

Synthesis of zeolites from coal fly ash: an overview

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Abstract

Coal combustion by-products production in USA and EU is estimated in around 115 million tons per year. A large portion of this production is accounted for the coal fly ash (CFA). Cement and concrete manufacturing consumes most of the CFA produced. Zeolite synthesized from CFA is a minor but interesting product, with high environmental applications. Zeolites may be easily obtained from CFA by relatively cheap and fast conversion processes. This paper provides an overview on the methodologies for zeolite synthesis from CFA, and a detailed description of conventional alkaline conversion processes, with special emphasis on the experimental conditions to obtain high cation exchange capacity (CEC) zeolites. Zeolitic products having up to 3 meq g^{-1} may be easily obtained from high-glass CFA by direct conversion. A review of potential applications of different zeolitic products for waste water and flue gas treatment is also given. The examination of the data presented by different authors reveals that one of the main potential application of this material is the uptake of heavy metals from polluted waste waters. The zeolitic material may be also used for the uptake of ammonium from polluted waters but high concentrations of other cations may considerably reduce the ammonium absorption efficiencies due to ion competition. Some of the zeolites synthesized may be also used as molecular sieves to adsorb water molecules from gas streams or to trap SO_2 and NH_3 from low-water gaseous emissions.

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1. Introduction

The inorganic residues arising from coal combustion processes are known as ‘coal combustion by-products’ (CCBs in USA, or CCP in Europe). CCBs are mainly fly ash, bottom ash, slag, and fluidized bed combustion and flue gas desulfurization by-products. Although a large proportion of global CCBs is used

by the building industry, there is still a proportion which is disposed of in ponds or landfills.

The use of coal fly ash (CFA; the more abundant CCB) has important economical and environmental implications. Thus, it is believed that a ton of fly ash used to replace a ton of cement saves the use of an equivalent of nearly one barrel of oil.

Following the European Association for Use of the By-Products of Coal-Fired Power Stations (ECOBA, <http://www.ecoba.com/>) classification, the major CCBs are:

- Pulverized coal fly ash (PFA). The European standard EN450—defines fly ash as a fine-grained

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powder, which is mainly composed of spherical glassy particles, produced during the combustion of pulverized coal. Fly ash has pozzolanic properties and consists essentially of SiO_2 and Al_2O_3 . Fly ash is obtained by electrostatic or mechanical precipitation of dust-like particles from the flue gases of furnaces fired with pulverized coal. Cenospheres (or hollow glassy spherical particles, with a relative density $< 1.0 \text{ kg dm}^{-3}$) may be recovered from fly ash disposal ponds, bag houses ESP and mechanical collectors.

- Furnace bottom ash (FBA) is a coarse grained material arising from wet ash removal of dry-bottom furnaces.

- Boiler slag is a vitreous grained material derived from wet ash removal of wet-bottom furnaces.

- Flue gas desulfurization (FGD) product is a fine gypsum powder obtained by desulfurization of flue gas coal-fired power plants.

- Fluidized-bed combustion by-products (FBCB) are CCBs, some of which may have high Ca and S contents, resulting from fluidized-bed combustion processes.

As reported by the American Coal Ash Association (ACAA, <http://www.aaa-usa.org/>), in 1998, 74.9 million tons of CCBs were produced in USA (60% fly ash, 15% bottom ash, 1% boiler slag, and 24% FGD materials). ECOBA reported a CCB production for Europe in 1999 of 55 million tonnes (70% fly ash, 11% bottom ash, 4% boiler slag and 15% FGD products).

CCBs are mainly used as building materials and in other civil engineering works. Bulk and agglomerate utilization is classically differentiated as follows (Goumans et al., 1994):

- Agglomerate applications, such as cement and concrete manufacturing, production of bricks and light weight aggregates and refractory materials, and additives for the ceramic industry.
- Bulk applications, such as road and rail bases, pavements, land filling in mining activities, and soil amendment material.

ECOBA reported that, within the EU, the utilization of bottom and fly ash in the construction industry is currently about 44% and 48%, respectively, of the annual production, while the utilization rate for boiler slag is 100%. Additionally, around 20% of the CCBs

production is used for land reclamation activities. However, 37% of the European and 70% of the American CCBs production is still stored in disposal sites.

Since the 1950s, the primary use of fly ash has been in concrete and cement manufacturing (as reported by ECOBA, in USA and EU, 6 and 9 million tonnes, respectively, are used annually to this end). However, novel potential applications have been developed or are in the progress of development. Examples of these applications are:

- Additives for immobilization of industrial and water treatment wastes (Dirk, 1996; Andres et al., 1995).
- Extraction of valuable metals, such as Al, Si, Fe, Ge, Ga, V, Ni (Pickles et al., 1990; Font et al., 2001).
- Land stabilization in mining areas (Jarvis and Brooks, 1996).
- Sorbents for flue gas desulfurization (Garea et al., 1997).
- Fire-proof materials (Vilches et al., 2001).
- “slash” (fly ash/sludge blend) production for soil amendment (Reynolds et al., 1999).
- Filter material for the production of different products (Kruger, 1997).
- Ceramic applications (Anderson and Jackson, 1983; Stoch et al., 1986; Queralt et al., 1997).
- Synthesis of high cation exchange capacity (CEC) zeolites.

The compositional similarity of fly ash to some volcanic material, precursor of natural zeolites, was the main reason to experiment with the synthesis of zeolites from this coal by-product by Höller and Wirsching (1985). Although this potential application may consume only a small proportion of the fly ash production, the final products obtained may reach a relatively higher added value than when applied in current construction applications.

2. Synthesis of zeolites from fly ash

Zeolites are crystalline aluminum–silicates, with group I or II elements as counterions. Their structure is made up of a framework of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$

tetrahedra linked to each other at the corners by sharing their oxygens (Fig. 1). The tetrahedra make up a three-dimensional network, with lots of voids and open spaces. It is these voids that define the many special properties of zeolites, such as the adsorption of molecules in the huge internal channels (Fig. 2). The substitution of Si (IV) by Al (III) in the tetrahedra accounts for a negative charge of the structure (Fig. 1) which may give rise to high CEC (up to 5 meq g^{-1}) when the open spaces allow the access of cations. Zeolites may be found in natural deposits, generally associated with the alkaline activation of glassy volcanic rocks, or synthesized from a wide variety of high-Si and Al starting materials. As a consequence of the peculiar structural properties of zeolites, they have a wide range of industrial applications (Breck, 1984), mainly based on:

- Ion exchange: Exchange inherent $\text{Na}^+/\text{K}^+/\text{Ca}^{2+}$ for other cations on the basis of ion selectivity.
- Gas adsorption: Selective absorption of specific gas molecules.
- Water adsorption: Reversible adsorption of water without any desorption chemical or physical change in the zeolite matrix.

Since the initial studies by Höller and Wirsching (1985), many patents and technical articles have proposed different hydrothermal activation methods

to synthesize different zeolites from fly ash (see as examples: Hemni, 1987; Mondragón et al., 1990; Shigemoto et al., 1992, 1993, 1995; Kolousek et al., 1993; Bang-Sup et al., 1995; Chang and Shih, 1995; Park and Choi, 1995; Querol et al., 1997a, 2001a; Singer and Berggaut, 1995; Amrhein et al., 1996). All the methodologies developed are based on the dissolution of Al–Si-bearing fly ash phases with alkaline solutions (mainly NaOH and KOH solutions) and the subsequent precipitation of zeolitic material. Table 1 shows the zeolite types that have been synthesized from coal fly ash by different studies. The potential industrial application of these zeolitic materials is varied. Thus, zeolite X has a large pore size (7.3 Å) and a high CEC (5 meq g^{-1}), which make this zeolite an interesting molecular sieve and a high-cation exchange material. However, the small pore size of hydroxy-sodalite (2.3 Å) accounts for the low potential application for both molecular sieving and ion exchange. The main limitation of the processes for synthesizing zeolites from fly ash is that to speed the reaction, relatively high temperatures (125–200 °C) have to be applied to dissolve Si and Al from the fly ash particles. Under these conditions, many of the high-CEC and large pore zeolites (zeolites A and X) cannot be synthesized. If temperature is reduced, then the synthesis yield is reduced considerably and a very long activation time is required. However, KM (equivalent to phillipsite), NaP1, Na-chabazite (herschelite),

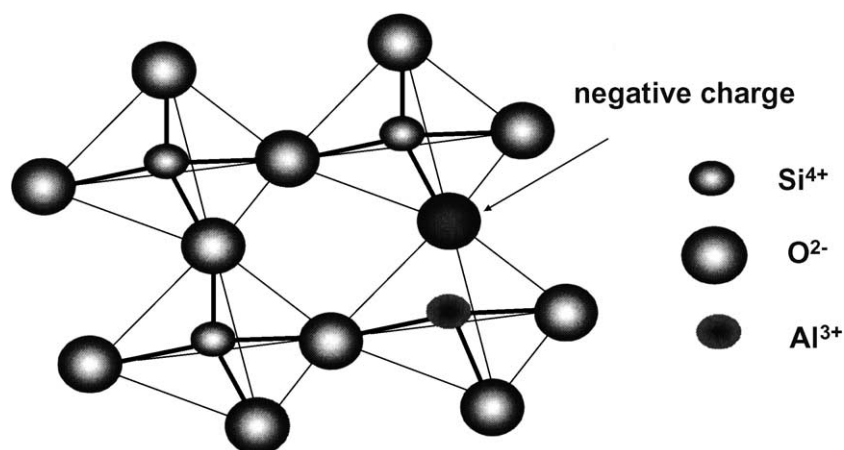


Fig. 1. Idealized structure of zeolite framework of tetrahedral $[\text{SiO}_4]^{4-}$ with a Si/Al substitution ($[\text{AlO}_4]^{5-}$) yielding a negative charge, and consequently a cation exchange capacity.

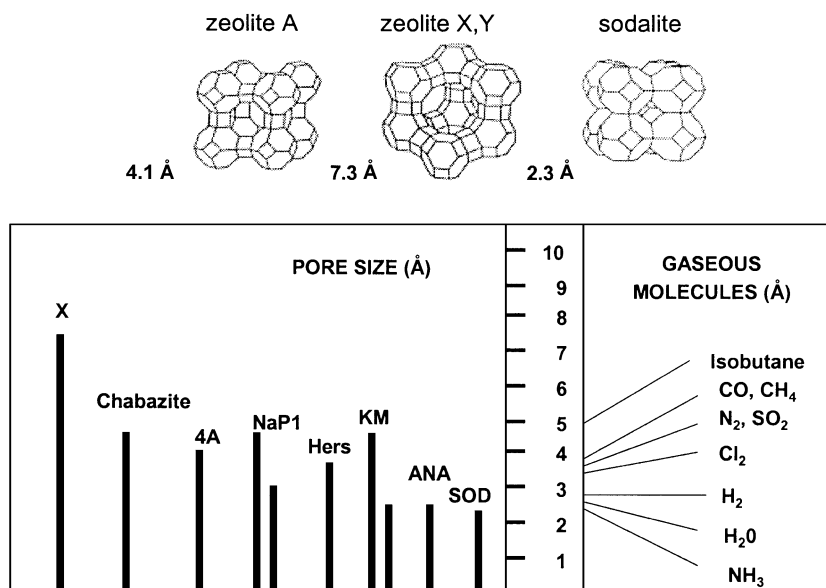


Fig. 2. Top: The channel diameter of zeolites is dependent on the structure. The sodalite cage (truncated cube–octahedron) is the base unit of A, X zeolite and hydroxy-sodalite, but depending on the arrangement of the polyhedral unit, the structures have channels with very different diameter. Bottom: Examples of channel size for selected zeolites which may be synthesized from fly ash compared with the diameter of some gaseous molecules (modified from Breck, 1984). ANA, analcime; zeolite A, X, zeolite X, Hers, herschelite (Na-chabazite), SOD, sodalite; KM, phillipsite. Note that NaP1 and KM have two channel types with different pore size.

K-chabazite, Linde F, and other high-CEC zeolites may still be obtained with high synthesis yields in the range of 125–200 °C.

Table 1

Zeolites and other neomorphic phases synthesized from fly ash and Joint Committee of Powder Diffraction Standard (JCPDS) codes for XRD identification

Zeolitic product	JCPDS
NaP1 zeolite	39-0219
phillipsite	30-0902
K-chabazite	12-0194
zeolite F linde	25-0619
herschelite	31-1271
faujasite	12-0228
zeolite A	43-0142
zeolite X	39-0218
zeolite Y	38-0239
perialite	38-0395
analcime	19-1180
hydroxy-sodalite	31-1271
hydroxy-cancrinite	28-1036
kalsilite	33-0988
tobermorite	19-1364

Although the synthesis method are based on hydro-thermal alkaline conversion of fly ash, the following types of processes may be used:

- Classic 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. Sodium or potassium hydroxide solutions with different molarity, at atmospheric and water vapor pressures, from 80 to 200 °C and 3 to 48 h have been combined to synthesize up to 13 different zeolites from the same fly ash (Querol et al., 2001a). The zeolite contents of the resulting material varied widely (40–75%) depending mainly on the activation solution/fly ash ratio and the reaction time. This methodology has been applied at a pilot plant scale by Querol et al. (2001a) for the production of 2.7 tonnes of zeolitic material in 8 h in a single-batch experiment. The application of the microwave to the conventional synthesis parameters at a laboratory scale (Querol et al., 1997b) resulted in a drastic reduction of the reaction time to 30 min.

- Shigemoto et al. (1992, 1993, 1995) and Berggaut and Singer (1995) varied the process by introducing an alkaline fusion stage before the conventional zeolite synthesis, resulting in very interesting zeolites such as zeolite A and faujasite.

- Dry or molten-salt conversion. To avoid a synthesis process with the generation of waste water, Park et al. (2000a,b) developed a synthesis strategy based on the use of salt mixtures instead of the aqueous solutions as the reaction medium. This interesting process has limitations since, up to now, only low-CEC zeolites are obtained to the high temperature needed in the activation process.

- Hollman et al. (1999) developed a two-stage synthesis procedure that enables the synthesis of >99% pure zeolite products from high-Si solutions obtained from a light alkaline attack of fly ash. Moreover, the solid residue from this attack could be converted into classic zeolitic products by using the conventional conversion method. This process has the advantage of producing pure zeolitic material, instead of the blend zeolite/residual fly ash particles obtained from other strategies. Moreover, high-pore volume zeolites, including zeolites X and A, may be obtained in this process.

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(III)/Si(IV) ratio of this type of zeolite accounts for a high ion exchange potential, especially for heavy metals and ammonium. Therefore, the synthesized zeolitic material may have significant application in waste water decontamination technology.

2.1. Classic alkaline conversion of fly ash

In most studies, the fly ash activation is usually carried out in digestion bombs or autoclaves, varying the activation agent (mainly KOH and NaOH), temperature (100 and 200 °C), conversion time (3–48 h), solution concentration (0.5, 1, 2, 3 and 5 M), pressure (the vapor pressure at the temperature selected), and solution/sample ratio (1–20 ml g⁻¹).

After synthesis experiments, the zeolitic material obtained is filtered and washed with water, dried at room temperature and analyzed by means of XRD. The determination of the CEC value and comparison with that of the pure zeolite is recommended for a semi-quantitative estimate of the zeolite contents of the synthetic materials.

Most of the previously referenced studies demonstrated that the NaOH solutions have a higher conversion efficiency than the KOH solutions under the same temperature. Although most of the zeolites reported in Table 1 may be obtained for a specific fly ash, the reaction time needed to reach acceptable

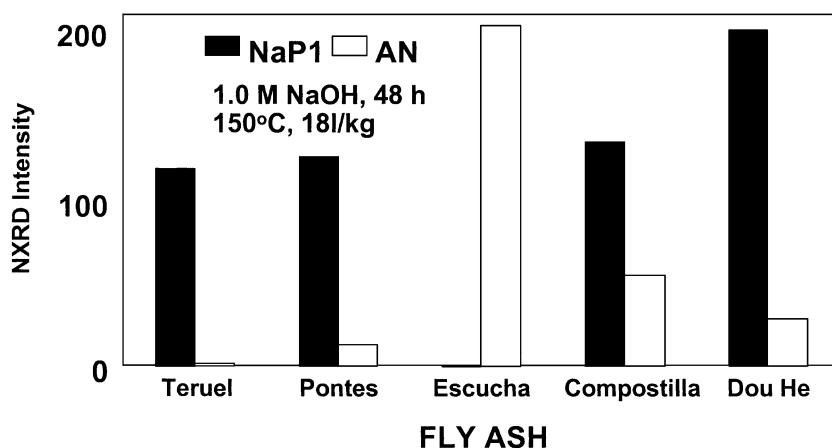


Fig. 3. Under the same synthesis conditions (1 M NaOH, 48 h, 150 °C and 18 l kg⁻¹), different fly ashes may give rise to different zeolitic products. Note that Teruel and Escucha fly ashes have a similar SiO₂/Al₂O₃ (1.8 and 1.9) ratio but under the experimental condition used. Teruel fly ash give rise to NaP1 zeolite and Escucha to analcime (AN).

synthesis yields is inversely proportional to the aluminum–silicate glass content of the fly ash. The conversion efficiencies are also dependent on the contents of non-reactive phases (mainly hematite, magnetite, lime) and resistant aluminum–silicate phases, such as mullite and quartz, and the grain size distribution. Thus, for higher aluminum–silicate glass content, shorter activation periods and lower solution/fly ash rates are needed to reach high zeolites synthesis yields.

Given that the Al- and Si-bearing phases are dissolved during different stages of the zeolitization (glass>quartz>mullite), different zeolite synthesis behavior using the same activation conditions for a similar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio might be obtained for fly ashes with a diverse mineral composition. Thus, two fly ashes having similar bulk $\text{SiO}_2/\text{Al}_2\text{O}_3$ but different quartz–mullite/glass proportions, will have a very different composition of the glass matrix, and consequently the nucleation processes will take under two different scenarios concerning the ratio Al/Si of synthesis solutions. Therefore, it is the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of the glass matrix and not the bulk ratios that exert an important influence on the type of zeolite obtained. Fig. 3 shows an example of different zeolitic materials obtained by applying the same synthesis conditions to different fly ashes with similar bulk $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios.

Other important parameters for the zeolitization of fly ash are the activation time, the concentration of the activation agents and fly ash/solution ratio.

- As previously stated, the time needed to obtain a high synthesis yield is inversely proportional to the glass content. High-glass fly ashes are zeolitized in short period (6–8 h), but longer reaction times (24–48 h) are required to obtain similar synthesis yields from high-mullite or quartz fly ashes.

- The highest synthesis yields are obtained in 12–24 h using a high-activation solution/fly ash ratio ($10\text{--}20 \text{ ml g}^{-1}$) due to the total dissolution of mullite, quartz, and the glassy matrix (see Fig. 4). However, this process suffers from a number of disadvantages such as high water consumption and the need for high activation periods. The use of the lower activation solution/fly ash ratio (2 ml g^{-1}) led, in addition to less water consumption, to a drastic reduction in the activation time down to several hours. However, total dissolution of quartz and mullite is not achieved.

- Both temperature and concentration of the activation agent have also a very important influence on the zeolite types obtained. Thus, by increasing both parameters (i.e. 5 M and 200°C), low-CEC zeolites such as hydroxy-cancrinite and hydroxy-sodalite are obtained. Conversely, low temperature and concentration (i.e. 0.5–3 M and $<150^\circ\text{C}$) allows the synthesis of high-CEC zeolites such as NaP1, A, or

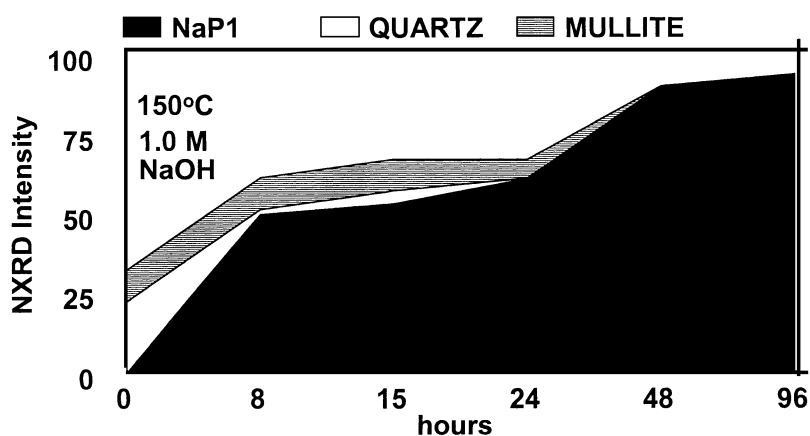


Fig. 4. Time evolution of normalized XRD intensity of the highest reflection of quartz, mullite and NaP1 zeolite during the zeolite conversion using a solution/fly ash ratio of 18 ml g^{-1} . Note that from the initial stages, NaP1 grows from the dissolution of the glass matrix, and that quartz is completely dissolved after 24 h of activation, and mullite after 48 h.

Table 2

Zeolites and other neomorphic phases synthesized from fly ash as a function of activation agent (NaOH or KOH), T, C and activation solution/fly ash ratio (ml g⁻¹)

		10–18 ml g ⁻¹
<i>NaOH</i>		
0.5–3.0 M	90–175 °C 175–225 °C	NaP1 analcime, hydroxy-sodalite, tobermorite, nepheline-hydroxy
3.0–5.0 M	150–200 °C	hydroxy-sodalite, hydroxy-cancrinite, tobermorite
<i>KOH</i>		
0.5–1.0 M	150–200 °C	KM, tobermorite
3.0 M	<150 °C	linde F, tobermorite
5.0 M	<150 °C	linde F, kalsilite, tobermorite
3.0–5.0 M	>150 °C	kalsilite, tobermorite
		1–3 ml g ⁻¹
<i>NaOH</i>		
5.0 M	150–200 °C	low activation for all temperatures
1.0 M	150 °C	low activation, NaP1 (herschelite)
	200 °C	NaP1 and herschelite for 8 h activation
2.0–3.0 M	90 °C	A zeolite
	150 °C	NaP1 (herschelite traces), faujasite (if aging)
5.0 M	200 °C 150–200 °C	NaP1, herschelite herschelite, analcime, hydroxy-sodalite, hydroxy-cancrinite
<i>KOH</i>		
2.0 M	150–200 °C	KM zeolite
5.0 M	150 °C	KM, chabazite and linde F traces
	200 °C	kalsilite and KM, perialite and tobermorite traces

chabazite. Table 2 summarizes the zeolite types that may be synthesized from fly ash as a function of T and C and solution/fly ash ratio.

High-NaP1 zeolitic material was obtained at a pilot plant scale from the Narcea fly ash (Moreno et al., 2001a,b) by using 3 M NaOH solutions with a ratio of 2 ml g⁻¹, 125 °C in 8 h. The zeolitic material obtained reached a CEC of 2.7 meq g⁻¹, equivalent to 60% zeolite content.

3. Potential applications zeolites synthesized from fly ash

Simultaneously with the development of synthesis methods, intensive research has been carried out on the potential application of the zeolites synthesized from fly ash. The high Al (III)/Si (IV) ratio of these zeolites accounts for the high CEC of some of them such as NaP1, 4A, X, KM, F, chabazite, herschelite, and faujasite. Owing to this high CEC (up to 5 meq g⁻¹ of some pure zeolites), these zeolites have a high potential for application in water decontamination. In particular, the removal of heavy metals and ammonium from solutions was tested extensively (Kolousek et al., 1993; Catalfamo et al., 1993; Singer and Berkgaut, 1995; Berkgaut and Singer, 1995, 1996; Lin and His, 1995; Park and Choi, 1995; Querol et al., 1997b, 2001a,b; Amrhein et al., 1996; Suyama et al., 1996; Patane et al., 1996a,b; Lin et al., 1998; Moreno et al., 2001a,b). The possibility of the use of these zeolites as molecular sieves in gas purification technology has also been investigated in a number of studies (Querol et al., 1999; Srinivasan and Grutzeck, 1999; Querol et al., 2001b). The readers are preferred to Breck's (1984) handbook of zeolites for detailed information on applications.

3.1. Ion exchange

Most of the studies on the use of fly ash-derived zeolites in the field of water purification have been performed for selected pollutants by using synthetic solutions under laboratory conditions. These studies have shown that the zeolitic material obtained may reach CECs from 0.3 to 4.7 meq g⁻¹ (Table 3), and that there is a competition between cations in a solution to occupy exchangeable places in zeolites. In other words, the matrix effect of the solution exerts considerable influence on the pollutant uptake efficiencies by zeolites from a solution. Thus, high-Fe³⁺ or Ca²⁺ solutions in urban and industrial waste waters may considerably reduce the uptake of ammonium (Juan et al., 2001). However, Moreno et al. (2001a,b) tested the heavy metal uptake capacity from acid mine waters of zeolitic material synthesized from fly ash with zeolite doses from 5 to 40 g l⁻¹ depending on the water matrix patterns (mainly, high Ca²⁺ and Mg²⁺ or Fe³⁺ contents) and the zeolite type. The

Table 3

Cation exchange capacity (meq g⁻¹) obtained for zeolitic material synthesized from fly ash using the methodology of ISRIC (1995)

Zeolitic product	CEC
4A-X	4.7
NaP1	2.7
herschelite	2.1
KM	1.9
linde F	1.9
analcime	0.6
sodalite	0.3
fly ash	<0.05

Mean CEC values of Spanish fly ashes are also reported. The 4A-X zeolite blend was obtained from silica extracts from fly ash, and the other zeolitic material was obtained by direct conversion.

results demonstrated that these pyrite mining waste waters may be efficiently decontaminated by a direct cation exchange treatment using low zeolite doses (Fig. 5). The cation exchange decontamination may be advantageous in cases, such as extraction wells, where it can be performed with no solid waste (precipitates) in the bottom as it occurs when pH treatments are applied to precipitate heavy metals. From the results, a tentative order for the affinity of different ions to the zeolite exchange sites was obtained: Fe³⁺>Al³⁺≥Cu²⁺≥Pb²⁺≥Cd²⁺=Ti⁺>

Zn²⁺>Mn²⁺>Ca²⁺=Sr²⁺>Mg²⁺ (Moreno et al., 2001a). These results demonstrate that NaP1 and 4A zeolites have a higher affinity for metal ions than for Ca²⁺ and Mg²⁺. Thus, solutions containing up to 600 mg l⁻¹ of these heavy metals and up to 800 mg l⁻¹ of Ca can be treated with zeolite to reduce the metal content down to <0.5 mg l⁻¹, with relatively high levels of Ca still being present in solution. In addition to the ion exchange, precipitation of metal-bearing solid phases may enhance efficiency of the decontamination tests since a drastic pH rise was induced by the zeolite addition (from 2.5 to 5 pH). Although cation exchange is the leading process, the quantification of the metal uptake due to precipitation was unclear from the experiments performed.

Jeong Hwan et al. (1996) found high ammonium and heavy metals (Mn, Cd, Pb, Cu, Cr, Zn) removal efficiencies by treating municipal landfill leachates with a 1:1 blend of activated carbon and zeolitic material synthesized from fly ash.

An important limitation for the application of the zeolitic material for the cation uptake from waste waters is the possible occurrence of potentially hazardous leachable elements (such as Mo, As, Cr, V) in the residual fly ash particles when direct conversion products are used. However, in most of

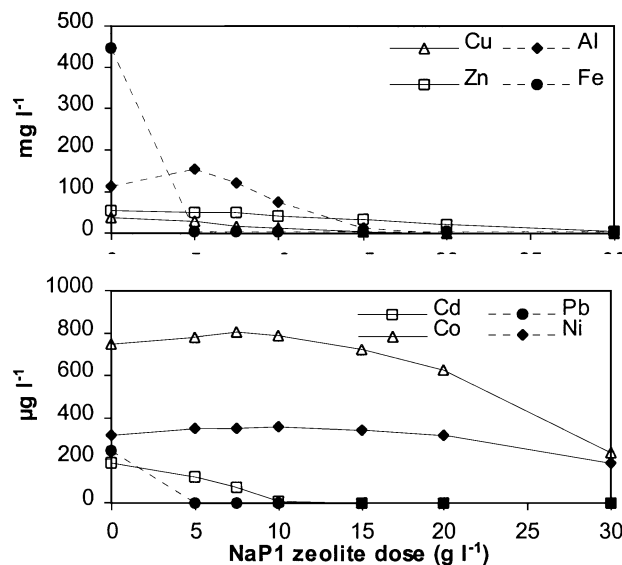


Fig. 5. Decrease of concentration of heavy metals as a function of the zeolite dose (g l⁻¹) in the treatment of acid mine waters with a high NaP1 product synthesized from coal fly ash (based on data from Moreno et al., 2001a).

the experiments carried out in the literature cited, the content of these leachable elements in the treated solutions was low enough to compete with the benefits of the cation uptake. If pure zeolitic material synthesized from Si fly ash extracts is used, this limitation does not exist.

Another use of the zeolitic material synthesized from coal fly ash is the immobilization of heavy metals in contaminated soils. When phyto-remediation strategies are adopted for the final recovery of polluted soils, the immobilization of metals is necessary to avoid leaching of the metals and the consequent ground water pollution. Zeolitic material synthesized from fly ash has been applied using different doses (from 15 to 54 tons per hectare) to different experimental fields by Moreno et al. (2001b). The zeolitic material was manually applied by mixing the powder with the soil. One of the fields was maintained without zeolite addition to compare the reduction of the metal leaching with the other fields. Sampling was carried out 1 and 2 years after the zeolite addition. The preliminary results show that the application of the zeolitic material considerably decreases the leaching of elements such as Cd, Co, Cu, Ni, and Zn (Fig. 6). Although the reduction of the leachable proportion is mainly due to the ion exchange, the precipitation of insoluble phases (as a consequence of the pH rise from 3.3 to 7.6 due to the

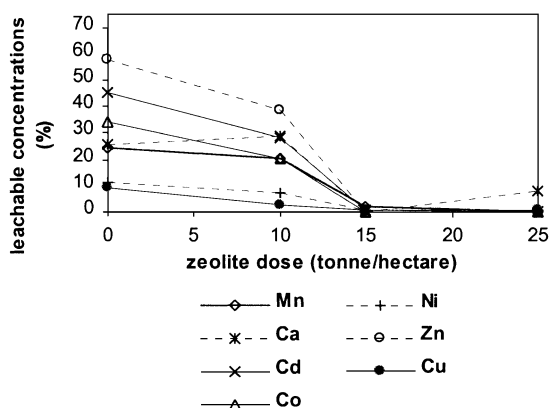


Fig. 6. Decrease of the leachable proportions of heavy metals from soils as a function of the zeolite dose after 2 years treatment of contaminated soils from sulfide mining areas with a high NaP1 product synthesized from coal fly ash (based on data from Moreno et al., 2001b).

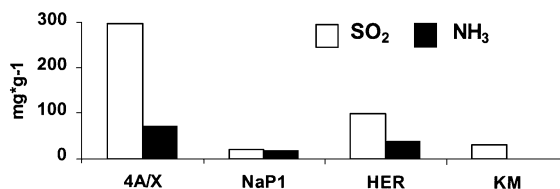


Fig. 7. SO₂ and NH₃ sorption capacity (mg g⁻¹) of zeolitic products synthesized from coal fly ash (based on data from Querol et al., 2001a,b). These are high NaP1, 4A, KM zeolites, and herschelite (HER) products.

zeolite addition) also contributes to immobilize the pollutants.

Similar studies have been performed by Lin et al. (1998) to immobilize Cd in contaminated soils. A drastic reduction of the leachable Cd contents (from 88% to 1%) was obtained by adding zeolitic products synthesized from fly ash to polluted soils with a dose of 16% wt.

3.2. Molecular sieves

The use of zeolites synthesized from fly ash as molecular sieves for flue gas treatment and separation and recovery of gases such as CO₂, SO₂, and NH₃ has been tested. Fig. 2 shows the pore size of different zeolites synthesized from fly ash and the molecular size of selected gaseous molecules. As evidenced by this figure, zeolite X has a channel size of 7.3 Å, larger than the diameter of molecules of H₂O, SO₂, and NH₃.

CO₂, SO₂ and NH₃ adsorption capacities of the zeolitic materials are usually determined using thermogravimetric analysis or instrumentation for gas sorption analysis with direct detection of desorbed gases. Both methodologies are based on a sorption chamber with a flow of gas mixture through a sample holder. The gas carrier is usually He or N₂. Samples are placed into a glass reactor and activated under 200–400 °C before the adsorption runs to extract water molecules from the zeolite. The saturation of the samples is reached by passing through the blend of the gas carrier with fixed concentrations of CO₂, SO₂ or NH₃. After saturation, the samples are purged at temperatures from 20 to 80 °C. The desorbed gas concentrations are usually measured directly by thermal conductivity or indirectly by thermogravimetry.

Zeolites 4A, and specially zeolites X, have a larger diameter channels than the above-mentioned gas mol-

ecules (4.1 Å), but other zeolites such as sodalite and analcime have very small channels (around 2.3 Å) which will not trap these species. Other zeolites such as KM or NaP1 have a complex structure with two types of channel size (one with a very small diameter and the other with a size close to the 4A zeolite), which makes trapping of these molecules difficult. Thus, the SO₂ and NH₃ adsorption capacities measured for sodalite and analcime usually reach only 1–6 mg g⁻¹ as reported by Srinivasan and Grutzeck (1999) and Querol et al. (2001b). The last study also showed that for KM and NaP1, the sorption values may increase to 20 mg g⁻¹, whereas a very high SO₂ sorption capacity was measured for henschelite (Na-chabazite), 4A and X zeolites (100, 300 and 380 mg g⁻¹, respectively) in accordance with the wider channels of these zeolites (Fig. 7).

It is important to note that the presence of water vapor in the flue gas may considerably reduce the gas uptake capacity of these zeolites in actual industrial applications. Consequently, the major potential applications of this zeolitic material for gas treatment may be both the water vapor uptake or SO₂ or NH₃ sorption from low-water gaseous effluents.

From the point of view of flue gas cleaning, the most interesting zeolites are 4A and X zeolites, followed by Na-chabazite. The two first zeolites may be obtained in significant amounts from silica extracts from fly ash, but not from direct conversion since their synthesis yield from fly ash is strongly limited by temperature (<100 °C). If this low-temperature range is used in direct conversion, the low dissolution of the fly ash glass matrix accounts for the low synthesis yield. Although 4A and X zeolites have been obtained by direct conversion from fly ash, the content of the zeolite in the end product is very low. In the direct conversion, higher temperatures are needed to dissolve, partially or totally, the Al–Si fly ash phases before the precipitation of neomorphic zeolites.

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