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CO2 capture using zeolites from coal fly ash

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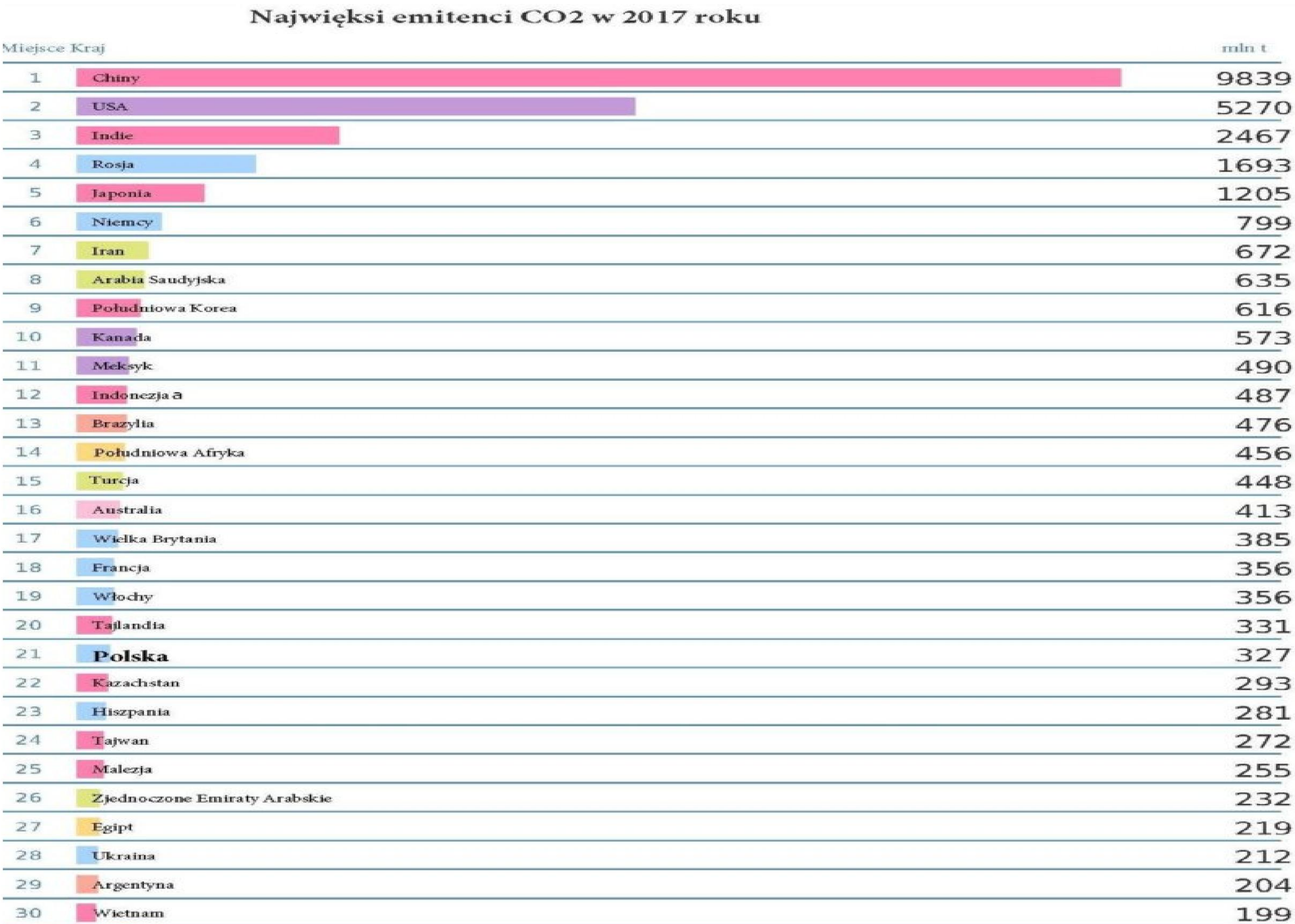
The content of the presentation

1. CO2 emissions in Poland
2. Production of coal ashes in Poland
3. Ways of managing ashes
4. Methods of synthesizing zeolites
5. X type zeolites as the most prospective for CO2 sorption
6. Characteristics of Na-X zeolites
7. Preliminary cost analysis

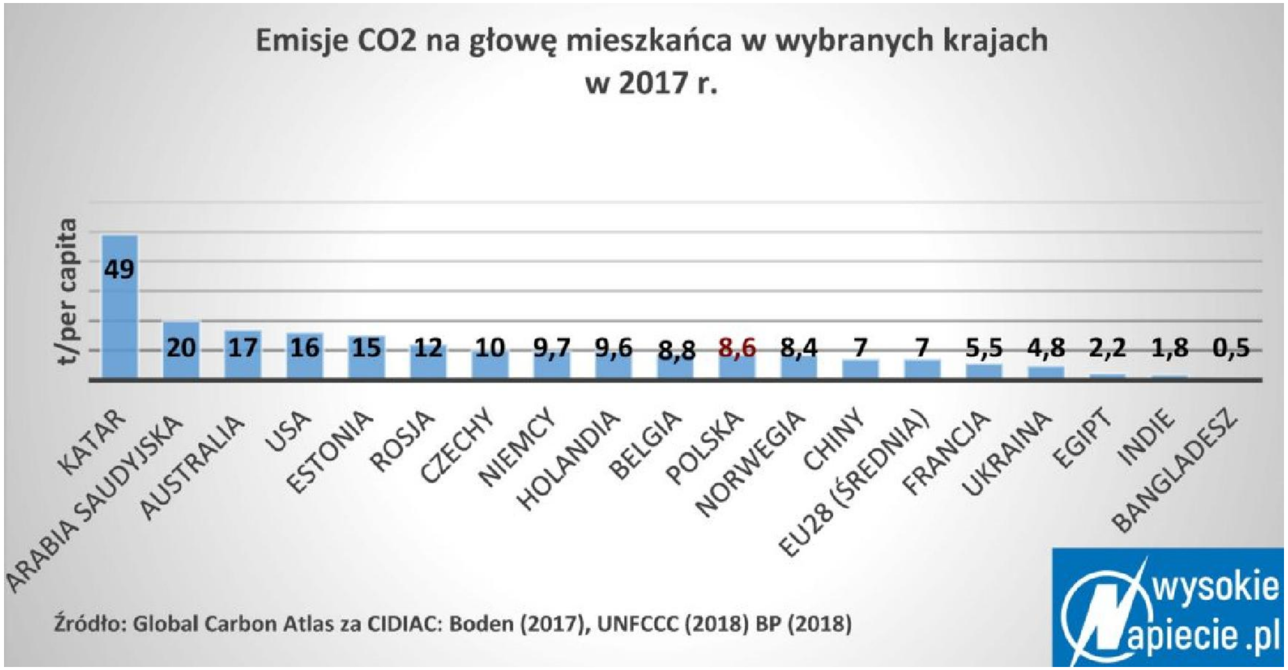
9. Evaluation of the possibility of implementing this method in Poland

Major emitters of CO2 in 2017



Źródło: Global Carbon Atlas, dane za CDIAC: Boden (2017), UNFCCC (2018), BP (2018)

CO2 emission per capita



Production of coal ashes in Poland

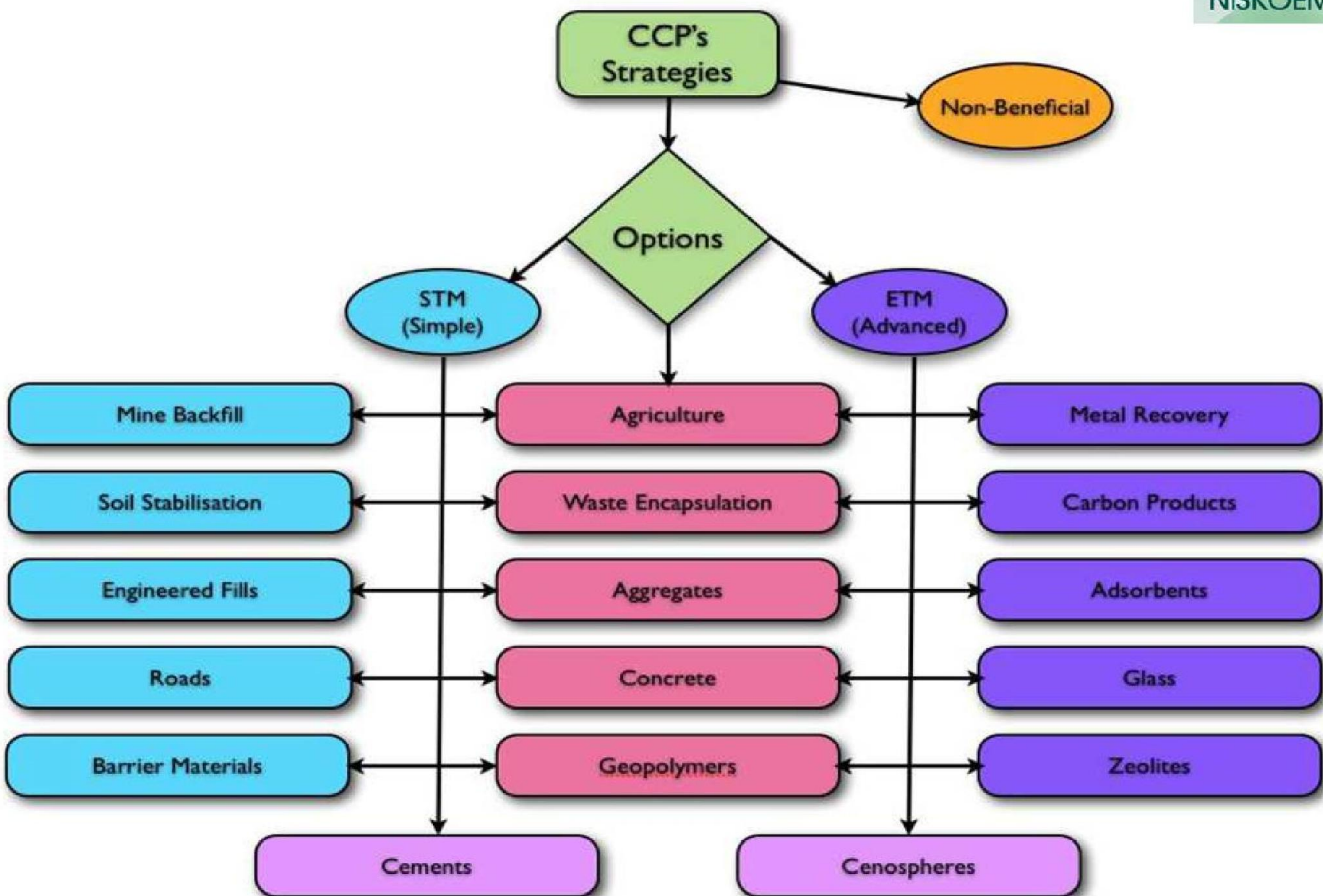
Utilisation and storage of the wastes from coal combustion is a large problem to the power industry.

- ~ 23 million tonnes of furnace wastes from coal were generated in Poland in 2016.
- Ash-and-slag mixtures had the largest share (65 per cent which accounts for 15 million tonnes).
- Fly-ashes from hard coal combustion (12 million tonnes) constitute the remaining part of the wastes.
- Currently furnace wastes are utilised in around 57 per cent.

Production of coal ashes in Poland

Power plant wastes (mainly ashes) as the coming from current production as the dumped ones may be a significant resource for zeolite production, which widens possibilities to utilise them. Utilisation of wastes as raw materials supports activities aimed at lithosphere protection, which is consistent with guidelines to balanced development.

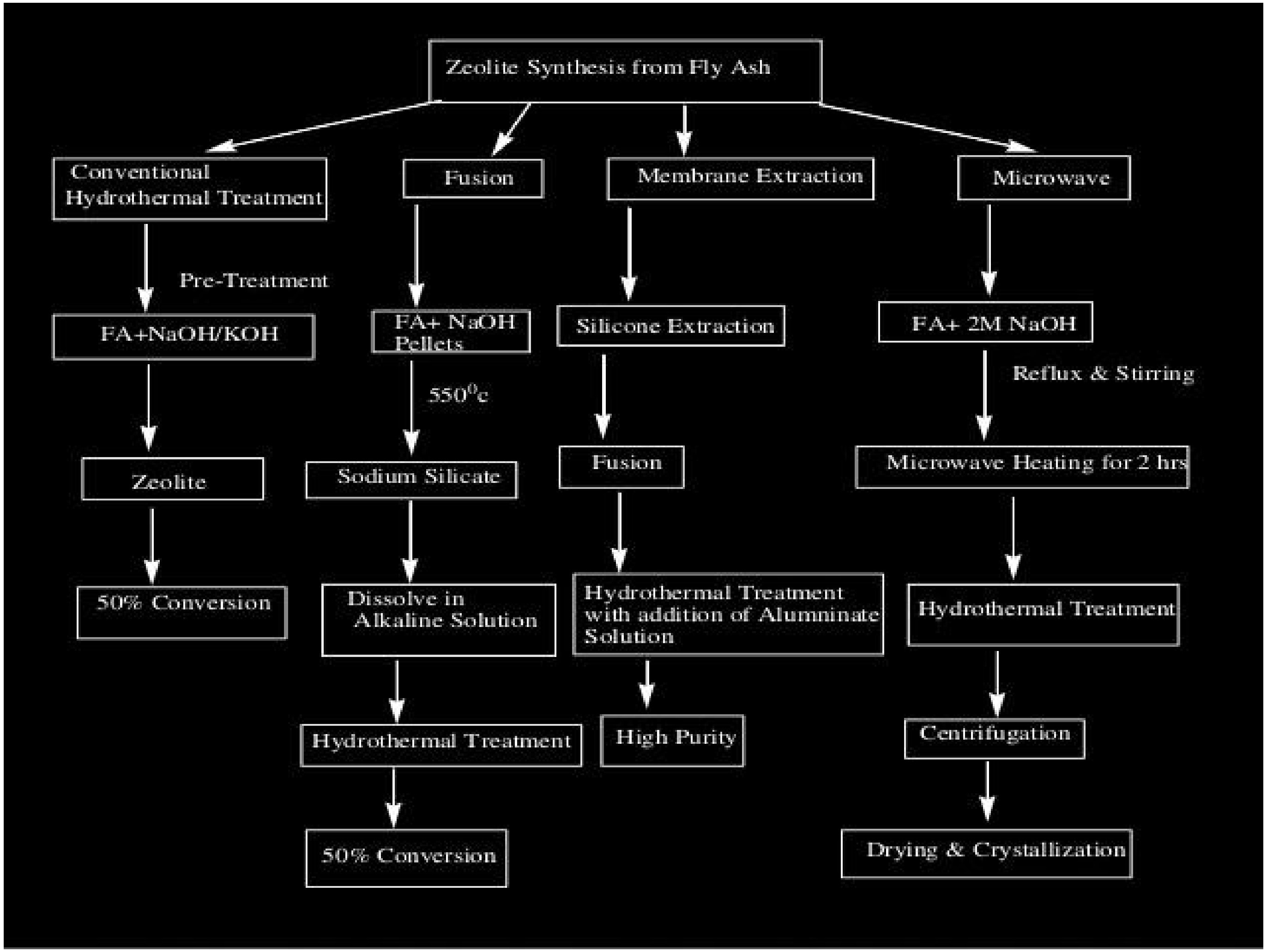
The ways of managing ashes

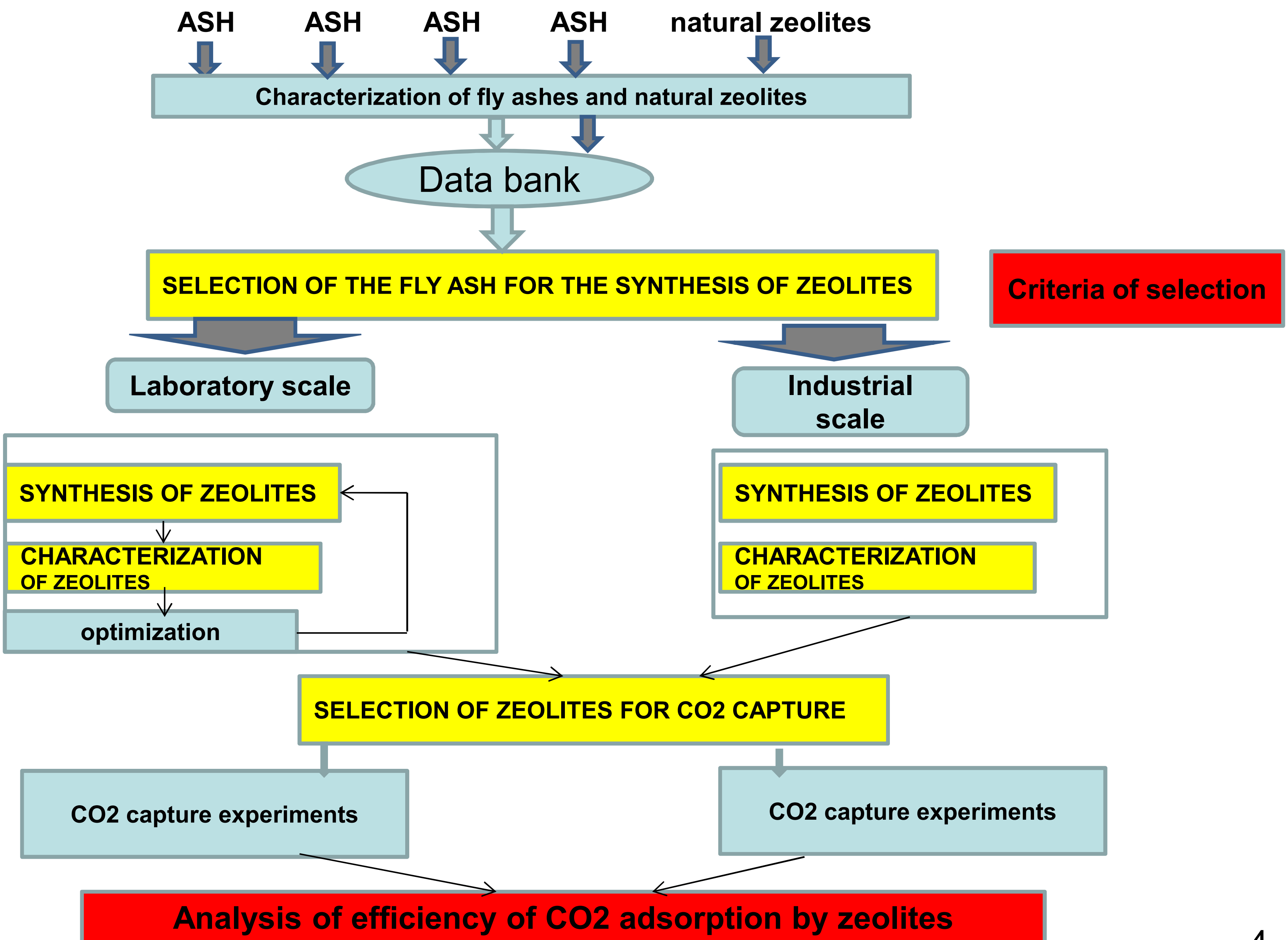


Zeolites

Zeolites are mostly hydrated aluminosilicates of alkaline elements, alkaline soils elements, or on rare occasions other cations. The very useful properties of zeolites (sorption, catalytic, molecular-sieve, ion exchange, and other properties) are the results of the specific structure of its aluminosilicate skeleton. This zeolitic structure comprises a system of channels and cavities, which are a result of sequential combining of alumino-silico-oxygen tetrahedra rings. These tetrahedra rings form so-called secondary building units (SBU), which are the most often used criteria for zeolite separation into different structural types.

The methods of synthesizing zeolites





ASH
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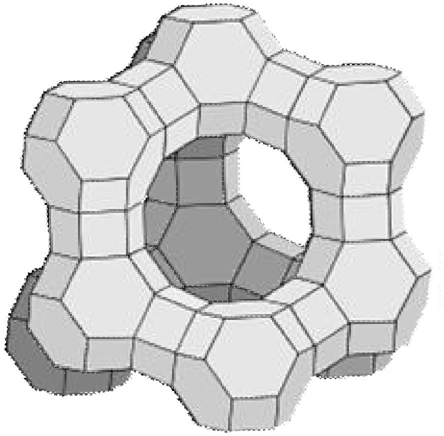
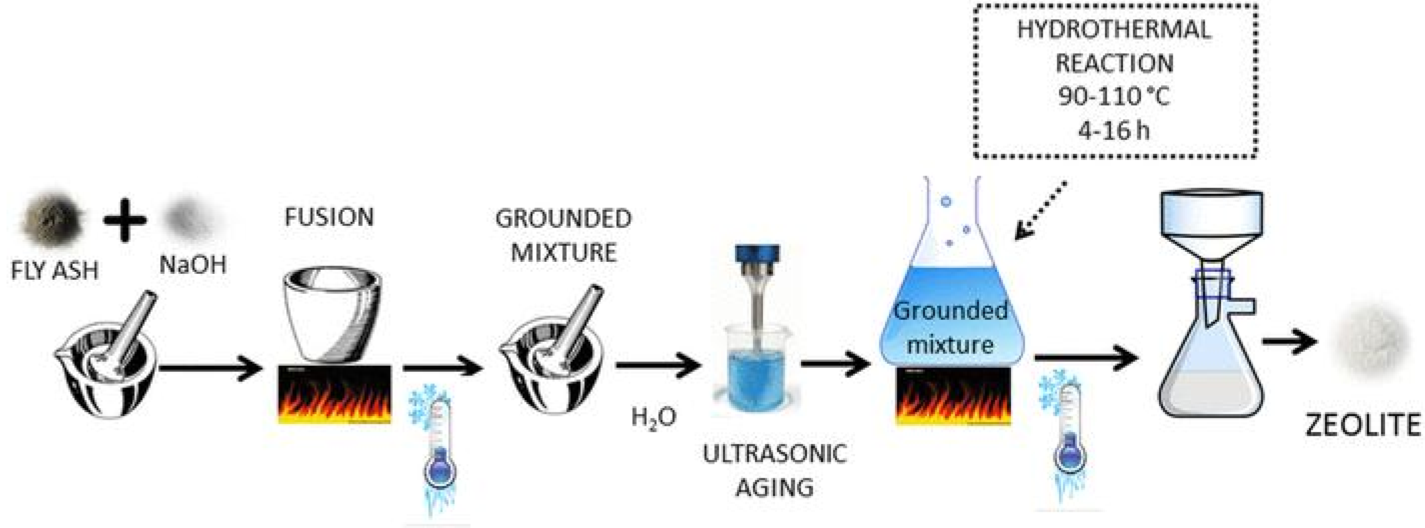
natural zeolites
Characterization of fly ashes and natural zeolites
Data bank
SELECTION OF THE FLY ASH FOR THE SYNTHESIS OF ZEOLITES
Criteria of selection
Laboratory scale
Industrial scale
SYNTHESIS OF ZEOLITES
CHARACTERIZATION OF ZEOLITES
optimization
SYNTHESIS OF ZEOLITES
CHARACTERIZATION OF ZEOLITES
SELECTION OF ZEOLITES FOR CO2 CAPTURE
CO2 capture experiments
CO2 capture experiments
Analysis of efficiency of CO2 adsorption by zeolites

X type zeolites as the most prospective for CO2 sorption

One of the most distinguished types of natural structural zeolites is fajausite (FAU), for which the synthetic analogue is Na-X zeolites (its commercial names: X and 13X).



The methods of synthesizing zeolites



X type zeolites as the most prospective for CO2 sorption

A large channel diameter 0.74 nm and high content of sodium is characteristic of this type of structure. That makes zeolites an attractive material used in industrial purposes as molecular sieves and ion exchangers.

Zeolitic material (rich in Na-X phase), because of the presence of micropores and their large volume as well as high thermostability, may be useful for adsorption of industrial gases. Previous studies have confirmed the high adsorption of CO2 on Na-X zeolites synthetisized from fly ash.

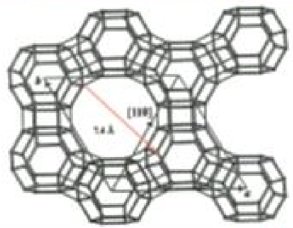
ZEOLITES DATA SHEET

ID	**ZS1**
Type of zeolites	**Na-X**

Synthesis conditions

Material: fly ash (sample ID), Kozienice Power Station
Synthesis method: hydrothermal
Process parameter: mass of fly ash 20 g; reactant volume 0,5 dm^3 NaOH 3M; reaction time 24 h; temperature 80°C
Sample preparation: wash with water, drying (105°C, 12 h)

Structure

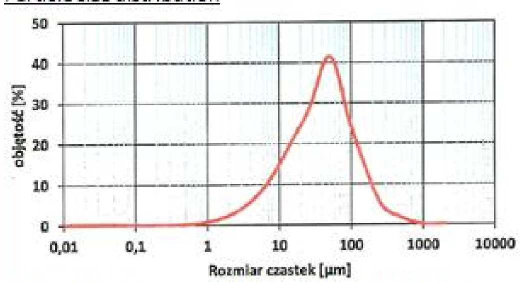


RESULTS

Physical properties

Density: 2 ,535 g/cm^3
Apparent density: 1,913 g/cm^3
Bulk density: 0,472 g/cm^3

Particle size distribution

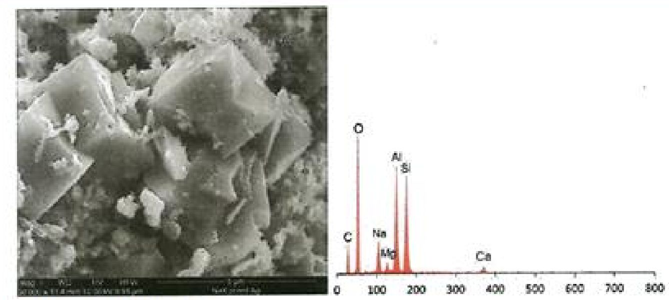


The particle size test covers the range: 0,5-1000 µm
Average particle size is 75,5 µm

Chemical composition

Oxide	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
%wt.	34,50	1,63	19,75	6,62	11,69	2,17
Oxide	**K_2O**	**Na_2O**	**P_2O_5**	**C**	**LOI**	
%wt.	0,54	6,23	0,82	7,08	15,61	

Morphology and microstructure



Composition relations:
(Na+K)/Si= 0,57
(Na+K+Ca+Mg)/Si= 0,59
(Na+K)/Al = 0,66
(Na+K+Ca+Mg)/Al = 0,78
Si/Al =1,14

Mineral composition

63% zeolite
Unreacted mineral phases: mullite, quartz,

Textural properties

Textural parameters of material determined on the basis of mercury porosimetry MIP

V_{int} (cm^3/g)	S (m^2/g)	D_p (µm)	P (%)
1,384	80,236	0,035	75,33

Textural parameters of material determined on the basis of adsorption / desorption isotherm of nitrogen

S_{BET} (m^2/g)	S_{mic} (m^2/g)	S_{ext} (m^2/g)	V_{mic} (cm^3/g)	V_{tot} (cm^3/g)	D_{av} (Å)
94,49	10,63	83,86	0,005	0,240	103,27

V_{int} – total intrusion volume,
S – total surface area,
D_p – average pore radius (2V/A),
P – porosity,
S_{BET} – specific surface area,
V_{tot} – total pore volume,
S_{mic} – micropore surface,
S_{ext} – external surface,
V_{mic} – micropore volume,
D_{av} – average pore diameter.

Preliminary cost analysis

1. The research included searching for zeolite with high CO2 absorption capacity and high chemical stability.
2. In the carried out studies, the hydrothermal reaction of fly ash with sodium hydroxide gave the Na-X mesoporous material.
3. According to preliminary calculations, it allows the recovery of about 80% of the CO2 emitted.
4. The production costs on a semi-technical scale of Na-X material mainly include energy and material inputs. They were calculated on the basis of syntheses carried out by the authors. The cost of production of mesoporous material from fly ash (1kg) is:

   - about 5.70 PLN (hydrothermal reaction)
   - 6.90 PLN (hydrothermal reaction with fusion).

Conclusions

- The aim of this study was to present the possibility of using fly ash for the production of synthetic zeolites. In comparison with the natural zeolites, synthetic zeolites may be a more promising mineral sorbent for use in environmental engineering and protection because have a well-defined channel size for the removal CO2.

- The synthesis reactions that were carried out have shown that, depending on the synthesis conditions of the process (i.e., NaOH concentration and reaction temperature), several types of zeolites with different channel system sizes can be obtained. From laboratory work, we obtained three types of synthetic zeolite materials: Na-X , Na-P1 and sodalite .

Conclusions

- We compared the properties and characteristics of the zeolitic material to assess which synthesis reaction was most effective. The zeolites obtained seem to be most promising in their practical application as a mineral sorbent.
- Mineralogical analysis indicated that this type of laboratory scale reaction yielded a high percentage (>70 wt%) of a particular zeolite in relation to the residue.
- Analysis of the textural parameters showed that Na-X displayed the best properties with a surface area of 166 m2 · g−1, the ion exchange capacities 1.8,meq · g−1.
- The production and use the zeolites from fly ashes must be economically rational.

Thank you for your attention