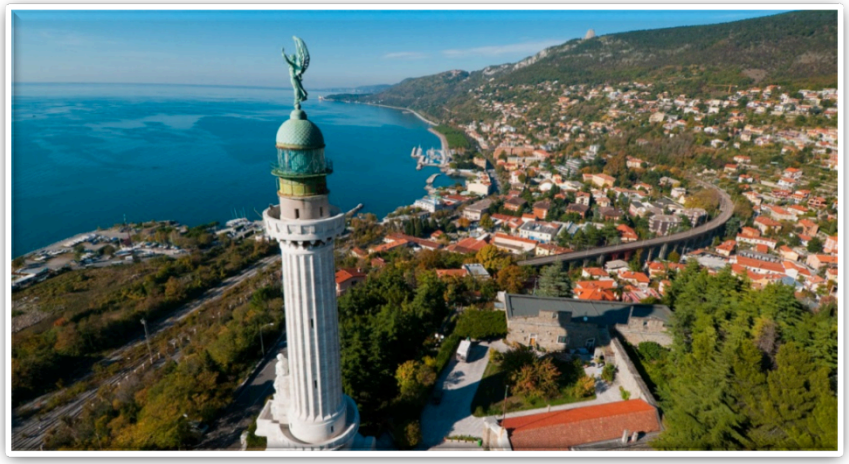
Structure – dissolution relationship of a Zn/Ca modified base glass for UK high level waste

Adam J. Fisher

3rd Year Ph.D. Student, The University of Sheffield, UK

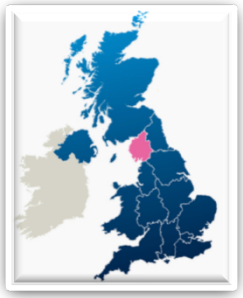
Supervisors: Dr. Claire Corkhill, Prof. Neil Hyatt & Prof. Russell Hand



Joint ICTP-IAEA Workshop on Fundamentals of Vitrification and Vitreous Materials for Nuclear Waste Immobilization 9th November 2017

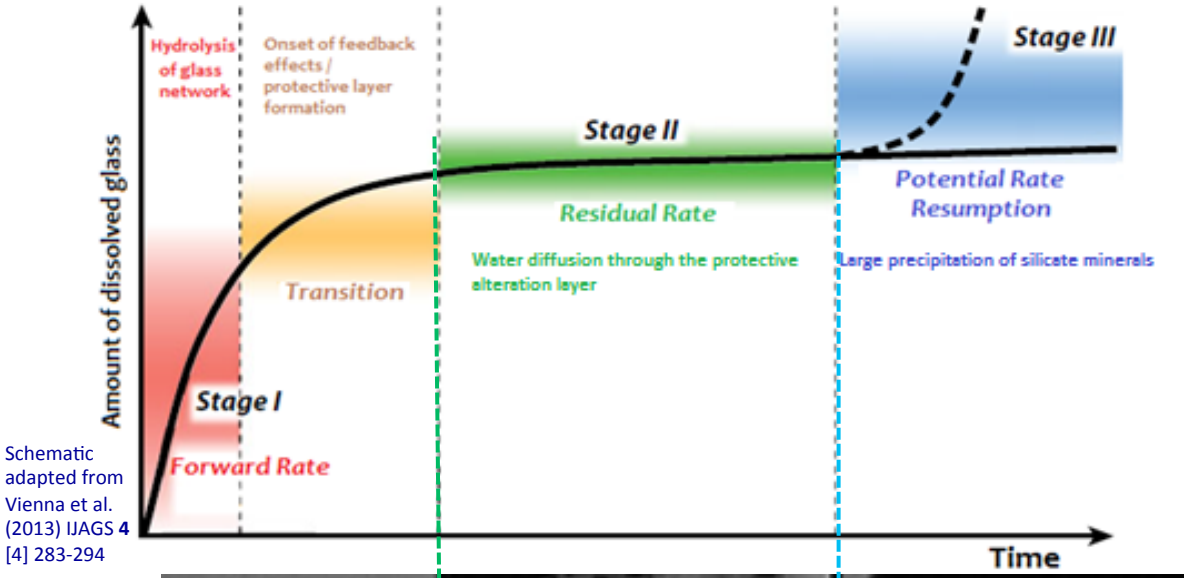
Background

- In the UK (Sellafield) the waste arsing from the reprocessing of spent nuclear fuel is vitrified.
- Reprocessing leads to liquid waste stored in Highly Active Storage Tanks (HAST).
- Produces waste containing large amounts of Mo

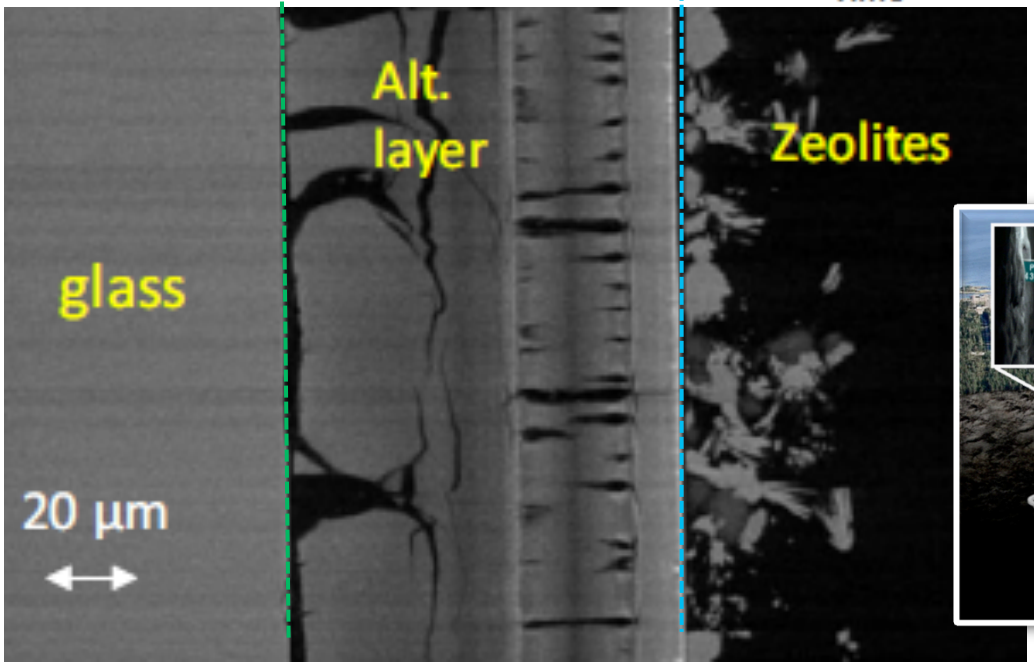


	Amec (2017) Final report on studies of simulant HLW glasses RWM005105	Estimated number of HLW containers			
		Made to date (year 2015)	Yet to be made (2015-2022)	To repository (year >2040)	To overseas customers
MAGNOX -type	**Magnox waste glass**				
	18wt% (low incorp.)	100	0	3009	
	25wt% baseline glass	2700			
	28wt%	209	0		
OXIDE -type	**Blend waste glass (Oxide:Magnox 75:25)**				
	17wt% (low incorp.)	100	0	1487	1780
	25wt% baseline glass	2400			
	28wt% highest currently, and currently the highest spec for overseas customers	767	0		
	Blend waste glass (Oxide:Magnox 50:50)				
	28 to 35wt% incorporporation		1694-x	1694-x	
	Butex-containing glass (Butex + Oxide:Magnox 50:50 or +Magnox)				
	Up to 35wt% with Blend feed		x = 60-120	x = 60-120	
POCO	**Post operational clean out, research phase**				
	Waste loading strategy to be defined		1340	1340	
	Tech wastes, research phase				
	Waste loading strategy to be defined				
	Melter heels		70	70	
	Filters and swarf		70	70	
Sub-totals		6276	3174	7670	1780

Background – Glass Dissolutio

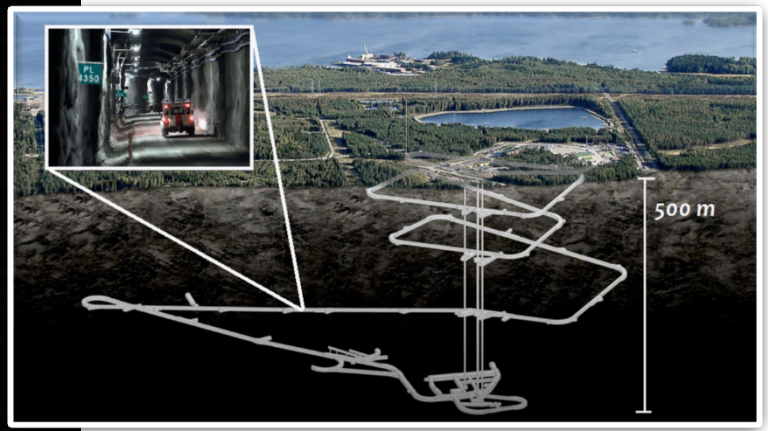


Schematic adapted from Vienna et al. (2013) IJAGS **4** [4] 283-294



SEM taken from Gin et al. (2015) Geochimica et Cosmochimica Acta **151** 68–85

- Glass composition, solution composition, pH, temperature etc. affect rates and timescales.
- Vitrified HLW in a Geological Disposal Facility has the potential to be stable for 100,000+ years if dissolution stays at the Residual Rate.
- Stage III – important – active area of interest.



Background – Glass Dissolutio

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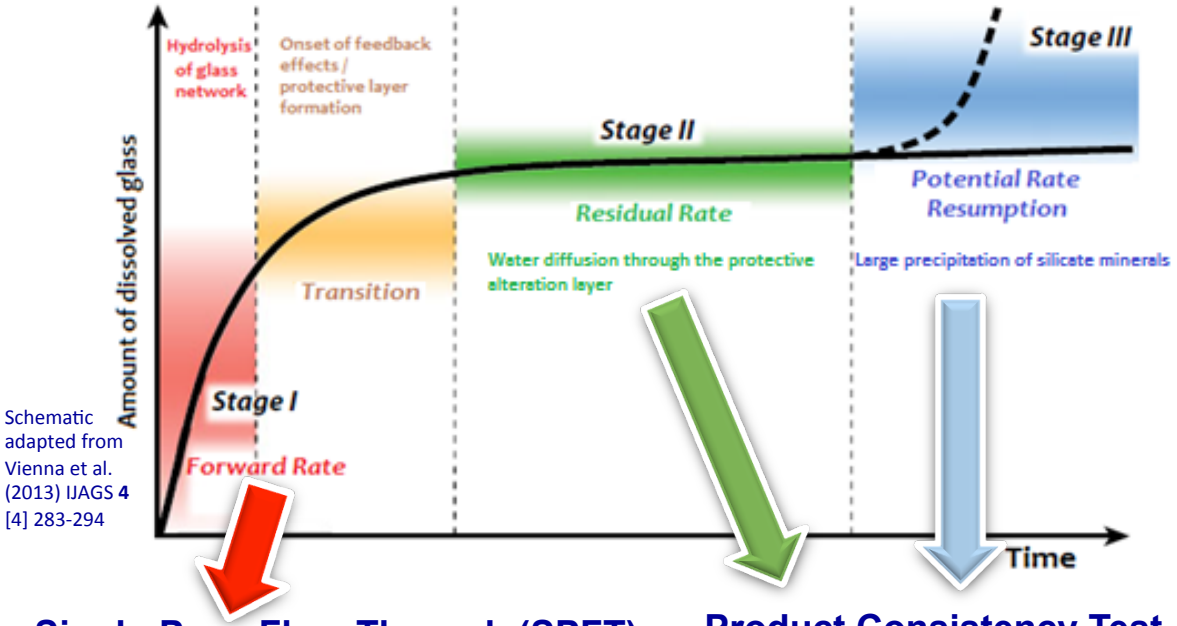
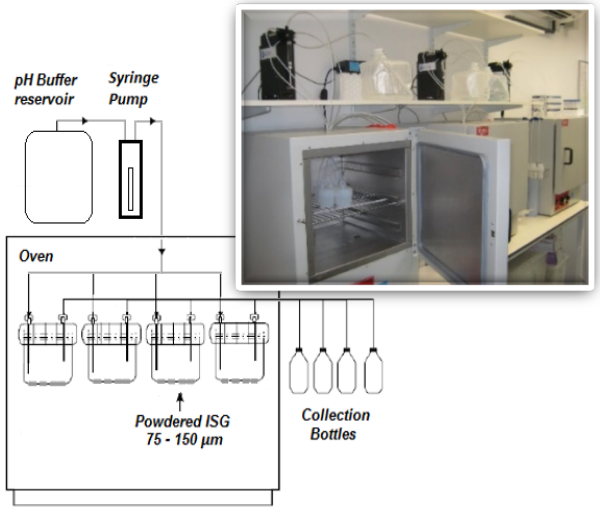


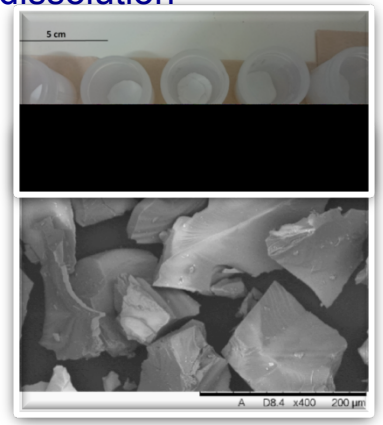
Schematic adapted from Vienna et al. (2013) IJAGS **4** [4] 283-294

Different experimental techniques used to investigate stages of glass dissolution.

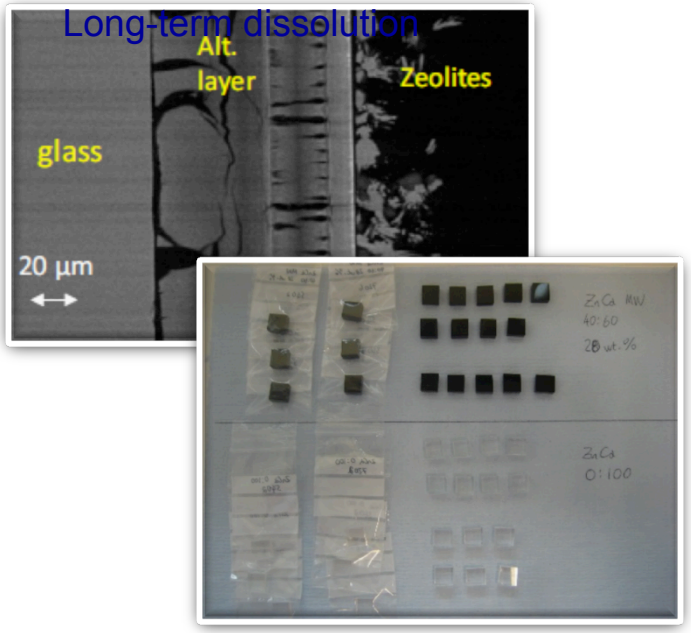
Single-Pass-Flow-Through (SPFT)
Maintains dilute conditions



Product Consistency Test – B
(PCT-B) Saturated conditions
Short-term accelerated dissolution



Materials Characterisation Centre – 1
(MCC-1) Saturated conditions
Long-term dissolution



Aim

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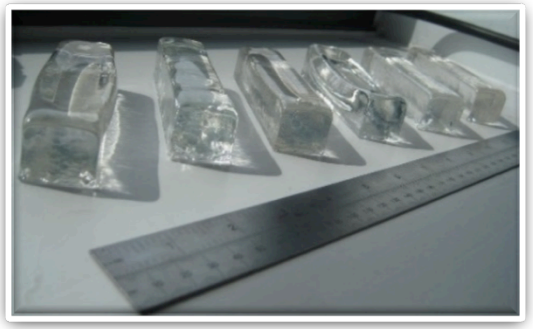
- Understand how varying ***Zn/Ca*** ratios influence the structure of the glass and how this relates to the durability of simple base glasses & 28 wt. % waste loaded ZnCa MW.

Achieved through NMR (Si-29 & B-11), Raman, SPFT, PCT-B & MCC-1 investigations.

Sellafield Ltd

wt. %

	MW	*ZnCa 100:0 MW*	*ZnCa 80:20 MW*	*ZnCa 60:40 MW*	*ZnCa 40:60 MW*	*ZnCa 20:80 MW*	*ZnCa 0:100 MW*
SiO_2	*61.7*	*46.76*	*46.76*	*47.18*	*47.61*	*48.05*	*48.5*
B_2O_3	*21.9*	*22.99*	*22.99*	*23.2*	*23.41*	*23.63*	*23.85*
Na_2O	*11.1*	*8.44*	*8.44*	*8.52*	*8.6*	*8.68*	*8.76*
Li_2O	*5.3*	*4.13*	*4.13*	*4.17*	*4.2*	*4.24*	*4.28*
Al_2O_3	-	*4.13*	*4.13*	*4.17*	*4.2*	*4.24*	*4.28*
ZnO	-	*14.45*	*11.56*	*8.75*	*5.89*	*2.97*	-
CaO	-	-	*1.99*	*4.02*	*6.08*	*8.18*	*10.33*



T_{melt} : 1200 °C
T_{anneal} : 450 °C

Si-29 NMR Results – Structure

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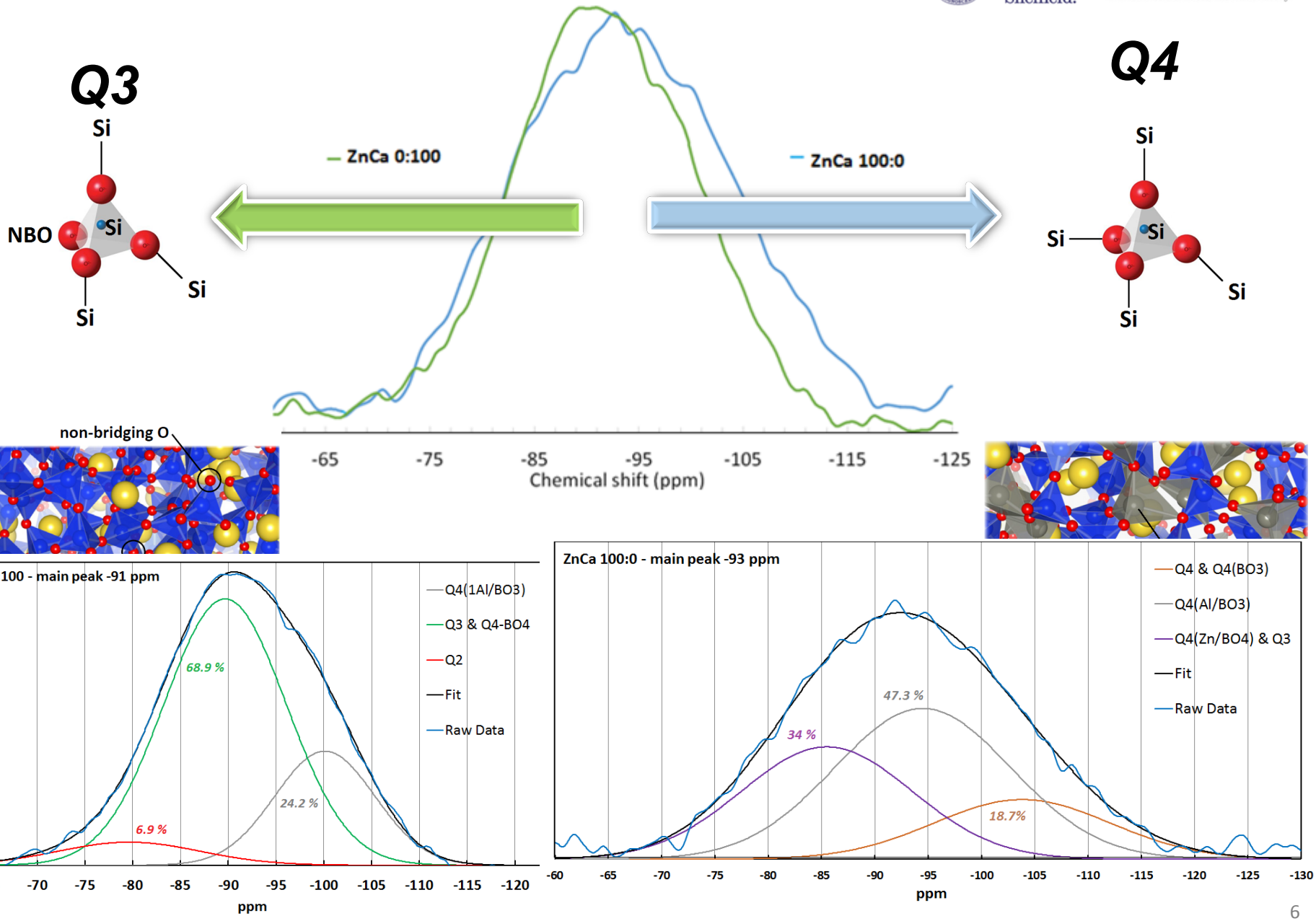
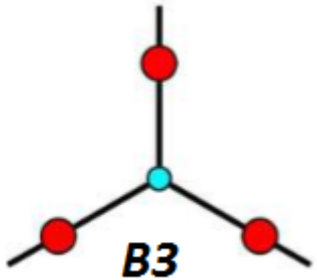
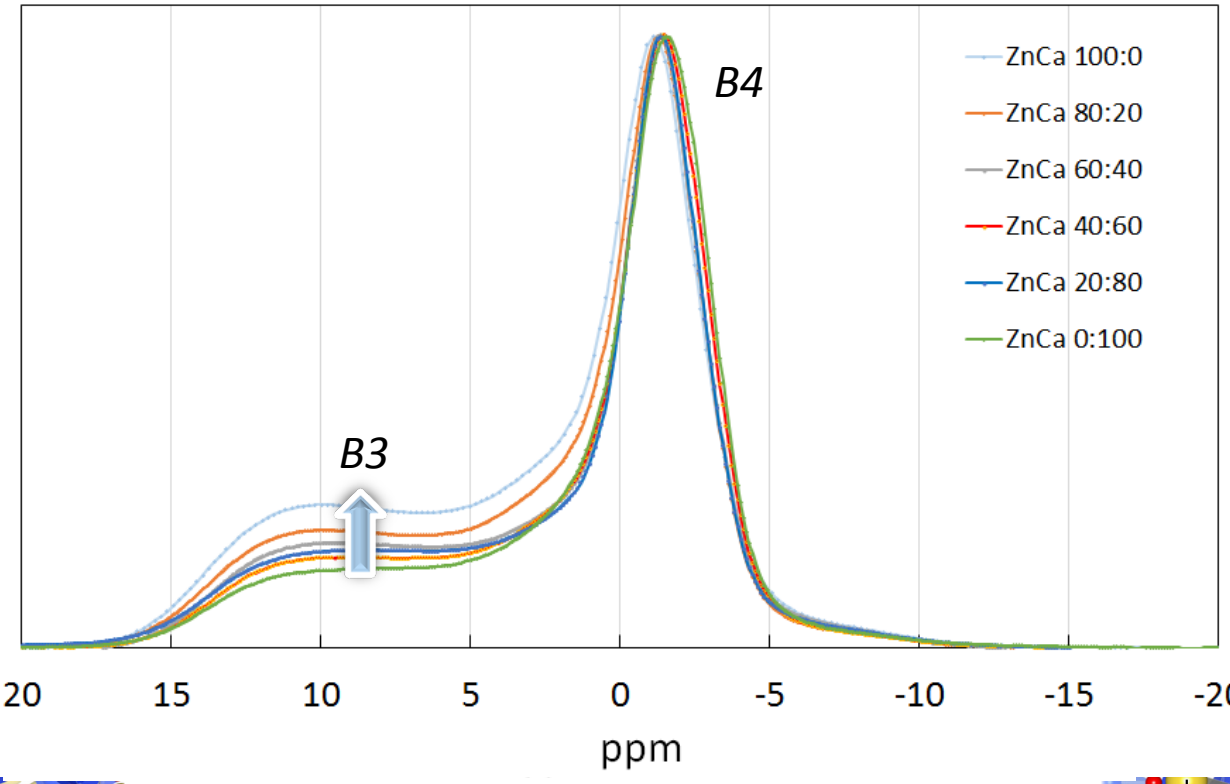
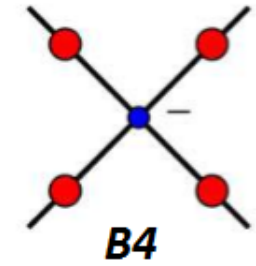
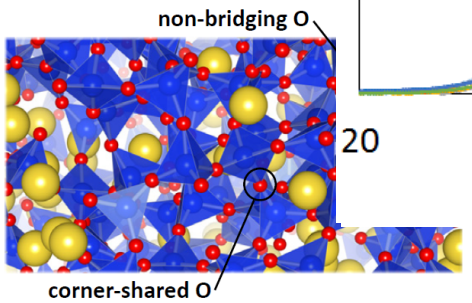


B-11 NMR Results

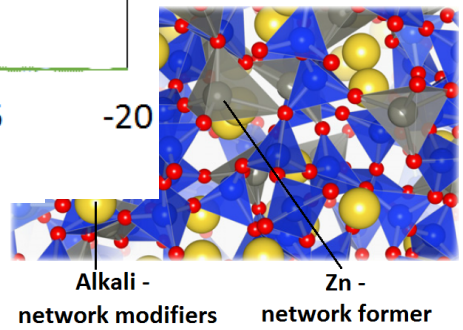








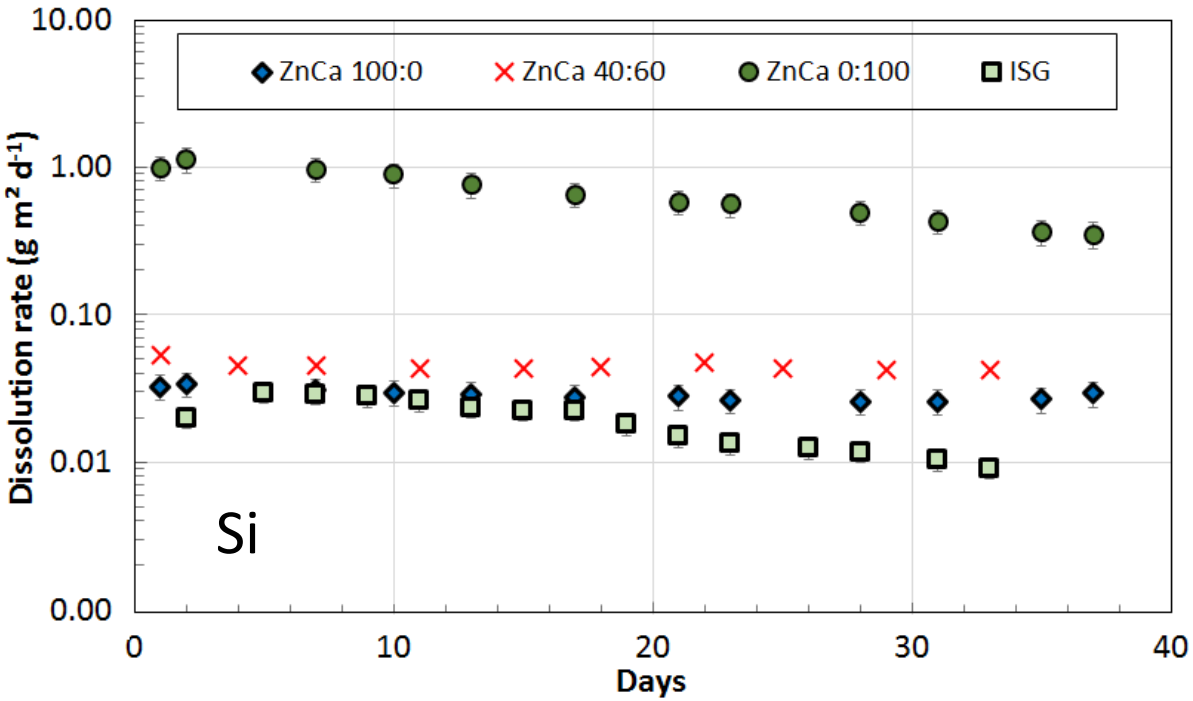
Images adapted from Stechert et al. (2013) J. Am. Cer. Soc. **96** [5] 1450-1455.

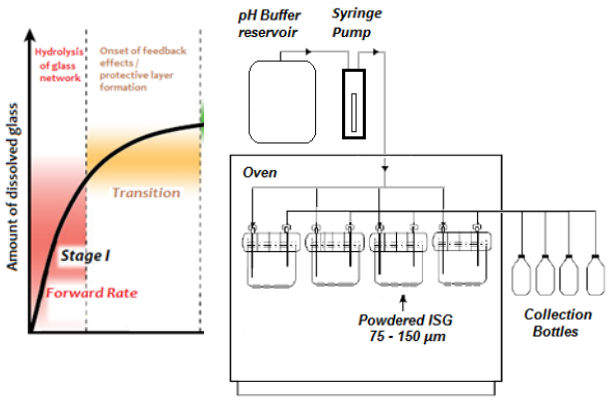


- Generally more Q4 units in ***Zn*** containing glasses ➔ glass more polymerised (better connected) ➔ should be more durable.
- Currently deconvoluting other spectra. Possible to distinguish Q4(Zn) peak?
- Currently analysing B-11 spectra. More ***Zn (less Ca)*** ➔ more B3.

Durability Results – Stage I - SP

- 40 °C, pH 9 (TRIS buffer), 1-35 days, crushed glass 75-150 µm
- Flow-Rate log [Q/S] = -6.78, confident that this maintains dissolution at the Forward Rate. Based on extensive ISG studies

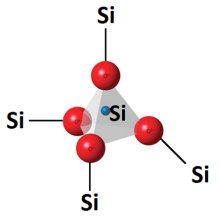




wt. %

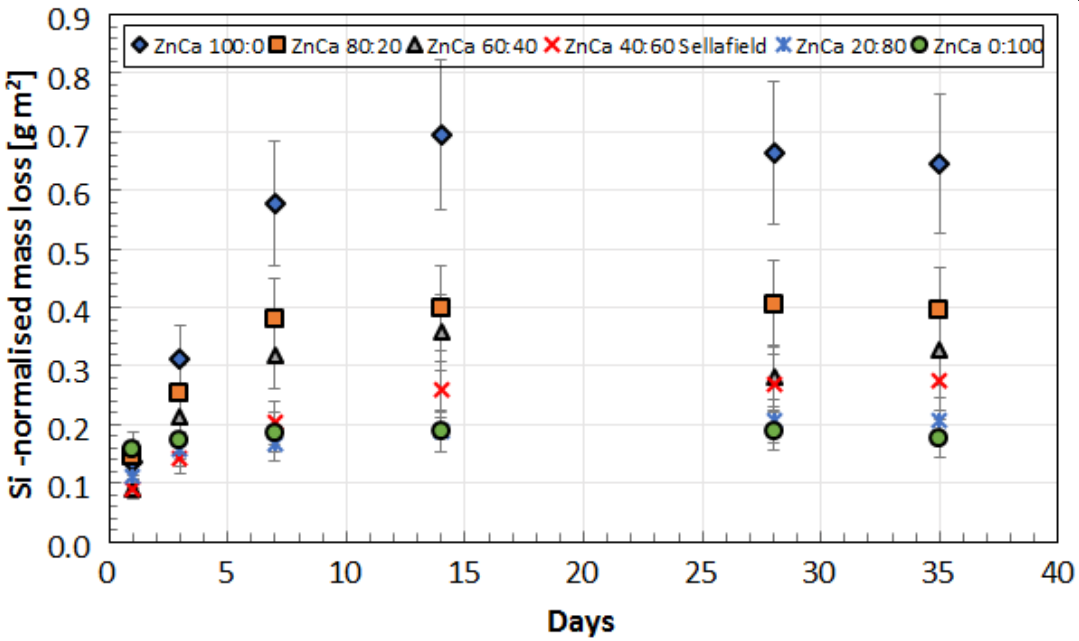
	ZnCa 100:0 MW	ZnCa 60:40 MW	ZnCa 0:100 MW	ISG
SiO_2	46.76	47.18	48.5	56.2
B_2O_3	22.99	23.2	23.85	17.3
Na_2O	8.44	8.52	8.76	12.2
Li_2O	4.13	4.17	4.28	-
Al_2O_3	4.13	4.17	4.28	6.1
ZnO	14.45	8.75	-	-
CaO	-	4.02	10.33	5
ZrO_2	-	-	-	3.3

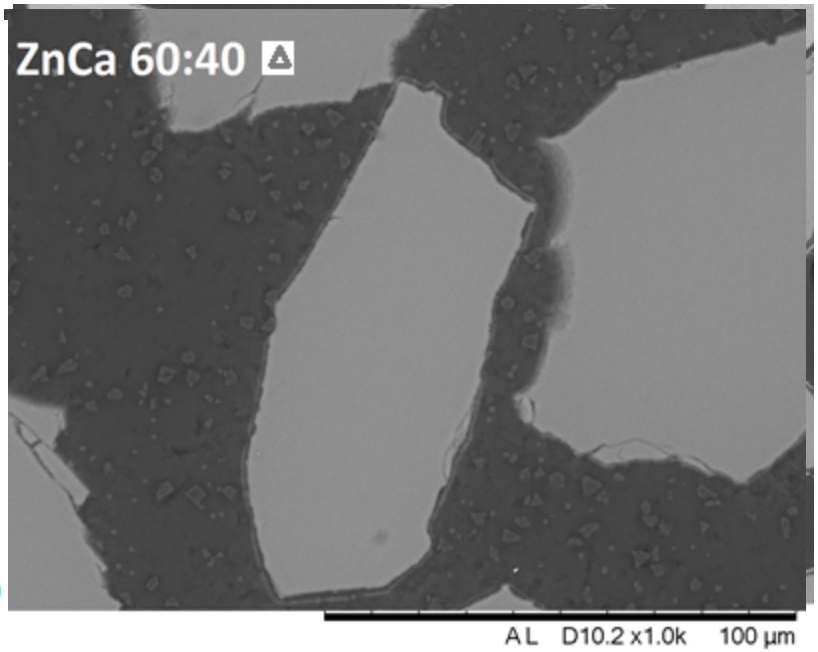
- ***Forward Rate*** - Durability follows the trend ***ZnCa 100:0 > ZnCa 0:100***
- Expected? Yes, the most polymerised glass (based on 29-Si NMR) is the most durable.
- More Si-O-M bonds need to be broken (hydrolysis) in ***ZnCa 100:0*** ➔ more durable.



Durability Results –Stage II - PC

- 90 °C, 1-35 days, crushed glass 75-150 µm, UHQ, SA/V = 2,000 m^{-1}, pH 9.6-10 post dissolutior
- Normalised mass loss ➔ $NL_i = C_i - C_{i,b} / f_i \ (SA/V)$





No evidence for 'large' alteration layers on ZnCa 40:60, 20:80, 0:100.

- Durability follows the trend ***ZnCa 0:100 > ZnCa 100:0***. *Reverse of Stage I*.
- Is this result expected? Note: the most polymerised glass (based on 29-Si NMR) is the least durable (for stage II).

Results – SEM EDX

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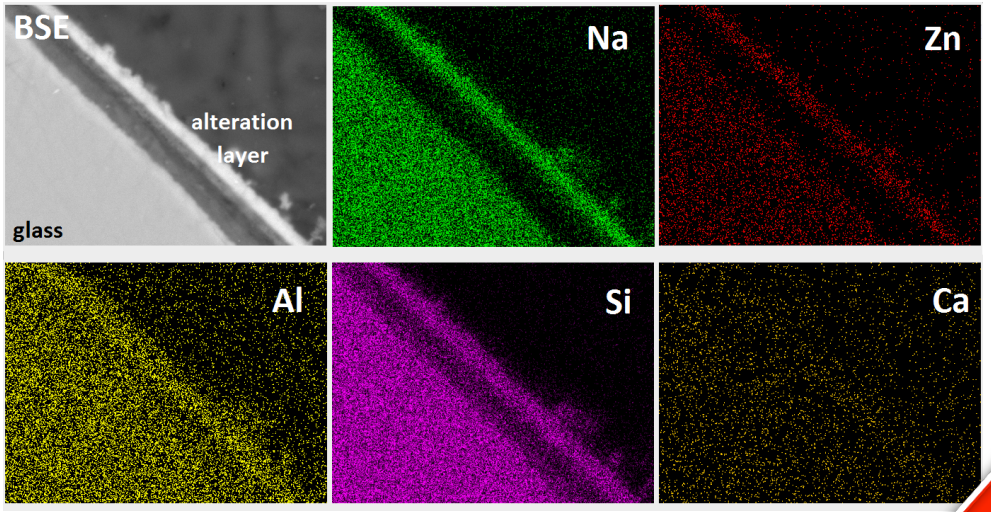
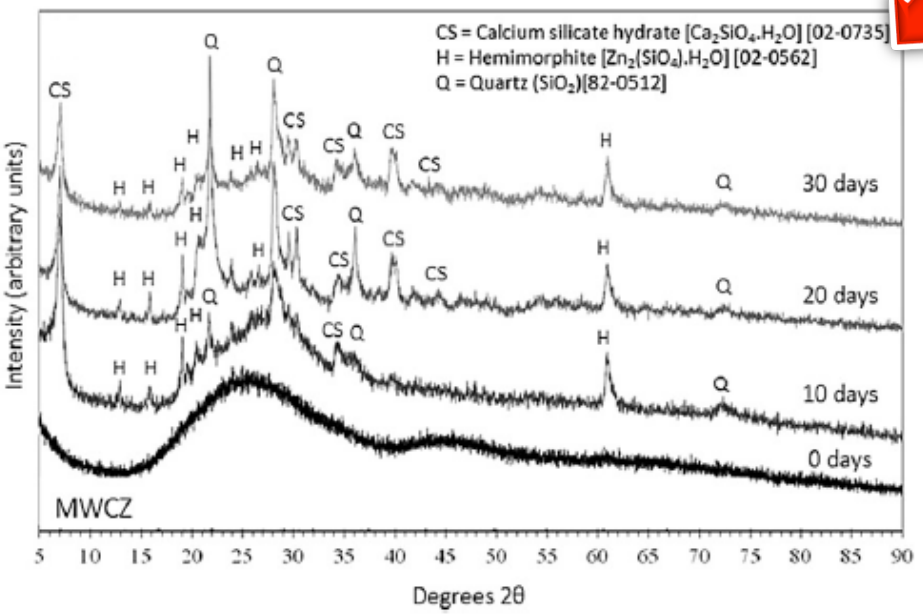
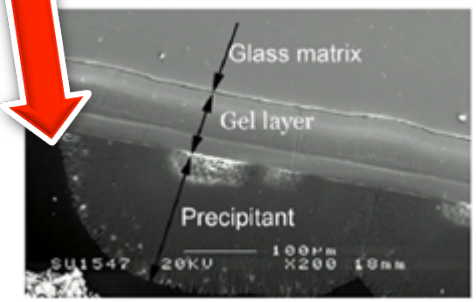
ZnCa 100:0

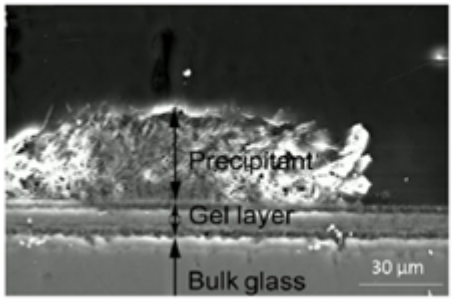


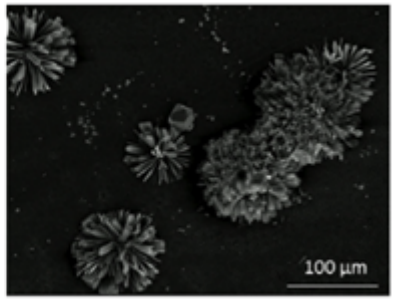
- Stratified alteration layers
- ***Zn*** concentrated in outer layer, negligible detection in solution.
- ***Zn***-silicate precipitate phases identified in literature (VHT on waste loaded ZnCaMW)

Cassingham et al. (2016) J. Nuc. Mat. **479** 639-646,
Zhang et al. (2015) J. Nuc. Mat. **462** 321-328.









Base glass - Conclusion

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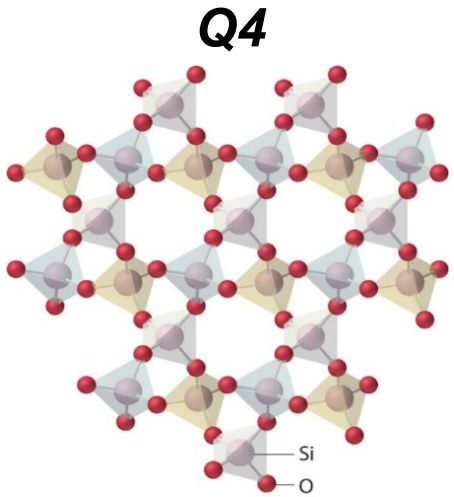
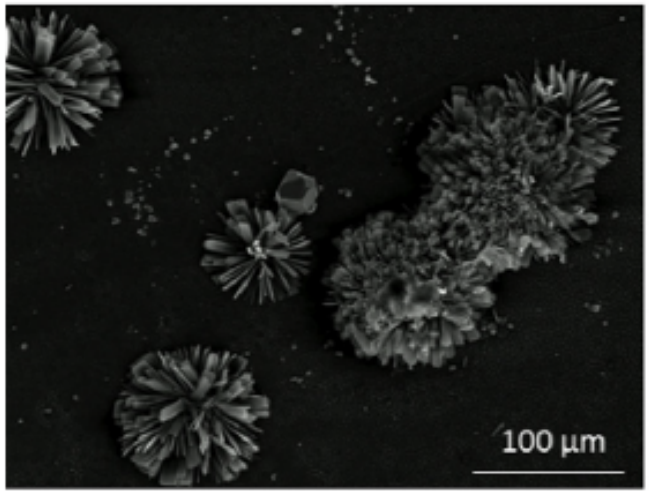
Original Aim - Understand how the varying ***Zn/Ca*** ratios influence the structure of the glass and how this relates to the durability of simple base glasses.



- More ***Zn*** (less ***Ca***) ➔ more polymerised structure (Q4) ➔ intrinsically more durable (stage I) BUT….in saturated conditions (stage II) ***Ca*** containing glasses are more durable

Why?

- ***Ca*** rich alteration layers are effective at passivating the glass.
  Chave et al. (2011) Geochimica et Cosmochimica Acta **75** 4125-4139.
- ***Zn*** – Zn-silicates precipitating out, local under saturation wrt Si ➔ less durable glass in the long-term.



Zhang et al. (2015) J. Nuc. Mat. **462** 321-328.
SEM/EDX after 28 days VHT on simulant ZnCaMW 20 wt. %

Waste-loaded glass: ZnCa MW 28 wt. %

- Investigate varying *ZnCa* ratios on 28 wt.% waste-loaded glass durability.

Three Compositions

MW ZnCa 100:0 28 wt.%

MW ZnCa 40:60 Sellafield 28 wt.%

MW ZnCa 0:100 28 wt.%

Oxide Component	wt. % ZnCa 100:0 MW - 28 wt. %	ZnCa 40:60 MW - 28 wt. %	ZnCa 0:100 MW - 28 wt. %
Al_2O_3	3.08	3.15	3.21
B_2O_3	17.13	17.56	17.89
CaO	-	4.56	7.74
Li_2O	3.07	3.15	3.21
Na_2O	6.29	6.45	6.57
SiO_2	34.83	35.71	36.38
ZnO	10.77	4.41	-
BaO	0.96	0.97	0.97
CeO_2	1.50	1.51	1.51
Cr_2O_3	0.54	0.55	0.55
Cs_2O	1.68	1.69	1.69
Fe_2O_3	2.29	2.31	2.31
Gd_2O_3	3.99	4.01	4.01
HfO_2	0.06	0.06	0.06
La_2O_3	0.77	0.77	0.77
MgO	1.63	1.65	1.65
MnO_2	0.00	0.00	0.00
MoO_3	2.56	2.58	2.58
Nd_2O_3	2.38	2.40	2.40
NiO	0.36	0.36	0.36
P_2O_5	0.48	0.48	0.48
PrO_2	0.79	0.79	0.79
RuO	0.59	0.59	0.59
SO_3	0.03	0.03	0.03
Sm_2O_3	0.49	0.49	0.49
SrO	0.52	0.52	0.52
TeO_3	0.30	0.31	0.31
TiO_2	0.00	0.00	0.00
Y_2O_3	0.30	0.31	0.31
ZrO_2	2.61	2.63	2.63
Total	100	100	100

Waste-loaded glass: ZnCa MW 28 wt. % - Characterisation

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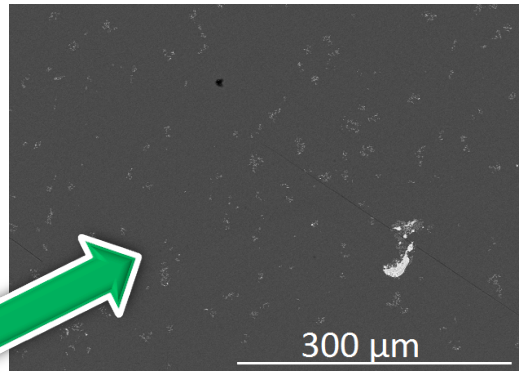
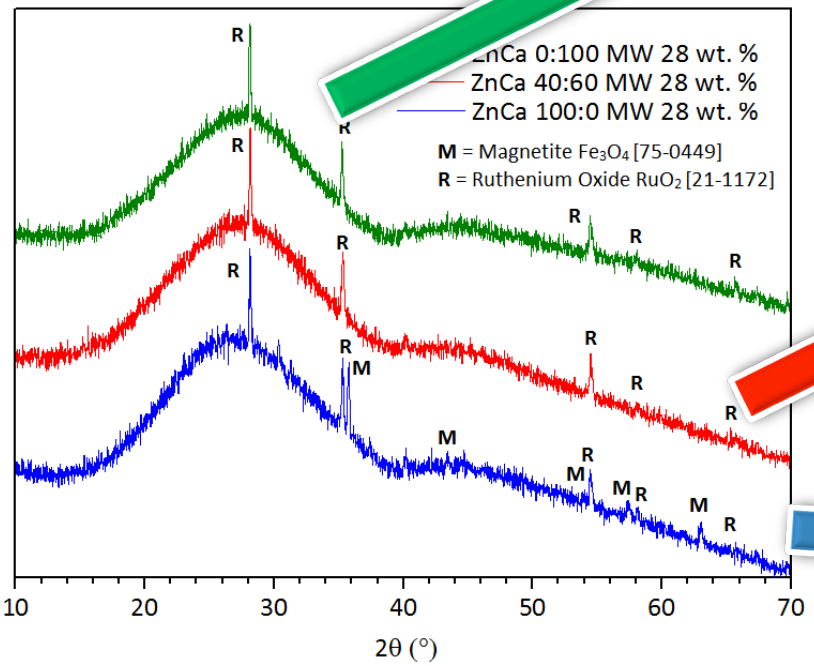
Three Compositions

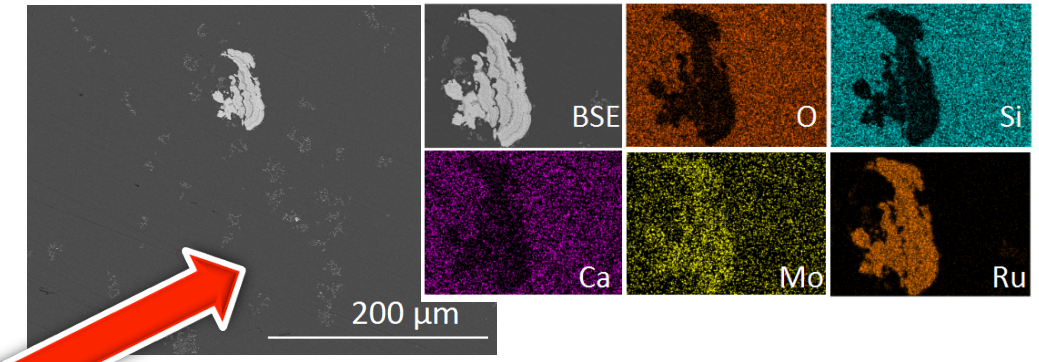
ZnCa 100:0 MW 28 wt.%

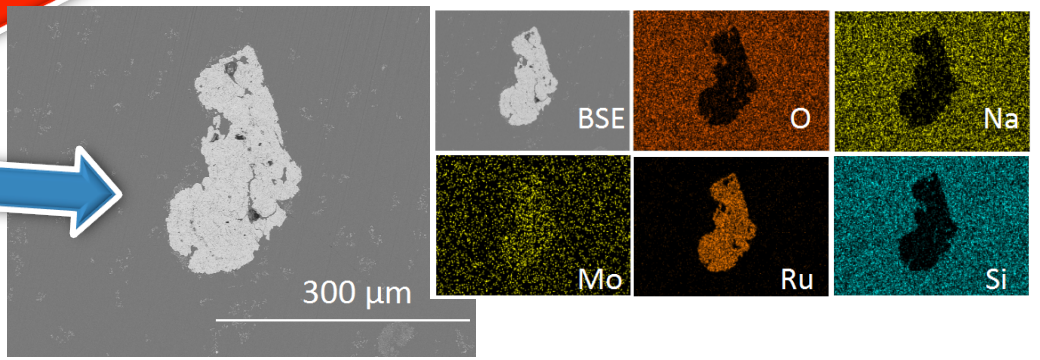
ZnCa 40:60 MW Sellafield 28 wt.%

ZnCa 0:100 MW 28 wt.%



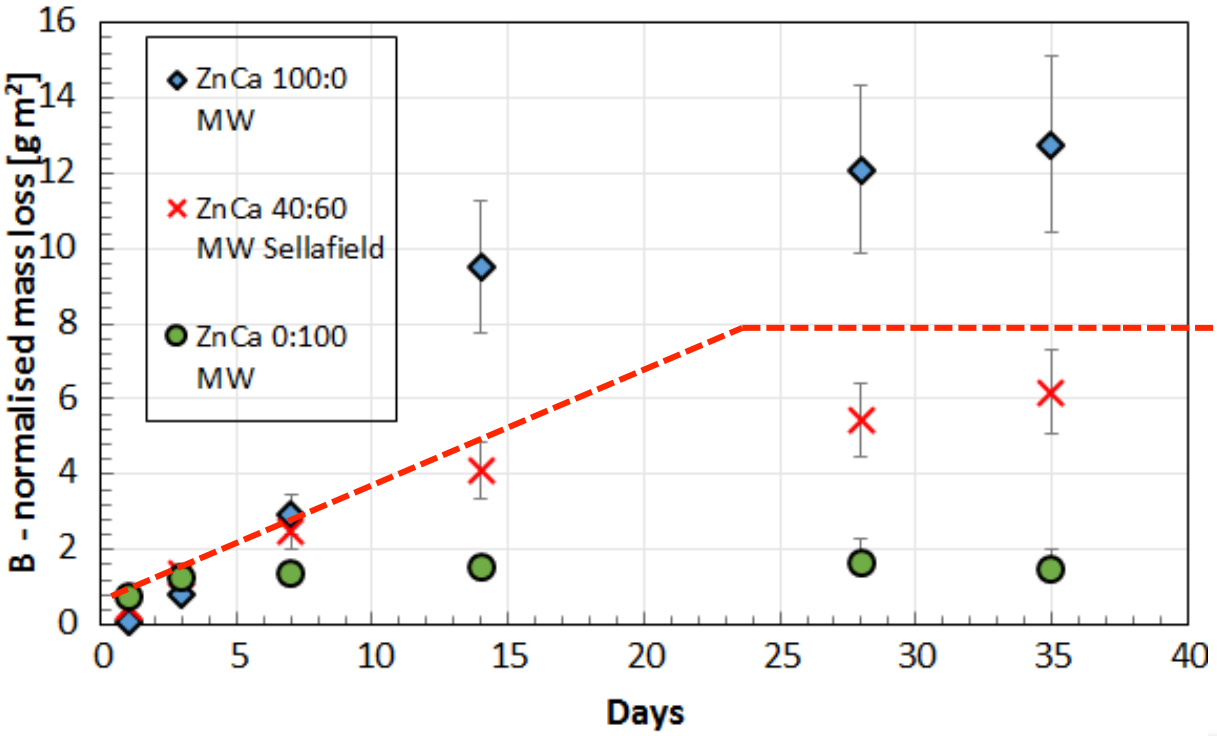






Durability Results –Stage II - PC

- On 28 wt. % waste loaded samples (75:25 , Oxide:Magnox)
- 90 ^{o}C, 1-35 days, crushed glass 75-150 µm, UHQ, SA/V = 2,000 m^{-1}, pH 9.6-10 post dissolutior
- Normalised mass loss ➔ $NL_i = C_i - C_{i,b} / f_i \ (SA/V)$



Standard
MW 25 wt. % (75o:25m)
Harrison (2011) Procedia Materials Science **7** 186-192.

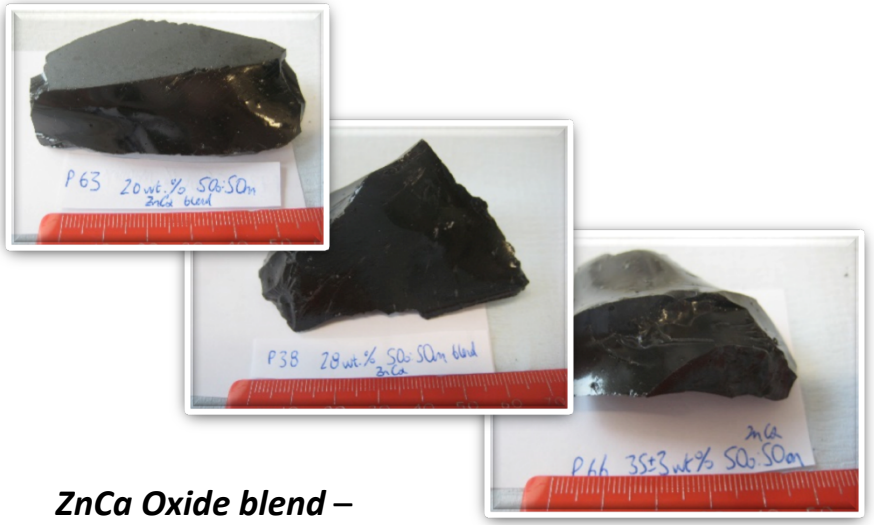
120 day PCT-B

- Durability follows the trend ***ZnCa MW 0:100*** **>** ***ZnCa MW 100:0***.
- *Assume the reverse is true for stage I (based on base glass results)*
- ***ZnCa 40:60 28 wt. % MW Sellafield*** *similar durability as* ***Standard MW 25 wt. %***

Future work

- Investigate varied waste loaded ***ZnCa MW*** (20, 28 & 35 wt.% waste (Magnox & Oxide blend)). Waste-loaded glass optimization (ZnCa ratio 40:60). Does Zn inclusion allow for greater waste loading (in terms of durability)?

ZnCa Magnox –
High Mg (~6 wt. %) & Al (~6 wt. %)



ZnCa Oxide blend –
Mg (~2 wt. %) & Al (~2 wt. %)

- Long term PCT-B & MCC-1 (>2 years) on base and waste loaded glasses to investigate possible rate-resumption due to ***Zn*** precipitates (stage III).Gin et al. (2013) IJAGS 4 [4] 371-382, Arena et al. (2016) J.Nuc.Mat. 470 55-67.
- UHQ, expected groundwater and near-field solutions (UK cement backfill).

➔ Zn addition expected to be problematic.

Impact of results

- Potential to impact waste treatment at the Sellafield site (optimisation of MW glass formulation).
- Provide the robust data to support a safety case for geological disposal of nuclear waste in the UK.
- This investigation also highlights the important fact that glass formulations (in terms of durability) for geological disposal should not be selected based solely on forward (maximum) dissolution rates.
- **Discussion – what do we mean by a durable glass?**

Acknowledgments:

Dr. Clare Thorpe……*dissolution*
Dr. Brant Walkley……*NMR*
Dr. Laura Gardner……*NMR*
Colleen Mann……*dissolution*
Daniel Backhouse……*dissolution*
Sean Barlow……*SEM/XRD*
Dale Prentice……*computing*

This research was performed in part at the MIDAS Facility, at the University of Sheffield, which was established with support from the Department of Energy and Climate Change.

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Society of Glass Technology 1916 Centenary 2010

EPSRC Engineering and Physical Sciences Research Council

National Nuclear Laboratory

NGN CDT Next Generation Nuclear

Radioactive Waste Management

Sellafield Ltd

The University Of Sheffield.

NucleUS
Immobilisation Science Laboratory

Thanks for listening.
Questions?

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@ISL_Sheffield ajfisher1@Sheffield.ac.uk

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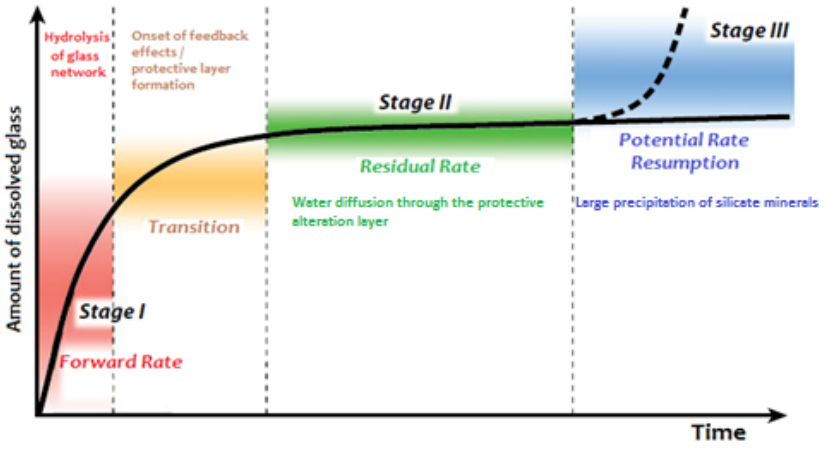
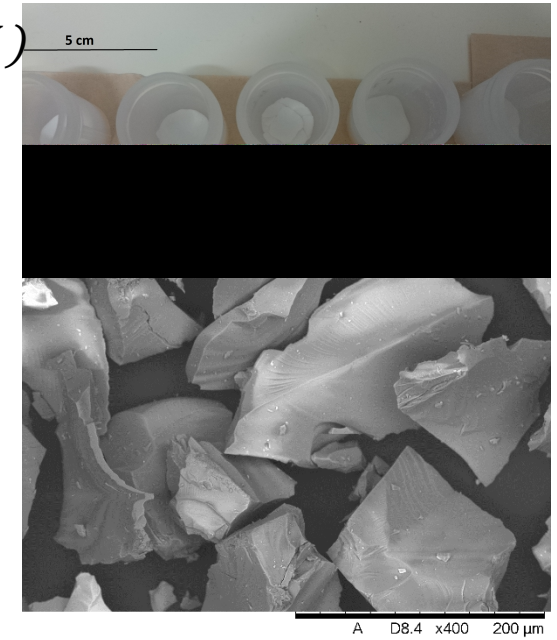
TO DO Results – Durability Stage II - F

- 90° C, 1-35 days, crushed glass 75-150 µm, UHQ, SA/V = 2,000 m^{-1}, pH COMMENT ON PLOTS post dissolution
- Normalised mass loss ➔ $NL_i = C_i - C_{i,b} / f_i \ (SA/V)$



Zn>Ca

Zn<Ca

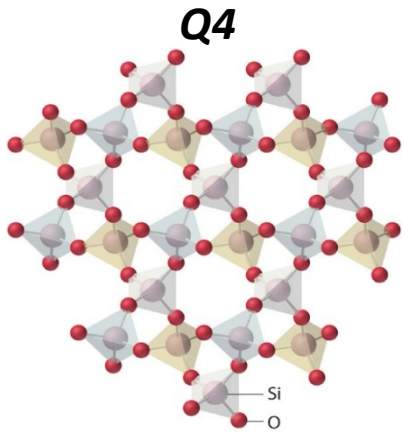


No evidence for 'large' alteration layers on ZnCa 40:60, 20:80, 0:100.

- Durability follows the trend ***ZnCa 0:100 > ZnCa 100:0***.
- Is this result expected? Note, the most polymerised glass (based on 29-Si NMR) is the least durable (for stage II).
- Passivating effects of ***Ca*** in the alteration layers can explain the durability.
  [Chave et al. (2011) Geochimica et Cosmochimica Acta 75 4125-4139].

Discussion

1. What is the effect of ***ZnCa*** additions on the structure?
2. Should a more polymerised glass (high Q4) be more durable?
3. Main durability factor? Connectivity or solubility?
4. How much ***ZnCa*** is necessary in ***ZnCa*** MW? Note, addition of ***Zn*** to base glass formulation is *expected* to have adverse effects in the long-term by increasing the dissolution rate. [Gin et al. (2013) IJAGS **4** [4] 371-382, Arena et al. (2016) J.Nuc.Mat. **470** 55-67].



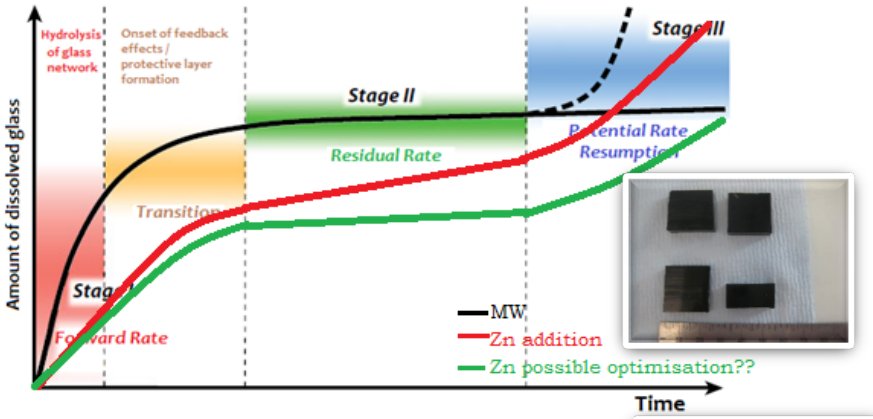
Conclusion

- RETURN TO OVERALL AIM understand how the varying Zn/Ca ratios influence the structure of the glass and how this relates to the durability.
- More Zn (less Ca)➔ more polymerized structure ➔ intrinsically more durable BUT in saturated conditions Ca containing glasses are more durable!

- Initial studies suggest ***ZnCa 0:100*** most durable base glass (PCT-B 1-35 days).
- ***ZnCa 100:0*** intrinsically more durable when dissolving at forward rate (SPFT).
- ***Ca*** rich alteration layers are effective at passivating the glass.
- ***Zn*** addition – trade off between processing benefits and long-term durability.

Further work

- Part 2 - experiments on waste loaded ***ZnCa MW*** (28 wt.% waste).
- Long term MCC-1 dissolution experiments (>2 years) on base and waste loaded glasses to investigate possible rate-resumption due to ***Zn*** addition.
- Raman spectroscopy, comparison with NMR.



Impact of results

- Potential to impact waste treatment and decommissioning at the Sellafield site (optimisation of MW glass formulation).
- Provide the robust data and mechanistic understanding required to support a safety case for geological disposal of nuclear waste.
- Safety case for geological disposal should not be based on forward rate dissolution. NEEDED – SPFT ON STAGE 3 DISSOLUTION!!