

# Synthesis of merlinoite from Chinese coal fly ashes and its potential utilization as slow release K-fertilizer

Jing Li <sup>a,\*</sup>, Xinguo Zhuang <sup>a</sup>, Oriol Font <sup>b</sup>, Natalia Moreno <sup>b</sup>, V. Ramon Vallejo <sup>c</sup>, Xavier Querol <sup>b</sup>, Aurelio Tobias <sup>b</sup>

<sup>a</sup> Key Laboratory of Tectonics and Petroleum Resources, China University of Geosciences, Ministry of Education, Wuhan 430074, China <sup>b</sup> Institute of Environmental Assessment and Water Research, CSIC, C/Jordi Girona 18-26, Barcelona 08034, Spain <sup>c</sup> Department of Plant Biology, Faculty of Biology, University of Barcelona, Av. Diagonal, 643, Barcelona 08028, Spain

\* Corresponding author. Tel.: +86 13697348536.

E-mail addresses: lijing02003140@163.com, crystalj06@163.com (J. Li).

## 1. Introduction

China is the country with the largest coal consumption, accounting for 49% of global coal consumption [1]. In the near future, Xinjiang will be the largest and most important coal-producing and consuming province in Northwest China because of its enormous coal reserves and high coal quality [2]. Enormous coal consumption in PCC power plants in Xinjiang will promote economic development, but on the other hand, it will generate large amounts of coal combustion by-products (CCPs), gaseous pollutants, and particulate matter emitted to the atmosphere that may cause serious environmental problems [3]. Meanwhile, more and more open pit coalmines are being and will increasingly be explored in Xinjiang, which gives rise to large areas of degraded soil in the opencast coal mine areas. Consequently, from environmental and economic point of view, the need for emission reduction and for research on potential high value-added applications for large-amount fly ash generated from the PCC power plants in Xinjiang is of high environmental and economic relevance. Reclamation of large-area opencast coal mine areas after mining is also necessary to recover the ecological and landscape values of the exploited areas. Currently, fly ash produced in China has mainly been used in some applications with low economic benefits, e.g. in brick manufacture and road or dam construction [4–6]. Nevertheless, large amounts of Chinese fly ashes are still dumped into ponds or piled on land [7,8]. Synthesis of zeolites from coal fly ash is one of the promising applications of fly ashes with high added value [9]. Since the initial studies of zeolite synthesis from fly ash by Höller and Wirsching

**Table 1**  
Mineralogical, and major and trace elements concentrations of the studied fly ashes.

%	WEI		HONG	%	WEI		HONG
	WAc	Waf			WAc	Waf	
Quartz	9.6	4.3	3.7	Calcite	<dl	<dl	<dl
Mullite	7.8	3.2	3	Lime	5.1	0.4	1.5
Hematite	2.4	1.2	1.6	Dolomite	0.8	0.4	0.5
Magnetite	<dl	<dl	0.4	Anorthite	0.5	<dl	<dl
Anhydrite	1.6	0.3	0.4	Glass	73	90	89
%							
SiO <sub>2</sub>	49	58	53	SO <sub>3</sub>	1.6	0.6	0.7
Al <sub>2</sub> O <sub>3</sub>	20	23	20	MgO	2.5	2	2.8
CaO	7.1	3.2	9	TiO <sub>2</sub>	0.9	1	0.8
K <sub>2</sub> O	1.7	2.4	1.9	P <sub>2</sub> O <sub>5</sub>	0.4	0.3	0.2
Na <sub>2</sub> O	0.9	2.4	1.3	MnO	0.05	0.06	0.09
Fe <sub>2</sub> O <sub>3</sub>	4.9	5.5	7.4	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	2.4	2.5	2.7
mg/kg							
Li	38	67	44	Ba	1076	1290	1475
Be	4	5	5	La	48	37	42
B	46	122	182	Pr	12	10	11
Sc	21	23	20	Nd	53	47	49
V	153	144	185	Sm	11	10	11
Cr	68	65	81	Eu	2	2	2
Co	16	35	25	Gd	11	9	10
Ni	35	76	58	Tb	1	1	1
Cu	88	113	100	Dy	8	7	7
Zn	90	201	131	Ho	1	1	2
Ga	26	44	27	Er	4	4	4
Ge	2	3	4	Yb	4	5	5
As	17	28	37	Lu	<0.1	1	1
Se	2	3	5	Hf	4	6	4
Rb	77	95	80	W	9	6	7
Sr	957	808	1044	Tl	<0.1	1	1
Nb	53	53	47	Pb	36	47	40
Mo	6	9	25	Th	19	16	22
Cd	<0.1	1	<0.1	U	7	4	25
Sn	4	5	4	Hg	0.15	0.05	0.19
Sb	3	3	3	Cl	444	417	595
Cs	9	10	8	F	670	691	462

Abbreviation: <dl, under detected limit of XRD (~<1%).

(1985) [10], various methods and patents have been proposed, improved and applied by many authors to synthesize different types of zeolites [11–34], among which direct conversion is a common synthesis method [19,22–25]. Due to the peculiar structural properties of zeolites, they have a wide range of industrial applications, such as ion exchange, and gas and water adsorption, among others [35,36]. The potential industrial application of the zeolitic materials obtained depends on zeolite type. Since most of the Na-zeolites have a higher CEC most of the studies and field applications reported above have been performed with Na-zeolites. The high CEC and large pore size, of Na-zeolites (e.g. NaP1, X, and A zeolite), than K-zeolites promoted their application for polluted soils and waters remediation [22,24,26,33,37,38]; although, the use of natural zeolites (clinoptinolite) in agriculture and for soil remediation started from the 80 s, studies on K-zeolites synthesized from fly ash and its fertilizer efficiency are scarce [39]. The present study focuses on the synthesis of merlinoite by KOH direct conversion, using fly ashes from Xinjiang PCC power plants, being subsequently applied to determine their potential for a novel use: as an efficient slow release K-fertilizer both for potential application on degraded opencast mine reclamation and for agricultural use in conventional high-nutrient demanding crops (such as sunflower). The synthesis of zeolites from a potentially hazardous waste (fly ash) and its use in the restoration of degraded lands is a challenge for the valuation of this residue, increasing their economic value while reducing environmental and economic costs of landfill.

## 2. Materials and methods

### 2.1. Sampling

Three fly ash samples (HA, Waf, and WAc) were simultaneously collected from the electrostatic precipitators (ESP) of two PCC power plants fed with Jurassic subbituminous coals in Xinjiang Province, Northwest China (Fig. 1). HA was collected from the 800 MWh HONG power plant. The fine and coarse fraction of the fly ash (Waf and WAc) were collected from different rows of the ESP in the 250 MWh WEI power plant. Mineralogical and geochemical composition of these fly ashes is summarized in Table 1. Detailed information on characteristics of these fly ashes is reported elsewhere [40].

### 2.2. Synthesis experiments

Zeolite synthesis experiments were processed using three collected fly ashes (HA, Waf, and WAc), which were first mixed with different doses of KOH solutions of different concentrations in 45 ml 4744 Parr digestion bombs with Teflon reactors in closed systems, and then activated at different activation temperature and time in a Memmert laboratory oven (Table 2). The synthesized zeolitic products were filtered through Whatman filter paper and repeatedly washed with MilliQ water until pH 10–11. The filter residues were dried at 60 °C and analyzed by Powder X-Ray Diffraction (XRD). The XRD patterns were collected on a Bruker D8 Advance diffractometer with monochromatic Cu K $\alpha$ 1,2

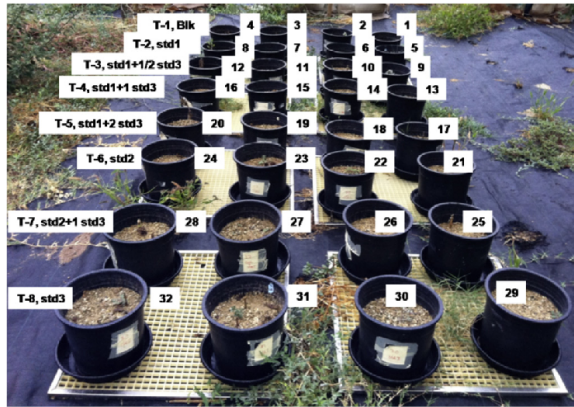


**Table 3**

Sunflower growing treatments with different doses of fertilizers.

Treatments	Pots	Reference	Doses		
			K-zeolite	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	Struvite
T-1	1–4	Blank	–	–	–
T-2	5–8	std1	–	10 g N/m <sup>2</sup>	–
T-3	9–12	1/2K + std1	10 g K/m <sup>2</sup>	10 g N/m <sup>2</sup>	–
T-4	13–16	1K + std1	20 g K/m <sup>2</sup>	10 g N/m <sup>2</sup>	–
T-5	17–20	2K + std1	40 g K/m <sup>2</sup>	10 g N/m <sup>2</sup>	–
T-6	21–24	std2	–	4.5 g N/m <sup>2</sup>	10 g P/m <sup>2</sup>
T-7	25–28	1K + std2	20 g K/m <sup>2</sup>	4.5 g N/m <sup>2</sup>	10 g P/m <sup>2</sup>
T-8	29–32	std3 (1 K)	20 g K/m <sup>2</sup>	–	–

Abbreviation: T, treatment; std, standard.

**Fig. 2.** The sunflower growing treatments carried out with different doses of nutrients. Abbreviations: Blk, blank; std, standard; T, treatment.

most of the KOH-activation conditions tested (Fig. 3, the XRD intensities of the synthetic products are provided in Table A1, Appendix: supplementary materials). Traces of tobermorite ( $\text{Ca}_5(\text{OH})_2\text{Si}_6\text{O}_{16}\cdot 4\text{H}_2\text{O}$ ), perialite ( $\text{K}_9\text{NaCaAl}_{12}\text{Si}_{24}\text{O}_{72}\cdot 15\text{H}_2\text{O}$ ), and K-aluminum silicate ( $\text{KAlSiO}_4$ ) of much lower industrial interest than merlinoite were also crystallized in specific synthesis conditions. Unconverted quartz, mullite, and hematite from the relict fly ash were also detected by XRD in zeolitic products synthesized at low KOH molarities and temperatures. Similar to natural merlinoite (IZA, 2005) [42], morphology of the synthesized merlinoite observed by SEM-EDX is pseudotetragonal prisms, forming radiating groups or fibrous spheroidal aggregates (Fig. 3). Different fly ashes presented different synthesis yields under the same experimental conditions. HA showed relatively low synthesis efficiency under the same activation conditions. Higher merlinoite synthesis yields were obtained from Waf and WAc, and perialite is more likely synthesized from Waf (Fig. 4). Minor contents of perialite were also crystallized from HA and WAc when activated under at least two of the following conditions (Table A1): (a) high KOH concentration ( $\geq 5$  M); (b) high activation temperature ( $\geq 200^\circ\text{C}$ ); (c) long activation time ( $\geq 12$  h); (d) high KOH/fly ash ratio ( $\geq 5$  l/kg). That is, synthesis results also depend highly on synthesis conditions: activation temperature and time, KOH concentration, and KOH/fly ash ratio (Figs. 5–8). Increasing activation temperature increases the conversion efficiency, which is evidenced by the reduction of quartz, mullite and other residual phases from fly ashes with the increase of temperature (Table A1). On the other hand, higher activation temperature ( $200^\circ\text{C}$ ) gave rise to the crystallization of tobermorite and perialite with low actual CEC (Fig. 5). Prolonging activation time, the amounts of the unconverted quartz, mullite and other residual phases from the fly ashes decreased, indicating that increasing activation time also promotes zeolite synthesis efficiency (Fig. 6). However, longer activation time ( $\geq 12$  h) favored the synthesis of tobermorite and perialite with very low industrial interest (Fig. 6). Increasing KOH concentration also gave rise to reduction of quartz, mullite phases from fly ashes (Table A1), indicating that higher KOH concentration gives rise to higher synthesis efficiency (Fig. 7). It is worth noting that relatively high KOH concentration ( $\geq 3$  M) was needed to obtain high synthesis yields, probably due to the lower conversion efficiency of KOH solution than NaOH solution [22]. Proportion of synthetic merlinoite was reduced with the increase of KOH solution/fly ash ratio from 2 to 5 l/kg (Fig. 8). Instead higher KOH solution/fly ash ratio favors the synthesis of more perialite with low industrial interest (Fig. 8). From economic point of view, the increase of activation temperature, time, KOH concentration or KOH solution/fly ash ratio will increase the production cost. Taking into account both synthesis results and economic cost, the optimal synthesis efficiency for obtaining a high quality merlinoite product from HA could be obtained with a KOH solution/fly ash ratio of 2 l/kg at 3 M KOH solution,  $200^\circ\text{C}$  for 8 h, or at 5 M KOH solution,  $150^\circ\text{C}$  for 8 h. As for WAc, the optimal merlinoite synthesis condition is with KOH/fly

The dried sunflowers were crushed, milled, and acid-digested following the same procedure reported above [41]. Major and trace element concentrations in the sunflowers were determined by ICP-AES and ICP-MS, respectively. Nitrogen contents in sunflowers were determined by conventional combustion-reduction elemental process by thermal conductivity in a Thermo Finnigan flash 1112 analyser. One-factor ANOVA was applied to test the statistical significance of weight and macronutrients variability among treatments. Linear regression was performed to determine the relationships among weight and macronutrient content with the following groups of treatments: Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O addition (T2), struvite addition (T6), merlinoite addition (T8), struvite + merlinoite (T7), and merlinoite + Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (T3, T4, T5), with respect to the Blank (T1), based on total dry weight and weight-normalized concentrations of the sunflowers in 30 experiments. Results for merlinoite + Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O group indicate the variability with respect to the Blank per unit of merlinoite dose. Analyses were done using Stata statistical software, release 12 (StataCorp, TX, College Station, 2012).

### 3. Results and discussion

#### 3.1. Zeolite synthesis results

A high quality merlinoite ( $\text{K}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}$ ) product was synthesized under

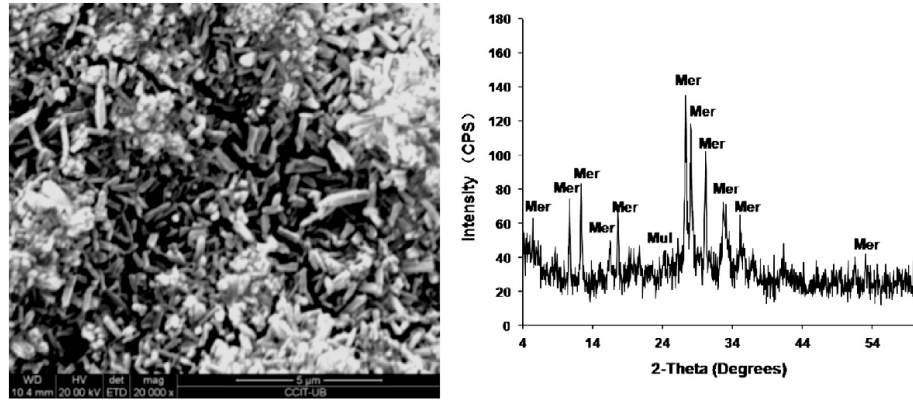


Fig. 3. Morphology and XRD spectra of synthesized merlinoite from the studied fly ashes by KOH direct conversion. Abbreviations: Mer, merlinoite; Mul, mullite.

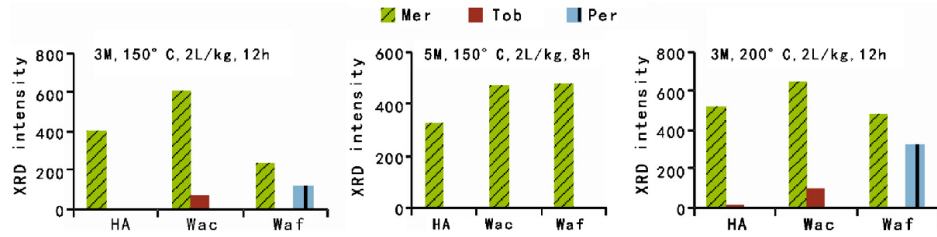


Fig. 4. Synthesized results of different fly ashes under the same condition through KOH direct conversion. Abbreviations: Mer, merlinoite; Tob, tobermorite; Per, perillite.

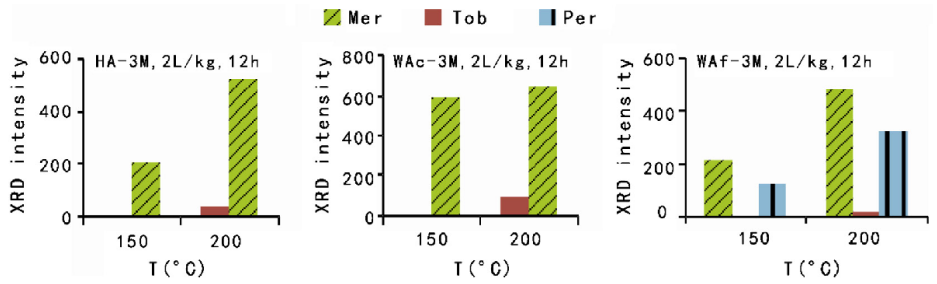


Fig. 5. Synthesized results by KOH direct conversion under different activation temperature. Abbreviations: Mer, merlinoite; Tob, tobermorite; Per, perillite.

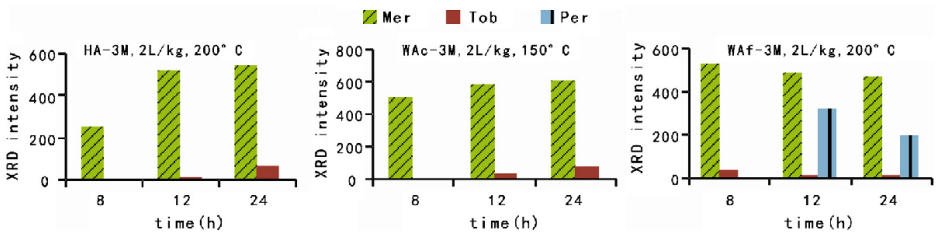


Fig. 6. Synthesized results by KOH direct conversion under different activation time. Abbreviations: Mer, merlinoite; Tob, tobermorite; Per, perillite.

ash ratio of 2 l/kg at 3 M KOH solution and 150 °C for 8 h. With respect to Waf, the highest amounts of merlinoite are synthesized when activated with a KOH solution/fly ash ratio of 2 l/kg at 5 M KOH solution and 150 °C for 8 h, or at 3 M KOH solution and 200 °C for 8 h.

### 3.2. Cation exchange capacity

CECs of the merlinoite products synthesized under selected con- ditions are given in Table 4. The synthetic merlinoites reached CECs ranging from 60 to 340 cmol kg<sup>-1</sup> (Table 4).

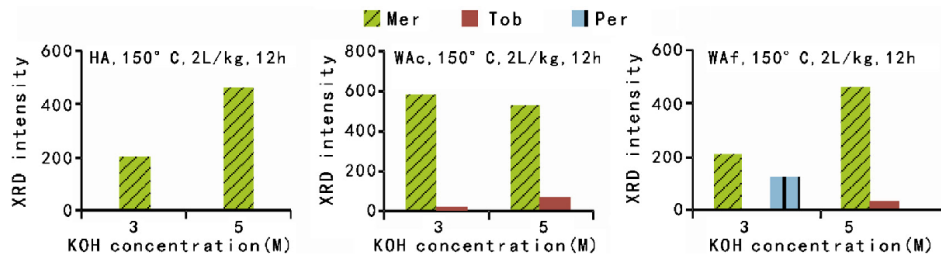


Fig. 7. Synthesized results by KOH direct conversion under different KOH concentration. Abbreviations: Mer, merlinoite; Tob, tobermorite; Per, perlialite.

**Table 4**  
CEC of the synthetic zeolite products by KOH direct conversion compared to the NaP1-IQE and A-IQE zeolite reference.

	Conc (M)	T (°C)	T (h)	Ratio (l/kg)	CEC (cmol kg <sup>-1</sup> )
NaP1-IQE	–	–	–	–	490
A-IQE	–	–	–	–	540
WAc	5	150	2	24	190
Waf	5	150	2	24	220
HA	5	150	2	24	160
WAc	5	150	5	24	340
HA	5	150	5	24	310
Waf	5	150	5	24	290
WAc	5	150	2	8	130
Waf	5	150	2	8	160
HA	5	150	2	8	170
WAc	3	150	2	24	90
WAc	3	150	2	8	90
WAc	3	150	2	12	100
WAc	5	150	2	12	60
Waf	5	150	2	12	120
HA	5	150	2	12	100
WAc	5	150	2	8	100
Waf	3	200	2	8	130
HA	3	200	2	8	190
Waf	5	150	2	8	160
pilot scale					

The merlinoite products synthesized from WAc, Waf and HA at relatively lower economic cost with shorter activation time (8 h), present CEC of 130, 160 and 170 cmol kg<sup>-1</sup>, respectively (Table 4), which are relatively lower compared to that of the natural clinoptilolite marketed as an ion exchanger (220 cmol kg<sup>-1</sup>) [35,43], but still higher compared to the similar synthetic merlinoite products used for K-fertilizer (50–60 cmol kg<sup>-1</sup>) [39]. Relatively lower CECs of the synthetic merlinoite products are ascribed to the partial conversion of fly ash to zeolite products.

### 3.3. Merlinoite synthesis at pilot plant

The synthesis of merlinoite using pilot-scale reactor was carried out under the optimal conditions for synthesizing merlinoite from Waf (5 M KOH, 150 °C, 2 l/kg and 8 h) to obtain large amounts of merlinoite for fertilizer application test. It presents a CEC of 160 cmol kg<sup>-1</sup> (Table 4), same as that obtained using lab-scale digestion bomb under the same synthesis conditions, indicating the repeatability and viability of the synthesis experiments when up-scaling the process. CEC of 160 cmol kg<sup>-1</sup> results in an exchangeable K of 62.5 g/kg of merlinoite, corresponding to 60% of K available as fertilizer for KG of merlinoite. This accounts for a 60% merlinoite purity in the zeolitic products obtained, and 40% unconverted material. Consequently, the yield of merlinoite is around 600 g for 1 kg of ash used, and 1071 g/kg of KOH used, viz. 1538 g/kg of K used. This purity is relatively high taking into account the conversion method applied (direct hydrothermal activation) which is the most easy and low cost method for the synthesis of zeolites from fly ash. Washed and acidified merlinoite products are characterized by a K content of 12–14% and low

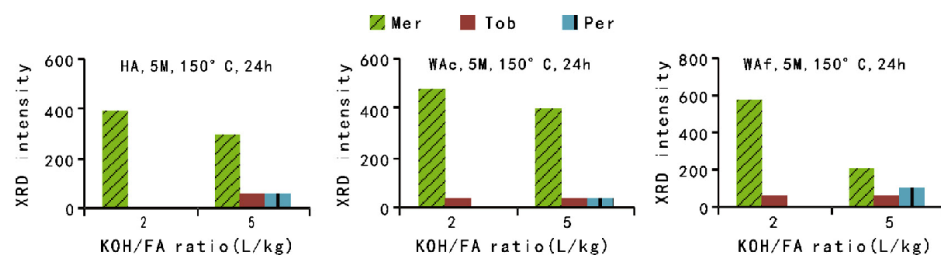


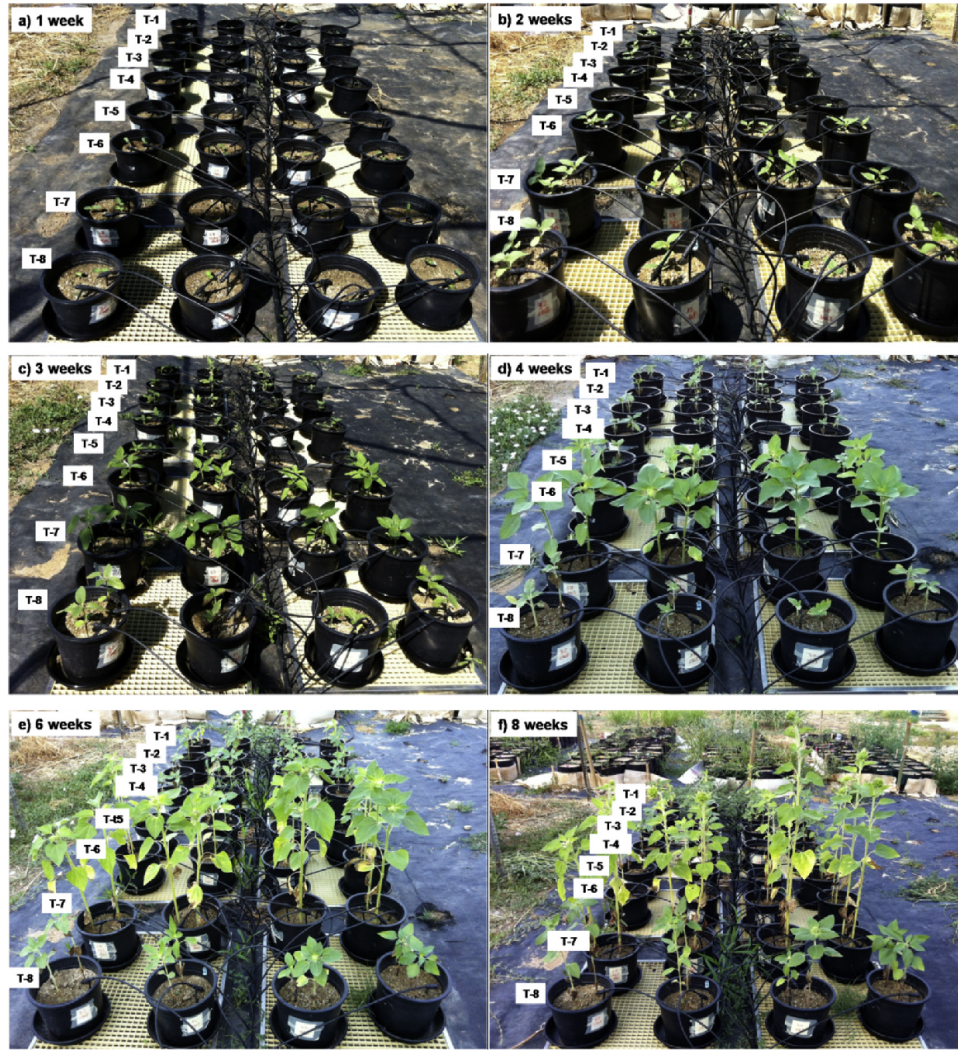
Fig. 8. Synthesized results by KOH direct conversion under different KOH/fly ash ratios. Abbreviations: Mer, merlinoite; Tob, tobermorite; Per, perlialite; FA, fly ash.

concentrations of trace elements with the exception of Ba and Sr (Table 5). The leachate of washed pilot-plant merlinoite show an alkaline pH (9.2), high K release (2623 mg/kg) and low leachable levels for most elements (Table 5). With the exception of B (2.3 mg/kg), most trace elements shows extractable contents < 1 mg/kg. The acidification of merlinoite decreases alkaline pH to slightly acidic (5.3), and increases K release to 17,793 mg/kg (Table 5). The slightly acidic pH also modify the leachability of a number of elements, increasing the extractable content of B, Co, Ni, Rb, Se, Y, Ba, Zn and REEs (by a factors of 1.3–12, and up to 133 for Sr) and decreasing that of As, Cr, Mo, Sc and V (by factors of 2–49). The leachable contents from acidified merlinoite are still low, falling within the range of inert landfill material [44] and suitable to be used as fertilizer.

### 3.4. Use of merlinoite as slow release K-fertilizer

Images of sunflower growth in the different treatments after different growing time (see methodology) are shown in Fig. 9. As shown in Table 5 and Table A2 (Appendix: supplementary materials), the leachability of the merlinoite, soil and struvite are very low, consequently the potential uptake by sunflowers does not include undesirable elements, and no toxic effects of pollutants





**Fig. 9.** The growth photos of sunflowers after different sowing time. *Abbreviation:* T, treatment.

were observed in the fertilization experiment (neither in plant growth nor in visual symptoms of toxicity, Fig. 9). After one week sowing, all sunflower seeds started to germinate (Fig. 9a), except those in pot 14 of T-4 and pot 18 of T-5 (probably due to a problem of seeds). After two-week sowing, all sunflowers grew similar (Fig. 9b), probably indicating that the nutrients used did not show obvious effects for sunflower growth at the early growth stage. Three weeks later, sunflowers grown from different treatments started to present different growth rate (Fig. 9c). The different growth rate is emphasized as sowing progresses (from 4 to 8 weeks). Sunflowers with full fertilization in T-7, showed the best growing efficiency, which grew much taller, stronger and greener compared to those in other treatments along the sowing process (Fig. 9c–f). In T-6, sunflowers with a recommended dose of struvite presented the second highest growth but generally they were not so strong and leaves of them were much yellower than those in T-7. In T-8, sunflowers with the addition of only merlinoite grew very slow, similar to those grown in the other treatments (T-1–T-5, Fig. 9d) but the leaves of them were green (Fig. 9e). Furthermore, with the addition of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  or the mixture of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and merlinoite, the sunflowers in T-2, 3, 4, and 5 grew to similar height as those grown in soil only (T-1), but the leaves of them were much greener than those in T-1 (Fig. 9e). After eight weeks, sunflowers grown in T-6 and 7 started to bloom (Fig. 9f). Sunflowers in T-7 grew to up to 1 m, much stronger than those in T-6 and other treatments (Fig. 9f). With the addition of merlinoite (T-8), or  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (T-2), or mixture of both (T-3, 4 and 5), the sunflowers grew very slowly, only slightly taller than two weeks before (Fig. 9e and f), but the leaves of them were green compared to those grown only in soil (T-1). The weight of sunflowers after cutting and drying, the moisture as well as the macro nutrient contents (K, P, N, Ca, and Mg) in sun- flowers of each treatment are listed in Table 6 (the corresponding values of sunflowers in each pot are provided in Table A3, Appendix: supplementary materials). Sunflowers in all treatments present moisture contents ranging from 74% to 80%. With the addition of merlinoite and struvite,

**Table 5**

Major and trace element concentrations and leachable concentrations in the merlinoite synthesized at pilot plant.

Bulk content	Washed	Acidified	Leaching	Washed	Acidified
			pH	9.2	5.3
			K ( $\mu\text{S}/\text{cm}$ )	830	9524
			mg/kg		
%					
Al <sub>2</sub> O <sub>3</sub>	17.7	16.2	Al	33	<dl
CaO	2.9	2.4	Ca	19	7684
Fe <sub>2</sub> O <sub>3</sub>	4.8	4.4	Fe	7.0	<dl
K <sub>2</sub> O	14.4	12.5	K	2623	17,793
MgO	1.3	1.2	Mg	<dl	615
Na <sub>2</sub> O	0.2	0.1	Na	186	634
P <sub>2</sub> O <sub>5</sub>	<dl	<dl	P	<dl	<dl
SO <sub>3</sub>	0.2	<dl	S	<dl	<dl
SiO <sub>2</sub>	na	na	Si	771	285
mg/kg					
Li	47.9	41.2	Li	0.4	10.9
Be	3.0	2.5	Be	<dl	<dl
B	38.3	28.8	B	2.3	5.9
Sc	22.3	19.1	Sc	0.2	0.1
Ti	4823	4324	Ti	1.0	0.03
V	25.8	21.0	V	0.4	0.01
Cr	70.6	57.9	Cr	0.3	0.05
Mn	431	367	Mn	0.1	12.3
Co	22.2	18.9	Co	<dl	0.2
Ni	39.6	34.2	Ni	<dl	0.5
Cu	66.4	57.1	Cu	0.02	0.1
Zn	132	110	Zn	<dl	1.3
Ga	30.0	25.0	Ga	<dl	0.1
Ge	1.4	1.1	Ge	<dl	0.04
As	6.7	5.6	As	0.6	0.1
Se	1.3	2.7	Se	0.03	0.1
Rb	65.3	59.1	Rb	0.3	3.0
Sr	700	567	Sr	0.2	133.6
Y	46.8	36.9	Y	0.01	6.0
Zr	193	197	Zr	0.1	<dl
Nb	44.8	39.5	Nb	0.02	<dl
Mo	1.3	1.1	Mo	0.1	<dl
Cd	<dl	<dl	Cd	<dl	<dl
Sn	4.5	3.9	Sn	<dl	<dl
Sb	1.5	1.4	Sb	0.1	<dl
Cs	6.5	5.8	Cs	0.01	0.1
Ba	986	868	Ba	0.2	0.6
La	40.2	33.4	La	0.01	5.1
Ce	95.5	78.5	Ce	0.04	11.9
Pr	11.3	9.2	Pr	<dl	1.5
Nd	43.6	34.5	Nd	0.02	5.8
Sm	10.1	7.8	Sm	<dl	1.1
Eu	1.7	1.3	Eu	<dl	0.2
Gd	9.5	7.4	Gd	<dl	1.1
Tb	1.5	1.1	Tb	<dl	0.2
Dy	9.4	7.4	Dy	<dl	0.9
Ho	1.9	1.4	Ho	<dl	0.2
Er	5.5	4.4	Er	<dl	0.5
Tm	<dl	<dl	Tm	<dl	0.1
Yb	5.4	4.3	Yb	<dl	0.4
Lu	<dl	<dl	Lu	<dl	0.1
Hf	6.2	5.8	Hf	<dl	<dl
Ta	7.6	9.2	Ta	<dl	0.02
W	2.3	2.2	W	0.1	0.03
Tl	<dl	<dl	Tl	<dl	<dl
Pb	34.1	28.2	Pb	<dl	<dl
Bi	<dl	<dl	Bi	<dl	<dl
Th	15.6	12.1	Th	<dl	<dl
U	10.1	6.8	U	<dl	<dl

Abbreviations: Washed, washed merlinoite; Acidified, acidified merlinoite; <dl, under detected limit; na, not analyzed.

**Table 6**  
The average weight, moisture contents and nutrient contents of sunflowers in each treatment.

Mean (s)	Weight (g)		Moisture (%)		Macronutrient concentration (%)					Weight-normalized concentration (total load, %)				
	Wet mass		Dry mass		K	P	N	Ca	Mg	K	P	N	Ca	Mg
T-1	11 (2.0)	2.6 (0.3)	77 (1.6)	1.9 (0.2)	0.6 (0.1)	0.1 (0.01)	2.8 (0.5)	0.6 (0.1)	4.9 (1.1)	0.3 (0.03)	0.3 (0.03)	1.6 (0.5)	7.1 (1.0)	1.4 (0.2)
T-2	18 (5.4)	4.2 (1.5)	77 (1.3)	1.8 (0.1)	2.3 (0.2)	0.1 (0.03)	2.8 (0.6)	0.8 (0.2)	7.6 (2.4)	0.4 (0.05)	0.4 (0.05)	9.3 (2.6)	12 (4.7)	3.0 (0.6)
T-3	14 (4.9)	3.0 (1.3)	78 (2.3)	2.0 (0.4)	2.8 (0.9)	0.1 (0.02)	3.5 (0.9)	1.0 (0.2)	5.8 (2.4)	0.3 (0.1)	0.3 (0.1)	7.9 (3.8)	9.6 (2.9)	3.0 (1.6)
T-4	13 (1.4)	2.7 (0.4)	78 (1.9)	1.9 (0.1)	2.9 (0.2)	0.1 (0.01)	3.4 (0.5)	1.0 (0.3)	5.1 (1.0)	0.3 (0.02)	0.3 (0.02)	8.0 (0.9)	9.2 (0.7)	2.7 (0.7)
T-5	14 (10.7)	3.1 (2.5)	80 (5.7)	1.8 (0.1)	2.8 (0.2)	0.1 (0.01)	4.0 (0.6)	1.0 (0.2)	8.2 (0.6)	0.3 (0.1)	0.3 (0.1)	12 (2.5)	18 (0.2)	4.3 (1.5)
T-6	36 (6.8)	8.9 (1.8)	75 (2.2)	2.7 (0.3)	1.0 (0.2)	0.2 (0.02)	4.1 (0.6)	0.9 (0.1)	23 (2.7)	1.9 (0.4)	1.9 (0.4)	9.0 (1.3)	37 (12)	7.7 (2.1)
T-7	98 (6.2)	26 (1.8)	74 (0.3)	2.0 (0.5)	1.4 (0.2)	0.1 (0.04)	3.2 (0.8)	0.9 (0.3)	52 (12)	3.5 (1.1)	3.5 (1.1)	35 (7.3)	81 (19)	22 (7.1)
T-8	14 (1.5)	3.2 (0.4)	77 (0.9)	2.3 (0.4)	2.3 (0.5)	0.1 (0.02)	2.4 (0.4)	0.9 (0.1)	7.2 (1.2)	0.4 (0.1)	0.4 (0.1)	7.3 (2.1)	7.8 (2.1)	2.9 (0.7)
p	<0.001	<0.001	<0.001	<0.05	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Abbreviations: T, treatment, standard deviation; p, significant level.

sunflowers in T-7 attain the highest biomass by most, with average wet and dry weight of 98 and 26 g, respectively (Table 6). As regards macronutrients, small differences, but statistically significant ( $p < 0.01$ ) are found on the concentrations in sunflowers among different treatments, reaching maximum differences of 0.8%, 0.1%, 2.3%, 1.7%, and 0.4% for K, P, N, Ca, and Mg, respectively (Table 6). Maximum differences were found for N in T-1 (no



**Table 7**  
Results of the linear regression analysis for determining fertilization effects of different treatments.

Treatment group		<i>b</i>	<i>se</i>	<i>p</i>	<i>R</i> <sup>2</sup> (%)
Ln (weight)	std1	0.24	0.19	0.22	88.9
	std2	1.23	0.21	<0.001	
	mer	0.23	0.21	0.28	
	std1 + mer	-0.20	0.25	0.43	
	std2 + mer	0.85	0.30	0.01	
	cons.	0.93	0.15	0	
Ln (K)	std1	0.23	0.18	0.21	91.0
	std2	1.57	0.20	<0.001	
	mer	0.39	0.20	0.06	
	std1 + mer	-0.36	0.23	0.13	
	std2 + mer	0.39	0.28	0.18	
	cons.	1.58	0.14	0	
Ln (P)	std1	0.27	0.23	0.26	89.3
	std2	1.92	0.26	<0.001	
	mer	0.43	0.26	0.11	
	std1 + mer	-0.57	0.30	0.07	
	std2 + mer	0.18	0.36	0.62	
	cons.	-1.31	0.18	0	
Ln (N)	std1	1.63	0.18	<0.001	91.5
	std2	1.77	0.20	<0.001	
	mer	1.54	0.20	<0.001	
	std1 + mer	-1.40	0.23	<0.001	
	std2 + mer	-0.20	0.49	0.49	
	cons.	0.42	0.14	0.01	
Ln (Ca)	std1	0.28	0.19	0.17	90.4
	std2	1.63	0.21	<0.001	
	mer	0.08	0.21	0.71	
	std1 + mer	0.14	0.25	0.58	
	std2 + mer	0.71	0.30	0.03	
	cons.	1.95	0.15	0	
Ln (Mg)	std1	0.67	0.22	0.005	88.0
	std2	1.70	0.24	<0.001	
	mer	0.73	0.24	0.005	
	std1 + mer	-0.58	0.28	0.05	
	std2 + mer	0.31	0.34	0.36	
	cons.	0.31	0.17	0.08	

Abbreviations: *b*, regression coefficient (slope of the correlation line); *se*, standard error; *p*, significant level; *R*<sup>2</sup>, correlation coefficient; cons., constant term of the correlation line; std1, Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O; std2, struvite; mer, merlinoite.

(Table 6), together with the highest growth rate. T-6, with only struvite addition showed intermediate growth rate but clear deficiency in N (Table 6), as evidenced by the low N concentration and by the yellow color of older leaves (this is a clear symptom of N-deficiency in crops). NO<sub>3</sub> content in merlinoite, incorporated after the synthesis process (not quantified), accounts for the differences between T-7 and T-6. T-2, 3, 4, 5 and 8 without struvite addition showed similar N uptake but reduced growth rate than T-6. Total load of Ca and Mg is related to the plant growth as those nutrients, particularly Ca, are uptaken in part through transpiration flow [47].

The above issues are supported by the linear regression analyses (Table 7). As regards the influence on sunflower weight, the addition of struvite (std2) and struvite + merlinoite have a positive slope (then increasing doses favors the sunflower growth) and its contribution to the weight is statistically significant (Table 7, *p* < 0.05). The addition of only Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and the increase of merlinoite doses (up to two times of the recommended dose) have low relevance on sunflower weight (positive slope but *p* > 0.05, Table 7). Struvite is the main source for the uptake P, K, Ca, Mg, and N by sunflowers and the only fertilizer, which is statistically significant (*p* < 0.05) for P and K uptake. Although is not statistically significant, merlinoite fertilization has a *p* value close to 0.05 and a positive slope indicating that it is a minor source for K uptake when compared with struvite. This is in line with the aforementioned effect of P deficiency on K uptake and the synergistic effect on K and P uptake when P is available. Furthermore, the increase on K uptake given by the addition of merlinoite in the struvite + merlinoite fertilization (indicated by the positive slope, Table 7) is not significant (*p* = 0.1–0.2) with respect to that produced with only struvite. With the exception of struvite + merlinoite fertilization, treatments with only Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, only struvite and containing merlinoite have a positive effect and are statistically significant for the uptake of N (Table 7). As regards Ca, struvite and the struvite + merlinoite fertilization are statistically significant. In the case of Mg uptake, the merlinoite fertilization, and the treatment with only struvite, only

fertilizer addition) and T-6 (low N-NH<sub>4</sub> addition rate), showing the lowest N concentrations (Table 6). Note that highest nutrient concentrations are not produced with full fertilization (T-7). In view of this, the concentrations of K, P, N, Ca, and Mg were normalized with respect to the dry weight of sunflowers. The weight-normalized concentrations (or total load of macronutrients in plant) reveal differences on macronutrient contents among treatments (Table 6). Full fertilization (T-7) shows by far the highest total load of macronutrients (K, P, N, Ca, and Mg, Table 6). With the addition of only struvite, sunflowers in T-6 obtain average wet and dry weight of 36 g and 3.2 g, respectively, which are much lower compared to those in T-7 but higher than those in Blank (T-1) and other treatments (Table 6). These sunflowers also show the second highest total load of macronutrients, which are 2–4 times lower than those in T-7, but much higher than in Blank T-1 and other treatments (Table 6). By contrast, with the addition of only merlinoite, the weight of sunflowers in T-8 are slightly higher compared to those in T-1 and the total load of macronutrients, especially K, N, and Mg in them are also higher than in T-1 (Table 6). Grown only in the poor soil without any nutrients, sunflowers in T-1 obtain the lowest wet and dry weight as well as the lowest total load of macronutrients (Table 6). The sunflowers grown in the remaining treatments (T-2, 3, 4 and 5) obtain similar or relatively higher weights and total load of macronutrients compared to those in T-8, which are also slightly higher than those in T-1 but obviously lower than those in T-6 and T-7 (Table 6). The variation of concentration of a given nutrient depends on its availability, competition between nutrients, and plant growth rate (i.e. plant nutrient demand). Nutrient availability had clear consequences on plant growth (Table 6). As can be deduced from the total load of macronutrients (Table 6), low P availability clearly limited sunflower growth after four weeks of sowing in all treatments without struvite. Phosphorous deficiency strongly limits photosynthetic activity [45]. A synergistic effect in K and P uptake was suggested comparing T-6 and T-7. With the same dose of P (struvite), T-7 showed almost twice as much P and K concentration as T-6. Moreover, T-6 showed relatively high K content in spite of having no merlinoite fertilization, much higher than the rest of treatments where struvite was not added or even with merlinoite addition. The deficiency of essential macronutrients, especially P, may limit the uptake of other nutrients such as K [46]. For instance, K uptake in the treatments without struvite is much lower than in treatments including struvite (T-6 and T-7) and only slightly higher (1.1–1.2 times higher) than in treatment with only soil (T-1). It is also noticeable that K uptake attain similar values when only merlinoite (T-8) and only Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (T-2) are applied. Potassium is retained by merlinoite through the cation exchange mechanism, the same as the natural clays in soils. Exchangeable cations are released to the soil solution as they are uptaken by plants and/or leached from soil solution. Therefore, plant uptake promotes the release of exchangeable K from merlinoite. The process is of slow release because it is, in large part, biologically regulated (by plant uptake). As regards N, full fertilization (T-7) shows by far the highest uptake of this essential nutrient

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  favor the uptake of Mg, especially the treatments with only struvite (indicated by the high positive slope, Table 7), since Mg is in the framework structure of this mineral. Nevertheless, combining struvite or  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  with merlinoite do not have a significant increase in the Mg uptake (Table 7). On the whole, N, P and K are the three essential macronutrients for plant growing. Blank, without any fertilizer inputs, produced poor growth of the high-nutrient demand sunflowers. With struvite and merlinoite, the sunflowers in T-7 grew the best due to the supply of N, P and K in optimal quantities. With only struvite, the sunflowers in T-6 also grew taller than other treatments, due to the supply of N and P from struvite; however, the leaves of them were yellow, indicating N-deficiency, and they did not grow as strong and tall as those in T-7 because of an unbalance between macronutrients supply (especially N/P). This indicates that merlinoite shows good fertilizer efficiency, making the sunflowers grew much faster, and with equilibrated nutrition. Nevertheless, with only merlinoite, the sunflowers in T-8 grew green but not tall and strong, probably due to shortage of P and N, indicating that the fertilizer efficiency of merlinoite cannot be fully achieved unless they are mixed with the two other essential macronutrients. Treatments with no P addition showed poorer growth than the two treatments with P addition (T-6 and T-7), indicating that low P availability limited the plant growth in the non P-fertilized treatments.

#### 4. Conclusions

Large amounts of coal fly ashes are increasingly being generated from two PCC power plants in Xinjiang, NW China, which may pose serious threat to the environment. High quality merlinoite zeolitic materials were synthesized from these fly ashes by KOH direct conversion method. Zeolite synthesis by this method is influenced by fly ash characteristics and various synthesis conditions. Different fly ashes present different synthesis results under the same activation conditions. As for the same fly ash, increasing activation temperature, time and KOH concentration gave rise to the increase of merlinoite synthesis efficiency. Relatively high KOH concentration ( $\geq 3\text{ M}$ ) is needed to obtain high synthesis efficiency of merlinoite. However, the relatively high activation temperature ( $\geq 200^\circ\text{C}$ ), long activation time ( $\geq 12\text{ h}$ ) and high KOH/fly ash ratios ( $> 2\text{ l/kg}$ ) are more favorable for the crystallization of tobermorite and perialite with low CECs, rather than a high merlinoite yield. The synthesized merlinoite products reached CECs ranging from 60 to 340  $\text{cmol kg}^{-1}$ . Considering the economic cost, pilot-scale merlinoite product synthesized from Waf under optimal synthesis conditions (5 M KOH,  $150^\circ\text{C}$ , 2 l/kg and 8 h) attained a CEC of 160  $\text{cmol kg}^{-1}$ . This merlinoite product presented good fertilizer efficiency, and can be used as an efficient slow release K-fertilizer for plant growing in poor soils when mixed with N and P-bearing fertilizers (such as struvite), indicating its high application potential for large-area soil reclamation in the opencast coal mines around the power plants in Xinjiang in the near future, or in high productive crops growing in nutrient-limited soils.

#### Acknowledgements

This study is funded by the National Natural Science Foundation of China (No. 40972104). The authors would like to acknowledge the Huadian Power Corporation in Xinjiang, China for providing feed coal and combustion by-product samples, acknowledge the Clariant Ibérica Producción, S.A Company in Barcelona, Spain for providing the pilot-scale reactor for synthesis of large-amount merlinoite, and the University of Barcelona for providing the experimental fields for growing sunflowers.

#### References

- [1] BP Statistical Review of World Energy, 2012, June, [http://www.bp.com/assets/bp\\_internet/globalbp/globalbp\\_uk\\_english/reports\\_and\\_publications/statistical\\_energy\\_review\\_2011/STAGING/local\\_assets/pdf/statistical\\_review\\_of\\_world\\_energy\\_full\\_report\\_2012.pdf](http://www.bp.com/assets/bp_internet/globalbp/globalbp_uk_english/reports_and_publications/statistical_energy_review_2011/STAGING/local_assets/pdf/statistical_review_of_world_energy_full_report_2012.pdf)
- [2] J. Li, X.G. Zhuang, X. Querol, O. Font, N. Moreno, J.B. Zhou, G.M. Lei, High quality of jurassic coals in the southern and eastern junggar coalfields, Xinjiang, NW China: geochemical and mineralogical characteristics, *International Journal of Coal Geology* 99 (2012) 1–15.
- [3] D.H. Klein, A.W. Andren, J.A. Carter, J.F. Emery, C. Feldman, W. Fulkerson, W.S. Lyon, J.C. Ogle, Y. Talmi, R.I. Van, N. Bolton, Pathways of 37 trace elements through a coal fired power plant, *Environmental Science and Technology* 9 (1975) 973–974.
- [4] J. Wang, X. Teng, H. Wang, H. Ban, Characterizing the metal adsorption capability of a class F coal fly ash, *Environmental Science and Technology* 38 (2004) 6710–6715.
- [5] T. Hsu, C. Yu, C. Yeh, Adsorption of  $\text{Cu}^{2+}$  from water using raw and modified coal fly ashes, *Fuel* 87 (2008) 1355–1359.
- [6] D. Wu, Changes of mineralogical–chemical composition, cation exchange capacity, and phosphate immobilization capacity during the hydrothermal conversion process of coal fly ash into zeolite, *Fuel* 87 (2008) 2194–2200.
- [7] N. Koukouras, R. Zeng, V. Perdikatis, W. Xu, E.K. Kakaras, Mineralogy and geochemistry of Greek and Chinese coal fly ash, *Fuel* 85 (2006) 2301–2309.
- [8] G. Lu, F. Xue, J. Zhao, Some advice to the fly ash of China, *China Mining Magazine* 20 (2011) 193–200 (in Chinese with English abstract).
- [9] X. Querol, N. Moreno, Novel products and applications with combustion residues-zeolites, in: M. Cox, H. Nugteren, M. Janssen-Jurkovićová (Eds.), *Combustion Residues-Current, Novel and Renewable Applications*, Wiley, England, 2008, pp. 240–261.
- [10] H. Höller, U. Wirsching, Zeolites formation from fly ash, *Fortschr Mineral* 63 (1985) 21–43.
- [11] T. Hemmi, Synthesis of hydroxy-sodalite (“zeolite”) from waste coal ash, *Journal of Soil Science and Plant Nutrition* (Tokyo) 33 (3) (1987) 517–521.
- [12] F. Mondragón, F. Rincon, L. Sierra, C. Escobar, J. Ramírez, J. Fernandez, New perspectives for coal ash utilization: synthesis of zeolitic materials, *Fuel* 69 (1990) 263–266.
- [13] N. Shigemoto, S. Shirakami, S. Hirano, H. Hayashi, Preparation and characterization of zeolites from coal fly ash, *Nippon Kagaku Kaishi* 5 (1992) 484–492.
- [14] N. Shigemoto, H. Hayashi, K. Miyaura, Selective formation of Na-X, zeolite from coal fly ash by fusion with sodium hydroxide prior to hydrothermal reaction, *Journal of Materials Science* 28 (1993) 4781–4786.
- [15] N. Shigemoto, S. Sugiyama, H. Hayashi, Characterization of Na-X, Na-A, and coal fly ash zeolites and their amorphous precursors by IR MAS NMR and XPS, *Journal of Materials Science* 30 (1995) 5777–5783.
- [16] D. Kolousek, V. Seidl, E. Prochazkova, J. Obsasnikova, L. Kubelkova, I. Svetlik, Ecological utilization of power-plant fly ashes by their alteration to phillipsite: hydrothermal alteration, application, *Acta Universitatis Carolinae: Geologica* 37 (1993) 167–178.
- [17] H.L. Chang, W.H. Shih, Conversion of fly ash to zeolites for waste T, *Ceramic Transactions* 61 (1995) 81–88.
- [18] H.L. Chang, W.H. Shih, Synthesis of zeolites A and X from fly ashes and their ion-exchange behavior with cobalt ions, *Industrial and Engineering Chemistry Research* 39 (2000) 4185–4191.
- [19] A. Singer, V. Berkgaot, Cation exchange properties of hydrothermally treated coal fly ash, *Environmental Science and Technology* 29 (7) (1995) 1748–1753.
- [20] C. Amrhein, G.H. Haghnia, T.S. Kim, P.A. Mosher, R.C. Gagajena, T. Amanios, L. de la Torre, Synthesis and properties of zeolites from coal fly ash, *Environmental Science and Technology* 30 (1996) 735–742.
- [21] V. Berkgaot, A. Singer, High capacity cation exchanger by hydrothermal zeolitization of coal fly ash, *Applied Clay Science* 10 (1996) 369–378.
- [22] X. Querol, F. Plana, A. Alastuey, A. López-Soler, Synthesis of Na-zeolites from fly ash, *Fuel* 76 (8) (1997) 793–799.
- [23] X. Querol, A. Alastuey, A. López-Soler, F. Plana, J.M. Andrés, R. Juan, P. Ferrer, C.R. Ruiz, A fast method for recycling fly ash: microwave-assisted zeolite synthesis, *Environmental Science and Technology* 31 (9) (1997) 2527–2533.
- [24] X. Querol, J.C. Umaña, F. Plana, A. Alastuey, A. López-Soler, A. Medinaceli, A. Valero, M.J. Domingo, E. Garcia-Rojo, Synthesis of Na zeolites from fly ash in a pilot plant scale. Examples of potential environmental applications, *Fuel* 80 (2001) 857–865.
- [25] X. Querol, N. Moreno, J.C. Umaña, A. Alastuey, E. Hernández, A. López-Soler, F. Plana, Synthesis of zeolites from coal fly ash: an overview, *International Journal of Coal Geology* 50 (2002) 413–423.
- [26] X. Querol, N. Moreno, A. Alastuey, R. Juan, J.M. Andrés, A. López-Soler, C. Ayora, A. Medinaceli, A. Valero, Synthesis of high ion exchange zeolites from coal fly ash, *Geologica Acta* 5 (2007) 49–57.
- [27] G.G. Hollman, G. Steenbruggen, M. Janssen-Jurkovicova, A two-step process for the synthesis of zeolites from coal fly ash, *Fuel* 78 (1999) 1225–1230.

- [28] S. Rayalu, S.U. Meshram, M.Z. Hasan, Highly crystalline faujasitic zeolites from fly ash, *Journal of Hazardous Materials B77* (2000) 123–131.
- [29] S. Rayalu, J.S. Udhoji, K.N. Munshi, M.Z. Hasan, Highly crystalline zeolite – a from fly ash of bituminous and lignite coal combustion, *Journal of Hazardous Materials B88* (2001) 107–121.
- [30] O. Font, N. Moreno, S. Diez, X. Querol, A. López-Soler, P. Coca, Garcia, F. Pena, Differential behaviour of combustion and gasification fly ash from Puertollano Power Plants (Spain) for the synthesis of zeolites and silica extraction, *Journal of Hazardous Materials B166* (2009) 94–102.
- [31] M. Ahmaruzzaman, A review on the utilization of fly ash, *Progress in Energy and Combustion Science* 36 (2010) 327–363.
- [32] N. Koukoulas, C. Vasilatos, G. Itskos, I. Mitsis, A. Moutsatsou, Removal of heavy metals from wastewater using CFB-coal fly ash zeolitic materials, *Journal of Hazardous Materials B173* (2010) 581–588.
- [33] N. Moreno, X. Querol, F. Plana, J.M. Andres, M. Janssen, H. Nugteren, Pure zeo- lite synthesis from silica extracted from coal fly ashes, *Journal of Chemical Technology and Biotechnology* 77 (2002) 274–279.
- [34] N. Moreno, X. Querol, A. López-Soler, J.M. Andres, M. Janssen, H. Nugteren, M. Towler, K. Stanton, Determining suitability of a fly ash for silica extraction and zeolite synthesis, *Journal of Chemical Technology and Biotechnology* 79 (2004) 1009–1018.
- [35] D.W. Breck, *Ion Exchange Reactions in Zeolites Zeolite Molecular Sieves, Structure, Chemistry, and Use*, Robert E. Krieger Publishing, Malabar, FL, 1984 (Chapter 7; TIC: 245213).
- [36] J.D. Sherman, Synthetic zeolites and other microporous oxide molecular sieves, *Proceedings of the National Academy of Sciences of the United States of America* 96 (1999) 3471–3478.
- [37] N. Moreno, Recovery of Fly Ash for the Synthesis of Zeolites by Silica Extraction and Direct Conversion. *Environmental Applications* (Ph.D. thesis), Department of Environmental Geology, Institute of Earth Sciences (CSIC) and Department of Engineering and Natural Resources, Polytechnical University of Catalonia (UPC), 2002, 250 pp. (in Spanish with English abstract) <http://www.tdx.cat/handle/10803/6986>
- [38] C. Wang, J. Li, X. Sun, L. Wang, X. Sun, Evaluation of zeolites synthesized from fly ash as potential adsorbents for wastewater containing heavy metals, *Journal of Environmental Sciences* 21 (2009) 127–136.
- [39] L.S. Ferret, Zeolites from coal ash: synthesis and use (Doctoral thesis), Federal University in Brazil, 2004 (in Portuguese with English abstract).
- [40] J. Li, X.G. Zhuang, X. Querol, O. Font, N. Moreno, J.B. Zhou, Environmental geochemistry of the feed coals and their combustion by-products from two coal-fired power plants in Xinjiang Province, Northwest China, *Fuel* 95 (2012) 446–456.
- [41] X. Querol, M.K.G. Whateley, T.J.L. Fernandez, E. Tuncali, Geological controls on the mineralogy and geochemistry of the Beypazari lignite, central Anatolia, Turkey, *International Journal of Coal Geology* 33 (1997) 255–271.
- [42] IZA, Commission on Natural Zeolites, 2005 <http://www.iza-online.org/natural/Data-sheets/Merlinoite/merlinoite.htm>
- [43] GSA Resources, 2000, <http://www.gsaresources.com/cationexchange.htm>
- [44] European Council Decision 2003/33/EC, Official Journal of the European Communities L6 (2003) 27–49.
- [45] F.J.M. Maathuis, Physiological functions of mineral macronutrients, *Current Opinion in Plant Biology* 12 (2009) 250–258.
- [46] B.K. Das, S.P. Sen, Effect of nitrogen, phosphorus and potassium deficiency on the uptake and mobilization of ions in Bengal gram (*Cicer arietinum*), *Journal of Bioscience* 3 (1981) 249–257.
- [47] H. Marschner, *Mineral Nutrition of Higher Plants*, 2nd ed., Academic Press, London, 1995.

