Scottish Research Partnership in Engineering

University of Strathclyde Glasgow

Nuclear Waste Services

LLW Repository Ltd

# Development of sustainable substitutes for Pulverised Fly Ash in Cement and Concrete


Student: Andrea Kozlowski

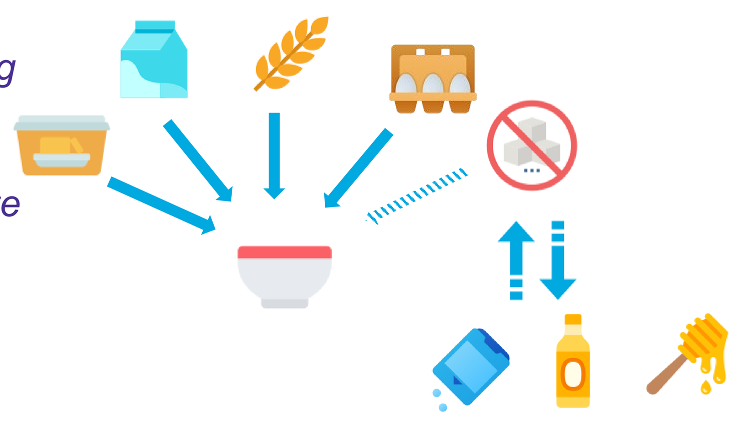
Industry Sponsor: Low-Level Waste Repository (part of Nuclear Waste Services)

Academic Supervisors: Joanna Renshaw, Katherine Dobson


## Industry Challenge

*Imagine:*

- *You promised to bake a cake for tomorrow in the morning and it's already 11PM*
- *You start making the dough and you just miss sugar*
- *No sugar available anymore, but alternatives (stevia, date sugar, sorghum, …)*
- *You're a passionate researcher, so you want to try the alternatives to see if they can replace sugar*
- *So, you make small batches, testing each alternative by adding the same amount you would have added sugar*
- *Requirements for the cake:*
  - *Fluffiness*
  - *Stability (should not fall apart)*
  - *Homogeneity (hold the blueberries evenly throughout the whole cake)*
  - *Dissolution resistance (you know several people like to dip the cake in coffee/tea)*
- *Starting your experiment…*



**Project this on a widely used blended cement "recipe":**
**25% Ordinary Portland Cement (OPC) + 75% Pulverised Fly Ash (PFA)**

**ISSUE: No domestic PFA from 2024**

### BACKGROUND

- Cement and concrete industry produces **~10% of global $CO_2$ emissions**[1]
  → substitute cement clinker= huge $CO_2$ reduction potential [2]
- PFA (from coal-fired power stations) commonly used clinker material
- UK Net Zero: **decarbonisation power sector** (removing coal plants in 2024)
  → no domestic PFA supply, reliance on overseas supply
- Low-Level Waste Repository Ltd. (LLWR)/Nuclear Waste Services (NWS) use blended cement with PFA as clinker, for safe encapsulation of low-level waste → Critical **need for PFA substitute** whilst **maintaining the properties & performance** of the blended cement

NET ZERO 2050

### OBJECTIVE

- Identify sustainable, cost-effective substitutes for PFA
  - Low $CO_2$ emissions
  - Gives same or better properties
  - Locally available
- Study alternatives for their physical, chemical, and mechanical properties in blended cements
- Assessing performance for industrial use

**Buy PFA from other countries?**
- PFA composition origin dependent → influences cement properties
- Global trend to stop coal → increased prices & higher competition
- Dependence from supplier & susceptible to disruptions
- For continued disposal, Environmental Safety Case needed
  → higher standards for $CO_2$ emissions

**Change the whole cement formula?**
- Testing currently ongoing (performed by NWS)
- Political decision taken in 2019
  → new cement formula needs licensing, and this takes about 10 years

**Research novelty?**
- Until now PFA used to replace OPC or SCMs but **not vice versa**

**Company's motivation?**
- Environmental aspects of increasing importance
- Ensure continuation of operation and completions of remit

## Proposed Research

1. Make cement according to formula [*Fig. 1*]
2. Identify characteristics of material samples with experiments [*Fig. 2*]
3. Compare SCM cement properties (chem., phy., mech.) to references [*Tab. 1*]
4. Check compliance with waste acceptance criteria for low-level waste[3]

| Supplementary Cementitious Material (SCM) | Abbrv. |
|---|---|
| Beneficiated Fly Ash | BPFA |
| Metakaolin | MK |
| Pozzolanic Sand | PS |
| Wastepaper Ash | WPA |
| Volcanic Ash | VA |
| Olivine | OL |
| Biomass Fly Ash | BMFA |
| **Reference Material** | **Abbrv.** |
| Ordinary Portland Cement | OPC |
| Pulverised Fly Ash | PFA |

*Tab. 1: Overview used SCMs*

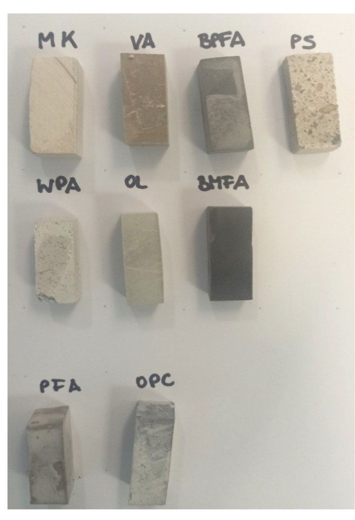



*Fig. 1: Cement samples made with SCM & reference materials. 2.95:1 (SCM:OPC) with 2.43% Superplasticiser added to the water (2.13% for WPA)*

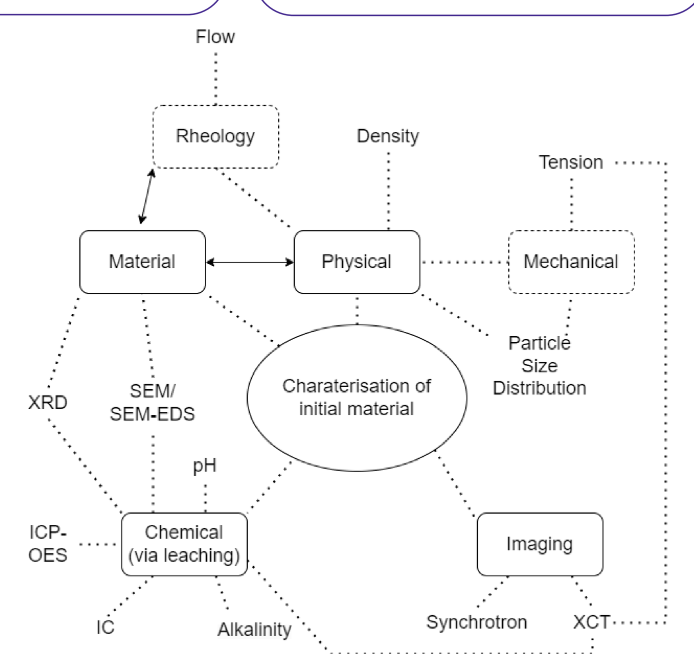



*Fig. 2: Overview of all experiments performed/planned to characterise the initial materials*

**Leaching (washing out material from sample)**

- 3 main leaching experiments performed with **deionised water (DW)** & **synthetic groundwater (GW)**[4]:

| Name | Duration | Measurement interval | Water replacement per interval |
|---|---|---|---|
| Short | 24 h | 1 h every 5 min, then every 15 min | None |
| Medium | 11 d | After 24 h | Total replacement |
| Long | Months | Every 4 weeks | 10ml+1ml |

- Liquid probes (11 ml) extracted & chemically analysed (*Fig. 2*)

**SEM/SEM-EDS (Scanning Electron Microscopy)**

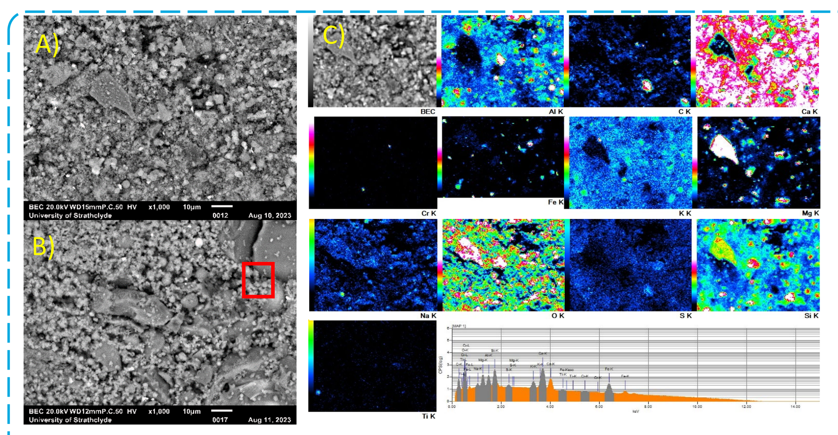


*Fig. 3: Exemplary SEM pictures and SEM-EDS analysis for PFA samples. (A) Untreated sample, (B) Sample after a 11d leaching experiment, (C) SEM-EDS analysis for an unleached sample*

- Comparison of leaching experiments Example (*Fig. 3*):
- Main elements identified: Al, Ca, K, Mg, Na, Si, O (**C**)
- Much more Ca visible on surface (example red box) (**B**) compared to unleached sample (**A**)

**XCT (X-ray Computerised tomography)**

- Non-destructive imaging
- Imaging samples at 5-15 µm
- 3D image analysis for identification and quantification all key phases & pores/fractures [*Fig. 4*, **B**, **D**]
- Some samples show more homogeneous grout distribution & have higher porosity (**A**, **B**) than other (**C**, **D**)
- Used with leaching experiments & mechanical testing to match microstructure to structural change & failure mechanisms

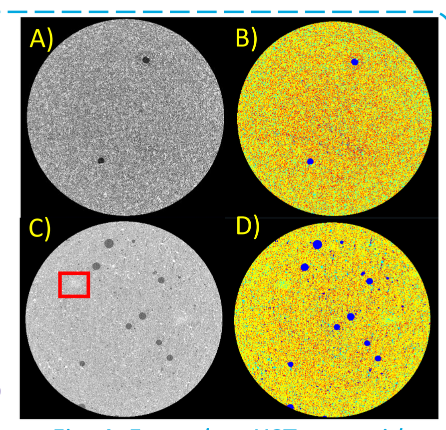


*Fig. 4: Exemplary XCT scan with composition analysis (Avizo) of an unleached OL sample (A+B) and unleached BPFA (C+D).*

**Chemistry pH/IC (Ion Chromatography)/ ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy)**

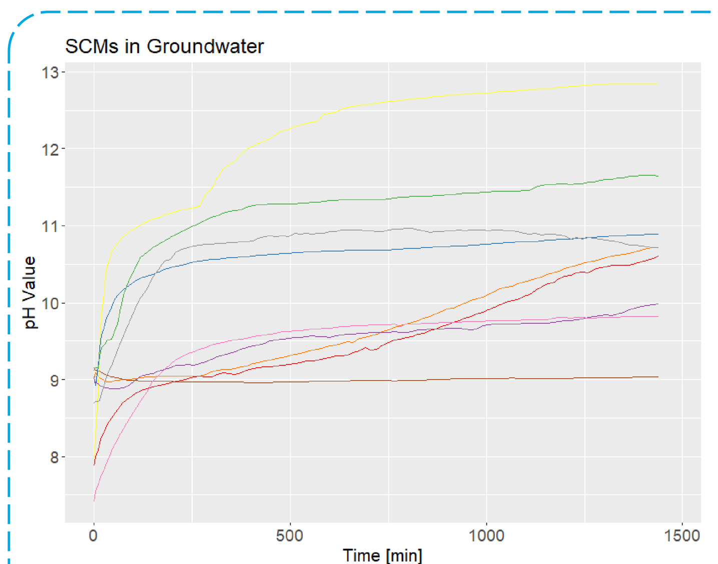



*Fig. 5: 24-hour experiment, samples in GW, change in pH over time. Orange: BMFA, yellow: WPA, red: OPC, blue: VA, green: BPFA, purple: PFA, brown: MK, pink: PS, grey: OL.*

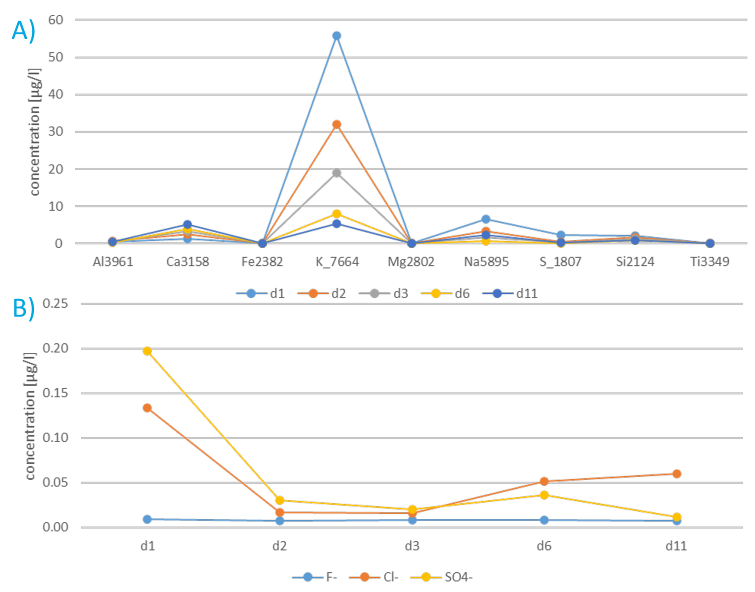



*Fig. 6: ICP-OES (A) and IC (B) results of BMFA during the 11-day leaching experiment in DW. In B, $NO_3^-$ is on the second y-axis.*

**pH**

- Interaction of samples with DW (harsher environment) and GW (realistic conditions, *Fig. 5*)
- Equilibration of water & sample (short leaching) dependant of material (*Fig. 5*, samples vary between pH 9 and 12.8 after 24 h)
- Dissolution of material influences pH of liquid (medium and long-term)

**IC/ICP-OES**

- Used to identify dissolution elements from reaction between sample & water
- Elemental (**A**) & anion (**B**) concentrations decrease over time [*Fig. 6*]

**Added value of research:**

- Intensive study of chemical, physical, & mechanical properties of SCMs
- Accelerated long-term behaviour study by crushed samples in DW/GW (high surface area-to-liquid ratio)
- In accelerated conditions (DW, room temperature) or real conditions (GW, 4ºC)

## Desired Outcomes/Impacts

### INTENDED OUTCOME: Find replacement for PFA

- List alternatives by checking for fulfilment of waste acceptance criteria and overall performance
- Recommend best material to be used at NWS from End 2024 (after transition period)

### FUTURE BENEFIT TO SOCIETY

- Continuation safe long-term disposal low level nuclear waste
- Reduction of $CO_2$ emissions by the NWS
  → might be only small fraction but is example for the sector for feasibility
- Cement & concrete industry might face same/similar issue in the future
  → first solution, giving time to invest into better possibilities

## References


**[1]** Lehne, J., Preston, F. (2018): Making Concrete Change Innovation in Low-carbon Cement and Concrete, Chatham House for the Royal Institute of International Affairs, London, UK, ISBN 978-1-78413-272-9. **[2]** World Business Council for Sustainable Development (2002): The Cement Sustainability Initiative: Our agenda for action, Energy Environm. Sci. 7 (1), p.30-189. **[3]** Huntington, A. (2016): Waste Acceptance Criteria – Low Level Waste Disposal, LLW Repository Ltd. **[4]** May, C. C., et al. (2012): The effect of EDTA on the groundwater transport of thorium through sand, Water Research 46(15), p.4870-4882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