (100–600 rpm) were investigated. Crystallization in an alkaline medium of MFA that was previously amorphized (the fusion method) was also explored using the same experimental design. In this case, the alkali/MFA ratio varied from 0.62 to 1.46, and the crystallization temperature varied from 90 to 150 °C. Additionally, the effect of temperature (200–600 °C) and time (0.5–2 h) of the thermal amorphization pretreatment were studied.

To enhance the anion adsorption capacity, W zeolite was modified with ammonium and aluminum salts. In addition to this work, it could be investigated the possibility of preparing zeolite A from MFA due to its potential use in the formulation of detergents, water softeners, and adsorbents. Zeolite Y and high silica alumina ratio zeolites could also be studied due to the amount used as catalysts in the petroleum refining and petrochemical industries.

Mexico, as well as many other countries, faces the problem of arsenic contamination in surface and groundwater, which directly affects human health [25–29]. Several common treatment technologies are used for the removal of inorganic contaminants, including arsenic [24], from drinking water supplies. Large scale treatment facilities often use conventional coagulation with alum or iron salt followed by filtration to remove arsenic. Lime softening and iron removal are also common. Other technologies that have been used for arsenic removal are iron-based adsorption media, manganese green sand, reverse osmosis, electrodialysis reversal, nanofiltration, and adsorption by activated materials [30]. All of these processes have good performance, but one of the main problems is that sophisticated equipment and expensive reagents are required. New methods and new functional materials should be developed to reduce the arsenic removal costs, to increase its efficiency, and to facilitate the implementation in rural zones where people lack purified drinking water.

Continuous investigation of the available arsenic removal technologies is essential to develop economical and effective methods for removing arsenic to reach the new Maximum Contaminant Level (MCL) standard ( $10 \mu g L^{-1}$ ) recommended by the World Health Organization (WHO). Among the present methods of arsenic removal are nanofiltration [31], precipitation-coprecipitation using aluminium salts [32], photo-oxidation [33], and adsorption processes [34,35] with alumina [36], natural zeolites [37–39], and synthetic zeolites [40]. To increase the anionic species adsorption capacity, the zeolites must be modified by acid treatment, ion exchange [41], or surfactant functionalization [37,42,43]. Modified zeolites, with aluminum salts and coated zeolites with iron have shown high arsenic (V) removal [44,45]. Some of the low cost adsorbents have low efficiency in removing arsenic. As an example, the mixture of natural zeolites chabazite-phillipsite has an efficiency of 60–80% in the better cases, whereas clinoptilolite has an efficiency of 40–60% [39]. To increase the arsenic removal up to 98% of  $H_3AsO_3$  (as an example) from a  $500 \mu g As L^{-1}$  solution, a contact time of 70 days is required [46].

In this work, two methods to obtain synthetic zeolites at low cost were studied. MFA has been selected as a potential raw material to produce low cost zeolites because it has no commercial value, is locally available, and most importantly, has a high reactivity due to its high silica and amorphous phase content [1]. To

select the alkali, the upward ionic nature of the alkaline hydroxides (lithium < sodium < potassium) was taken into account. The hypothesis is that in using potassium hydroxide as the mineralizing agent and MFA as the source of silica and alumina, it would be possible to obtain zeolites with a good yield in only one step and under soft reaction conditions. The other circumstances that motivated the realization of this study were the fact that Coahuila and other states in México have an endemic problem related with arsenic pollution in drinking water; there is evidence that potassic zeolites (merlinoite, chabazite, phillipsite, and edingtonite) have good ionic exchange capacity and selectivity for heavy metals [47] and chabazite has strong affinity for both arsenite and arsenate species [48].

The advantages of zeolite compared with other materials are given by its particular structural and chemical properties that can be controlled by its crystallization. There are zeolites with low, medium, and high pore size. Their nano-porosity gives rise to a high specific surface area and, consequently, they have many possible active sites. The properties of the zeolites can be modified by substituting the aluminum atoms in the  $\text{SiO}_2\text{-Al}_2\text{O}_3$  structure with Si, P, B, Ge, Co, Fe, among others [6]. Additionally, the chemistry of the zeolite surface can be modified by exchanging the alkaline metal that typically has by  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{M}^{n+}$ , where M is any cation and  $n$  is its valence. Following these modifications, it is possible to change the nature, strength and concentration of acid sites in the zeolite surface. This means that it is possible to regenerate the exhausted zeolites and extend their lifetime. Finally, it can be concluded that it is possible to design a zeolite with the properties required for a specific process, in this particular case, to remove arsenic from aqueous solutions.

Zeolitization of fly ash is based on a hydrothermal alkali treatment that can be done by two methods: classic alkaline conversion (the direct method) and the fusion method. The main disadvantage of the first method is the low speed of the reaction between the fly ash and the alkaline medium. High concentrated alkali solutions (0.5–5 M of NaOH) are required during long periods of time (8–24 h) at high temperature (150–200 °C) to obtain acceptable crystallization of useful zeolites such as P zeolite [5]. If soft conditions are applied, a mixture of zeolites and the crystalline phases of fly ash are obtained [49]. The fusion method consists of applying an alkali fusion (550–600 °C, 2 h) stage prior to hydrothermal treatment [4] to amorphize the mullite and quartz in the fly ash and to reduce the crystallization temperatures and times [5]. A higher amount of alkali is used in this method than the direct one. The product obtained from alkali fusion is previously aged before the crystallization. The selection of the method must be done according to the zeolite required. The most common zeolites are the sodic ones. To promote direct MFA zeolitization with NaOH, high concentrations and temperatures are required. Furthermore, the zeolites obtained by the direct conversion procedure have low cation exchange capacities and low pore sizes (analcime); their properties limit their potential applications. In the case of potassic medium at the studied conditions, no zeolites were obtained by the fusion route [49].

This study focused on the development of a straightforward method to prepare low cost zeolites from MFA, which is potentially useful to remove arsenic (V) present in aqueous solutions. To carry out the present work, a random sample of MFA from the landfill of the “Jose Lopez Portillo” coal-fired plant was taken and re-sampled by the quarter method [50]. MFA without any additional treatment was used as the raw material, and two zeolitization routes followed: direct fly ash zeolitization and MFA alkaline fusion were applied to carry out the re-crystallization process. Using direct hydrothermal MFA zeolitization, zeolite W with KOH and analcime with NaOH were obtained. Hydrothermal zeolitization of previously amorphized MFA resulted in zeolite W or chabazite with

KOH and zeolite X or P with NaOH. None of these contained any residual crystalline phases. When LiOH was employed, no unique crystalline phases were obtained. It was demonstrated that W zeolite has the ability to remove 99% of the arsenic (V) from an aqueous solution of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  originally containing 740 ppb in 5 min.

## 2. Experimental

### 2.1. Materials and chemical reagents

MFA was obtained from the “Jose López Portillo” coal-fired power plant, located in North Coahuila state, Mexico. The fly ash samples were dried at 110 °C for 12 h prior to zeolitization. The MFA chemical composition (%) was:  $\text{SiO}_2$  (56.7),  $\text{Al}_2\text{O}_3$  (23.7),  $\text{Fe}_2\text{O}_3$  (6.0),  $\text{CaO}$  (3.9),  $\text{K}_2\text{O}$  (1.5),  $\text{TiO}_2$  (1.0),  $\text{MgO}$  (0.7),  $\text{SO}_3$  (0.7),  $\text{Na}_2\text{O}$  (0.4) and volatile material (5.0). Moreover, five fly ash samples from the same coal-fired plant were sampled and analyzed weekly (5). The variation in chemical and mineralogical composition was minimal; the content of  $\text{Al}_2\text{O}_3 + \text{SiO}_2$  was 80–85%. All chemicals that are used in this study, i.e., potassium, sodium and lithium hydroxide (Riedel de Haën), sodium aluminate and sodium silicate (Spectrum) were of analytical grade. In addition, deionized water was used in all experiments.

### 2.2. Characterization of raw materials and obtained zeolites

MFA and its zeolitic products were characterized by X-ray diffraction (XRD) using a Philips model XPert PW3040 diffractometer. Quantification of zeolitic phases was performed using Sietronics Traces 3.0 software. The area under the peaks from 10 to 50° was quantified, and the content of zeolitic phases was determined.

Morphology was examined by scanning electron microscopy using a Philips XL30 ESEM microscope. Chemical composition was measured by X-ray fluorescence (XRF) using a Bruker AXS spectrometer. Nitrogen adsorption and desorption isotherms were measured using a Quantachrome Autosorb 1C. Samples were degassed at 300 °C prior to adsorption. The analyses were carried out at –196 °C with nitrogen. The specific surface area was calculated by a multipoint BET equation. Pore volumes were calculated from maximum nitrogen adsorption values at  $P/P_0 \sim 0.99$ .

The concentration of residual arsenic was measured by plasma emission spectrophotometry (Thermo Elemental Instrumental, Iris Intrepid II) according to ASTM standard E-1097-07.

### 2.3. MFA zeolitization strategy

Two alternative methods were applied to study the MFA re-crystallization. In a direct method, MFA was hydrothermally treated with a mineralizing agent. In accordance with a report of the fusion method [51], MFA was thermally treated with the mineralizing agent, and the resulting product was aged by the application of slow stirring prior to the hydrothermal zeolitization process. The effect of seven factors on the zeolitization process was studied at three levels. These factors included: nature and amount of mineralizing agent, temperature and time of the fusion process, temperature and time of the hydrothermal crystallization process and stirring rate. Fusion temperature and time were not applied in the direct method. Experimental conditions were selected on the basis of conditions from previous reports in the literature [52,53]. Factors and levels evaluated in both direct and fusion methods are shown in Table 1.

An orthogonal array  $L_{27}(3^{13})$  proposed by Taguchi [54] was used to define the critical factors and the optimum conditions for the MFA zeolitization process. Twenty-seven experiments ( $L_{27}$ ) were derived from each zeolitization method (see Tables 2 and 3).

**Table 1**  
Factors and levels evaluated in MFA zeolitization process.

Direct method						
MOH	MOH/MFA ratio <sup>a</sup>	Temperature crystallization (°C)		Time crystallization (h)	Stirring rate (rpm)	
NaOH	0.23;0.29;0.35	120		8	100	
KOH	0.33;0.41;0.50	150		16	350	
LiOH	0.25;0.31;0.37	175		24	600	
Fusion method						
MOH	MOH/MFA ratio <sup>a</sup>	Fusion temperature (°C)	Fusion time (h)	Temperature crystallization (°C)	Time crystallization (h)	Stirring rate (rpm)
NaOH	0.62;0.83;1.04	200	0.5	90	8	100
KOH	0.87;1.16;1.46	400	1	120	16	350
LiOH	0.65;0.87;1.09	600	2	150	24	600

<sup>a</sup> In (g/g); MOH: mineralizing agent; MFA: Mexican fly ash.

Eighteen of the fifty-four experiments involved the activation of MFA by KOH, which led to W zeolite formation. The hydrothermal MFA conversion process was carried out in a set of 8 serially connected 100 mL high pressure stainless steel reactors (Parr<sup>TM</sup>), which were continuously stirred and temperature-controlled. The flow diagram of the zeolitization process is shown in Fig. 1. The percentage of zeolitic phase produced in each trial was used as the measured response variable.

### 2.3.1. Synthesis by the direct method

Sixteen grams of dry MFA were added to 48 mL of aqueous MOH (M = Li, Na, K). This mixture was put into a Parr<sup>TM</sup> reactor and tightly closed. The hydrothermal treatment was carried out at 120, 150 and 175 °C for periods of 8, 16 and 24 h. The products were washed with deionized water to remove any excess hydroxide and then dried at 110 °C for 12 h.

Considering that NH<sub>4</sub>-Y zeolite has demonstrated its ability to remove arsenic from aqueous solutions [41], the Na-Y was prepared by the reported method [55].

**Table 2**  
Experimental conditions of zeolitization of MFA by direct method.

Test	MFA (g)	H <sub>2</sub> O (mL)	KOH/MFA ratio	NaOH/MFA ratio	LiOH/MFA ratio	Hydrothermal conditions			Zeolitic phase	Residual phases	Zeolitic content (%)
						T (°C)	t (h)	Stirring (rpm)			
ED1	16	48	0.33			175	16	100	W	–	71
ED2	16	48	0.33			175	16	350	W	–	74
ED3	16	48	0.33			175	16	600	W	–	75
ED4	16	48	0.41			120	24	100	W	M, Q	52
ED5	16	48	0.41			120	24	350	W	M, Q	55
ED6	16	48	0.41			120	24	600	W	M, Q	54
ED7	16	48	0.50			150	8	100	W	M	52
ED8	16	48	0.50			150	8	350	W	M	55
ED9	16	48	0.50			150	8	600	W	M	55
ED10	16	48		0.23		120	8	100	NaP	Q, M	39
ED11	16	48		0.23		120	8	350	NaP	Q, M	41
ED12	16	48		0.23		120	8	600	NaP	Q, M	41
ED13	16	48		0.29		150	16	100	ANA	M	47
ED14	16	48		0.29		150	16	350	ANA	M	50
ED15	16	48		0.29		150	16	600	ANA	M	49
ED16	16	48		0.35		175	24	100	ANA	–	63
ED17	16	48		0.35		175	24	350	ANA	–	66
ED18	16	48		0.35		175	24	600	ANA	–	66
ED19	16	48			0.25	150	24	100	ABW	M, Q	23
ED20	16	48			0.25	150	24	350	ABW	M, Q	22
ED21	16	48			0.25	150	24	600	ABW	M, Q	19
ED22	16	48			0.31	175	8	100	ABW	M, Q	34
ED23	16	48			0.31	175	8	350	ABW	M, Q	23
ED24	16	48			0.31	175	8	600	ABW	M, Q	35
ED25	16	48			0.37	120	16	100	ABW	M, Q	31
ED26	16	48			0.37	120	16	350	ABW	M, Q	31
ED27	16	48			0.37	120	16	600	ABW	M, Q	26

W: W zeolite; NaP: P zeolite; ANA: analcime; ABW: ABW zeolite; Q: quartz; M: mullite.

### 2.3.2. Synthesis by the fusion method

MFA (7.6 g) was mixed with MOH in a predetermined ratio (Table 3). The resultant mixture was homogenized by milling and thermally treated at different temperatures for periods of 0.5, 1 and 2 h. Fused products were cooled and added to a flask with 63 mL of deionized water before stirring at room temperature for 17 h. The aged products were then put into a Parr<sup>TM</sup> reactor and crystallized at 90, 120 and 150 °C for 8, 16 and 24 h. After that, the final product was washed with deionized water and dried at 110 °C for 12 h.

### 2.4. Modification of W zeolite and arsenic removal trials

To compare the W zeolite prepared in this work and a Y zeolite such as that reported by Shevade and Ford [41], an experimental Y zeolite was synthesized by sodium silicate and sodium aluminate as described by Ginter et al. [55] but with an alumina content of 75%. The molar composition of the reaction mixture was 0.33 Na<sub>2</sub>O:0.06 Al<sub>2</sub>O<sub>3</sub>:0.72 SiO<sub>2</sub>:12.6 H<sub>2</sub>O. The generated gel was hydrothermally crystallized at 100 °C for 6.5 h with stirring. The final product was

**Table 3**  
Experimental conditions of MFA zeolitization process by fusion method.

	MFA (g)	H <sub>2</sub> O (mL)	KOH/MFA ratio	NaOH/MFA ratio	LiOH/MFA ratio	Alkaline fusion			Hydrothermal conditions			Majority zeolitic phase	Residual phases	Zeolitic Content (%)
						T (°C)	t (h)	Aging (h)	T (°C)	t (h)	Stirring (rpm)			
EF1	7.6	63	0.87			400	2	17	90	16	600	–	Q, M	0
EF2	7.6	63	0.87			400	2	17	120	24	100	W	–	65
EF3	7.6	63	0.87			400	2	17	150	8	350	W	–	88
EF4	7.6	63	1.16			600	0.5	17	90	16	600	W	–	0
EF5	7.6	63	1.16			600	0.5	17	120	24	100	CHA	–	62
EF6	7.6	63	1.16			600	0.5	17	150	8	350	W	–	89
EF7	7.6	63	1.46			200	1	17	90	16	600	–	–	0
EF8	7.6	63	1.46			200	1	17	120	24	100	–	–	0
EF9	7.6	63	1.46			200	1	17	150	8	350	W	–	76
EF10	7.6	63		0.62		200	0.5	17	90	8	100	FAU	Q, M	27
EF11	7.6	63		0.62		200	0.5	17	120	16	350	NaP	M	50
EF12	7.6	63		0.62		200	0.5	17	150	24	600	ANA	M	47
EF13	7.6	63		0.83		400	1	17	90	8	100	FAU	Q, M	19
EF14	7.6	63		0.83		400	1	17	120	16	350	NaP	Q, M	50
EF15	7.6	63		0.83		400	1	17	150	24	600	ANA	–	48
EF16	7.6	63		1.04		600	2	17	90	8	100	FAU	–	66
EF17	7.6	63		1.04		600	2	17	120	16	350	NaP	–	62
EF18	7.6	63		1.04		600	2	17	150	24	600	SOD	Q	49
EF19	7.6	63			0.65	600	1	17	90	24	350	ABW	Q, M	20
EF20	7.6	63			0.65	600	1	17	120	8	600	ABW	Q, M	23
EF21	7.6	63			0.65	600	1	17	150	16	100	ABW	Q, M	55
EF22	7.6	63			0.87	200	2	17	90	24	350	–	–	0
EF23	7.6	63			0.87	200	2	17	120	8	600	ABW	Q, M	7
EF24	7.6	63			0.87	200	2	17	150	16	100	ABW	Q, M	10
EF25	7.6	63			1.09	400	0.5	17	90	24	350	ABW	Q, M	10
EF26	7.6	63			1.09	400	0.5	17	120	8	600	ABW	Q, M	6
EF27	7.6	63			1.09	400	0.5	17	150	16	100	ABW	Q, M	8

W: W zeolite; FAU: faujasite zeolite; NaP: P zeolite; ANA: analcime; SOD: sodalite; ABW: ABW zeolite; Q: quartz; M: mullite.

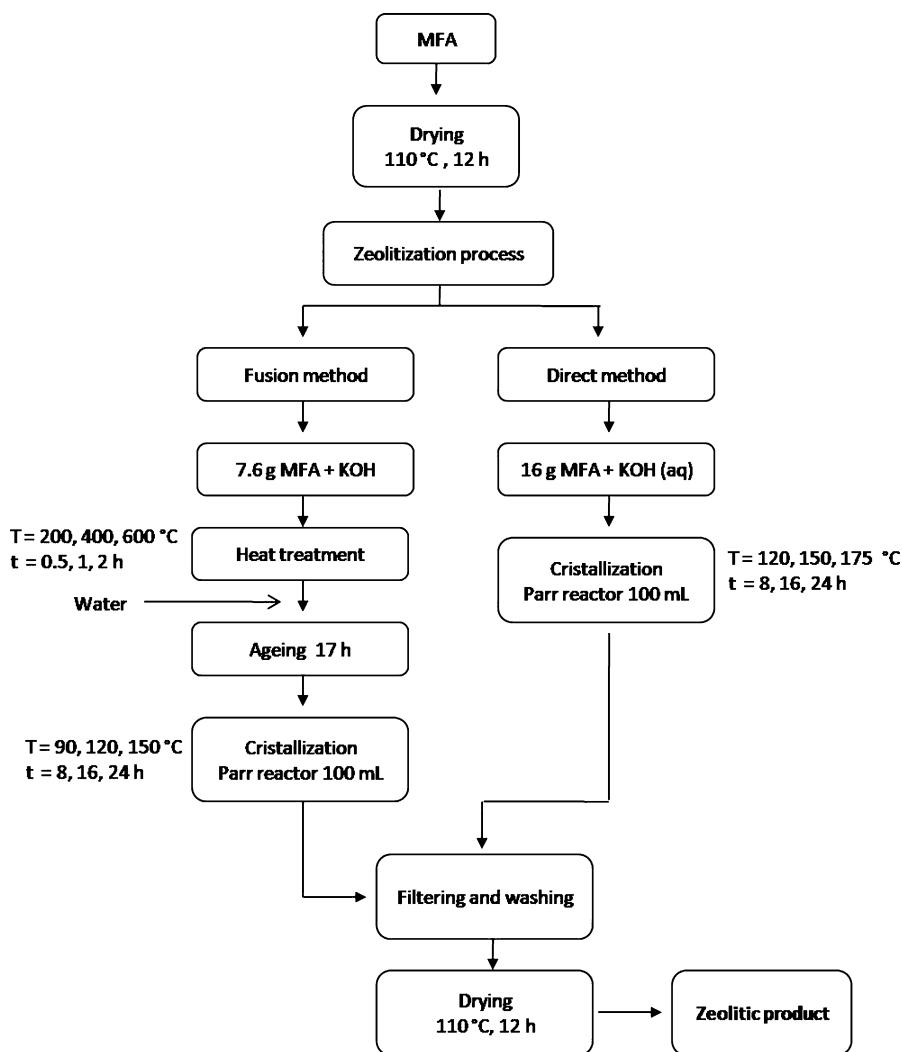


Fig. 1. Flow diagram of MFA zeolitization by direct and fusion method.

recovered, filtered and washed by deionized water, then dried at 110 °C for 24 h. The zeolite obtained was labeled as Y75.

As it was commented in the introduction, the zeolite surface has to be modified to promote the capacity for anionic species removal. For improvement of the arsenic removal, zeolites were treated with ammonium chloride and aluminum sulfate, according to procedure described below.

#### 2.4.1. Ammonium forms of W and Y75 zeolites

Fifteen grams of the low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio Y zeolites (Y75) or W zeolites synthesized by the direct method were submitted to ionic exchange with 53 mL of 5 M NH<sub>4</sub>Cl stirred at boiling temperature (105 °C) for 2 h. This process was repeated four times, and samples were washed with 230 mL of deionized water after each treatment. Exchanged zeolite was filtered, washed with deionized water and dried at 110 °C for 12 h. Ammonium forms of W (10 g) and Y75 (11 g) zeolites were obtained and labeled as WNH<sub>4</sub> and Y75NH<sub>4</sub>, respectively.

#### 2.4.2. W zeolite modified with aluminum sulfate

This process was carried out according to a procedure in the literature [56]. Ten grams of potassium W zeolite obtained by the direct method was added to a 1 L of solution of Al<sub>2</sub>SO<sub>4</sub> 0.007 M. The resultant slurry was kept under stirring at room temperature for 15 h. Subsequently, the modified zeolite was washed three times

with 200 mL of deionized water, filtered and dried at 110 °C for 12 h. Nine grams of modified W zeolite was obtained and labeled WMOD.

#### 2.4.3. Arsenic removal test

To carry out these trials, 1 g of experimental zeolite (WNH<sub>4</sub>, WMOD or Y75NH<sub>4</sub>) was added to 100 mL of aqueous Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O containing 740 ppb of As (V). The solution was adjusted to a pH of 7 and maintained at 25 °C. The system was kept well-stirred to ensure that the zeolite was homogeneously dispersed. Ten milliliter aliquots were collected at various time intervals and filtered through a 0.45 μm syringe filter before the remaining arsenic concentration was measured.

### 3. Results and discussion

#### 3.1. MFA zeolitization

Data obtained from the MFA zeolitization process were submitted to statistical analysis (ANOVA) using a confidence level of 95%. The response variable was the content of W zeolite (wt.%). An ANOVA was performed for each zeolitization method; the results are summarized in Table 4. It can be observed that for the direct method, the most important factor was the mineralizing agent, which contributed 96% to the response variable.

**Table 4**  
ANOVA of W zeolite synthesis from MFA by direct and fusion methods.

	Factor	df <sup>a</sup>	S <sup>b</sup>	V <sup>c</sup>	F <sup>d</sup>	F <sup>e</sup> (0.05, 2,16)	P <sup>f</sup>
Direct method	Mineralizing agente	2	21942.144	10971.072	15120.434 <sup>*</sup>	3.6337	96.7470
	MOH/fly ash ratio	2	240.1816	120.09081	165.5103 <sup>†</sup>	3.6337	1.0590
	Crystallization temperature	2	240.1816	120.09081	165.5103 <sup>†</sup>	3.6337	1.0590
	Time crystallization	2	240.1816	120.0981	165.5103 <sup>†</sup>	3.6337	1.0590
	Stirring	2	5.6208	2.8104	3.8733 <sup>†</sup>	3.6337	0.0247
	Error	16	11.6092	0.7255			0.0511
	Total	26	22679.919				100
	Factor	df <sup>a</sup>	S <sup>b</sup>	V <sup>c</sup>	F <sup>d</sup>	F <sup>e</sup> (0.05, 2,12)	P <sup>f</sup>
Fusion method	Mineralizing agente	2	7442.6904	3721.3452	25.1122 <sup>*</sup>	3.8853	34.1872
	MOH/fly ash ratio	2	380.15496	190.0773	1.2827	3.8853	1.7462
	Fusion temperature	2	380.15496	190.0773	1.2827	3.8853	1.7462
	Fusion time	2	380.15496	190.0773	1.2827	3.8853	1.7462
	Crystallization temperature	2	3802.9793	1901.4896	12.8315 <sup>*</sup>	3.8853	17.4861
	Time crystallization	2	3802.9793	1901.4896	12.8315 <sup>*</sup>	3.8853	17.4861
	Stirring	2	3802.9793	1901.4896	12.8315 <sup>*</sup>	3.8853	17.4861
	Error <sup>g</sup>	12	1778.2615	148.1884			8.1682
	Total	26	21770.354				100

<sup>a</sup> Degree freedom.

<sup>b</sup> Sum of squares.

<sup>c</sup> Mean squares.

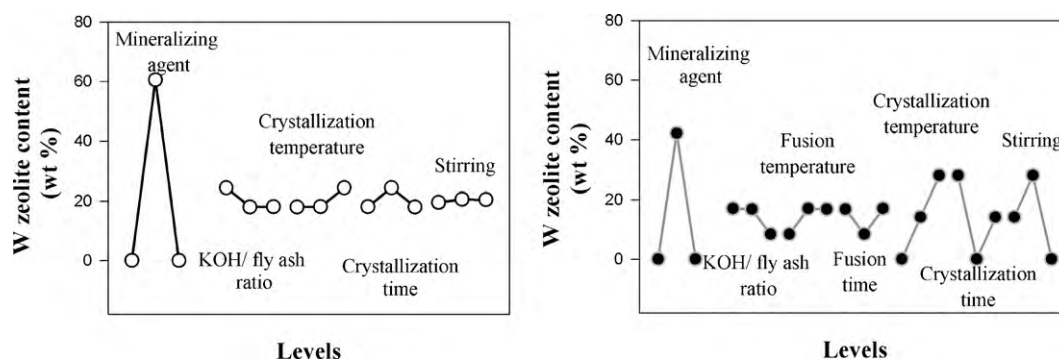
<sup>d</sup> Variance ratio.

<sup>e</sup> F tables.

<sup>f</sup> Percentage of contribution.

<sup>g</sup> Experimental error.

<sup>\*</sup> Factor statistically significant at 5%.



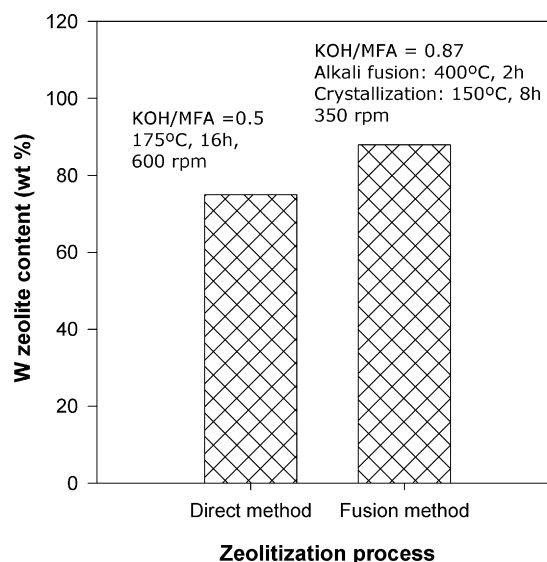
**Fig. 2.** Main effects of zeolitization process by the (○) direct and (●) fusion method.

On the other hand, the most important factor for the fusion method was the type of mineralizing agent (34.18%) followed by the crystallization temperature and time, and finally, the stirring rate.

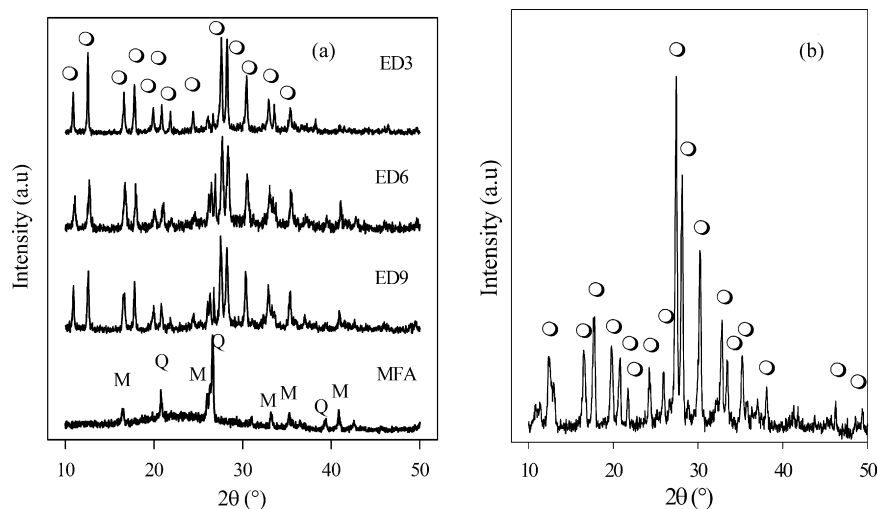
Fig. 2 shows a plot of the main effects of the factors evaluated in the direct and fusion methods. It can be observed that the most important factor for W zeolite synthesis was the mineralizing agent, followed by the KOH/MFA ratio, temperature and crystallization time. Stirring level was not a significant factor. These results are consistent with those obtained from the variance analysis. Considering both of the analyses, the mineralizing agent appears to be the most important factor in W zeolite synthesis.

By the direct method, the highest content of W zeolite was obtained at the lowest KOH/MFA ratio and at the highest crystallization temperature studied. At medium crystallization time, W zeolite was the majority crystalline phase produced.

The optimum conditions of W zeolite synthesis for each zeolitization method were calculated and the experiments were carried out at these conditions to verify the results. Fig. 3 shows the W zeolite content obtained for each method. Using the direct method, the optimal conditions were: KOH/MFA ratio (0.50), crystallization temperature (175 °C), time (16 h) and stirring rate (600 rpm); from this experiment, a 75% yield of W zeolite was obtained. On the



**Fig. 3.** Optimal conditions of synthesis of W zeolite by direct and fusion methods.



**Fig. 4.** XRD patterns of (a) MFA and zeolitic products obtained by the direct method under the conditions given in Table 2 and (b) zeolite obtained under optimal conditions: KOH/MFA of 0.5, 175 °C, 16 h [○: W zeolite; □: quartz; △: mullite].

other hand, using the fusion method, the optimal conditions were the following: KOH/MFA ratio (0.87), fusion temperature (400 °C) and time (2 h); crystallization temperature (150 °C), time (8 h) and stirring rate of 350 rpm; these conditions are the same that EF3 experiment. The W zeolite content was 87.9%.

It is worth noting that the KOH/MFA ratios were between 0.87 and 1.16, and their fusion temperatures were between 400 and 600 °C for periods of 0.5–2 h, followed by hydrothermal treatment at 150 °C for 8 h. All of them led to high W zeolite yields by the fusion method (around 88%). In both cases, high W zeolite yields were obtained when the experiments were run at the set of calculated optimal conditions, validating the statistical analysis.

The control parameter in both the direct and fusion methods was the amount of KOH added to the reaction mixture. The quantity of used alkali was higher in the fusion method than the direct one; therefore, the pH could be higher in the fusion method. The highest yields of W zeolite were 88% (fine needles) and 75% (rectangular prismatic crystals) by the fusion and direct methods, respectively. Following the obtained data, it can be concluded that the highest yield of W zeolite is acquired at high pH. Additional studies must be done to establish the effect of the pH on the yield and morphology of the W zeolite.

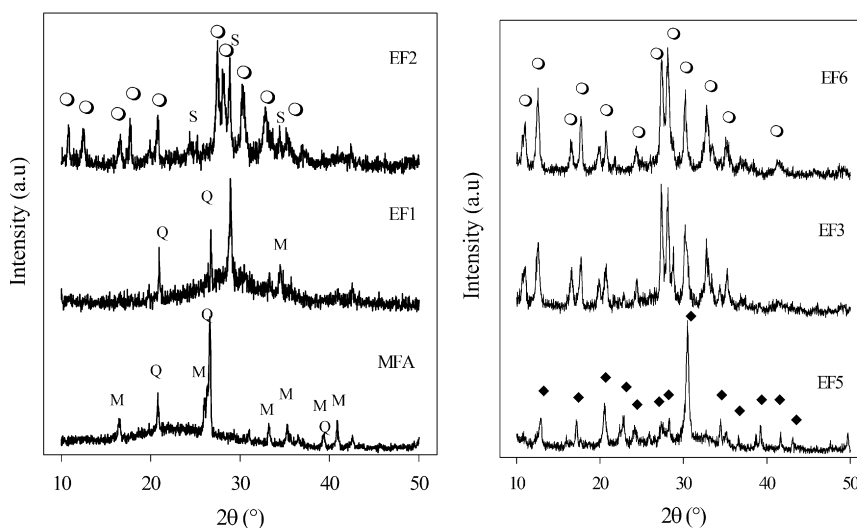
Although the W zeolite yields obtained by the fusion method (88%) were higher than those obtained by the direct method (75%), the zeolites obtained by the former method, were not used in arsenic removal trials. Their morphology of aggregated needle-like crystals limits their utility as adsorbents in drinking water, for example.

To examine the reproducibility of the zeolitization method using different batches of fly ash, another five fly ashes from the same coal-fired plant sampled weekly were submitted to a zeolitization process under the optimal conditions obtained by the direct method. In all of the cases, W zeolite was obtained as the unique crystalline phase with an average of zeolite of 74.8% with standard deviation of 3.4 vs (75% with MFA). These results support that the variations in the composition of the MFA were not significant to the synthesis of zeolitic materials.

### 3.2. Characterization of MFA zeolitization products

#### 3.2.1. XRD W zeolite obtained by direct and fusion methods

XRD results provided evidence that all experiments performed using KOH by the direct hydrothermal method led to the formation of W zeolite (Fig. 4). W zeolite per-



**Fig. 5.** XRD patterns of products obtained by the fusion method [○: W zeolite; □: quartz; △: mullite; S: silicalite; ◆: chabazite].



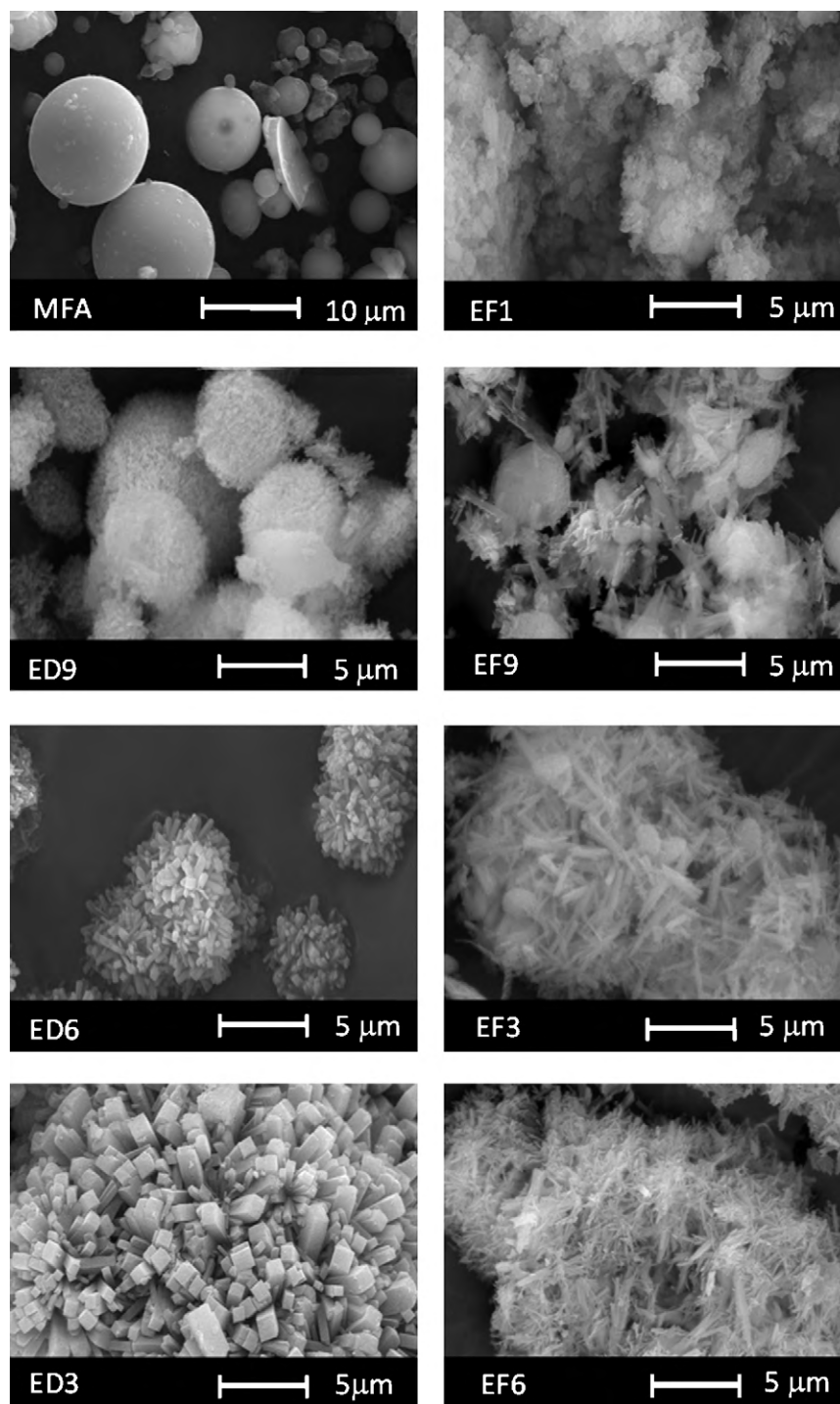


Fig. 6. SEM images of MFA and W zeolite obtained by the direct and fusion method. Experimental conditions are showed in Tables 2 and 3.

centages obtained by each condition are summarized in Tables 2 and 3.

It was found that at higher crystallization temperature, a high yield of the zeolite can be obtained. Thus, the percentage of the zeolitic phase is correlated directly to the crystallization temperature. At 120 and 150 °C, the W zeolite percentage was 52–55%, and the proportion increased to 75% at 175 °C. This result is attributed to the fact that dissolution of aluminum and silicon species from MFA is enhanced at high temperatures. The solution is saturated with de-polymerized and reactive species, which promote the formation of W zeolite. At these studied

conditions, over 8 h were required to form the W zeolitic structure.

Nevertheless, the KOH/MFA ratio calculated as the most suitable to promote zeolitization was 0.5. A ratio of 0.33 resulted in a similar percentage of zeolitic phase (75% and 74%) when crystallization temperature and time were kept constant. In addition, morphology of the obtained products was similar for both ratios. Therefore, it can be concluded that a KOH/MFA ratio of 0.33 is adequate to produce W zeolite.

The amorphous material obtained from the MFA alkaline fusion and crystallized by hydrothermal treatment at 90 °C for 16 h was

**Table 5**  
Chemical composition of MFA and W zeolite obtained from MFA by direct and fusion methods, wt.%.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	CaO	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MgO	SO <sub>3</sub>	ZrO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SrO	LOI
MFA	56.70	23.74	1.49	0.41	3.90	5.98	1.09	0.74	0.66	0.05	0.05	0.05	5.06
ED3 <sup>a</sup>	43.43	17.92	15.09	0.20	2.61	3.96	0.71	0.61	0.10	0.04	0.04	0.03	15.23
EF6 <sup>b</sup>	41.85	19.18	19.58	–	2.52	4.04	0.75	0.53	0.04	0.03	–	0.03	11.32

<sup>a</sup> By direct method (KOH/MFA ratio 0.33, 175 °C, 16 h).

<sup>b</sup> Synthesis by fusion method (KOH/MFA ratio 1.16, alkaline fusion: 600 °C, 0.5 h; crystallization: 150 °C, 8 h).

unsuccessful regardless of the fusion conditions applied (Fig. 5, EF1). Low temperatures delayed the formation of the aluminum and silicate reactive species required to form the zeolitic structure. This phenomenon was confirmed by the observation that when the crystallization temperature was increased to 120 °C, a mixture of W zeolite and silicalite was obtained (Fig. 5, EF2). When the KOH/MFA ratio and fusion temperature were increased, chabazite was obtained after hydrothermal treatment (Fig. 5, EF5). Crystallization of the amorphous material obtained from the thermal treatment of MFA with KOH, carried out at 150 °C for 8 h, led to the formation of W zeolite as the unique crystalline phase in all of the studied cases, (Fig. 5, EF3 and EF6). The content of W zeolite in trials EF3 and EF6 was 87.9 and 88.4%, respectively.

### 3.2.2. Comparative morphology of W zeolite

The morphology of the MFA used as a raw material and the W zeolites obtained by direct and fusion methods are shown in Fig. 6. The MFA mainly consists of spherical hollow particles (censpheres and pleurospheres), but it also contains unburned organic materials and different irregular agglomerations immersed in an amorphous matrix (Fig. 6, MFA). W zeolite obtained by the direct method consists of aggregates of bar-like crystals (Fig. 6, ED3, ED9). The crystal size was higher when the crystallization times exceeded 8 h (Fig. 6, ED6 and ED3). The largest agglomerates were obtained when zeolite W was crystallized at 175 °C for 16 h using a KOH/MFA of 0.33 (Fig. 6, ED3). XRD results suggest that high temperatures and longer crystallization times enhance W zeolite formation and promote crystal growth, resulting in W zeolite peaks that were narrower under these conditions. Regardless of the method used to prepare the W zeolites, the XRD pattern was largely the same. However, the morphological characteristics of the W zeolites obtained by the fusion method (Fig. 6, EF6) were completely different from those obtained by the direct method (Fig. 6, ED3). An amorphous phase was observed for the experiments carried out at low temperatures (90 °C) (Fig. 6, EF1). Instead of aggregates of bar-like crystals obtained by the direct method, W zeolite was obtained as agglomerates of needle-like crystals by the fusion method. Needles were thinner when the crystallization temperature was increased from 120 to 150 °C (Fig. 6, EF6). When a KOH/MFA ratio of 1.46 was applied, no agglomerates were observed, but needle-like crystals were randomly distributed with some amorphous material (Fig. 6, EF9).

Different experimental conditions resulted in a different nucleation process, and a product with different morphological

**Table 6**  
Textural properties of MFA and experimental zeolitic products.

	Area BET (m <sup>2</sup> /g)	Pore total volume (cm <sup>3</sup> /g)	Average pore size (Å)
MFA	4.73	0.0323	273.9
EF6	55.31	0.2416	174.7
ED3	28.48	0.1319	185.2
WMOD <sup>a</sup>	17.26	0.0842	195.1
WNH4 <sup>a</sup>	40.55	0.1346	138.0
Y75NH4	588.20	0.3542	24.00

<sup>a</sup> Obtained from ED3.

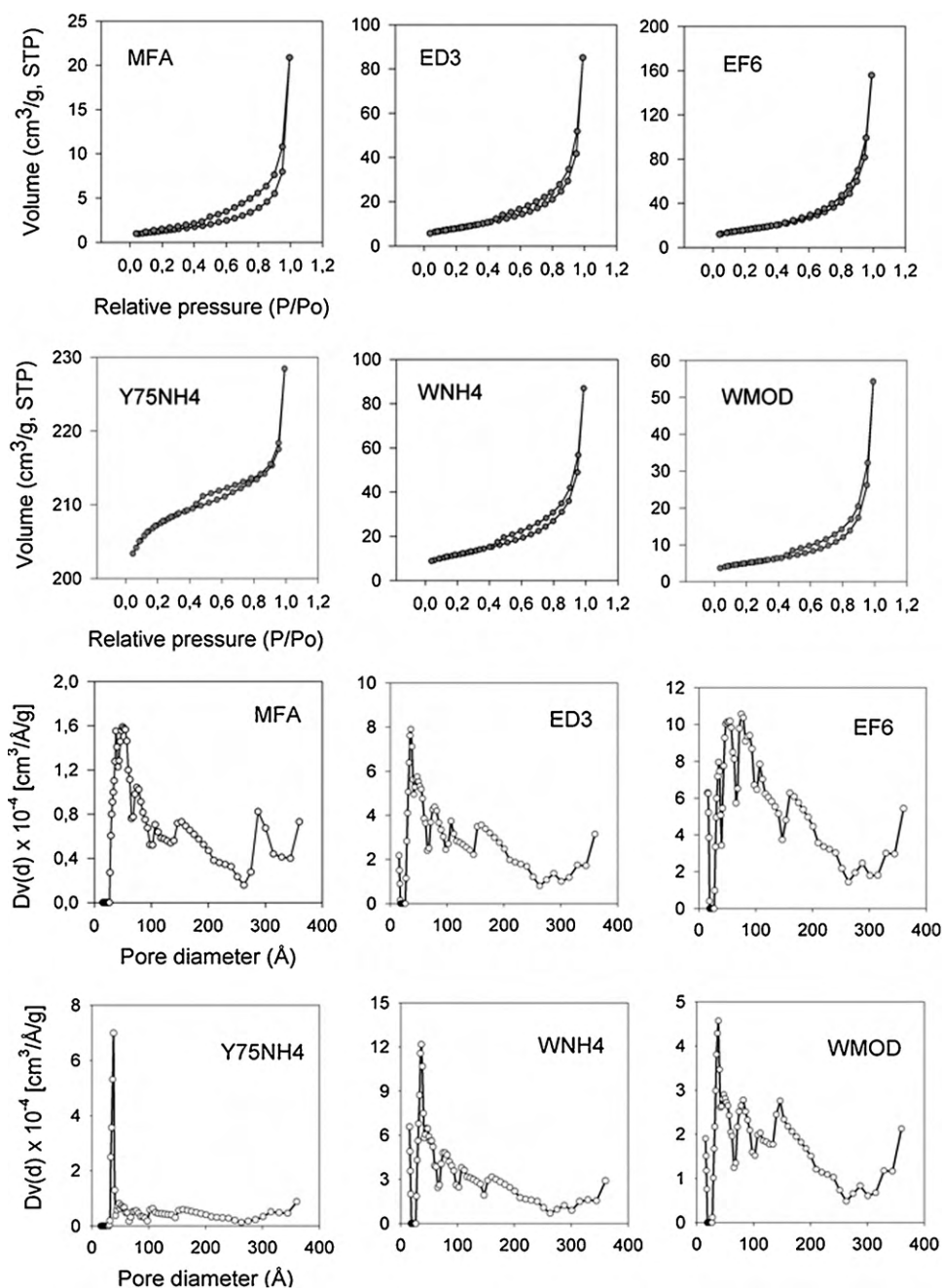
characteristics was obtained. The difference in mineralizing agent concentration used in each zeolitization method, as well as the ageing step, results in materials with the same XRD pattern but different size and morphology. Thus, it can be summarized that the kinetics of the nucleation and crystallization process are dependent on the amount of alkali, temperature, and chemical composition of the initial reaction mixture, among other factors. Some of these findings were explained by Valtchev et al. [57], who demonstrated that during the polymerization step, the cation (potassium) is not integrated into the gel network. At this early stage, the cation is concentrated at the surface or in a close environment to the gel particles. Valtchev et al. [57] says that the cation progressively enters into the solid matrix, breaks the structure, and reorganizes the aluminosilicates species. Thus, this mechanism will be favored at high potassium concentration.

During the ageing step carried out at room temperature of the fusion method, slower nucleation rates dominate with respect to crystal growth and thus relatively small crystallites are obtained [57]. In contrast with the direct method, few nuclei overcome the energetic barrier at elevated temperature and continue their growth.

The difference in crystal size obtained for W zeolites can be explained in terms of the difference in the alkalinity in the direct (low) and fusion (high) methods. It has been found that the alkalinity affects the rate of nucleation more than the rate of crystal growth [58]. The crystallites tend to be larger at low OH<sup>-</sup> concentrations, presumably because of formation of fewer nuclei [58]. The small amount of KOH required by the direct method for MFA zeolitization results in the low alkalinity and large crystal size obtained.

The nature of the starting silica and alumina species required to assemble zeolitic structures may account for the differences in size, number, and morphology of crystals formed in W zeolite from the direct method. The formation of building units occurs slowly, and, consequently, a very small number of nucleation centers are formed. The final result is a low number of large zeolitic crystals [59]. On the other hand, when an initial MFA/KOH heating treatment is applied, the de-polymerization process is accelerated and an amorphous material is produced. Dissolution of reactive species from the amorphous material is faster than in the direct method [60]. During the aging step, a large number of nucleation centers are generated, and as a consequence a large number of small crystals are formed [53].

Comparing the yields and properties of W zeolite obtained from MFA by the direct and fusion methods using KOH as a mineralizing agent in both procedures, it was possible to define the most efficient and convenient route to prepare W zeolite that would be potentially useful in the arsenic removal from drinking water. The direct re-crystallization of the MFA was carried out using only 48% of the volume of the reactor at 175 °C, 16 h. H<sub>2</sub>O/MFA and KOH/MFA ratios of 3 and 0.333 in weight were used, respectively, to obtain 25% of W zeolite more than the weight of MFA fed to the reactor. Large crystalline aggregates of W zeolite are generated in this single step. This morphology and size facilitate the operations of filtration and washing. The method of MFA amorphization implies two stages prior to the crystallization. The first stage consists of transforming the thermodynamically stable crystalline species that compose the



**Fig. 7.** Adsorption and desorption isotherms of  $N_2$  ( $-196^\circ\text{C}$ ) and pore size distribution of MFA, W zeolite obtained by the direct (ED3) and fusion methods (EF6); Y75NH4; and W zeolite modified with ammonium chloride (WNH4) and aluminum salt (WMOD).

MFA by potassic fusion (KOH/MFA ratio of 1.3 in weight,  $600^\circ\text{C}$ , 0.5 h) in an amorphous material that in the second stage is aged in  $H_2O$ /MFA ratio of 8.24 in weight and stirred ( $25^\circ\text{C}$ , 17 h). Finally, the resultant amorphous mixture is crystallized ( $150^\circ\text{C}$ , 8 h). Sixty-three percent of the volume and eighty-six percent of the weight of MFA fed to the reactor was obtained. Small and fine needle crystals are produced; this morphology limit has possible application for drinking water treatment.

A comparison between the direct and fusion methods used to prepare W zeolite led to the selection of the direct one as potentially useful to produce W zeolite at a larger scale. First of all, the amorphization method requires two additional steps that imply higher energy consumption (alkaline fusion and aging) than the direct method. Additionally, because using low volume of the reactor (48% vs. 63%) and a concentrated system given by  $H_2O$ /MFA ratio

in weight (3.0 vs. 8.24) and low KOH/MFA ratio in weight (0.333 vs. 1.16), a higher amount of the W zeolite was produced by weight unit of MFA (1.25 vs. 0.86). Another important attribute that the direct method had over the fusion method was the size and the shape of the zeolitic crystals. Aggregates of rectangular prismatic large crystals are obtained by the direct method while fine needles crystals are obtained by the fusion method.

### 3.3. Chemical and textural properties of W zeolite

As a result of the MFA zeolitization process, the experiments that led to the highest W zeolite content by each method were selected for further characterization. They were ED3 (KOH/MFA ratio 0.33,  $175^\circ\text{C}$ , 16 h) and EF6 (KOH/MFA ratio 1.16, alkali fusion:  $600^\circ\text{C}$ , 0.5 h; crystallization:  $150^\circ\text{C}$ , 8 h) by the direct and fusion method,

respectively. Chemical and textural properties of these materials were measured. In Table 5, the chemical composition of W zeolite obtained by the direct and fusion method is shown; the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of W obtained by the direct method was 4.12 while that of W synthesized by fusion method was 3.71.

After W zeolite modification of the (ED3) with aluminum salt, the contents of potassium, sodium and calcium were reduced by 21%, 68% and 66% respectively and replaced by  $\text{Al}^{3+}$  ions. In the case of W zeolite modification with ammonium chloride, 93% of potassium and 87% of sodium present in W zeolite was removed and replaced by ammonium cations. This means that the modifier agents ( $\text{Al}^{3+}$  and  $\text{NH}_4^+$ ) are located inside the zeolite pores, where the  $\text{Na}^+$  or  $\text{K}^+$  are neutralizing the zeolite surface.

Nitrogen adsorption isotherms are shown in Fig. 7 for MFA and experimental W zeolites synthesized by both the direct method (ED3) and the fusion method (EF6) as well as for W zeolite modified with ammonium (WNH4) and aluminium (WMOD) salts. These isotherms fit the description of a type IIb isotherm according to the IUPAC classification system [61]. The Y75NH4 zeolite isotherm exhibited a type I isotherm. The shape of the fly ash and zeolitic isotherms was related to the presence of pores with narrow and elongated sections and to the possible presence of interconnecting channels [62]. Zeolites typically display a type I isotherm, but several factors such as crystal size, zeolite content, and amorphous silica or aluminosilicate content can generate distortions on the isotherm shape [61]. Differences observed in isotherms were related to differences in pore size and geometry, which were inferred by pore size distribution (Fig. 7).

Specific surface area and total pore volume of fly ash and W zeolite synthesized by both methods are summarized in Table 6. The zeolitization process led to an increase in BET area and pore volume over the MFA starting material, particularly for W zeolite obtained by the fusion method.

As a result of the modification with aluminum sulfate of ED3, the BET area and their pore size were decreased, which it can be attributed to the partial filling of pore spaces by aluminum [63]. Ammonium exchange of ED3 led to an increase in specific surface area. Y75NH4 showed a high BET area characteristic of faujasite-type zeolites.

The W zeolite structure did not show significant changes either after ammoniacal exchange or modification with aluminum sulfate.

#### 3.4. Arsenic (V) removal

The arsenic (V) adsorption capacity of W zeolite in its different forms was evaluated: as it was obtained from the direct method (ED3), modified with  $\text{NH}_4\text{Cl}$  (WNH4), and modified with aluminum sulfate (WMOD). As a reference, an experimental Y zeolite was also evaluated in its sodic form (Y75Na) and in its exchanged with  $\text{NH}_4\text{Cl}$  form (Y75NH4). The results obtained are shown in Fig. 8.

Sodium Y zeolite (Y75Na) taken as a reference demonstrated poor As (V) removal under the studied conditions. The modification of sodium Y zeolite with ammonium chloride by ion exchange (Y75NH4) increases the As (V) removal. In contrast, ammonium W zeolite (WNH4) obtained by the same procedure demonstrated no significant changes in its sorption behavior upon ion exchange (Fig. 8). This can be explained by the differences in pH observed during the adsorption process. Using WNH4 zeolite, the initial pH of the suspension was 7.0, which increased to 7.5 during the removal process. The experimental Y zeolite showed the opposite behavior, with Y75NH4 tending to decrease the pH of the arsenic solution from 7.0 to 6.0. Increase of the pH indicates that surface sites are being hydrolyzed and zeolite particles are becoming negatively charged, which reduces arsenic adsorption rates [64]. On the other hand, when the pH is reduced, particles become positively charged, and arsenic adsorption is favored. During the adsorption process,

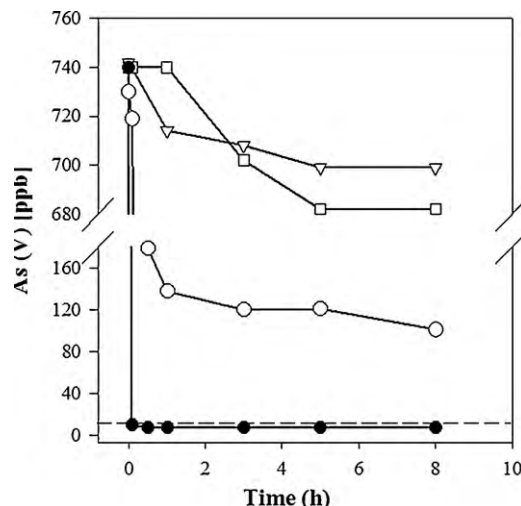


Fig. 8. Adsorption As (V) on W zeolite ( $\nabla$ : ED3;  $\square$ : WNH4;  $\bullet$ : WMOD) and  $\circ$  Y75NH4.

WMOD zeolite showed a sharply decreasing in pH (7 to 4.5) and the concentration of arsenic (V) also decreased from 740 to 10 ppb in five minutes. At these pH conditions, there are two species in equilibrium.  $\text{H}_2\text{AsO}_4^{1-}$  dominates at a pH lower than 6.9, while at higher pH,  $\text{HAsO}_4^{2-}$  is dominant. Arsenic (V) does not change its oxidation state at the studied pH (7.0 at the beginning). In these trials, the effect of pH was not evaluated; however, it will be considered in further works.

Shevade and Ford [41] found that another important factor related to arsenic removal efficiency is the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in the zeolitic structure. They recommend zeolites with low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio ( $2 < \text{SiO}_2/\text{Al}_2\text{O}_3 \leq 12$ ) for efficient As (V) removal. Thus, experimental faujasite Y75NH4 ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio equal to 4) was prepared and used as an internal reference to compare with W zeolites obtained by MFA zeolitization. The arsenic removal efficiency shown by Y75NH4 was 85% at the conditions studied. On the other hand, the WMOD zeolite with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 3.5 removed 99% of arsenic.

The high arsenic removal shown by a W zeolite modified with an aluminum salt is attributed to the generation of new sites with different electric charge as is reported by Onyango et al. [64] using a commercial modified faujasite to remove arsenic (V). This charge tends to be positive, which favors the attraction of arsenic species in aqueous solutions.

Although the present results highlight the high potential of modified W zeolite as a nanostructured material for arsenic (V) removal, additional studies are in progress to clarify the effects of parameters such as temperature, pH, and arsenic concentration, among other factors, on the arsenic adsorption capacity of W zeolite and to elucidate the mechanisms of arsenic removal. Furthermore, low cost zeolites will be synthesized by using other industrial wastes such as geothermal waste and applying microwave as the energy source to reduce crystallization times.

#### 4. Conclusions

The studied Mexican fly ash is so reactive that it can be applied in the synthesis of low cost zeolites, whose chemical, morphological, and textural properties can be tailored by adjusting the synthesis conditions. The obtained zeolites can be modified to achieve the properties required for a specific process. These properties could be an advantage to obtain a versatile material that can be used in specific applications. In this particular case, the chemical nature of the W zeolite surface could be modified to force the adsorption of

anionic arsenic (V) species instead of the cationic species that zeolites naturally adsorb. The alkaline hydroxide plays an important role in the amorphization of the crystalline phases included in the fly ash. With potassium hydroxide, it is possible to prepare W zeolite with textural and morphological properties that depend on the synthesis route. This particular finding can be used to apply the synthesized W zeolite in processes such as cationic species removal, anionic species removal, organic compounds adsorption, and acid catalysis.

The direct method to obtain the W zeolite described in this work implies the use of a MFA without any pretreatment; in addition, the KOH/MFA and H<sub>2</sub>O/MFA ratios are low, the re-crystallization conditions are relatively soft, and the obtained yield is one of the highest reported in literature. Furthermore, it is possible to modify its surface to promote the adsorption of anionic species. With these attributes, the direct method to convert fly ashes in zeolites is considered a significant contribution. Both the zeolite W and its modified version developed in this study are strongly recommended to be scaled up at the pilot plant level and to study the possibility to be applied in cationic removal species (unmodified zeolite), and to reach less than 10 ppb of arsenic in aqueous solution, which is the limit recommended by worldwide health organizations for drinking water. The remaining challenge is to develop a method to regenerate the surface of the zeolite saturated with arsenic to extend its useful life and, finally, to develop a method to recover arsenic and to dispose of the exhausted zeolite.

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