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Development of an immobilisation process for High Dose Spent Adsorbents from Fukushima

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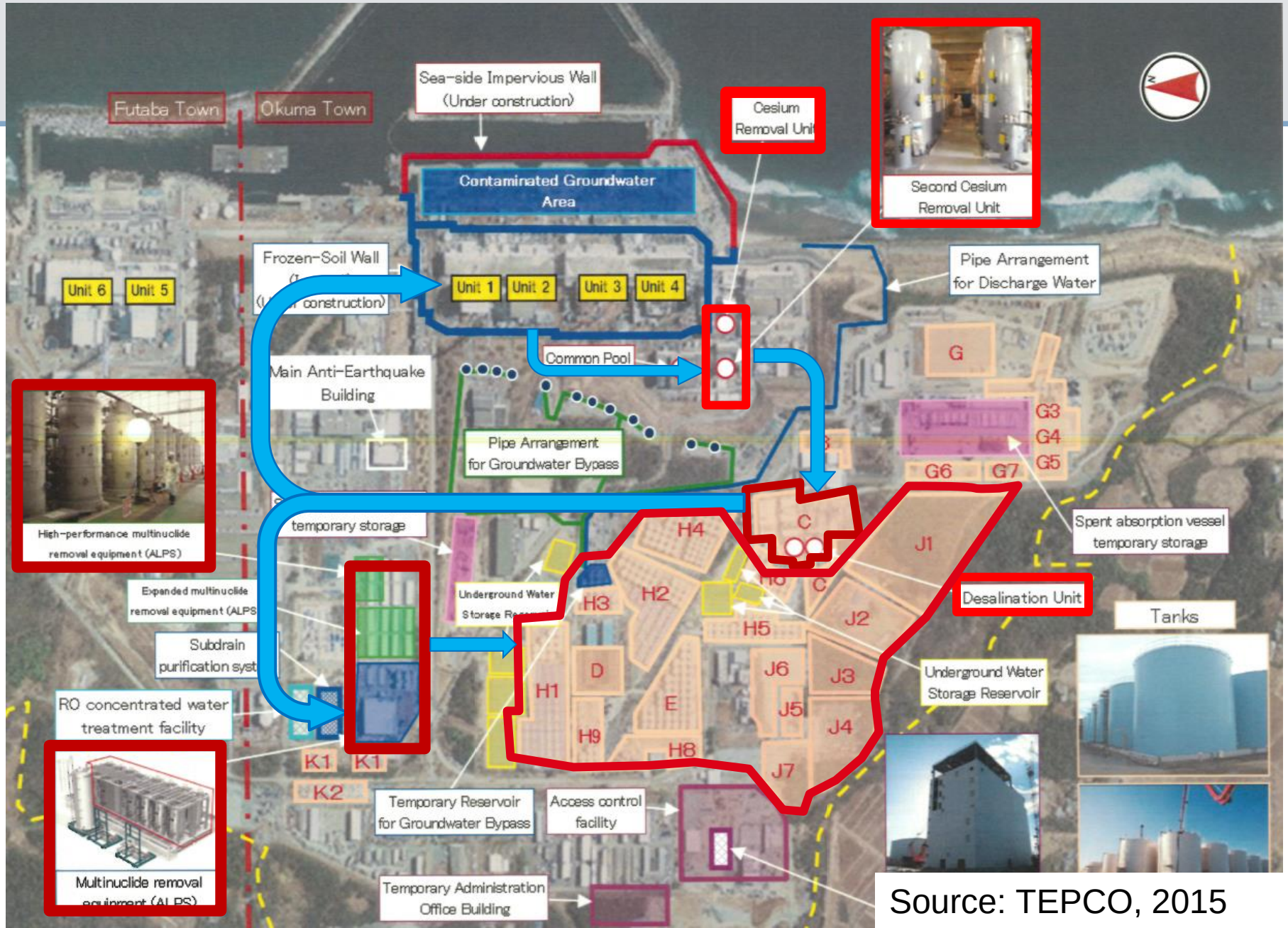


Source: TEPCO, 2015

High Dose Spent Adsorbent (HDSA)

- Water purification systems generate highly radioactive spent ion exchange adsorbents, termed High Dose Spent Adsorbents (HDSA)

- Many types of adsorbents used
  - SARRY system uses Honeywell UOP products
  - Hitachi HP-ALPS uses proprietary adsorbents
  - Possible zeolitic and crystalline silicotitanate compositions

- HDSA
  - 10^7 -10^8 Bq/cm^3
  - High radiogenic heat production

Nuclide	Half-life
^{134}Cs	2.06 years
^{136}Cs	13.04 days
^{137}Cs	30.08 years
^{90}Sr	28.90 years

- Simulant HDSA
  - Chabazite
  - Zeolite, general formula: $Mx[(AlO_2)x(SiO_2)y] \cdot zH_2O$ [M=Na,K,Ca,Mg]

Long term disposal of HDSA

- Search for a suitable disposal matrix for long term disposal of HDSA
- Selected matrix is a low melting glass

<u>Project parameters</u>

- Very low maximum process operating temperature: 600°C
  - Avoid volatilising Cs and Sr species
- Radionuclides have very high dose and short half-life
  - Estimated repository lifetime 300 years
  - “High” heat production
- Multiple possible waste streams into one wasteform
  - Flexible glass system
- Reasonable solidification technology and process

Glass composition

- Lead borosilicate glass composition chosen based on work done among others by Fu *et al.*[1]

Glass composition (from base oxides)

- 63 wt% PbO
- 25 wt% B_2O_3
- 12 wt% SiO_2

Glass composition (mol%)

- 33 mol% PbO
- 43 mol% B_2O_3
- 24 mol% SiO_2

Thermal characteristics

- Softening point of 451 ^oC
- Flow point of 582 ^oC
- Melting point of 1126 ^oC

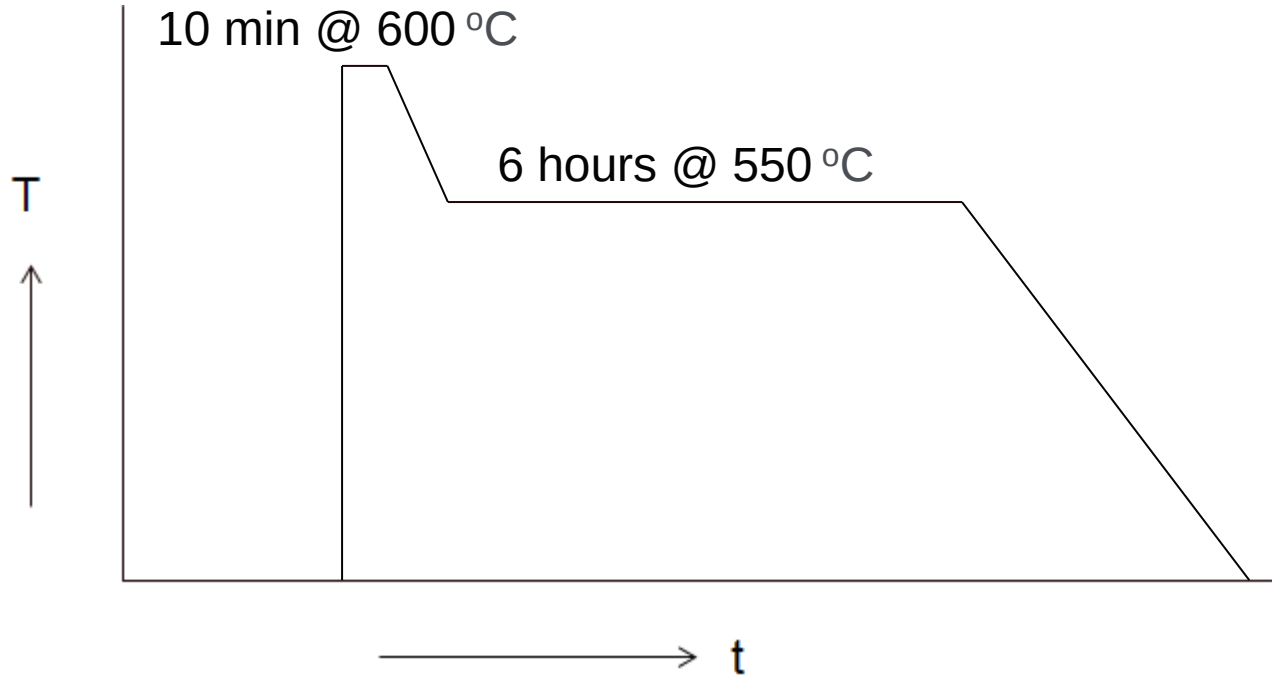
1) S.L. Fu, L.S. Chen, and J.H. Chou, *Sintering of Cordierite Glass-Ceramic with Lead Borosilicate Glass. Ceramics International, 1994.* ***20****: p. 67-72*

Wasteform production

- Sintering of glass frit with zeolitic model waste to form Glass-Composite Material (GCM) wasteform
- K-chabazite model waste, procured from Verdi Sp.A. in Italy
- Chabazite (100 – 125 micron) mixed with PBS glass frit (≤38 micron)
- Range of wasteloadings trialled (up to 40 wt%)
- Sintering profiles tuned with cold-pressed wasteforms
- Pressureless sintered wasteforms produced

Two step sintering

- First step done under direct heat. Note the glaze on the picture of the pellet
- At the end left to cool at equilibrium in the furnace to avoid thermal stress
- Resulting pellet was robust, but looked "bloated"



Temperature profile

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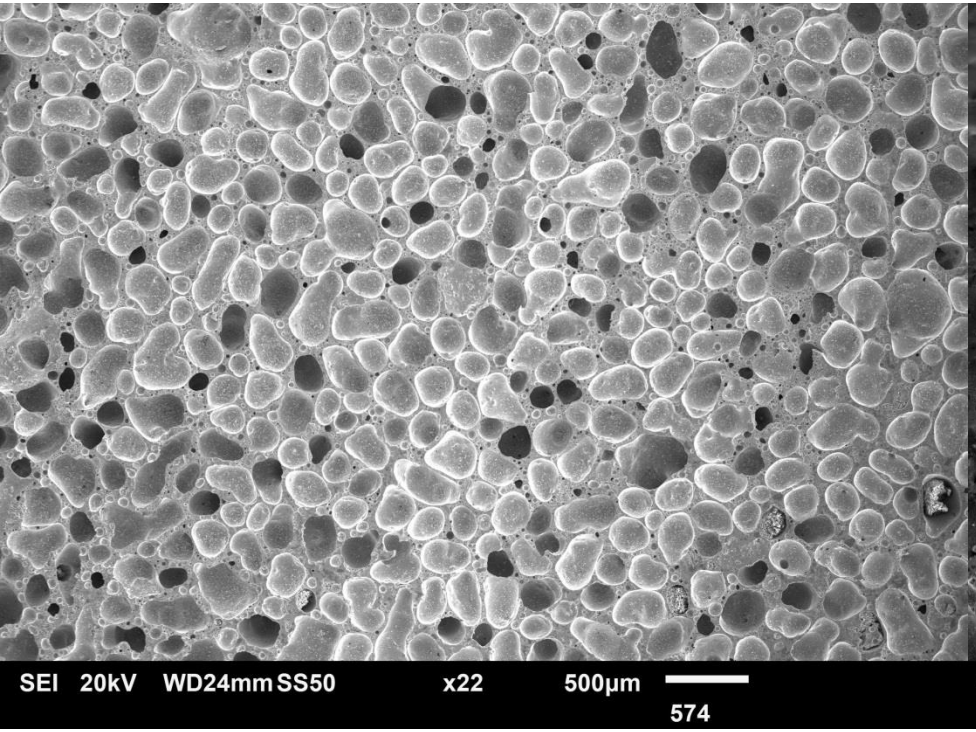
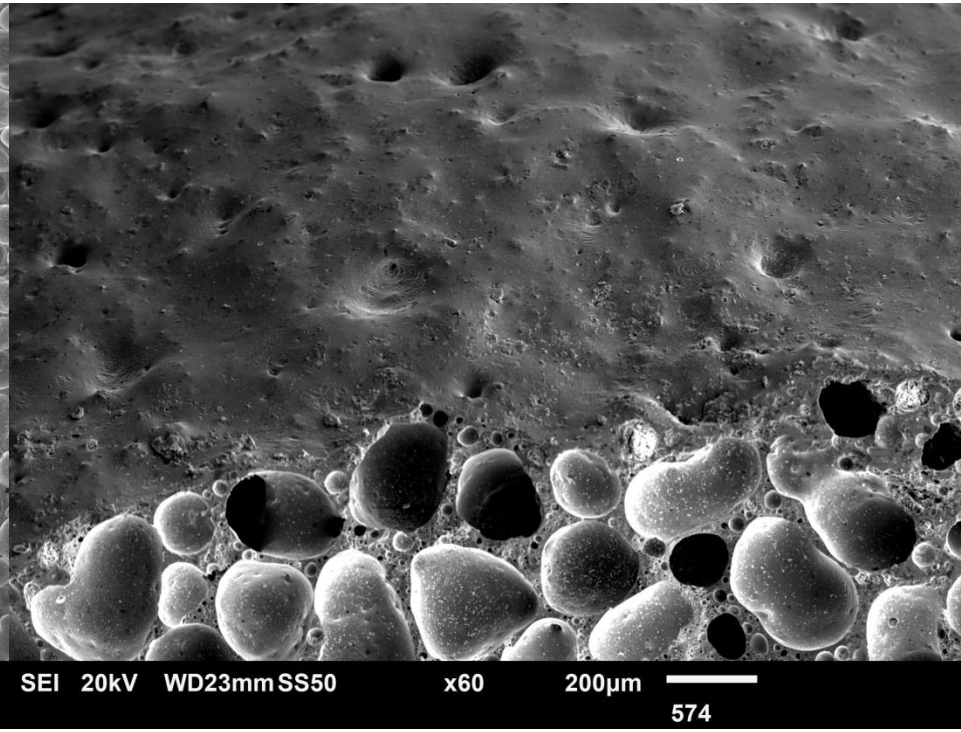
Two step sintering microstructure





Cross section middle

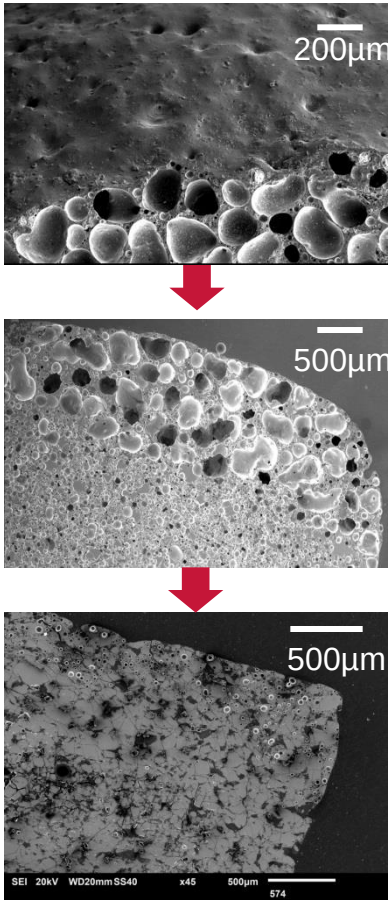
- Bubbles formed during viscous flow sintering
- Foamed microstructure

Cross section crust

- Foamed microstructure
- Smooth “glazed” crust prevents diffusion of gas

Waste form production – Sintering optimisation

- Sintering of PBS glass frit with zeolitic model waste to form Glass-Composite Material (GCM) wasteform
- Chabazite mixed with PBS glass frit and cold-pressed before sintering
- Sintering profiles were optimised to produce a dense wasteform
  - various thermal heat treatment steps and particle size distributions trialled
- Final iteration contained:
  - Chabazite thermal pre-treatment step at 600°C
  - Three step sintering profile



Cross-sectional SEM images. Show the progressive densification with improving sintering profiles

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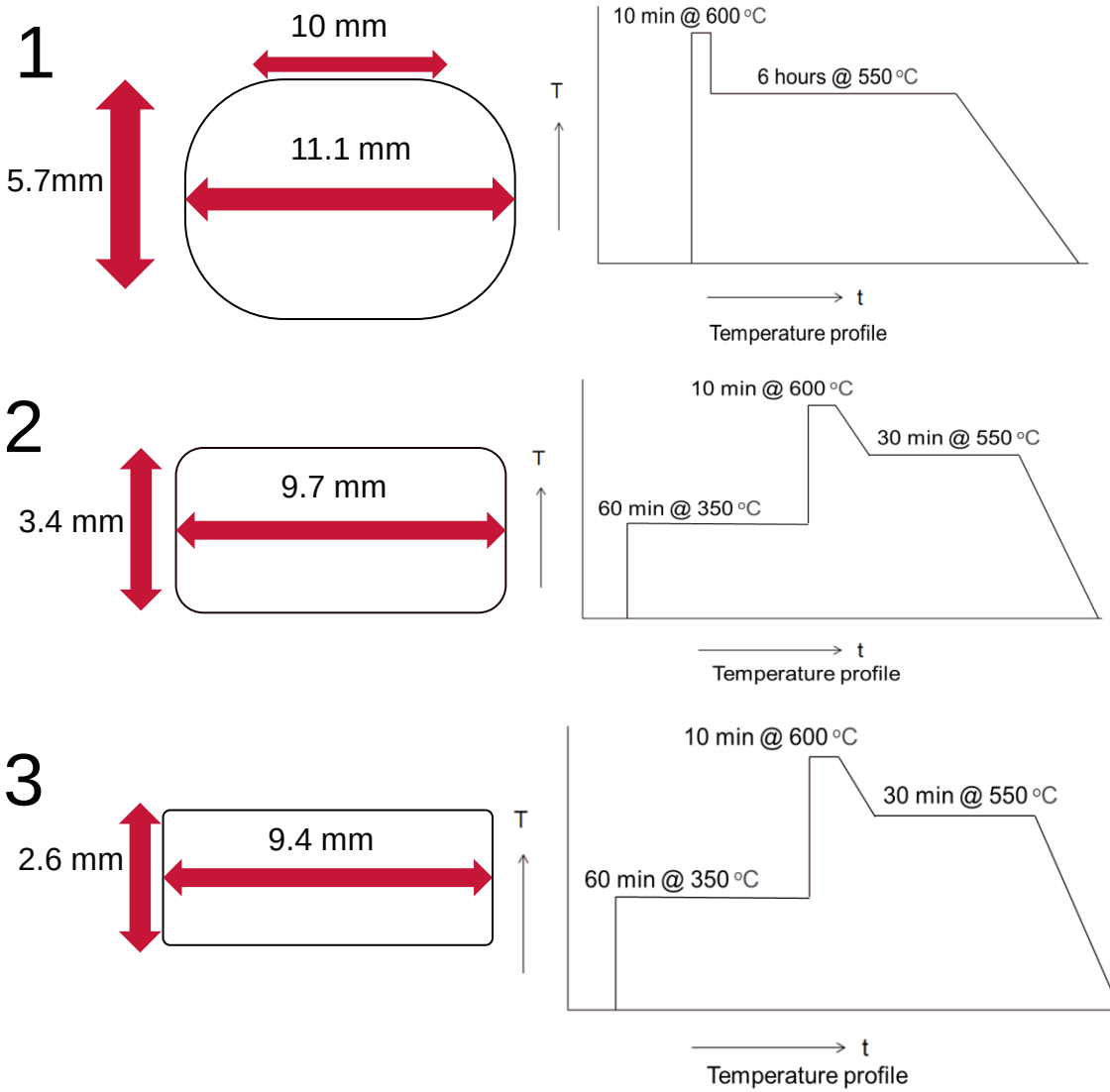
Sintering optimisation - comparison



- Zeolitic model wasteform successfully sintered with lead borosilicate glass frit
- Maximum processing temperature of 600°C
- Sintering parameter optimisation performed with cold-pressed 10 wt.% waste loading
- Thermal pre-treatment step of chabazite implemented

Simplified industrial process

- Final waste treatment process required simplification
- Cold-pressing of wasteform not representative of final processing conditions
- Final (envisaged) process
  - Loaded HDSA have high activity and heat load
  - Final vitrification process envisaged to use radiogenic heat to drive vitrification
  - In – canister vitrification batch process
  - Natural convection cooled storage

Wasteform production

- PBS glass frit (≤38 micron) and pre-treated chabazite (100-125 micron) mixed for 12 hours
- Loaded in stainless steel molds and subjected to pressureless sintering
- Wasteloading first refined to 5 wt.% increments (5wt% - 10 wt.% - 15 wt.%)
- Later increased to 10 wt. % increments, with a maximum of 40wt.% loading
- Similar sintering profiles observed

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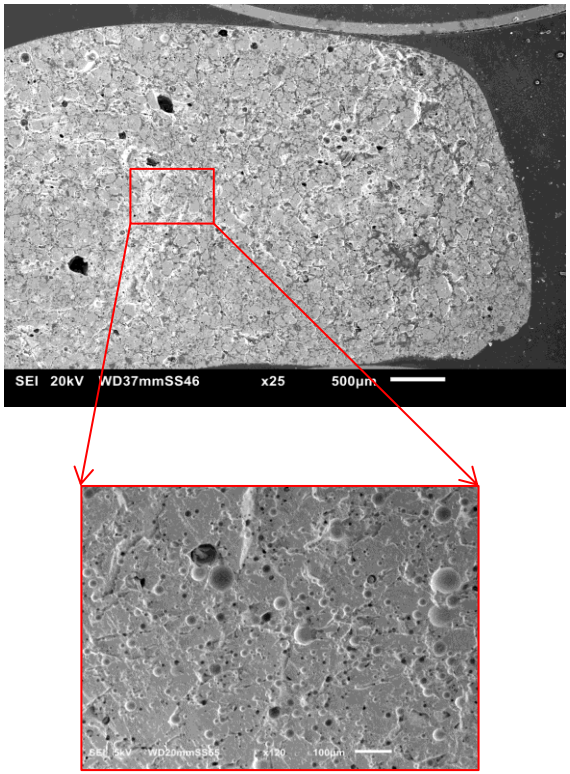
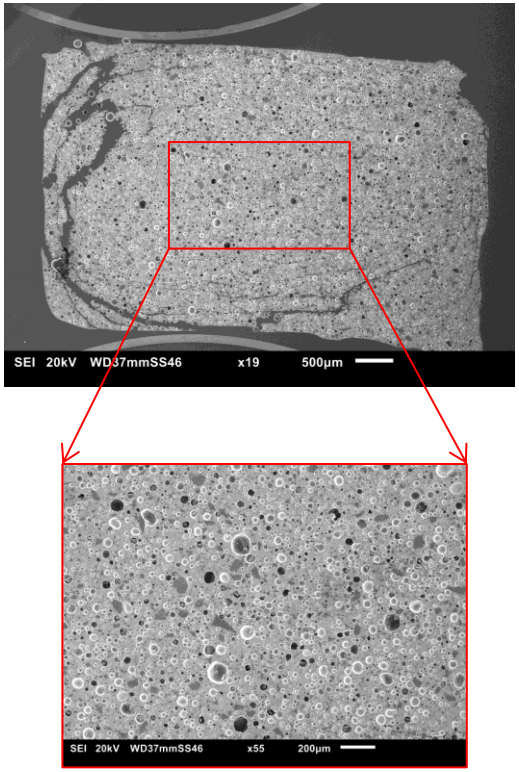
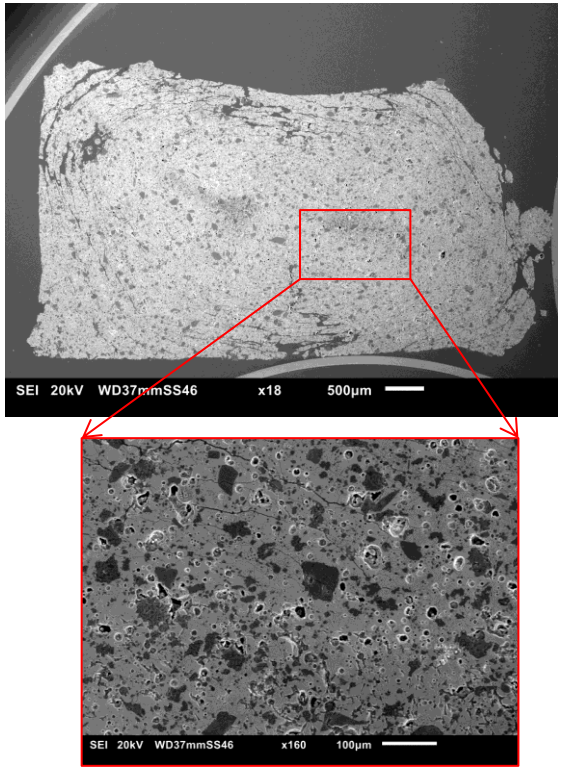
Pressureless sintered wasteforms



5 wt% chabazite



10 wt% chabazite

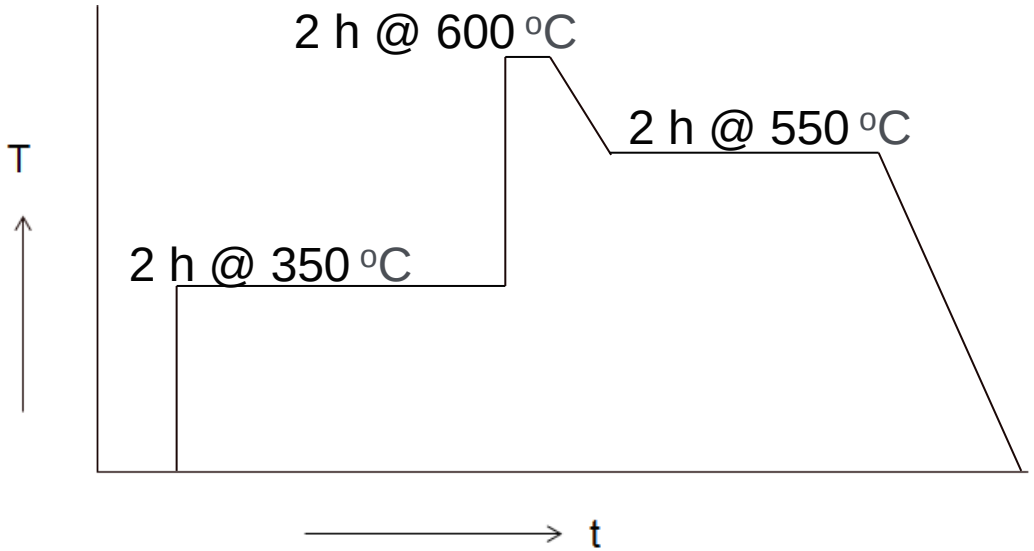


15 wt% chabazite

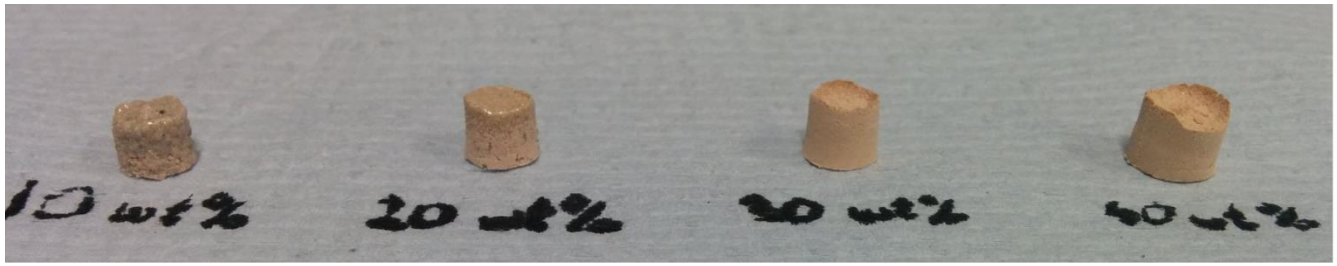
- Initial waste loading for trials was kept purposely low
- Samples prone to macroscopic circumferential cracking
- Dense GCM microstructure achieved

Refined sintering

- Higher wasteloading
  - Longer pre-treatment
  - Longer sintering



Temperature profile



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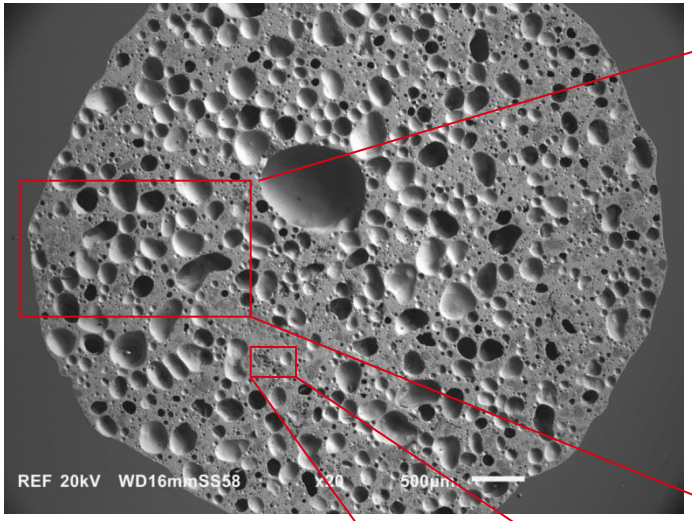
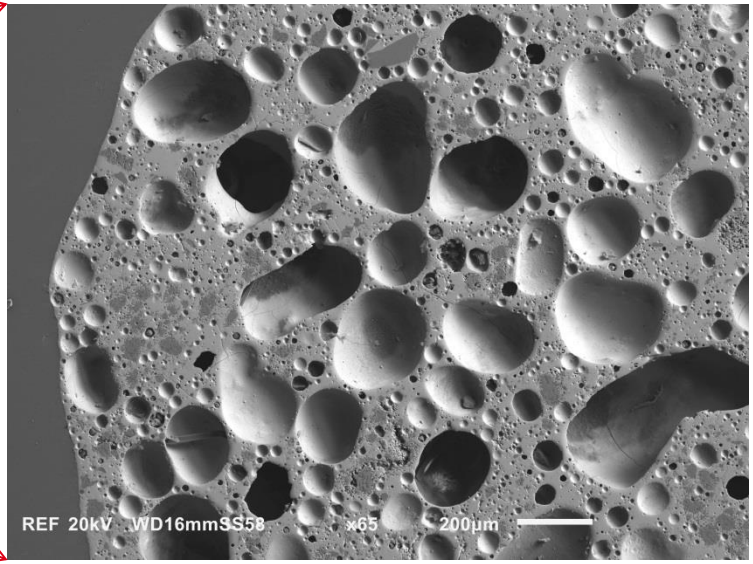
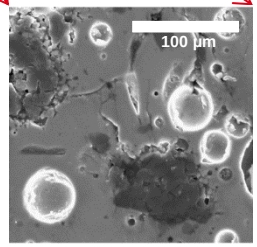
10 wt.% chabazite

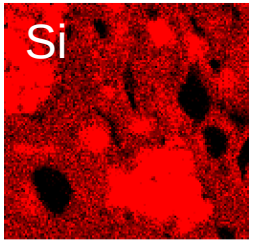


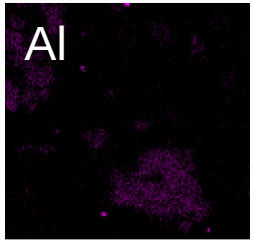


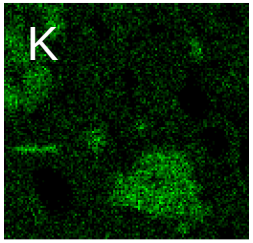
- No circumferential cracking
- Increased foaming

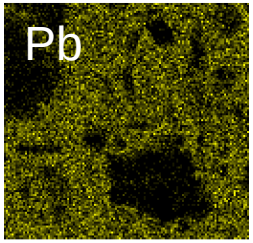


Electron Image 1









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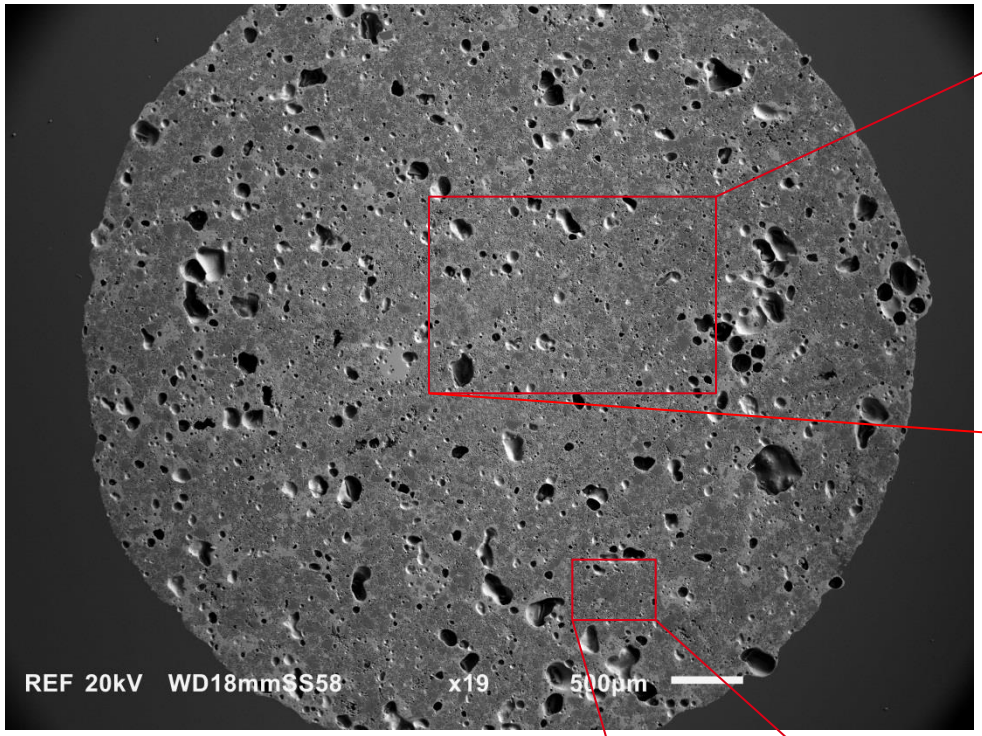
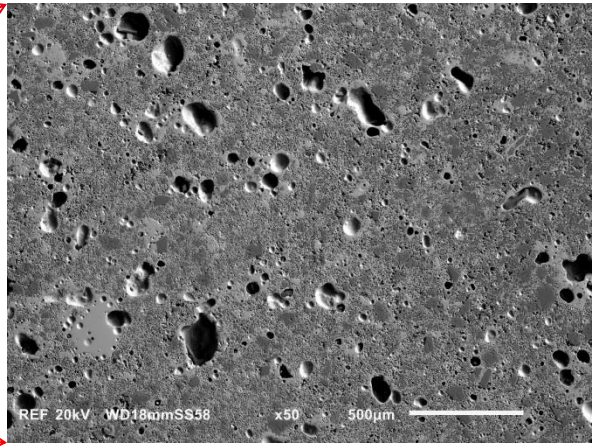
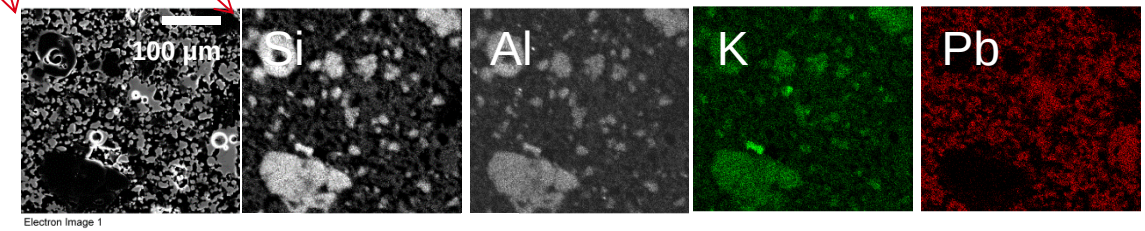
20 wt.% chabazite





- No cracking
- Signs of foaming



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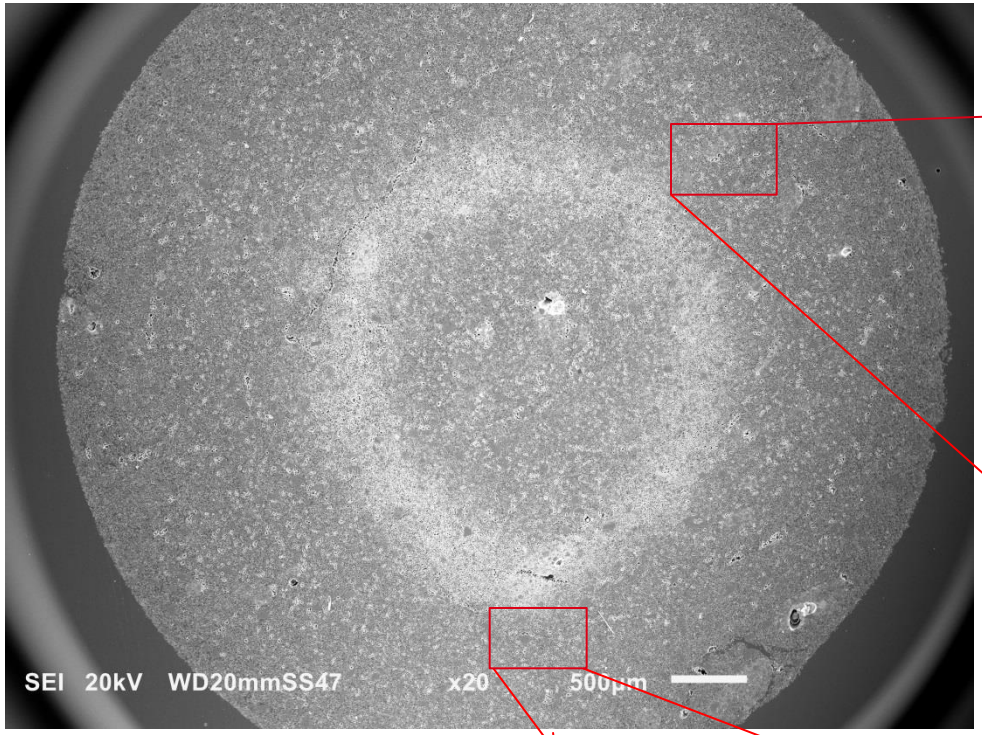
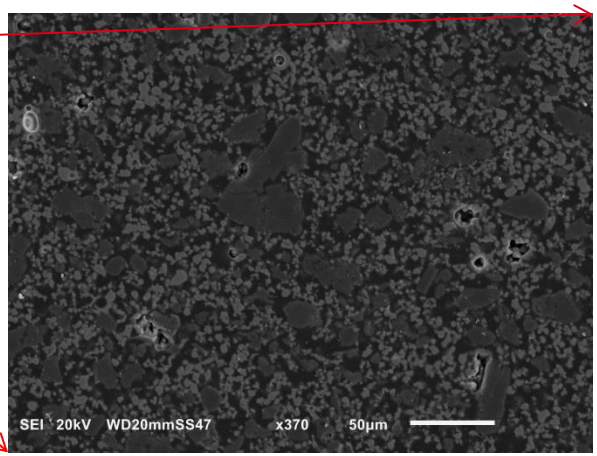
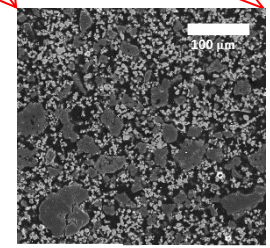
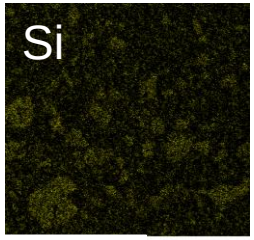
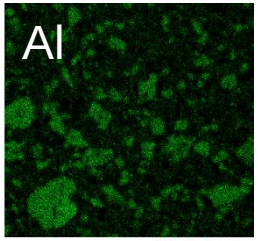
30 wt.% chabazite

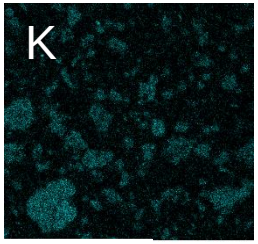


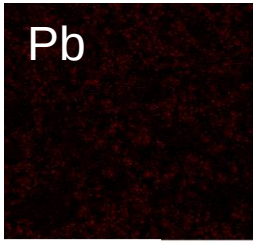












- Dense microstructure
- No cracking
- Halo effect artifact

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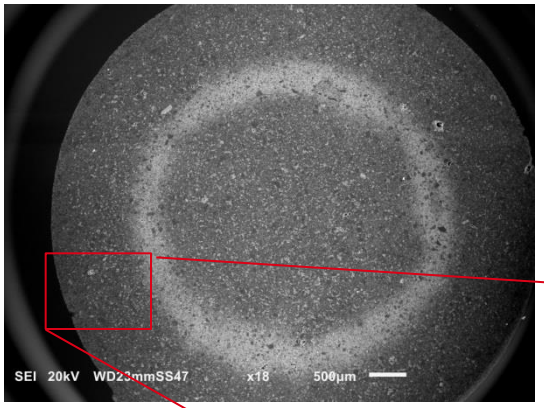
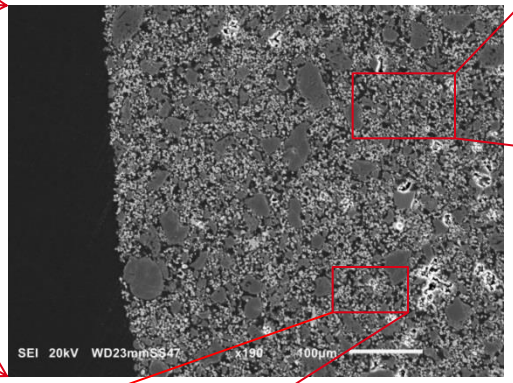
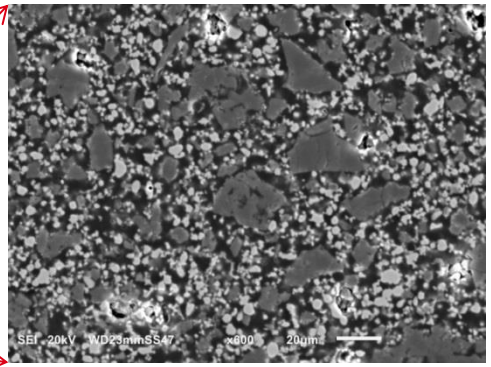
40 wt.% chabazite







- Cross section shows dense microstructure
- No cracking observed
- Halo effect artifact

Electron Image 1

Conclusions

- Glass composition suited to accommodating model wasteform at given maximum processing temperature of 600°C
- Sintering parameters optimisation performed with pelletised 10 wt.% waste loading
- Pressureless wasteforms produced
  - Full sintering accomplished
  - 40 wt.% wasteloading achieved
- Microstructure of final product finely tuned by controlling composition, sintering and thermal treatment regimes

Acknowledgement

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