Zeolite development from fly ash and utilization in lignite mine-water treatment

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Introduction

Background

- Over 10 Mtn lignite fly ash produced annually in Greece;
- Composition: Mainly Class C (ASTM C618);
- No more than 10% of the total FA output is industrially utilized, the rest is dumped;
- Rep. Kazakhstan: major coal producer and consumer –coal properties similar to Greek lignite;
- Overall target: To establish a new utilization path for Greek FA --Knowledge transfer to NU and the emerging market of Kazakhstan.

Research Interests & Targets

- Development & characterization of novel, zeolite-based sorbents for coal mine-water treatment;
- Material to be field-tested in Upper Silesia, Poland (*MANAGER* RFCS 2013 Project) and compared with a basket of potential m-w sorbents, incl. biofilms; algae; and phosphate gel.

Current Research Highlights

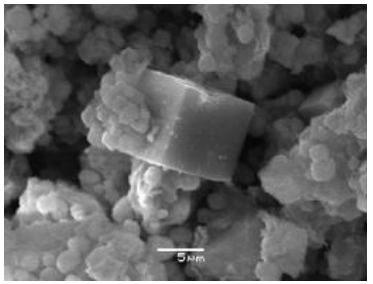
- Fly ash has been modified to zeolite with largely upgraded surface properties;
- Phillipsite and thomsonite-like minerals were the main zeolitic crystals developed;
- The products totally & quickly removed Cr, Cu and Pb from artificial aqueous media;
- Sorbent effectiveness was verified by treating actual lignite mine-waters.

Introduction

Coal-fired power plant

Coal fly ash

Hydrothermal activation



Zeolites (Na & K)

Product Development

K-fertilizer

Industrial Wastewater Treatment

Agriculture

Materials & Methods

FA Sampling & Zeolite Development

- FA samples collected from the ESP's of Megalopolis (850 MW) and Meliti (330 MW) power stations;
- MG-FA and MT-FA samples underwent alkaline hydrothermal treatment at 90°C, using 1 L NaOH 1M per 50 g FA;
- Incubation period set at 24 h and mixing took place at 150 rpm;
- Filtering and then drying at 40°C for 24 h. Leaching with water until no NaOH was detected.

Material characterization

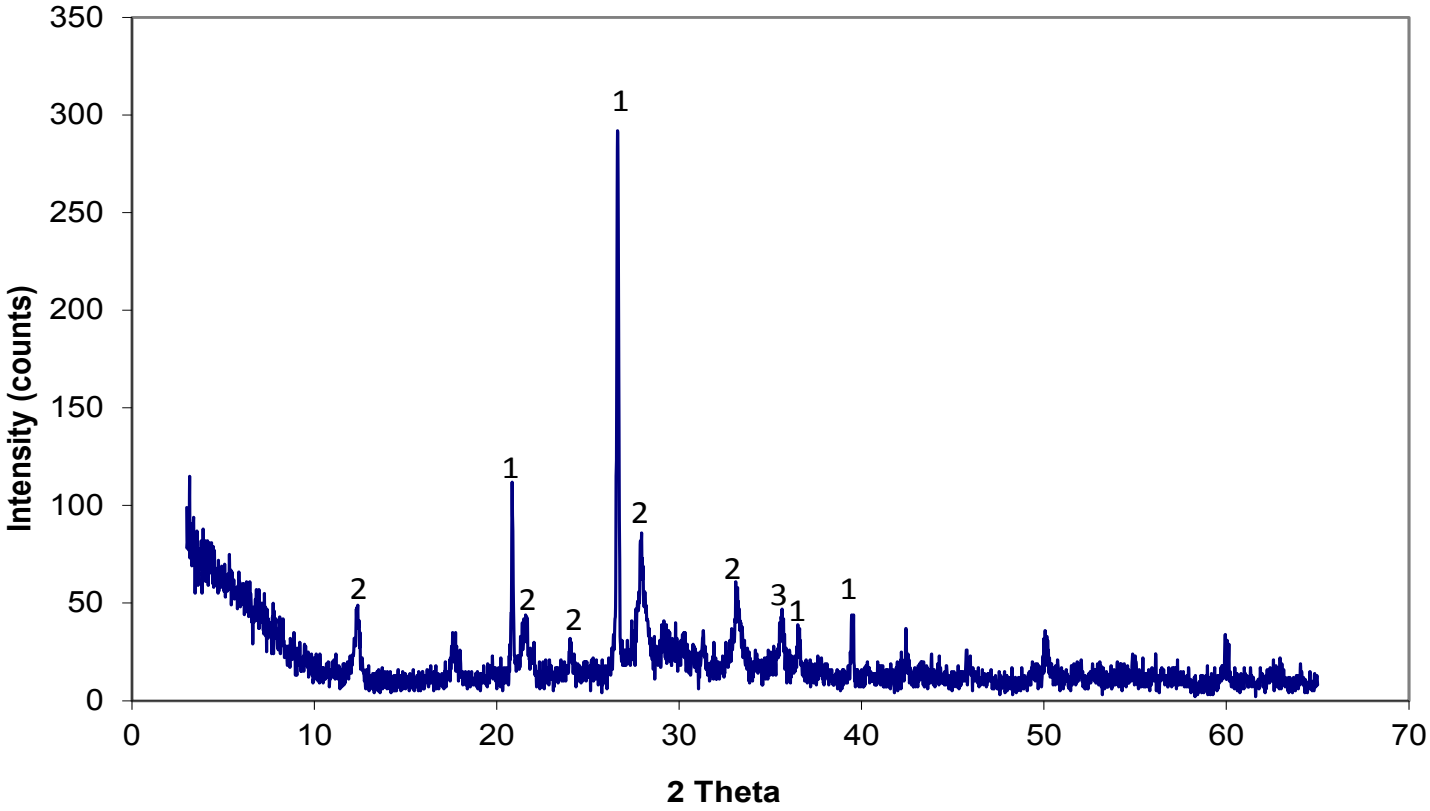
- XRD; AAS; EDS-SEM; PSD determination; N_2-porosimetry.

Heavy metal uptake testing

- Aqueous solution of about 1000 mg / L (each) of Cr, Cu, Ni, Pb, Zn and 20 mg/L Cd was prepared;
- Filling a series of glass tubes with 50 ml of solution, adding 1 g of each zeolitic material and then implementing mechanical stirring at 200 rpm for 2 h;
- Supernatant solution filtered and subjected to: a) GFAAS for the determination of the remaining concentration of Cr (total), Cu, Ni, Cd and Pb and b) FAAS for Zn;
- Field mine-water testing: rep. samples collected from 2 sampling points (A & B) in the Southern Field of the West Macedonia Lignite Centre in West Macedonia, Greece.
- Adsorption tests with mine-water samples have been designed and executed identically to the artificial aqueous solution.

Results -Mineralogy

X-Ray Diffractogram –MG Zeolitic Product

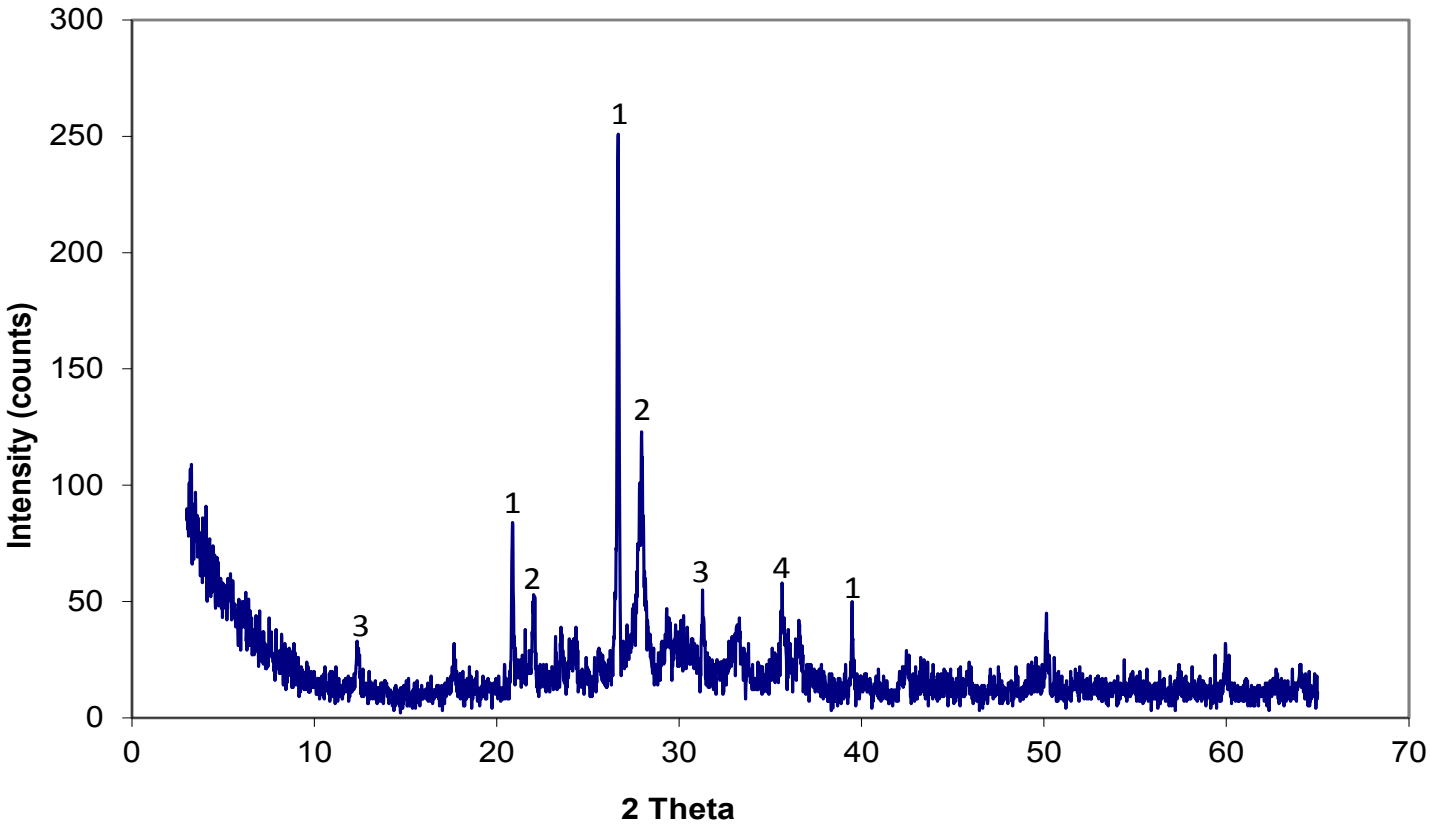


1: Quartz (SiO_2);

2: Phillipsite ($(Ca,Na_2,K_2)3Al_6Si_{10}O_{32}\cdot 12H_2O$; 3: Hematite ($Fe_2O_3$)

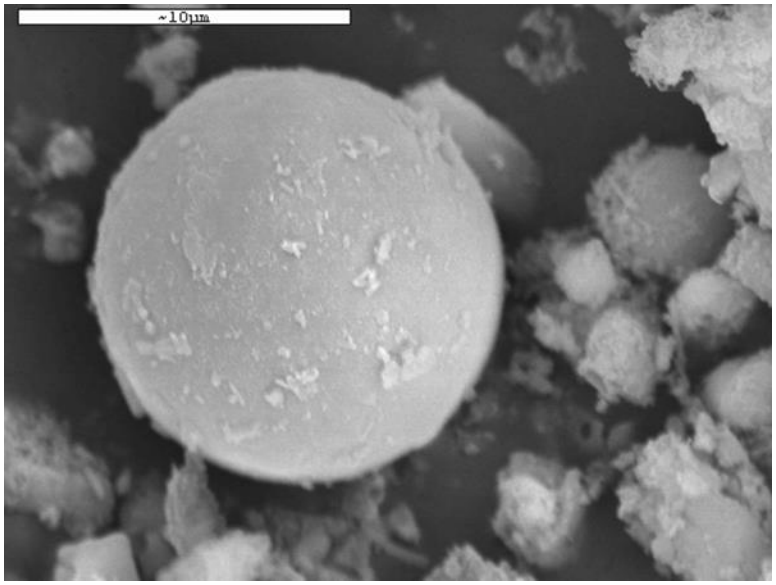
Results -Mineralogy

X-Ray Diffractogram –MT Zeolitic Product

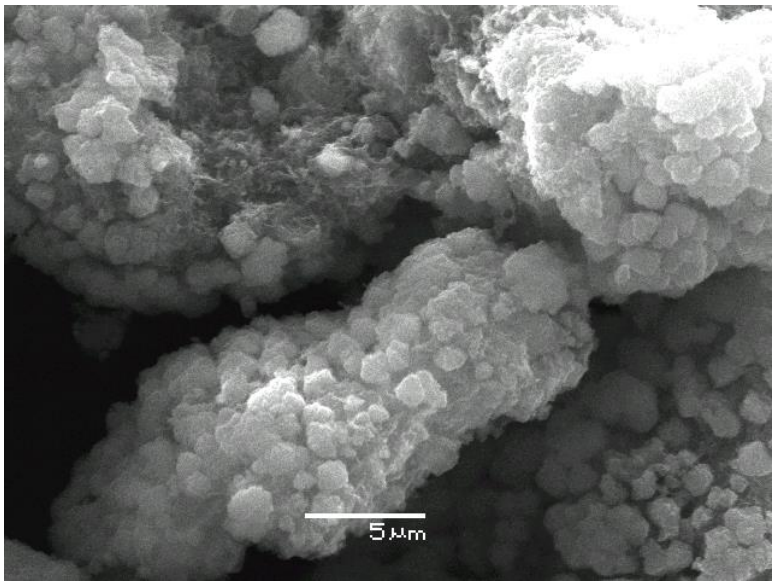


1: Quartz (SiO_2); 2: Albite ($NaAlSi_3O_8$) ;
3: Thomsonite ($NaCa_2Al_5Si_5O_{20}•6H_2O$); 4: Hematite ($Fe_2O_3$)

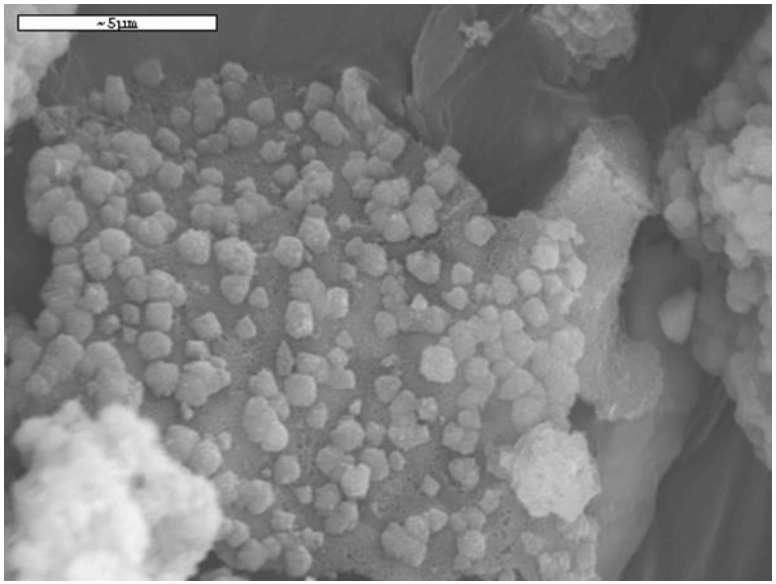
Results –effect on microstructure



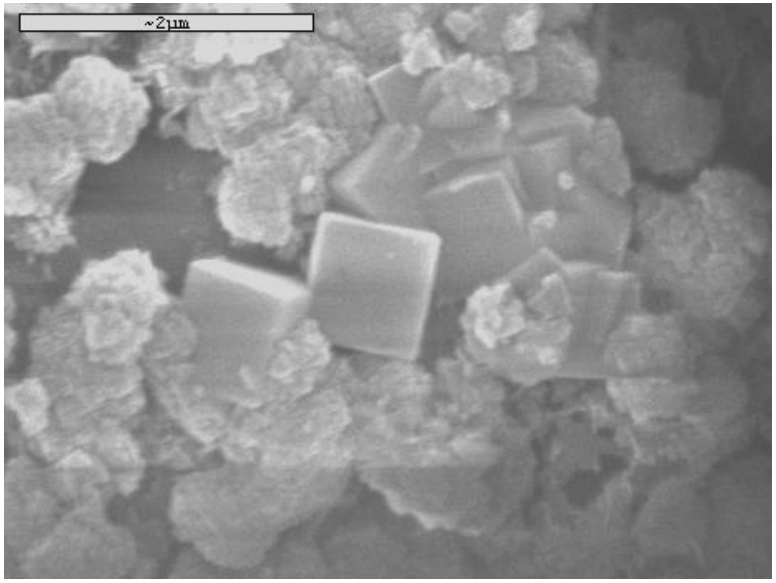
MT-FA



MG-Z

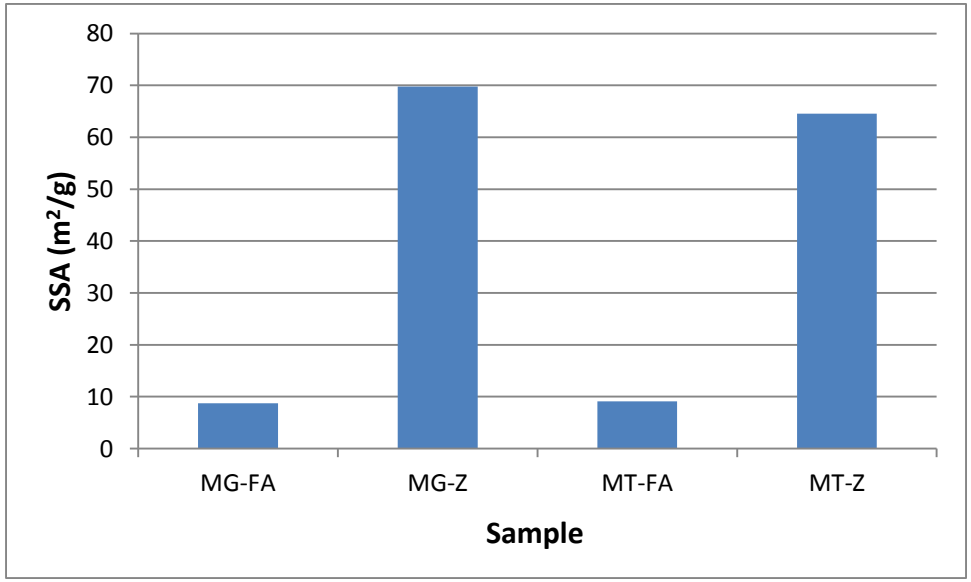


MT-Z

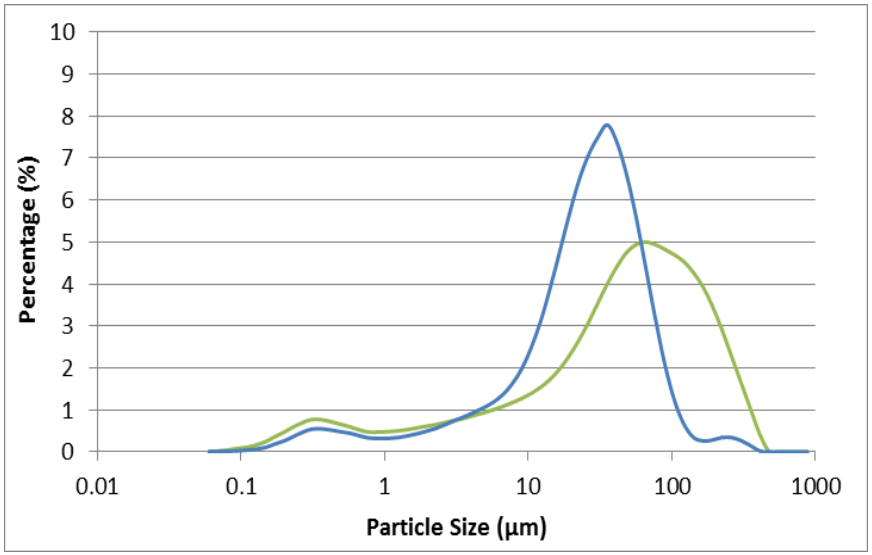


MT-Z

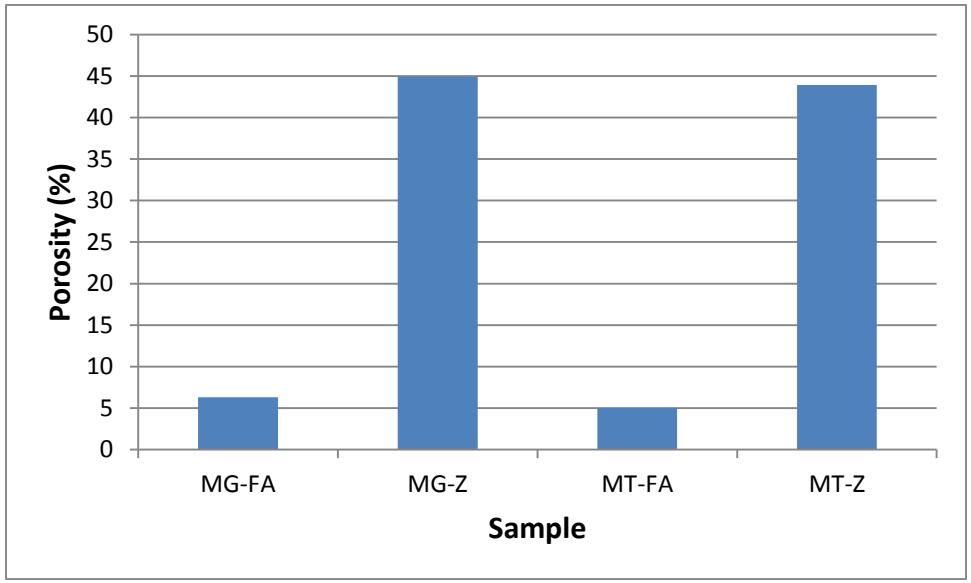
Results –effect on SSA, Porosity, and PSD



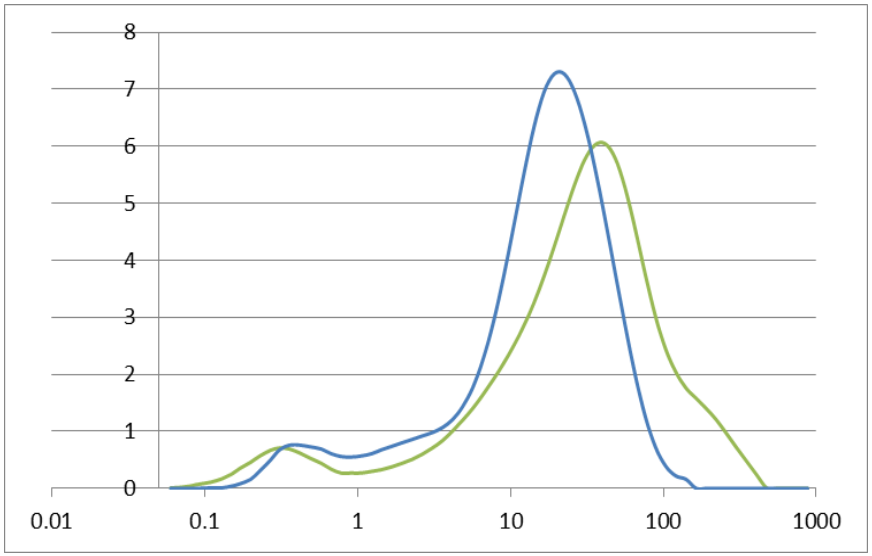
Spec. Surface Area



MG-PSD



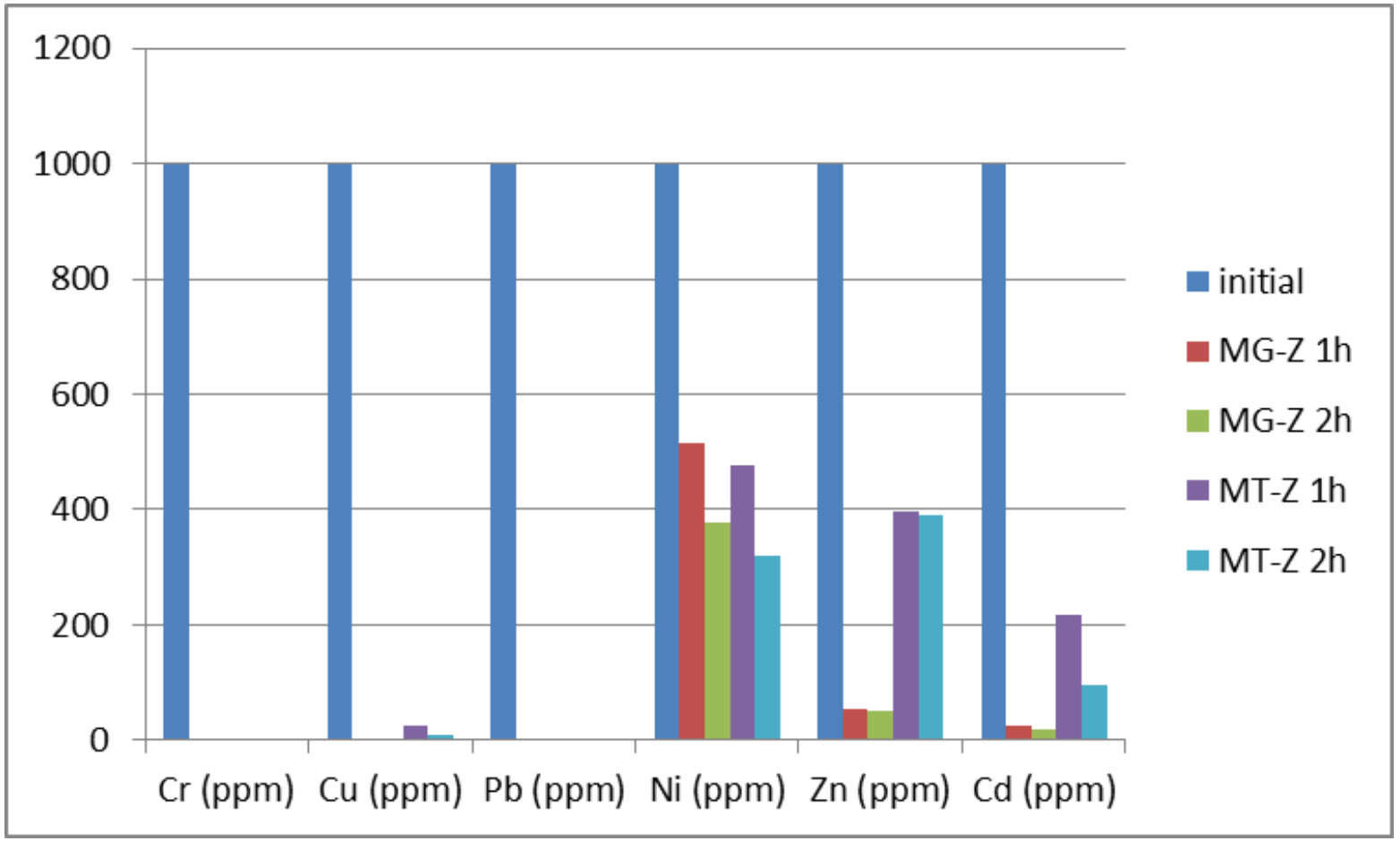
Porosity



MT-PSD

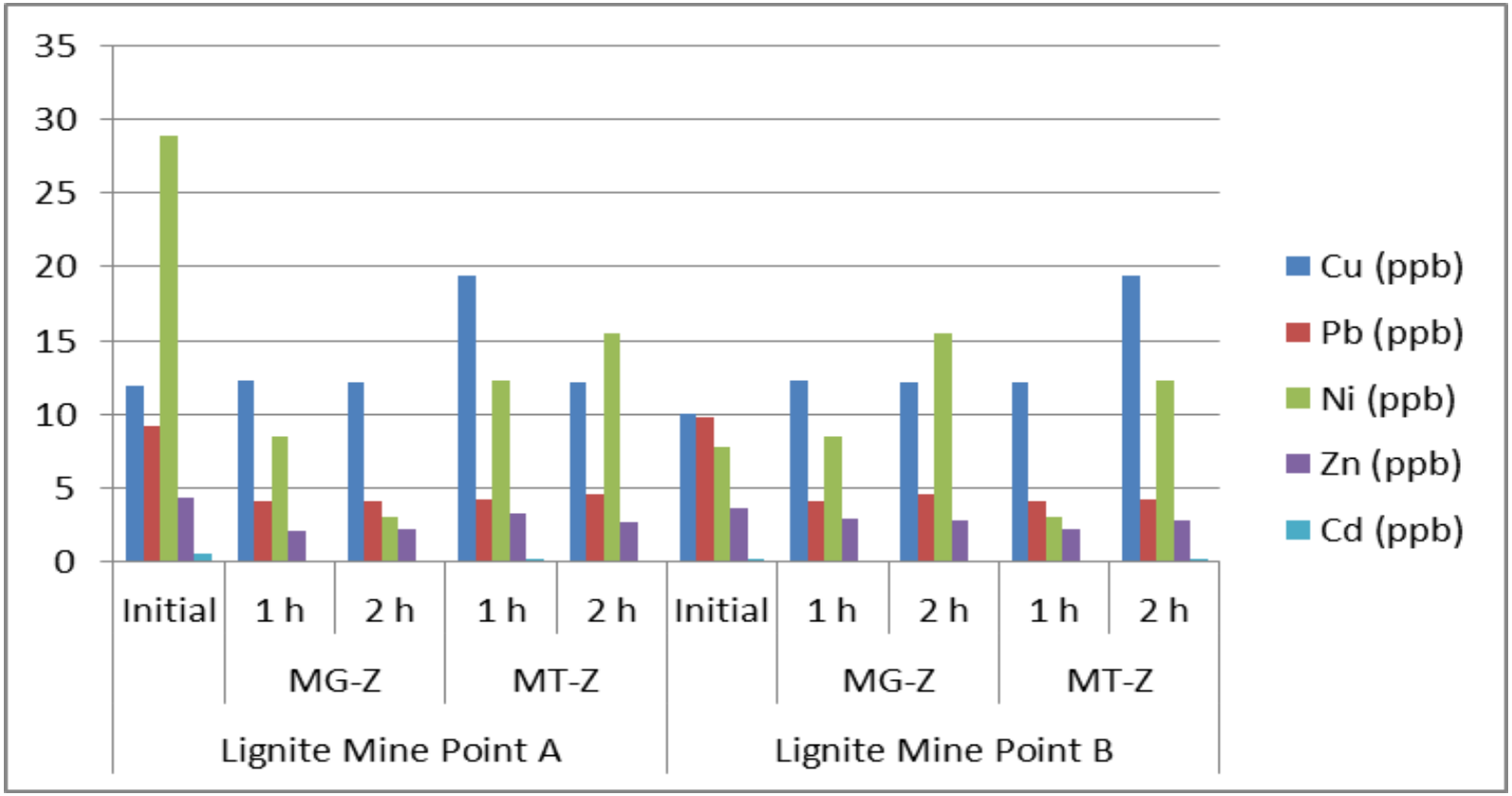
Results –HM removal testing

Uptake of HM cations by MG-Z and MT-Z, after 1 and 2 h.



Results –HM uptake from lignite minewater

Uptake of HM cations by MG-Z and MT-Z, after 1 and 2 h.



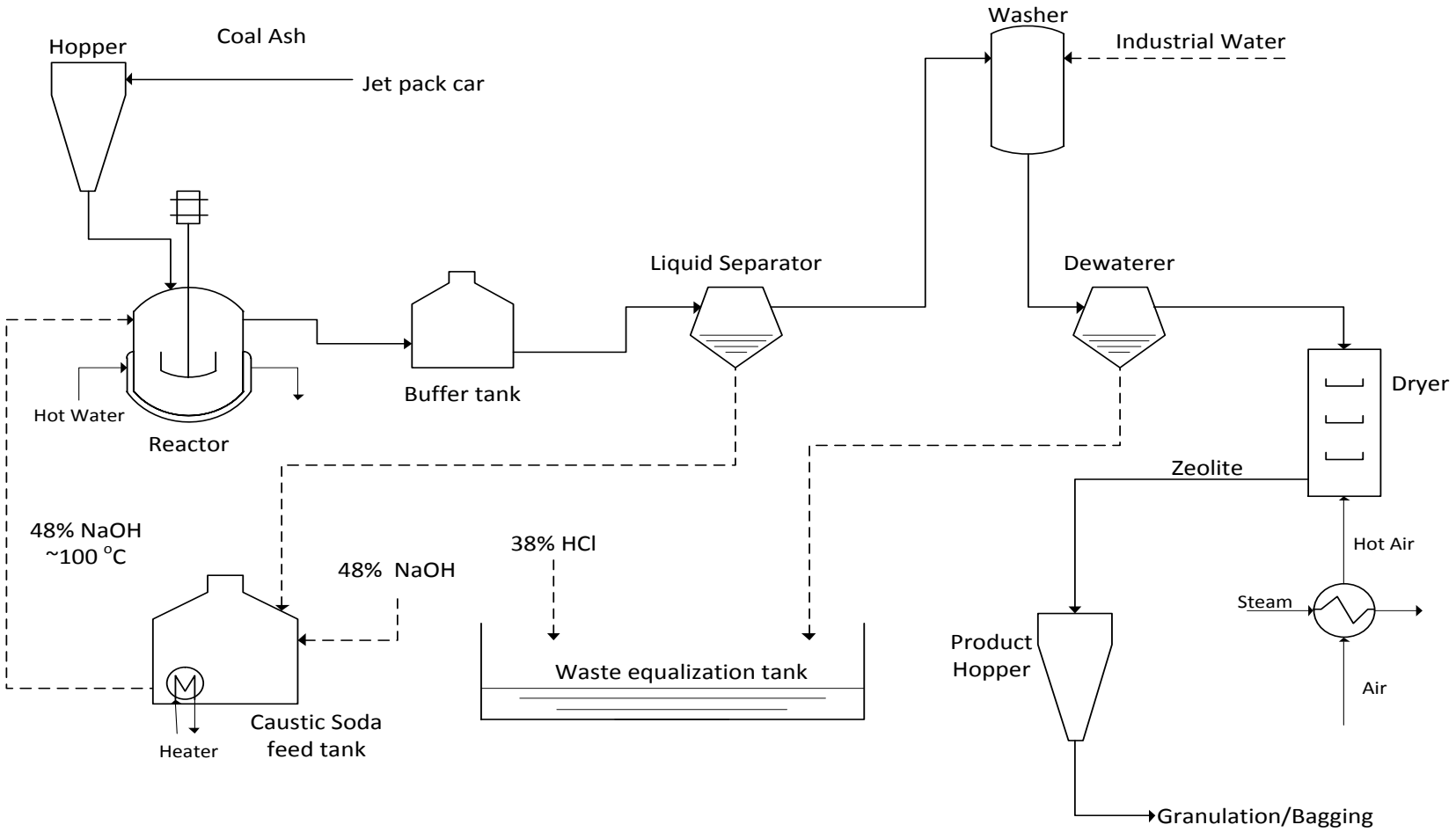
- ✓ *Initial concentration of pollutants in the collected samples was fairly low, exceeding the EU & EPA drinking water limits only in the case of Ni, while being marginally close to the limits in the case of Pb.*

Conclusions

- Siliceous fly ash with moderate CaO concentration can be modified to zeolite-structured material with largely upgraded surface properties and porosity (improved by 600%);
- Phillipsite and thomsonite-like minerals were the main zeolitic crystals developed by hydrothermally treating lignite fly ash from Megalopolis and Meliti power stations, respectively;
- Both zeolitic products were proven absolutely effective in quickly removing Cr, Cu and Pb from aqueous solutions. On the other hand, 1 h-uptake rates of Ni, Zn and Cd were much lower in both cases, although MG-Z was proven much more efficient than MT-Z in uptaking Zn and Cd after 2 h;
- Water samples collected from two sampling points of an active lignite mine were also tested and both MG-Z and MT-Z were proven appropriate sorbents for their effective remediation;
- Given the minimal transportation cost from the production to the application site, the obtained experimental results are considered quite encouraging for the prospective market value of the products.

Future Activities

Zeolitization Plant



Detailed layout of a pattern for zeolitization plant, to be in detail designed by CERTH.

Thank you