COALBYPRO

Effective methods for managing coal by-products towards CO_2 emissions reduction

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Coal fly ash and CO_2 reducing applications - Workshop
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The idea behind...

- An important **goal** of the EU: significant reduction of the CO_2 footprint
- The biggest issue of the big industries, is the cost of capturing the CO_2

Carbonation employs a reaction of carbon dioxide with metal oxides (usually those of Ca and Mg), and mimics the naturally occurring process of rock weathering.

Mineral carbonation of waste materials provides a promising method for CO_2 capture, due to its potential as a finishing step in industries which produce **CO_2** and **alkaline solid by-products**.

The idea of using mineral carbonation to bind CO_2 was first proposed back in the 90s. Since then there has been a lot of research around it.

Why…

(a) Carbonation products ($CaCO_3$ or $MgCO_3$) are thermodynamically stable under ambient conditions

(b) Great sequestration capacity due to the high availability of deposits

(c) No transport at sites is required $\rightarrow$ cost-effective

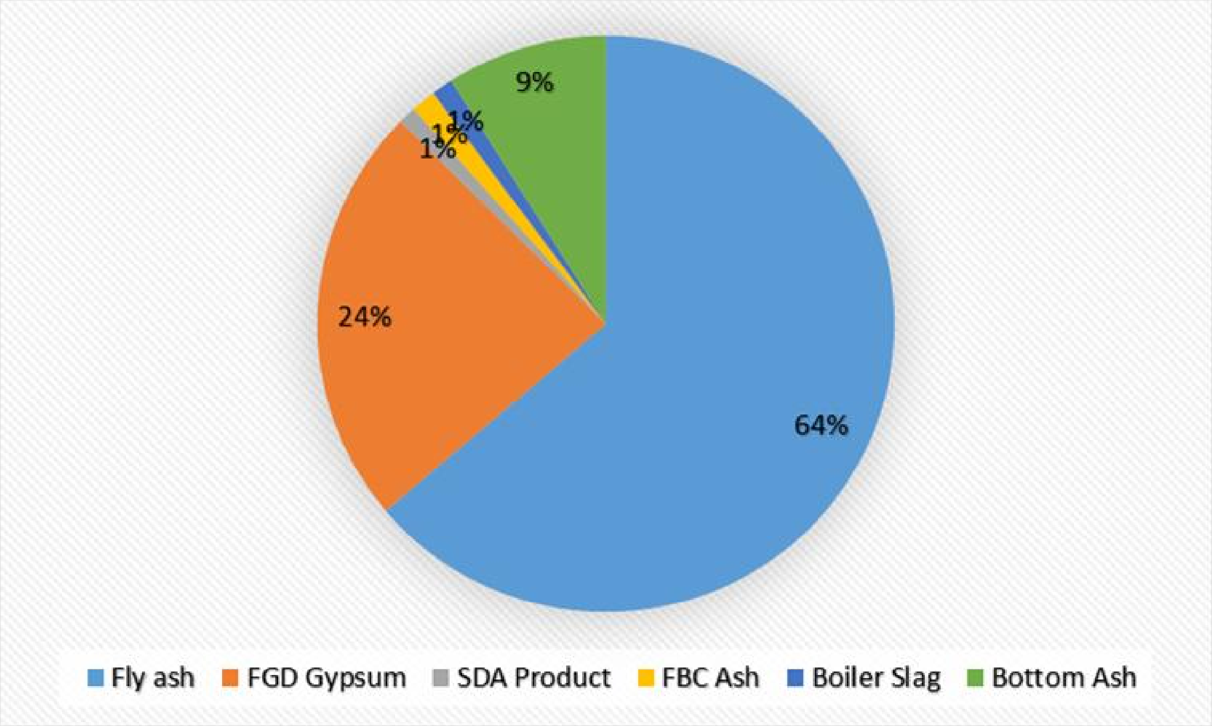
(d) Products may be beneficially reused in a variety of applications

(e) Decreased leaching of heavy metal trace elements such as Pb, Ni, and Cd from residues and stabilizing of the waste leading to an improvement of environmental quality

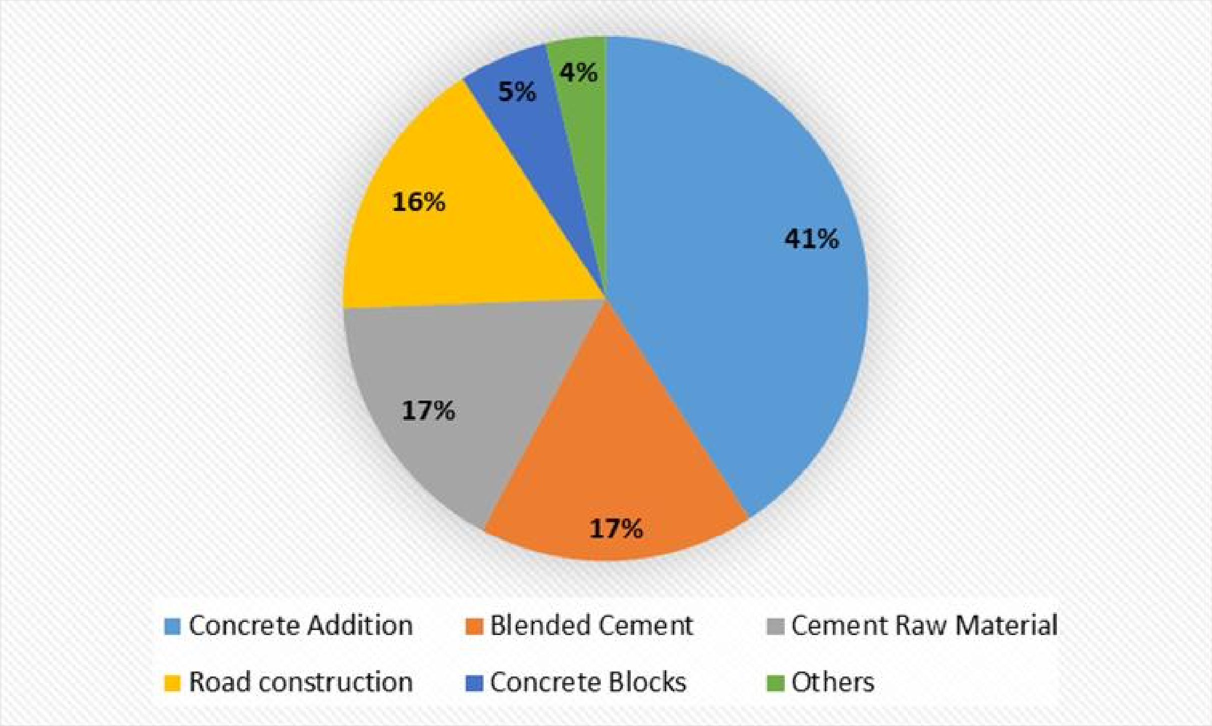
Fly ash in general…

- Current chemical absorption technologies are very energy intensive.
- Physical and chemical adsorption processes for CO_2 capture using high-surface area solids have also been proposed.
- The sorbents used thus far are very expensive and hinder the economical viability of the process.
- There is a need to find cost-effective precursors that can compete with expensive commercial sorbents.
- Use of coal combustion by-products, like Ca containing ashes, can be very progressive approach from an economical point of view

Fly ash in general…



Production of CCPs in Europe (EU15) in 2016. Total production: 40 million tonnes (http://www.ecoba.com/ecobaccputil.html)



Utilisation of Fly Ash in the construction industry and underground mining in Europe (EU15) in 2016. Total utilisation: 11,4 million tonnes (http://www.ecoba.com/ecobaccputil.html)

utilization ratio remains less than 30% of the total generated amount in terms of the worldwide production

The procedure…

Sampling of fly ash → Laboratory analyses

Determination of sorption properties

Synthesis of zeolites

Determination of sorption properties

Verification of parameters in the pilot unit

Innovation and added value

Added value of the project:

- Chemical sorption of CO_2 in the materials in high temperature
- Structural bonding of CO_2 in the zeolites
- 2 particle size scales will be tested: powder and pellets
- Industrial scale experiments
- Use of the carbonated end product for the environmental management of the coal/ lignite mine
- the cost of CO_2 transport in the storage site is eliminated

Applicable in Europe and internationally.
The company that operates the power plant or the mine can benefit as it compensates the expenses of the mineralisation process.

CO_2 capture in fly ash

Fly ash contains high content of alkali components, such as Ca, Mg, Na and K that are essential for the mineral carbonation.

Important characteristics of fly ash for CO2 capture are:

- porosity
- relatively high surface area and
- reactivity

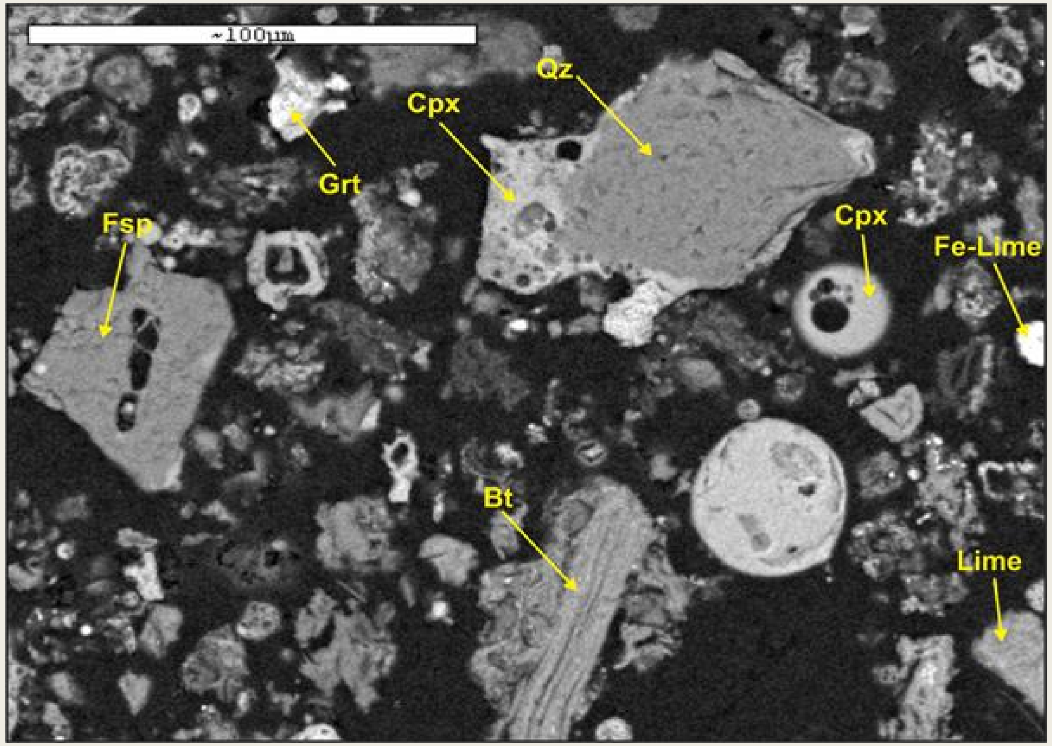


Image from a fly ash samples after the SEM/EDS analysis

CO_2 capture in fly ash

1st Step: Laboratory tests

- Preliminary sorption properties of the samples,
- determination of the ratio between the contribution of physical sorption and chemisorption of carbon dioxide
- Use of in-house constructed fixed bed reactor testing CO_2 sorption
- This laboratory apparatus enables determination of sorption capacities using dynamic method of measuring breakthrough curves at defined gas flow.

CO_2 capture in fly ash

2[nd] Step: Simulation of real conditions

- fluidised bed reactor for simulation of the real conditions,
- similar to industrial-scale high temperature CO_2 sorption systems.
- gas circulation at low pressure near the atmospheric conditions.

CO_2 capture in fly ash

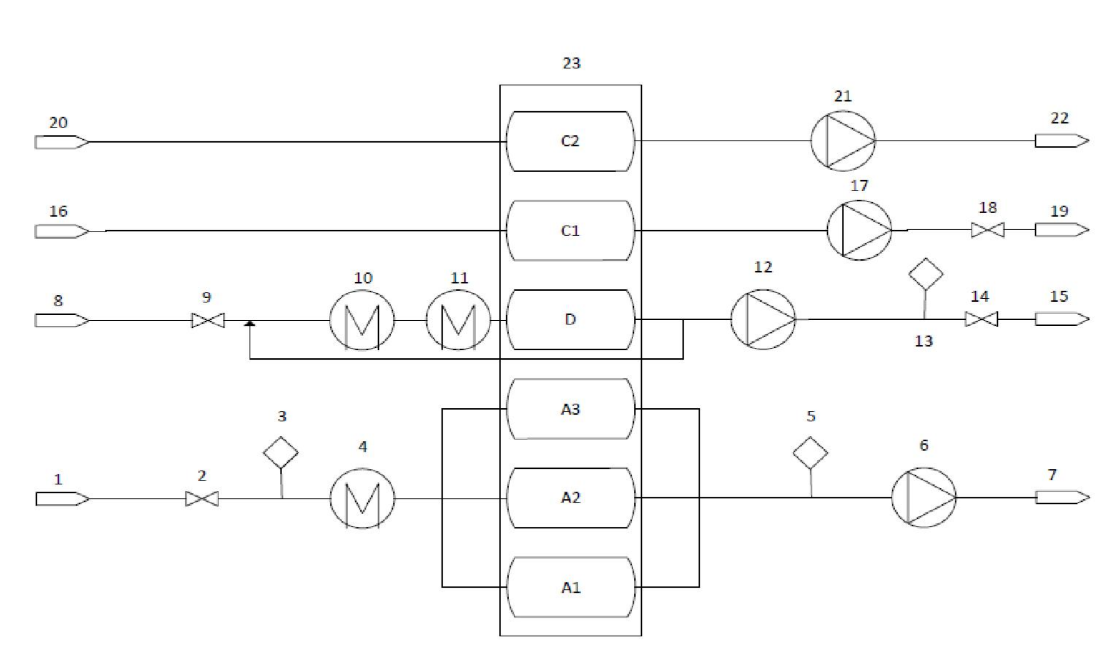
3rd Step: Experimental testing on the industrial unit

- The main purpose of the PSEA is testing of solid sorbents (materials) for CO_2 capture from flue gas.
- The unit is not usable for the wet-based process.
- Modification (impregnation) of adsorbent is necessary. From powder to pellets
- These tests will provide information about the kinetics of competitive reaction of SO_2 and its influence on the process of CO_2 carbonation
- testing of sorption on fly ashes the regenerative adsorption-desorption regime is not estimated.
- Flue gas feeding for this pilot scale unit is taken directly from the main duct of the energetic block before the FGD unit. Therefore the flue gas pre-treatment includes its own separation of NOx, SO_2 and SO_3.

CO_2 capture in fly ash

4th Step: Long-term experimental testing on the industrial unit

- A set of repeating tests to achieve the corresponding reliable trusted data about the sorption capacity for CO_2 capture
- Use of the industrial PSEA unit in CEZ power station
- Granulated samples will be used
- Duration of the experiments: 1 month each sample



A columns: adsorption, D column: desorption, C columns: two-stage cooling

CO_2 capture in zeolites

Zeolites: porous crystalline allumino-silicate minerals

- Si/Al ratio of fly ash, which should be between 2 and 3

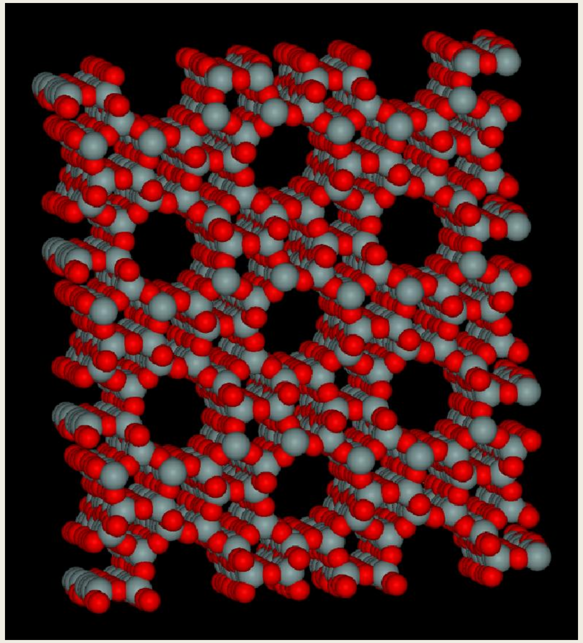
In favour of:

- Large pore volume
- High adsorption capacity
- High ion-exchange capacity and
- Selectivity for polar molecules

The adsorption and gas separation properties of zeolites are heavily dependent on:

- size
- charge density
- distribution of cations (e.g. Na^+, K^+, Ca^{2+}, Mg^{2+}) in the porous structure

Structures to be tested: Na-X and Na-P1



Structure of zeolite

CO_2 capture in zeolites

Experimental procedure and CO_2 capture experiments:

1) selection of the most appropriate zeolites for the CO_2 capture - (natural and synthetic zeolites)
2) measurement of CO_2 adsorption in natural zeolites in laboratory scale
3) measurement of CO_2 adsorption in synthetic zeolites in laboratory scale
4) measurement of CO_2 adsorption in zeolites in industrial scale
5) structural, textural, phase and chemical analysis of zeolites after CO_2 capture

For the lab and industrial testing the prepared zeolite samples need to be modified again in the form of granules or pellets.

Environmental management of the carbonated products

Use of carbonated products:

- mine backfilling as it happens with the fly ash. Advantages:
  - ➢ increase of structural stability of the mine
  - ➢ prevention of land subsidence
  - ➢ suppression of mine fires and the reduction of acid mine drainage due to the alkalinity of the carbonates
- fertilizers in restored sites of mine fields

Innovative aspect:

- Management of the carbonated products
- Examine the possibility of leaching of the elements due to intense acidic conditions

Environmental management of the carbonated products

Conduct a Cost Benefit Analysis (CBA) for the sustainability of the procedures

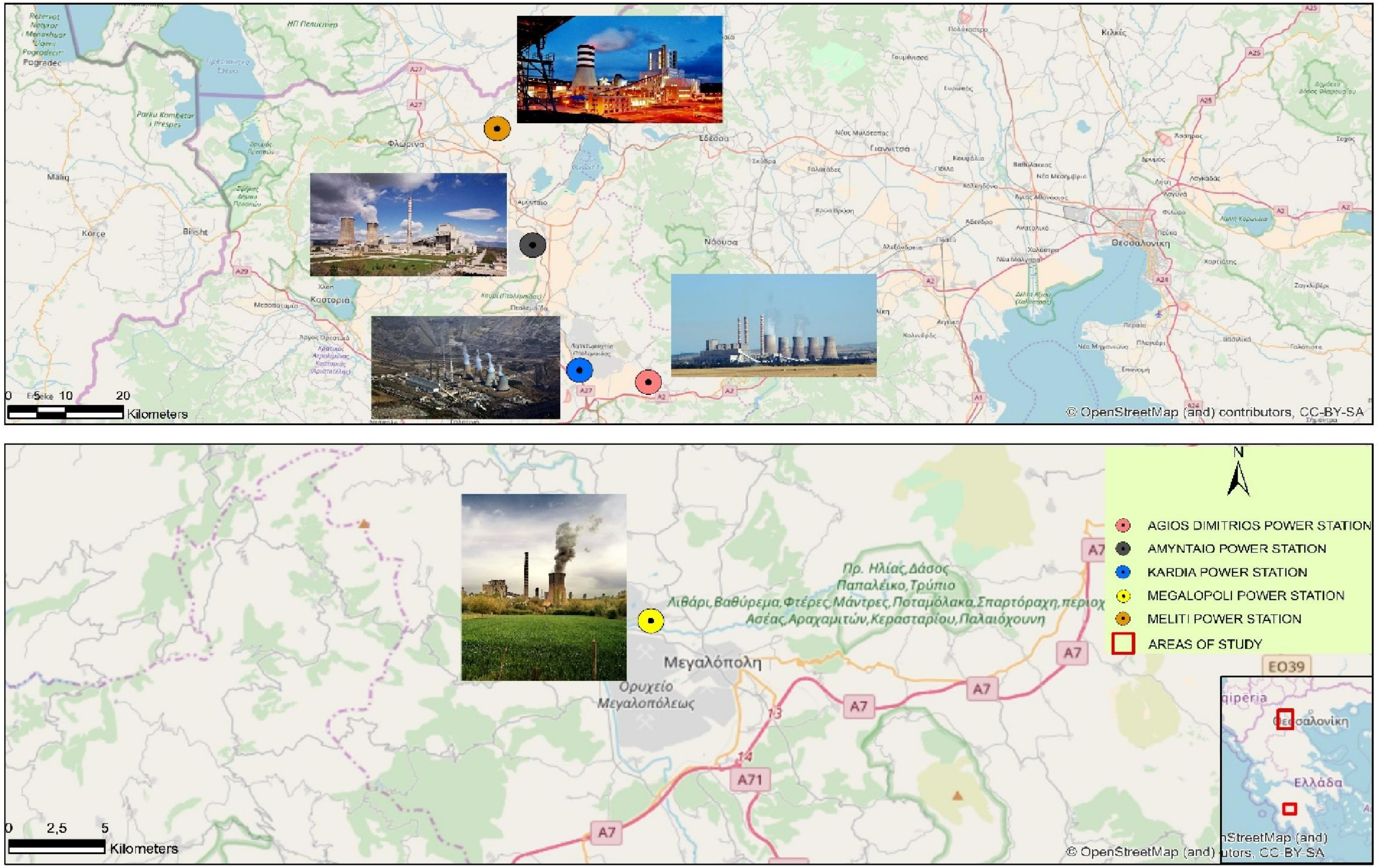
Using coal combustion products (CCPs) in an environmentally safe manner reduces energy consumption, saves virgin resources, and lessens greenhouse gas emissions

Current green building practices encourage using recycled materials such as coal ash and other industrial by-products

The parameters that will be considered are:

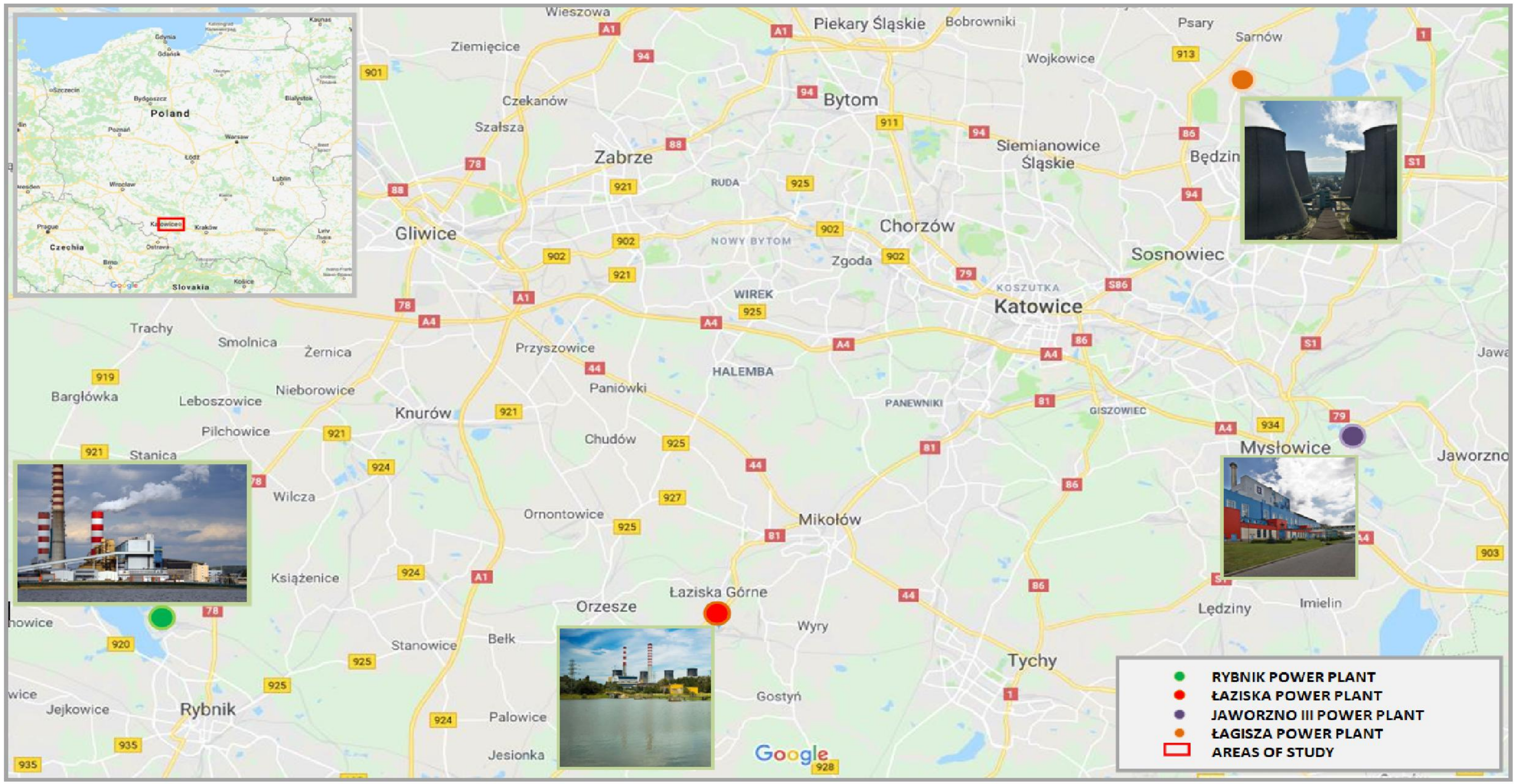
- Energy consumption/ saving
- Reduction of GHG emissions
- Avoiding land filling of fly ash

Initial work…



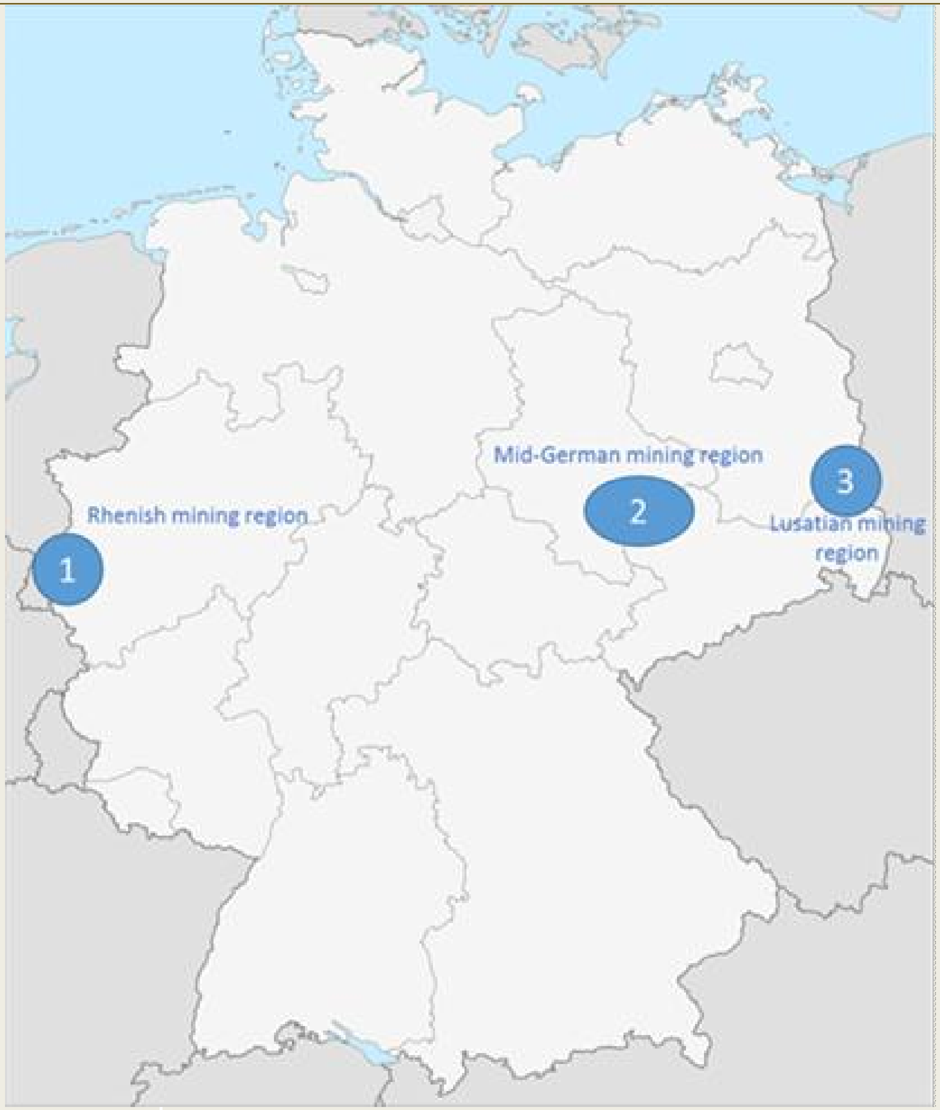
Sampling areas of the selected **Greek** fly ashes

Initial work…



Sampling areas of the selected **Polish** fly ashes

Initial work…



Overview of the **German** mining and sampling regions

Initial work…

	Greek FA	Polish FA	Czech FA	German FA
# samples	23	10	20	7
Parameters measured				
CHNS	√			
BET surface area	√	√	√	√
Total pore volume	√	√	√	√
Porosity	√			√
PSD	√	√	√	√
Major & trace elements	√	√	√	√
Mineralogy	√	√		√
SEM	√	√		

THANK YOU

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