Crucial parameters determining efficient use of fly ashes from energy sector as raw materials for dedicated advanced applications

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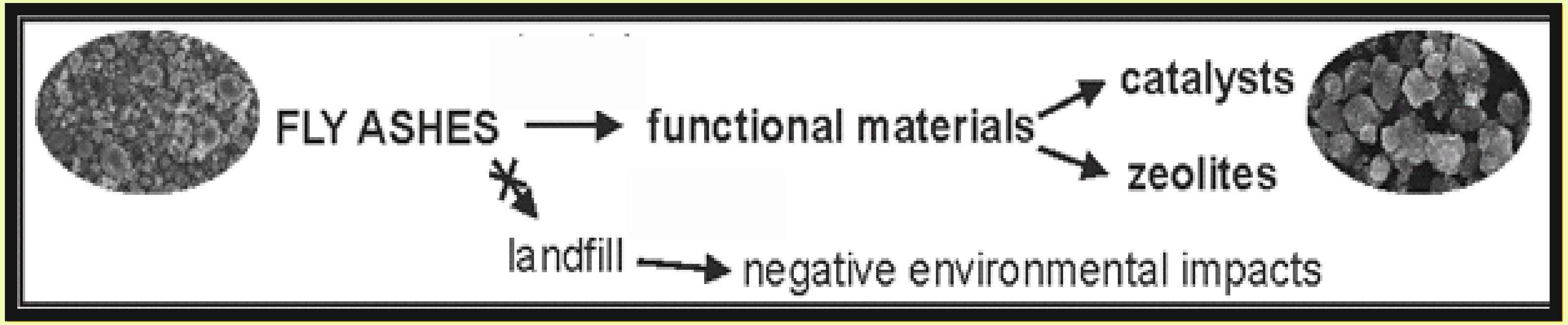

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What we call fly ash ?

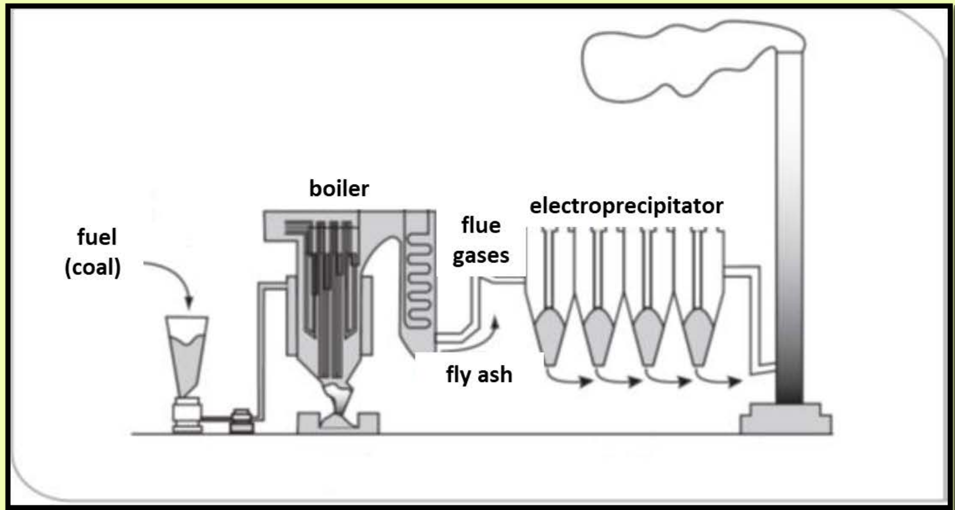
Fly ashes are solid coal combustion products (CCPs), having a form of very fine mineral powders. Fly ashes are built of four main groups of components:

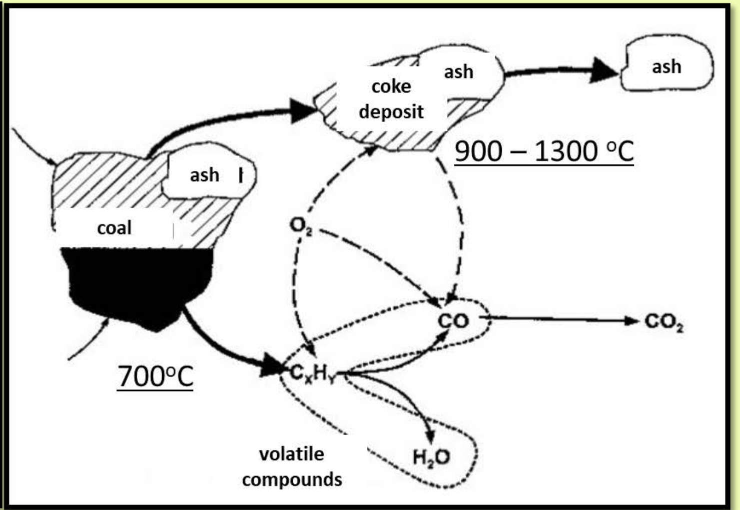
- major: SiO_2, Al_2O_3, Fe_2O_3, CaO
- additional: MgO, SO_3, Na_2O, K_2O
- trace: TiO_2, P_2O_5, Mn_xO_y
- residual: unburned carbon

component	USA	GB	Japan
	wt. (%)		
glassy phase	50 - 90	50 - 90	69 - 84
mullite	0 - 16	9 - 35	8 - 18
hematite	1 - 8	5	0,5 - 5
quartz	0 - 4	1 - 6	5 - 12

component	wt. (%)
SiO_2	2 - 68
Al_2O_3	3 - 39
Fe_2O_3	3 - 29
CaO	0,2 - 31
MgO	0,4 - 12
K_2O	0,2 - 8
Na_2O	0,2 - 8
TiO_2	0,5 - 2
P_2O_5	0,08 - 6
MnO	0,02 - 0,2
C	0,1 - 25
SO_3	0,1 - 7

A simplified scheme of a typical high-scale industrial plant for energy generation from solid fuels



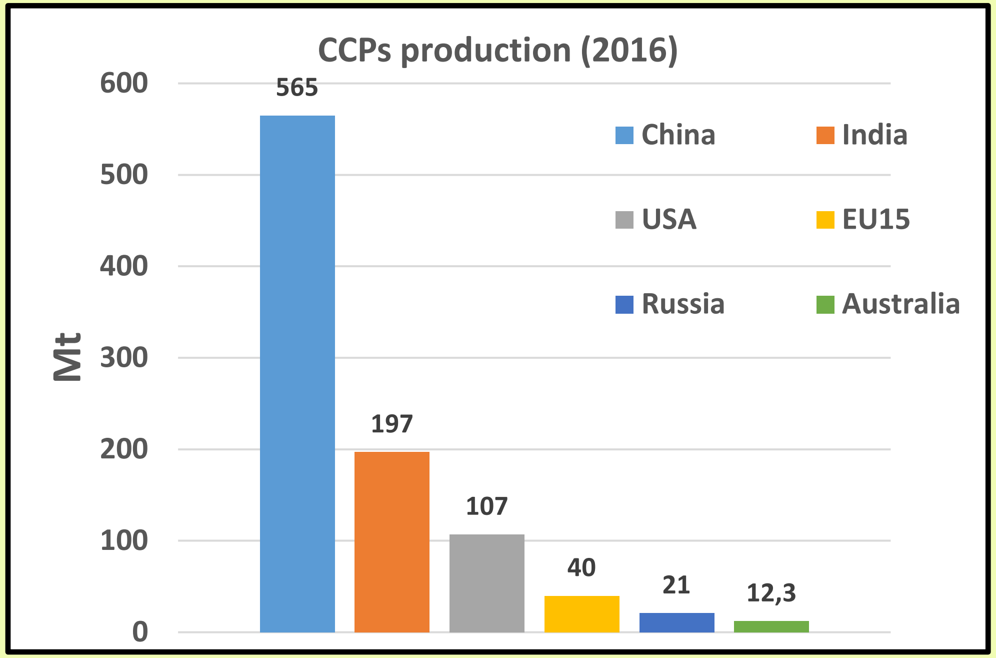


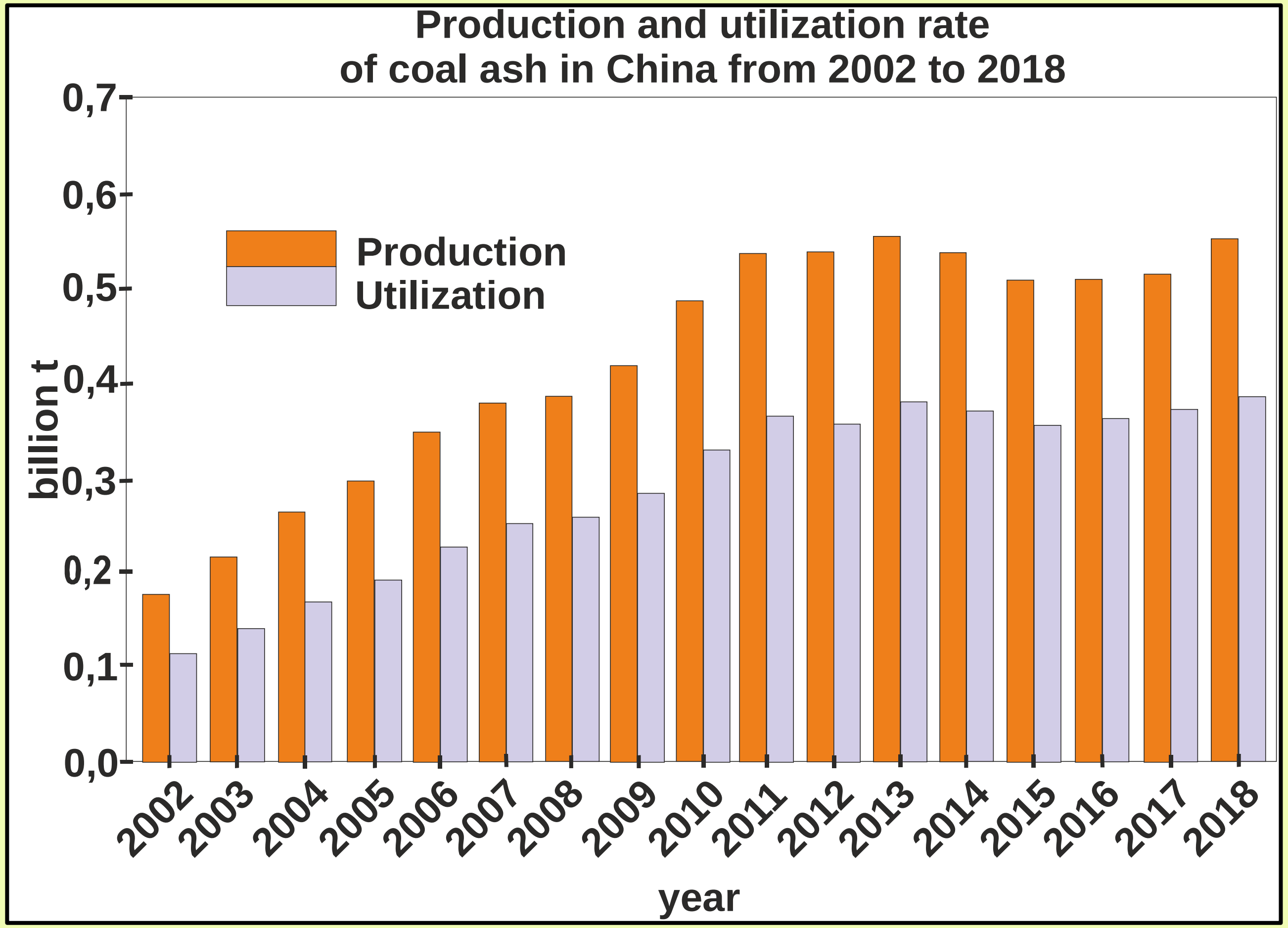
Fly ash is a fine 1-500µm fraction, which leaves a combustion chamber with flue gases and is collected in dedusting instalation using an electroprecipitator.

Roy, W.R., Thiery R, Schuller R, Suloway J, Coal Fly Ash: A Review of the Literature and Proposed Classification System with Emphasis on Environmental Impacts. Environmental Geology 96 (1981),
Thomas M, University of New Brunswick, Optimizing the Use of Fly Ash in Concrete, Portland Cement Association, 2007

Scale of the problem and environmental impact of fly ash storage

https://www.coaltrans.com/insights/article/global-aspects-on-coal-combustion-products





A large-scale storage of fly ashes requires not only an adequate localization but also generates additional costs, due to e.g. protection of landfills against dusting and leachates. The low fly ash particle sizes (0.01-100) µm and a possible content of noxious substances (heavy metals, hydrocarbons) are responsible for relatively high environmental impact of fly ashes.

https://file.ejatlas.org/docs/Bokosheflyash.jpg

Luo, Y., Wu, Y., Ma, S. et al. Utilization of coal fly ash in China: a mini-review on challenges and future directions. Environ Sci Pollut Res 28, 18727–18740 (2021). https://doi.org/10.1007/s11356-020-08864-4

Motivation, aim of work and experimental methods used in the current studies

Reusing fly ashes generated during industrial energy production from solid fuels is an important element of the circular economy. Fly ash as a material with tunable properties, largely dependent on, among others: the properties of an initial fuel, the technology and conditions of combustion, as well as methods of separation of ashes from the tale gases.

Therefore, it is absolutely crucial to accurately identify the physicochemical properties of such materials, so that it is possible to select the best method of utilizationof fly ashes.

Structural properties – chemical and phase compositions:

- X-ray fluorescence – XRF
- X-ray diffractometry – XRD
- Raman spectroscopy - RS

Textural properties – particle size distribution, specific surface area, porosity:

- BET/Porosimetry
- SEM - EDS

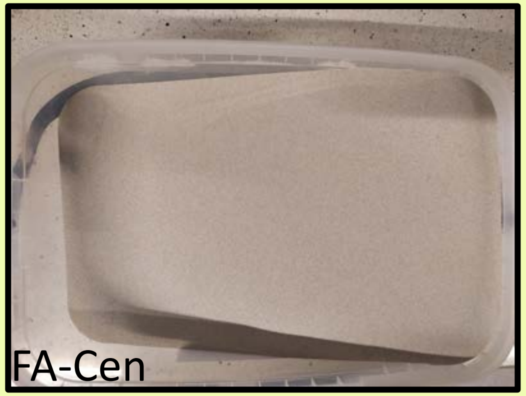
Functional characterization:

- DRIFT spectroscopy

Samples

The tested samples can be divided into 3 types: the first ones come directly from power plant electrostatic precipitator, the second ones were collected from fly ash warehouses, the third are commercial cenospheres with a specific grain size (150 µm).

The origin of the samples	Samples notation
Power plant	FA-Pp
Fly ash warehouses	FA-Mix
Comercial cenosheres	FA-Cen



Chemical composition

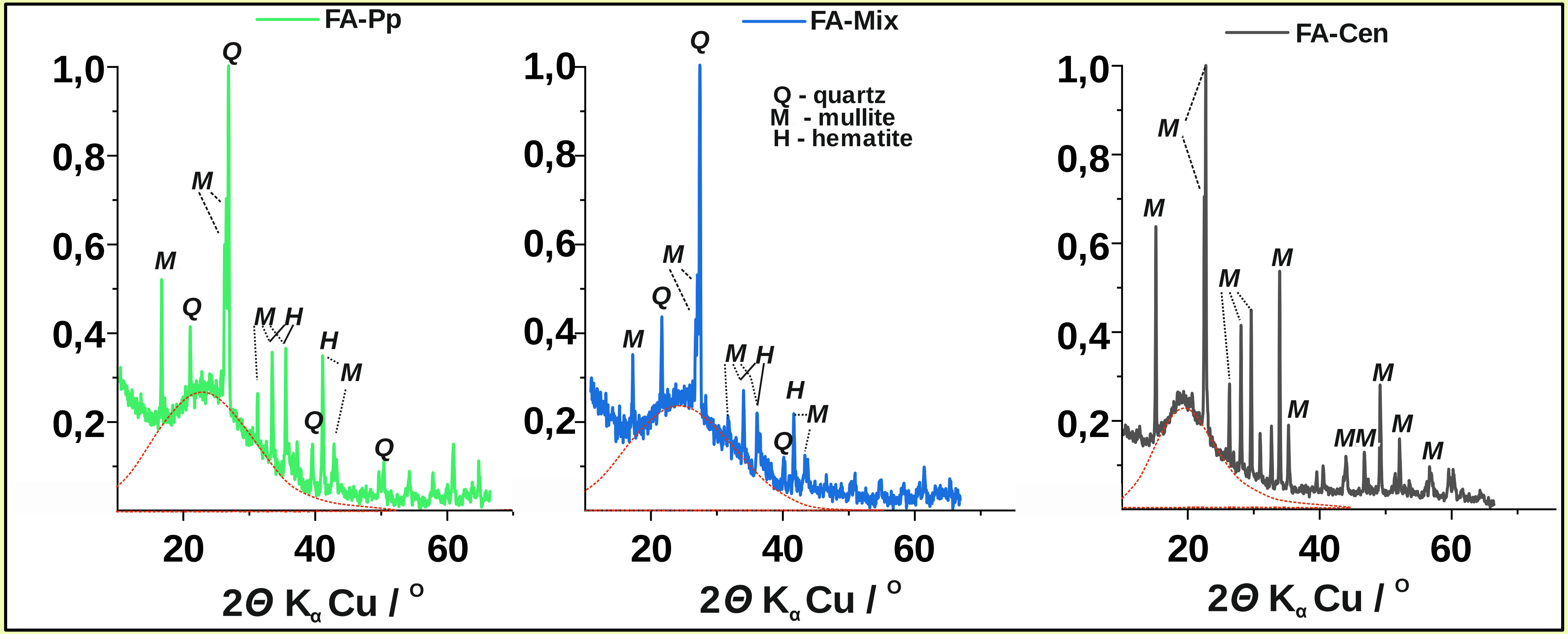
Component %wt	FA-Pp	FA-Mix	FA-Cen
SiO_2	53,4	49,1	55,0
Al_2O_3	16,9	29,4	34,0
Fe_2O_3	11,3	5,4	2,5
K_2O	3,9	2,5	0,9
CaO	3,9	2,5	2,5
MgO	3,7	2,2	1,1
TiO_2	1,5	1,1	1,7
LOI	5,4	4,0	4,5

Fly ash composition can be very variable.

The content of potentially valuable metals that can be recovery, such as iron or titanium, is particularly important.

The proportion of silicon and aluminum content is also important, which may determine the usefulness of ashes in the synthesis of zeolites.

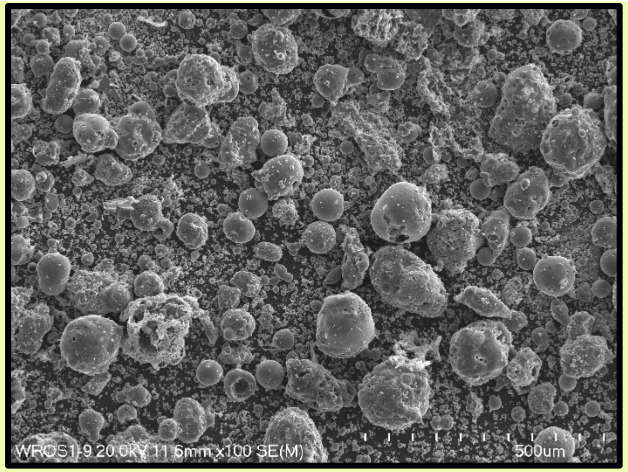
Mineral and phase composition

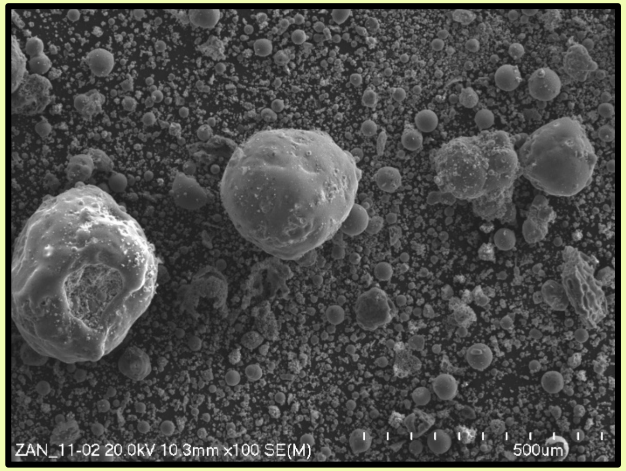


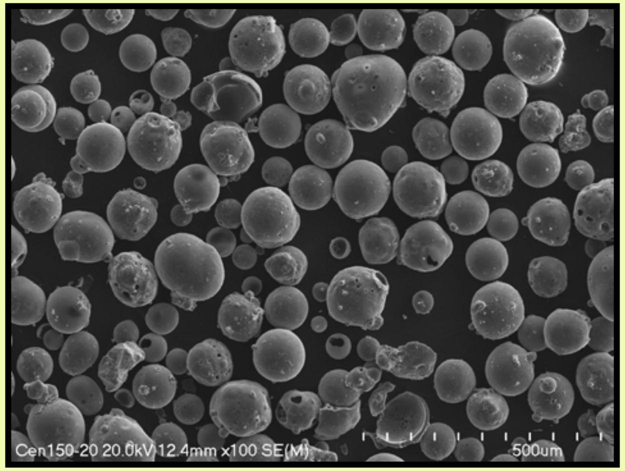
Relative intensity of signals for individual phases	FA-Pp	FA-Mix	FA-Cen
Quartz	0,52	0,59	0,00
Mullite	0,31	0,23	0,79
Amorphous glassy phase	0,18	0,18	0,21

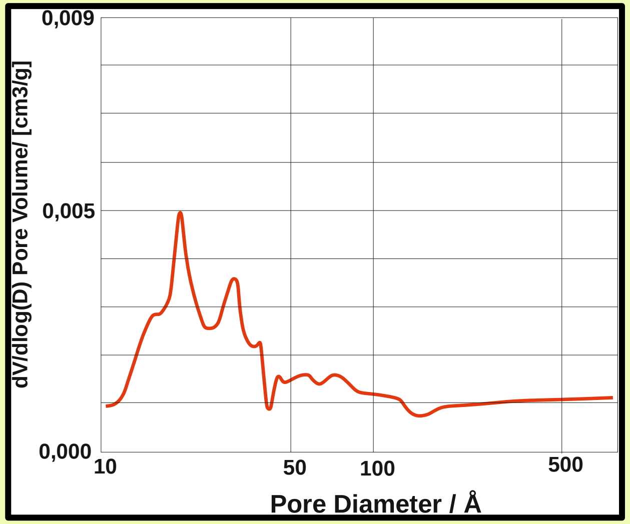
Textural properties

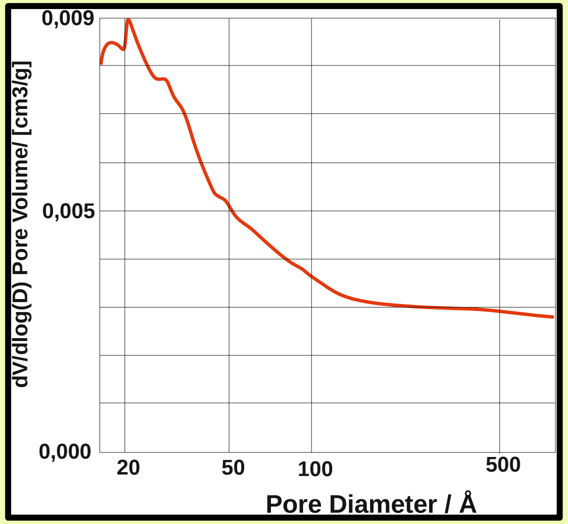
FA-Pp	FA-Mix	FA-Cen
Specific surface area / [m²/g]		
3,1	4,9	3,8

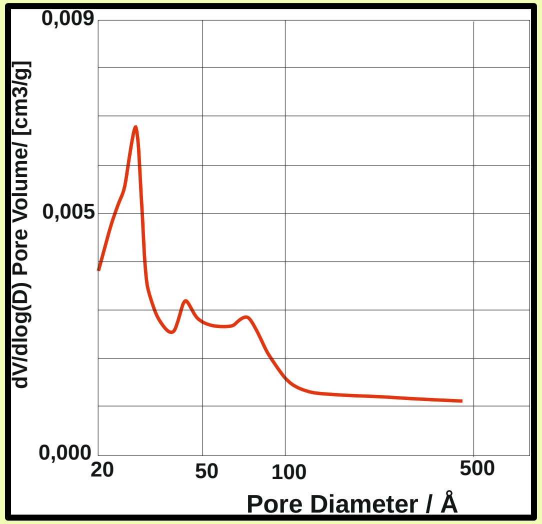




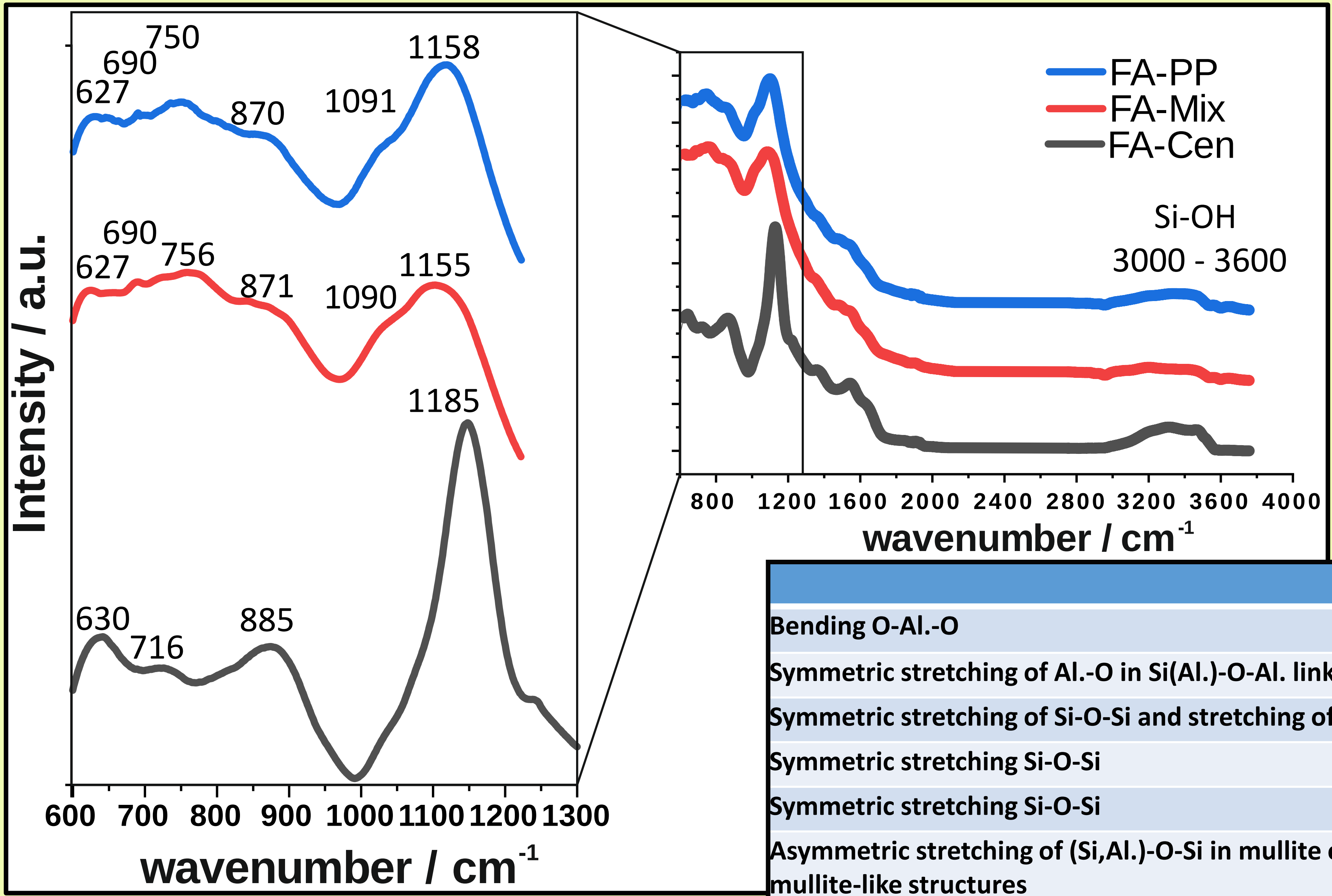








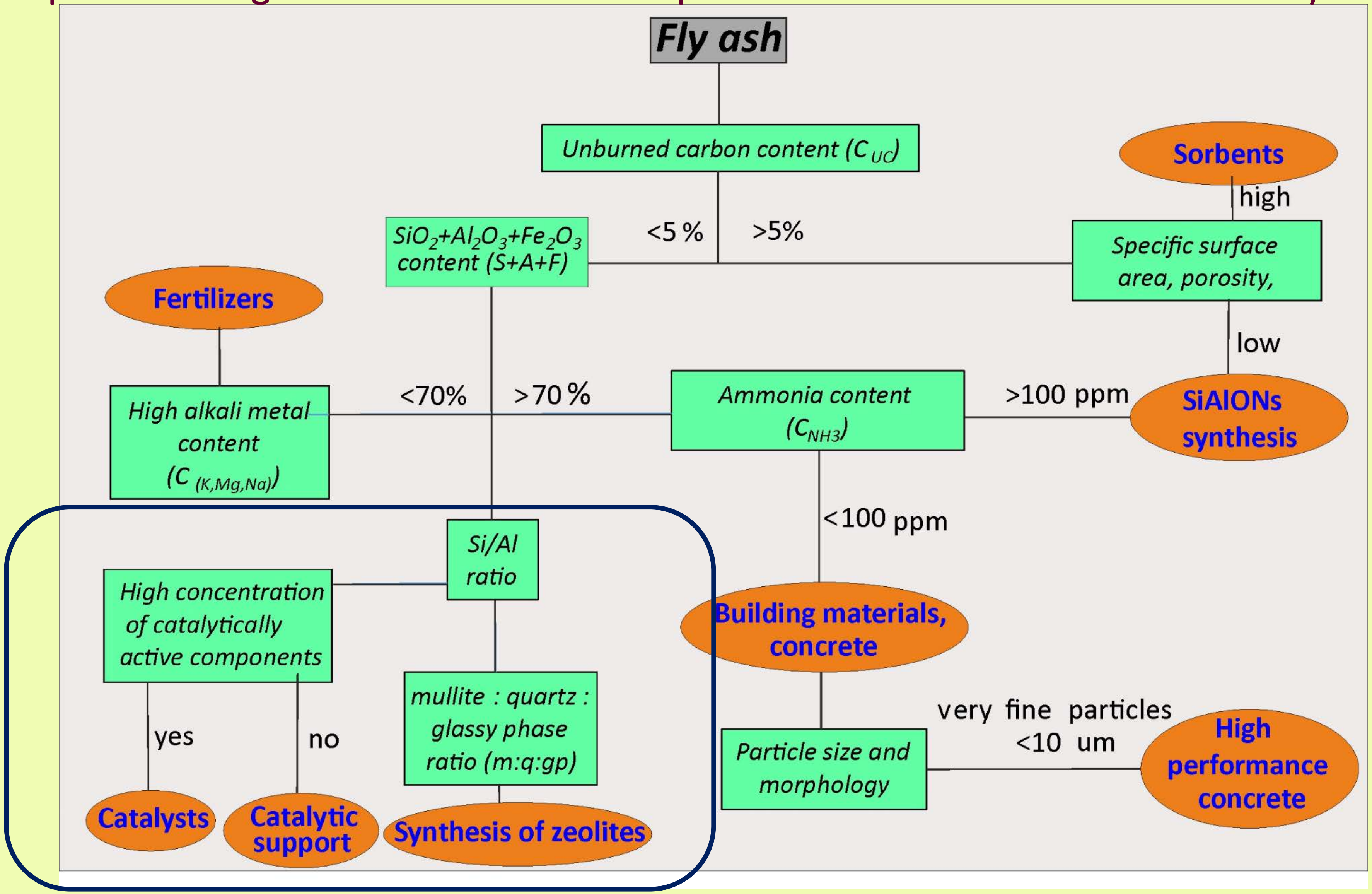
Functional characterization



	FA-PP	FA-Mix	FA-Cen
Bending O-Al.-O	627	627	630
Symmetric stretching of Al.-O in Si(Al.)-O-Al. linkages	690	690	-
Symmetric stretching of Si-O-Si and stretching of Al.-O	750	756	716
Symmetric stretching Si-O-Si	870	871	885
Symmetric stretching Si-O-Si	1091	1090	-
Asymmetric stretching of (Si,Al.)-O-Si in mullite or mullite-like structures	1158	1155	1185

Different routes of reuse of fly ashes

Operational algorithm to determine the preferential methods of utilization of fly ashes



P. Rybowicz, M. Mochnaczewski, M. Kozieł, Ł. Uruski, A. Łagosz, M. Michalik, L. Chmielarz, A. Adamski, Key Parameters of Fly Ashes Generated from the Industrial Energy Sector Decisive for Their Pro-ecological Applications, Energy & Fuels. 34 (2020) 6229–6238. https://doi.org/10.1021/acs.energyfuels.9b04426.

Crucial parameters for using fly ash as raw materials for dedicated advanced applications

Catalytic active materials

thermal resistance

morphology

acid sites on surface

specific surface area

SiO_2, Al_2O_3
as a catalytic support

Catalytic active metals
on surface

Zeolites synthesis

Si/Al. ratio

Relative content of crystalline(quartz, mullite)
and amorphous phase

Content of alkali metal

Conclusions

Fly ash is a by-product of fuel combustion. Annually, about 1 billion tons of them are produced. The largest producers are China and India.

The storage of fly ash is associated with costs and the risk of negative impact on the environment. Therefore, new methods of ash management and obtaining advanced functional materials are sought.

The presented results of research on the physicochemical properties of three types of ashes show possible differences in their parameters. Mainly in chemical composition, the content of individual crystalline phases (quartz, mullite) and differences in morphology.

Due to the diversity of fly ash properties, the selection of the optimal management path requires a thorough analysis.

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