

## Novel process for high value utilization of high-alumina fly ash: valuable metals recovery and mesoporous silica in situ preparation

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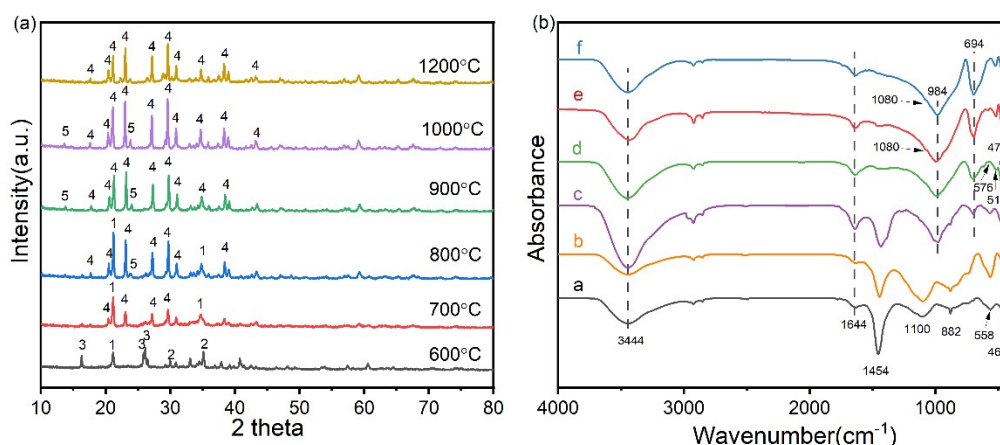
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### Supplementary data



**Fig.S1 XRD patterns and FTIR spectra of FN system (with 40% addition of  $\text{Na}_2\text{CO}_3$ ) after calcined at 600-1200 °C**

**XRD: 1  $\text{NaAlSiO}_4$ , orthorhombic; 2  $\text{Na}_2\text{CO}_3$ ; 3 Mullite; 4  $\text{NaAlSiO}_4$ , hexagonal; 5 Zeolite;**

**FT-IR: a FA- $\text{Na}_2\text{CO}_3$  mixture; b 400 °C; c 600 °C; d 800 °C; e 1000 °C; f 1200 °C**

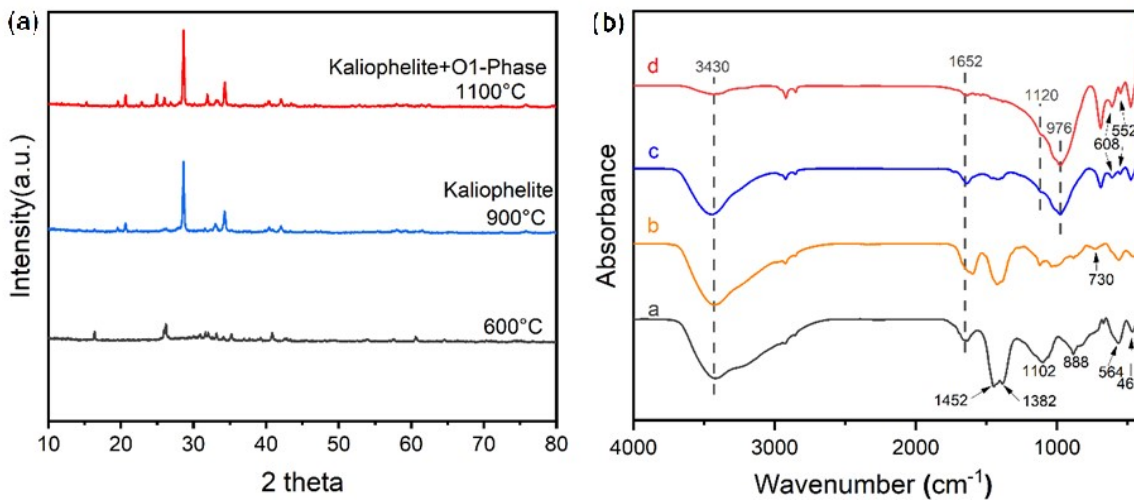
The mineral composition of fly ash mainly includes crystalline phase minerals (mullite, quartz etc.) and amorphous phase minerals (amorphous silica, glass etc.). Fig. S1a shows the XRD patterns of raw fly ash and FN calcined at 600-1200 °C for 2 h. At the calcination temperature of 600 °C, the diffraction

peaks appear at 21.0° and 34.7°, which correspond to the low temperature carnegie phase of sodium aluminosilicate (NaAlSiO<sub>4</sub>, low carnegieite, orthorhombic), implying that mullite in fly ash have been transformed under the calcination action of Na<sub>2</sub>CO<sub>3</sub>. The disappearance of quartz and amorphous silica in fly ash indicates that they are involved in the mineral phase transformation of mullite into carnegie phase as shown in Eq. 3.1. When the calcination temperature is increased to 800 °C, the mineral phases of mullite and Na<sub>2</sub>CO<sub>3</sub> completely disappear, and the diffraction peaks of NaAlSiO<sub>4</sub> (Nepheline, hexagonal, JCPDS No. 35-0424) appear at 21.3°, 23.2°, 27.6°, 29.8° and 31.4°, indicating that the sodium ions enter and destroy the mullite lattice to generate new sodium aluminosilicate minerals. While the calcination temperature is further increased to 1000 °C or even higher, the sodium chalcocite phase is stable.



The structural evolution of fly ash calcined with Na<sub>2</sub>CO<sub>3</sub> at different temperatures was detected by FTIR spectra as shown in Fig. S1b. For uncalcined FN, the broad bands appear at 3444 cm<sup>-1</sup> and 1644 cm<sup>-1</sup> are attributed to the presence of surface hydroxyl groups due to adsorbed water. The absorption peaks located at 1100 and 468 cm<sup>-1</sup> correspond to the stretching and bending vibrations of Si-O in the skeleton [SiO<sub>4</sub>]. The absorption band at 558 cm<sup>-1</sup> indicates the internal vibrations of Si-O-Al oct (aluminum octahedra) in the mullite lattice. In addition, the absorption bands at 882 and 1454 cm<sup>-1</sup> are attributed to the bending and stretching vibrations of the CO<sub>3</sub><sup>2-</sup>. After calcination at 400 °C, the structure of mullite and Na<sub>2</sub>CO<sub>3</sub> decomposed, corresponding to the weakness and disappearance of the characteristic absorption bands intensity (b). At 600 °C, the absorption band shifted from 1100 to 984 cm<sup>-1</sup> position and appeared at 694 cm<sup>-1</sup> due to irregular stretching vibrations of Si-O, indicating a

transition from Si-O-Al<sub>oct</sub> (Al octahedron) to Si-O-Al<sub>tet</sub> (Al tetrahedron) (c). At 800°C, the main absorption bands appear at 984, 694 and 472 cm<sup>-1</sup>, indicating the complete transformation of aluminum octahedra to aluminum tetrahedra and the formation of structurally stable hexagonal sodium chalcocite (d). The appearance of new absorption peaks at 518 and 576 cm<sup>-1</sup> demonstrates the formation of the shelf structure of the sodium-aluminosilicate as well as the hexagonal ring. With the increase of temperature to 1000-1200 °C, the absorption peaks at 984, 694, and 472 cm<sup>-1</sup> hardly change, indicating the hexagonal sodalite can be stable above 800 °C. The high temperature changed the spatial symmetry of hexagonal crystals and adjusted alignment of the skeletal [SiO<sub>4</sub>] and [AlO<sub>4</sub>], therefore the shoulder band formed at 1080 cm<sup>-1</sup>, and the absorption peaks in the range of 516-570 cm<sup>-1</sup> adjust the position and shape above 1000 °C(e-f).

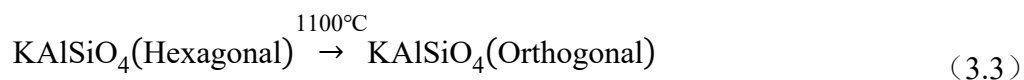
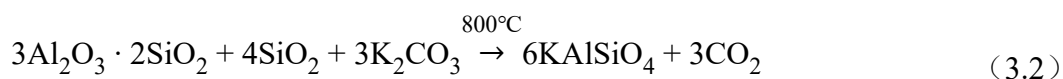


**Fig.S2 XRD patterns and FT-IR spectra of FK system (with 50% addition of K<sub>2</sub>CO<sub>3</sub>) after holding at 600~1100 °C**

**FT-IR: a FA-K<sub>2</sub>CO<sub>3</sub> ; b 600 °C ; c 800 °C ; d 1100 °C**

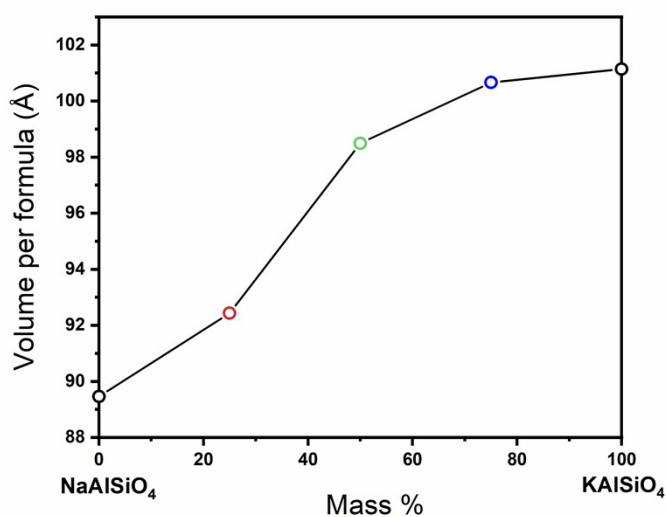
After calcination of K<sub>2</sub>CO<sub>3</sub> as activator with fly ash, potassium ions entered the mullite crystalline

phase and destroyed the original crystal structure. Figure S2a shows the XRD patterns of the raw fly ash and the FK at 600-1100 °C for 2 h. With the increase of temperature, the FK firstly generated new amorphous material, indicating a large amount of unreacted mullite crystalline phase and K<sub>2</sub>O in the system. It can be regarded as precursors of potassium aluminosilicate minerals. Then the temperature increased again and the potassium aluminosilicate crystalline phase appeared. The diffraction peak became intense and sharp with the increase of temperature, indicating that the increase of temperature promotes the reaction of mullite with K<sub>2</sub>CO<sub>3</sub> reaction. At 900°C, the diffraction peaks appeared at 19.2°, 20.7°, 28.5°, 34.4°, 40.4° and 42.4°, due to the formation of potassium feldspar (Kaliophilite, KAlSiO<sub>4</sub>) crystals. It corresponds to the standard card JCPDS No. 12-0314. At 1100°C, the XRD pattern showed new diffraction peaks at 14.2°, 15.3°, 24.9°, and 26.0°, indicating the transformation of hexagonal potassium feldspar into potassium aluminosilicate (PAS, KAlSiO<sub>4</sub>) with orthogonal crystalline phases. The XRD pattern is consistent with the standard JCPDS No. 33-0989. The reaction is shown in Chemical formula (3.2 3.3).



The structural evolution of fly ash calcined with K<sub>2</sub>CO<sub>3</sub> at different temperatures was detected by FTIR spectra as shown in Fig. S2b. For the uncalcined FK system, the characteristic absorptions of mullite and K<sub>2</sub>CO<sub>3</sub> can be observed(a). The broad spectral bands centered at 3430 and 1652 cm<sup>-1</sup> belonged to surface hydroxyl groups. The absorption bands at 1102, 564 and 466 cm<sup>-1</sup> correspond to the stretching and bending vibrations of Si-O and the internal vibrations of Si-O-Al oct (aluminum octahedra) in the mullite lattice. The absorption bands at 888, 1452 and 1382 cm<sup>-1</sup> are attributed to the bending and

stretching vibrations of the  $\text{CO}_3^{2-}$ . At 600 °C, the absorption at  $730\text{ cm}^{-1}$  occurred, which is the out-of-plane bending vibration of Si-O. It marked the transition from Si-O-Al<sub>oct</sub> (Al octahedron) to Si-O-Al<sub>tet</sub> (Al tetrahedron), accompanied by a decrease in the intensity of the two characteristic stretching bands of the hydroxyl group (b). After calcination at 800 °C, the intensity of the characteristic absorption bands diminished or even disappeared, indicating the structural decomposition of mullite and  $\text{K}_2\text{CO}_3$ . The formation of an absorption band at  $976\text{ cm}^{-1}$  with a shoulder at  $1120\text{ cm}^{-1}$  indicated the complete transformation of aluminum octahedra to aluminum tetrahedra and the formation of a stable shelf aluminosilicate structure (c). The peaks at 608 and  $552\text{ cm}^{-1}$  were sharper by the temperature above 1100 °C, indicating the formation of the orthorhombic  $\text{KAlSiO}_4\text{-O1}$  phase (d).



**Fig.S3 Volume per formula in  $\text{NaAlSiO}_4\text{-KAlSiO}_4$  system**

**Table S1 Addition ratio of FNK mixed samples at 900 °C**

Samples	Quality/g
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	FA	K <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>
K <sub>1</sub> Na <sub>0</sub>	10	5	0
K <sub>0.75</sub> Na <sub>0.25</sub>	10	3.75	1.25
K <sub>0.5</sub> Na <sub>0.5</sub>	10	2.5	2.5
K <sub>0.25</sub> Na <sub>0.75</sub>	10	1.25	3.75
K <sub>0</sub> Na <sub>1</sub>	10	0	5

**Table S2 Variation of lattice parameters and grain size of kaliophilite during acid leaching for different time**

Sample	Time(h)	(102)FWHM	(102)I/I <sub>0</sub>	Grain size (nm)	I <sub>(102)</sub> /I <sub>(002)</sub>
1	0	0.144	1	90.4	8.09
2	0.5	0.158	0.18	67.2	6.66
3	2	0.184	0.05	52.2	5.13
4	4	0.195	0.03	47.3	4.41

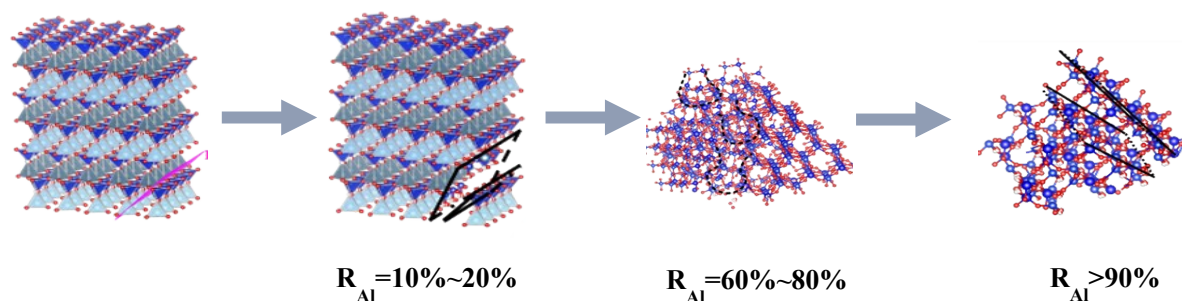
**Table S3 Variation of lattice parameters and grain size of Nepheline during acid leaching for different time**

Sample	Time (h)	(201)FWHM	(201)I/I <sub>0</sub>	Grain size (nm)	I <sub>(201)</sub> /I <sub>(002)</sub>
1	0	0.212	1	43.3	1.34
2	0.5	0.214	0.62	42.8	1.37
3	2	0.233	0.50	38.6	1.33
4	4	0.239	0.42	37.3	1.31

**Table S4 Chemical compositions of PC fly ash and mesoporous silica**

Components	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	MgO
FA	45.63	43.88	4.95	2.65	1.91	0.43	0.33	0.22
MS	91.10	6.46	0.272	0.233	1.09	0.01	0.21	0.11

The content of SiO<sub>2</sub> is above 91% in the mesoporous silica. Compared to fly ash, the impurity content is reduced, such as Al, Ca, Fe etc.



**Fig.S4 The mechanism of pore formation during acid leaching for kaliophilite**

Taking kaliophilite as an example, after 2.5% HCl treatment, the leaching efficiency of Al is about 20%, the sample is dominated macropore with low specific surface area. After being treated with higher concentration of acid, mesopores become abundant. When the acid concentration is 15%, the macropore gradually transformed into mesopore due to the continuous leaching of Al and other valuable metals. The specific surface area is about 400m<sup>2</sup>/g. After treatment with 30% HCl, the dissolved Al adsorbs on the surface of the mesopore material and generates the large wedge shape pores, the specific surface area decreases.