



BNFL

Characterisation of Full-Scale Inactive Cement-Based Intermediate Level Wasteforms After One Decade of Storage

Robert J. Caldwell, Newton J. Bowmer,
Ed J. Butcher, and I. Hugh Godfrey

Nuclear Sciences and Technology Services, BNFL

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Introduction to project

- Initial concept for ILW ~ 50 years above ground storage then 50 years below ground.
- UK Repository delayed - now ~ 10^2 years above ground storage and similar period of monitoring in repository to allow retrieval if necessary. More emphasis on life of product.
- Objective - analysis of aged (>10 years) inactive samples to **increase** understanding of wasteform evolution and **reinforce** evidence of stability.

Overview

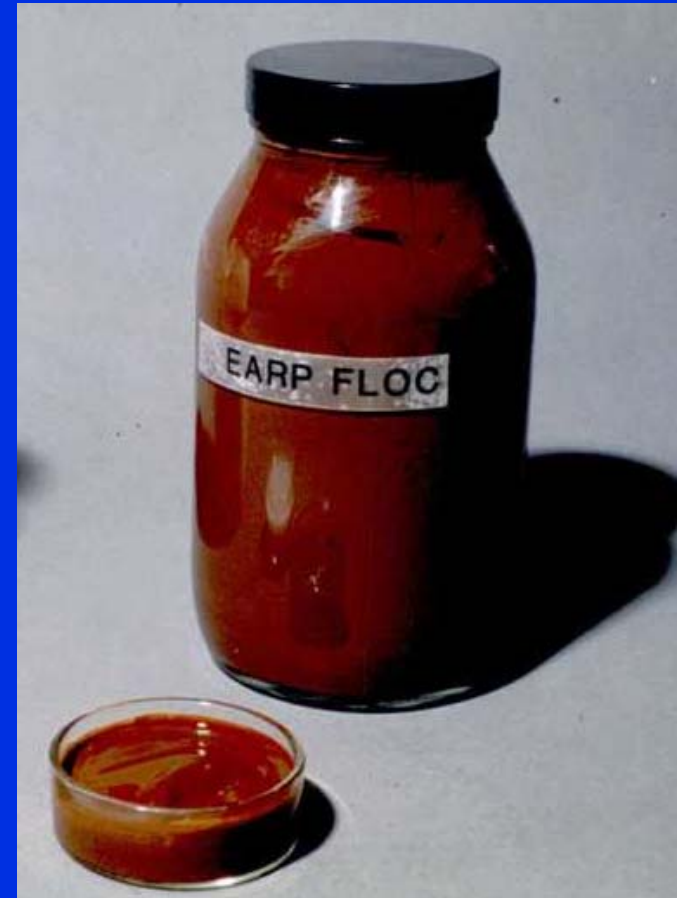
- Background
 - Waste description
 - Encapsulation process
- Characterisation of 10 year old samples
- Conclusions
- Future work

UK Waste Categories

- High Level
 - Heat Generating
 - Fission Products from reprocessing
- Intermediate Level
 - Exceeds low level criteria
 - Not significantly heat generating
- Low Level
 - <4 GBq /Tonne α
 - <12 GBq /Tonne $\beta\gamma$

Floc - waste description

- Acidic liquid effluent
- Acid feed neutralised with NaOH
- Precipitates $\text{Fe}(\text{OH})_3$ floc + alpha & metals (Cr, Pb, Ni), (beta by adding other materials)
- Ultrafilter to concentrate waste
- Wash out soluble salts - water



Specific issues for floc waste

- Retardation - overcome by formulation selection
- Chemical reaction or crystallisation of floc - shrinkage during curing - overcome by pre-treatment
- High w/s ratio (~ 1) samples susceptible to water loss and shrinkage / cracking

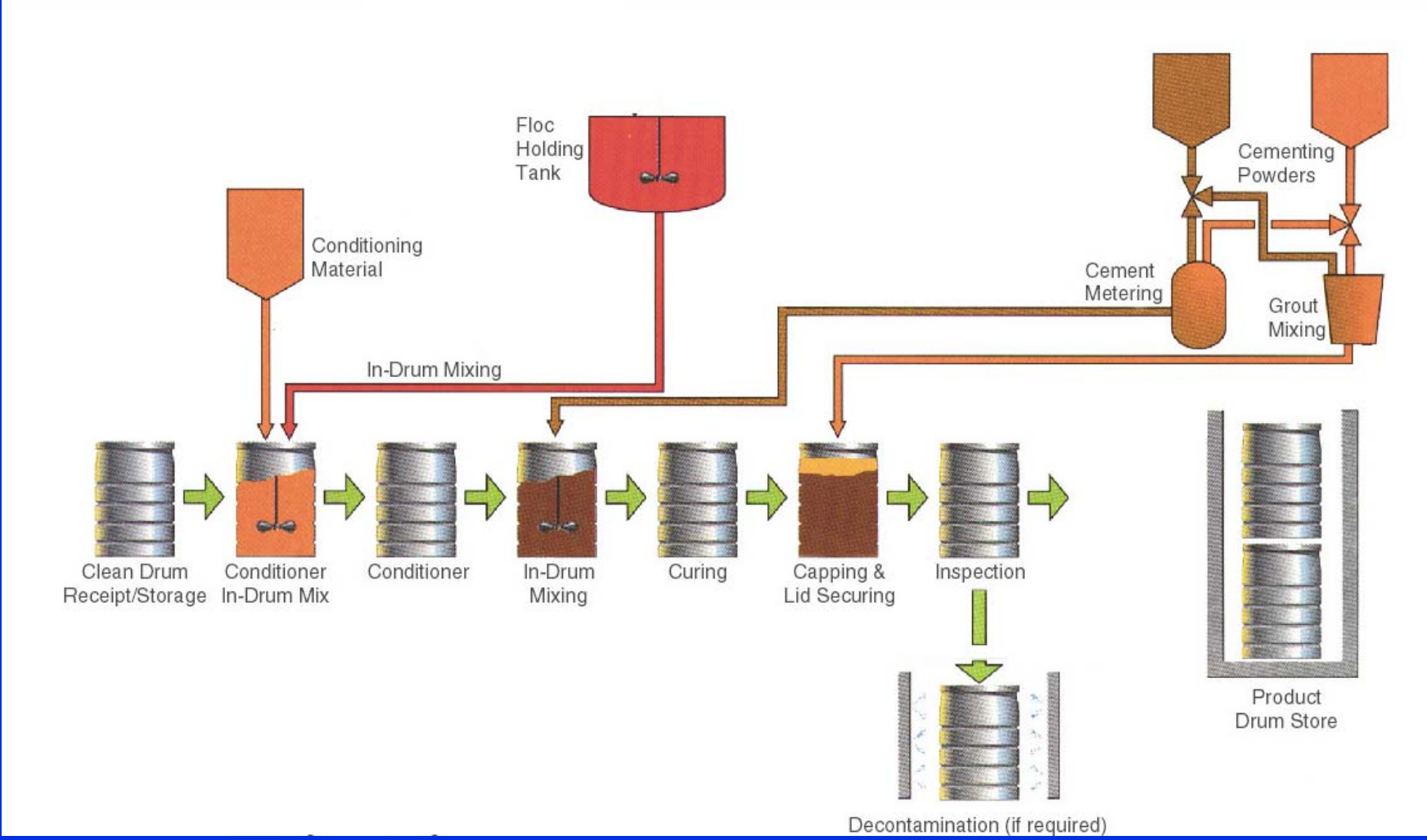
Floc encapsulation process

- Waste metered into 500 litre drum with integral paddle.
- Waste pre-treated in the drum for a set time to condition the floc.
- PFA and OPC powders fed at specified blend ratio to drum and mixed with paddle.
- Allowed to cure till grout set.

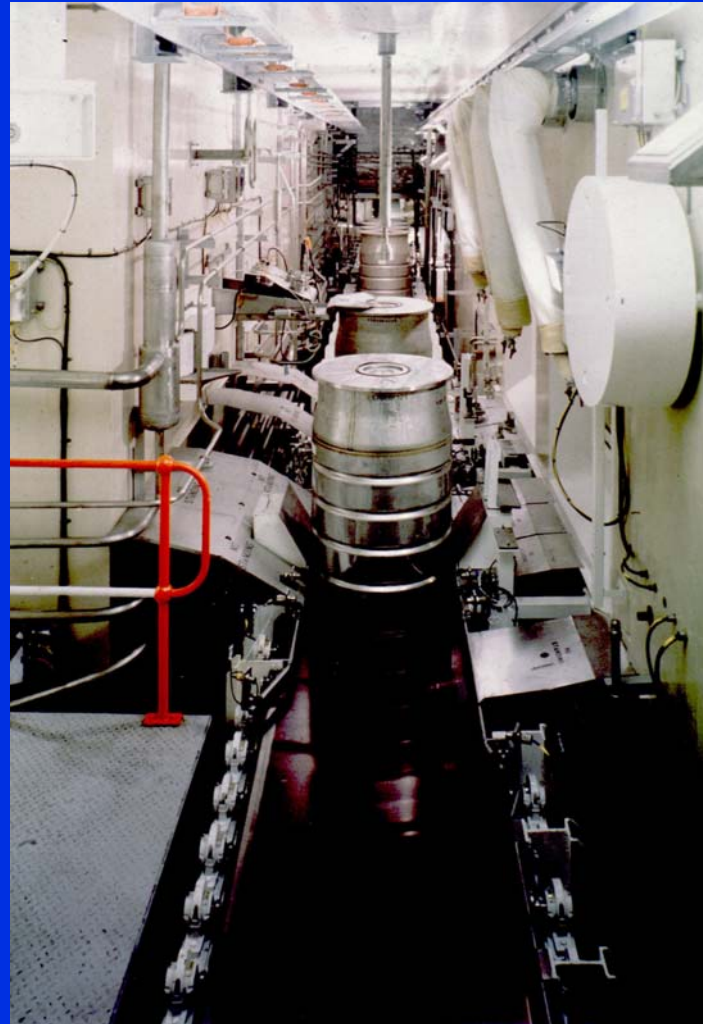
Floc encapsulation process

- PFA/OPC grout cap added to fill voidage and immobilise loose activity.
- Drum lidded, decontaminated then to store.
- Operational since 1994 > 3000m³ of waste treated.

Encapsulation process



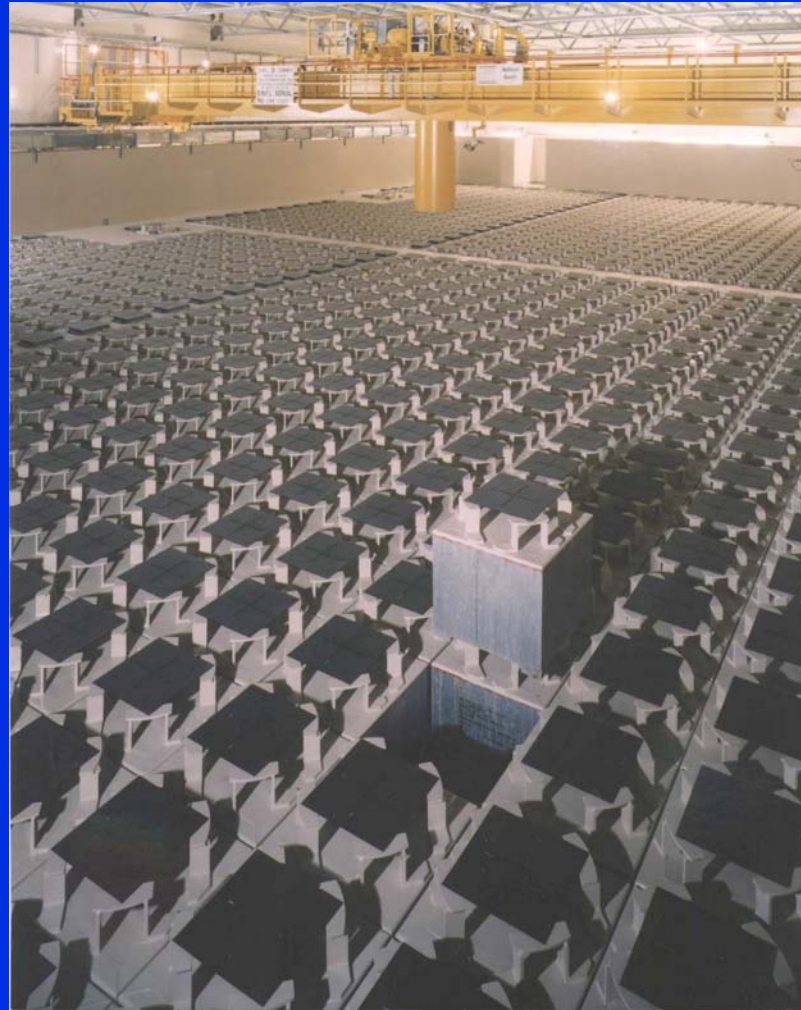
Floc encapsulation line



Encapsulated floc Product



Store



Samples investigated

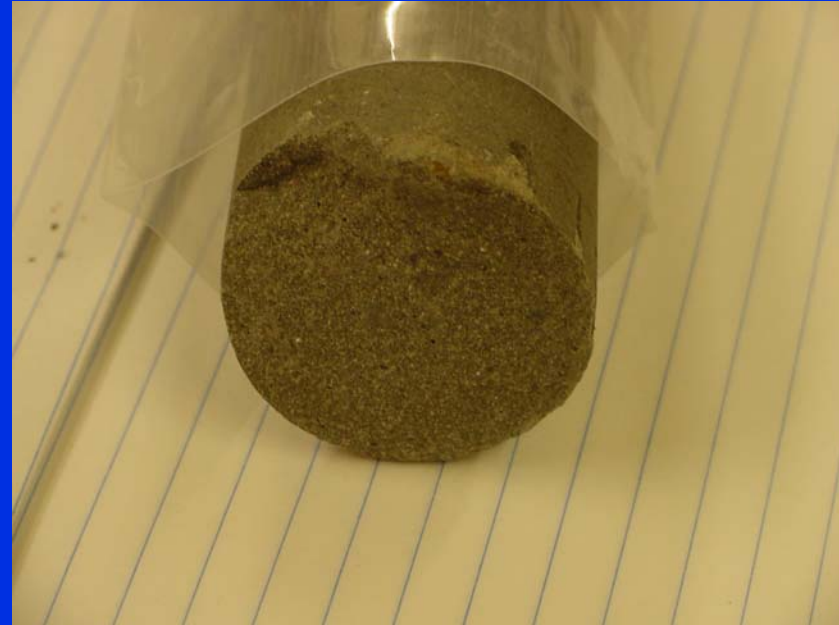
- 6 full-scale, non-active, 10 - 12 years old, stored in a BNFL warehouse. Various floc compositions (total of 4 flocs produced and treated at WPEP).
- Storage conditions similar to target stores conditions.
- Samples cast in drum mould, several sectioned during previous investigation.
- All surfaces exposed - worst case.

Typical sample



Sampling

- 50mm diameter diamond drilled cores wet (to depth) and dry (300mm),
- Stored under argon to prevent oxidation/ carbonation, then sealed in double plastic sleeves.



Characterisation

Initial Characterisation

- Logging of cores physical characteristics,
- Logging of bore hole to identify historic faults,
- BD, SG, MC for moisture density relationships - porosity, degree of saturation,
- pH and redox profiles through low L/S extraction, and carbonation profiles using standard indicator method, and
- ANC profiles to indicate degree and form of alkalinity present.

Characterisation

Instrumental Characterisation

- Analysis of grout by SEM with elemental analysis using energy dispersive x-ray spectroscopy (EDS),
- Analysis of grout with x-ray diffraction (XRD) analysis to investigate CSH incorporation, and
- Thermogravimetric Analysis (TGA) of cores to confirm/refute presence of phases (e.g., $\text{Ca}(\text{OH})_2$).

Summary of Results

Core and Borehole Logging

- Two historic cracks found - one probably due to handling methods, the other due to paddle- investigated with SEM.
- Uniform appearance of wasteforms.
- Matrix homogeneous and well mixed.

Summary of Results

Moisture Density Relationships

- The bulk density of the wasteforms were consistent throughout with little evidence of densification at depth.
- Moisture content remains consistent throughout wasteform.
- solids specific gravity determination was made using a Micromeritics gas pycnometer.

Summary of Results

Moisture Density Relationships

- Calculated porosity ranged from 45 to 52% (50-60% after 90 days) and the degree of saturation was generally measured to be ~100%.
- Waste remains homogeneous, continued hydration after 90 days, no significant desiccation.



Summary of Results

Carbonation Profiles (Phenolphthalein method):

- Profiles from upper surfaces of cores indicate carbonation penetration of between 1 to 3 mm.
- Several samples did not show any carbonation due to core barrel damage during the coring operation.
- Salts coated historic cracks (lateral) identified at 370 mm of IDM/91/13 did not indicate carbonation.

Summary of Results

Equilibrium Extraction

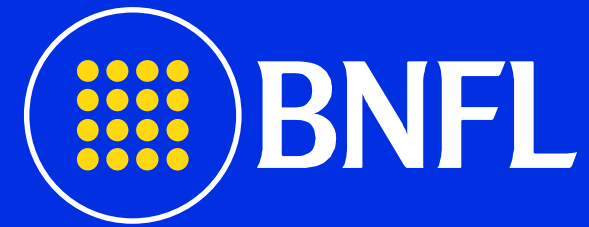
- pH ranging from 11.92 to 12.32 all below Ca(OH)_2 saturation for the ambient temperature.
- E_H ranging from 123.5 to 316.5 mV. Indicating that the oxidising conditions prevailed through the selection of the PFA blended grout.

Summary of Results

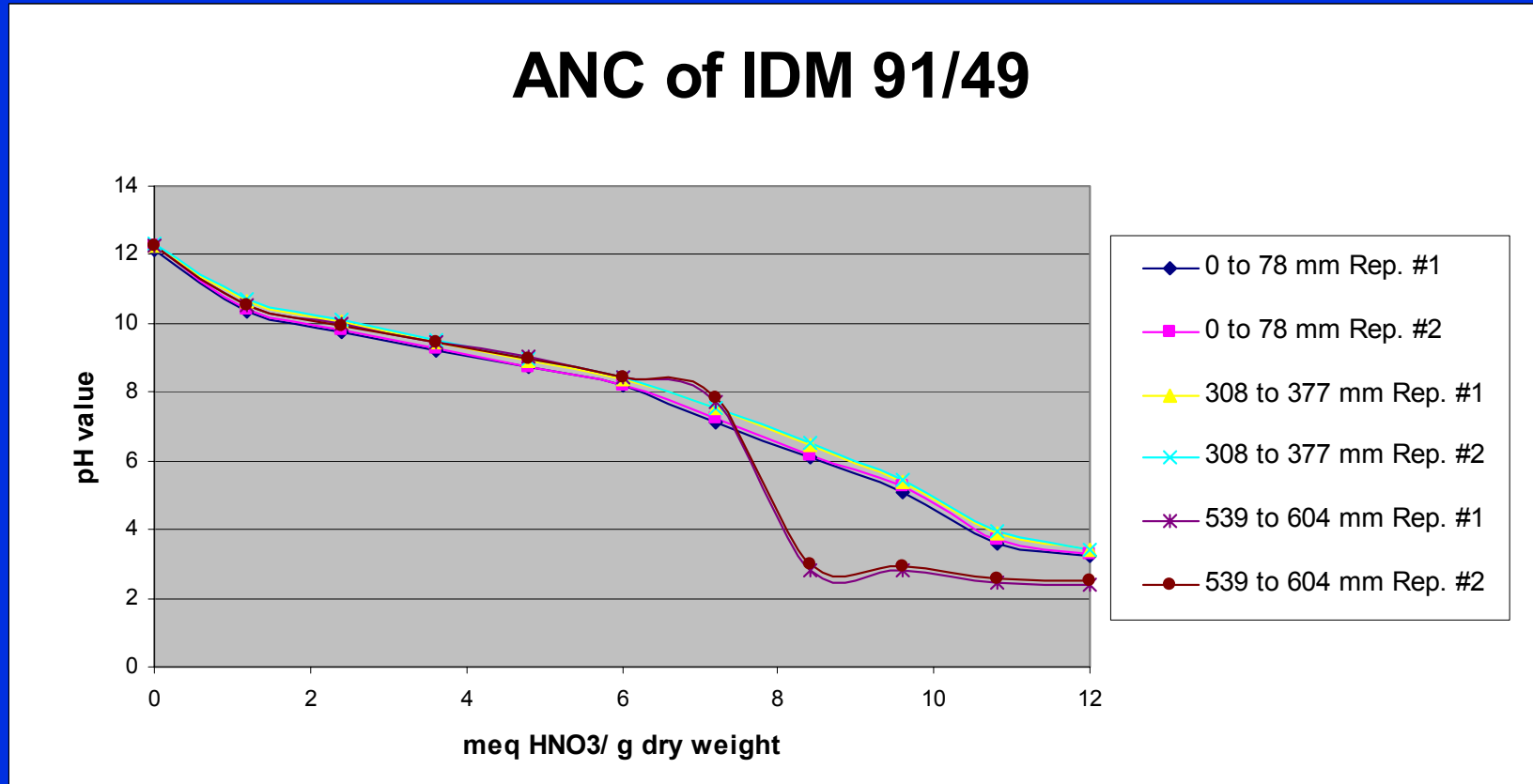
Acid Neutralisation Capacity

- Indicates that very little free $\text{Ca}(\text{OH})_2$ exists in all wasteforms.
- No carbonate buffering observed (pH 8.3 if vented).
- Upper section of SEC/Bulk wasteforms IDM/91/13 and IDM/91/49 have been depleted of alkalinity but do not show signs of carbonation.
- Wasteforms all have significant buffering ($>4\text{eq/kg}$) to pH=9. Relates to a 1 kg sample capable of neutralising 40,000 L of pH 4 mineral acid.

Summary of Results



Acid Neutralisation Capacity

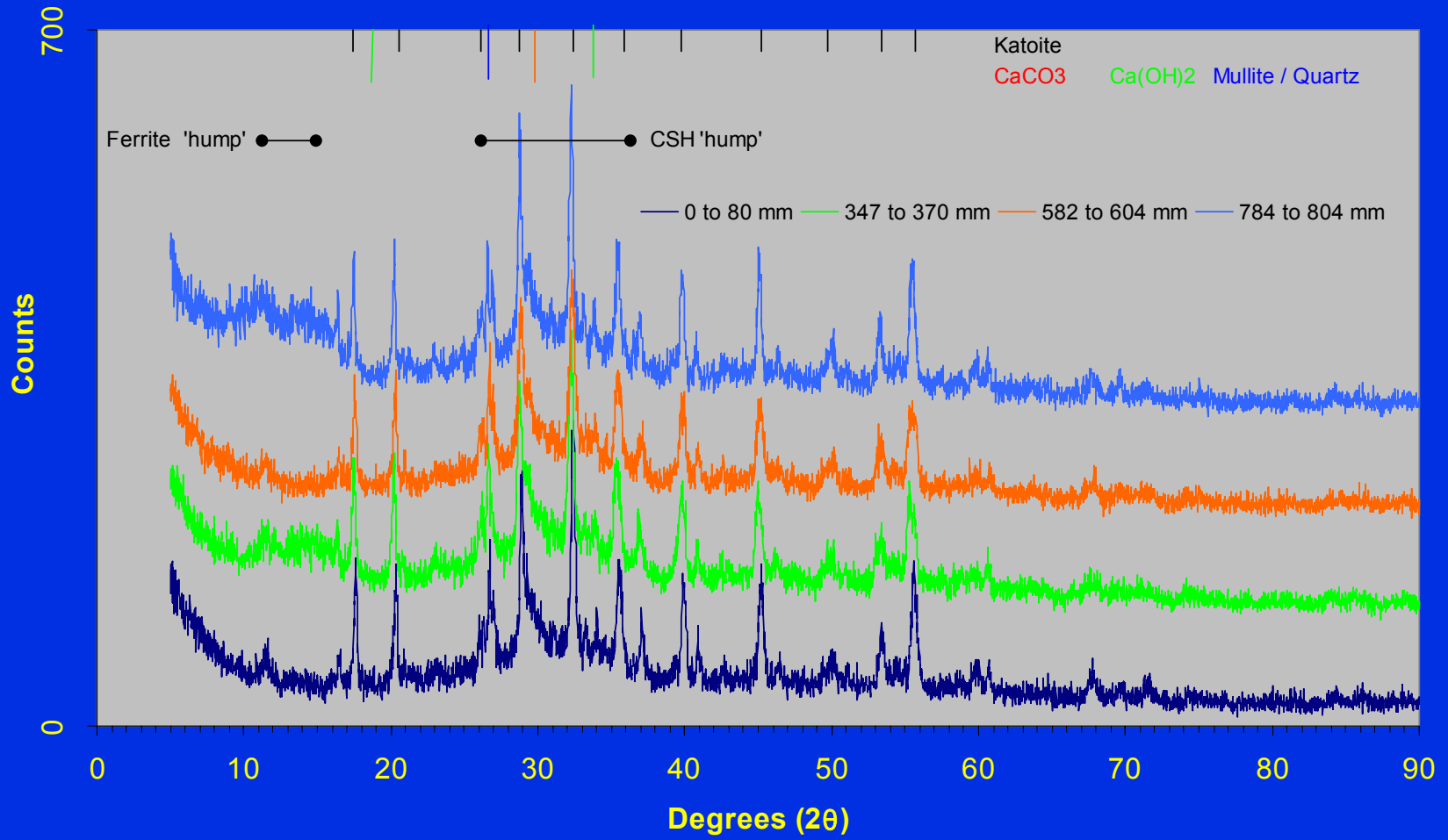


Summary of Results

XRD Analysis

- Peak intensities are related to degree of crystallinity.
- All wasteforms produced similar XRD peak pattern output with amorphous CSH and calcium ferrite humps.
- Software identified pattern as the hydrogarnet phase 'Katoite'.
- Mullite and quartz also identified (PFA).
- Portlandite and calcite not identified.
- No unexpected phases, portlandite consumed - product in steady state.

Typical XRD traces

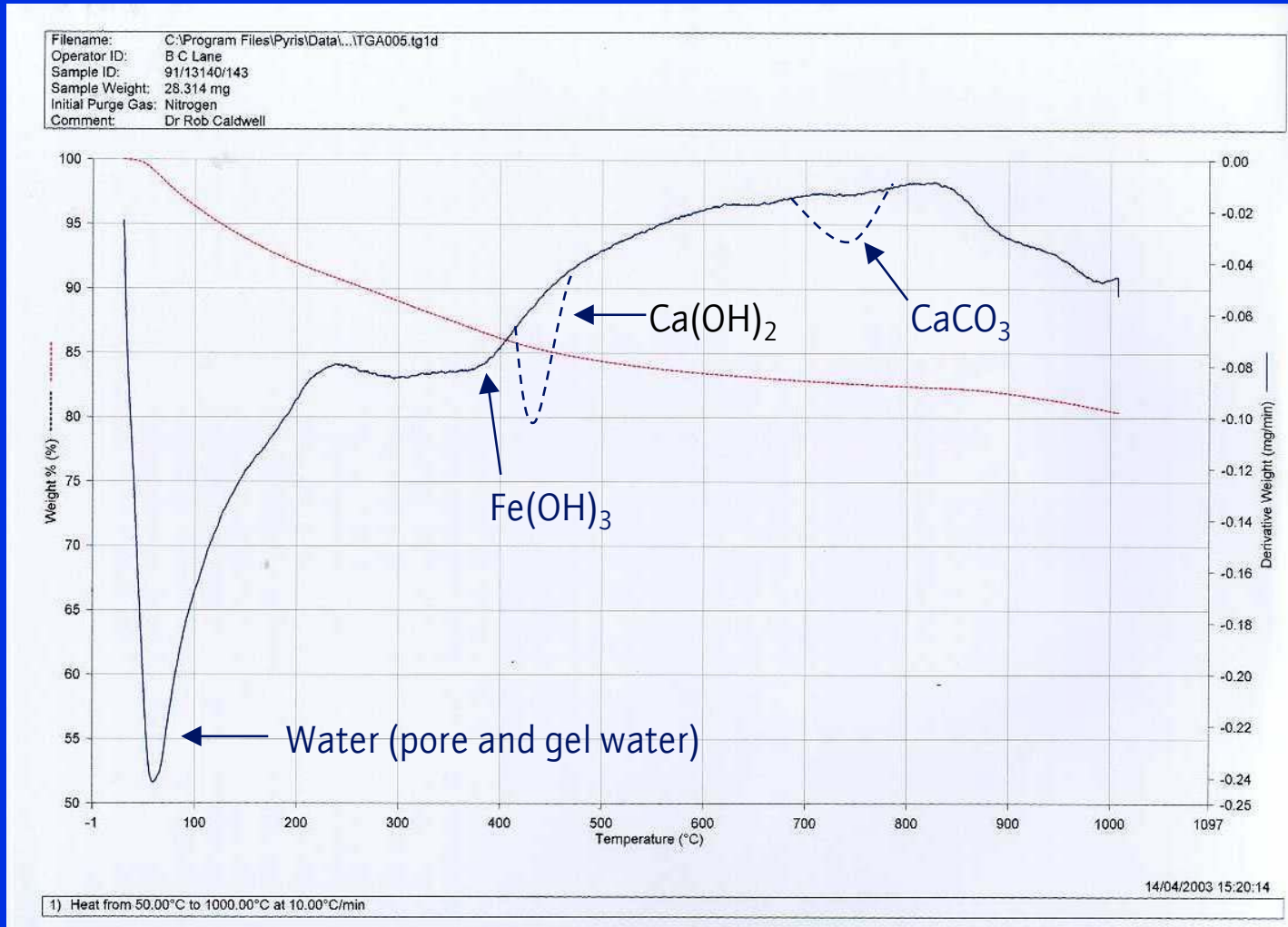


Summary of Results

Thermal Gravimetric Analysis

- All wasteforms produced similar TGA output with slight differences with sample depth.
- Generally large peak identified as the release of bound and evaporable water from the CSH up to 400°C.
- Again portlandite not identified (peak at 450°C absent).
- Calcite peaks generally observable at various depths (reagent carryover) with greater peaks at outer surfaces as would be expected (peak at 720°C).
- No unexpected phases.

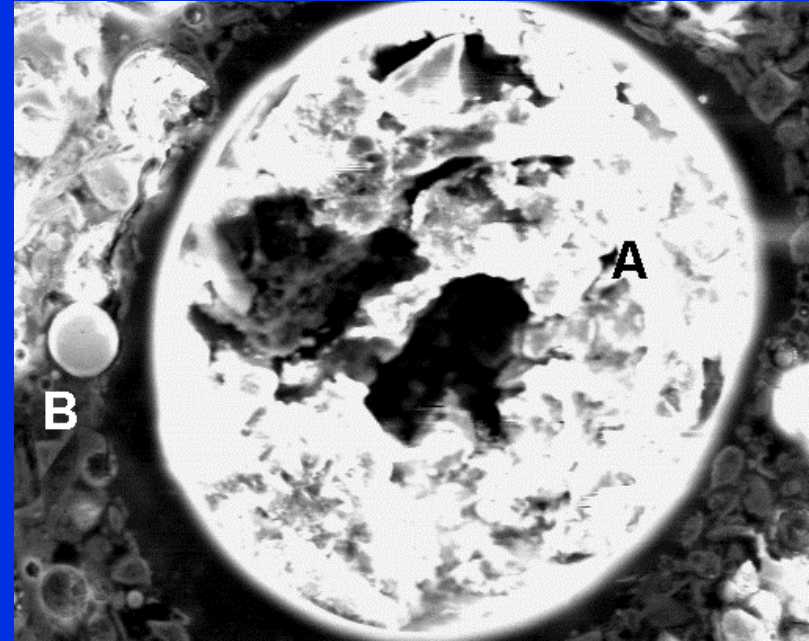
Typical TGA trace



Summary of Results

Scanning Electron Microscopy

- Normal calcium silicate hydrate field with flyash cenospheres/mullite crystals, magnetite spheres and small voids.
- Relatively dense matrix.
- Significant proportion of flyash remains available.
- **No unexpected phases.**



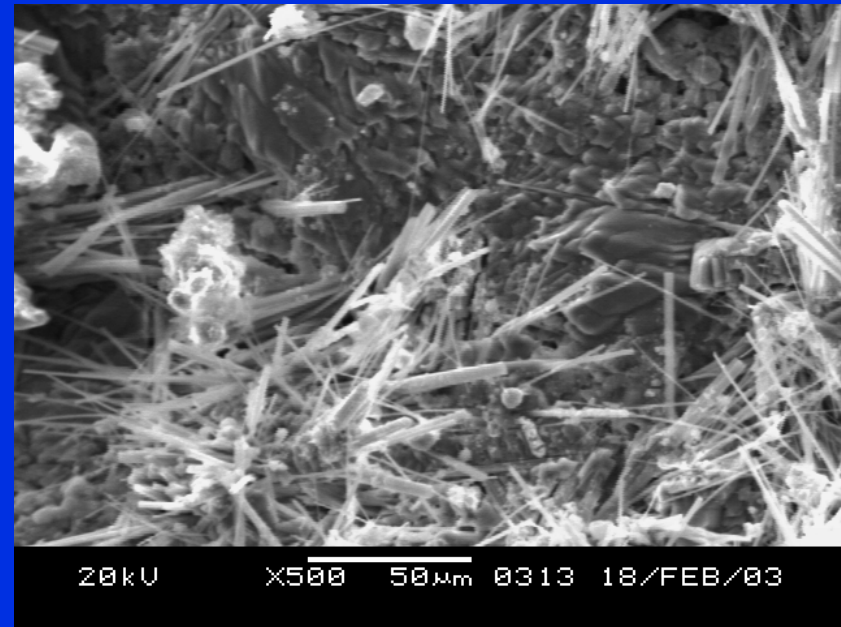
A= cenosphere/mullite crystals

B= magnetite sphere

Summary of Results

Scanning Electron Microscopy

- Historic fracture found in IDM 91/13 is covered in ettringite which degrades in the presence of CO₂.
- Suggests that fracture isolated from atmosphere – self sealing carbonation.



Conclusions

- Investigation represents a conservative evaluation of 10 to 12 year old WPEP wasteforms due to the absence of a stainless steel drum, a poured PFA/OPC cap, and controlled atmosphere (temperature and humidity).
- Desiccation has not been found to be significant after >10 years of curing.
- Only two cracks found, one was investigated and appeared to have resealed itself.

Conclusions

- Porosity and degree of saturation very consistent, regardless of wasteform and depth of core sample investigated.
- Moisture density data and relationships very consistent regardless of wasteform and depth of core sample investigated.
- wasteforms have a mature, relatively porous matrix, with no evidence of calcium hydroxide available to support further pozzolanic reactivity, wasteform reaching/reached a steady state.

What next?

- Floc wastes
 - Link to work at Immobilisation Science Laboratory.
- Other wastes treated at Sellafield:
 - Magnox metal, barium carbonate, centrifuge cake, filter pre-coat, stainless steel hulls, etc.
- Characterise early age wasteforms.

