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A mini-review on coal fly ash properties, utilization and synthesis of zeolites

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ABSTRACT

Coal fly ash is considered as a by-product of coal combustion power stations that may pertain unique properties and utilization fields. This review article gives an overview of different classification methods with comparative data on the chemical composition of coal and coal fly ash. Furthermore, a review describes in detail the utilization sectors of coal fly ash that expands from environmental application to materials production and possible recovery of precious elements. A particular interest is set on the synthesis of zeolites by applying modern production approaches along with state-of-the-art application fields starting from heavy metal removal to catalysis. It suggests to consider different methods of synthesis of zeolites by highlighting the main drawbacks and advantages.

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Coal fly ash; synthetic zeolites; synthesis; properties; application

Introduction

Coal is one of the world's most plentiful and widely disseminating fossil fuel, which proven resources are assessed for about 1000 billion tones worldwide (Bukhari et al. 2015; Tauanov et al. 2018a). It is still a commonly used type of combustible in various developing and progressive countries. In accordance with Yao et al. (2015), coal-burning power production considered to 29.9% of global power production in 2011 and it is predicted to reach almost 46% by 2030. According to the statistics of the past 10 years, PRC is the prevailing consumer of coal in the world with more than 50% of the global coal consumption in 2012 (Yao et al. 2015). This tendency is followed by the US and India with a yearly consumption rate of 11.7% and 8%, accordingly. The manufacturing Asian countries, such as Japan (3.3%), South Korea (2.2%) and Indonesia (1.4%) also use up a large percentage of the world share as shown in Figure 1.

Although the coal-fired power plants are still largely used, it should be noted that most of the developed countries strictly regulate the installation of special entrapment technologies to substantially decrease and control the release of toxic pollutants, such as SO₂, NO_x, mercury, toxic metals and acid gases. For example, current regulations of the US EPA require the use of special control technologies to significantly reduce the discharge of pollutants and to meet the concentration limits, which include wet and dry flue gas desulfurization or sorbent injection for SO₂ and activated carbon injection for mercury

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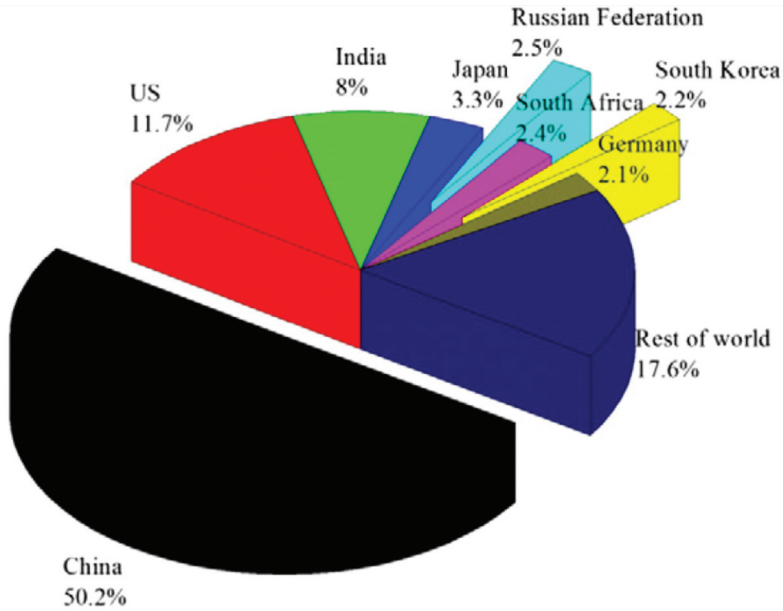


Figure 1. The coal consumption share worldwide in 2012 (Reprinted from Yao et al. (2015) with permission from Elsevier).

control measures (US Department 2011). Alternative measures of control usually implemented in coal-fired power plants, depending on pollutants nature, might include fabric filters, selective catalytic reduction, electrostatic precipitation and fuel switching.

It is well known that coal is the major source of energy (electricity) production and industrialization of many countries rely on the consumption of coal energy. For instance, in People’s Republic of China (PRC) almost 68.5% of energy is generated from coal in 2012 (Figure 2), while the percentages of energy produced from coal of progressed and

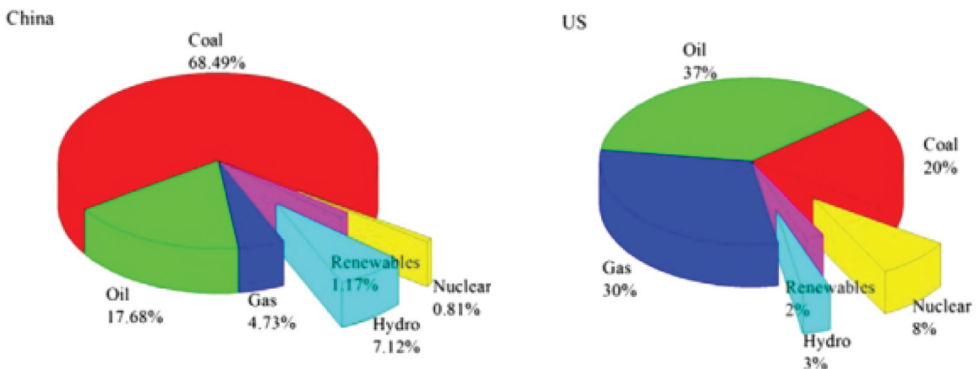


Figure 2. Consumption of energy by fuel type in 2012: PRC vs. USA (Reprinted from Yao et al. (2015) with permission from Elsevier).

progressing countries as the US, Japan and India are counted as 20%, 53% and 21.78%, respectively (Tauanov et al. 2017b).

Numerous reviews on coal fly ash and zeolites have been published, including pioneering review on synthetic zeolites produced from CFA (Querol et al. 2002a), zeolites for removal of gaseous pollutants (Ren et al. 2020), a critical review on the utilization of waste resources (Collins et al. 2020), zeolite synthesis from hazardous wastes (Mallapur and Oubagaranadin 2017), synthesis of nanoporous materials via recycling CFA and other solid wastes (Lee et al. 2017), environmental applications of zeolites produced from CFA (Franus et al. 2015) and characterization with possible industrial applications (Jha and Singh 2011). However, there is a need for an updated review of CFA properties, utilization fields and production of synthetic zeolites along with application sectors. The main goal of the current mini-review is to establish these data and broadly describe the state-of-the-art information in the literature to emphasize the importance of detailed analysis and utilization of value-added material.

Coal Fly Ash Classification and Composition

The study performed by the World Coal Institute (World Coal Institute 2005) shows an energy and moisture content of coal depending on origin with the valued reserves worldwide of each category and initial utilization fields as demonstrated in Figure 3. In general, according to their classification, coal is categorized into two groups: a low-rank coal that contains about 47% of total coal reserves (lignite and sub-bituminous) and hard coal (bituminous and anthracite) that includes about 53% of total coal amount.

One of the major disadvantages of energy consumption dependence on coal sources is the gathering of coal ash that causes environmental and health issues (Belviso 2017; Tauanov et al. 2017a, 2019). According to the literature, a burned coal produces about 5

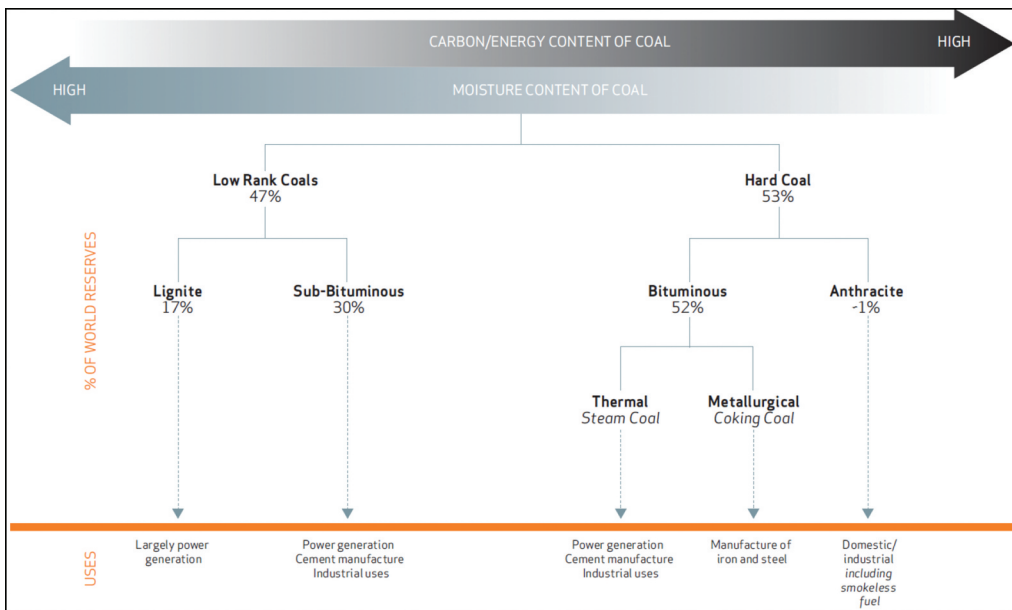


Figure 3. The world coal reserves classification (Reprinted from the World Coal Institute (2005)).

to 20 wt.% of ash, which includes both a coal bottom ash (CBA, 5–15 wt.%) and CFA (85–95 wt.%) (Yao et al. 2015). Normally, the coal ash is emitted in the form of wet and dry consumptions after being used in coal combustion reactors. The coal bottom ash (CBA) is a crude fraction of ash that is normally settled down at the bottom of combustion reactors and gathered mechanically after burning process. CFA is a finer fraction of burned ash that is electrostatically or mechanically precipitated and collected in ash disposal areas after combustion.

As for the usage of CFA, the statistics differ from country to country from a minimum of 3% to 90% (Belviso 2017). The utilization index of CFA is around 50% in the US and 90% in EU states, while the recycling and reprocessing in PRC and India are 67% and 60%, respectively (Belviso 2017). It should be mentioned that the average total ash utilization degree in the world has been enhanced by 9% and reached 25% (Bhattacharjee and Kandpal 2002; Wang, Terdkiatburana, and Tadé 2008), but it also indicates that almost 75% of the produced waste ash is still accumulated in disposal ponds and requires a relevant recycling or reprocessing method. The forecast of major cross-regional coal trade for the period of 2002–2030 conducted by the World Coal Institute (World Coal Institute 2005) reveals that in most of the countries, especially in developing regions the coal trade is predicted to expand; hence, it could be expected that the consumption will necessarily be increased (Figure 4). Consequently, it entails an urgent utilization of previously produced fly ash and to find other novel and immense methods of reprocessing.

CFA is a material with complex chemical and mineralogical composition that requires various advanced characterization methods to extract full data. Recent studies state that up to 316 specific minerals and 188 mineral groups are found in different samples of ash (Vassilev et al. 2003; Vassilev and Vassileva 2005, 1997). According to ASTM standards

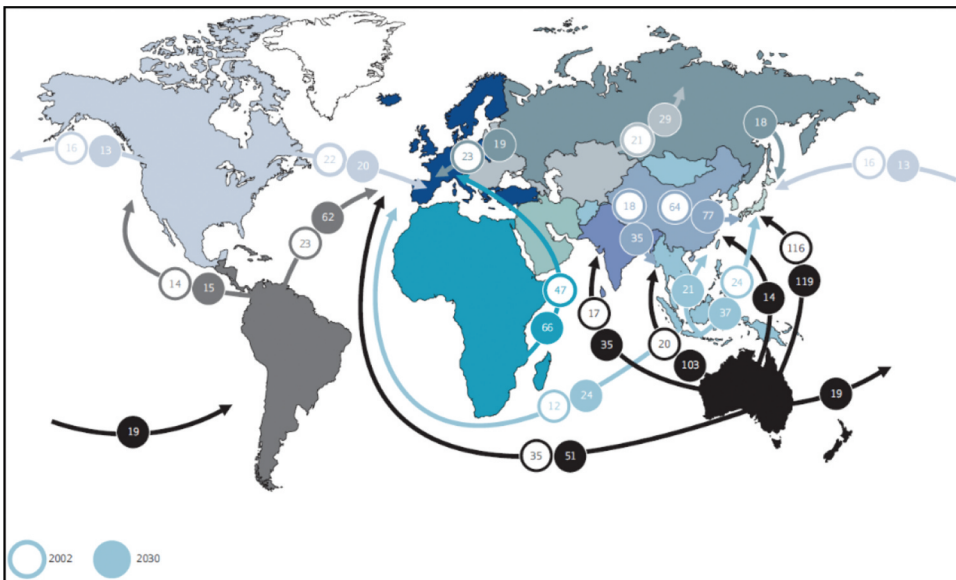


Figure 4. The world coal trade projection for 2002–2030 in Mt (Reprinted from the World Coal Institute (2005)).

(C618) CFA is classified into two classes: Class C, which contains more than 20% of CaO and more than 50% of combined SiO_2 , Al_2O_3 and Fe_2O_3 oxides; while Class F, has the combined content of SiO_2 , Al_2O_3 and Fe_2O_3 that is greater than 70% and the amount of CaO is less than 20% (Blissett and Rowson 2012). There are other CFA classification approaches, for instance, Canada groups CFA according to the concentration of CaO and lost on ignition (LOI) index (Belviso 2017). In this classification, CFA is grouped into Types F (<8%), CI (8–20%), CH (>20%) based on CaO content, whereas classification according to LOI indexes includes Type F with CaO amount 8–12%, while other Types C, CI and CH contain up to 6% CaO.

The UN classifies CFA into four groups according to $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and CaO content, where Group-I CFAs have $\text{SiO}_2/\text{Al}_2\text{O}_3 > 2$ and CaO amount up to 15%; Group II includes CFAs with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of up to 2 and CaO amount >15% with SO_3 content <3%. The Group III CFA, in contrast, has the amounts of CaO and SO_3 more than 15% and 3%, respectively, while the Group IV includes CFAs with CaO amount more than 15% with SO_3 less than 3% (Belviso 2017).

More recent classification of CFAs suggested by Vassilev and Vassileva is based on origin, mineralogy and chemical composition, physical and chemical properties. The system is complex and hence gives a more comprehensive method of classification that

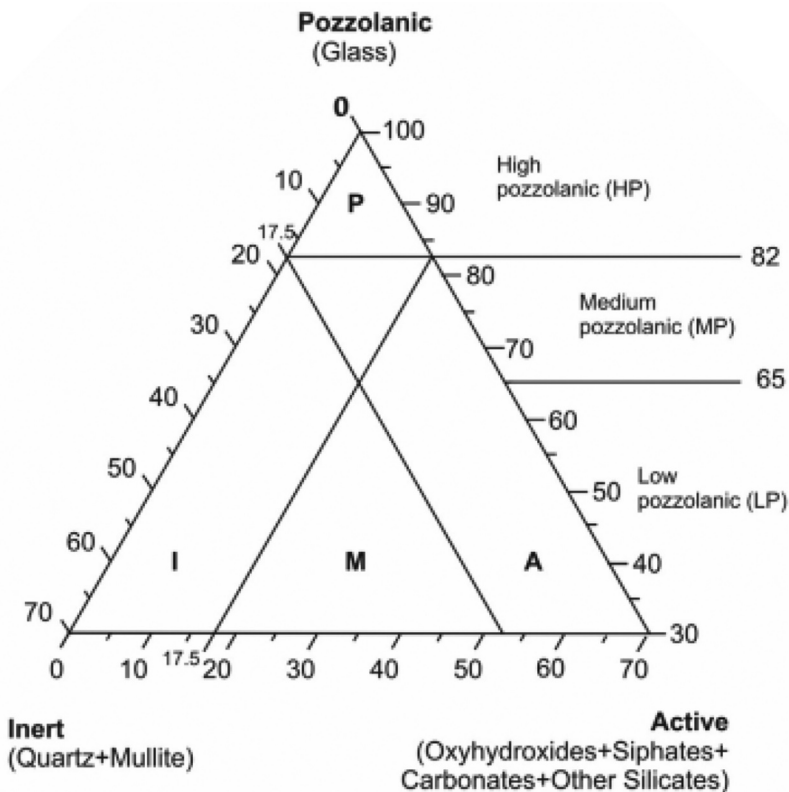


Figure 5. The phase-mineral classification of CFA (Reprinted from Belviso (2017) with permission from Elsevier).

Table 1. The chemical composition of CFAs produced from various coal types

Coal type	Component (wt.%)								
	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	SO ₃	Fe ₂ O ₃	LOI
Bituminous	0–4	0–5	5–35	20–60	0–3	1–12	0–4	10–40	0–15
Sub-bituminous	0–2	1–6	20–30	40–60	0–4	5–30	0–2	4–10	0–3
Lignite	0–6	3–10	10–25	15–45	0–4	15–40	0–10	4–15	0–5
Anthracite	0–1	1–4	18–36	28–57	0–4	1–27	0–9	3–16	1–8

is valuable for considering the application of CFAs in different fields of industry (Figure 5).

CFAs have generally a hydrophilic surface and have more fine particles formed upon exiting the combustor, therefore, tend to have a disordered structure that improves the reactivity (Iyer and Scott 2001). In general, CFA of Type F is produced when anthracite, bituminous or sub-bituminous coal is burned and is normally low in lime and contains more silica, alumina and iron oxide; although CFA of Type C origins from lignite coal that contains more lime (Fisher et al. 1978). The range of chemical composition of CFAs produced from these coal types is shown in Table 1 (Belviso 2017).

The composition and mineralogical phase content of CFA is mostly reliant on the origin and type of coal burned in power plants. For example, according to XRD analysis, most of the CFA samples contain inorganic phases as mullite, quartz and hematite or various ferric oxide forms (Duta and Visa 2015; Jha et al. 2009; Visa 2016; Xie et al. 2014). The principal chemical components of CFA are silica, alumina, ferrous oxide and calcium oxide with different amounts of remaining carbon and trace elements. Table 2 summarizes a comparative chemical composition of CFAs from different countries. The chemical characteristics of CFA have been completely investigated and it is acknowledged that CFAs include multiple components at concentrations of higher than 50 mg/kg. Some of those components

Table 2. The chemical composition of CFAs from different continents (Taken from Blissett and Rowson (2012) with permission from Elsevier)

Compound	Regions and component (wt.%)				
	Europe	US	PRC	India	Australia
SiO ₂	28.5–59.7	37.8–58.5	35.6–57.2	50.2–59.7	48.8–66.0
Al ₂ O ₃	12.5–35.6	19.1–28.6	18.8–55.0	14.0–32.4	17.0–27.8
Fe ₂ O ₃	2.6–21.2	6.8–25.5	2.3–19.3	2.7–14.4	1.1–13.9
CaO	0.5–28.9	1.4–22.4	1.1–7.0	0.6–2.6	2.9–5.3
MgO	0.6–3.8	0.7–4.8	0.7–4.8	0.1–2.1	0.3–2.0
Na ₂ O	0.1–1.9	0.3–1.8	0.6–1.3	0.5–1.2	0.2–1.3
K ₂ O	0.4–4.0	0.9–2.6	0.8–0.9	0.8–4.7	1.1–2.9
P ₂ O ₅	0.1–1.7	0.1–0.3	1.1–1.5	0.1–0.6	0.2–3.9
TiO ₂	0.5–2.6	1.1–1.6	0.2–0.7	1.0–2.7	1.3–3.7
MnO	0.03–0.2	No data	No data	0.5–1.4	No data
SO ₃	0.1–12.7	0.1–2.1	1.0–2.9	No data	0.1–0.6
LOI	0.8–32.8	0.2–11.0	No data	0.5–5.0	No data

Table 3. The trace element content of CFAs (ppm)

Elements	As	Ba	Cr	Cu	Li	Ni	Pb	Rb	Sr	V	Zn
Median value	55	1302	148	86	185	96	80	108	757	228	154

may cause an environmental issue (Izquierdo and Querol 2012; Tauanov, Lee, and Inglezakis 2020).

Table 3 presents the concentrations of trace elements in 23 European samples of CFA. They are in broad agreement with the elemental composition of Australian CFA analyzed by Jankowski et al. (2006). It is notable that heavy metals, such as Ba, Cr, Ni, Rb, Pb, Sr, Zn and V are existing in a significant amount. Due to this, mobility studies have been performed to evaluate the possibility of those elements leaving the surrounding environment. The leaching properties of elements are tightly linked with the phase compound that they are related to, as well as the leaching conditions such as the pH of solution (Azat et al. 2019).

Utilization Fields of Coal Fly Ash

The main application fields of CFA are currently attributed to construction, ceramic, environmental and agricultural sectors. According to statistics, the industrialized countries as US and EU mostly use the fly ash in concrete and cement production, waste stabilization, mining applications, as structural fills and embankments, for remediation and restoration that overall accounts for more than 60–70% of all CFAs (Yao et al. 2015).

Environmental Applications

The physical and chemical properties of CFA are advantageous for the preservation of various organic and inorganic pollutants and it is widely examined as an adsorbent in different environmental fields. The unburnt carbon containing in CFA adds some extra advantages, which increases an adsorption capacity of the material. Several studies have been made on the application of CFA for heavy and toxic metal removal from both gaseous and aqueous environment. The first studies were conducted in 1984, where CFA was used as an adsorbent of divalent copper (Cu^{2+}) from industrial wastewater (Panday, Prasad, and Singh 1985). More recently, Cho et al. investigated the adsorption of Zn^{2+} and Cd^{2+} in batch experiments at room temperature under various pH values of 3 to 10. According to the outcomes, the adsorption underwent by the Freundlich model and the experiments with real wastewater solutions suggested that CFA could be used as a low-cost adsorbent (Cho, Oh, and Kim 2005). CFA has also been studied for removal of other heavy metals, such as Pb^{2+} , Ni^{2+} and Cr^{3+} (Bayat 2002; Ayala et al. 1998; Alinnor 1993). Some research groups also examined the hazardous metals as Hg (II), As (III) and As (V). The experiments on adsorption elemental Hg using CFA showed attractive results (Diamadopoulos, Ioannidis, and Sakellaropoulos 1993; Banerjee, Joshi, and Jayaram 2005; Pattanayak et al. 2000), however, there are still gaps on interpretation the detailed mechanism of adsorption that might occur due to the interaction of unburnt carbon with Hg or fly ash and Hg, hence these variables require further investigations.

CFA has been favorably used for adsorption of organic pollutants. For instance, CFA has adsorbed phenol with adsorption capacity reaching 27.9 mg/g that is equivalent to commercially used activated carbon that shows an adsorption capacity of 108 mg/g (Aksu and Yener 1999). Yet another study on adsorption of halogenated phenols using CFAs showed the adsorption capacities of 98.7 mg/g and 118.6 mg/g for 2-chlorophenol and 4-chlorophenol, accordingly (Aksu and Yener 2001). CFA has also been considered as an effective

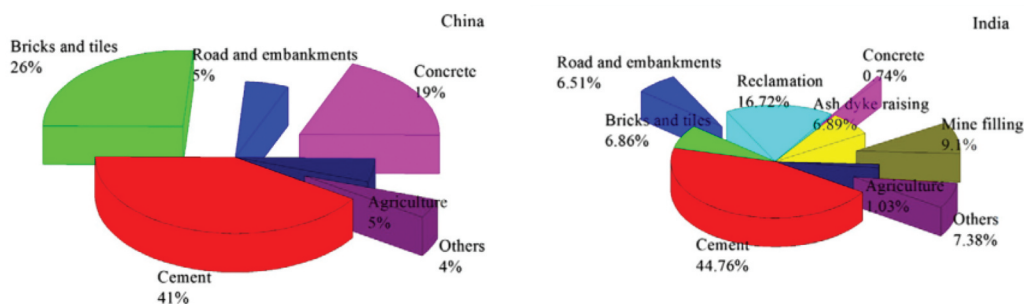


Figure 6. CFA utilization fields in PRC and India (Reprinted from Yao et al. (2015) with permission from Elsevier).

adsorbent for removal of polychlorinated biphenyls (Nollet et al. 2003), chrysoidine R dye (Matheswaran and Karunanithi 2007), herbicides, such as metribuzin and atrazine (Singh 2009) from water.

Another environmental use of CFA includes the adsorption of greenhouse emissions, namely CO₂, SO₂, and NO_x flue gases. The recent research on desulfurization of the flue gas using Ca(OH)₂ enriched CFA show that adsorption increase with the ratio of CFA to Ca(OH)₂ (Davini 1995). According to experimental results obtained by Lu and Do on adsorption of NO_x using CFA, the authors claim the positive effect of unburnt carbon on adsorption capacity, which could further improve the performance of material upon activation (Lu and Do 1991). A more recent study on capturing CO₂ using CFA-based composites proved that relatively cost-effective and abundant material could be an efficient alternative for CO₂ capture (Sarmah, Baruah, and Khare 2013).

In summary of the pollutant removal potential of CFA, it could be concluded that chemical and physical properties of CFA are favorable and in some cases, the crucial effect might occur due to the presence of unburnt carbon as it has a high surface area, which is significant for adsorptive methods of remediation.

Construction Industry

It is well known that the main field of utilization of CFA worldwide is in the construction industry. Figure 6 illustrates the breakdown of CFA utilization in PRC and India, two key countries that generate a huge amount of CFA annually (Yao et al. 2015). It is evident that in PRC a huge percentage of CFA is used in the manufacturing of bricks and tiles, alongside in cement (41%) and concrete production (19%). The statistics of India is comparable in terms of cement production (44.76%), followed by reclamation (16.72%) and mine filling (9.1%). The remaining proportion of CFA is shared with other application sectors, such as road construction and embankments, agricultural use and others (Yao et al. 2015).

There are specific reasons why the CFA is utilized for cement and concrete production as it is cheap and abundant. In addition, the pozzolanic nature of some CFAs makes them useful for cement replacement in concrete production (Alinnor 2007). CFA could also improve the long-term durability properties of concrete by decreasing the ingress of

aggressive agents such as chloride ions (Diamadopoulos, Ioannidis, and Sakellaropoulos 1993). The studies on low-lime CFA show that 45 wt.% of the material with portland cement could allow engineering practical strength despite the initial strength to be reduced to some extent (Banerjee, Joshi, and Jayaram 2005). The need and interest of scholars in high-volume fly ash (HVFA) concrete has grown over the last decade since it is more environmentally and economically feasible material. There are many studies on a laboratory scale and field trials up to 50–75% CFA in concrete production and testing (Pattanayak et al. 2000). In conformity with the literature, the main benefits of HVFA concrete contrasted with commonly used types are improved dimensional stability, superior durability (Blissett and Rowson 2012) and enhanced chloride permeability (Nassar, Soroushian, and Ghebrab 2013).

It must be pointed out that recent studies on geopolymers, which could be generated from aluminosilicate rich CFA by alkali-activation technology, become a promising cement alternative in civil engineering. Geopolymers have attractive physicochemical and mechanical properties that include low density, shrinkage, improved mechanical strength, micro and nanoporosity, thermal stability and chemical resistance (Blissett and Rowson 2012). All these characteristics of geopolymers increase the production of this material from CFA and application in the construction sector. Geopolymers are produced from CFA generally harden instantly at ambient temperature and have mortar compressive strength of 80–120 MPa (Kumar et al. 2007; Kumar, Kumar, and Mehrotra 2007) and concrete strengths of about 70 MPa (Djwantoro Hardjito, Sumajouw, and Vijaya Rangan n.d.) as reported in the literature. Another study on CFA-based geopolymer mortar manufacturing with different content of sand aggregate shows that material has 60 MPa compressive strength and 2.27 GPa Young's modulus with negligible change of these values up to 50 wt.% of sand aggregate content (Temuujin, van Riessen, and MacKenzie 2010).

The prevalence of CFA in the construction industry is justified with low cost and easiness in processing, and the above-mentioned new trends in materials manufacturing further extend the utilization fields, lower the expenses and adverse destructive impacts of conventional construction approaches.

Agriculture

The literature documents study on the application of CFA in soil amelioration processes as an agent for different purposes. The advantage of CFAs in the agriculture is their physical and chemical properties that allow monitoring and adjusting the pH level depending on surrounding conditions. CFA consists of chemical elements that typically present in the soil that includes macro- and micronutrients, namely Ca, K, P, Mg, Zn, Fe, S, Cu, Mn, Co, Mo and B which successively expands the potential of CFAs to be used in soil amelioration (Belviso 2017). As noted earlier in previous sections, CFAs have different chemical compositions: Class F fly ashes have a lower content of CaO, while Class C fly ash has a higher CaO amount. It is well known that most of the crops need a relevant pH level that varies from alkaline to acidic phase. For example, if the soil requires an alkaline pH level to grow crops, CFAs enriched with Ca, Na, Al and hydroxyl ions could be placed to raise the pH, which is explained by the gradual release of these ions into soil environment (Pandey and Singh 2010).

One study states increasing of pH up to 2.3 points when CFA obtained from coal containing the equivalent value of 2.43% CaCO_3 (Manoharan et al. 2010). According to Jala and Goyal (2006), the CFA enriched soil system that experienced Ca to Na exchange, kept the friability with consequent positive vegetative grown. This is especially crucial when soil fertility is low and needs additional amelioration approaches. A thorough study on the effect of CFAs for soil modification proved that both pH and biomass amount increased after using fly ash (González, Navia, and Moreno 2009). Another study states that CFA also allows controlling the amount and leaching of inorganic and organic phosphorus in soil that further expands the benefits of utilization. Innovative applications of CFAs include an ornamental plant production (Chen and Li 2006; Jayasinghe, Tokashiki, and Kitou 2010) and insecticide applications (Basu et al. 2009; Sankari and Narayanasamy 2007).

Ceramics Production

The vitrification technology, where the waste material is transformed into a new value-added raw material becomes popular in the last decade. CFA is a promising alternative material that could be used for the manufacturing of ceramics (Belviso 2017). CFA could be used for the production of glass and ceramics without adding additives and almost without pretreatment (Kumar, Kumar, and Mehrotra 2007).

In certain cases, a mixture of CFA with conventional raw materials shows enhancing of physical and mechanical properties that allow to reduce the costs and improve the properties (Kumar et al. 2007). Jing et al. (Djwantoro Hardjito, Sumajouw, and Vijaya Rangan n.d.) produced ceramic granules using CFA, clay and diatomite and used them in trickling filters. The results demonstrated that newly prepared granules have high porosity and large pore area that is appropriate for biofilters. Kockal (Temuujin, van Riessen, and MacKenzie 2010) investigated the effect of CFA addition and sintering conditions on the body of ceramic tiles, which indicated that CFA enriched ceramic tiles show comparable properties as of commercial ceramic materials. There are many studies on CFA utilization as a replacement for kaolinite in the production of ceramic cordierite (Manoharan et al. 2010; Pandey and Singh 2010), pressed ceramic tiles (Sokolar and Vodova 2011) and brick (Jayasinghe, Tokashiki, and Kitou 2010; Matsi and Keramidias 1999).

Materials Production and Recovery

CFA could be recycled for the production of different composite materials. For instance, CFA containing aluminum alloy composites obtained by stir casting method showed comparable hardness, elastic moduli and enhanced wear abrasive resistance, which allows the composites to be used for producing of pulleys, oil pans and valve covers (Rohatgi and Guo 1998). The composites gained from a combination of nickel and CFA were found to be improved wear resistant rather than simple nickel coating. The superior performance of composite is perceived to be due to the excellent bonding between CFA particles and nickel (Ramesh, Seshadri, and Iyer 1991).

Another aspect that is important when fabricating composites is the density of the material, which usually should be light and strong. In such cases, CFA could be applied to reduce the overall density of metal composites, which normally have a higher density, with cenospheres (hollow particles) that present in CFA that could add favorable properties as improved buoyancy,

insulation, reduced shrinking module and warpage values (Basu et al. 2009). CFA is also used for the fabrication of mullite. Ohtake et al. (1991), for example, heated CFA enriched with gamma-alumina up to 1400°C and produced synthetic mullite with 80% yield. The properties of sintered synthetic mullite were comparable with commercial mullite. Comparable studies carried out by Hwang, Huang, and Hein (1994) also demonstrate that high-quality mullite could be produced from CFA and alumina upon conventional sintering at 800–1000°C combined with microwave treatment. It is important to note that microwave-assisted sintering produced a dense and strong material with a crystalline mullite content (Fang et al. 1996).

Materials recovery is another field of application of CFAs. According to the literature, CFA could be a source of valuable metals as Ge, Ga, V, Ti and Al (Yao et al. 2015). These metals are valuable because they could be used for producing of diodes, infrared optics, photovoltaics and other optoelectronic devices that are in high demand. Ge, for example, could be obtained from CFA by leaching followed by separation from other elements that include precipitation, distillation, flotation, complexation, solvent extraction and other approaches (Yao et al. 2015). Ga is another metal that could be recovered from CFAs, which is 6–10 folds higher in amount than in parent coal due to enrichment after combustion (Yao et al. 2015). This metal might also be leached out by using strong acids followed by a two-step solvent extraction (Gutiérrez, Pazos, and Coca 1997). Recent studies report that CFA which is processed over arc-typed reactor might produce up to 90% of iron and ferrosilicon alloy with Si content of up to 40% (Pickles et al. 1990). Chromium could be recovered from CFA upon acidic conditions using packed bed CFA pellets with kaoline used as a binder (Iyer and Scott 2001). Silica and alumina extraction are also deemed as potential materials to be recovered from CFA. Silica is usually regained from CFA in an amorphous form, while alumina could be recovered in the solid state in the form of alpha- or gamma-alumina (Lin, Malts, and Shindler 1998).

Synthesis of Zeolites from Coal Fly Ash

One of the most attractive and desirable conversions of CFA into a cost-effective product is the synthesis of zeolitic sorbents. The main reason behind its potential utilization is the

Table 4. Common porous structures produced from CFA

Zeolite type	Formula
NaP1 zeolite	$\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$
Phillipsite	$\text{K}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot \text{H}_2\text{O}$
K-chabazite	$\text{K}_2\text{Al}_2\text{SiO}_6 \cdot \text{H}_2\text{O}$
Zeolite F Linde	$\text{KAlSiO}_4 \cdot 1.5\text{H}_2\text{O}$
Herschelite	$\text{Na}_{1.08}\text{Al}_2\text{Si}_{1.68}\text{O}_{7.44} \cdot 1.8\text{H}_2\text{O}$
Faujasite	$\text{Na}_2\text{Al}_2\text{Si}_{3.3}\text{O}_{8.8} \cdot 6.7\text{H}_2\text{O}$
Zeolite A	$\text{NaAlSi}_{1.1}\text{O}_{4.2} \cdot 2.25\text{H}_2\text{O}$
Zeolite X	$\text{NaAlSi}_{1.23}\text{O}_{4.46} \cdot 3.07\text{H}_2\text{O}$
Zeolite Y	$\text{NaAlSi}_{2.43}\text{O}_{6.86} \cdot 4.46\text{H}_2\text{O}$
Perliolite	$\text{K}_9\text{NaCaAl}_{12}\text{Si}_{24}\text{O}_{72} \cdot 15\text{H}_2\text{O}$
Analcime	$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$
Hydroxy-sodalite	$\text{Na}_{1.08}\text{Al}_2\text{Si}_{1.68}\text{O}_{7.44} \cdot 1.8\text{H}_2\text{O}$
Hydroxy-cancrinite	$\text{Na}_{14}\text{Al}_{12}\text{Si}_{13}\text{O}_{51} \cdot 6\text{H}_2\text{O}$
Kalsilite	KAlSiO_4
Tobermorite	$\text{Ca}_5(\text{OH})_2\text{Si}_6\text{O}_{16} \cdot 4\text{H}_2\text{O}$

analogy of CFA composition and physical-chemical properties to naturally occurring zeolites from volcanic materials (Xie et al. 2014). The research on synthetic zeolite production boomed after the first experiments made by Holler and Wirsching back in 1985 when scientists used CFA as a raw material for synthetic zeolite production (Brassell, Ojumu, and Petrik 2016). Since then there have been several articles published and patents filed in the world on using CFA for the production of zeolites. The elemental composition of zeolite and CFA is similar, yet the primary distinction separating those two is the structure of crystalline. CFA is normally formed of an amorphous structure, wherein a zeolite has a well-defined crystalline structure (Querol et al. 2002a).

There have been continuous studies in the search for better crystallinity, yield along with a suitable cation exchange capacity (CEC), high specific surface area, efficient pollutant removal and viability for production. Over the past years, numerous research on the synthesis of zeolites from CFA polished several commonly applied methods, like conventional alkaline hydrothermal treatment, fusion followed by hydrothermal treatment, microwave-assisted production, ultrasound-assisted synthesis and a multistep approach. Table 4 summarizes some of the research work performed on the synthesis of zeolites and other neo-morphic phases from CFA with Joint Committee Powder Diffraction Standard (JCPDS) codes for XRD diffraction (Querol et al. 2002a).

Hydrothermal Treatment

One of the widely employed methods for the production of zeolite is the hydrothermal conversion using alkaline solutions (Asokan, Saxena, and Asolekar 2005; Ramesh, Seshadri, and Iyer 1991; Rohatgi and Guo 1998). In accordance with this technique, the raw CFA is dissolved in the alkaline solution to extract aluminate and silicate constituents and then go through raised temperature treatment to produce zeolitic crystals. There are four main steps during zeolitization of CFA: first, a dissolution of Si and Al, then a condensation followed by nucleation and crystallization (Bukhari et al. 2015). The ratio of aluminate or silicate is normally varied to obtain a desired type of zeolite. Depending on reaction conditions as temperature, pressure, reaction time, Si/Al ratio, alkaline solution, pH and seeding of initial CFA this method allows producing different synthetic zeolites, such as zeolite X, zeolite P (Tauanov et al. 2018a; Wdowin et al. 2014a), analcime (Tauanov et al. 2018b; Wang 2003), chabazite or hydroxyl-sodalite (Franus, Wdowin, and Franus 2014; Luo, Zhang, and Yang 2016). Murayama, Yamamoto, and Shibata (2002) examined the effect of alkali solution nature on the mechanism of zeolite formation by varying the activation agent (NaOH, KOH, Na₂CO₃, NaOH/KOH, Na₂CO₃/KOH). It was determined that sodium ions in alkali solutions improved the zeolite synthesis, while the co-existence of potassium with sodium ions reduced the yield of production.

It is important to note that there are some disadvantages of conventional hydrothermal treatment, such as the partial dissolution of Si derived from CFA and a lower rate of dissolution of Al as compared with Si, which is because of low solubility and inertness of mullite containing in CFAs (Belviso 2017). These factors slightly modify using this approach since it might not completely dissolve the Si and Al content present in raw CFA, therefore producing zeolites with relatively low yield.

Fusion-assisted Hydrothermal Treatment

In the search for changing of yield and crystallinity of zeolites obtained from CFAs, Shigemoto, Hayashi, and Miyaura (1993) suggested applying a fusion step before conventional hydrothermal treatment. The samples of CFA with sodium hydroxide (NaOH) were fused at 550°C prior to conventional raised temperature treatment without stirring. This novel approach enabled to produce synthetic zeolite Na-X with a high conversion rate, CEC and improved crystallinity. A similar synthetic route was examined by Berggaut and Singer (1996), where authors fused a NaOH and CFA at slightly raised fusion temperature 170–180°C to produce aluminosilicate gel, which then followed by hydrothermal treatment at 100°C to yield a synthetic Na-P zeolite without aging and Na-X zeolite after 12 hours of aging. Another research group also used the pre-fusion step before hydrothermal treatment of CFA to produce zeolite P and faujasite (Chang and Shih 1998). The authors noted that the fusion-assisted method improved the dissolution of Si and Al content from parent CFA, hence enhancing the yield of zeolite synthesis.

The literature commonly recommends that a pre-fusion step improves the traditionally used hydrothermal treatment that has been confirmed with numerous studies. The major disadvantage could be the raised temperature treatment (500–600°C) that adds up the costs of the method and has to be examined before large-scale manufacturing.

Sonication Approach

Application of ultrasound energy is another novel approach in the synthesis of zeolites from CFA. The main drawback of this energy is that it allows to speed up the dissolution of Si and Al content in CFA, therefore promoting a faster poly-condensation process and transition of semi-crystalline phase into crystalline phase (Belviso et al. 2011; Bukhari et al. 2015; Bukhari, Rohani, and Kazemian 2016). There are numerous studies, where authors used an ultrasonic treatment on the synthesis of zeolites from CFA. More recently, Woolard, Strong, and Erasmus (2002) produced a synthetic hydroxyl-sodalite using CFA, while Musyoka, Petrik, and Hums (2011) synthesized a zeolite-A through the combination of ultrasound and microwave energies. The latter observed that a sonication for 40 minutes before conventional hydrothermal treatment improved the crystal formation of zeolite and significantly reduced the duration of the reaction. Wang and Zhu (2005) used ultrasound energy along with conventional hydrothermal incubation of CFA to synthesize zeolite. As stated in their research findings, the surface area and adsorptive properties were relatively higher and the treatment time was considerably reduced in comparison with a synthesis that does not involve sonication.

It is apparent from the literature that ultrasonic energy promotes the crystal growth and lowers the necessary synthesis temperature, which successively reduces the costs of production. Furthermore, there is a potential to increase the crystallinity of zeolites via sonication as it enables to saturate the crystalline phase during the nucleation stage.

Microwave-assisted Synthesis

Another method to improve the conventional hydrothermal treatment is the application of microwave for a short time during synthesis. For example, Querol et al. (1997) tried to use

both conventional and microwave irradiation and were able to synthesize zeolite-A in a comparatively faster mode. As stated in the results, the yield of zeolite was similar, however, the microwave-assisted method enabled to reduce the time necessary for activation step from a typical 24–48 hours applied in the traditional approach to 0.5 hours. Likewise, another group of scientists obtained zeolite Na-P1 from CFA in a microwave-irradiated closed-oven that also enabled to optimize the synthetic route (Andrés et al. 1999). Usually, the zeolite formation using this method could be separated into three phases: firstly, the dissolution of Si and Al content in CFA; secondly, the improvement of intermediate aluminosilicate gel; and lastly, the conversion of gel into a zeolite and growth of zeolitic crystals (Inada et al. 2005).

Generally, it could be constituted that the main drawbacks of microwave-assisted approach are the facilitation of reaction activation time and the possibility to produce comparatively smaller zeolite crystals. Apart from this, the reduction of total synthesis time enables cutting the costs and might be economically feasible for large-scale manufacturing of CFA-derived zeolites.

Applications of Coal Fly Ash-derived Zeolites

Heavy Metals Removal Manufacturing

One of the major application fields of synthetic zeolites derived from CFA is remediation of heavy metals from water. Penilla, Bustos, and Elizalde (2006), for example, produced a synthetic zeolite from a Spanish low-lime containing CFA of Class F applying conventional hydrothermal treatment with NaOH as an activation agent. The results proved that the synthetic zeolites P and analcime of GIS framework were the main species of production, which allowed removing all tested metals (Cs, Pb, Cd and Cr) from mine waters to some extent. Another study investigated that hydrothermal transformation of CFA into zeolites could also be used for the removal of Hg^{2+} and Pb^{2+} cations (Somerset, Petrik, and Iwuoha 2008). According to the research findings, CFA-derived zeolite was able to remove 30% and 95% of mercury and lead from water, respectively.

Woolard, Petrus, and Van der Horst (2000) performed a comparative examination of two types of synthetic zeolites derived from CFA. The authors produced synthetic zeolites Na-P1 and hydroxy-sodalite, then tested both zeolites for retention of Pb^{2+} from the water. The results showed that synthetic zeolite Na-P1 is more effective in removing lead ions than hydroxy-sodalite. Similar studies on removal of Pb^{2+} from water using CFA-based zeolites could be found elsewhere (Golbad, Khoshnoud, and Abu-Zahra 2017; Lee, Cheon, and Kam 2003; Scott et al. 2001). Some research works include a pilot-scale production of synthetic zeolites from CFA that was used for wastewater treatment from heavy metals, such as Ni^{2+} , Cd^{2+} , Zn^{2+} , Pb^{2+} , Cu^{2+} and Cr^{3+} (Koukouzas et al. 2010; Wdowin et al. 2014a). The results of the pilot-scale testing demonstrated that the CEC of synthetic zeolites differs from 68 to 260 meq per 100 g of sample.

Inorganic and Organic Pollutants Removal

Some research groups used CFA-derived zeolites to remove inorganic pollutants. Zhang et al. (Querol et al. 1997), for instance, applied synthetic faujasite to remediate ammonium

from water solutions. They determined that adsorbent is effective and demonstrate allowable kinetics and thermodynamics. Another study observed a simultaneous removal of ammonium and phosphate by applying synthetic zeolites obtained by fusion method and pre-saturated with cations, such as Al^{3+} , Ca^{2+} and Fe^{3+} (Wu et al. 2006). The results revealed that the removal efficiency of inorganic pollutants has been improved by the enrichment of cations. In the same way, Zhang et al. (2007) examined that ammonium and phosphate removal utilizing synthetic zeolite treated with sulfuric acid enhances the adsorption efficiency.

CFA-derived synthetic zeolites have also been studied for remediation of organic pollutants. Bandura et al. (2016) explored the removal of aromatic hydrocarbons, such as benzene, toluene and xylene, so-called as BTX, by means of synthetic Na-X zeolite. According to authors the improved adsorption capacity of zeolites is related to the standard framework of faujasites that normally have wide channels appropriate for BTX pollutants. The same group has explored another synthetic zeolite Na-P1, which removed 99% of xylene, 77% of toluene and 35% of benzene (Bandura and Skaskiv 2017). These results led to the assumption that the adsorption capacity of BTX is inverse to the degree of hydrophobicity and molecular weight of pollutants. Synthetic zeolites functionalized with alkyltrimethoxysilane groups have also found application in oil spill cleanup (Sakthivel et al. 2013). The alkyl chains enhanced the floating effect in water owing to their hydrophobicity that conversely enabled adsorbing the spilled oil from the water surface.

Molecular Sieves

The porous structure of synthetic zeolites facilitates the capture of various pollutant gasses, namely CO_2 , SO_2 , volatilized Hg and NH_3 . Srinivasan and Grutzeck (1999) obtained synthetic zeolites X, Y and Na-P1 using a Class F CFA. They observed the produced zeolites for the capture of SO_2 from a stack gas that initially contained 2000 mg/L of SO_2 . The results showed that the optimized CFA-based synthetic zeolite demonstrated an adsorption capacity of 6–7 mg SO_2 per 1 g of adsorbent. Likewise, Querol et al. (2002b) examined the capture of CO_2 and SO_2 by using CFA-derived zeolites. They explored that the adsorption

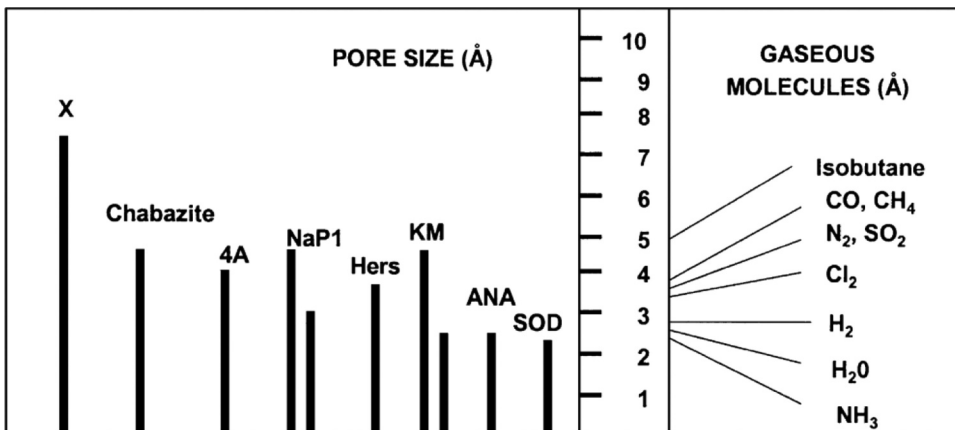


Figure 7. The pore size of synthetic zeolites (in Å) and molecular sizes of gases.

capacity of produced zeolites reached 74 mg of CO₂ per and 297 mg SO₂ per 1 g of adsorbent. The group also investigated the adsorption of SO₂ and NH₃ utilizing synthetic sodalite and analcime (Querol et al. 2002a). The maximum adsorption capacities of these two gases were as low as 1–6 mg per 1 g of adsorbent, which was mainly because of the small or tight size of channels (about 2.3 Å) rather than necessary minimum diameter. Particularly, the adsorption capacity of adsorbents used for flue gas purification and separation relies on the size of channels and the molecular size of targeted species. Figure 7 shows the size of pores of some widely known synthetic zeolites derived from CFA.

Another study carried out to observe the adsorption of CO₂ using CFA-based zeolite reports adsorption of 52 mg of CO₂ per 1 g of adsorbent (Majchrzak-Kucęba and Nowak 2005). Synthetic zeolites could be used for adsorption of hazardous metals like Hg from flue gas. Wdowin et al. (2015, 2014b) examined two different synthetic zeolites derived from CFA impregnated with Ag NPs to capture gaseous Hg from the flue gas stream. According to the results, the impregnation of silver into the zeolite matrix significantly improved the adsorption capacity with Hg breakthrough varying between 15% and 40%. The authors also stated that Hg adsorption from a flue gas stream relies on sorbent grain (powder or granulated), the flow rate of gas, temperature and contact time, which requires an optimization study.

Catalysis

An alternative application field of synthetic zeolites produced from CFA is catalysis, especially zeolite as a substrate for catalysts. A recent study conducted by Fotovat, Kazemini, and Kazemian (2009) determined that Co NPs impregnated synthetic zeolites could be successfully applied in Fischer-Tropsch reaction. The synthesis reaction carried out with pristine zeolite and CFA-based zeolite loaded with Co NPs showed a comparable activity. Ríos et al. (2012) reviewed the use of synthetic Na-X zeolite modified with ammonium and hydrogen ions in catalytic cracking reactions used for a petroleum refinery. In the same way, Yamamoto et al. (2007) noted that an ion exchange of zeolite structure with dissolved cations could improve the performance of catalysts. The author characterizes those ion-exchanged synthetic zeolites with transition metal ions have been used as catalysts in several organic reactions. For instance, the synthetic zeolites were utilized in polypropylene pyrolysis that was mentioned in research works conducted by Nam et al. (2004) and Kim, Kim, and Chung (2003).

The literature noted various main application fields of synthetic zeolites produced from CFAs. The advantages of synthetic zeolites obtained from CFAs are the low cost and diversity, which could allow to produce different types of zeolites depending on target pollutant and contamination conditions, such as pH, temperature and dosage. Some of these investigations went beyond the lab-scale and reached a pilot-scale production, testing and feasibility studies. It is apparent from the literature that the main interest of researchers is the utilization of CFA-based zeolites to ensnare and remove heavy metals from gaseous and aqueous media, which has already reached some degree of feasibility.

Conclusions

The review paper provides an overview on classification and composition of both coal and coal fly ash derived from the production of energy from power plants, the possible

and currently employed sectors of the utilization of coal fly ash. The section on synthetic zeolites derived from CFA describes how CFA could be converted into zeolites and provides a detailed overview on the possible ways of application. It is clear from the review that the chemical composition of CFA varies depending on location, burning conditions and origin of the parent coal. Moreover, the utilization fields of both CFA and synthetic zeolites show that some of the sectors are still reluctant to broadly employ CFA and zeolites. There are certain important and emerging fields of application as the recovery of elements, separation and extraction of valuable metals and cenospheres. This in turn requires further examination, laboratory and large-scale studies, and analysis of feasibility.

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