Zeolite formation utilizing fly ash from Greece and Kazakhstan

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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;
- Kazakhstan: major coal producer and consumer (FA: mainly Class F);
- Overall target: To establish a new utilization path for Greek FA & to promote knowledge transfer to NU and the emerging market of Kazakhstan (19 Mtn fly ash /year).

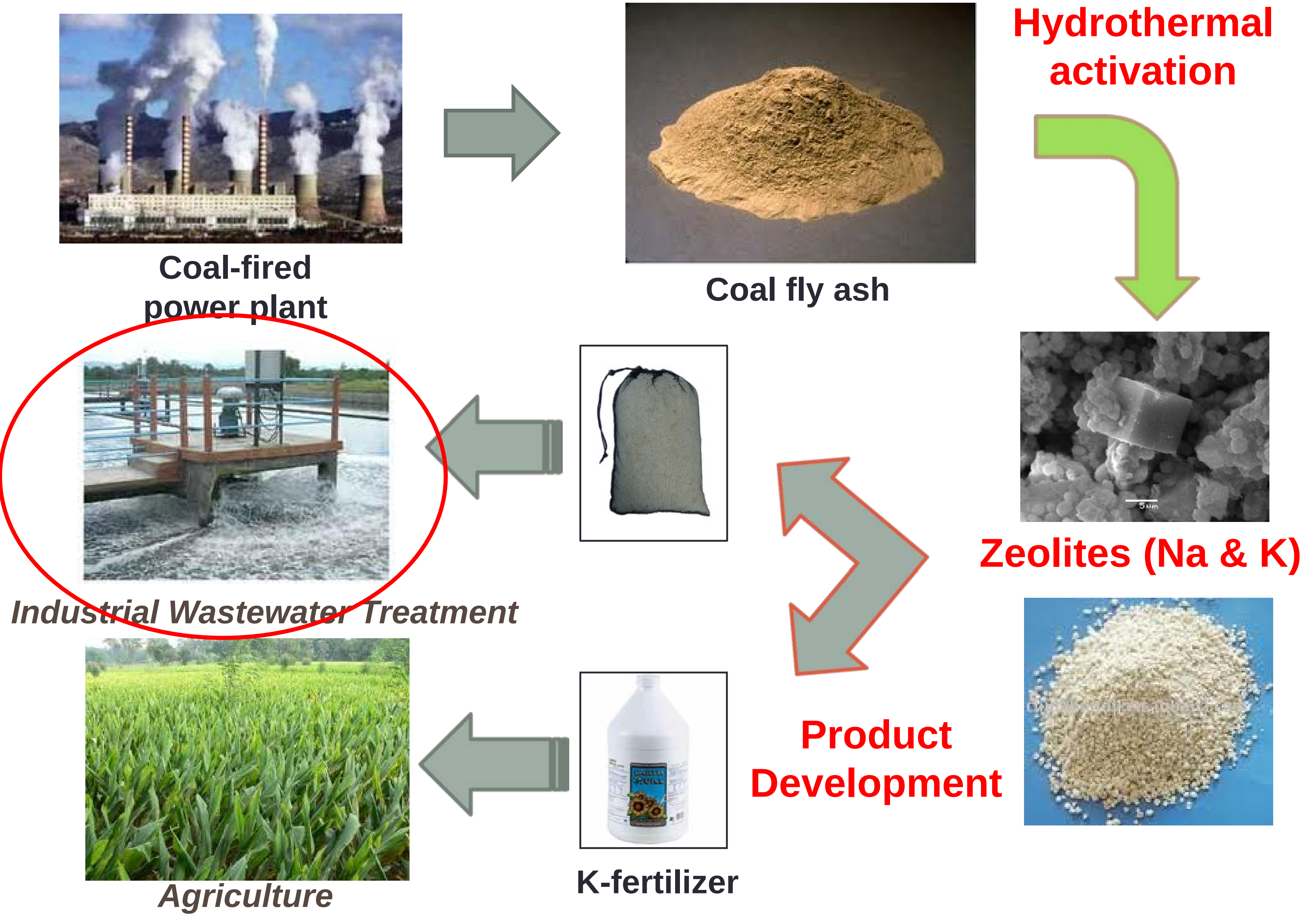
Research Interests & Targets

- Development & characterization of novel, zeolite-based sorbents for coal mine-water treatment;
- Material to be field-tested in Upper Silesia, Poland (*MANAGER* RFCS 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 by Hellenic ashes;
- Gobbinsite was the principal zeol. crystal in Kazakhstani-FA modified materials;
- The products totally & quickly removed Cr, Cu and Pb from artificial aqueous media;
- Sorbent effectiveness was verified by treating actual lignite mine-waters.

Introduction



Materials & Methods

FA Sampling & Zeolite Development

- FA samples collected from the ESPs 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;
- Kazakhstani ashes: Petropavlovsk CHP plant belonging to JSC "SevKazEnergo" (434 / 922 MW) and from Astana city CHP-2 plant belonging to JSC "Astana Energia" (360 / 1077 MW) -Both CHP plants use Ekibastuz coal as primary fuel;
- Alkaline hydrothermal treatment: 110°C, using NaOH 4M as activation solution (50g/l);
- 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

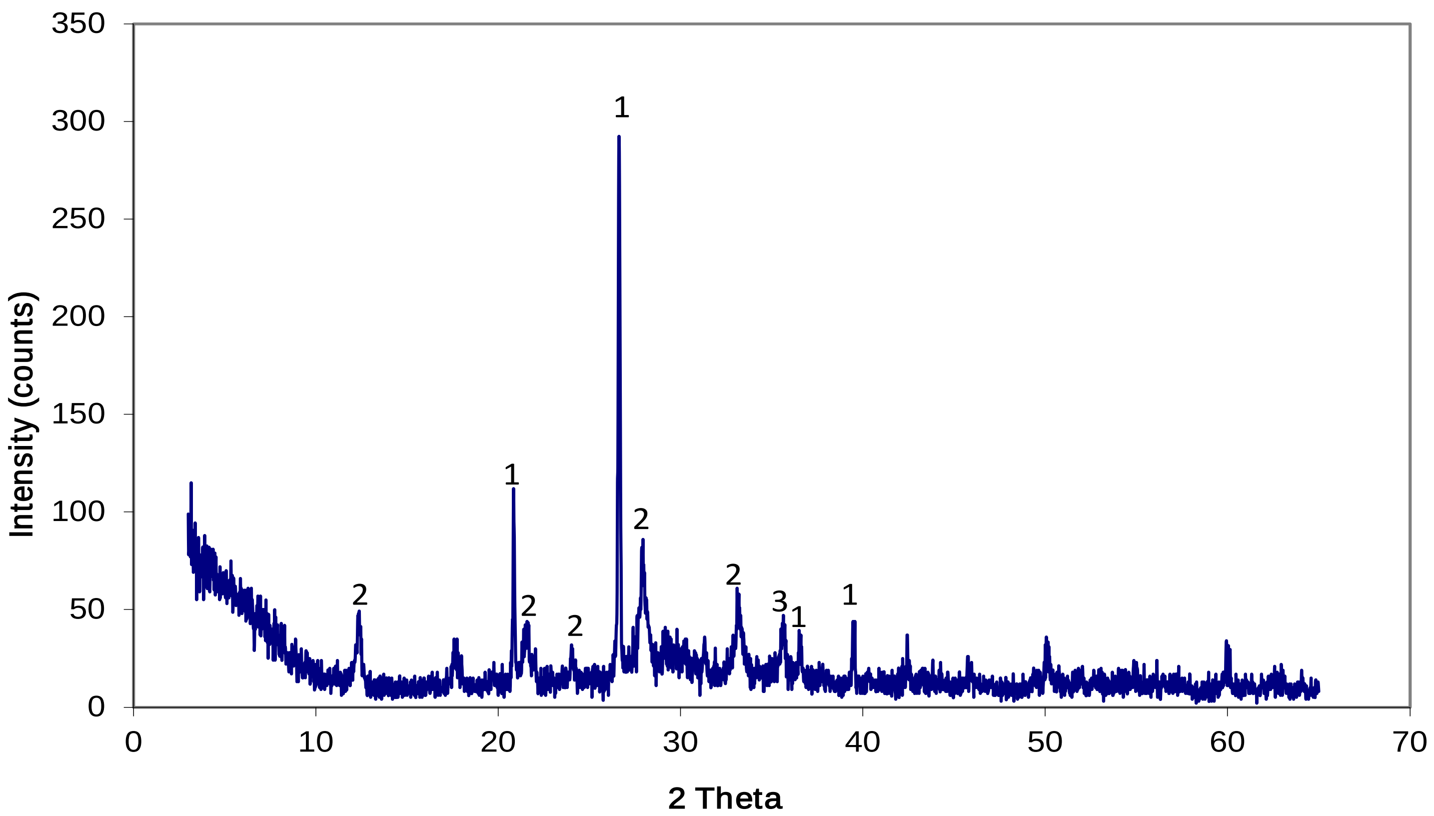
- XRD; AAS; EDS-SEM; PSD determination; N_2-porosimetry.

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.

Results -Mineralogy

X-Ray Diffractogram –MG Zeolitic Product

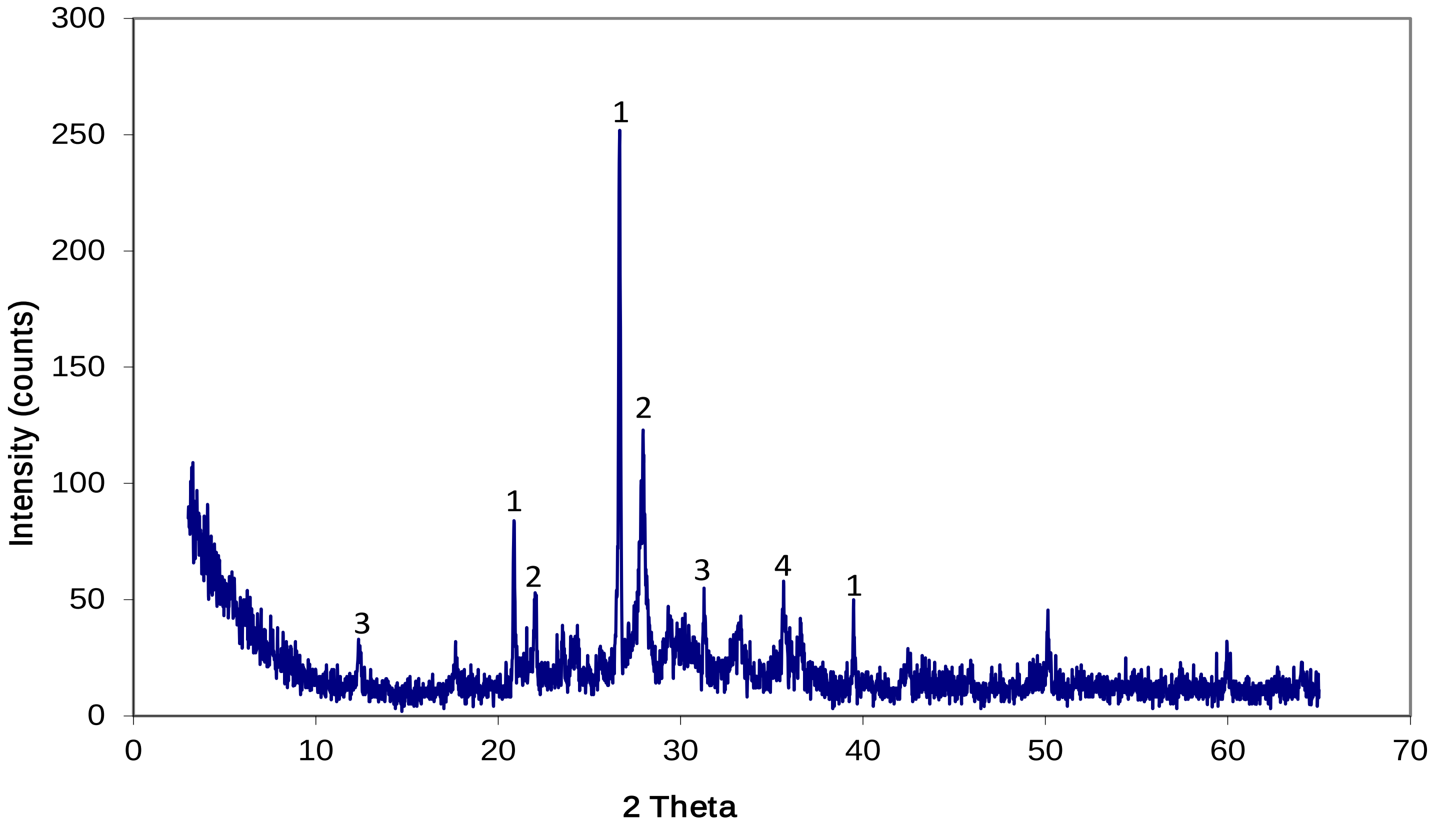


1: Quartz (SiO_2);

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

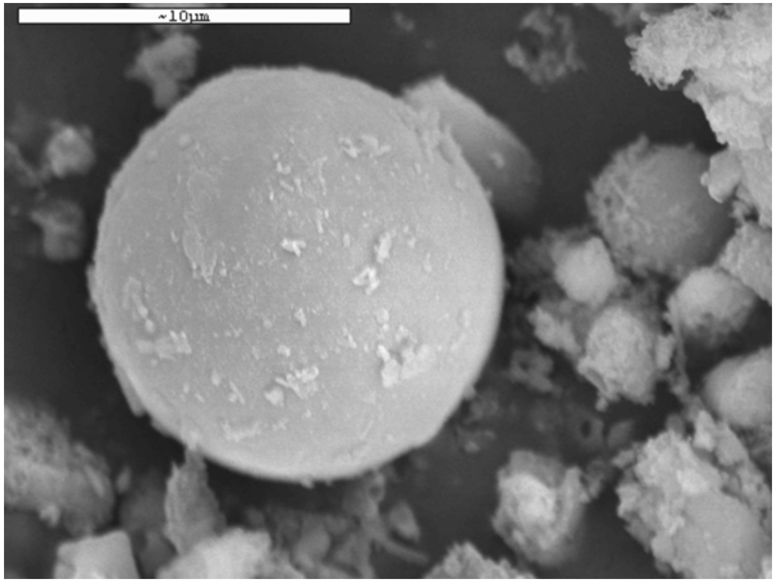
Results -Mineralogy

X-Ray Diffractogram –MT Zeolitic Product

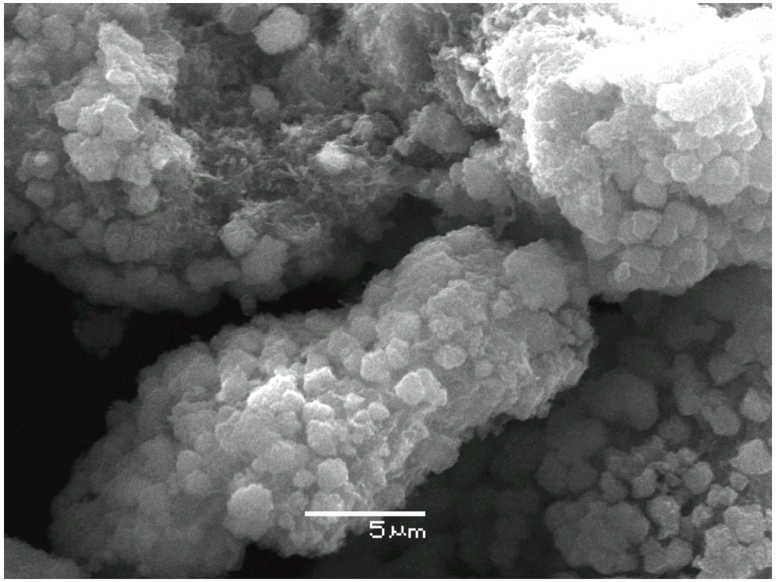


1: Quartz (SiO_2); 2: Albite ($NaAlSi_3O_8$) ;
3: Thomsonite ($NaCa_2Al_5Si_5O_{20}$•$6H_2O$); 4: Hematite (Fe_2O_3)

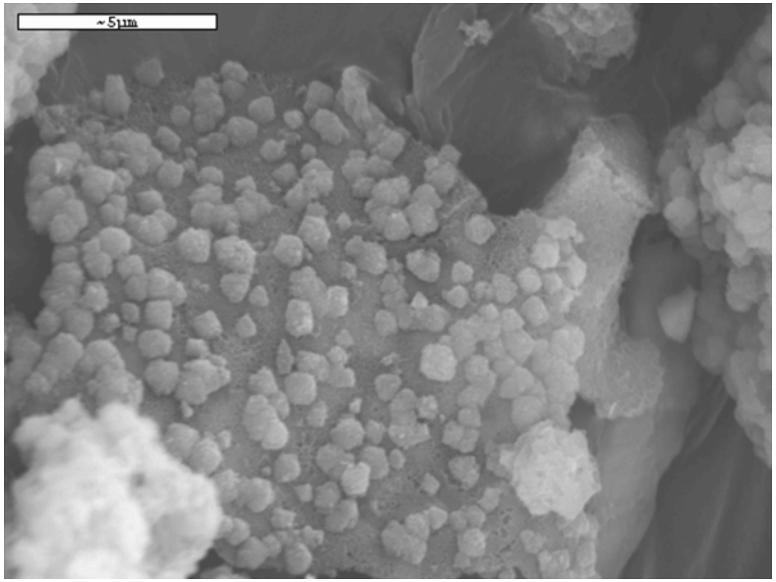
Results –effect on microstructure



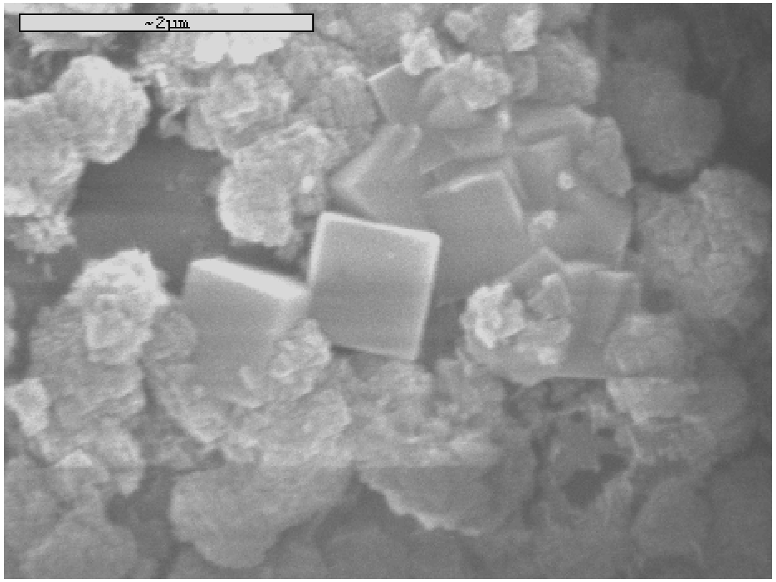
MT-FA



MG-Z

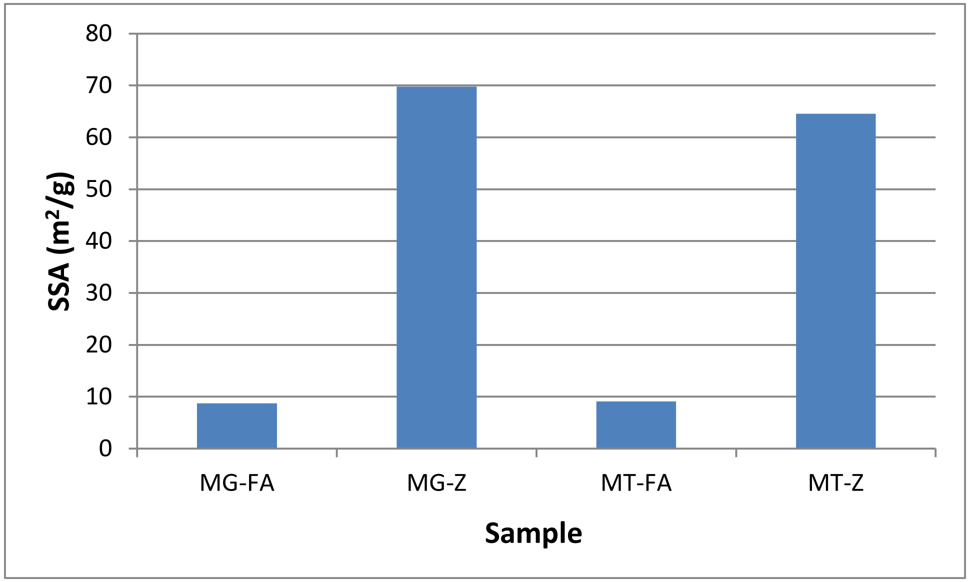


MT-Z

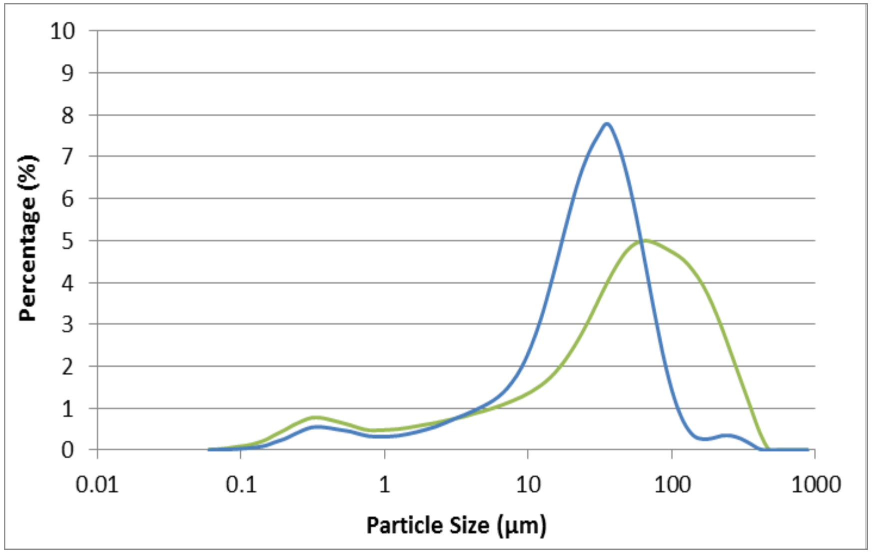


MT-Z

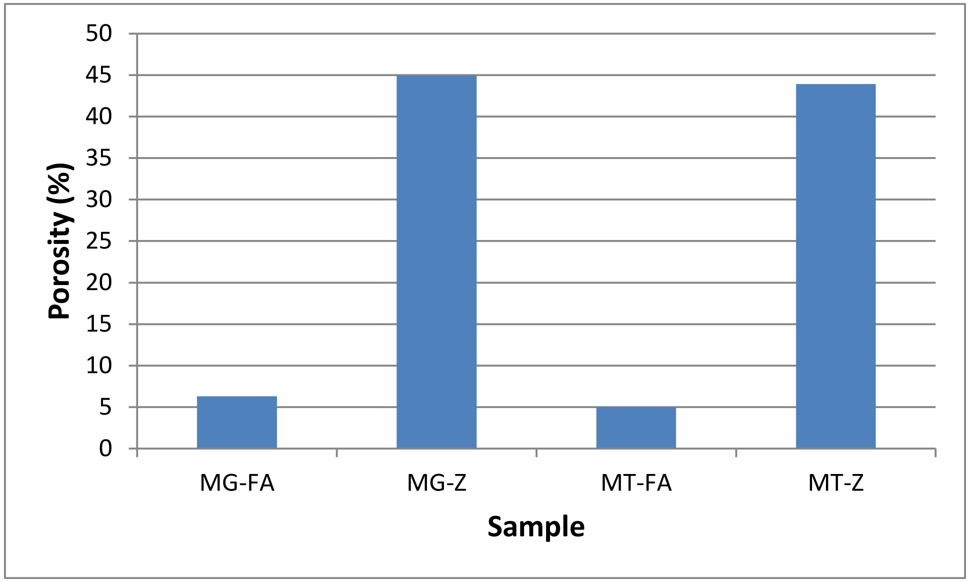
Results –effect on SSA, Porosity, and PSD



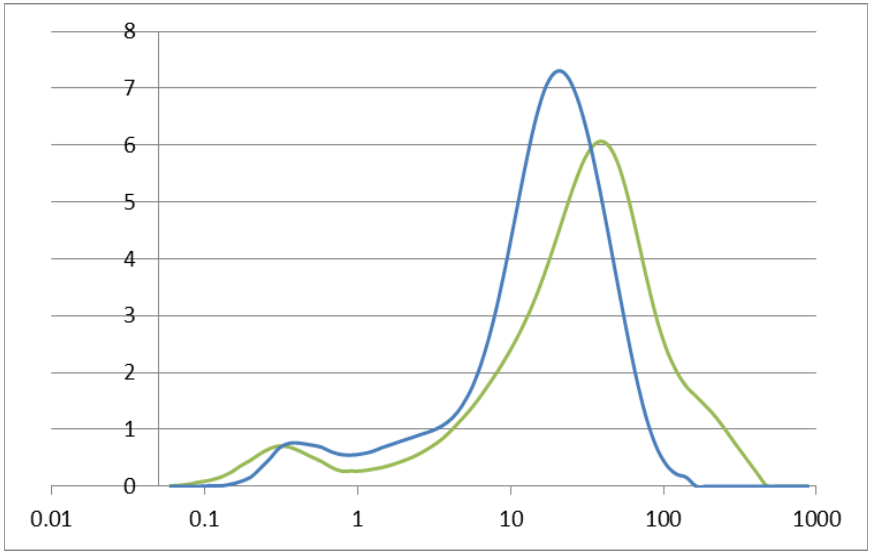
Spec. Surface Area



MG-PSD



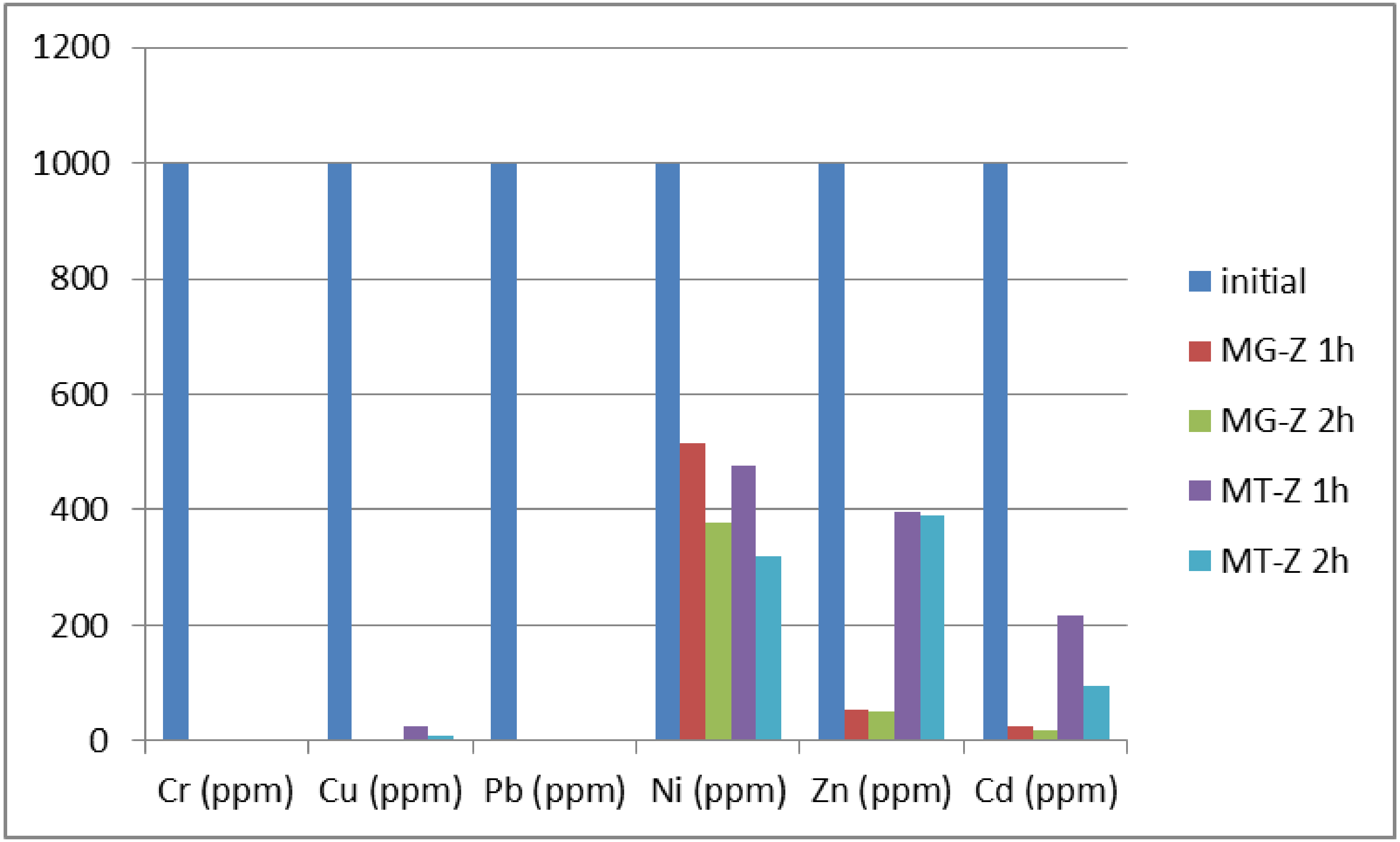
Porosity



MT-PSD

Results –HM removal testing

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

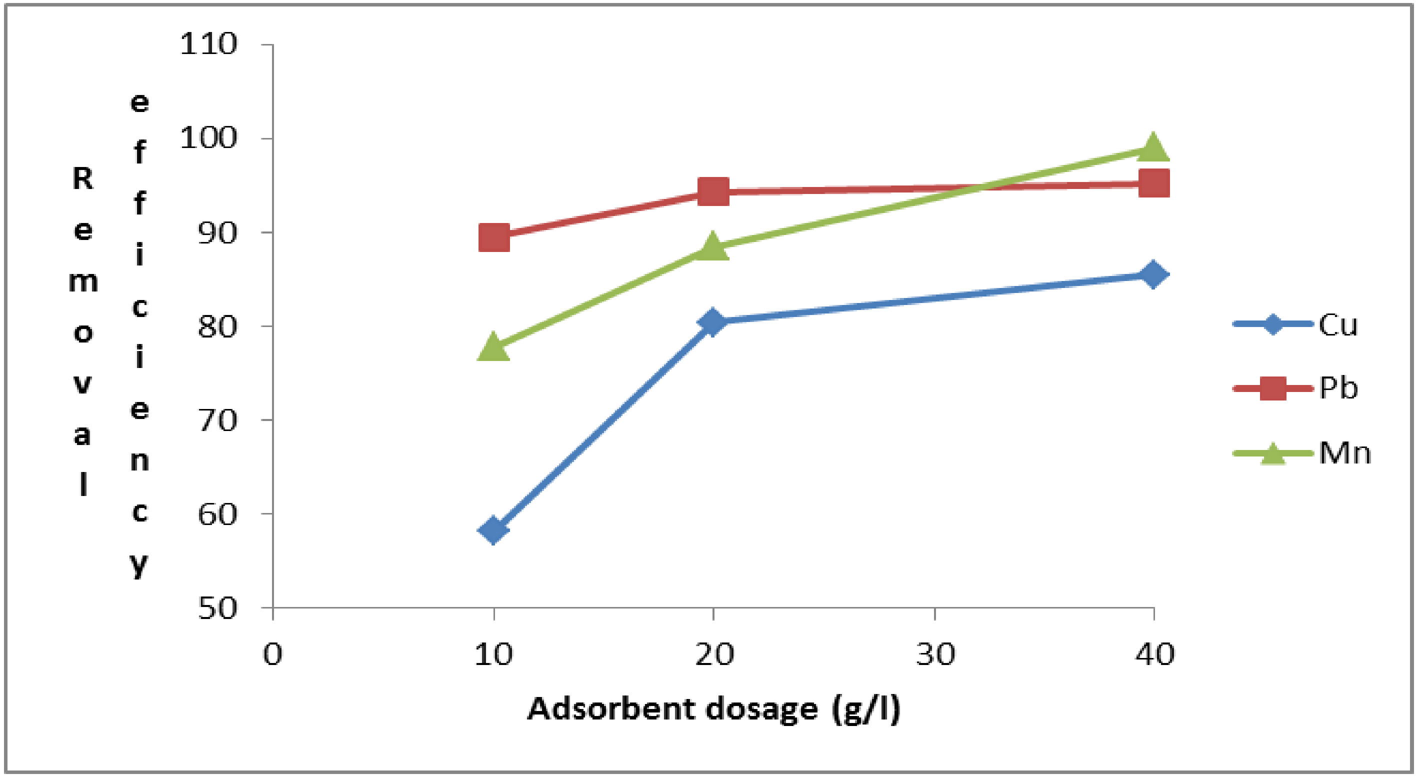


Results –HM removal testing

Effect of Adsorbent Dosage on HM retention yield

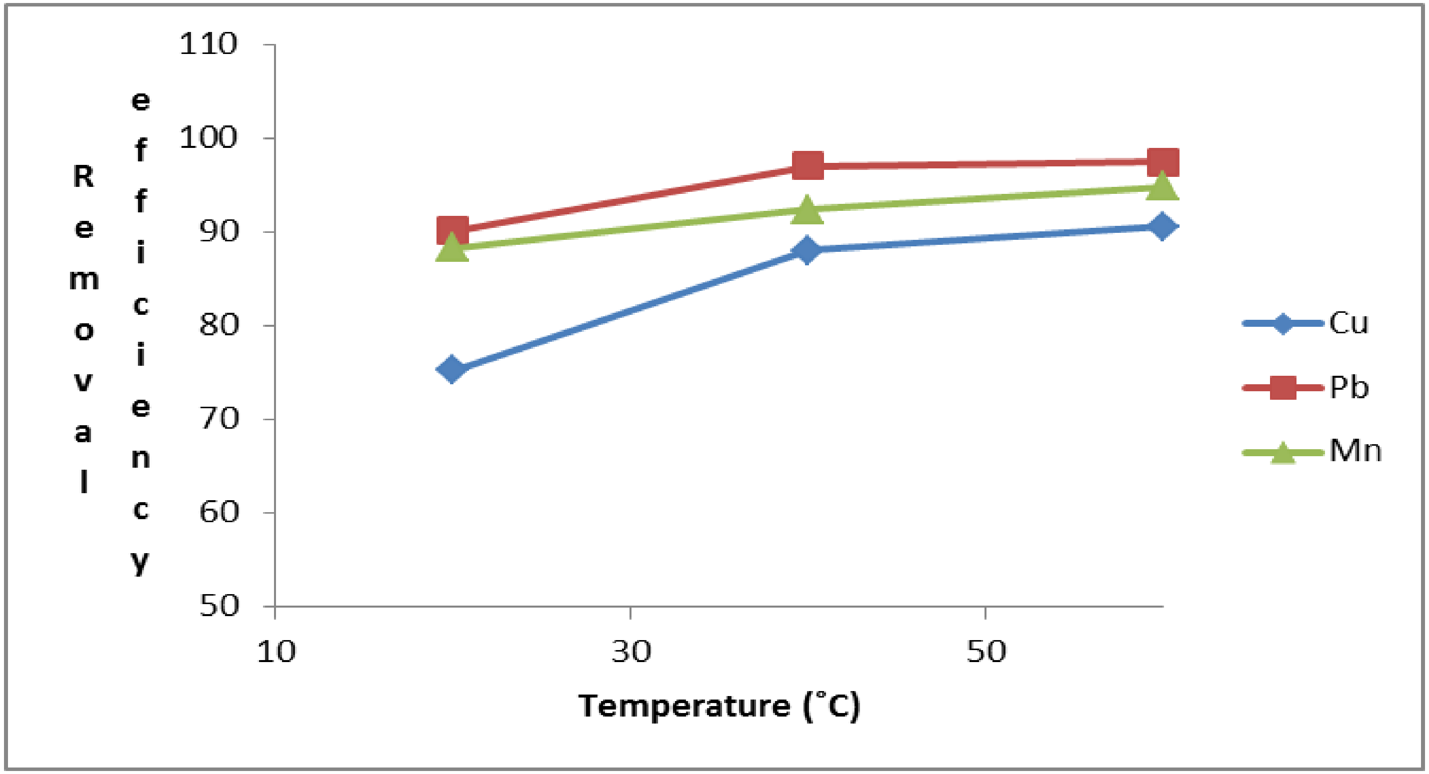
Element	Concentration (ppm)
Na	8300
K	180
Mg	450
Ca	1000
Mn	18.823
Pb	0.472
Cu	0.117
Ni	0.125

- ✓ *The pollutant concentrations were selected so as to be similar to intermediate salinar, flooding mine-waters.*



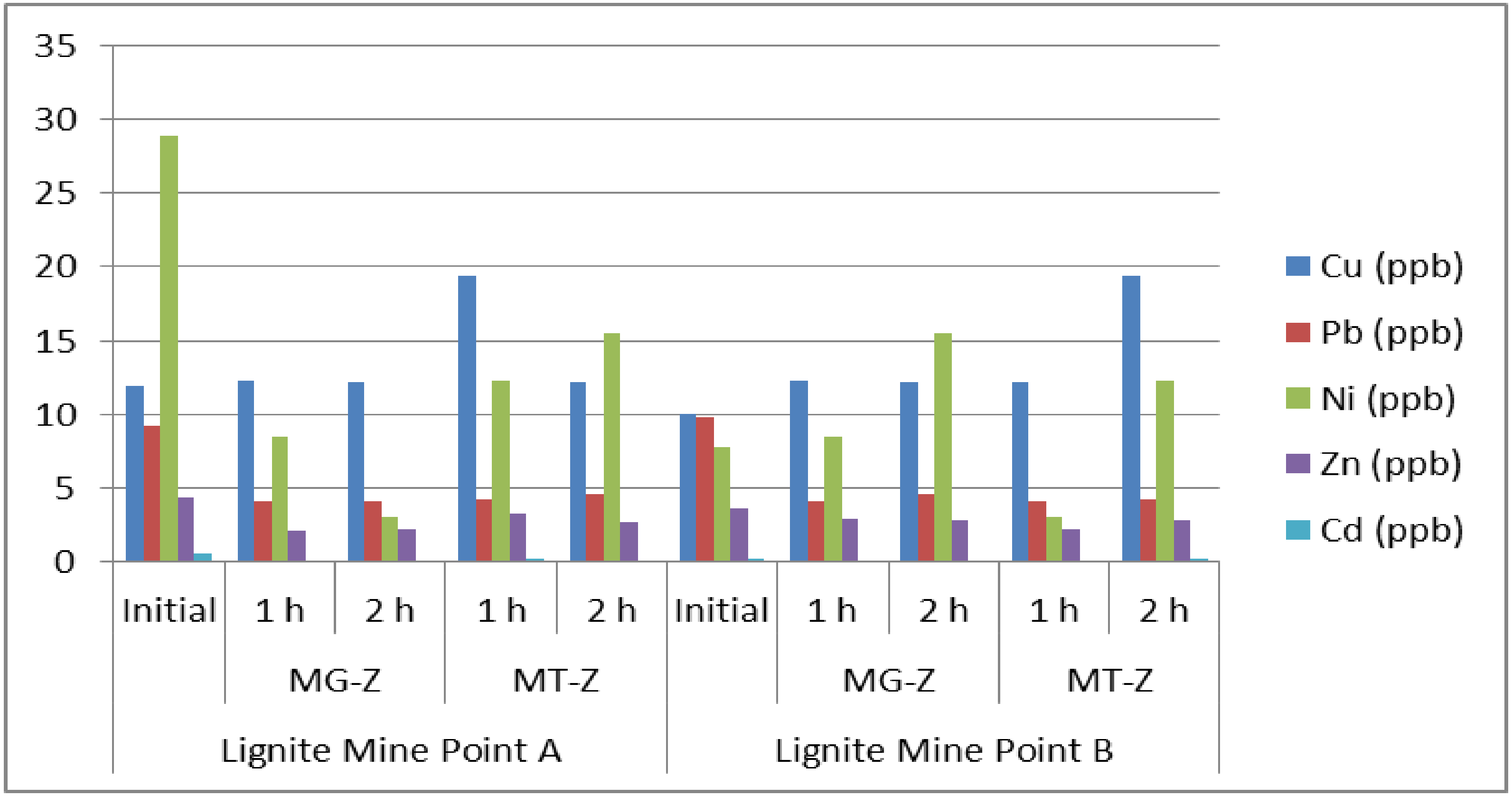
Results –HM removal testing

Effect of Adsorption Temperature on HM retention yield



Results –HM uptake from lignite minewater

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

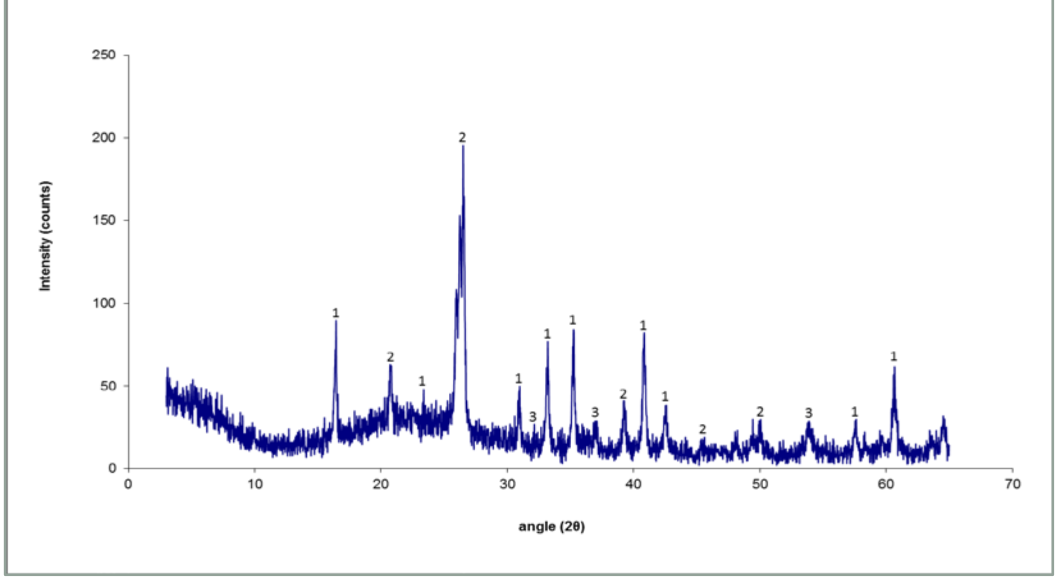


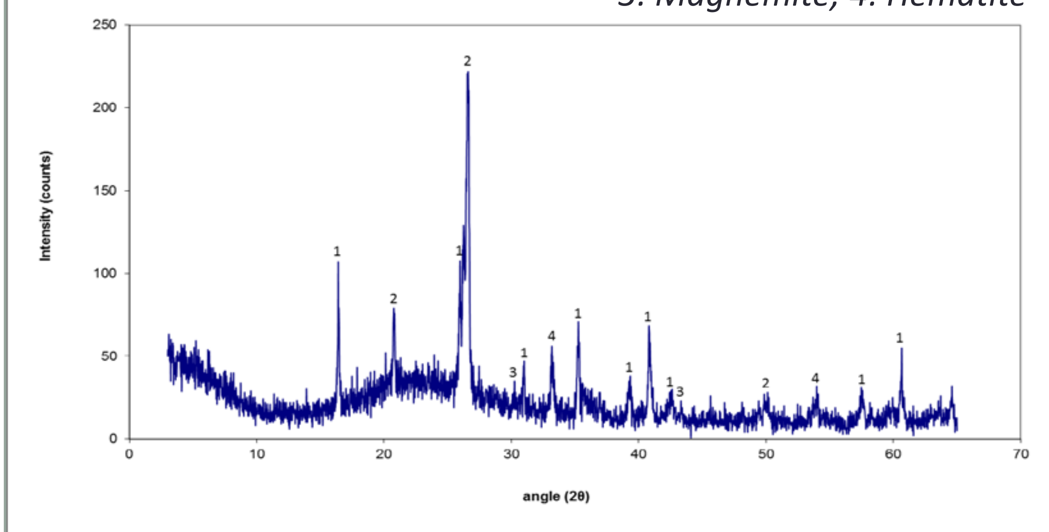
- ✓ *Initial concentration of pollutants in the collected samples was fairly low, exceeding the EU & EPA drinking water limits only in the case of Ni, while being marginally close to the limits in the case of Pb.*

Results –Kazakhstani FA

Parameters	UoM	Parameter value		Average
		from	to	value
Moisture of fuel as received, W_r^2	%	3.8	7	5.4
Ash content on dry basis, A^d	%	34.8	38	36
Volatile-matter yield, W^{dat}	%	24	40	32
Sulfur total, S_t^d	%	0.4	1	0.7
Lowest combustion heat of working fuel, Q_t^2	kcal/kg	4700	4200	4500
Ash residue composition:				
- SiO_2	%	56.9	67.3	62.1
- $Al_2 O_3$	%	24.4	31.6	28
- $Fe_2 O_3$	%	4.4	7.26	5.83
- CaO	%	0.68	3.29	1.98
- Mg O	%	0.19	1.26	0.72
- TiO_2	%	1.09	1.65	1.37
- SO_3	%	0.55	2.31	1.43
- P_2O_5	%	0.32	1.29	0.8
- $K_2O + Na_2O$	%	0.56	0.95	0.75
Element-by-element composition of combustible mass				
Carbon		79.8	83.2	81.5
Hydrogen		5.6	4.9	5.3
Nitrogen		1.5	1.7	1.6
Oxygen		9.6	12.2	10.9

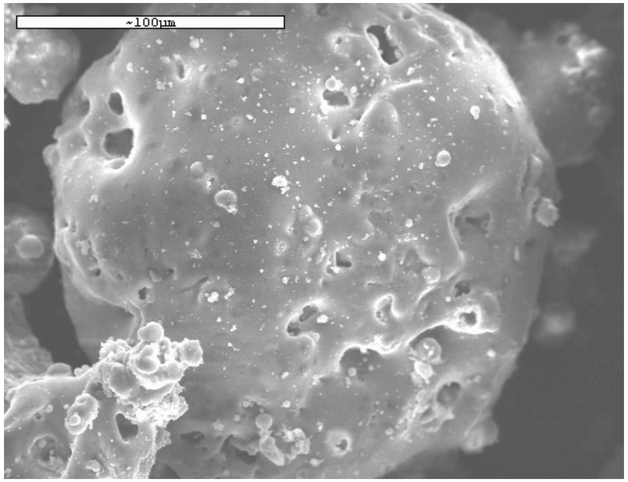
Results -Kazakhstani FA





Sample	KAZ1-FA	KAZ2-FA
SiO_2	56.16	56.48
Al_2O_3	30.99	24.93
Fe_2O_3	5.92	7.43
MgO	0.55	0.86
CaO	1.84	2.48
Na_2O	0.21	0.3
K_2O	0.38	0.5
TiO_2	1.24	1.09
P_2O_5	0.46	0.41
MnO	0.1	0.14
LOI	1.9	5.1

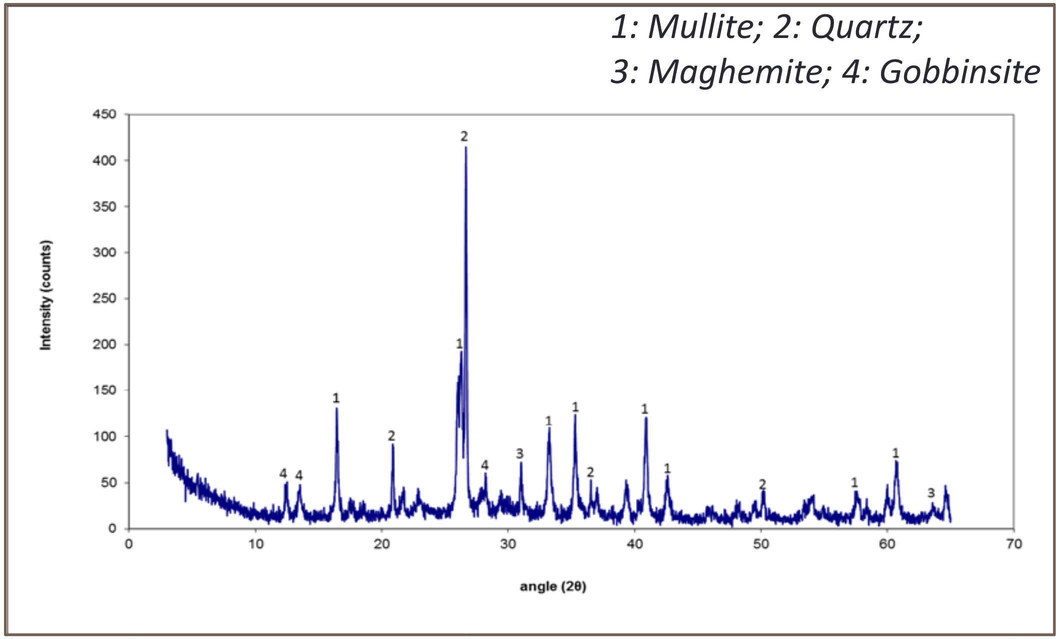
KAZ1: Petropavlovsk; KAZ2: Astana

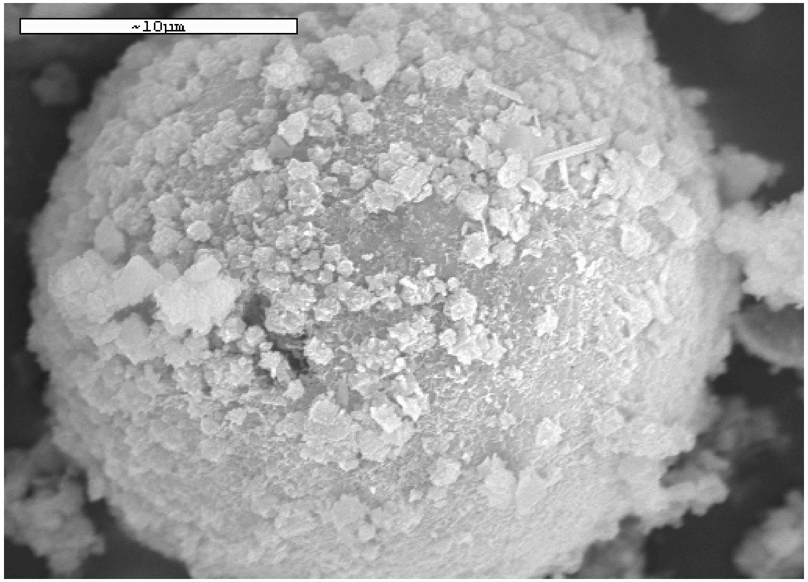


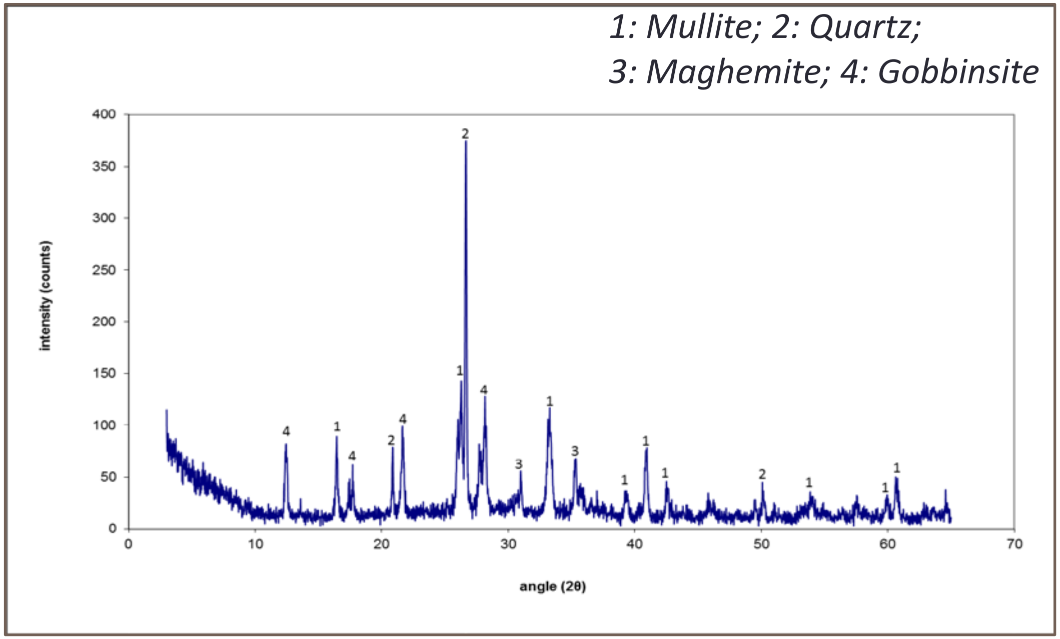
FA cenosphere

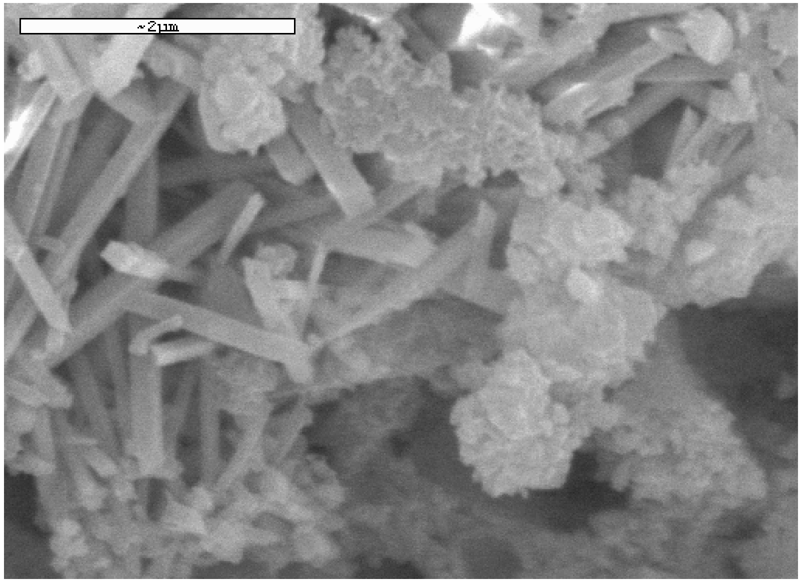
Mullite ($3Al_2O_32SiO_2$); Quartz (SiO_2); Lime (CaO); Maghemite (Fe2O3, γ-Fe_2O_3); Hematite (Fe_2O_3); Gobinsite: ($(Na_2; Ca)_2K_2Al_6Si_{10}O_{32}$)

Results -Kazakhstani FA/zeol materials









Mullite ($3Al_2O_32SiO_2$); Quartz (SiO_2); Lime (CaO); Maghemite (Fe2O3, γ-Fe_2O_3); Hematite (Fe_2O_3); Gobinsite: ($(Na_2; Ca)_2K_2Al_6Si_{10}O_{32}$)

Conclusions -Hellenic FA/zeol products

- 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;

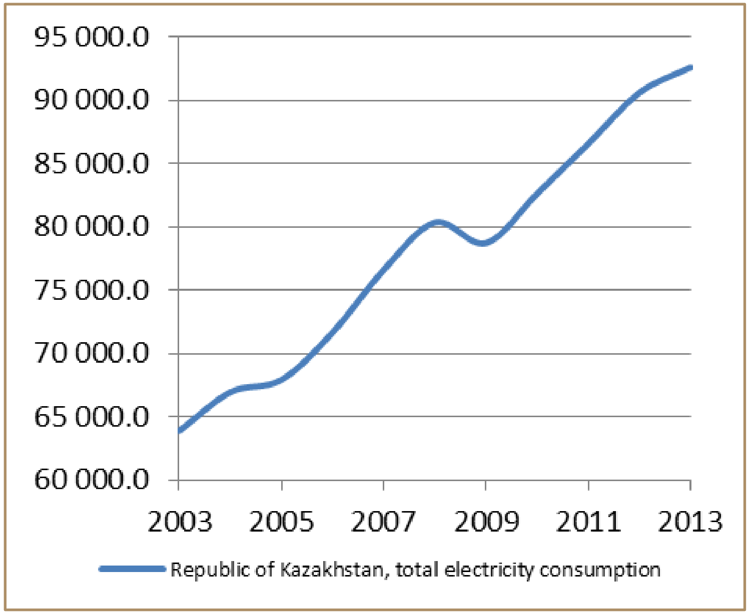
- Both zeolitic products were proven absolutely effective in quickly removing Cr, Cu and Pb from aqueous solutions. On the other hand, 1 h-uptake rates of Ni, Zn and Cd were much lower in both cases, although MG-Z was proven much more efficient than MT-Z in uptaking Zn and Cd after 2 h;

- 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.

Initial Conclusions -KAZ FA

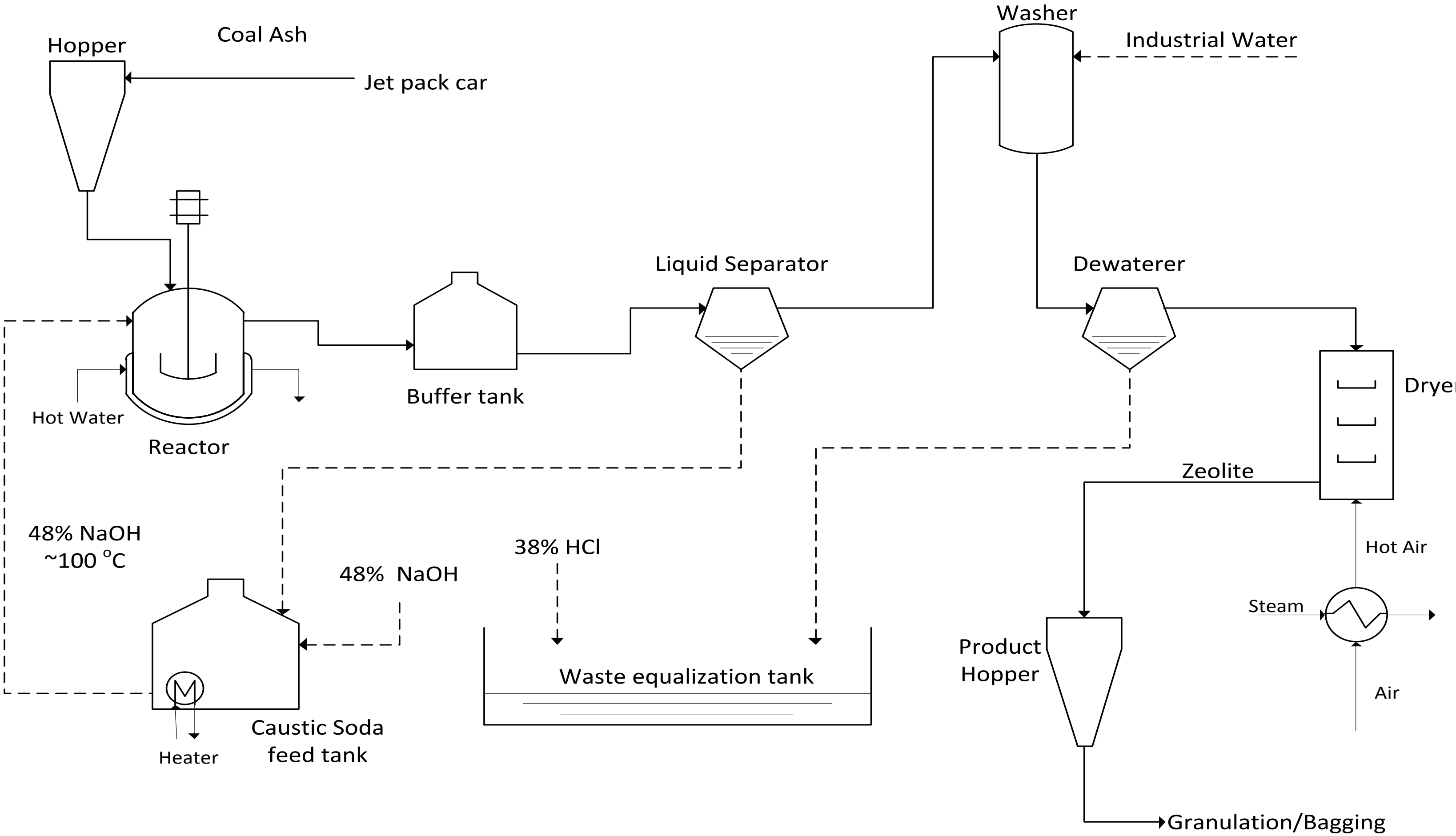
- Siliceous fly ash by Ekibastuz coal has been modified to zeolite-structured material with gobbinsite as the primary zeolitic crystal and upgraded surface properties and porosity;
- Next step: testing against artificial and actual minewater samples.



✓ *Electricity consumption (kWh) in Kazakhstan is on the rise.*

Future Activities

Zeolitization Plant



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

Thank you