

# Differential Behavior of Combustion and Gasification Fly Ash from Puertollano Power Plants (Spain) for Zeolite Synthesis and Silica Extraction

**Oriol Font<sup>1</sup>, Natalia Moreno<sup>1</sup>, Sergi Diez<sup>1</sup>, Xavier Querol<sup>1</sup>, Angel López-Soler<sup>1</sup>, Pilar Coca<sup>2</sup>, Francisco García Peña<sup>2</sup>**

<sup>1</sup>Institute of Earth Sciences "Jaume Almera", (CSIC), Lluís Solé i Sabarís str, s/n, 08028 Barcelona, Spain. <sup>2</sup>ELCOGAS S.A., Carretera de Calzada a Puertollano km 27, 13500 Puertollano, Ciudad Real, Spain.

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## ABSTRACT

Coal gasification (IGCC) and pulverised coal combustion (PCC) fly ashes (FAs), obtained from two power plants fed with the carboniferous bituminous coal from Puertollano (Spain), were characterized. Both FAs were used as raw materials for zeolite synthesis by direct conversion and by alkaline fusion, and SiO<sub>2</sub> extraction at laboratory scale. The Puertollano FAs are characterised by a high SiO<sub>2</sub> content (59 %) with respect to EU coal FAs. The zeolite synthesis and SiO<sub>2</sub> extraction yields obtained for the two types of FAs were compared. High zeolite synthesis yields were obtained from both FAs by using conventional alkaline activation. However, the SiO<sub>2</sub> extraction yields were very different. In the IGCC FA the occurrence of Al<sub>2</sub>O<sub>3</sub> only in the highly soluble glass matrix, limits drastically the SiO<sub>2</sub> extraction with respect to the very high extraction yields obtained for the PCC FA. In the PCC FA, the occurrence of mullite (a highly insoluble Al-bearing phase) accounts for the trapping of Al<sub>2</sub>O<sub>3</sub> and prevents the fast dissolution of Al<sub>2</sub>O<sub>3</sub> when SiO<sub>2</sub> is extracted. If both Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> are extracted simultaneously, the extraction solution is saturated in Al<sub>2</sub>O<sub>3</sub> and the SiO<sub>2</sub> extraction is limited by the precipitation of zeolitic material in the extraction residue. The results of the zeolite synthesis from the Si-bearing extracts from both FAs demonstrated that high purity zeolites with high cation exchange capacity (CEC, between 4.3 and 5.3 meq/g) can be produced. Furthermore, the solid residue arising from SiO<sub>2</sub> extraction is also a relatively high NaP1 zeolite product (CEC from 2.4 to 2.7 meq/g) equivalent to the direct conversion products. The zeolitic materials synthesised from both FAs by alkaline fusion showed an intermediate (between the high purity zeolites and the direct conversion products) zeolite content with CEC values from 3.4 to 3.7 meq/g. Low leachable metal contents were obtained from high purity A and X zeolites and zeolite material synthesised by alkaline fusion for PCC FA. Conversely, the high metal content leached from zeolites synthesised from IGCC FA limits the possible applications of these products.

## INTRODUCTION

More than 43 million tonnes (metric) of coal FA are produced annually in the European Union<sup>1</sup>. Although the main proportions of these FAs are produced by Pulverized Coal Combustion (PCC) process, a small amount of FA are generated from the Integrated Coal Gasification Combined Cycle (IGCC). In the PCC plants the 80% of coal combustion by-products are produced as FAs and 20% as slag. Conversely, most of the gasification by-products are obtained as slag (around 90 %), and a small proportion (around 10 %) is collected as FA. Apart from these differences, the PCC and IGCC processes generate FAs with different mineralogical compositions.<sup>2</sup> The PCC FAs are made up of aluminosilicate glass (52-90% for European FAs<sup>3</sup>), with Ca, Fe, Na, K, Ti, Mn impurities, and variable minor amounts of quartz, mullite, lime, hematite, magnetite, gypsum and feldspars, as well as traces of sillimanite, cristobalite-trydimite, wollastonite, and Fe-Al spinels. IGCC FAs are characterized by a predominant aluminosilicate glass matrix and a wide variety of fine crystalline reduced species (mainly sulphides).<sup>2</sup>

Owing to the large volume of FA generated from power generation, their use has been mainly based in the manufacture of concrete and cement since 1950s. However, other novel potential applications such as the synthesis of zeolites from FA have been proposed. Höller and Wishing<sup>4</sup> prompted the synthesis of zeolites from FAs due to the compositional similarity of these products to some volcanic materials, precursor of natural zeolites. Afterwards, many patents and technical articles have proposed different methods to synthesize different types of zeolites from FAs.<sup>5-20</sup> However, most of these methodologies are based on the alkaline hydrothermal activation (mainly by means of NaOH and KOH solutions). Shigemoto et al.<sup>21</sup> optimized the traditional direct conversion by the introduction of an alkaline fusion step prior to synthesis. This fact permitted to obtain different types of zeolites with potential industrial application (such as NaP1, chabacite, herchelite). The direct conversion method was also applied by the use of dry conversion systems.<sup>22-23</sup> Recently the alkaline fusion procedure has been improved to obtain high porous size and CEC zeolitic material<sup>24-26</sup>. Other studies on direct conversion allowed to reduce the synthesis time (from hours to few minutes) by microwave assisted method.<sup>27</sup> However, the zeolitic products obtained by direct conversion have low CEC values due mainly to incomplete conversion of the FA in zeolite. Hollman et al.<sup>28</sup> prompted the synthesis of zeolites from SiO<sub>2</sub> extracts from FAs obtaining high purity zeolites (>95% of A and X zeolite), and Moreno et al.<sup>29-30</sup> optimised this method synthesising in the same process zeolites with high purity from SiO<sub>2</sub> extracts and another zeolitic product (the solid residue from SiO<sub>2</sub> extracts), equivalent to zeolites obtained by direct conversion method.

As a consequence of the peculiar structural properties of zeolites, intensive research on the potential industrial applications of zeolites synthesised from FA was also carried out. The high Al<sup>3+</sup>/Si<sup>4+</sup> ratio of some types of zeolites accounts for the high CEC (up to 5 meq/g) of some zeolites such as A, NaP1, X, KM, F, chabazite and herschelite. For these reasons, the heavy metals and ammonium uptake has been the major application field tested.<sup>9,10,17,27,29,31-37</sup> Moreover, the use of these zeolites as molecular sieves for the gas cleaning technology has also been investigated by a few studies<sup>38-39</sup>. In this case, it is important to note that the presence of water vapour

in the flue gas may considerably reduce the gas uptake capacity of these zeolites in actual industrial applications.<sup>33</sup>

In spite of these interesting properties, nowadays the use of zeolitised FAs is limited due to the following key questions:

- The use of high CEC resins is preferred instead zeolites due to the higher CEC and the lack of large zeolites deposits in Europe.
- The zeolitic products synthesised by the direct conversion method contain a non-converted part of FA. Consequently, the CEC of these products is much lower than that of the pure commercial synthetic zeolites. Moreover, the residual FA fraction may contain leachable B, Mo and Se, which may limits the utilization of this zeolitic material in specific water purification processes. However, this zeolitic material may be used for industrial wastewater treatments
- Although the synthesis of zeolites from SiO<sub>2</sub> extraction from FA has the advantage of producing high purity zeolitic materials with a large pore volume (equivalent to commercial products), the extrapolation of the synthesis conditions to an industrial scale supposes high economic costs.
- Other limitations are:
  - Low resistance to acidic attack of most synthetic zeolites.<sup>40</sup> Although this fact supposes a low applicability of zeolites employed in long-term processes (such as passive geochemical barriers), their use lead to very good results in short time treatments.
  - The application of zeolitic materials for NH<sub>4</sub><sup>+</sup> uptake treatments from actual waste waters may be limited by the ionic competition between major cations and NH<sub>4</sub><sup>+</sup><sup>33</sup>. However, this effect is lower in the uptake of metals.
  - Low mechanical resistance of zeolitic products. With the aim of increasing the potential applications (such as permeable columns or barriers), the pelletisation of the zeolitic material was tested.<sup>39</sup> However, the results showed that the pelletisation supposed an important reduction of CEC of the zeolitic product.

The main objectives of this study were to investigate and compare the behaviour of PCC and IGCC FAs for the synthesis of zeolite by using three different zeolite synthesis methods: SiO<sub>2</sub> extraction, direct conversion and alkaline fusion. In addition, it was evaluated the quality of the zeolitic products obtained in view to evaluate some of the above limitations. To this aim, the FAs produced in the ENECO PCC and ELCOGAS IGCC powers plants from Puertollano (Spain), fed with the metal-rich carboniferous bituminous Puertollano coal, were characterized and used as raw materials for the zeolite synthesis. The Puertollano FAs were selected because the high SiO<sub>2</sub> contents (59%) with respect to the EU coal FAs.

## METHODOLOGY

### Fly ashes

With the aim of comparing the different behaviour of PCC and IGCC FAs during zeolite synthesis, two FAs samples from ENECO PCC and ELCOGAS IGCC power plants, fed with the carboniferous bituminous coal from Puertollano (Spain), were

selected. The IGCC plant is fed with a 50:50 mixture of coal and petroleum coke from a nearby refinery, whereas the PCC plant is fed with 100% of coal.

The chemical composition of these FAs was determined by means of an acid digestion method devised for the analysis of trace elements in coal and combustion wastes.<sup>41</sup> In addition, the FA international reference material NBS 1633<sup>b</sup> was also analysed to check the accuracy of the analytical and digestion methods. The silica, C and Hg contents were determined directly in solid samples by X-Ray Fluorescence (XRF), LECO elemental analysers, and Hg Gold amalgam AAS analyser, respectively. The rest of the elements were analysed in the acid digestions by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

The mineral composition of the FAs was determined by X-Ray diffraction (XRD) using a SIEMENS D501 powder diffractometer with a graphite monochromator, NaI(Tl) detector and Cu K $\alpha$  radiation. Final quantitative XRD analysis of the original FAs was obtained by the Internal Reference Method, using fluorite as an internal standard.<sup>42-44</sup>

The physical characterisation included proximate analysis (moisture content at 105 °C and loss on ignition at 1050°C), BET surface area and particle size determinations. The particle size distributions were determined by means of laser diffraction particle sizer (Malvern Mastersizer/E®). The BET surface area was measured with a multi-point volumetric apparatus (Micromeritics® model ASAP 2000) by adsorbing and desorbing nitrogen on samples previously dried and out-gassed (150 °C, 12Hrs under a vacuum of 0.1mm Hg).

Details on chemical, mineralogical and physical characterisation of these FAs are shown in Table 1. From the point of view of these material reactivity for the zeolite synthesis and SiO<sub>2</sub> extraction, the main difference is the high content of aluminosilicate glass matrix (90%) and a wide variety of fine crystalline reduced species (mainly sulfides) in IGCC FA. However, PCC FA is made up of a lower proportion of aluminosilicate glass (66%) and variable small amounts of quartz, mullite and magnetite. Other differences between the FAs were that the content in most trace elements is much higher in IGCC than PCC FA, probably due to the lower IGCC FA/slag ratio. In addition, the IGCC FA exhibits finer grain size than PCC.

### Zeolite synthesis

Three ways for the zeolitisation of the two cited FAs were compared in this study: a) SiO<sub>2</sub> extraction followed by a synthesis process to obtain A (Na<sub>12</sub>Al<sub>12</sub>Si<sub>12</sub>O<sub>48</sub>·27H<sub>2</sub>O) and X (Na<sub>86</sub>Al<sub>86</sub>Si<sub>106</sub>O<sub>384</sub>·264H<sub>2</sub>O) zeolites with high purity, b) direct conversion to obtain NaP1 (Na<sub>6</sub>Al<sub>6</sub>Si<sub>10</sub>O<sub>32</sub>·12H<sub>2</sub>O) products and, c) fusion method to produce high X zeolitic material.

### *Synthesis of zeolites by SiO<sub>2</sub> extraction*

PCC and IGCC FAs are characterised by high SiO<sub>2</sub> and high glass content, as well as, high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio (Table 1), therefore these FAs may be suitable for obtaining high SiO<sub>2</sub> extraction yields for further synthesis of zeolites.<sup>45</sup> Also, the relatively high

SiO<sub>2</sub> extraction yield obtained for PCC FA in prior studies on SiO<sub>2</sub> extraction from EU Fas,<sup>30,45</sup> provides a justification for testing this zeolite synthesis method.

Based on the results obtained in these studies, the SiO<sub>2</sub> extraction tests were carried out at temperatures between 50 and 150 °C, NaOH solution/FA ratios between 2 and 5 L/kg, NaOH concentrations from 0.5 to 3 M and extraction times from 1 to 24h. These SiO<sub>2</sub> extraction tests were performed with magnetic stirring, using closed heated system in 60 mL Savillex PFA reactors on hot plates for experiments at 50-90 °C. The reactors were immersed in a water bath for a better control and a homogeneous application of temperature. For the tests at temperatures >90 °C, a Parr 2L 4843 autoclave reactor with continuous stirring by mechanical agitation, temperature and pressure controls was used. The SiO<sub>2</sub> extracts obtained were used as starting solutions to optimise the pure A and X zeolite synthesis. This method is based on combining SiO<sub>2</sub>-rich and Al<sub>2</sub>O<sub>3</sub>-rich solutions to obtain high purity zeolites, after gelification, aging and crystallization steps. The Al<sub>2</sub>O<sub>3</sub> source used for this study was an Al<sub>2</sub>O<sub>3</sub>-rich waste solution supplied by an Al-anodising industry (Fuertes S.L Parets del Vallés, Barcelona). This high Al<sub>2</sub>O<sub>3</sub> solution contained 168.1 g Na<sub>2</sub>O/L of and 192.0 g Al<sub>2</sub>O<sub>3</sub>/L. The molar ratios tested for synthesis of high pure A and/or X zeolites were: Na<sub>2</sub>O/SiO<sub>2</sub> from 1.3 to 4.5, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> from 1.0 to 2.5 and, H<sub>2</sub>O/Na<sub>2</sub>O from 25 to 50, based on typical synthesis conditions for pure zeolites<sup>46-47</sup>, and IQE S.A, recommendations for zeolites synthesised from SiO<sub>2</sub> extracts arising from FA by Hollman et al.<sup>28</sup> and Sáez<sup>48</sup>. Likewise, the synthesis strategy was based on the following steps: a) gelification (between 40°C to 80°C, from few minutes to 2h), b) aging to 25°C until 23h and, c) crystallisation (between 70°C to 90°C, from 1 to 72h). The synthesis procedure was optimised to avoid the aging step and to reduce the synthesis time.

Table 1. Chemical, physical and mineralogical characteristics of the IGCC and PCC FAs from Puertollano power plants (Spain ) selected for this study

	PCC	IGCC	PCC	IGCC	PCC	IGCC
Major oxides (%)	Trace elements (mg/kg)					
SiO <sub>2</sub>	58.6	58.5 B	534	89Mo	11	135
Al <sub>2</sub> O <sub>3</sub>	27.4	20.6 Ba	460	433Rb	139	302
Fe <sub>2</sub> O <sub>3</sub>	7.3	4.3 Be	14	13Sb	120	381
CaO	0.8	3.6 Co	31	53Se	7	19
MgO	1.0	0.6 Cu	75	392Sn	10	67
Na <sub>2</sub> O	0.3	0.6 Ga	34	320Sr	131	102
K <sub>2</sub> O	2.4	3.8 Ge	61	420Th	30	22
P <sub>2</sub> O <sub>5</sub>	0.1	0.5 Hq	1.3	<0.01U	15	6
TiO <sub>2</sub>	0.7	0.6 Mn	511	222Zn	924	7230
SO <sub>3</sub>	0.2	2.7				
C	0.7	4.5				
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	2.1	2.8				
Physical characteristics	<b>Mineralogy</b>		<b>PCC</b>	<b>IGCC</b>		
grain size distribution (µm)	Glass		66	90		
percentile 10	4.7	1.4 Mullite	20	No		
median	26.2	3.7 Quartz	10	No		
percentile 90	123.8	26.3 Magnetite	3	No		
H <sup>a</sup> (%)	0.1	0.3 Galena	No detected		4	
LOI (%)	1.1	5.1 Sphalerite	No detected		3	
BETSA (m <sup>2</sup> /g)	2.7	7.3 Wurtzite	No detected		2	
		Nickeline	No detected		1	

### *Synthesis of zeolites by direct conversion*

The solid residue arising for the SiO<sub>2</sub> extraction is in fact a direct conversion product, as demonstrated by Moreno et al.<sup>30</sup>. Consequently, characterisation of these residues was used to evaluate the direct conversion efficiencies. Furthermore, for higher temperatures (150 to 200 °C), conventional direct conversion experiments were carried out on PCC and IGCC FAs using PARR 4744 reactors 2 L/kg, from 0.5 to 5 M NaOH and from 8 to 24 h.

### *Synthesis of zeolites by alkaline fusion*

Based on the method prompted by Rayalu et al.<sup>24-25</sup> high X zeolitic material was synthesised from FA by NaOH fusion. The homogeneous fusion mixture was obtained by mixing pulverized FA and NaOH at different ratios (from 1.2 to 2, by weight). This mixture was heated at a temperature ranging between 550 and 600 °C for 2h. The fused mixture was then cooled at room temperature, carefully milled and mixed thoroughly in distilled water (1 g FA/10 mL H<sub>2</sub>O). In fact, this fused mass obtained was agitated mechanically for several hours (12-16 h). The resultant gel was then subjected to crystallisation and kept at 90 °C at two different times (6 and 8 h). Afterwards, the solid crystalline product was filtered and repeatedly washed with distilled water to remove excess NaOH until the filtrate pH was 10-11. Finally, the precipitate was dried at a temperature of 50-60 °C.

### Quality evaluation

The zeolitic products obtained from the different experiments were filtered and washed with distilled MilliQ water, dried at room temperature and analysed by means of XRD. Their morphology was examined by means scanning electron microscope (SEM-Jeol). Furthermore, the purity of the zeolitic products synthesised in this work was evaluated by comparing of the CEC, determined by the method of ISRIC<sup>49</sup>, with pure commercial A, X and NaP1 zeolites supplied by IQE S.A (Indústrias Químicas del Ebro). Moreover, to determine the potential mobility of trace elements from the zeolitic products, a leaching test (DIN-38414), was applied to all zeolitic materials. Major and trace element contents in the leachates were determined by means of ICP-AES and ICP-MS.

## RESULTS

### Zeolite synthesis

#### *Synthesis of zeolites by SiO<sub>2</sub> extraction*

The highest SiO<sub>2</sub> extraction yields obtained for both FAs were: 66.5 g SiO<sub>2</sub>/L (equivalent to 200 g SiO<sub>2</sub>/kg of FA) from PCC FA, at 120 °C, 9h and 3 L/kg of 3M NaOH, and 40 g SiO<sub>2</sub>/L (equivalent to 120 g SiO<sub>2</sub>/kg of FA) using the IGCC FA at 90 °C, 9h and 5 L/kg of 3M NaOH.

The results on SiO<sub>2</sub> extraction from PCC FA demonstrated that increasing temperature from 50 to 120 °C, increased SiO<sub>2</sub> extraction yields from 27 to 200 g SiO<sub>2</sub>/kg; however the yields decrease down to 131 g SiO<sub>2</sub>/kg for temperature >120

°C, due to the precipitation of SiO<sub>2</sub>-bearing species. Also, high SiO<sub>2</sub> extraction yields were obtained when reducing the NaOH/FA ratio from 4 to 2 L/kg, at 150 °C, but at 120 °C, the SiO<sub>2</sub> extraction yields attained at 3L/kg were even higher. Consequently, the optimal SiO<sub>2</sub> extraction conditions for IGCC FA may be fixed at 120 °C, 3 L/kg and 3M NaOH. The extraction experiments performed using this optimal conditions allowed fixing the optimal extraction time at 9h.

The SiO<sub>2</sub> extraction tests carried out with IGCC FA reached extraction yields ranging from 1 to 120 g/kg. The highest SiO<sub>2</sub> extraction yield was attained at 90 °C, 3M NaOH, 5 L/kg and 9h. The SiO<sub>2</sub> extraction yields increased for high NaOH/FA ratios and high temperature (up 90-120 °C), while decreased if temperature exceed 120 °C. Also, higher SiO<sub>2</sub> extraction yields (by a factor 1.5-2) were obtained for 5 L/kg than 3 L/kg at <90 °C. However, increasing temperature to 90 and 120 °C this factor is reduced down to 1 to 1.3. Based on this results, optimal SiO<sub>2</sub> extraction conditions were fixed at 90-120 °C, 3 L/kg and 2M NaOH. Although high SiO<sub>2</sub> extraction yields (80-110 g SiO<sub>2</sub>/kg) were reached at 90 °C for a high extraction times (>10h), similar extraction yields (100 g SiO<sub>2</sub>/kg) were obtained at 120 °C in only 6h. For these conditions but for increased extraction times, synthesis yields were reduced to 20 g SiO<sub>2</sub>/kg. These results evidenced the fast dissolution and precipitation of SiO<sub>2</sub> while increasing temperature. Moreover, using the optimal extraction conditions the lowest Na<sub>2</sub>O/SiO<sub>2</sub> molar ratio was attained in the leachates. Low Na<sub>2</sub>O/SiO<sub>2</sub> molar ratios favour the synthesis of high CEC zeolites instead low CEC zeolites, such as sodalite and analcime. Combining the need of a low NaOH/FA ratio and a high SiO<sub>2</sub> extraction yield, the optimal SiO<sub>2</sub> extraction conditions from IGCC FA were fixed at 120 °C, 3 L/kg, 2 M NaOH and 6h (obtaining 100 g SiO<sub>2</sub>/kg).

The results showed higher SiO<sub>2</sub> extraction yields for PCC FA than IGCC FA. This fact is probably due to the high proportions of Al<sub>2</sub>O<sub>3</sub> extracted for IGCC FA (from 3 to 26 times higher than for PCC FA). The occurrence of high insoluble Al-bearing phases, such as mullite (3Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>) in the PCC FA accounts for the trapping Al and preventing the saturation of Al<sub>2</sub>O<sub>3</sub> in the leachate, with the consequent precipitation of zeolites in the solid residue. However, in the IGCC FA, Al<sub>2</sub>O<sub>3</sub> occurs in the highly soluble glass matrix and consequently, a fast and simultaneous dissolution of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> accounts for the precipitation of these species as zeolitic material in the solid residue, with the consequent reduction of the SiO<sub>2</sub> extraction yields. This fact was demonstrated by the results of SiO<sub>2</sub> extraction tests carried out with thermally treated IGCC FA at 1050 °C, which allows the crystallization of highly insoluble Al-bearing phases giving rise to higher SiO<sub>2</sub> extraction yields (by a factor from 2.2 to 2.4 compared with not thermally treated FA).

The low SiO<sub>2</sub> extraction yields and the high Na<sub>2</sub>O/SiO<sub>2</sub> molar ratio in the leachates may be the main limitations for the synthesis of zeolites by SiO<sub>2</sub> extraction from IGCC FA. Conversely, the high SiO<sub>2</sub> extraction yields obtained from PCC FA, make suitable this FA for the synthesis of zeolites by SiO<sub>2</sub> extraction.

Although the above mentioned limitations, the SiO<sub>2</sub> extracts from PCC and IGCC FAs were selected for the subsequent synthesis of zeolites. The results demonstrated that the following high crystalline zeolites may be produced using the SiO<sub>2</sub> extracts from these FAs (Figure 1 and 2):

- X zeolite (#1): this zeolite was obtained by combining the highest SiO<sub>2</sub> extract from PCC and the high Al<sub>2</sub>O<sub>3</sub> waste solution extract ( Na<sub>2</sub>O/SiO<sub>2</sub>= 1.2, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>= 1.9 and H<sub>2</sub>O/Na<sub>2</sub>O= 41.0), by gelification at 60 °C during 15 min, without stirring and subsequent crystallisation at 90 °C and 7h.
- A zeolite (#2): obtained by combining the highest SiO<sub>2</sub> extract from PCC and the high Al<sub>2</sub>O<sub>3</sub> waste solution (Na<sub>2</sub>O/SiO<sub>2</sub>= 1.3, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>= 1.7 and H<sub>2</sub>O/Na<sub>2</sub>O= 41.0).
- A zeolite (#3): obtained by combining the highest SiO<sub>2</sub> extract from IGCC and the high Al<sub>2</sub>O<sub>3</sub> waste solution (Na<sub>2</sub>O/SiO<sub>2</sub>= 4, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 2 and H<sub>2</sub>O/Na<sub>2</sub>O= 31).

These high purity A zeolites products were obtained after a first gelification step at 60 °C, and 15 min without stirring and a crystallisation step at 90 °C and 8h.

The use of these synthesis conditions demonstrated that is possible the production of high crystalline zeolites avoiding the aging step (applied in a number of experiments), and consequently the synthesis time was reduced drastically from 28h to 7-8h. The crystallinity of zeolites synthesised from SiO<sub>2</sub> extracts was compared with that of pure commercial A and X zeolites (Figure 1 and 2).

### *Synthesis of zeolites by direct conversion*

Relatively high contents of NaP1 were obtained in the zeolitized fly ash at 120 °C, 3M NaOH, 3L/kg, 4 to 10h and at 150 °C, 3M NaOH, from 2 to 4 L/kg, 9h. Based on these results, the following direct conversion conditions were selected for the NaP1 zeolite synthesis (Figure 1 and 2):

- NaP1 (#4): obtained by direct conversion at 120°C, 9h and 3 L/kg of 3M NaOH from PCC FA.

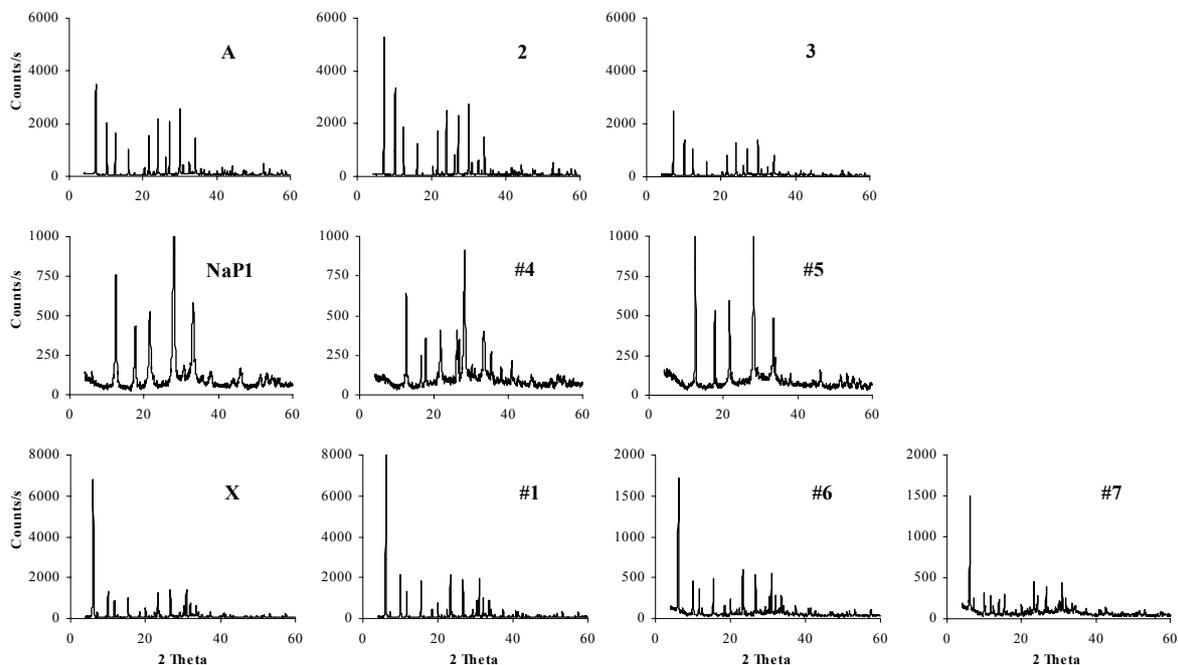


Figure 1. XRD patterns (Cu K<sub>α</sub> radiation) of commercial pure zeolites supplied by IQE S.A (A, X and NaP1), A zeolite obtained mixing the Al-waste solution and SiO<sub>2</sub> extracts from PCC and IGCC (#2 and 3, respectively), X zeolite synthesised with the Al-waste solution and SiO<sub>2</sub> extracts from PCC (#1), zeolitic material obtained by direct conversion from PCC and IGCC (#4 and #5, respectively), and zeolitic material obtained by the fusion method (#6 and #7, from PCC and IGCC, respectively)

As expected from the glass composition and mineralogy, the results on the experiments of direct conversion using the IGCC FA evidenced a higher content of NaP1 zeolite (by a factor of 1.2-3.0 compared with PCC FA). Furthermore, high synthesis yields were obtained at lower temperature (90 °C, 2M NaOH, 3L/kg, 9 to 24h, and 5 L/kg, 24h; as well as 120 °C, 2M NaOH, 3 and 5 L/kg, ≥4h). However, lower NaP1 contents were obtained for IGCC FA than for PCC FA, when using NaOH>2M at 90 and 120 °C, and also at higher temperatures (150 °C) due to the conversion of NaP1 zeolite into low CEC species such as sodalite and analcime. The high sodalite and analcime production on IGCC FA at 90-120 °C is also the consequence of the high content of soluble Al glassy species. For higher temperatures (>150 °C), the results evidenced a similar composition of the resulting zeolitic material with respect to that produced for < 150 °C, with a relatively higher content of NaP1 zeolite at 175 °C, 2M NaOH, 2 L/kg, 9h and at 150 °C, NaOH 3M, and 2L/kg and 9h. For these reason the following zeolitic material was selected for the quality evaluation:

- NaP1 (#5): obtained by the conventional direct conversion procedure at 175 °C, NaOH 2M, 2L/kg and 9h, with the highest NaP1 content.

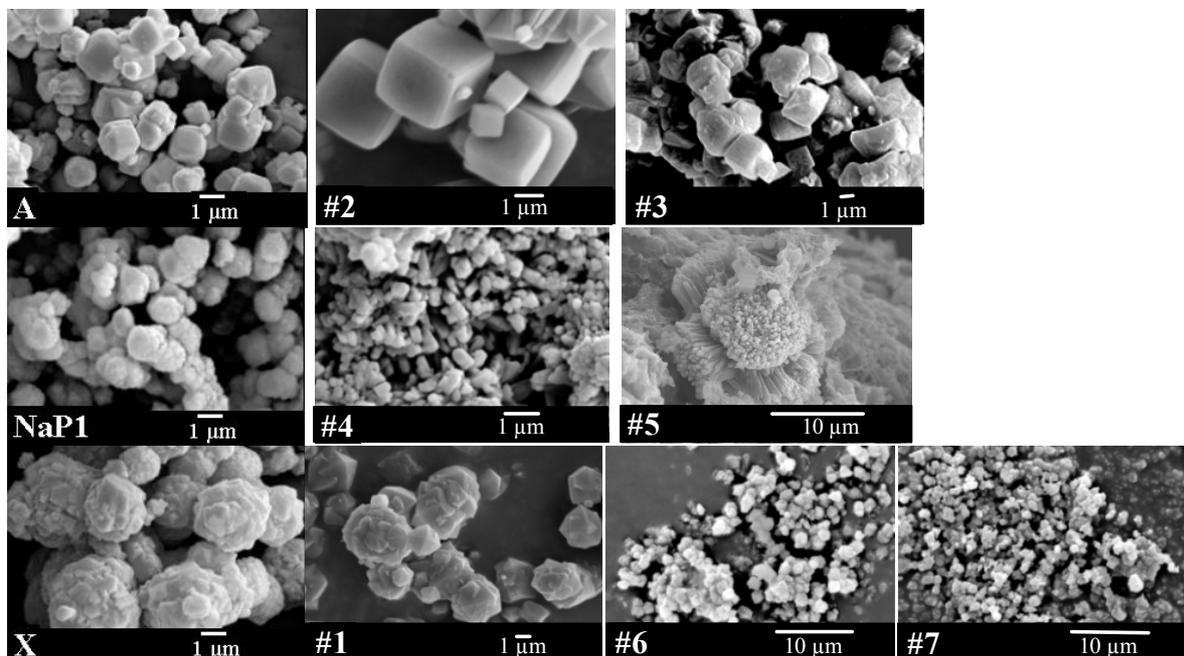


Figure 2. SEM micro-photograph of commercial pure zeolites supplied by IQE S.A (A, X and NaP1), A zeolite obtained mixing the Al-waste solution and SiO<sub>2</sub> extracts from PCC and IGCC (#2 and 3, respectively), X zeolite synthesised with the Al-waste solution and SiO<sub>2</sub> extracts from PCC (#1), zeolitic material obtained by direct conversion from PCC and IGCC (#4 and #5, respectively), and zeolitic material obtained by the fusion method (#6 and #7, from PCC and IGCC, respectively).

### *Synthesis of zeolites by alkaline fusion*

High crystalline X zeolites from FAs, sometimes with traces of A zeolite or sodalite, were produced by alkaline fusion. The results demonstrated that the zeolite synthesis yields and the zeolite types obtained depends on the FA composition and the synthesis conditions. Both FA types showed a similar behaviour during the fusion step, allowing the formation of a fused mass with relatively high proportions of crystalline phases, such as Na<sub>2</sub>SiO<sub>3</sub> and Na-rich nepheline. However, the different behaviour during aging and zeolite crystallization steps accounts for the differences on the zeolitic products obtained from two types of FAs. The increase of the FA/NaOH ratio from 1.2 to 2 results of the increase of the X zeolite yields for both FAs. Thus, for PCC FA, the highest contents of X zeolite with traces of A zeolite

were produced at FA/NaOH ratio of 2 kg/kg, aging during 16h, FA/H<sub>2</sub>O ratio of 10 L/kg and crystallization at 90 °C and 6h (Figures 1 and 2). Also high proportions of X zeolite were obtained at these conditions for IGCC FA, but traces of sodalite instead A zeolite were produced. When the FA/H<sub>2</sub>O ratio was reduced down to 5 L/kg, only sodalite was synthesised due to the high Na concentration in the FA/H<sub>2</sub>O mixture. However, if conditions were kept but the crystallization time increased up to 8h, a high X zeolite product with traces of A zeolite was obtained. Based on the results, the following zeolitic product were selected for the quality evaluation:

- X zeolite (#6): obtained by fusion at 600 °C from PCC FA, 2h with FA/NaOH ratio=2 kg/g, aging during 16h, FA/H<sub>2</sub>O ratio=10 L/kg and crystallization at 90 °C and 6h.
- X zeolite (#7): obtained by fusion at 600 °C from IGCC FA, 2h with FA/NaOH ratio=2 kg/g, aging during 16h, FA/H<sub>2</sub>O ratio=10 L/kg and crystallization at 90 °C and 8h.

### Evaluation of the CEC and potential leaching

Table 2 summarises the results of the CEC and leachable contents of selected elements from the zeolitic products synthesised in this study. The CEC of commercial zeolitic products were also determined and compared with that of synthesised from FAs. For the commercial pure zeolites, the results evidenced that the CEC for A and NaP1 zeolites (5.4 and 5.0 meq/g) were slightly higher than for X zeolite (4.3 meq/g). The comparison of CEC values obtained for commercial zeolites and synthesised from FAs allowed the evaluation of the purity of these zeolitic materials. The results evidenced higher purity for zeolites synthesised from PCC FA than that from IGCC FA with the exception of the optimal direct conversion products. Furthermore, for the two FA types the highest and lowest zeolite contents were reached for the synthesis from SiO<sub>2</sub> extracts and by direct conversion, respectively. Thus, it should be pointed out that the highest purity (100 and 98%) was found for X and A zeolites obtained from SiO<sub>2</sub> extracts from PCC FA (#1 and #2 samples), with CEC values of 4.3 and 5.3 meq/g, respectively. Also high purity A zeolite (80%, CEC of 4.3 meq/g) was obtained from SiO<sub>2</sub> extracts from IGCC FA (#3). Relatively high purity (83 and 70 %) X zeolites with traces of A zeolite were synthesised by alkaline fusion, for PCC and IGCC FAs, respectively (#6 and #7 samples). Since FAs are only partially zeolitised during direct conversion, the NaP1 zeolitic material obtained for this process attained the lowest CEC and purity, reaching 49 and 54 % purity when using PCC and IGCC FA, respectively (#4 and #5 samples). However, the CEC (2.4 and 2.7 meq/g) of the NaP1 zeolitic product obtained using PCC and IGCC FAs, respectively are slightly higher than the CEC of commercial natural zeolites, such as clinoptilolite or mordenite.

The leachable contents of major and trace elements for the zeolitic materials synthesised from IGCC and PCC FAs using the DIN-38414 tests are shown in Table 2. The results evidenced that the mobility of most elements (such as, B, Li, Mo, Sb, Se and Zn) was higher for the IGCC than PCC zeolitic products arising for the three synthesis methodologies. Concerning the IGCC FA, conversely to the results expected, the leachable contents of Co, Cu, Ga, Ge, K, Mn, Na, Rb, P and Sn contents were higher in the high purity zeolites obtained from SiO<sub>2</sub> extracts and the Al waste solution than in direct conversion and fusion products. It is important to note that the leachable contents of most elements are higher in direct conversion material

than the fusion products, conversely to the CEC values. In relation to the PCC FA, the highest leachable fraction for the studied elements were the obtained from the direct conversion products, whereas the lowest leaching behaviour was found for the high purity zeolites obtained from SiO<sub>2</sub> extracts for the majority of elements. Low leachable metal contents were obtained from high purity A and X zeolites and zeolite material synthesised by alkaline fusion for PCC FA. Conversely, the high metal content leached from zeolites synthesized from IGCC FA limits the possible applications of these products.

Table 2. Results on CEC, purity and leachable contents for major (mg/L) and trace elements (µg/L) in commercial pure and synthesised zeolites from IGCC and PCC Puertollano FAs. Si: SiO<sub>2</sub> extraction; Fu: fusion method; DC: direct conversion.

Oriaen Synthesis method # sample	IQE			PCC				IGCC		
	A	P	X	Si 2	Si 1	Fu 6	DC 4	Si 3	Fu 7	DC 5
Zeolitic material	A	NaP1	X	A	X X (traces A)	NaP1		A X (traces A)	NaP1	
CEC (meq/g)	5.4	5	4.3	5.3	4.3	3.7	2.4	4.3	3.4	2.7
<b>Zeolite content</b>	100%	100%	100%	98 %	100 %	83%X, 3%A	49 %	80 %	70%X, 7%A	54 %
<b>Leaching test</b>										
pH	9.8	9.8	10.5	9.6	10.2	9.9	9.7	11.6	10.1	9.1
Conductivity (µS/cm)	3187	538	889	1766	904	3011	6890	22	6766	4477
Al	90.9	12.7	24.9	1.4	5.6	7.3	<2.0	<2.0	10.9	3.1
Ca	<0.8	<0.4	<0.4	<0.4	<0.4	1	2.1	<2.0	5.1	9.5
Fe	0.1	0	0.2	0.2	0.2	11.7	0.4	0.7	4.5	5.1
K	4.2	8.4	7	7.5	3.7	12.4	57	238.3	41.1	44.5
Mg	<0.2	<0.1	<0.1	<0.1	<0.1	1.8	<0.5	<0.5	0.8	1.1
Na	815.1	143.4	110.5	424.6	178.6	731	1887.3	4329.5	1821.9	537.6
P	<0.4	<0.2	<0.2	0.2	0.2	<0.4	5.3	49	1.2	<1.0
S	10.5	0.2	<0.2	0.6	0.5	<0.4	13	112.1	7.9	583.2
Si	2.5	9.6	8.2	2	5.8	7.5	216.1	15	167.6	23.5
B	216	3	4	386	144	50	783	5435	288	9378
Ba	<1	<1	<1	<1	2	96	2	1	41	12
Co	<1	<1	<1	<1	<1	6	<1	65	2	4
Cu	1	<1	<1	2	4	21	11	102	15	63
Ga	693	4	19	7	6	5	<1	1201	13	185
Ge	<1	<1	<1	12	3	12	198	871	39	148
Li	75	3	1	14	6	142	154	246	600	1957
Mn	<1	<1	<1	1	1	116	3	1498	13	23
Mo	4	<1	<1	17	10	4	178	1257	104	2940
Rb	4	<1	1	26	10	29	102	945	81	88
Sb	<1	<1	<1	7	190	138	237	321	139	2594
Se	1	4	<1	6	47	3	65	40	16	334
Sn	3	<1	<1	3	6	3	<1	172	5	6
Sr	<1	<1	<1	<1	1	23	19	<1	13	12
Th	1	0	2	0	6	3	1	1	3	4
Ti	25	8	18	36	475	1323	28	107	262	467
Zn	<1	<1	<1	5	15	294	21	128	368	1422

## CONCLUSIONS

The results demonstrated that high purity A and X zeolites and relatively high NaP1 zeolitic material may be obtained from both, PCC and IGCC FAs using SiO<sub>2</sub> extraction, alkaline fusion and direct conversion methods for the synthesis. The occurrence of Al only in the highly soluble glass matrix, in the IGCC FA, limits

drastically the SiO<sub>2</sub> extraction with respect to the very high extraction yields obtained for the PCC FA.

Consequently, the feasibility of zeolite synthesis by SiO<sub>2</sub> extraction is highly limited for IGCC FA, but increase by direct conversion. Very low leachable metal contents from A and X zeolites were obtained by SiO<sub>2</sub> extraction and alkaline fusion for PCC FA. Conversely, the high metal content leached from zeolites synthesized from IGCC FA may limit their use for the uptake of metals in polluted areas.

For IGCC FA a high purity X zeolite with relatively low leachable metal contents was obtained if alkaline fusion method was applied. These results pointed out the significance of the occurrence of mullite in FA for the synthesis of zeolites with potential environmental applications.

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