Natural analogues for nuclear waste; a window into the future?

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Introduction

Glassy materials, those with no long-range atomic structure, are ubiquitous in our modern lives. Glass is formed when a molten liquid is cooled rapidly and, although many substances can be induced to form a glass, few do so as readily as SiO_2 making silicate glasses the most common. Other elements may substitute into the glass structure, either as network formers like B and Al that form covalent bonds in place of Si, or as network modifiers like Na^+, K^+, Ca^{2+} or Fe^{2+}, that form ionic bonds with oxygen from the silicate network. The addition of other elements to silicate glass has variety effects, from decreasing melting temperatures, to improved physical or chemical durability, to changing the colour of the glass.

The longevity of glass, across a range of natural environments, is of interest from the point of view of building construction, the manufacture of components such as semiconductors and fibre optics, the preservation of art and archaeological artefacts, and the safe disposal of vitrified waste. The impetus to understand glass degradation over very long time-periods >10,000 years comes, primarily, from the need to ensure that vitrified radioactive waste emplaced in subsurface disposal facilities will not pose a hazard to future generations.

In the UK, and in many countries including the USA, France, Russia, Germany and Japan, high level waste, resulting from spent fuel reprocessing, is immobilized in a borosilicate glass matrix and destined for eventual disposal in an engineered geological facility. In addition, vitrification is also under consideration for lower activity waste streams due to the wide range of elements that glass can incorporate, its chemical durability and resistance to radiation damage. The glass waste form is usually contained in a steel canister to keep it isolated from groundwater ingress for tens to hundreds of years, even after the backfill material is saturated. However, radioactive waste needs to be isolated for thousands to tens of thousands of years (depending on the isotope in question) to allow radioactivity to decay to safe levels and so the rate of corrosion of the glass matrix is an important factor in the safety case for disposal of vitrified radioactive wastes.

There is scientific consensus that glasses start to corrode when in contact with water or water vapour, and that the general mechanism begins with ion exchange between H^+/H_3O^+ from the water and alkali metals (e.g. L^+, Na^+, K^+) from the glass. Concurrently, there is hydrolysis of the glass

network breaking down Si-O and B-O bonds (Gin et al., 2013). Elements released from the glass accumulate in solution until sufficient silica is freed to allow formation of an amorphous gel layer on the glass surface. This layer densifies over time and can crystalize into secondary mineral phases (Gin et al., 2015) meaning further corrosion of the bulk glass is limited by the diffusion through this surface alteration layer and the rate of release of elements from the glass decreases (Figure 1). The rate of glass dissolution can continue at this reduced rate indefinitely, or, under some conditions, the precipitation of certain minerals, for example zeolites, can drive an increase in the glass dissolution rate (Fournier et al., 2017; Neeway et al., 2020).

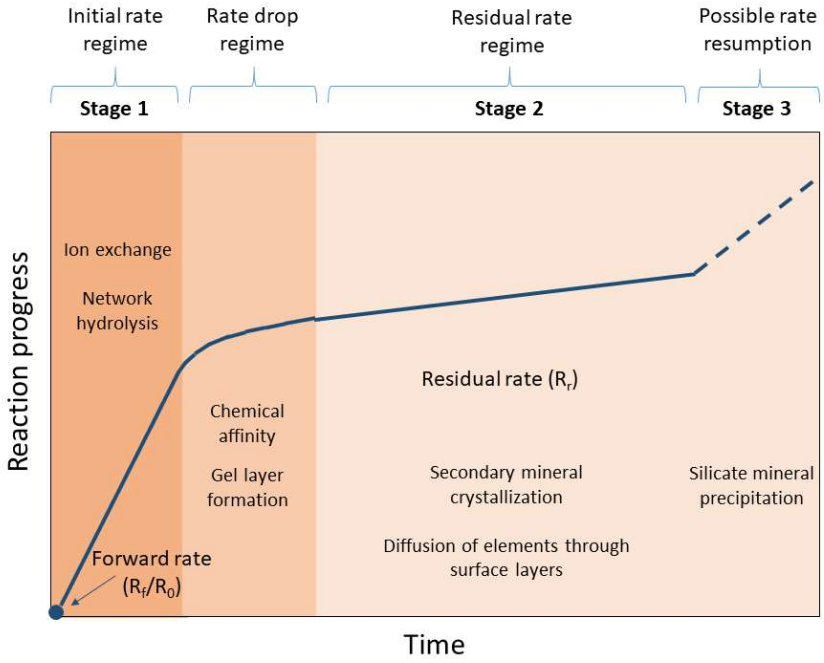

Figure 1: currently accepted mechanism for glass corrosion.

Although the glass corrosion mechanism is well established, the rates and timescales remain unpredictable, as the progress of glass degradation is dependent on a number of factors including pH, temperature, glass composition and solution chemistry. Rates of glass corrosion increase with increasing temperature and at the extremes of pH where both acidic and alkaline conditions promote hydrolysis of the silicate network. The initial durability of the glass is highly dependent on its chemistry with more polymerised networks, those with more 'bridging' oxygens, showing the greatest durability. Additionally, both the solution chemistry and glass chemistry can greatly influence the composition of the gel layer formation and secondary mineral precipitates.

To date, most estimates of glass corrosion rates have been derived from accelerated laboratory tests. In order to achieve measurable results over a short time period, laboratory tests are accelerated by increasing the glass surface area and raising the temperature, often to ≥ 90°C. In

addition, processes that occur only in complex natural environments and are not observable in simplified, sterile laboratory tests may influence corrosion. These include, the direct and indirect effect of microbial metabolism, the effect of changing or fluctuating geochemistry and variable saturation which are, as yet, poorly understood.

Natural and Archaeological Analogues

One way to validate the results obtained from static laboratory testing is by comparison with natural and ancient glasses that have been exposed to a known environment for a known period of time. These samples have come to be termed 'natural analogues' meaning their behaviour provides an analogue for that of modern nuclear waste glasses that have only been manufactured in the last 50 years.

Natural glasses include igneous glasses of basaltic (rich in Fe and Mg) and rhyolitic (rich in Si) compositions, fulgurites (petrified lightning strikes), glass observed in meteorites and impact glasses (Figure 2).

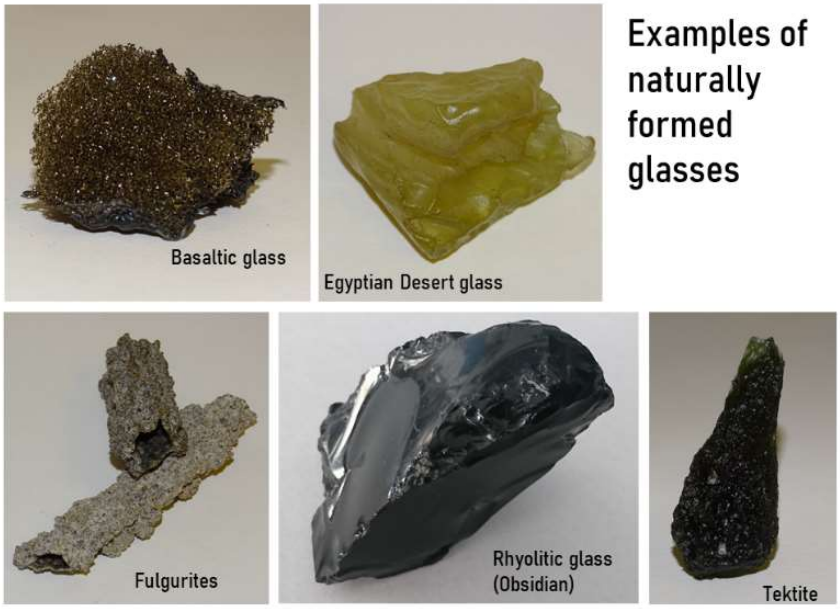

Figure 2. Examples of naturally formed silicate glasses. Samples were photographed from the Manchester Museum Collection.

Ancient glass samples include those found at Roman and Medieval burial sites, the walls of vitrified Hill Forts, and those retrieved from shipwrecks where the date that they began to contact water or soil can be well constrained (Figure 3). These sources provide a surprising range of glass

compositions from soda-lime and lead silicates used to make bottles and decorative artefacts to metal rich vitreous slags produced as a by-product from copper smelting.

Figure 3: example of man-made (unnatural glasses) that have been exposed to aqueous environments.

The major limitation when comparing the dissolution of natural or ancient glasses with that of nuclear waste glasses lies in compositional differences and, notably, the absence of boron. Boron oxide (B_2O_3) is included in most nuclear waste glass composition at 5-25 weight % where it substitutes into the silicate network and improves chemical durability. As borosilicate glass was only commercially manufactured from the early 1900s, and nuclear waste compositions only from the 1970s, there are no older samples available to study. Therefore, purposeful long-term burial experiments have been established under a variety of conditions relevant to geological waste disposal (granite, salt, limestone and clay lithologies) (Wicks, 2001; Jantzen et al., 2008; Van Iseghem et al., 2001; Bacon et al., 2018). Sometimes referred to as 'field tests', these studies aim to bridge the gap between precise, short term, laboratory studies and observations from natural analogue studies where differences in glass composition and exact environmental conditions can lead to uncertainty.

UK examples of field and natural analogue studies ongoing at the University of Sheffield

The University of Sheffield, Immobilization Science Laboratory specialises in developing new Thermal Treatment solutions for radioactive wastes and in assessing the long-term durability of both new and existing vitreous waste forms. A number of natural analogue studies are underway to compliment laboratory based dissolution testing and probe glass corrosion in complex natural environments.

Ballidon Long-Duration Experiment

The Ballidon Quarry, Derbyshire, UK, hosts one of the longest running glass burial experiments in the world. Now in its 50th year, this site was originally established to test the degradation of archaeological glasses under alkaline conditions compared to a sister experiment in acidic soil (Fletcher, 1972). Later, simulant (non-radioactive) nuclear waste glasses were added to the experiment, along with climate monitoring equipment to ensure conditions at Ballidon are well constrained ahead of removal of the next set of samples in 2022.

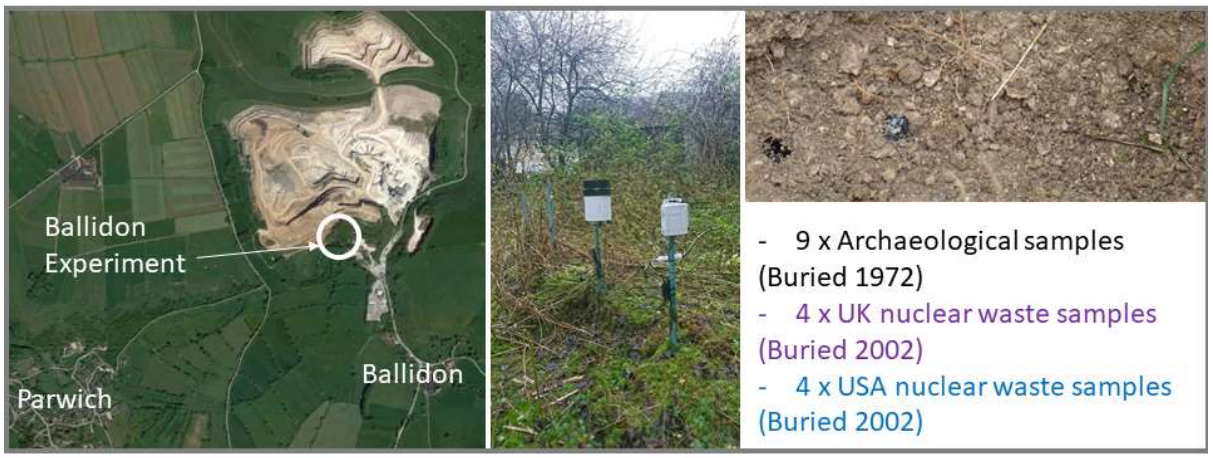

Figure 4: *Left*, location of the Ballidon Long Burial Experiment, *middle*, weather monitoring equipment on top of the burial site, *right*, summary of glass to be unearthed in 2022

Peak Dale Cave

Peak Dale, Derbyshire, UK, a man-made tunnel beneath a lime workings provides a stable environment with hyper alkaline, Ca-rich, water chemistry analogous to cement-leachates expected to evolve over time within a geological disposal facility where a cementitious engineered barrier is used. In addition to analysing glass samples found in the cave estimated at > 70 years old (the date the tunnel was closed) (Mann et al., 2016; Tjin et al., 2018), researchers at the University of Sheffield

have established a new field test including nuclear waste glass compositions from the UK and USA set to run for 30 years (Figure 5).

Figure 5: *Left,* location of Peak Dale, *Middle,* images of the cave and calcium rich precipitates, *right*, sample rig emplaced in 2020 containing eight UK and US glass samples of interest.

Albion Shipwreck Glasses

Analysis of a unique set of 265-year-old glass ingots (Figure 6), from a marine environment, gives an opportunity to compare corrosion in a low temperature environment to that in high temperature tests. In addition, these samples show evidence of biological colonisation and an opportunity to assess the effect of minor metal constituents of the glass (e.g. Cu, Co and Mn) added as colorants for their effect as a biocide. This work is underway and funded by the Royal Society of Chemistry Research Fund.

Figure 6: *Left,* location of the shipwreck of the Albion where the glass ingots were found, *middle and right,* images of the ingots coloured blue (Co), clear (Mn) and green (Cu).

Black Bridge slag samples

Archaeological vitreous slag samples found within the town of Hayle, situated in west Cornwall, may provide a close natural analogue to some heterogeneous glasses produced from mixed wastes such as plutonium contaminated materials (Hyatt et al., 2014; Michelin et al., 2015; Figure 7). The Copperhouse foundry, located in Hayle and first founded in 1758, and the Black Bridge, constructed circa 1811 can be used to date Hayle slag samples as ~ 250 years old. As the slag blocks have been fixed in position their exposure environment is known and, depending on location, they have been exposed to saline water, brackish water or rainwater. A study is planned to investigate the corrosion of these materials, and slags from other locations as an analogue for iron rich nuclear waste glasses.

Figure 7: *Left,* location of Hayle, Cornwall, UK, *middle,* a vitreous slag sample, *right,* slag sample held in position for 250 years by inclusion in a bridge across the Hayle estuary.

No single natural analogue, or field test site, can tell us everything we need to know about the long-term behaviour of glass. However, using a combination of many we can increase our understanding of corrosion mechanisms under a wide variety of environments and decrease even further, the margin of uncertainty around elemental release from vitrified radioactive wastes.

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