SECOND INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

KATHOLIEKE UNIVERSITEIT LEUVEN

Imperial College London

GEOPOLYMERISATION POTENTIAL OF METALLURGICAL SLAGS AND PLASMA TREATED APC RESIDUES

K. Komnitsas, I. Kourti, S. Onisei, Y. Pontikes, C. Cheeseman, P. Moldovan, A. Boccaccini

centre

SMART-PRO^2

Content:

- Geopolymers from FeNi slag
- Geopolymers from lead slag
- Geopolymers from plasma treated APC residues
- Conclusion

Geopolymers from FeNi slag
FeNi slag

- Electric arc slag is produced at LARCO S.A. ferronickel plant in Greece
- Annual slag production reaches 1,700,000 t; cement industry uses 450,000 t
- Slags are currently disposed of on surface heaps or under the sea
- Slag was dried and crushed (-120 μm and d_{50}: -12 μm) to increase surface area

	%		%		%
Fe_2O_3	*43.83*	***Cr_2O_3***	*3.07*	***C***	*0.11*
SiO_2	*32.74*	***MgO***	*2.76*	***Ni***	*0.1*
Al_2O_3	*8.32*	***Mn_3O_4***	*0.44*	***Co***	*0.02*
CaO	*3.73*	***S***	*0.18*		

Geopolymers from FeNi slag

Synthesis

Pulverised slag + **Activating solution** **Na_2SiO_3 + KOH pellets + water** → **Homogeneous paste**

- The paste was cast in moulds (5 cm edge)
- Specimens were pre-cured at room temperature for 2 days before heated at 80 ^{o}C for 48 hours
- Aging took place for 7 days at room temperature

Geopolymers from FeNi slag
Tests

- Long term durability:

  - immersion in distilled, seawater, acid rain and 0.05N HCl solutions for a max period of 8 months

  - pH, Eh, EC and metal ion concentration were monitored monthly

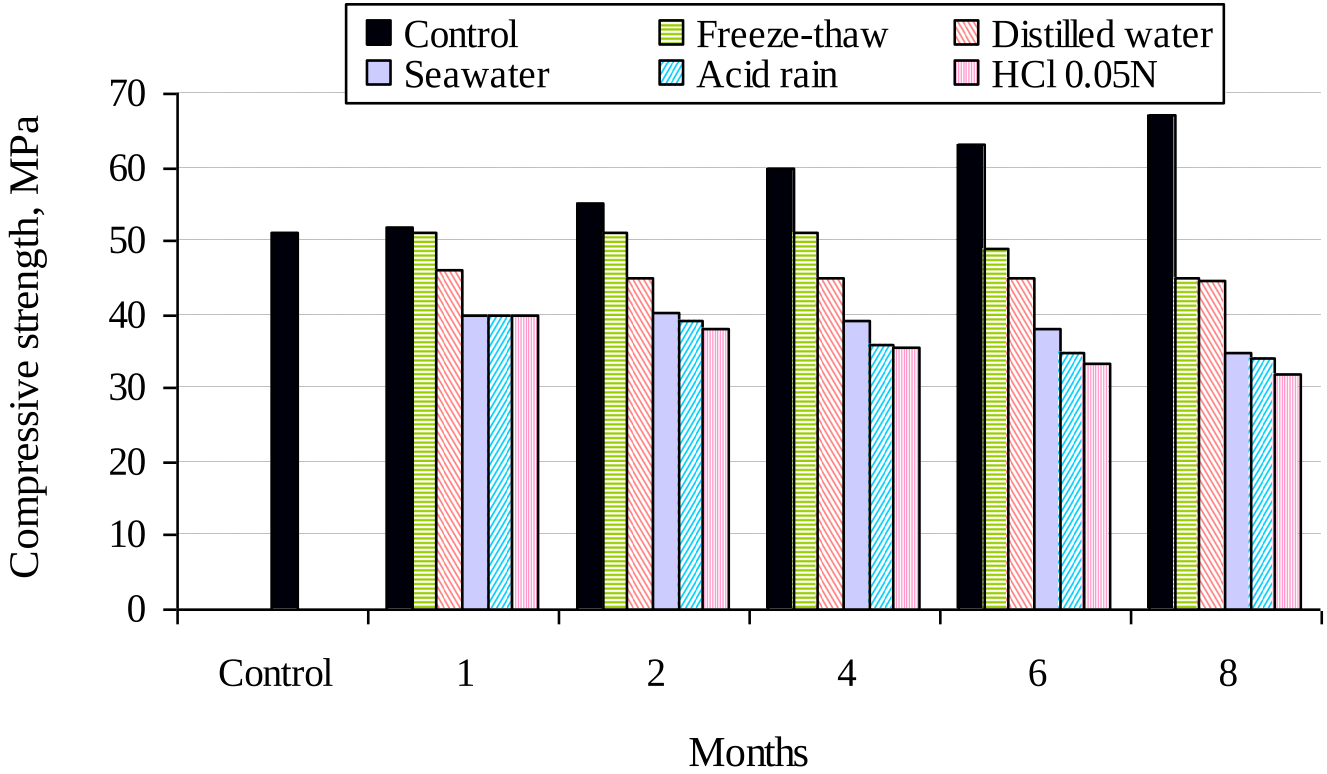
  - weekly freeze-thaw cycles (-15 and +60 ^{o}C) and high temperature heating up to 800 ^{o}C

- Compressive strength was measured using an MTS 1600 load frame

- Elucidation of geopolymerisation mechanisms by analytical techniques (XRD, SEM, FTIR, TG)

Geopolymers from FeNi slag

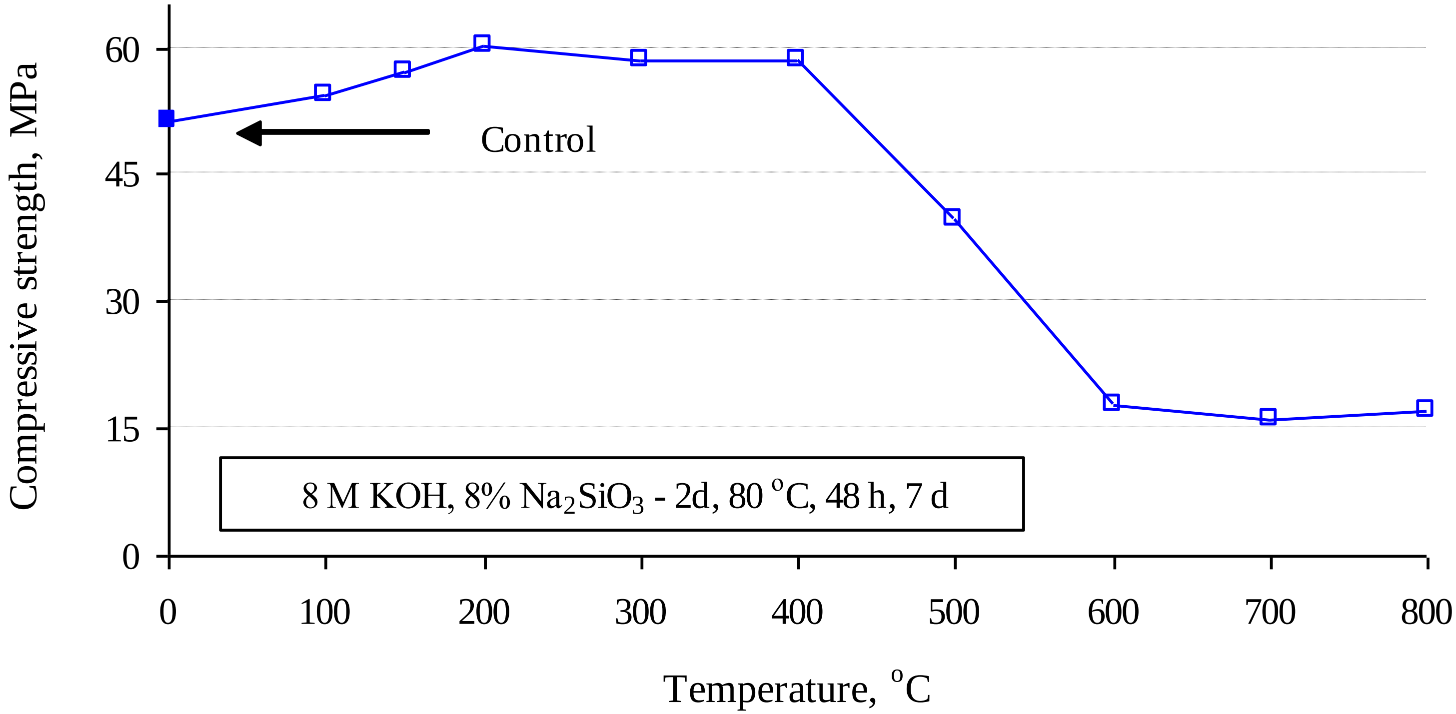
Results and discussion



Evolution of the compressive strength of geopolymers immersed in various solutions or subjected to freeze-thaw cycles over 8 months

Geopolymers from FeNi slag

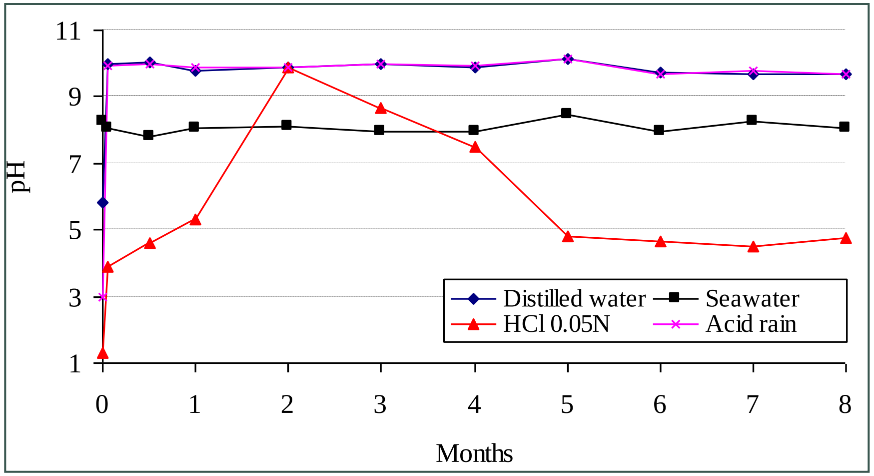
Results and discussion



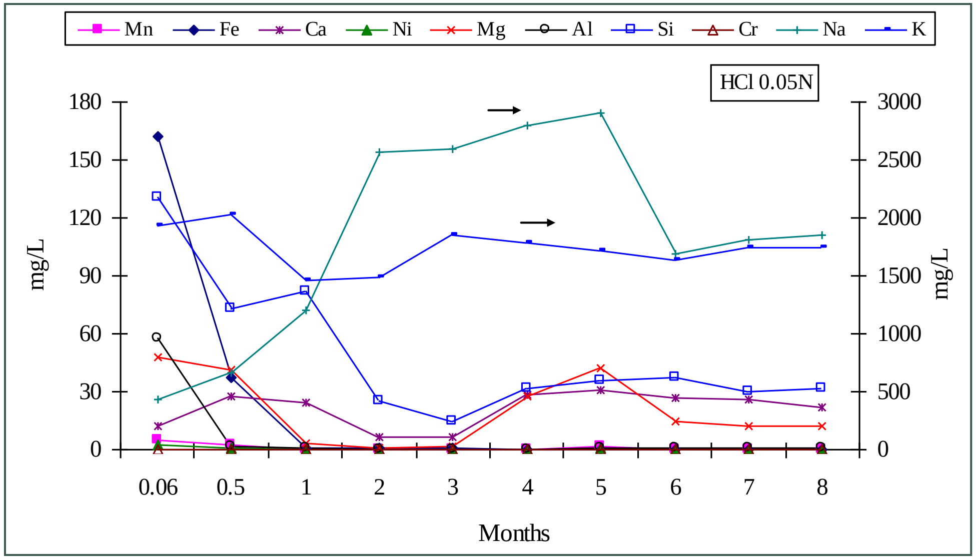
Evolution of the compressive strength of geopolymers vs. temperature

Geopolymers from FeNi slag

Results and discussion



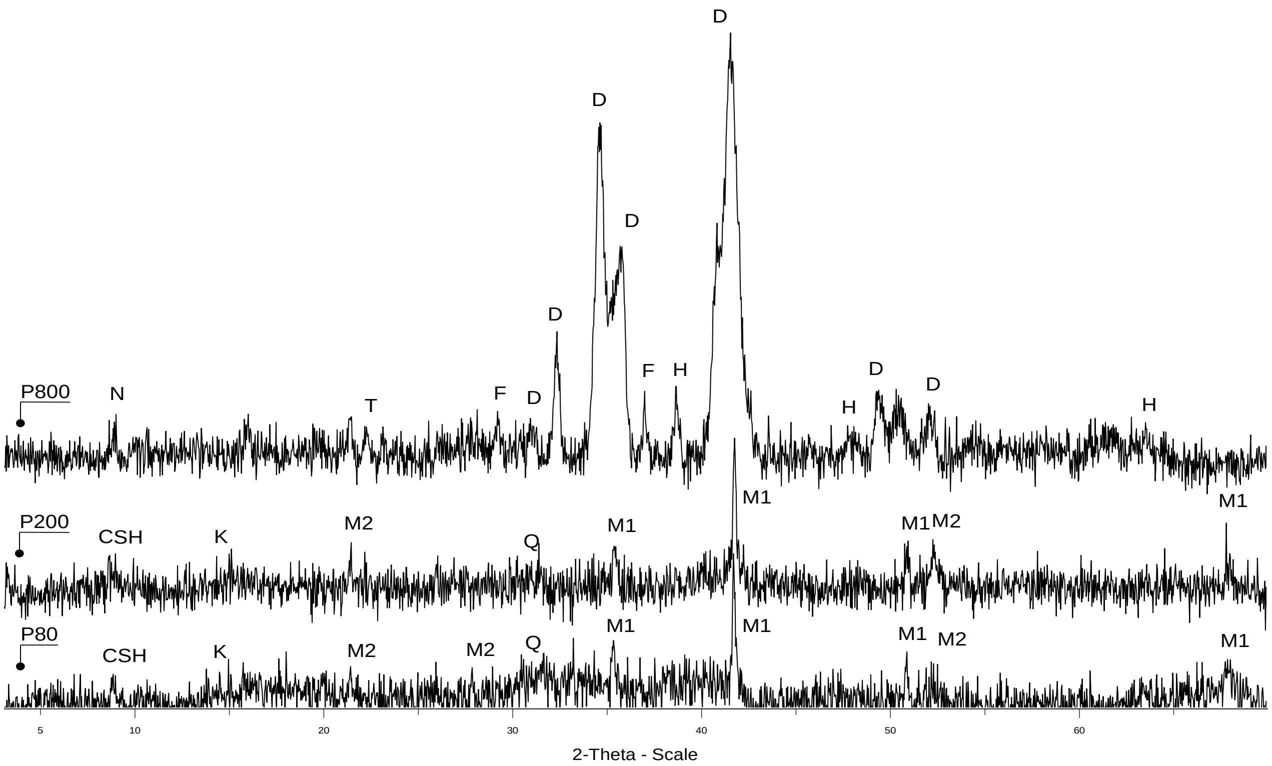
pH vs. time when geopolymers are immersed in various solutions



Dissolution of Mn, Fe, Ca, Ni, Mg, Cr, Na, K, Al and Si (mg/L) when geopolymers are immersed in 0.05N HCl solution

Geopolymers from FeNi slag

Results and discussion

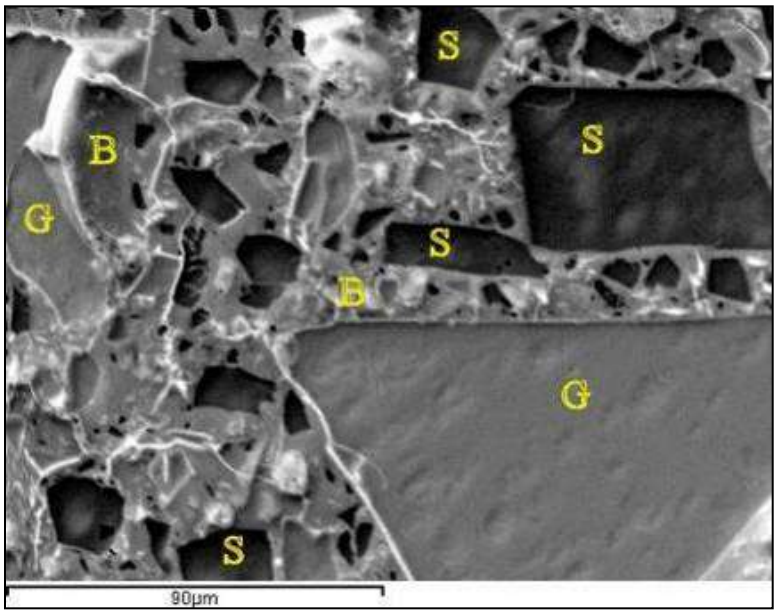


XRD patterns of geopolymers subjected to high temperature heating (P80, P200 and P800 heated at 80, 200, 800 ^oC, respectively)

(Q: quartz, K: kaolinite, M1: magnetite, M2: maghemite, F: fayalite, CSH: calcium silicate hydroxide, D: diopside, T: tridymite, H: hematite, N: $NaAl_{11}O_{17}$)

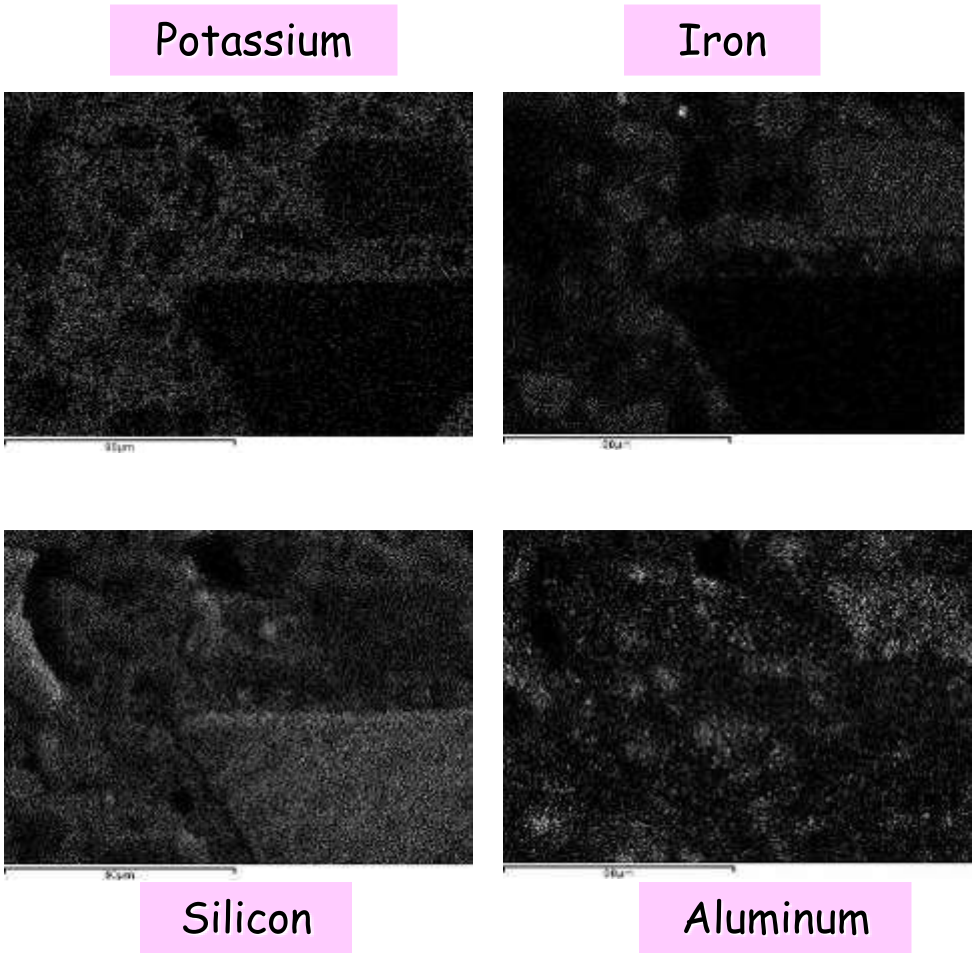
Geopolymers from FeNi slag

Results and discussion



Slag-glass geopolymer 50% w/w

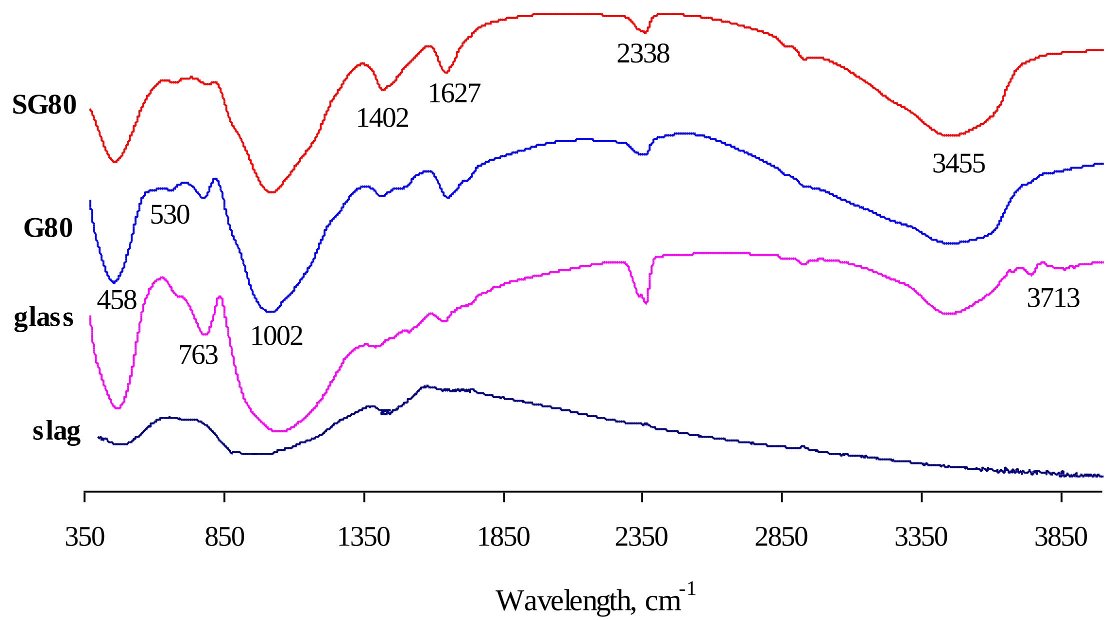
G: glass grains
S: slag grains
B: geopolymeric gel



Geopolymers from FeNi slag
Results and discussion

Infrared absorption bands ➡ identification of bonds

- Asymmetric stretching vibration T–O–Si (T:Si ή Al) [950-1200 cm^{-1}]
- In plane Si–O bending and Al–O linkages [460-465 cm^{-1}]
- Atmospheric carbonation or/and Na_2CO_3 [1410-1570 cm^{-1}]

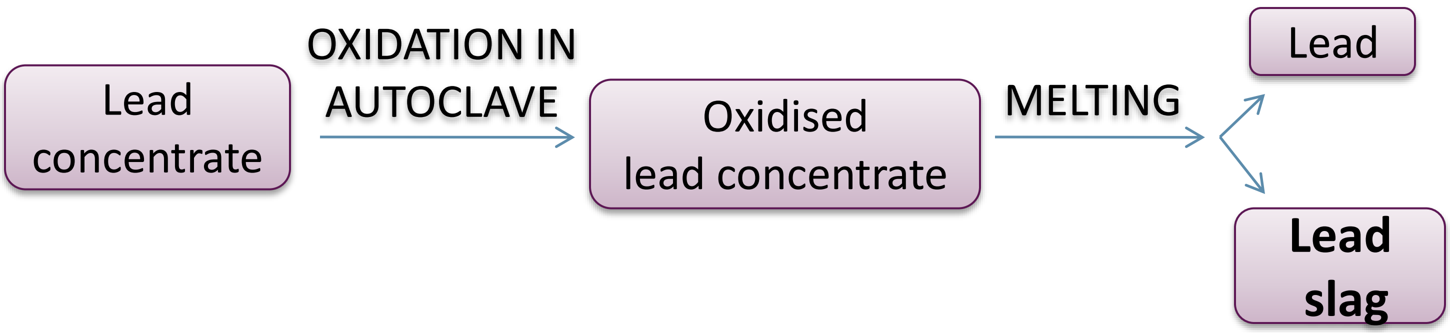


FTIR spectra of slag, glass and G80 glass-based geopolymer, SG80 slag-glass geopolymer

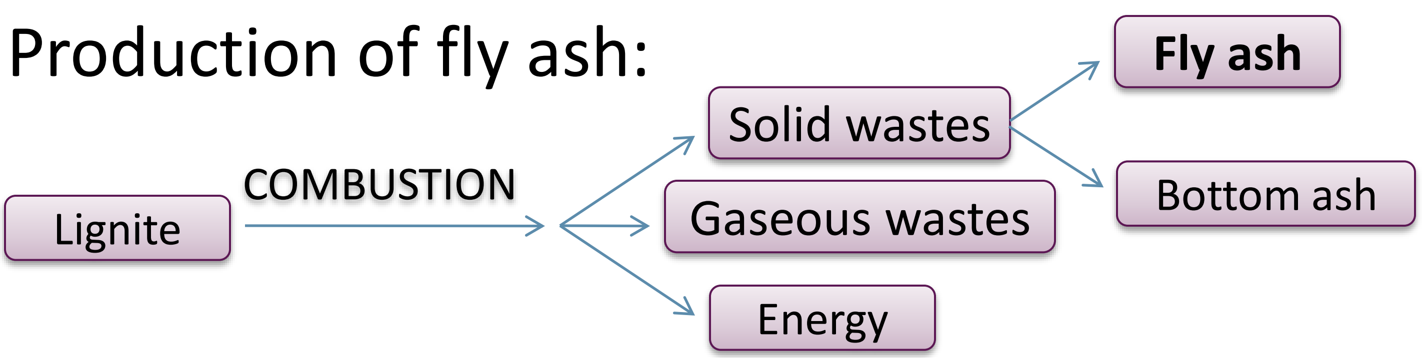
Geopolymers from lead slag

Introduction

- Production of lead slag:



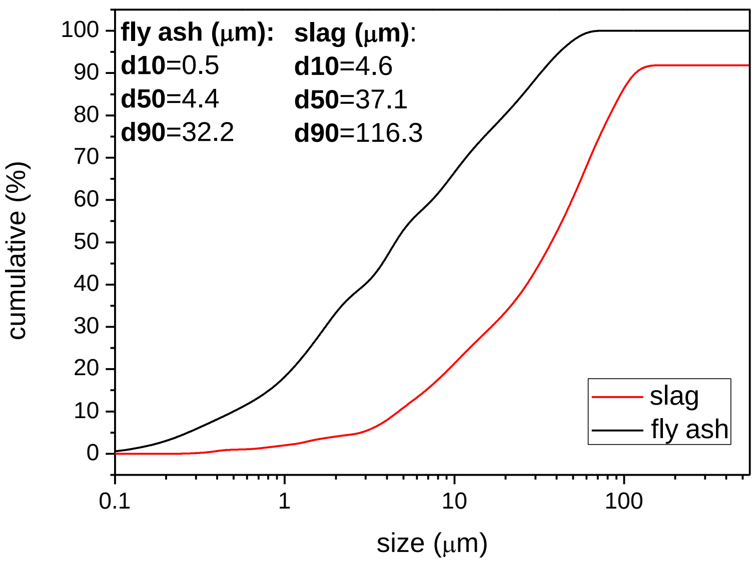
- Fly ash is also used in order to compensate the small amount of Si-, Al- source in lead slag
- Production of fly ash:



Geopolymers from lead slag

Materials

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	PbO
Slag	21.58	1.71	35.9	2.78	0.2	15.83	0.3	8.3	13.4
Fly ash	51.4	23.5	7.73	9.21	1.69	0.89	1.45	2.66	-



Slag	Fly ash
Litharge, PbO	**Quartz,** SiO_2
Wuestite, FeO	**Gehlenite,** $Ca_2Al_2SiO_7$
Sodium aluminium silicate, $Na_6Al_4Si_4O_{17}$	**Magnetite,** Fe_3O_4
Magnetite, Fe_3O_4	**Anorthite,** $CaAl_2Si_2O_8$
Sodium zinc silicate, Na_2ZnSiO_4	**Anhydrite,** $CaSO_4$

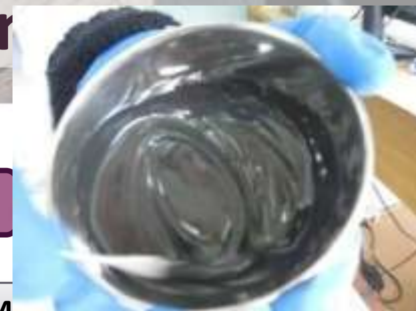
Geopolymers from lead slag

Sample preparation

materials → GRINDING → MIXING → CASTING →

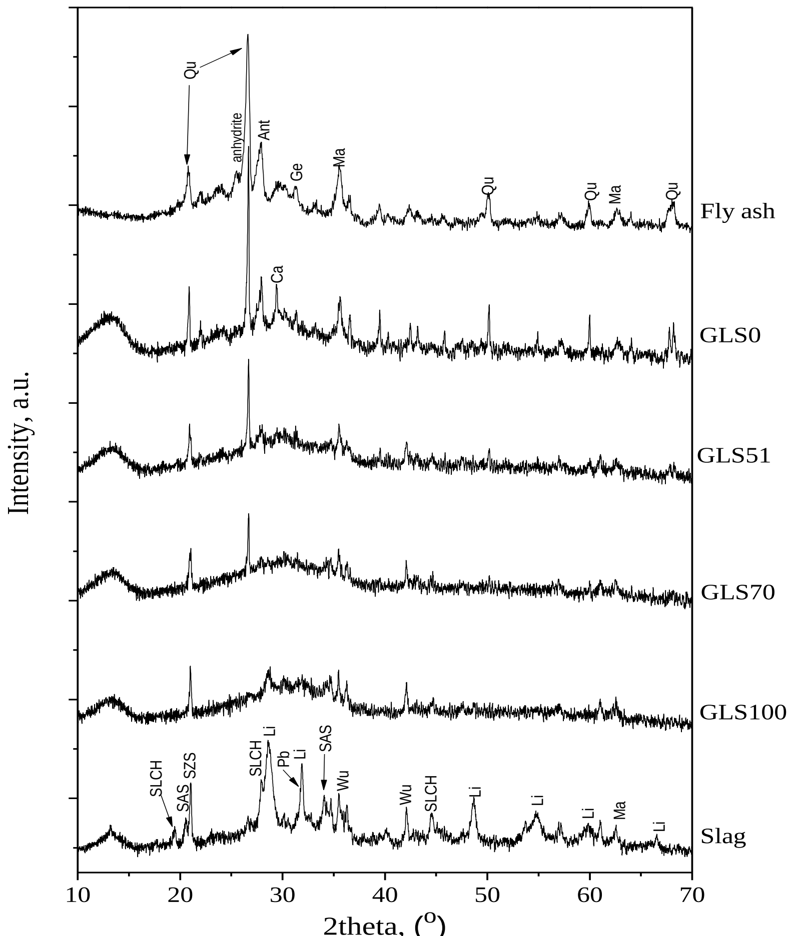
SS

H



		Slag			S/W	Si/Al
		28.2	25.4	20.8	3.59	5.04
GL51	48.9	51.1	22.0	15.7	4.31	5.97
GL70	29.8	70.2	19.4	11.5	5.19	7.63
GL86	13.8	86.2	17.2	8.0	6.31	11.3

Geopolymers from lead slag
Results and discussion: Crystalline phases



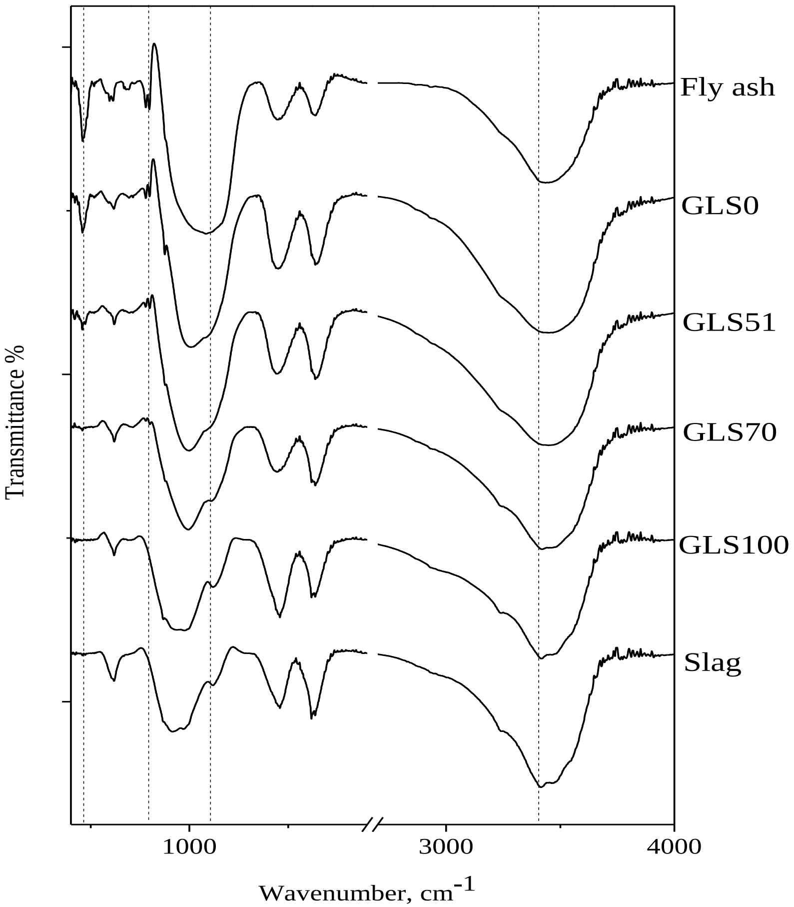
Qu-quartz , An-anorthite , Ma-magnetite, Ge-gehlenite
Ca-calcite, Li-litharge , SAS-sodium aluminium silicate
Wu- wuestite , SZS-sodium zinc silicate, Pb-lead

Fly ash		
Phase	**Before**	**After**
Anorthite	Y	Y
Gehlenite	Y	Y
Magnetite	Y	Y
Quartz	Y	Y
Anhydrite	Y	N
Calcite	N	Y

Slag		
Phase	**Before**	**After**
Litharge	Y	traces
Wüstite	Y	Y
Sodium aluminium silicate	Y	Y
Magnetite	Y	Y
Sodium zinc silicate	Y	Y
Sodium lead carbonate hydrate	(after storing)	

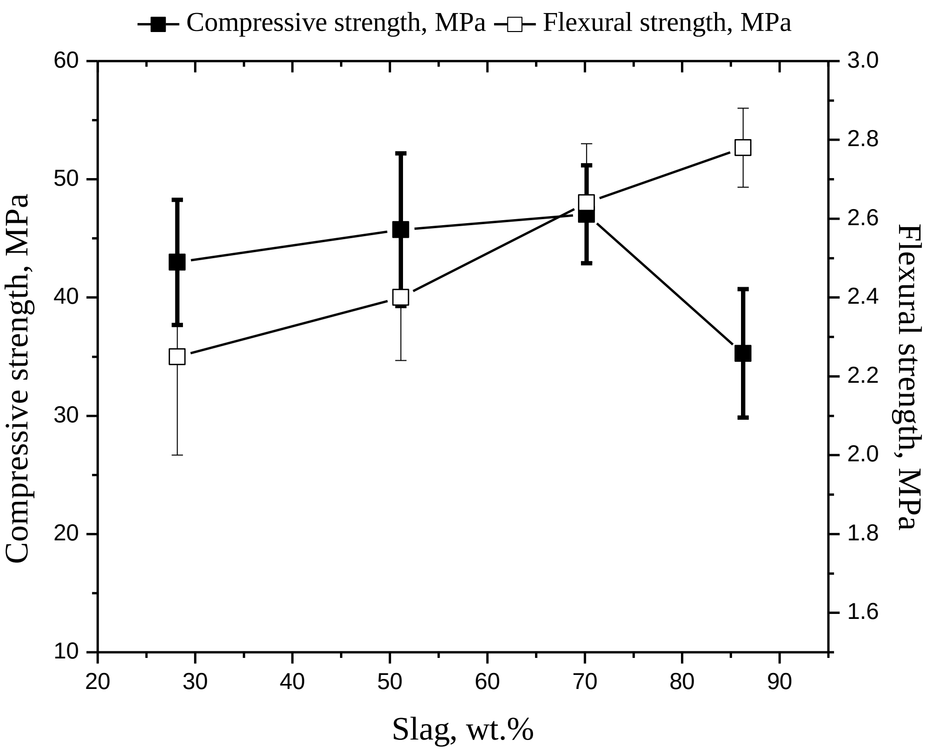
Geopolymers from lead slag

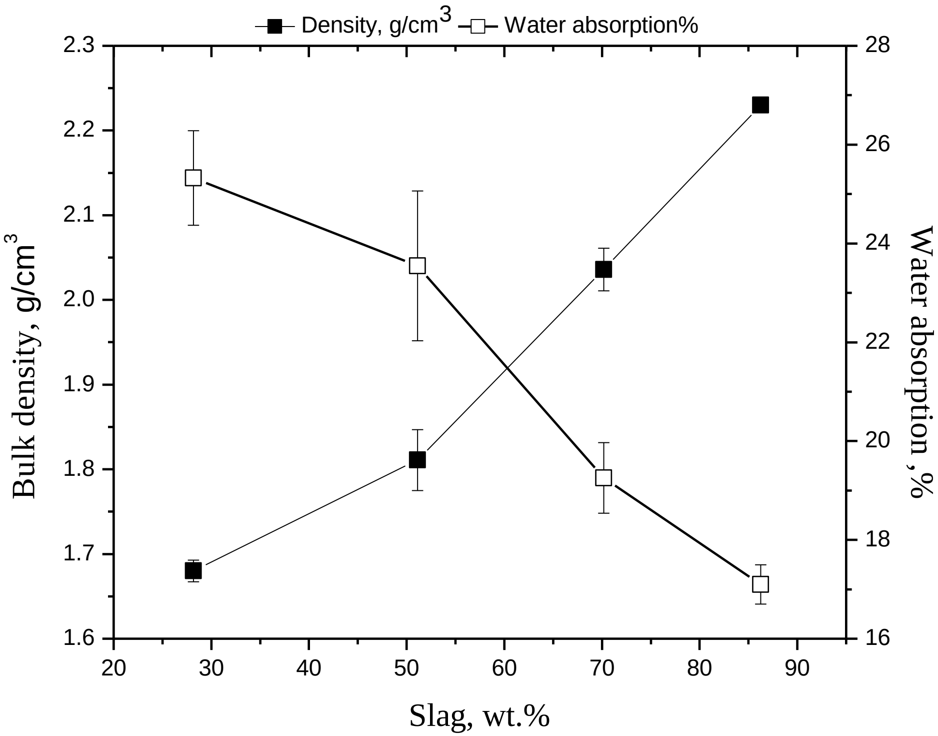
Results and discussion: Bonds characteristics



- The sharpening and shifting of the main band for the geopolymer with 100% fly ash, attributed to asymmetric stretching vibrations of Si – O – Si and Al – O – Si, indicates the formation of the aluminosilicate gel
- When only lead slag was used, the FTIR pattern of the geopolymers produced appears almost identical to the raw material
- For specimens produced using both fly ash and lead slag as the percent of slag in the body increases, the IR patterns resemble more the 100% slag geopolymer

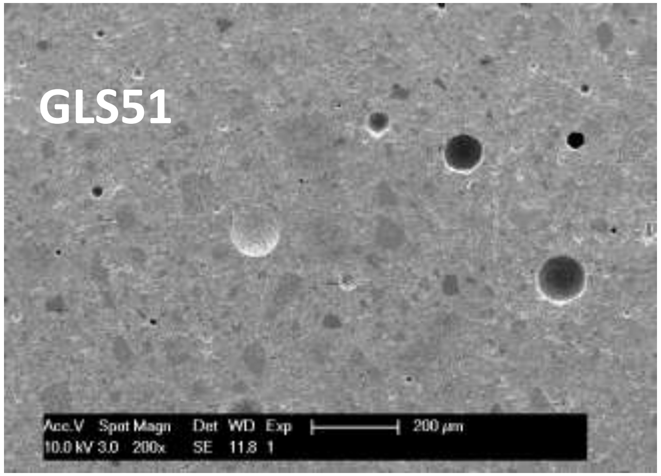
Geopolymers from lead slag
Results and discussion: physical properties

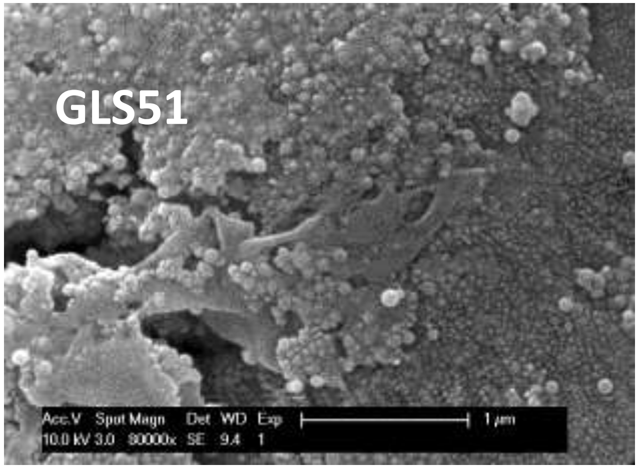


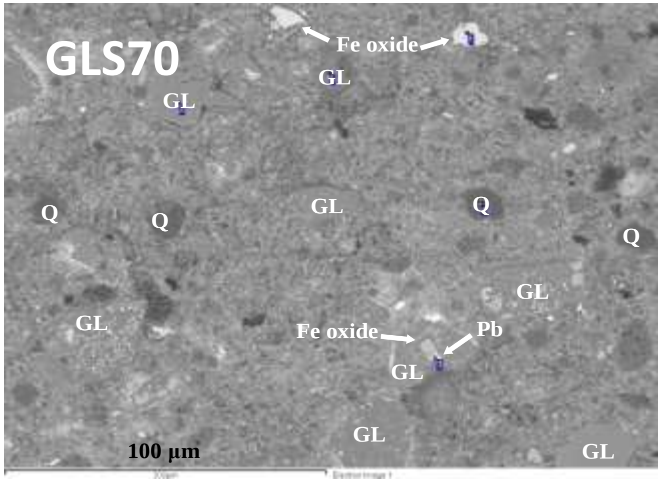


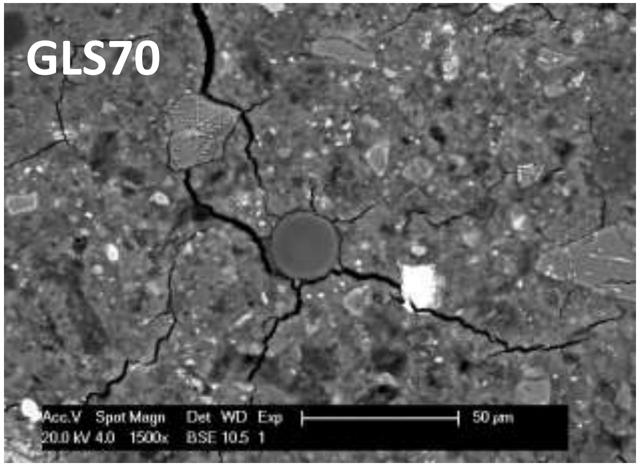
Geopolymers from lead slag

Results and discussion: Microstructure





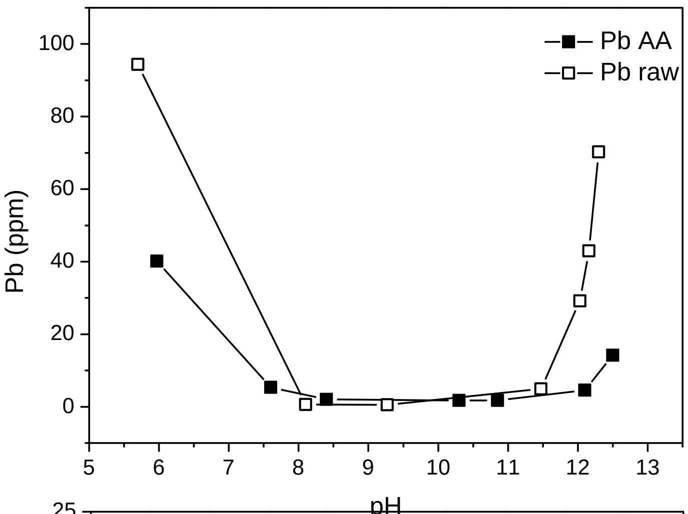


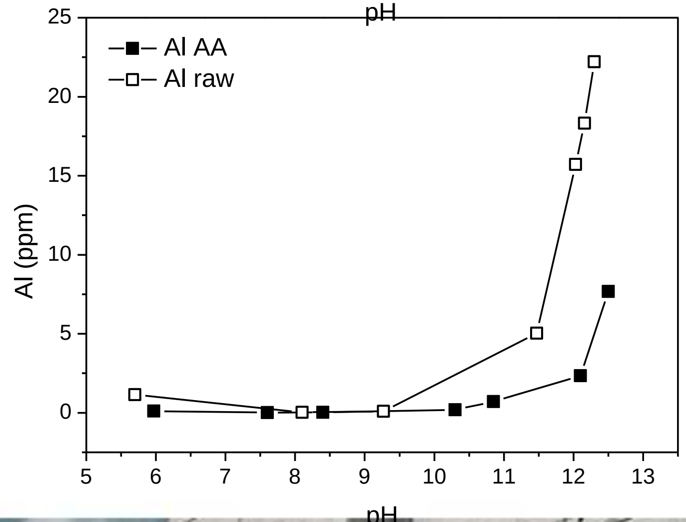


Geopolymers from lead slag

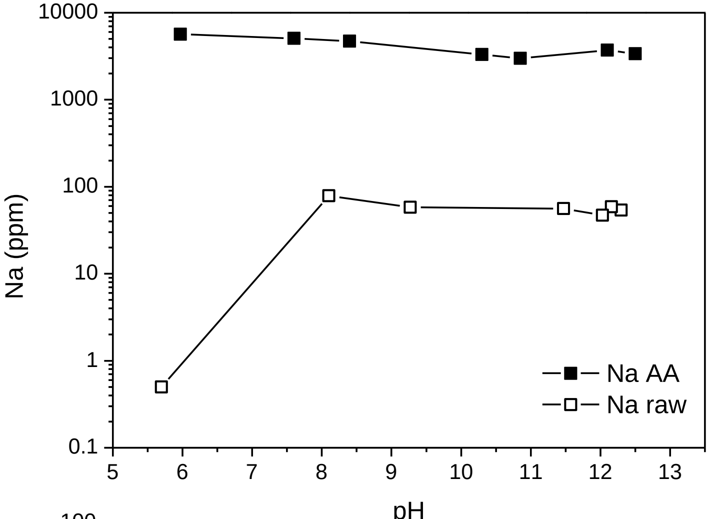
Results and discussion: Leaching

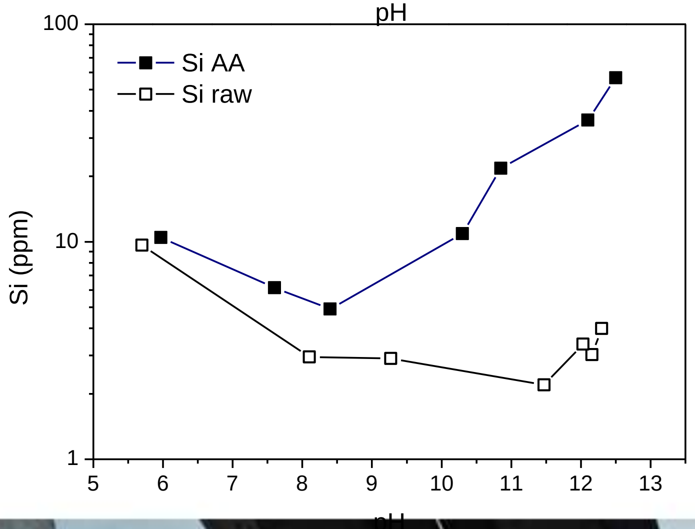
Decreased leaching





Increased leaching





Geopolymers from plasma treated APC residues

APC residues

SELCHP Energy from Waste facility, London

INCINERATOR BOTTOM ASH (IBA)

FLY ASH

AIR POLLUTION CONTROL (APC) RESIDUES

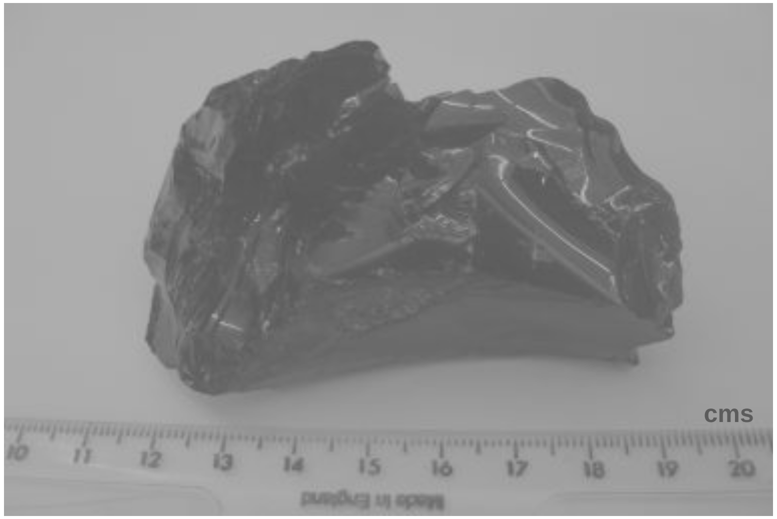
APC RESIDUES

- Hazardous waste from cleaning gaseous emissions
- Mixture of lime, fly ash and carbon
    - Fine particles removed by high efficiency filters
- Issues with APC residues are:
    - Heavy metals
    - High alkalinity
    - High soluble salt content, particularly leachable chloride (Cl^-)

Geopolymers from plasma treated APC residues

APC residue plasma derived glass

- DC plasma treatment of APC residues blended with SiO_2 and Al_2O_3 → Volume reduction ~70–75%
- Amorphous aluminosilicate glass
- Dark green colour
- Inert material



Research aim: Use APC glass as raw material for geopolymer's production

Geopolymers from plasma treated APC residues

Preparation of geopolymers

1. Preparation of activating solutions:

Water → Activating Solution

Alkali Source (NaOH) → Activating Solution

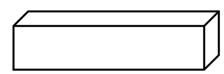
Silicate Source (Sodium silicate solution) → Activating Solution

2. Preparation of mix:

APC glass (SiO_2 = 41.1%, CaO = 32,6%, Al_2O_3 = 14.8%) → Mixing Bowl

Activating Solution → Mixing Bowl

3. Mixing for 10min



80x25x25 mm

4. Casting in rectangular moulds

5. Curing in the moulds for 24hr

(Compressive strength sample 40x25x25 mm)

6. Samples ready for further curing

Geopolymers from plasma treated APC residues
Results and discussion

- Strong and dense geopolymers over a wide range of S/L ratios
- Process highly affected by:
  - Particle size distribution of APC glass:
    - Fine particles improve early compressive strength
    - Broad particle size distribution of APC glass powder improves later strengths
  - NaOH concentration in the activating solution:
    - [NaOH] up to 10M → High strength geopolymers

Geopolymers from plasma treated APC residues
Results and discussion

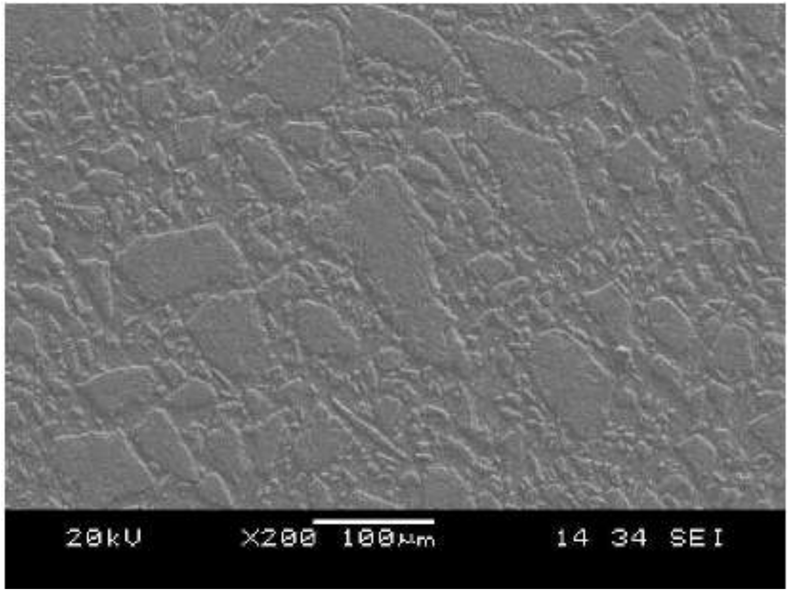
- Optimum APC glass geopolymer's composition:
  - Si/Al = 2.6
  - S/L = 3.4
  - [NaOH] = 6M in the activating solution

- Properties of APC glass geopolymers:
  - Very high strength (110 MPa @ 28 days)
  - High density (2300 kg/m^3)
  - Low porosity and water absorption
  - No leaching of heavy metals
  - High acid resistance
  - High freeze-thaw resistance

- <u>Not a pure geopolymer</u>

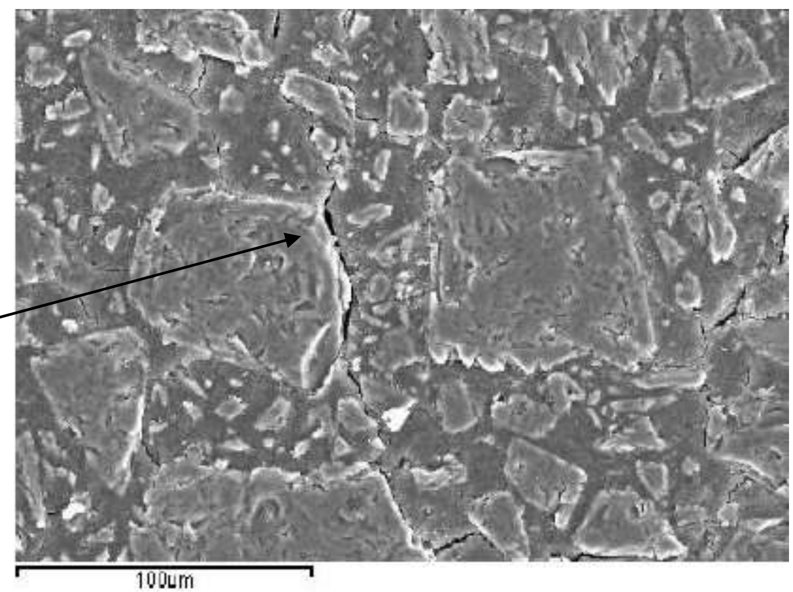
Geopolymers from plasma treated APC residues

Composite microstructure of APC glass geopolymers



- Material resembles a particle reinforced composite
- Geopolymer-glass composite
- Unreacted APC glass have a strengthening and toughening effect

Crack deflection mechanism



Geopolymers from plasma treated APC residues
Binder phase characterisation

- APC glass geopolymer contains both geopolymer gel incorporating calcium and hydration products
- High compressive strength can be attributed to:
  - Calcium present in the material
  - Microstructure with the unreacted APC glass particles acting as rigid inclusions.
- Similarities with both metakaolin and GGBFS geopolymers

Geopolymers from plasma treated APC residues

Potential applications

- Properties similar or better than concrete, cement geopolymer and some types of tiles
- Potential applications:
  - Replacement of cement or concrete in non-structural applications (eg. Pre-cast products, paving blocks)
  - Tile production
  - Hazardous and toxic waste management (Further research)
- Further testing is required for commercial applications

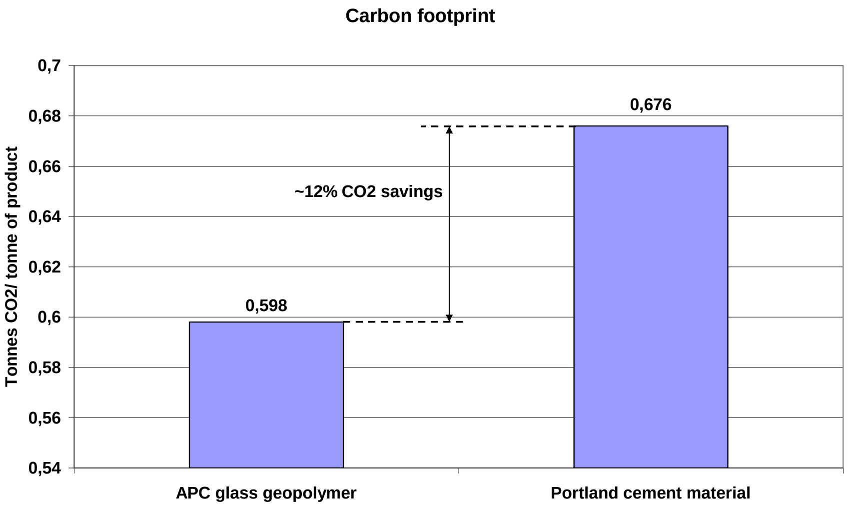
Geopolymers from plasma treated APC residues
Carbon footprint

- Carbon footprint assessment based on Greenhouse Gas Protocol
- Comparison with similar material prepared with Portland cement
- Plasma process:
  - Higher energy consumption than alternative APC residues management options
  - Proven technology which maximises resource efficiency
- DC plasma process on-site WtE plant:
  - On-site solution for APC residues
  - Minimises carbon footprint of process (renewable energy used)
  - Economically attractive. Cost of process independent of energy price variations

Geopolymers from plasma treated APC residues

Carbon footprint

- CF of APC glass geopolymer and PC material is affected:
  - Additional materials used
  - Milling (if required)
- Reuse of APC glass in geopolymers → Savings in use of natural resources



Reuse of APC glass in geopolymers helps to mitigate climate change as CO2 emissions are significantly lower compared to Portland cement use

Conclusions

Geopolymers from FeNi slag
Conclusion

- Geopolymerisation potential of low Ca FeNi slags (high compressive strength ~60 MPa is seen for optimum Si/Al ratio)
- Geopolymers exhibit very good behaviour in various aggressive environments, over a period of 8 months

  - sustain temperature variations between -15 & 60 ^{o}C

  - immersion in distilled water does not practically affect strength

  - immersion in seawater, acid rain or 0.05N HCl solutions decreases strength gradually but still remains above 30 MPa after 8 months

- Analytical techniques (XRD, SEM, FTIR, TG) may be used to elucidate mechanisms involved

Geopolymers from lead slag

Conclusion

- Geopolymers can be made from 100% fly ash, 100% lead slag and mixtures of them
- The main change occurring after geopolymerisation revealed by XRD and IR is that litharge and calcium sulphate dissolve and a new amorphous aluminosilicate gel phase is formed.
- The system of larger particles originating from lead slag in a geopolymeric matrix mainly derived from fly ash, behaves as a composite structure, where the larger particle act as rigid inclusions and contribute in crack deflection during crack propagation.

Geopolymers from plasma treated APC residues
Conclusion

- Plasma treated APC residues is a raw material suitable for geopolymers' production
- Formed amorphous, high strength geopolymer-glass composites
- Unreacted APC glass particles are embedded in the binder phase and provide reinforcement
- The binder phase contains both geopolymer gel incorporating calcium and hydration products
- Existence of both phases contributes to the excellent properties of the material
- Carbon footprint of APC glass geopolymers in ~12% lower than similar products from Portland cement