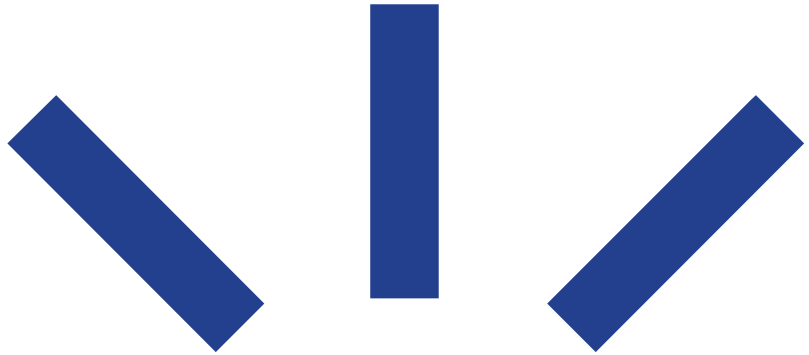

Reactivity of electric arc furnace (EAF) slag investigations & Effect of organic ligands on BFS dissolution and reactivity

Juho Yliniemi

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Inorganic circular materials group

Fibre and Particle Engineering Research Unit
University of Oulu, Finland

- 4 professors, 2 senior research fellows
- 8 postdocs, 28 doctoral researchers
  - Master students, trainees, laboratory technicians
- Budget: ~3 M€/year
- External funding: >80 %
  - Funding: EU Horizon, Business Finland, Research Council of Finland, Private foundations, ERDF, direct company projects
- >50 publications/year in top journals
- High international collaboration network
- High company collaboration

- Topics:
  - Utilization, characterization, and processing of industrial inorganic side streams
  - Magnesia-based binders, CO_2 capturing
  - Environmental applications, water purification
  - Construction materials, aggregates
  - Materials chemistry, dissolution, surface interphase reactions

Principal investigators:

Professor Mirja Illikainen

Professor Päivö Kinnunen

Senior research fellow Katja Ohenoja

Associate professor (tenure) Juho Yliniemi

Associate professor (tenure) Tero Luukkonen

Senior Researcher Priya(dharshini) Perumal

Materials chemistry of inorganic side streams and applications

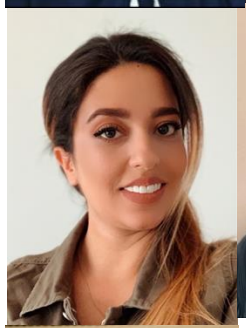
Group leader – Juho Yliniemi

Postdoctoral researchers:

- Dr. Elijah Damilola Adesanya
- Slags; iron-rich clinkers; SCMs; AAMs; fresh and hardened properties of low-CO_2 cements

- Dr. Recep Kurtulus
- Visiting research associate
- Glasses; slags; material synthesis; irradiation research

- Dr. Marco Cantaluppi
- Slags; clinker phase synthesis; mineralogy; beamline investigations; XRD; tomography



Doctoral researchers:

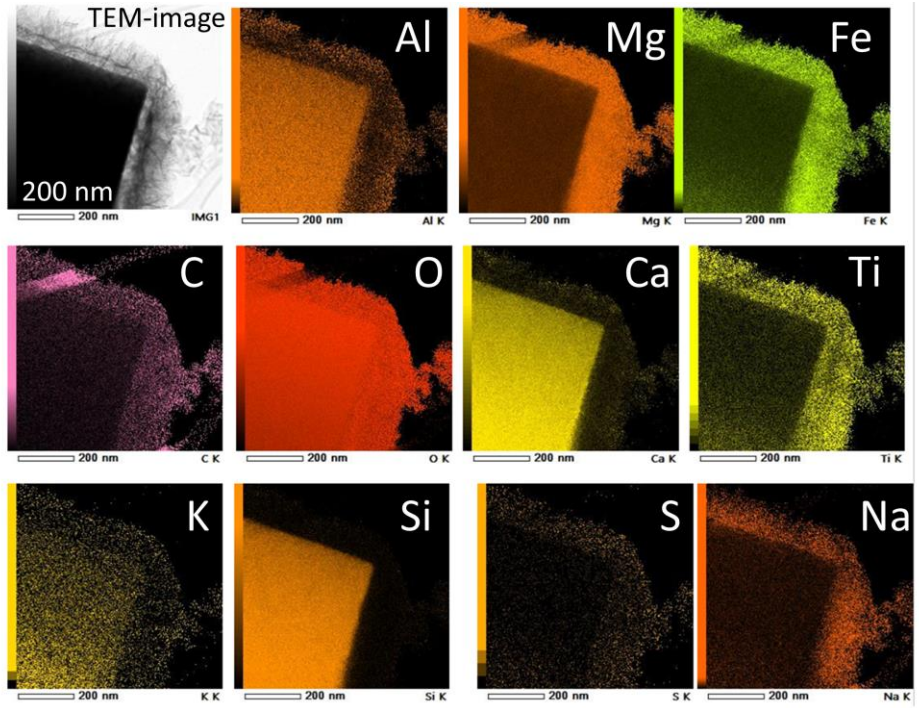
- Milad Eskandarinia, 2023-
- Mechanical activation of slags; Chemical admixtures for low-CO_2 cementitious materials
- Julson Tchio, 2023-
- Fresh and hardened properties of slag cements; pore solution chemistry; Impedance spectroscopy
- Mahtab Akbarzadeh, 2022-
- Mechanochemical activation of minerals; surface interface reactions of aluminosilicates; zeta potential
- Sepideh Bagheri, 2021-
- Organometallic complexation chemistry in cementitious binders, NMR
- Rajeswari Ramaswamy, 2019-
- Glass dissolution-precipitation reactions at high alkaline conditions; SEM/TEM-EDX

Materials chemistry of inorganic side streams and applications-subgroup
at Fibre and Particle Engineering Reseach Unit (FPE)

”How to improve reactivity of side streams and to use them in cementitious applications?”

Research areas:

- Advanced characterization of inorganic side streams
- Low-CO_2 cement binder chemistry
  - Dissolution, precipitation, and hydration reactions
  - Admixtures
  - Metal-ligand complexes
  - Solid surface-liquid interface reactions
- Performance of low-CO_2 cementitious materials
  - Fresh and hardened properties of mortars Characterization of hardened cements in nano- and microscale



[Ramaswamy, Yliniemi, Illikainen. *Dissolution-precipitation reactions of silicate mineral fibers at alkaline pH*. Cement and Concrete Research, 2022.]

Research vision for EAF slags

- **180-280 Mt/year of steel slags is produced globally***
  - 16.8 Mt/year in Europe**
- **At the same time, construction sector needs new low-CO_2 cementitious materials**
- **Our aim is to find suitable utilization pathways for EAF slags with main focus on cementitious materials**
- **7-9 researcher at FPE research unit are working on this topic**

Electric Arc Furnace (EAF) slag composition

- **Main minerological components based on literature:**
  - Larnite (Ca_2SiO_4), wüstite (FeO), merwinite ($Ca_3Mg(SiO_4)_2$), gehlenite ($Ca_2Al_2SiO_7$), mayanite ($C_{12}A_7$), etc.

- **Direct reduction of iron ore (DRI) slag sample (named as AS)**
- **From the analysis done, the slag contains following mineral phases**
  - Magnesiowüstite (Mg,FeO), Åkermanite ($Ca_2Mg(Si_2O_7)$, Gehlenite ($Ca_2Al_2SiO_7$), Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Perovskite ($CaTiO_3$), dicalcium silicates, Calcium aluminate (CA)
- **Mainly poor hydraulic minerals**

Electric Arc Furnace (EAF) slag composition

- **DRI slag has similar chemical composition as EAF slags**

  *EAF slags chemical compositions from literature

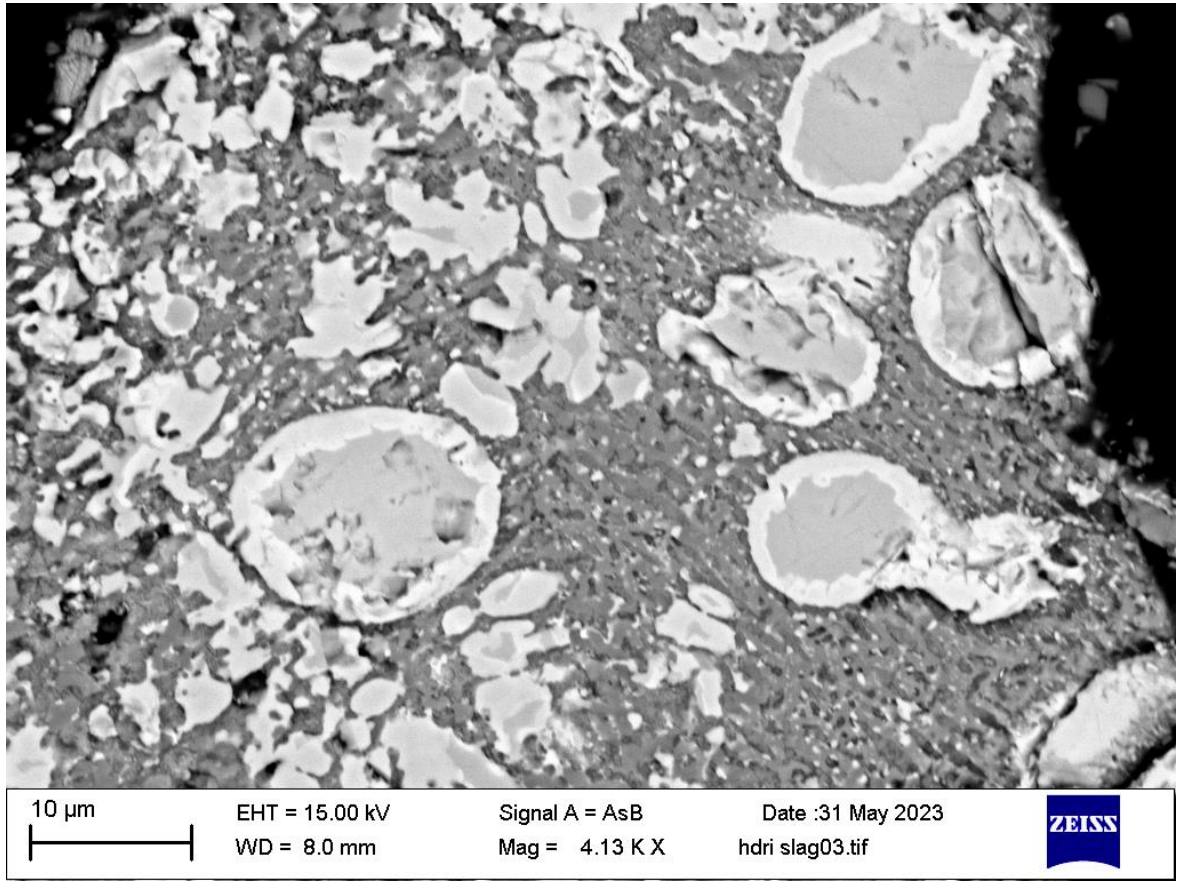
- **Major chemical components include Fe, Ca, Si and Al**

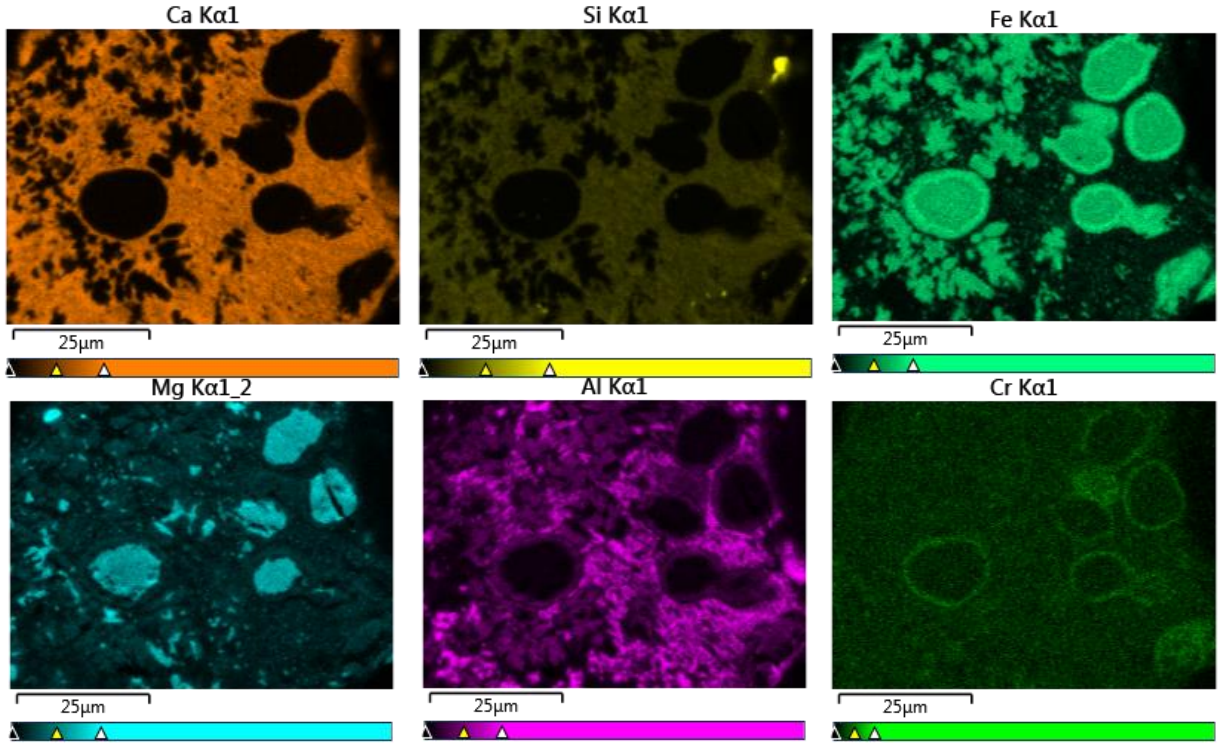
XRF

	#AS [%]	EAF*
CaO	24.6	24-40
SiO_2	16.2	14-18
Al_2O_3	9.6	4.5-25
MgO	6.4	5-13
SO_3	0.1	0-2
Fe_2O_3	35.3	20-35
Na_2O	0.3	-
K_2O	0.1	-
MnO	2.1	2-8
P_2O_5	0.3	0-2
Cr_2O_3	0.2	-
TiO_2	1.3	0-1
F-CaO	0.01	0-7

EAF slag composition

- **The elemental composition of the embedded grains are rich in Mg & Fe, while the darker regions consist majorly of Ca, Al and Si.**





Effect of organic ligands on BFS dissolution and reactivity

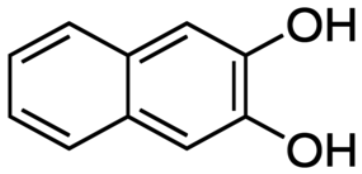
Na_2CO_3-activated BFS pastes

Table 2: Mix proportions of the samples. SC amount equals to 5% Na_2O equivalent of mass of GBFS and water-to-binder ratio of 0.35 for all samples.

Sample name	GBFS (wt.%)	Na_2CO_3 (wt.%)	Water (wt.%)	Ligand dosage in activator solution (mmol/L)
Reference	68	6	26	-
TEA_{25}	68	6	26	25
TEA_{100}	68	6	26	100
TEA_{150}	68	6	26	150
$TIPA_{25}$	68	6	26	25
$TIPA_{100}$	68	6	26	100
$TIPA_{150}$	68	6	26	150
NTA_{25}	68	6	26	25
NTA_{100}	68	6	26	100
NTA_{150}	68	6	26	150
$TKPP_{25}$	68	6	26	25
$TKPP_{100}$	68	6	26	100
$TKPP_{150}$	68	6	26	150
$DHNP_{25}$	68	6	26	25
$DHNP_{100}$	68	6	26	100
$DHNP_{150}$	68	6	26	150

From: Ramaswamy, Illikainen, Yliniemi. *Influence of ligands as chemical admixtures in the early hydration of sodium carbonate-activated blast furnace slag*. Construction and building materials, 2024 [accepted]

Isothermal calorimetry



DHNP=2,3-dihydroxynaphtalene

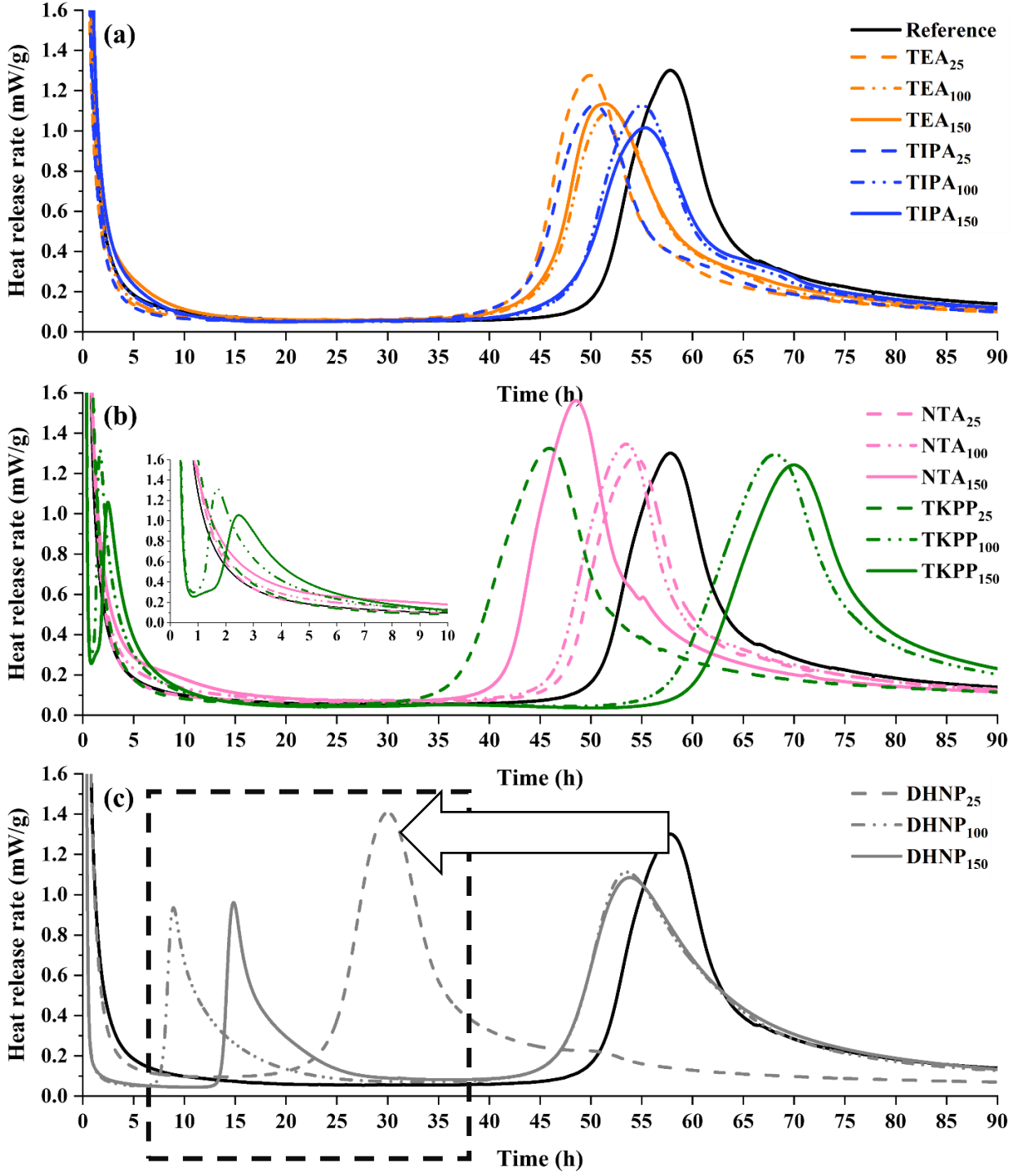


Fig. 1: Isothermal calorimetry results of SC-activated GBFS samples with ligands (a) TEA & TIPA, (b) NTA & TKPP, (c) DHNP with concentrations 25–150 mM, respectively.
From: Ramaswamy, Illikainen, Yliniemi. *Influence of ligands as chemical admixtures in the early hydration of sodium carbonate-activated blast furnace slag*. Construction and building materials, 2024 [accepted]

Compressive strength

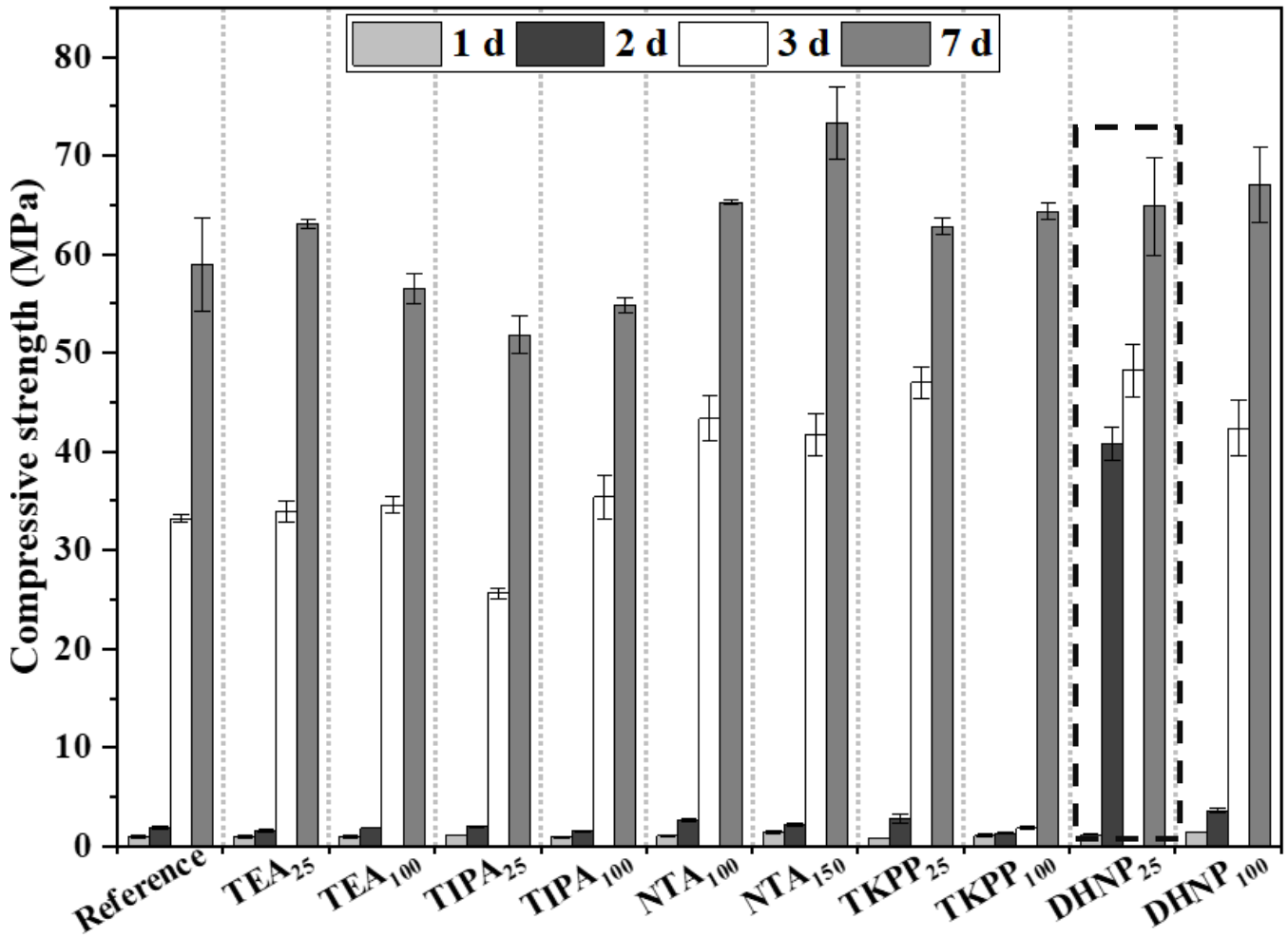


Fig. 2: Compressive strength of SC-activated GBFS samples with and without ligand (Reference). From: Ramaswamy, Illikainen, Yliniemi. *Influence of ligands as chemical admixtures in the early hydration of sodium carbonate-activated blast furnace slag*. Construction and building materials, 2024 [accepted]

Pore solution composition

- Ligands can influence the pore solution chemistry which may influence the IAP of the precipitating phases.
- All ligands increased Si concentration in the solution indicating increased extent of GBFS dissolution. Even though the ligands increased the pH of the system, DHNP which performed best, had lowest pH at initial stages.

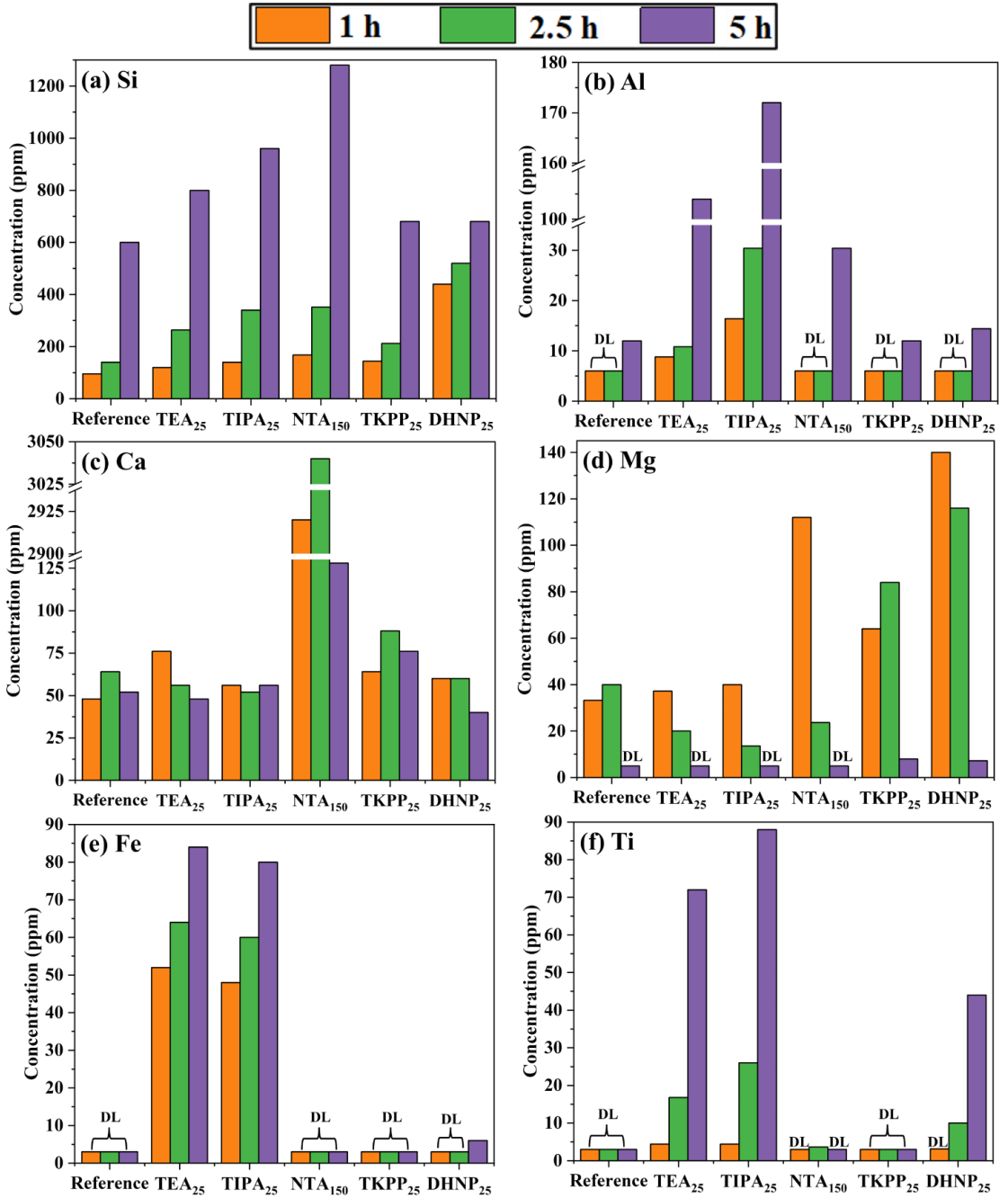


Fig. 6. Elemental concentration (in ppm) a) silicon, b) aluminium, c) calcium, d) magnesium, e) iron, and f) titanium from the pore solution for dissolution systems (at L/S ratio (w/w) of 1.05) with and without ligands after 1 h (orange), 2.5 h (green) and 5 h (purple) of dissolution, respectively.
From: Ramaswamy, Illikainen, Yliniemi. *Influence of ligands as chemical admixtures in the early hydration of sodium carbonate-activated blast furnace slag*. Construction and building materials, 2024 [accepted]

XRD

- **The main hydration products observed after 7 d were**
  - poorly ordered C-(A)-S-H gel
  - poorly ordered carbonate containing Mg-Al-LDH $Mg_{0.75}Al_{0.25}(CO_3)_{0.125}(OH)_2(H_2O)_{0.5}$
  - calcite $CaCO_3$,
  - gaylussite $Na_2Ca(CO_3)2.5H_2O$
- **DHNP did not affect the underlying carbonate salts precipitation kinetics unlike other ligands, instead affected the ion activity product (IAP) of other precipitation products such as LDHs and C-(A)-S-H, by altering the Mg and Si ions concentration in the pore solution.**

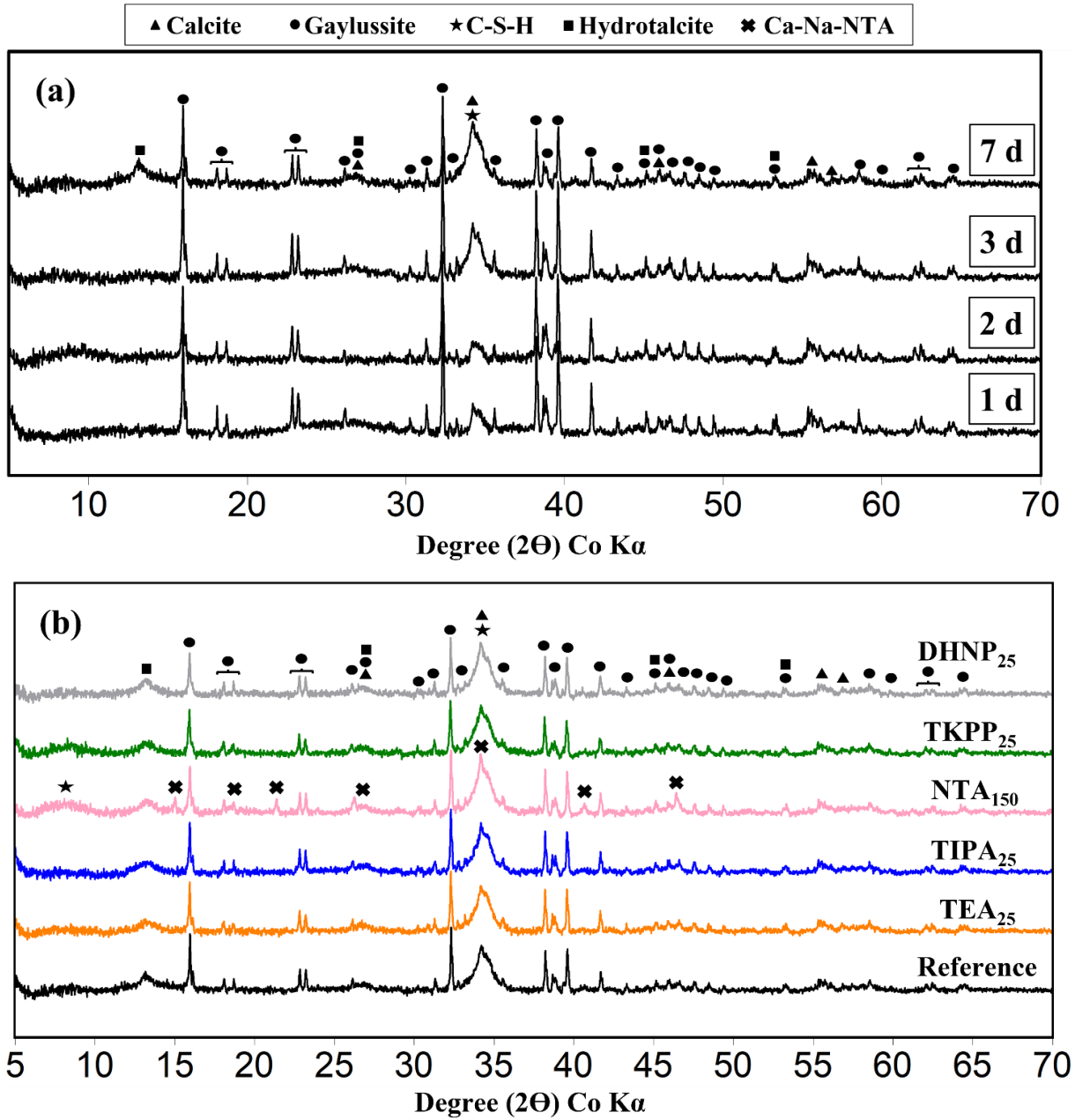
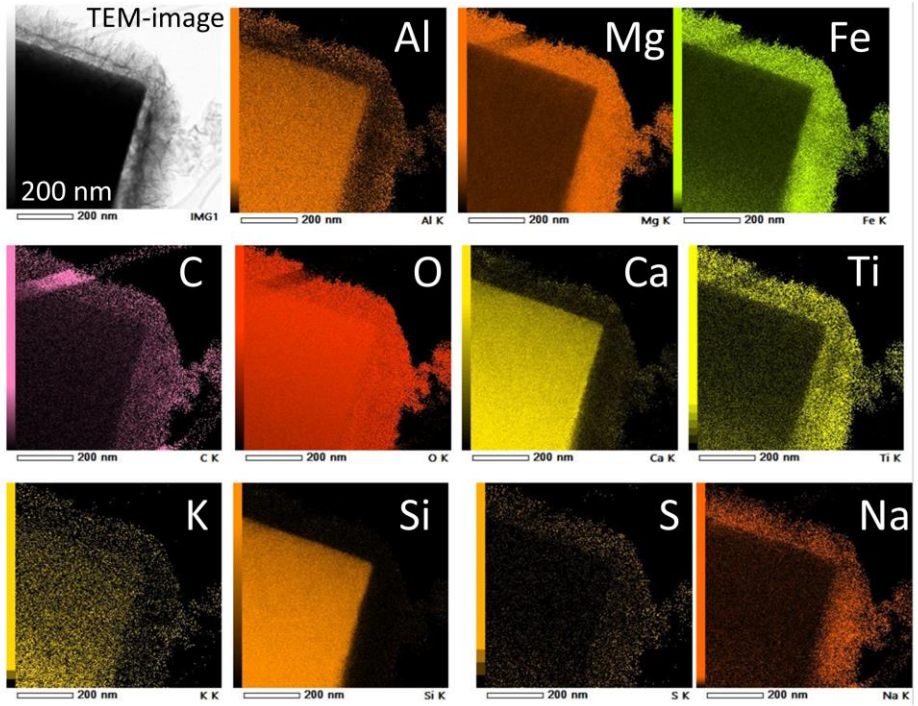


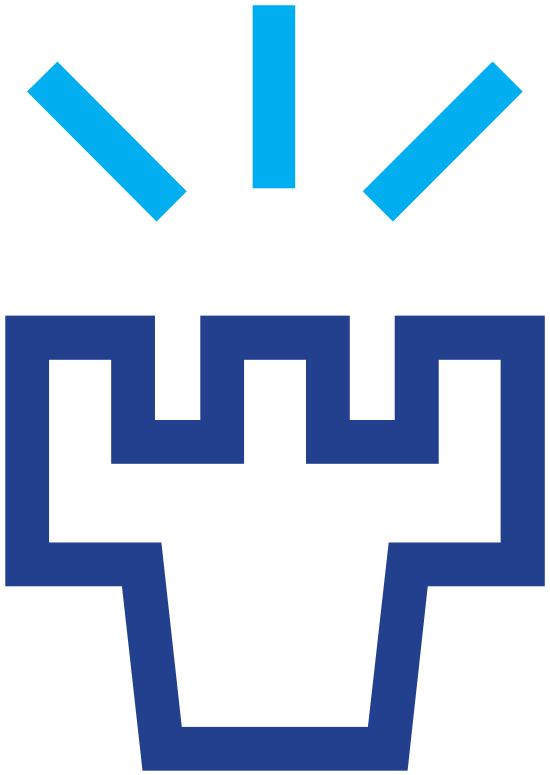
Fig. 3: XRD of SC-activated slag (a) Reference sample (1–7d); b) reference and ligand samples after 7 d (ligand dosages based on microcalorimetry results).
From: Ramaswamy, Illikainen, Yliniemi. *Influence of ligands as chemical admixtures in the early hydration of sodium carbonate-activated blast furnace slag*. Construction and building materials, 2024 [accepted]

Conclusions



- **EAF slags have low reactivity as cementitious material**
  - Main potential phases are dicalcium silicates
- **We are investigating methods to improve the reactivity of EAF slags for various cementitious systems: SCMs, AAMs, Fe-rich clinkers, etc.**
- **Organic ligands have potential to improve reactivity of inorganic side streams**
  - For example, 25 mM dosage of DHNP accelerated the hydration kinetics by 28 h and produced 2-day strength of 41 MPa compared to the reference of only 2 MPa
- **Ligands increase the extent of dissolution, affect speciation of metals in pore solution, and affect precipitation reactions**

Thank you!



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