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The Effect Of Crystal Precipitation On High Level Nuclear Waste Glass.

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Why Are We Concerned About Crystallisation?

1) Crystalline materials and their glassy counterparts contract at differing rates. This means it is more likely for cracks to form within nuclear waste glass in which crystals precipitate.

2) When crystals form, they can alter the composition of the surrounding glass making it less durable to corrosion attacks[1].

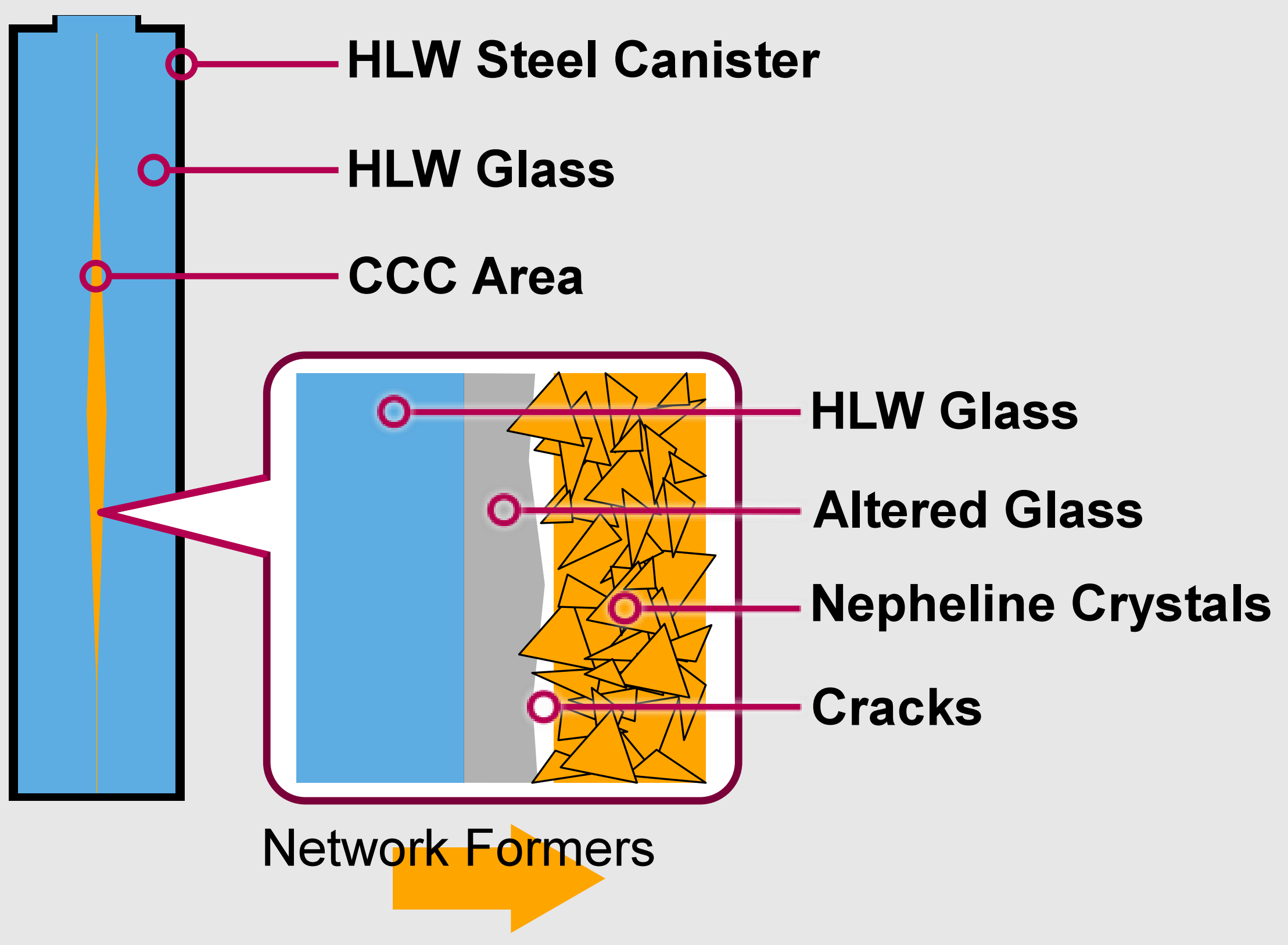
3) Crystals forming within the waste glass melter can result in costly operational issues or reduce the lifetime of the melter[2].

However more recent research suggests that imposed constraints may be excessively conservative, especially when it comes to nepheline precipitation in high alumina and sodium waste glasses[3].

Where Does Crystallisation Occur?

Crystallisation occurs along the centreline of the canister where cooling is slowest. High level nuclear waste canisters are made tall and narrow to alleviate this, but in high Al_2O_3 and high Na_2O waste loaded glasses crystallisation is still a problem[5].

What Happens Inside The Canister? - Nepheline



Nepheline ($Na_2O\ Al_2O_3\ 2(SiO_2)$), a common precipitate in nuclear waste glasses, tends to weaken the durability of the glass by removing two moles of network forming-oxides for each mole of network modifier it draws from the surrounding glass.
Slower cooling rates along the canister centreline afford more favourable nepheline crystallisation kinetics.

How Do We Test Durability?

There are multiple barrier systems protecting the release of radio-nuclides into the environment, however how the glass degrades when in contact with ground water is the last line of defence.
To test the durability of glass, they are placed in contact with water and the concentration and rate at which elements leach out of the glass into the water is measured and compared to standards[9].

Why Is This Research Important?

Nuclear energy is an important part of many countries strategies as they work towards Net Zero. Nuclear reactors are incredibly energy dense and allow for load following of national grids. Furthermore, nuclear power plants generate a considerably smaller volume of waste than the likes of coal power plants[7].

Since the geological storage of nuclear waste needs to be understood, fine-tuned and optimised to deal with legacy waste from endeavours such as the ***Manhattan Project***, it is key that we are organized and ready to use this knowledge-set in handling the forthcoming requirements of nuclear waste disposal.

What Will This Research Deliver?

This project will deliver a clearer understanding of the effects of crystallisation on nuclear waste glass durability as well as allowing for higher waste loading per unit volume of glass without compromising on durability.

Why Does Crystallisation Occur?

When a material cools from a molten state it will crystallise as it solidifies and different materials crystallise at differing rates. Glasses are amorphous solids which form as they cool too rapidly from their molten state for crystalline structures to form.

When waste glass is poured into a waste canister, it does not cool at a uniform rate resulting in some areas being more likely to crystallise.

The composition of the glass also affects the crystallisation.

What Affects Crystallisation?

Composition

Cooling rate

Impurities

What Oxides Induce Crystallisation?

$Al_2O_3 > Na_2O > Li_2O \approx K_2O \approx Fe_2O_3 > B_2O_3 > CaO > SiO_2$ [4]

How Is Crystallisation Modelled And Predicted?

Nepheline Discriminator

This was proposed to identify glass compositions that may be prone to nepheline precipitation. The calculation only depends on the mass fraction of SiO_2, Na_2O and Al_2O_3.

$$\boxed{ND = \frac{SiO_2}{SiO_2+Na_2O+Al_2O_3.}}$$

ND<0.62 is used as a predictor of nepheline precipitation[6].

Optical Basicity

Optical basicity is a measure of the glass compositions ability to accept cations and can represent an overall average state of oxygen in oxide glasses. It can be used to predict many glass properties including crystallisation and ionic solubility:

$$\boxed{\Lambda_{glass} = \frac{\sum x_i q_i \Lambda_i}{\sum x_i q_i}}$$

Where q_i is the number of oxygen atoms in the i-th component, x_i is the i-th oxide mole fraction and A_i is the i-th oxide optical basicity[3].

$\Lambda_{glass}>0.57$ is used as a predictor for nepheline precipitation[6].

Quadrant Map Showcasing High Crystallisation

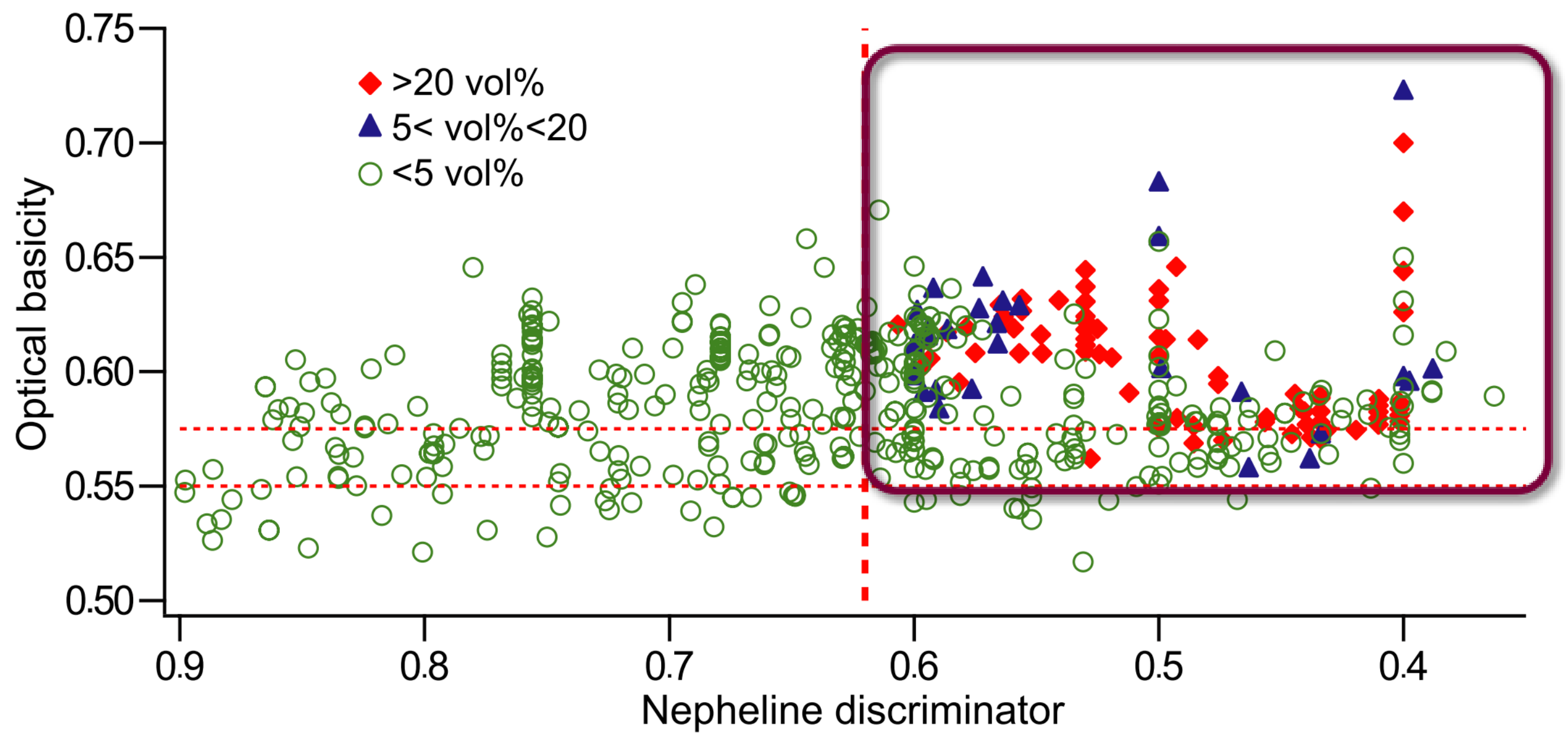


Fig - Quadrant map of 523 simulated waste glasses with ND and Λ_{glass} for each composition [6].

More contemporary modelling efforts focus on the use of machine learning and neural networks, however these will always require empirical data to validate.

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[3] McCloy J.S. & Vienna J.D. (2010). *Glass Composition Constraint Recommendations for Use in LifeCycle Mission Modeling.*
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[5] Marcial J. et al. (2020). *Effect of Cooling Profile On Crystalline Phases, Oxidation State, And Chemical Partitioning Of Complex Glasses.*
[6] McCloy J. S. et al. (2011). *Nepheline Crystallization in Nuclear Waste Glasses: Progress Toward Acceptance of High-Alumina Formulations.*
[7] Corkhill C. & Hyatt N. (2018). *Nuclear Waste Management.*

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