

Differential behaviour of combustion and gasification fly ash from Puertollano Power Plants (Spain) for the synthesis of zeolites and silica extraction

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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 characterised and used as raw materials for zeolite synthesis by direct conversion (DC) and by alkaline fusion (Fu), and SiO₂ extraction (Si-Ex) at laboratory scale. The Puertollano FAs are characterised by a high SiO₂ content (59%) with respect to EU coal FAs. High zeolite synthesis yields were obtained from both FAs by using conventional alkaline activation. However, the Si extraction yields were very different. 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. The solid residue arising from Si-Ex is also a relatively high NaP1 zeolite product (CEC 2.4–2.7 meq/g) equivalent to the DC products. The zeolitic materials synthesised from both FAs by Fu showed an intermediate (between the high purity zeolites and the DC 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 Fu for PCC FA.

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1. Introduction

More than 43 million tonnes (metric) of coal FAs are produced annually in the European Union [1]. The main proportions of these FAs are produced by Pulverised Coal Combustion (PCC) process, due to the low implementation at industrial scale of Integrated Coal Gasification Combined Cycle (IGCC) technology and to its low FA/slag ratio (0.1) with respect to that of PCC plants (4). In addition to the different FA production, the PCC and IGCC processes generate FAs with different mineralogical compositions [2]. The PCC FAs are made up of aluminosilicate (Al-Si) glass (52–90% for European FAs [3]), and variable minor amounts of quartz, mullite, lime, hematite, magnetite, gypsum and feldspars. The IGCC FAs are characterised by a predominant Al-Si glass matrix and a wide variety of fine crystalline reduced species [2].

Owing to the large volume of FAs generated from power generation, their use has been mainly based in the manufacture of concrete and cement since 1950s, much more than in other novel potential applications with high added value, such as the synthesis of zeolites. The synthesis of zeolites from FAs was prompted

by Höller and Wishing [4] 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 [5–25]. Most of these methodologies are based on the alkaline hydrothermal activation. Shigemoto et al. [16] optimised the traditional DC by the introduction of a fusion step prior to synthesis. This fact permitted to obtain different types of zeolites with potential industrial application (such as NaP1, chabazite, henschelite). The DC method was also applied by the use of dry conversion systems [17–18]. Recently the fusion (Fu) procedure has been improved to obtain high porous size and CEC zeolitic material [19–21]. Other studies on DC allowed reducing the synthesis time (from hours to few minutes) by microwave assisted method [23]. However, the zeolitic products obtained by DC have low CEC values due mainly to incomplete conversion of the FA in zeolite. Hollman et al. [24] prompted the synthesis of zeolites from SiO₂ extracts from FAs obtaining high purity zeolites (>95% of A and X zeolite), and Moreno et al. [25] optimised this method synthesising in the same process zeolites with high purity from SiO₂ extracts and another zeolitic product (the solid residue from SiO₂ extracts), equivalent to zeolites obtained by DC method.

As a consequence of the peculiar structural properties of zeolites, intensive research on the potential industrial applications of

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zeolites synthesised from FA was also carried out. The high Al^{3+}/Si^{4+} 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 have been the major application field tested [8,12,26–35]. The use of zeolites as molecular sieves for the gas cleaning technology has also been investigated [36–37] and is currently getting force in view to the CO_2 sorption. 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 [27].

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 zeolite deposits in Europe.
- the zeolitic products synthesised by the DC method contain a non-converted part of FA, with the consequent lower CEC of these products than that of the pure commercial synthetic zeolites. Moreover, the residual FA fraction may contain leachable B, Mo and Se, which may limit the utilization of this zeolitic material in specific water purification processes.
- although the synthesis of zeolites from Si-Ex 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.
- low resistance to acidic attack of most synthetic zeolites [38]. This fact supposes a low applicability of zeolites employed in long-term processes (such as passive geochemical barriers), but their use leads to very good results in short time treatments.
- the application of zeolitic materials for NH_4^+ uptake treatments from actual waste waters may be limited by the ionic competition

between major cations and NH_4^+ [27,34]. However, this effect is lower in the uptake of metals.

- low mechanical resistance of zeolitic products. The pelletisation, tested for its use as permeable columns or barriers, supposed an important reduction of CEC of the zeolitic product [39].

From the foregoing it is clear that the synthesis of zeolites was widely tested for PCC FAs but never for IGCC FAs. Since the considerable differences on their composition and speciation, and the expected implementation of IGCC technology at industrial scale, the main objectives of this study were to investigate and compare the behaviour of PCC and IGCC FAs for the synthesis of zeolites by using three different zeolite synthesis methods: Si-Ex, Fu and DC and to evaluate the quality of the zeolitic products obtained in view to assess some of the above limitations. To this aim, the FAs produced in the PCC and IGCC power plants from Puertollano (Spain), fed with a high metalliferous local coal were characterised and used as raw materials for the synthesis of zeolites. The Puertollano FAs were selected because the high SiO_2 contents (59%) with respect to the EU coal FAs.

2. Experimental

2.1. Fly ashes

Two FA samples from PCC and 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 Puertollano 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 [39]. The FA international

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
Major oxides (%)					
SiO_2	58.6	58.5	CaO	0.8	3.6
Al_2O_3	27.4	20.6	MgO	1.0	0.6
Fe_2O_3	7.3	4.3	Na_2O	0.3	0.6
K_2O	2.4	3.8	SO_3	0.2	2.7
P_2O_5	0.1	0.5	C	0.7	4.5
TiO_2	0.7	0.6	SiO_2/Al_2O_3	2.1	2.8
Trace elements (mg/kg)					
As	140	955	Mo	11	135
B	534	89	Ni	96	2296
Ba	460	433	Pb	1075	4796
Be	14	13	Rb	139	302
Cd	5	24	Sb	120	381
Co	31	53	Se	7	19
Cr	108	155	Sn	10	67
Cu	75	392	Sr	131	102
Ga	34	320	Th	30	22
Ge	61	420	U	15	6
Hg	1.3	<0.01	V	202	6256
Li	185	238	Zn	924	7230
Mn	511	222			
Physical characteristics					
	PCC	IGCC	Mineralogy (%)		
Grain size (μm)			Glass	66	90
Percentile 10	4.7	1.4	Mullite	20	No detected
Median	26.2	3.7	Quartz	10	No detected
Percentile 90	123.8	26.3	Magnetite	3	No detected
			Galena	No detected	4
Moisture (%)	0.1	0.3	Sphalerite	No detected	3
LOI (%)	1.1	5.1	Wurtzite	No detected	2
BETSA (m^2/g)	2.7	7.3	Nickeline	No detected	1

LOI indicates "loss on ignition".

reference material NBS 1633b was also analysed to check the accuracy of the analytical and digestion methods. The SiO_2 , 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 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 [40].

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, 12 h under a vacuum of 0.1 mm Hg). Details on chemical, physical and mineralogical characterisation of these FAs are shown in Table 1.

From the point of view of the reactivity of these materials for the synthesis of zeolite and the extraction of silica, the main peculiarity is the high content of Al-Si glass matrix (90%) and the wide variety of fine crystalline reduced species of IGCC FA. The PCC FA is made up of a lower proportion of Al-Si glass (66%) and variable small amounts of quartz, mullite and magnetite. Other differences between these FAs are the finer grain size and higher content in most trace elements, probably due to the lower IGCC FA/slag ratio, in IGCC than in PCC FA.

2.2. Synthesis of zeolites

Three ways for the zeolitisation of the two selected FAs were compared in this study: (a) Si-Ex followed by a synthesis process to obtain high purity zeolites such as A ($\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}\cdot 27\text{H}_2\text{O}$) and X ($\text{Na}_{86}\text{Al}_{86}\text{Si}_{106}\text{O}_{384}\cdot 264\text{H}_2\text{O}$) (b) DC to obtain NaP1 ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}\cdot 12\text{H}_2\text{O}$) products and, (c) Fu method to produce high X zeolitic material.

2.2.1. SiO_2 extraction

The potential suitability of FAs for the synthesis of pure zeolites by combining SiO_2 and Al_2O_3 -rich solutions has a direct correlation with the high Si-Ex yields from FAs. Then a detailed research to determine the optimal Si-Ex conditions from PCC and IGCC FAs for the subsequent synthesis of pure zeolites was carried out. Both FAs are characterised by high SiO_2 , glass content, and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (Table 1), therefore these FAs have a significant potential for obtaining high Si-Ex yields for further synthesis of zeolites [41]. Based on the results obtained in these studies, the Si-Ex tests were carried out under the following conditions: Temperature: 50–150 °C, NaOH solution/FA ratio: 2–5 L/kg, NaOH: 0.5–3 M, extraction times: 1–24 h.

These Si-Ex tests were performed with magnetic stirring, using closed heated system in 60 mL Saville 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_2 extracts obtained were used as starting solutions to optimise the synthesis of pure A and X zeolites. This method is based on combining SiO_2 -rich and Al_2O_3 -rich solutions to obtain high purity zeolites, after gelification, aging and crystallization steps. The Al_2O_3 source used for this study was an Al_2O_3 -rich waste solution supplied by an Al-anodising

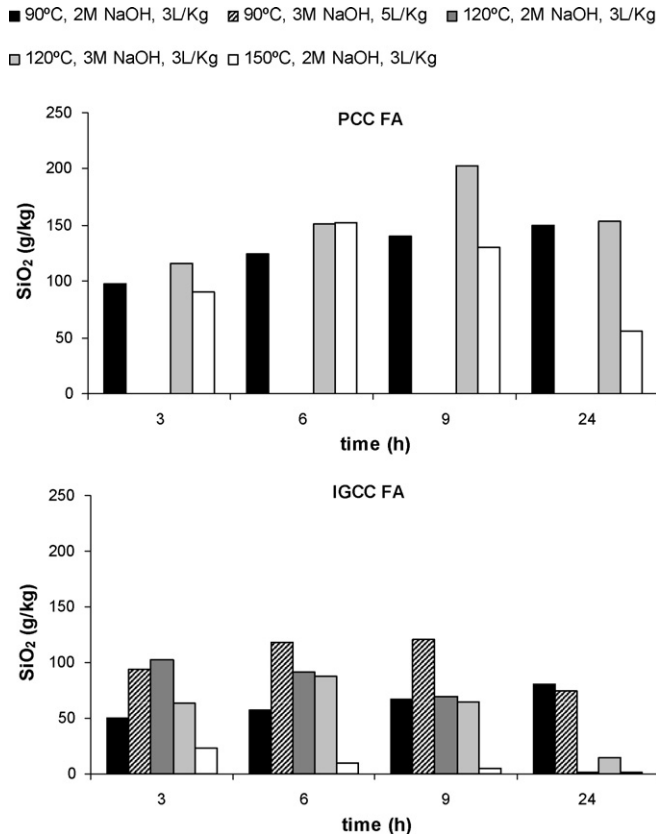


Fig. 1. Comparison of SiO_2 extraction yields attained for PCC (left) and IGCC (right) as a function of extraction time at different temperatures and NaOH concentrations.

industry (Fuentes S.L Parets del Vallés, Barcelona). This high Al_2O_3 solution contained 168.1 g $\text{Na}_2\text{O}/\text{L}$ of and 192.0 g $\text{Al}_2\text{O}_3/\text{L}$. The molar ratios tested for the synthesis of high pure A and/or X zeolites were: $\text{Na}_2\text{O}/\text{SiO}_2$ from 1.3 to 4.5, $\text{SiO}_2/\text{Al}_2\text{O}_3$ from 1.0 to 2.5 and, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ from 25 to 50, based on typical synthesis conditions for pure zeolites [42–43] and for zeolites synthesised from SiO_2 extracts arising from FA by Hollman et al. [24] and Sáez [44]. Likewise, the synthesis strategy was based on the following steps: (a) gelification (40–80 °C, from few minutes to 2 h), (b) aging (25 °C, until 23 h) and, (c) crystallization (70–90 °C, 1–72 h). The synthesis procedure was optimised to avoid the aging step and to reduce the synthesis time.

2.2.2. Direct conversion

The solid residue arising for the Si-Ex is in fact a DC product, as demonstrated by Moreno et al. [25]. Consequently, characterisation of these residues was used to evaluate the DC efficiencies. Furthermore, for high temperatures (150–200 °C), conventional DC 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.

2.2.3. Alkaline fusion

Based on the method prompted by Rayalu et al. [19–20], high X zeolitic material was synthesised from FA by NaOH fusion. The homogeneous fusion mixture was obtained by mixing pulverised FA and NaOH at different ratios (from 1.2 to 2, by weight). This mixture was heated at a temperature ranging from 550 to 600 °C for 2 h. The fused mixture was then cooled at room temperature, carefully milled and mixed thoroughly in distilled water (1 g FA/10 mL H_2O). In fact, this fused mass obtained was agitated mechanically for several hours (12–16 h). The resultant gel was then subjected to

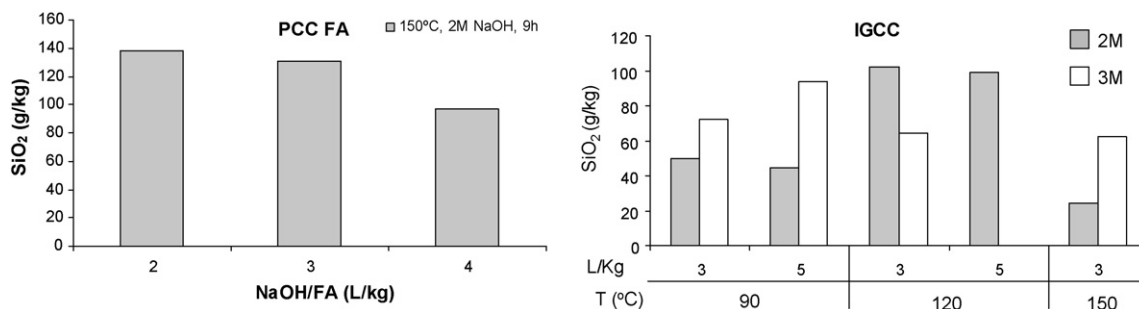


Fig. 2. Si-Ex vs NaOH/FA ratio at fixed extraction temperatures (150 °C) NaOH concentration (2 M) and synthesis time (9 h) for PCC (left) and vs at different temperatures and NaOH/FA ratio for IGCC FA (right).

crystallization 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 50–60 °C.

2.3. Quality evaluation

The zeolitic products were filtered and washed with distilled MilliQ water, dried at room temperature, and analysed by XRD. Their morphology was examined by means of JEOL 840 scanning electron microscopy with energy dispersive X-ray analyzer (SEM-EDX). Furthermore, the purity of the zeolitic products was evaluated by comparing of their CEC, determined by the method of ISRIC [45], with pure commercial A, X and NaP1 zeolites supplied by IQE S.A (Indústrias Químicas del Ebro). Moreover, a leaching test (DIN-38414) was applied to all zeolitic materials to determine the potential mobility of trace elements. Major and trace element con-

tents in the leachates were determined by means of ICP-AES and ICP-MS.

3. Results

3.1. Synthesis of zeolites

3.1.1. Si-Ex

The highest Si-Ex yields obtained for PCC and IGCC FAs were 200 and 120 g SiO₂/kg of FA, respectively. These highest Si-Ex yields were attained at 120 °C, 3 M NaOH, 3 L/kg and 9 h for PCC FA and at 90 °C, 3 M NaOH, 5 L/kg and 9 h for IGCC FA. As shown in Fig. 1, the Si-Ex yields obtained for IGCC FA were lower than PCC FA for whatever extraction conditions tested. For PCC FAs high Si-Ex yields (>150 g SiO₂/kg) were attained at: (a) 90 °C, 2 M NaOH, 3 L/kg and 24 h, (b) 120 °C, 3 M NaOH, 3 L/kg between 6 and 24 h, and (c) 150 °C, 2 M NaOH, 3 L/kg and 6 h.

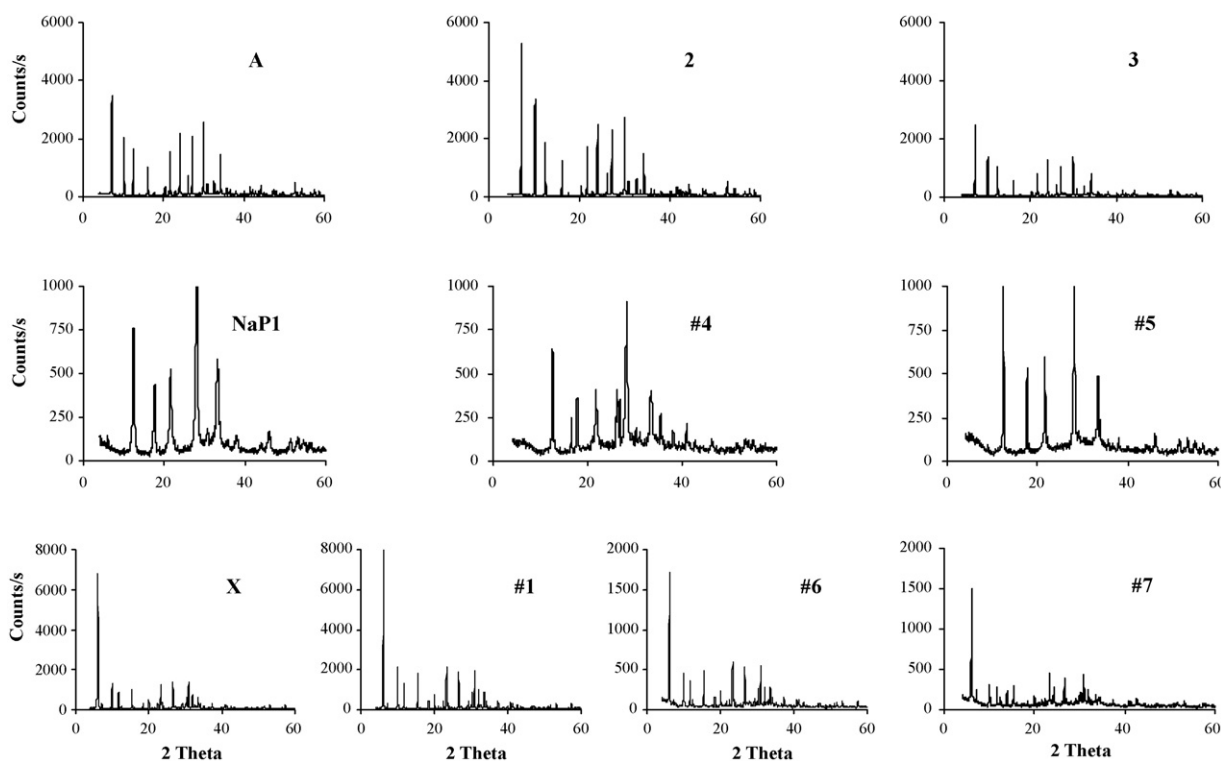


Fig. 3. XRD patterns (Cu K_α radiation) of commercial pure zeolites supplied by IQE S.A (A, X and NaP1), A zeolite obtained mixing the Al-waste solution and SiO₂ extracts from PCC and IGCC (#2 and 3, respectively), NaP1 zeolitic material obtained by direct conversion from PCC and IGCC (#4 and #5, respectively), X zeolite synthesised with the Al-waste solution and SiO₂ extracts from PCC (#1), and X zeolitic material obtained by the fusion method (#6 and #7, from PCC and IGCC, respectively). Relic quartz and mullite mineral phase from original fly ash also occur in the zeolitic product #4.

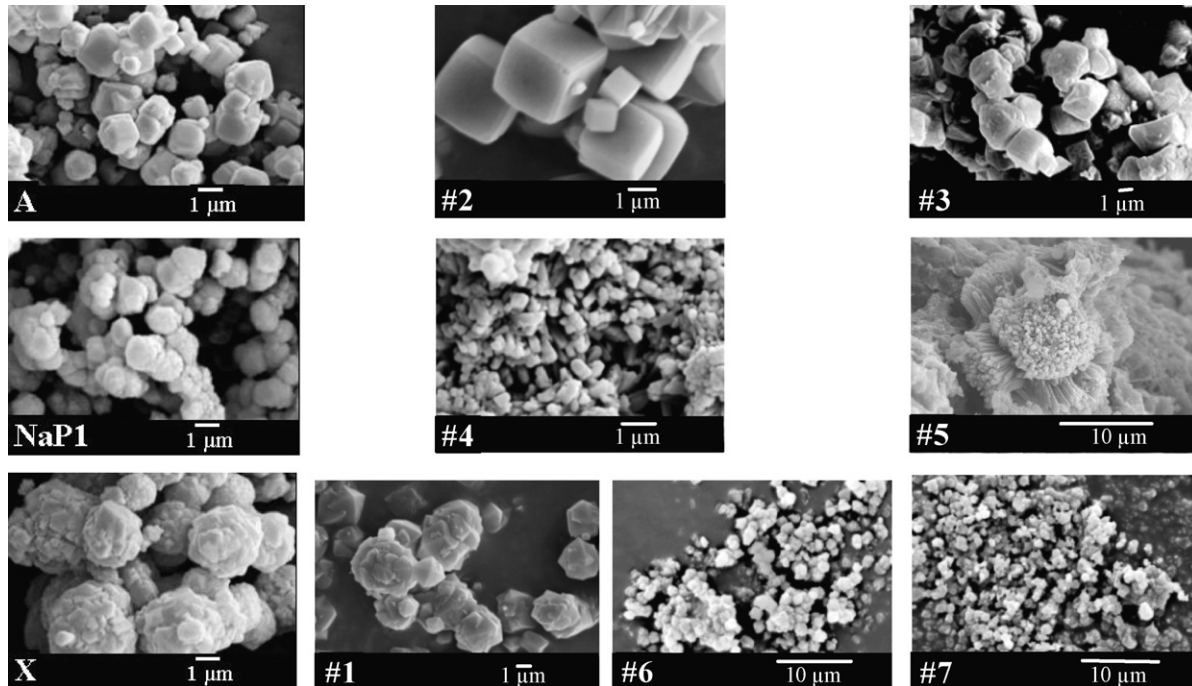


Fig. 4. SEM microphotograph of commercial pure zeolites supplied by IQE S.A (A, X and NaP1), A zeolite obtained mixing the Al-waste solution and SiO₂ extracts from PCC and IGCC (#2 and #3, respectively), NaP1 zeolitic material obtained by direct conversion from PCC and IGCC (#4 and #5, respectively), X zeolites synthesised with the Al-waste solution and SiO₂ extracts from PCC (#1), and X zeolitic material obtained by the fusion method (#6 and #7, from PCC and IGCC, respectively).

For IGCC FA, extremely low Si-Ex yields (<20 g SiO₂/kg FA) were achieved when using NaOH ≤ 1 M and relatively high Si-Ex yields (>100 g/kg) were achieved only when applying: (a) 90 °C, 3 M NaOH, 5 L/kg and 6 h and (b) 120 °C, 2 M NaOH, 3 L/kg and 3 h.

The high Si-Ex yields achieved from PCC FA than IGCC FA are probably due to the high proportions of Al₂O₃ extracted for IGCC FA (3–26 times higher than for PCC FA). In the PCC FA the occurrence of high insoluble Al-bearing phases, such as mullite (3Al₂O₃·2SiO₂), accounts for the trapping Al, preventing the saturation of Al₂O₃ in the leachate, and the consequent precipitation of zeolites in the solid residue. However, in the IGCC FA, Al₂O₃ occurs in the highly soluble glass matrix. As a result, a fast and simultaneous dissolution of Al₂O₃ and SiO₂ accounts for the precipitation of these species as zeolitic material in the solid residue, with the consequent reduction of the Si-Ex yields. This fact has been demonstrated by the Si-Ex tests carried out with thermally treated IGCC FA at 1050 °C, which allows the crystallization of highly insoluble Al-bearing phases, such as mullite and hercynite, giving rise to higher Si-Ex yields (by a factor from 2.2 to 2.4 compared with not thermally treated FA).

Besides the Al and Si in coal FAs is the main factor controlling Si-Ex yields, as deduced from the foregoing, the following extraction parameters are also important: (a) temperature: at a fixed concentration of NaOH, NaOH/FA ratio and time, both PCC and IGCC FAs increases the Si-Ex yields for temperatures up to 120 °C while reducing for temperatures >120 °C, due to the precipitation of SiO₂-bearing species (Fig. 1), (b) NaOH concentration: IGCC FA showed an increase of the Si-Ex yields as higher the NaOH concentration up to 3 M only for 90 °C (Fig. 1) and, (c) NaOH/FA ratio: generally, the increase of the NaOH/FA ratio from 3 to 5 L/kg showed reduction of the Si-Ex yields for IGCC FA except when applying 90 °C and 3 M NaOH (increasing SiO₂ extracted by a factor 1.5–2, Fig. 2). The reduction of Si-Ex yields when higher the NaOH/FA ratio was also observed for PCC FA at 150 °C (Fig. 2). The most probably cause is the easy precipitation of Na-Si-Al-rich species due to the high dissolution of Al obtained at high NaOH/FA. This effect is enhanced with the increase in the extraction temperature.

These results revealed the similar behaviour of Si-Ex as a function of the above extraction parameters for both FAs. The most important difference is the faster kinetics precipitation of SiO₂-bearing species for IGCC than PCC FAs, due to the high proportions of reactive Al₂O₃ and SiO₂ in the soluble IGCC FA glass matrix.

For the subsequent zeolite synthesis the optimal Si-Ex conditions may be fixed at: (a) 120 °C, 3 M NaOH, 3 L/kg and 9 h, for PCC FA, attaining the highest Si-Ex yields (200 g SiO₂/kg) and (b) 120 °C, 2 M NaOH, 3 L/kg and 3 h for IGCC FA, in which Si-Ex yields of 102 g SiO₂/kg were obtained in only 3 h coupled with the lowest Na₂O/SiO₂ molar ratio. The use of SiO₂ extracts with low Na₂O/SiO₂ molar ratios favours the synthesis of high CEC zeolites instead low CEC zeolites, such as sodalite and analcime.

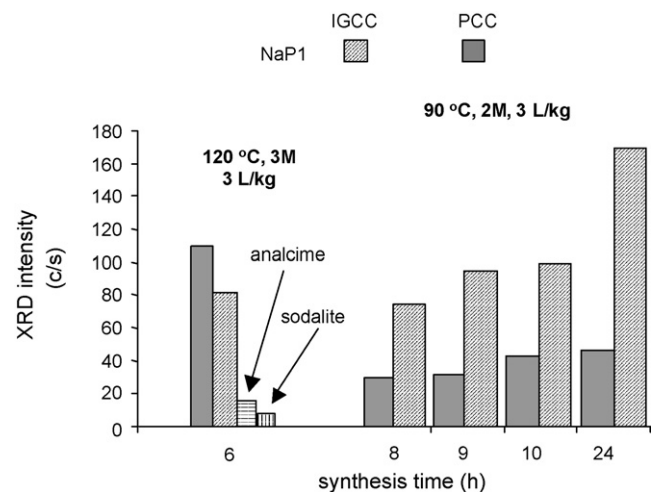


Fig. 5. Comparison among the zeolite content obtained by direct conversion for PCC and IGCC at 90 °C, 2 M NaOH, 3 L/kg and 120 °C, 3 M, 3 L/kg for different synthesis times.

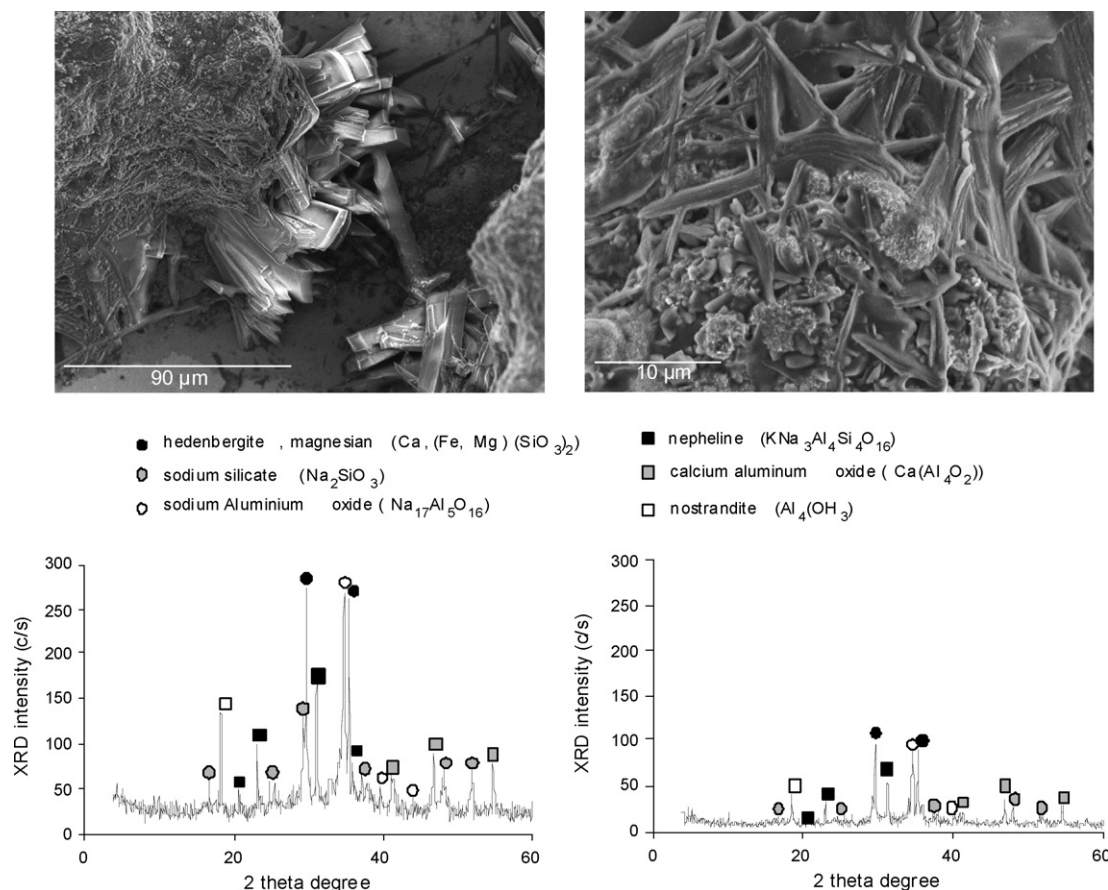


Fig. 6. SEM microphotograph and XRD patterns (Cu K_{α} radiation) of the fused material produced from PCC (left) and IGCC (right) after fusion step at 600 °C, FA/NaOH ratio of 2 kg/kg.

The high $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio in the leachates may be the main limitations for the synthesis of zeolites by Si-Ex from IGCC FA. Conversely, the high Si-Ex yields obtained from PCC FA make it suitable for the synthesis of zeolites by Si-Ex.

The results demonstrated that high crystalline zeolites may be produced using the SiO_2 extracts from these FAs (Figs. 3 and 4):

- X zeolite: (#1): obtained by combining the highest SiO_2 extract from PCC and the high Al_2O_3 waste solution extract ($\text{Na}_2\text{O}/\text{SiO}_2 = 1.2$, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.9$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 41.0$), by gelification at 60 °C during 15 min, without stirring and subsequent crystallization at 90 °C and 7 h.
- A zeolite (#2): obtained by combining the highest SiO_2 extract from PCC and the high Al_2O_3 waste solution ($\text{Na}_2\text{O}/\text{SiO}_2 = 1.3$, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.7$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 41.0$).
- A zeolite (#3): obtained by combining a high SiO_2 extract from IGCC and the high Al_2O_3 waste solution ($\text{Na}_2\text{O}/\text{SiO}_2 = 4$, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 31$).

The last zeolite products were obtained by a first gelification step at 60 °C, and 15 min without stirring and subsequent crystallization at 90 °C and 8 h (for A zeolitic products) and 7 h (for X zeolite). Using these conditions the synthesis method is optimised, avoiding the aging step (applied in a number of experiments) with a high reduction of the synthesis time (from 28 to 7–8 h).

3.1.2. Direct conversion

Relatively high contents of NaP1 were obtained in the zeolitised PCC FAs under the following synthesis conditions: (a) 120 °C, 3 M NaOH, 3 L/kg, 4–10 h, (b) 150 °C, 3 M NaOH, 2–4 L/kg and 9 h. The zeolitic material obtained under the following synthesis conditions was selected for subsequent quality evaluation of NaP1 products, (Figs. 3 and 4):

NaP1 (#4): obtained from PCC FA at 120 °C, 3 M NaOH, 3 L/kg and 9 h. Relic quartz and mullite mineral phase from original fly ash also occur in this zeolitic product (Fig. 3)

Given the high Al-Si glass content of IGCC FA, high NaP1 synthesis yields by DC were expected on this gasification by-product. In fact, IGCC FA yielded higher content of NaP1 zeolite (by a factor of 1.2–3.0) than for PCC FA at slight alkaline hydrothermal conditions (90–120 °C, 2 M NaOH, Fig. 5). However, lower NaP1 contents were obtained for IGCC FA than for PCC FA when using strong hydrothermal conditions ($\text{NaOH} > 2 \text{ M}$, $> 90^\circ\text{C}$), due to the fast conversion of NaP1 zeolite into Na-Al rich and low CEC species, such as sodalite and analcime (Fig. 5). The high sodalite and analcime production on IGCC FA at these synthesis conditions is also the consequence of the high content of soluble Al glassy species. For higher temperatures ($\geq 150^\circ\text{C}$), the results evidenced a similar composition of the resulting zeolitic material with respect to that produced for $< 150^\circ\text{C}$, attaining the highest NaP1 zeolite content at 175 °C, 2 M NaOH, 2 L/kg, 9 h. Therefore, the following zeolitic material, with the highest NaP1 content, was selected for the subsequent quality evaluation (Figs. 3 and 4):

NaP1 (#5): obtained from IGCC FA at 175 °C, NaOH 2 M, 2 L/kg and 9 h.

Table 2
Results on CEC, purity and leachable contents for major (mg/L) and trace elements ($\mu\text{g/L}$) in commercial pure and synthesised zeolites from IGCC and PCC Puertollano FAs.

Source	IQE			PCC FA			IGCC FA			
Synthesis method				Si-Ex	Fu	DC	Si-Ex	Fu	DC	
# Synthesis product	A	P	X	2	1	6	4	3	7	5
Zeolitic material	A	NaP1	X	A	X	X (A)	NaP1	A	X (A)	NaP1
CEC (meq/g)	5.4	5	4.3	5.3	4.3	3.7	2.4	4.3	3.4	2.7
Zeolite content (%)	100	100	100	98	100	83X, 3A	49	80	70X, 7A	54
Leaching test										
pH	9.8	9.8	10.5	9.6	10.2	9.9	9.7	11.6	10.1	9.1
Conductivity ($\mu\text{S/cm}$)	3187	538	889	1766	904	3011	6890	2200	6766	4477
mg/L										
Al	91	13	25	1.4	5.6	7.3	<2.0	36	11	3.1
Ca	<0.8	<0.4	<0.4	<0.4	<0.4	1.0	2.1	<0.1	5.1	9.5
Fe	0.1	<0.01	0.2	0.2	0.2	11.7	0.4	0.3	4.5	5.1
K	4.2	8.4	7.0	7.5	3.7	12.4	57.0	9.1	41	45
Mg	<0.2	<0.1	<0.1	<0.1	<0.1	1.8	<0.5	0.8	0.8	1.1
Na	815	143	111	425	179	731	1887	320	1822	538
P	<0.4	<0.2	<0.2	0.2	0.2	<0.4	5.3	21	1.2	<1.0
S	10.5	0.2	<0.2	0.6	0.5	<0.4	13.0	14	7.9	583
Si	2.5	9.6	8.2	2.0	5.8	7.5	216.1	6.6	168	24
$\mu\text{g/L}$										
As	2	<1	<1	74	97	18	2692	1288	552	7544
B	216	3	4	386	144	50	783	510	288	9378
Ba	<1	<1	<1	<1	2	96	2	<1	41	12
Cd	<1	<1	<1	<1	1	2	<1	<1	3	5
Co	<1	<1	<1	<1	<1	6	<1	<1	2	4
Cr	5	1	1	6	8	20	45	16	37	22
Cu	1	<1	<1	2	4	21	11	6	15	63
Ga	6	4	19	7	6	5	<1	1	13	185
Ge	<1	<1	<1	12	3	12	198	233	39	148
Li	70	3	1	14	6	142	154	129	600	1957
Mn	<1	<1	<1	1	1	116	3	2	13	23
Mo	4	<1	<1	17	10	4	178	33	104	2940
Ni	4	<1	<1	1	1	19	1	1	114	199
Pb	<1	<1	<1	7	176	258	13	3	407	711
Rb	4	<1	1	26	10	29	102	54	81	88
Sb	<1	<1	<1	7	190	138	237	79	139	2594
Se	1	4	<1	6	47	3	65	3	16	334
Sn	3	<1	<1	3	6	3	<1	3	5	6
Sr	<1	<1	<1	<1	1	23	19	1	13	12
Th	1	0.3	2	<0.1	6	3	0.8	<0.1	3	4
V	3	<1	<1	61	34	24	1039	520	3581	37870
Ti	25	8	18	36	475	1323	28	31	262	467
Zn	<1	<1	<1	5	15	294	21	26	368	1422

Si-Ex: SiO_2 extraction; Fu: fusion method; DC: direct conversion.

3.1.3. Alkaline fusion

High crystalline X zeolites, occasionally containing traces of A zeolite or sodalite, were produced by Fu from PCC and IGCC FAs. For both FAs similar fused material was produced during the fusion step (600 °C, 2 h, FA/NaOH ratio of 2 kg/kg). This fused material is characterised by a significant development of crystalline phases (Fig. 6), mainly Na and Ca silicates and Na and Ca oxides, such as Na_2SiO_3 , nepheline ($\text{KNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$), $\text{Na}_{17}\text{Al}_5\text{O}_{16}$, hedenbergite ($\text{Ca}(\text{Fe}, \text{Mg})(\text{SiO}_3)_2$) and $\text{Ca}(\text{AlO}_2)_2$. These phases are meta-stables at low temperatures showing a disordered structure after few days.

By subsequent aging and crystallization, high CEC X and A zeolite were produced for both FA types using similar synthesis conditions. For PCC FA the highest X zeolite content, with traces of A zeolite, was obtained when using 16 h and FA/ H_2O = 10 L/kg for aging step and 90 °C and 6 h for zeolite crystallization. Applying the same conditions for IGCC FA, also high proportions of X zeolite were produced but containing traces of sodalite instead A zeolite. To improve the zeolitic product obtained from IGCC FAs two synthesis parameters were modified: (a) the FA/ H_2O ratio was reduced to 5 L/kg on aging, but due to the high Na concentration in the FA/ H_2O mixture synthesis only sodalite was produced, and (b) the crystallization time was increased to 8 h, allowing the production of the highest X zeolite content with traces of A zeolite. Therefore, similar zeolitic product

was obtained for IGCC FA than for PCC FA using the same conditions but different crystallization time (8 and 6 h, respectively).

Based on the results, the following zeolitic products were selected for the quality evaluation:

X zeolite (#6): obtained by fusion at 600 °C from PCC FA, 2 h with FA/NaOH ratio = 2 kg/kg, aging during 16 h, FA/ H_2O ratio of 10 L/kg and crystallization at 90 °C and 6 h.

X zeolite (#7): obtained by fusion at 600 °C from IGCC FA, 2 h, FA/NaOH ratio of 2 kg/kg, aging during 16 h, FA/ H_2O ratio of 10 L/kg and crystallization at 90 °C and 8 h.

3.2. Evaluation of the CEC and potential leaching of metals

The comparison of CEC values obtained for commercial zeolites with those for zeolites synthesised from FAs allowed the evaluation of the purity of these zeolitic material. Table 2 summarises the results of the CEC and leachable contents of the selected elements from the zeolitic products synthesised in this study. For the commercial pure zeolites, the CEC obtained for A and NaP1 zeolites (5.4 and 5.0 meq/g), was slightly higher than for X zeolite (4.3 meq/g). As regards the purity of the zeolitic products synthesised from FAs

the following issues may be:

- a) those from PCC FA have a higher purity than those from IGCC FA, with the exception of NaP1 products.
- b) the highest and lowest zeolite contents were reached for the synthesis products obtained by Si-Ex and DC, respectively. The X and A zeolites obtained by Si-Ex from PCC FA (synthesis products #1 and #2) reached the highest purity (100 and 98%) with CEC values of 4.3 and 5.3 meq/g, respectively.
- c) a high purity A zeolite (around 80%, coupled with a CEC of 4.3 meq/g) was also obtained by Si-Ex from IGCC FA (synthesis product #3)
- d) relatively high purity (83 and 70%) X zeolites with traces of A zeolite were synthesised by Fu, for PCC and IGCC FAs, respectively (synthesis products #6 and #7).
- e) as stated above, the NaP1 zeolitic material obtained for DC attained the lowest CEC and purity, reaching 49 and 54% purity for PCC and IGCC FA, respectively (synthesis products #4 and #5). 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 using the DIN-38414 tests have revealed that the mobility of most elements (such as B, Li, Mo, Sb, Se and Zn) was higher for the IGCC than that for PCC zeolitic products obtained by the three synthesis methodologies, but especially by using the DC method.

Concerning the relative leachable fractions among synthesis methods, a similar tendency was observed, obtaining the highest and lowest leachable fraction for the studied elements on products synthesised by DC and Si-Ex, respectively. Low leachable metal contents were obtained from high purity A and X zeolites and zeolite material synthesised by Fu from PCC FA.

Nevertheless the leachability of elements in the IGCC zeolitic products differentiate from those from PCC by the following features: (a) the A zeolite synthesised by Si-Ex shows the highest leachable levels of P, Co, Ge, K and Mn, (b) the zeolitic product obtained by Fu shows the highest leachable levels of Al, Na, Si, Ba and Cr, most probably due to the partial conversion to zeolite of the silicates and aluminium oxide species crystallised during the fusion step, and (c) the zeolitic product obtained by Fu shows the lowest leachable levels of S, Fe, As, Cd, Co, Cu, Ga, Ge, Mn, and Ni. Most of these elements are bound to sulphide and oxide species in the raw IGCC fly ash, which can be easily dissolved during the aging step, not trapped in the zeolite framework structure and being partially leachable in the zeolitic end-product.

As deduced from the results the lower leachable fractions the higher the purity of the zeolitic material.

4. Conclusions

The comparative study on synthesis of zeolites by applying three different methods on two different FAs (PCC and IGCC) revealed the following:

- high purity (80–100%) A and X zeolites and relatively high NaP1 zeolitic material (49–54%) may be obtained from both FAs.
- the purity and leachable fractions of elements of the zeolitic products follow the same tendency among synthesis methods for both FA type, reaching the highest purity and the lowest leachable potential of elements in the zeolitic product synthesised by Si-Ex

and the lowest purity and highest leachability in that obtained by DC.

- For a given method the zeolitic products synthesised from PCC FA have a higher purity and low leachable fractions than those from IGCC, with the exception of NaP1 products obtained by DC method.
- the lower CEC and higher leachable content of metals showed for IGCC zeolitic products as compared to those from PCC FAs are due to the high metal content and to the different speciation of most elements of IGCC FAs with respect to PCC FAs. This may limit a few potential applications.
- furthermore, differences on speciation are also the cause for different Si-Ex yields between both FA types. The speciation of Al and Si in FA essentially controls the Si-Ex yields and the crystallization of NaP1 and points out the significance of the occurrence of mullite (a high insoluble Al-Si bearing phase) in FA for the synthesis of zeolites. The occurrence of only reactive Al, in the highly soluble glass matrix of IGCC FA, accounts for reducing drastically the Si-Ex due to the easy precipitation as zeolites. The optimal conditions for the synthesis of zeolites were then controlled by speciation of elements in FA.
- despite the above possible limitations of zeolites from IGCC FA, the zeolitic products from both FAs types can be used as a raw material for the synthesis of zeolites for environmental purposes.

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