HYDRAULIC BINDER FROM INDUSTRIAL SIDE-STREAMS IN FINLAND

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Nordic Recycling Day VIII, 26 - 27th September, 2017

UNIVERSITY OF OULU

OUTLINE OF PRESENTATION

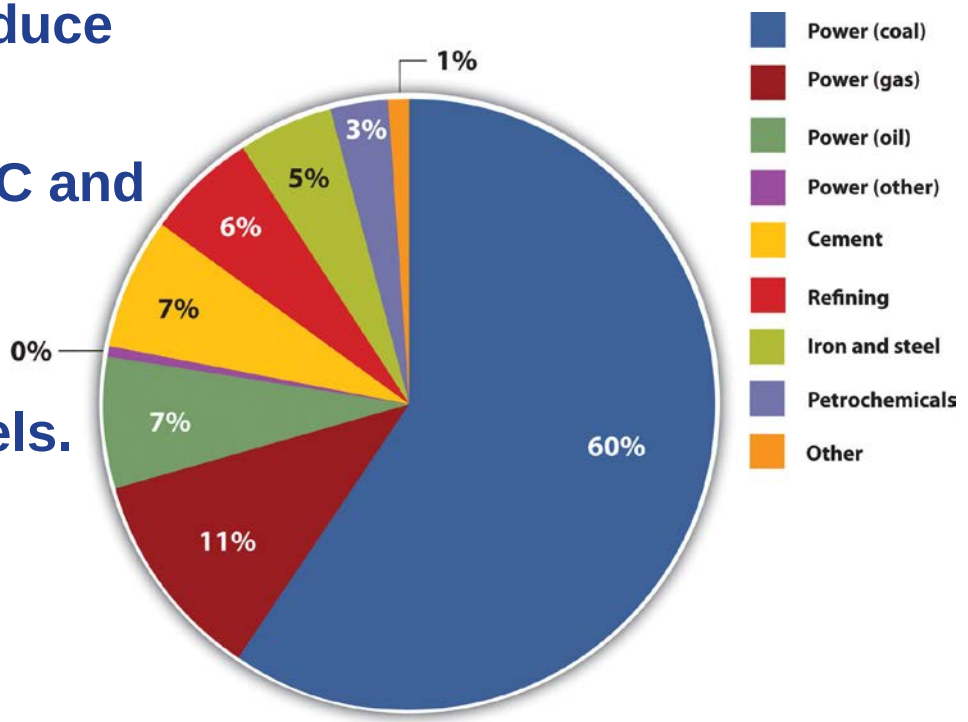
- **Background**
- **Research Objectives**
- **Preliminary Results**
- **Summary and Conclusion**

Background

- **Ordinary Portland Cement (OPC) production generates approx. 7% of total anthropogenic CO_2 emissions worldwide.**

- **Increasing infrastructure development worldwide will increase this number (5% annual increase in demand of OPC).**
- **EU 2050 climate & energy framework, plan to reduce 80% of these emissions by 2030.**
- **Several studies done on reducing the use of OPC and GHG emissions through:**

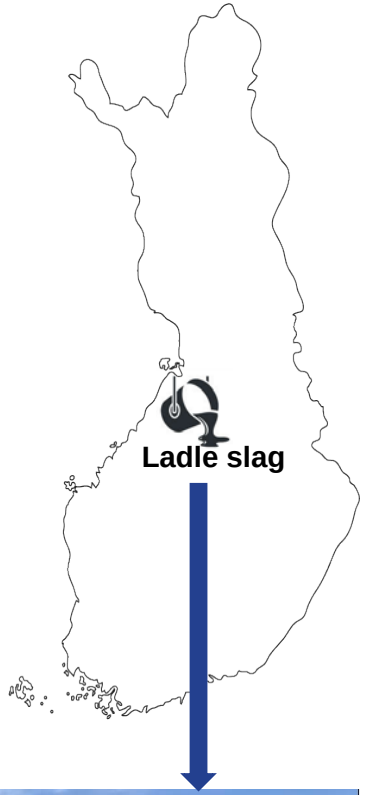
- **Partial replacement (blended cement)**
- **Replacing high-carbon fuels with low-carbon fuels.**
- **OPC-free cementitious binder**



Background

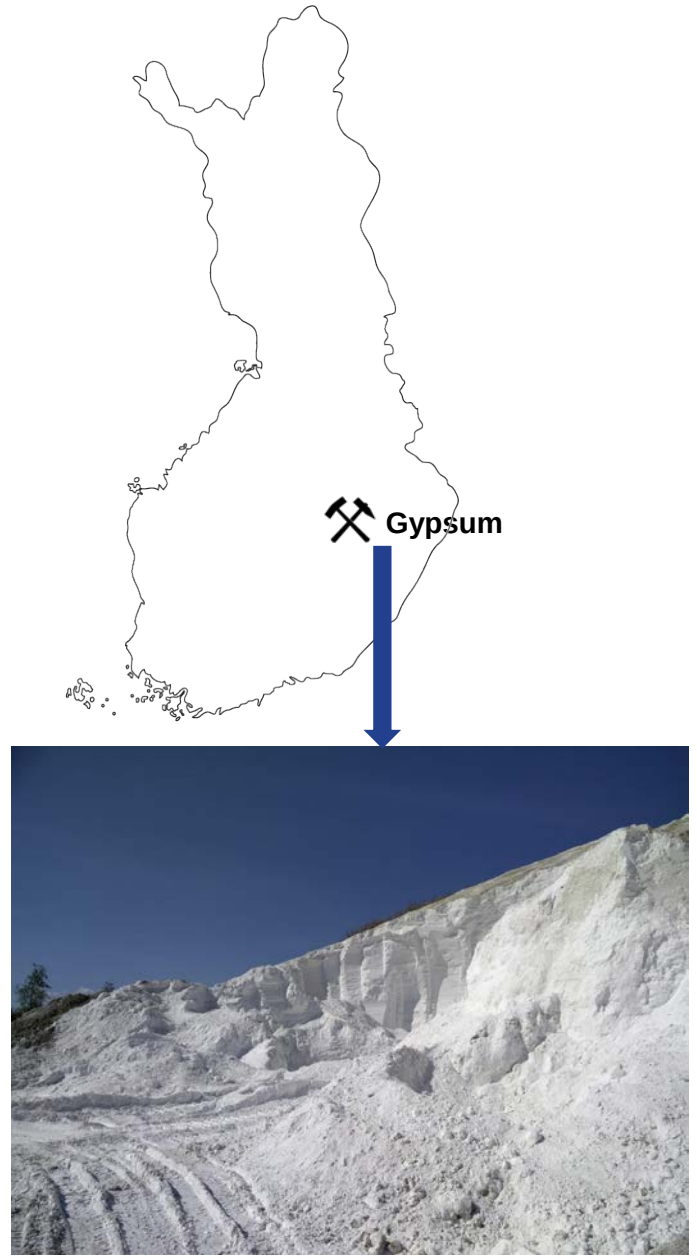
- **Millions of tons of mineral side streams produced in Finland from Metallurgy, Energy recovery, Pulp & Paper Industry, Mining etc.**
  - **Ladle slag is an industrial by-product generated during iron and steel making processes. 60 thousand tons of this slag is generated yearly in Finland and between 1.9 to 2.4 Mt generated in Europe.**

- Due to its physicochemical characteristics and mineralogy could be utilized in construction as a value added products.



Background

- In Silinjärvi Finland, exist a pile of gypsum, a waste product generated from phosphate production.
- The use of Gypsum in concrete dates back to ancient Egyptians using Lime and Gypsum to create a material that harden better.
- In OPC, 5% of Gypsum is used to control the setting and workability of cement.



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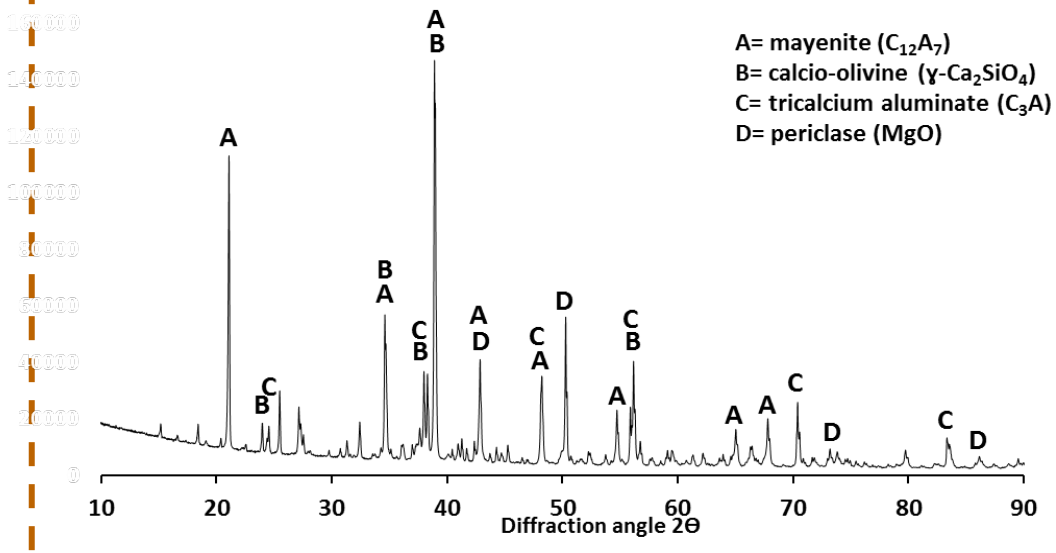
Research Objectives

- Considering the chemical and mineralogy composition of these industrial side streams, an **OPC-free slag cement** can be designed as an effective method for recycling in construction materials and reducing the use of OPC.

- Investigate the **hydraulic properties** and the influence of Gypsum addition to Ladle slag on the mortar properties and **reaction products** modification.

- Finally, **economical cost** and determination of conformity with standard specification or requirement for structural applications.

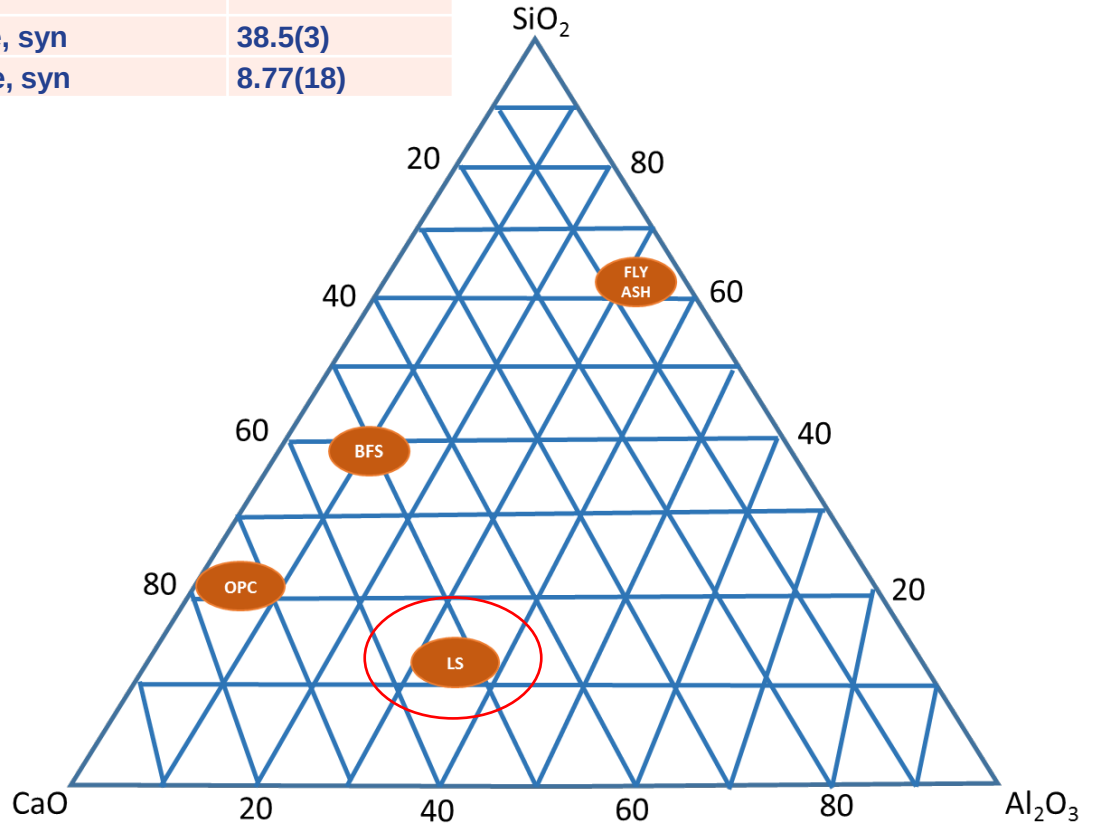
Research Approach



X-ray diffraction of ladle slag

Phase name	Content(%)
Calcio-olivine, syn	25.0(3)
Tricalcium aluminate	27.8(2)
Mayenite, syn	38.5(3)
Periclase, syn	8.77(18)

- Major crystalline phases in LS are Mayenite ($C_{12}A_7$), dicalcium silicate (y-C_2S) and Calcium aluminum oxide (C_3A).
- Major chemical compositions are CaO (50%), Al_2O_3 (28%) and SiO_2 (8%).



The phase diagram of LS in the ternary system

Research Approach

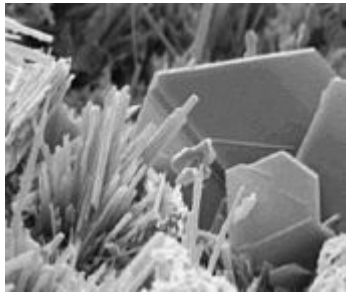
Macro-scale study

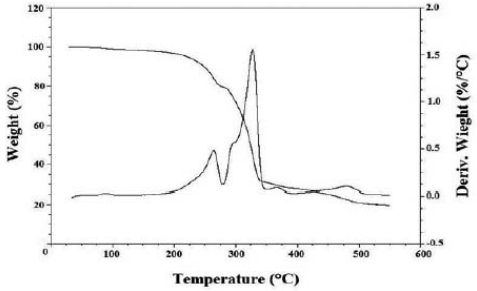
- Mayenite is a fast setting mineral, and therefore workability is poor when hydrated.
- Retarded the setting with several admixtures, best workability and retardation was achieved with citric acid (0.8-1% in H_2O).

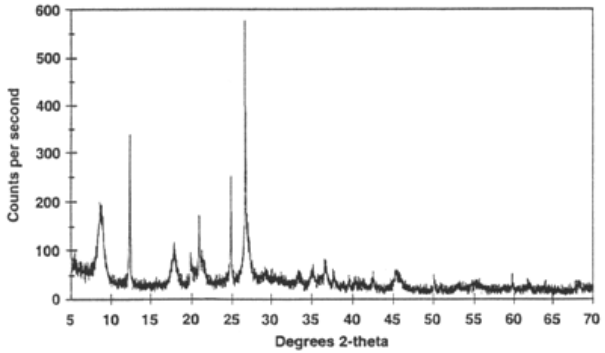
- Mix design was made of: Sand-to-slag ratio: 3:1, water-to-binder: 0.45 modified according to EN-196-1.
- Two samples; 100% LS and another batch with 30% Gypsum and 70% LS.
- Uniaxial compressive strength tests.
- Durability tests (ongoing)

Micro-scale study

- X-ray diffraction (XRD)
- Thermogravimetric analysis (TGA/DTG)
- Scanning electron microscopy (SEM)







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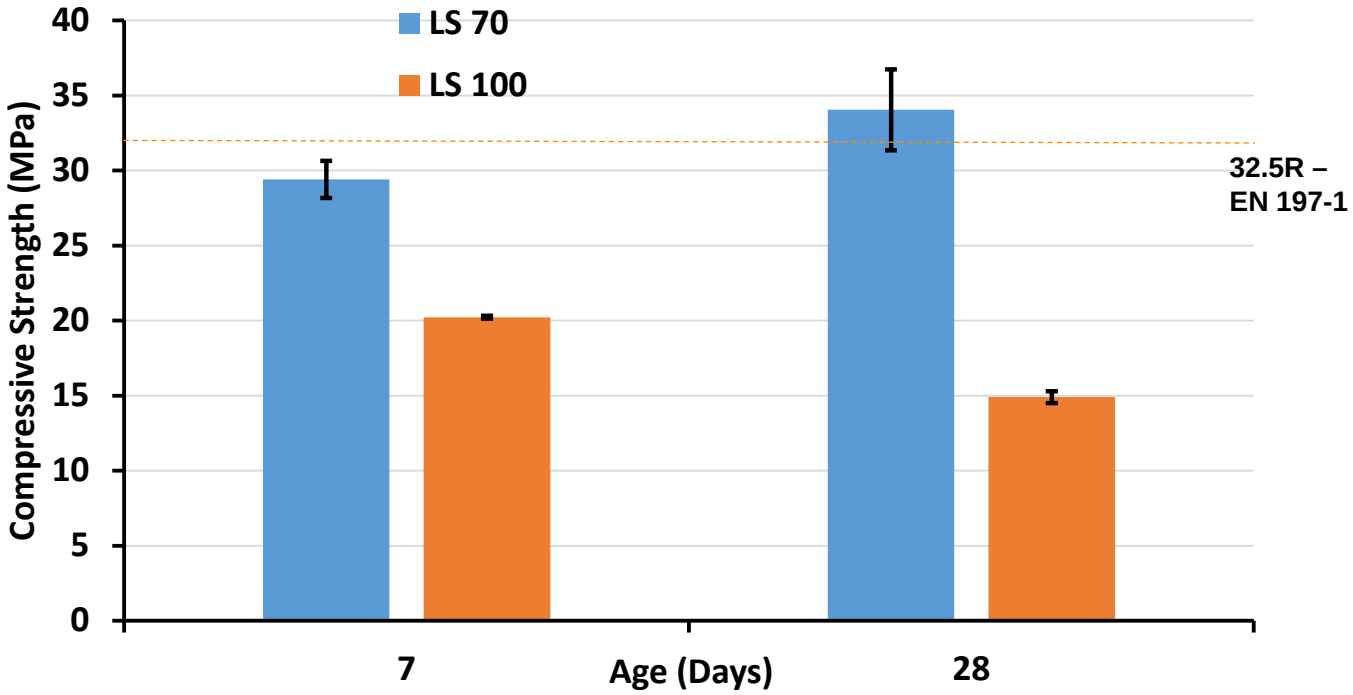
- Strength tests shows the reduction of strength due to conversion and also shows the effect of gypsum.
- Hydration reaction of ladle slag

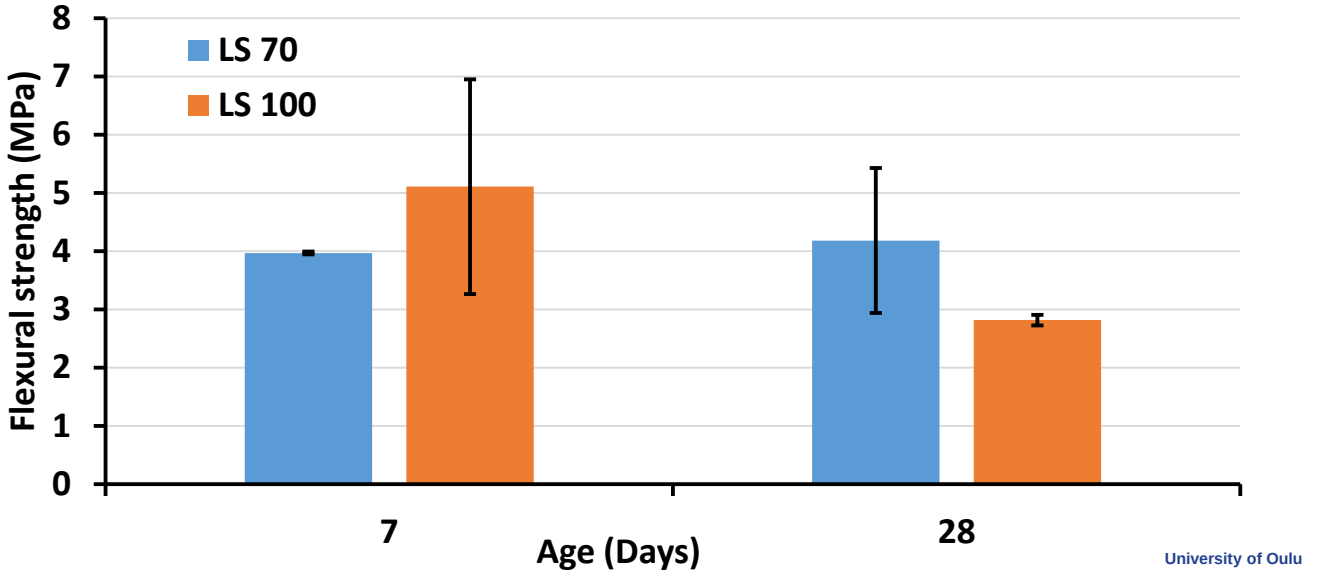
$$C_{12}A_7 + 51H_2O \longrightarrow (6C_2AH_8 + AH)^* \longrightarrow 4C_3AH_6 + 6AH + 18H_2O$$

* This phase of hydration can be prevented by reducing the water content of the mix ≤ 0.4.
* It can also be prevented by adding gypsum to achieve the below reactions.

$$C_{12}A_7 + 12CaSO_4 + 137H_2O \longrightarrow 4(C_3A{\bullet}CaSO_4{\bullet}32H_2O) + 6AH$$

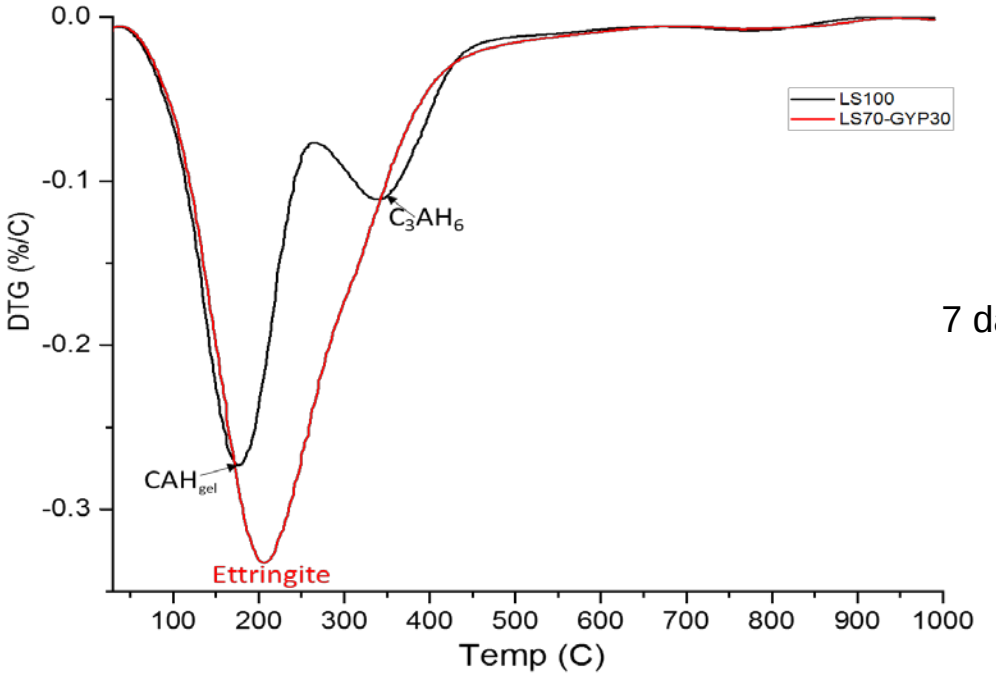
(ettringite)



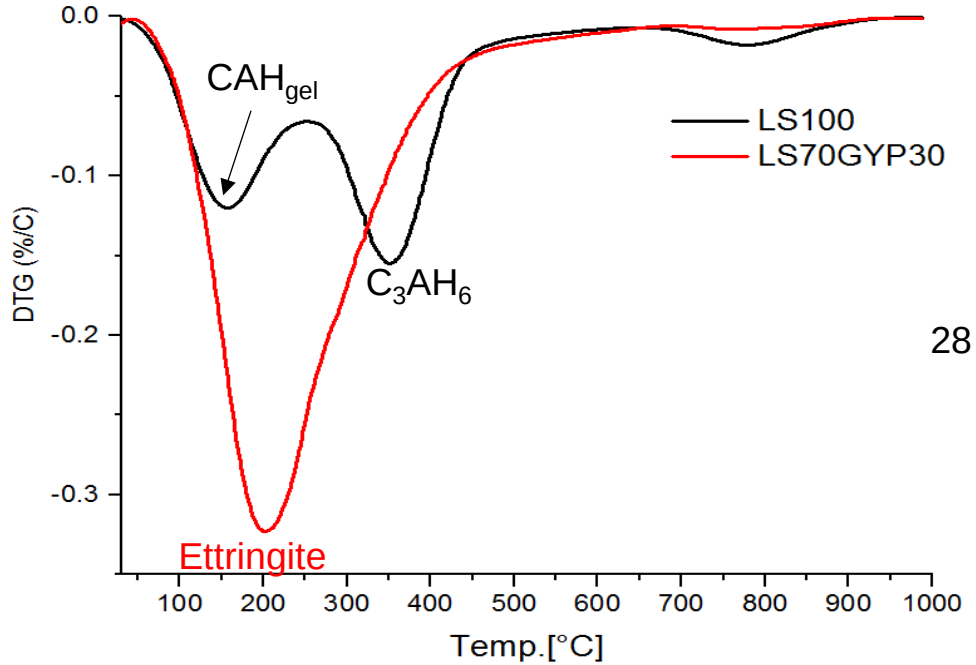


TGA/DTG

- Thermogravimetric analysis was utilized in analyzing the conversion process of the hydration products over time.
- The conversion is observed as a clear increase in the intensity of the stable product (C_3AH_6) with simultaneous decrease in the intensity of the peak of the metastable product (CAH_{gel}) over time.
- LS70GYP30 had similar intensity of peaks for ettringite at both days.



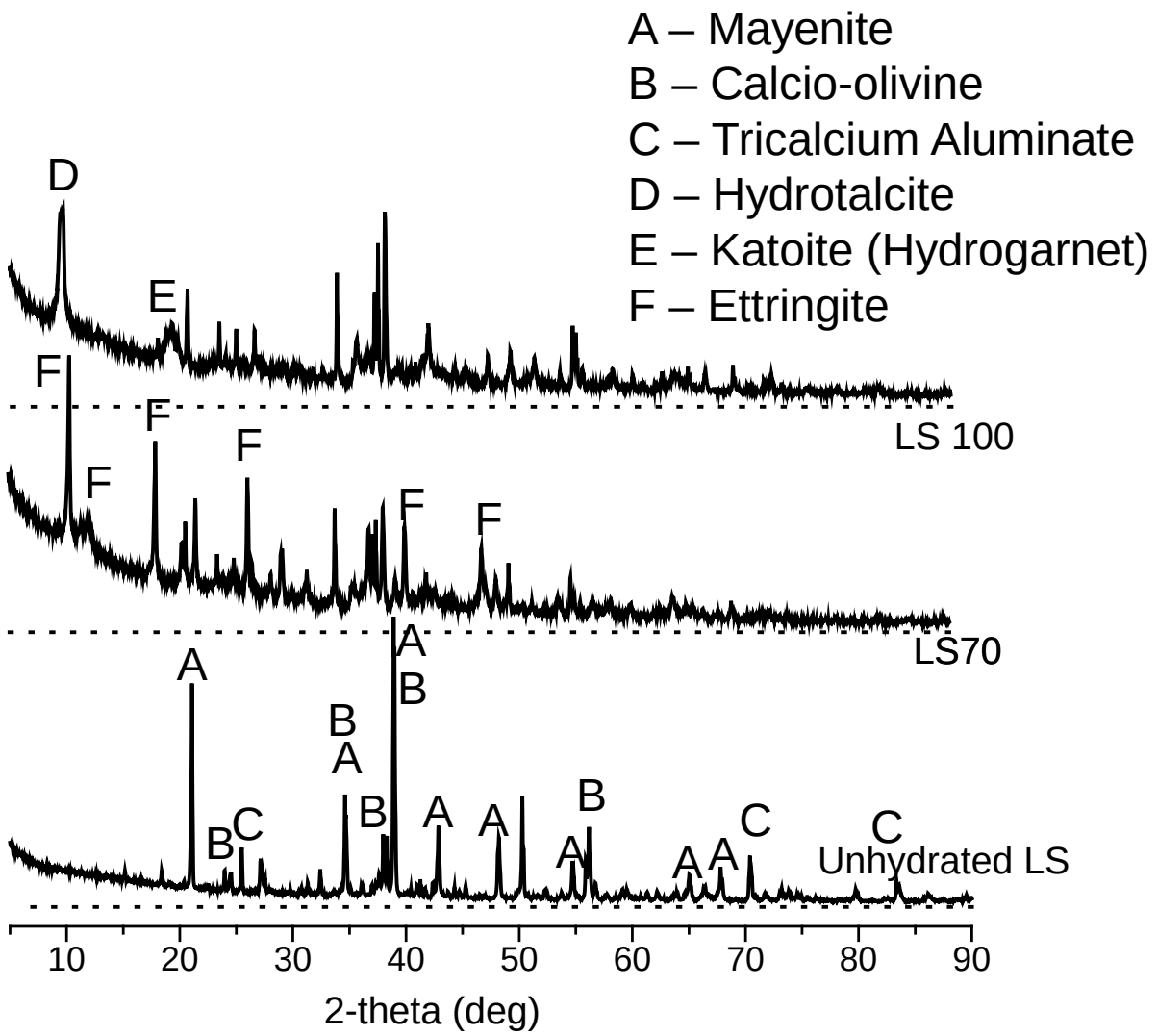
7 days



28 days

XRD

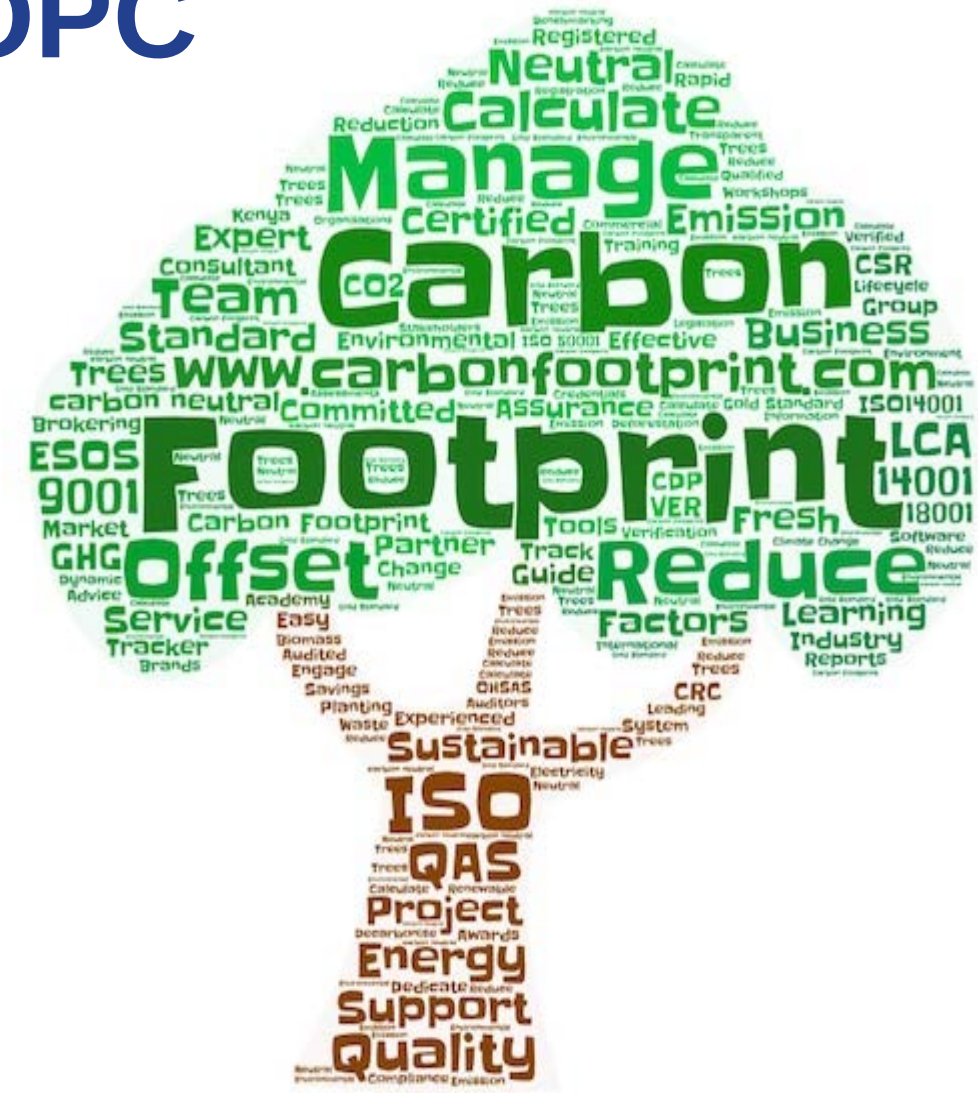
- New phases (ettringite) were observed with LS70GYP30.
- Two new phases were also observed in LS100, suggested as part of the reaction products -, Katoite and Hydrotalcite.
- XRD analyses conforms with DTG results on reaction products formation, although not yet definite with XRD - studies still on-going.



COST ANALYSIS vs. OPC

- For comparison OPC: 100 €/ton
- Ball milling machine (370W) (Laboratory scale mill, 10L capacity)
- Water 3.72e/m^3
- Electricity 0.08e kWh
- Citric acid 600 €/ton (Alibaba)

	Amount (kg/ton)	Cost (€/ton)
Milling electricity cost (2 h)	992 kg	30 €
Citric acid	8 kg	4.8 €
Total cost		34.8 €/ton



*Transportation price for citric acid, gypsum or slag was not added in the calculation.

*It is assumed that gypsum to be used is sourced freely.

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SUMMARY

- Ladle slag exhibits high hydraulic properties
- It’s conversion can be modified by optimizing gypsum content OR reducing water content.
- The resultant cement/mortar strength at 7 and 28 days conforms with EN 197-1 strength class (32.5R) specification
- The strength can be further increased by optimizing the particle packing of both materials (slag and gypsum) and curing conditions.
- In conclusion, utilization of ladle slag and gypsum as new cement is possible (and is promising OPC alternative)

SSAB

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The waste and side streams of today will provide new sources of raw material for tomorrow.

THANK YOU FOR YOUR ATTENTION!