Synthesis of Zeolites from Fly Ash in a Pilot Plant Scale. Examples of Potential Environmental Applications

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Zeolite synthesis is one of the potential applications of fly ash production to obtain high value industrial products with an environmental technology utilization.

The compositional similarity of fly ash to some volcanic material, precursor of natural zeolites, was the main reason to experiment the synthesis of zeolites from this waste material by Höller and Wrishing[1]. Since this initial studies, many patents and technical articles have proposed different methods for the synthesize this mineral from fly ash, and different applications of the zeolitic product. Although all these methods are based on an hydrothermal alkaline conversion of fly ash, the following types of processes may be used:

- Classical alkaline conversion of fly ash. This is based on the combination of different activation solution/fly ash ratios, with temperature, pressure and reaction time to obtain different zeolite types[2-18]. Sodium or potassium hydroxide solutions with different molarity, 80 to 200 ^{o}C, 3 to 48 h, and atmospheric to water vapor pressure have been combined to synthesize up to 13 different zeolites from the same fly ash. The zeolite contents of the resulting material varied widely (20 to 75 %), depending mainly on the activation solution/fly ash ratio and on the reaction time[18].
- Shigemoto and coworkers[6] and Berkgaut and Singer[10] varied the process by introducing an alkaline fusion stage prior to the conventional zeolite synthesis.
- The application of the microwave to the conventional synthesis parametres[19] allowed a drastic reduction in the reaction time down to 30 minutes.
- Janssen[20] and coworkers developed a two stages synthesis procedure which allows the synthesis of >90 % pure zeolite products from high-Si solutions resulting from a light alkaline attack of fly ash. In addition, the solid residue from this attack was converted in classical zeolitic products by using the conventional conversion method.

All these different processes resulted in the synthesis of low-silica sodium and potassium zeolitic (NaP1, A, X, KM, chabazite, faujasite) material. The high Al^{3+}/Si^{4+} of this type of zeolites accounts for a high ionic exchange potential, specially for heavy metals and ammonium. This

pattern confer to the zeolitic material obtained a high potential application in the waste water decontamination technology.

Although a lot of research has been developed in this field, there is a lack of experimentation in a pilot plant scale to reproduce experimental processes. This study focuses on the synthesis of zeolites from Spanish fly ashes at laboratory (g and kg sample size) and pilot plant (metric tonne sample size) scales and the potential application of the zeolitic material synthesized.

EXPERIMENTAL SECTION

The eleven Spanish fly ashes reported in Table 1 were selected for this study. In addition to the chemical data reported in this Table and a detailed physico-chemical characterization of these fly ashes are reported previously[21] demonstrate that this selection covers all possible types of pulverized coal fly ash produced in Spain.

Table 1. Fly ashes selected for this study with details of the power plant and major oxide contents.

Power Plant	Power (MW)	Company	Location
1. Teruel	1050	ENDESA	NE Spain
2. Escucha	160	FECSA	NE Spain
3. Robla	625	Unión FENOSA	N Spain
4. Compostilla	1312	ENDESA	N Spain
5. Meirama	550	Unión FENOSA	N Spain
6. Narcea	569	Unión FENOSA	N Spain
7. As Pontes	1400	ENDESA	NW Spain
8. Puertollano	220	ENECO	Central Spain
9. Puentenuevo (ESPIEL)	938	ENECO	S Spain
10. Los Barrios	550	SE	S Spain
11. Soto Ribera	672	IBERDROLA/E.Bierzo	N Spain

Fly ash	1	2	3	4	5	6	7	8	9	10	11
SiO_2	47.2	49.5	40.1	49.8	51.9	54.3	46.7	58.4	52.0	45.1	49.6
Al_2O_3	25.6	26.7	23.3	26.1	26.4	23	31	29.3	34.2	37.6	32.3
Fe_2O_3	16.6	14.3	14.3	8.4	4.8	7	9.4	7.5	6.1	2.8	7.7
CaO	5.6	2.3	8.9	2.7	7.5	4.2	6.7	0.9	2.1	9.0	3.2
MgO	1.2	1.1	2	2.4	2.3	2.7	1.9	1.0	1.6	2.2	1.7
Na_2O	0.2	0.3	0.3	0.8	0.4	0.8	0.3	0.4	0.6	0.4	0.7
K_2O	1.6	2.3	2.6	4.3	0.8	3.9	1.3	2.4	4.1	0.7	4.2
P_2O_5	0.2	0.3	0.8	0.5	0.4	0.2	0.2	0.1	0.4	1.7	0.1
TiO_2	0.8	1	0.9	1	1.5	1.1	1.2	0.7	0.9	1.5	0.9
MnO	0.04	0.03	0.1	0.08	0.05	0.09	0.1	0.1	0.1	0.1	0.0
SO_3	0.6	0.4	0.4	0.3	0.2	0.1	0.8	0.2	0.1	0.7	0.4
SiO_2/Al_2O	1.8	1.9	1.7	1.9	2	2.4	1.5	2.0	1.5	1.2	1.5

Synthesis experiments were first developed using 4 g of fly ash in 4744 Parr digestion bombs with Teflon reactors. The zeolite conversion was studied as a function of activation agent (KOH, and NaOH) temperature (150 and 200ºC), conversion time (3 to 48 hours), solution concentration (0.5, 1, 2, 3 and 5 M), pressure (from 4.7 atm to 15.3 atm), and solution/sample ratio (2 to 18 ml g^{-1}). The matrix of experimental parameters build for the synthesis was devised in order to

optimize the mono-mineral synthesis for the different fly ashes. Around 350 experiments were performed in the first stage. Secondly, laboratory experimentation with a kg sample size was performed in an autoclave reactor (BACHILLER, 5 L autoclave) with stirring, temperature and pressure control. The experimentation in this intermediate scale was applied only to a few fly ashes and to the lowest solution/sample ratio used (2 ml g^{-1}), with a higher application potential. Around 60 experiments were performed at this scale. Finally, the synthesis conditions in the pilot plant scale were selected from the results obtained at lab-scale experimentation to synthesize NaP1 zeolite (2M NaOH for the activation solution, a f solution/fly ash ratio of 2 l/kg, T=150ºC and t=24h). The pilot plant scale experiment was performed in a 10 m^3 R-410-A reactor made up of 304 steel, the experimental conditions are summarized in Table 2.

Table 2. Synthesis and post-synthesis parameters of the pilot plant experiment.

Reactor:	R-410-A, stainless steel 304, 10 m^3
Materials:	Osmitized water 1848 Kg, NaOH 50 % 352 Kg, Teruel fly ash 1100 Kg
Parameters:	T,149.5 ^{o}C reached in 1h 15', t, 24 hours, pressure, 3.55 Kg cm^{-2}, cooling t, 2 h
Filtration:	polypropylene press filters (F-406, 55 plates), 2 m^3 manual extraction membrane pneumatic pump (16 m^3 air/hour), T, 90 ^{o}C, t, 1 h
Washing:	T, 85 ^{o}C, t, 40 min, water drainage with air, t, 12 h
Evacuation:	manual with 400 Kg containers, total 2603 Kg (48 % moisture), 1354 Kg (dry)
Waste waters:	2926 litres to treat, residual NaOH, 8.4 % of the input, pH, 12.8.

The zeolitic material obtained from the different experiments was filtered and washed with distilled MilliQ water, dried at room temperature and analyzed by means of XRD using a SIEMENS D500 powder diffractometer with a graphite monocromator, NaI(Tl) detector and Cu Kα radiation. The morphology of zeolites was studied by means of scanning electron microscopy (JEOL 6400 SEM) equipped with an energy dispersive X-ray spectrometer (LINK LZ5).

The ionic exchange capacity (CEC) for NH_4^+, Cd^{2+}, Pb^{2+}, Zn^{2+} and Ba^{2+} was determined for most of the types of zeolitic material obtained. CECs were determined using pure solutions of soluble chlorides or nitrates. For CEC determinations 100 ml of single solutions containing 400 mg l^{-1} of each cation were mixed at room temperature with 1 g of each zeolitic product. After continuous stirring during 3 hours, the mixtures were filtered and the solutions stored at 4°C for subsequent analysis. The determination of the levels of Na^+ and K^+, as well as Cd^{2+}, Pb^{2+}, Zn^{2+} and Ba^{2+}, in the solutions after the experiments were determined by ICP-AES and the levels of NH_4^+ by colorimetry flow injection analysis (FIA).

RESULTS AND DISCUSSION

Synthesis

The results of this research allowed to reach high synthesis yields (from 25 % to 75 % of the fly ash converted into zeolitic material) for zeolites with high industrial interest in relatively short activation periods (24 to 3 hours). The highest synthesis yields were obtained using high activation solution / fly ash ratio 18 ml g^{-1} because the total dissolution of mullite, quartz and the glassy matrix. However, this process has some disadvantages such as the high water consumption and the need of high activation periods. The use of lower activation solution / fly ash ratio (2 ml

g^{-1}) tested previously by Koulosek[7] allowed, in addition to the minimization of the water consumption, a drastic reduction of the activation time down to 3 hours. Nevertheless, this low liquid/solid ratio did not reach total dissolution of quartz and mullite, but acceptable yield were achieved for several fly ashes (up to 70 % using the Narcea fly ash) in relatively short time (9 hours).

The results demonstrated a higher conversion efficiency of the NaOH versus the KOH solutions. The thirteen zeolitic phases reported in Table 3 were obtained from the fly ash by changing the synthesis parameters such as temperature, time, activation agent, concentration of the activation solution and solution/fly ash ratio. The Narcea, Compostilla, Soto de Ribera, Meirama, Los Barrios, Espiel and Teruel fly ashes showed the highest zeolite synthesis potential.

Table 3. Zeolitic phases synthesized from Spanish fly ashes using KOH and NaOH as activation agents, with the indication of their XRD JCPDS codes, divided into high and low industrial application groups based on the CEC.

Zeolitic product		JCPDS
High industrial application		
NaP1 zeolite	$Na_6Al_6Si_{10}O_{32}.12H_2O$	39-0219
Phillipsite/ KM-zeolite	$K_2Al_2Si_3O_{10}.H_2O$	30-0902
K-Chabazite	$K_2Al_2SiO_6.H_2O$	12-0194
F linde zeolite	$KAlSiO_4.1.5H_2O$	25-0619
Herschelite	$Na_{1.08}Al_2Si_{1.68}O_{7.44}.1.8H_2O$	31-1271
Faujasite	$Na_2Al_2Si_{3.3}O_{8.8}.6.7H_2O$	12-0228
Zeolite A	$NaAlSi_{1.1}O_{4.2}$	43-0142
Low industrial application		
Perlialite	$K_9NaCaAl_{12}Si_{24}O_{72}.15H_2O$	38-0395
Analcime	$NaAlSi_2O_6.H_2O$	19-1180
Hydroxy-sodalite	$Na_{1.08}Al_2Si_{1.68}O_{7.44}.1.8H_2O$	31-1271
Hydroxy-cancrinite	$Na_{14}Al_{12}Si_{13}O_{51}.6H_2O$	28-1036
Kalsilite	$KAlSiO_4$	33-0988
Tobermorite	$Ca_5(OH)_2Si_6O_{16}.4H_2O$	19-1364

Given that the Al- and Si- bearing phases are dissolved during different stages of the zeolitisation (glass>quartz>mullite), different zeolite synthesis behavior using the same activation conditions for a similar SiO_2/Al_2O_3 ratio may be obtained for fly ashes with different mineral composition. The SiO_2/Al_2O_3 ratios of the glass matrix have an important influence on the type of zeolite to be obtained. The higher aluminum-silicate glass content and the differences in the glass degradability are probably responsible for the higher synthesis efficiencies of the Meirama, Narcea, Soto de Ribera, Los Barrios and Espiel fly ashes.

From the point of view of the potential industrial application, the more interesting zeolitic products are herschelite, NaP1, faujasite and zeolite A, due to the high ionic exchange capacity. Table 4 and Figure 1 summarize the different zeolite types obtained for the experimental

conditions (temperature, concentration of the activation solution and solution/fly ash ratio) for the smallest sample size used.

Table 4. Zeolitic material synthesized as a function of reaction parameters using solution/fly ash ratios of 18 and 2 l Kg^{-1}.

alkali concentration	temperature	zeolitic product
18 ml g-^{1}		
NaOH		
0.5-3.0 M	<175 ^{o}C	NaP1 (herschelite, only Espiel fly ash)
	>175 ^{o}C	analcime, hydroxy-sodalite, tobermorite, nepheline hydrate
3.0-5.0 M	150-200 ^{o}C	hy-sodalite, hy-cancrinite, tobermorite
KOH		
0.5-1.0 M	150-200 ^{o}C	KM, tobermorite
3.0 M	<175 ^{o}C	F zeolite, tobermorite
5.0 M	<175 ^{o}C	F zeolite, kalsilite, tobermorite
3.0-5.0 M	>175 ^{o}C	kalsilite, tobermorite

alkali concentration	temperature	zeolitic product
2 ml g^{-1}		
NaOH		
0.5 M	150-200 ^{o}C	low activation for all temperatures
1.0 M	150 ^{o}C	low activation, NaP1 & herschelite (traces)
	200 ^{o}C	NaP1 and herschelite for 8 h activation
2.0-3.0 M	150 ^{o}C	NaP1 and traces of herschelite
	200 ^{o}C	NaP1 (Teruel, Los Barrios), herschelite and analcime traces (Narcea)
5.0 M	150-200 ^{o}C	herschelite, analcime (Narcea) hy-sodalite, hy-cancrinite (Teruel, Barrios)
KOH		
2.0 M	150-200 ^{o}C	KM zeolite
5.0 M	150 ^{o}C	KM, chabazite and linde F traces
	200 ^{o}C	Kalsilite and KM, perlialite and tobermorite traces

Selected synthesis conditions were reproduced in a kilogram scale using a water/sample ratio of 2 ml g^{-1} in the aforementioned autoclave with the Teruel and Narcea fly ashes. The results were found to be highly reproducible and relatively high NaP1 synthesis yields were obtained at 8 to 24 h, 150°C and 2.0 M NaOH. Figure 2 shows the high NaP1 synthesis yield as deduced from the XRD patterns. Finally, the same conditions fixed at 24 h were reproduced at a pilot plant scale in an 10 m^3 at Clariant, SA. Detailed data of the experimentation is given in Table 2.
The zeolitic material obtained at this scale was very similar to the product obtained in the intermediate scale, but trace levels of analcime were detected (Figure 2). The NaP1 zeolite content was estimated in 35 to 40 %. This pilot plant experiment showed that the following synthesis key questions have to be investigated in order to reduce production costs:

- There is a need to reduce the activation solution/fly ash ratio to diminish the water consumption, and to reduce the reaction time. Nowadays, acceptable yields may be obtained in 6h.

- Although the NaOH excess was only 8% of the original input, the pH of the waste waters was very high (12.8) and consequently, washing was carried out with the consequent increase of the production costs. From the point of view of the production costs, washing and filtering was found one of the key questions to be solved. An accurate stoichiometrical balance would allow to obtain acceptable yields without Na excess in waste. This balance coupled with a reduction of the activation solution/fly ash ratio could avoid the washing process and reduce the filtration to a minimum.
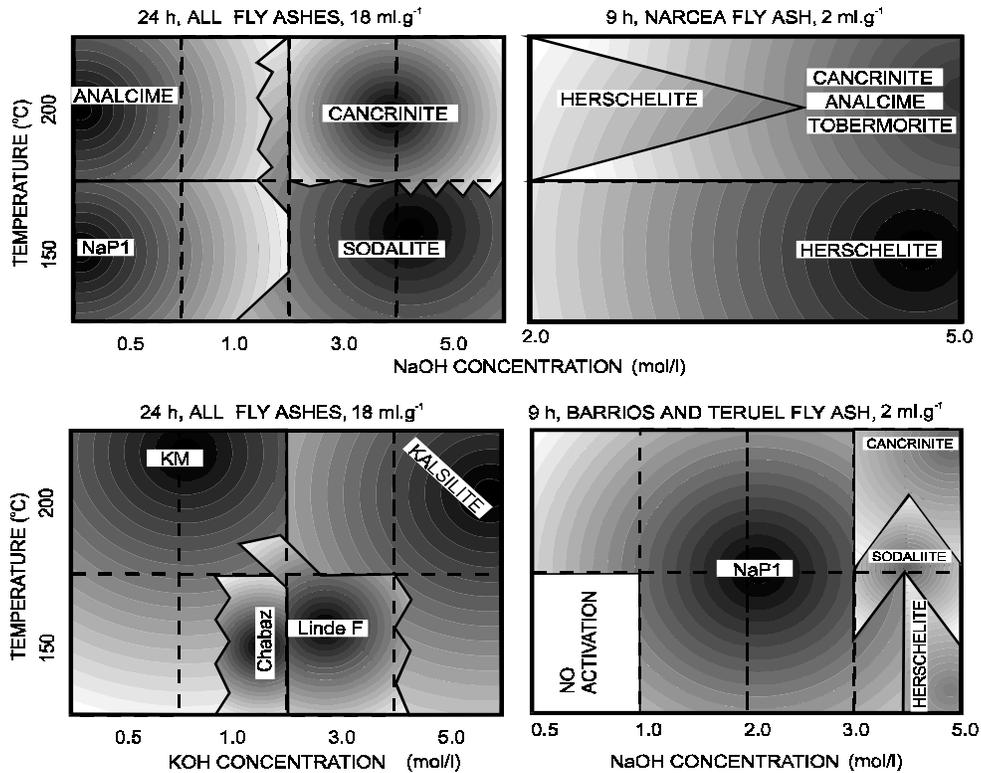

Figure 1. Zeolite products obtained from fly ash as a function of the synthesis parameters using a activation solution/fly ash ratio of 18 and 2 ml g⁻¹.
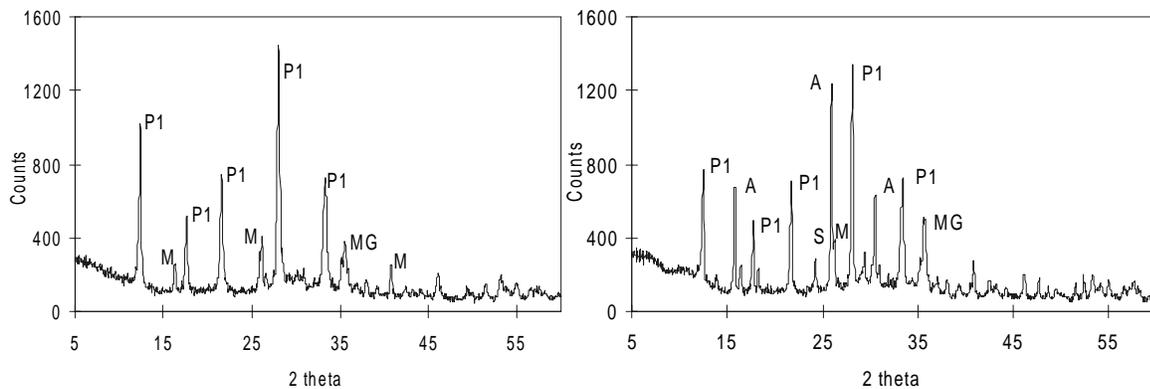

Figure 2. XRD patterns of the zeolitic material obtained from the synthesis experiments performed with the Teruel fly ash at the kilogram- (left) and pilot plant- scales. P1, NaP1 zeolite; A, analcime; S, Hydroxy-sodalite M, mullite; MG, magnetite.

<u>Applications</u>

Major potential application of the zeolites obtained are based on their use as high ion exchangers in industrial waste water and soil decontamination[10, 22-26]. Although some studies point towards the potential use in the gas cleaning technology, research has to be performed to find actual applications in this field.

The results of the CEC determinations are summarized in Table 5. CEC values from 160 to 260 meq $100g^{-1}$ (similar to CEC values of commercial clinoptilolite[7]) were obtained for NaP1, Herschelite, KM, linde F and K-chabazite for the majority of the cations investigated.

The untreated fly ashes showed a NH_4^+ retention capacity of 0.1-0.3 mg $NH_4^+.g^{-1}$. However, the treated fly ash reached retention capacities up to 38 mg $NH_4^+.g^{-1}$. Moreover, the experiments performed showed high ion exchange capacities after a few minutes, reaching the highest cation retention after 1 to 3 hours for NaP1 and KM zeolites, respectively[19]. These properties of the zeolitic products obtained from fly ash are very interesting from the point of view of their application as sorbents of NH_4^+ from waste waters, such as those arising from the farming activities. Once the NH_4^+ is retained in the sorbent, this could also be used as a soil conditioner since the release of this cation from the zeolites is very slow[7].

Concerning the heavy metals, the CEC capacity ranges from 80 to 260 meq $100g^{-1}$ (Table 5) for NaP1, KM, chabazite, herschelite, and linde F. With this CEC up to 198 mg Pb or 178 mg Ba may be trapped per gram of zeolitic material. The lowest CEC values were obtained for Zn^{2+}, whereas the highest CEC values were determined for Pb^{2+} and Ba^{2+}. The following CEC affinity for each zeolite and cation may be concluded from the results reported in Table 5: <u>NaP1:</u> Ba^{2+} >Pb^{2+}>NH_4^+=Cd^{2+}>Zn^{2+}, <u>KM:</u> NH_4^+>Pb^{2+}=Ba^{2+}>Cd^{2+}=Zn^{2+}, <u>Linde F:</u> NH_4^+=Ba^{2+}=Pb^{2+}>Cd^{2+}>Zn^{2+}, <u>K-Chabazite:</u> Ba^{2+}=Pb^{2+}>NH_4^+=Cd^{2+}>Zn^{2+}, <u>Herschelite:</u> NH_4^+= Pb^{2+}>Ba^{2+}=Cd^{2+}>Zn^{2+}.

Table 5. CEC values obtained for the different cations and zeolitic products in µeq g^{-1}.

	NH_4^+	Cd^{2+}	Pb^{2+}	Zn^{2+}	Ba^{2+}
NaP1	1324	1384	1821	809	2606
KM	1723	626	1451	512	1400
Analcime	611	258	563	279	438
Kalsilite	145	57	409	175	42
Sodalite	500	773	?	609	555
LindeF	1736	1094	1844	697	1746
Cancrinite	389	486	?	507	189
Tobermorite	548	798	?	503	630
K-chabazite	1087	1124	1535	662	1667
Nepheline	299	373	291	202	244
Herschelite	2075	1522	1908	873	1727

The zeolitic material synthesized from the pilot plant scale experiment gave rise to the following CECs for the heavy metals: 68 meqNi^{2+} $100g^{-1}$, 90 meqCd^{2+} $100g^{-1}$, 95 meqZn^{2+} $100g^{-1}$, 98 meqPb^{2+} $100g^{-1}$, 110 meqFe^{2+} $100g^{-1}$, 130 meqBa^{2+} $100g^{-1}$, 210 µeqCu^{2+} $100g^{-1}$ and 260 meqCr^{3+} $100g^{-1}$.

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