

Vitrified hillforts as anthropogenic analogues for nuclear waste glasses - project planning and initiation.

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Abstract

Nuclear waste must be deposited in such a manner that it does not cause significant impact on the environment or human health. In some cases, the integrity of the repositories will need to sustain for tens to hundreds of thousands of years. In order to ensure such containment, nuclear waste is frequently converted into a very durable glass. It is fundamentally difficult, however, to assure the validity of such containment based on short-term tests alone. To date, some anthropogenic and natural volcanic glasses have been investigated for this purpose. However, glasses produced by ancient cultures for the purpose of joining rocks in stonewalls have not yet been utilized in spite of the fact that they might offer significant insight into the long-term durability of glasses in natural environments. Therefore, a project is being initiated with the scope of obtaining samples and characterizing their environment, as well as to investigate them using a suite of advanced materials characterization techniques. It will be analysed how the hillfort glasses may have been prepared, and to what extent

they have altered under in-situ conditions. The ultimate goals are to obtain a better understanding of the alteration behaviour of nuclear waste glasses and its compositional dependence, and thus to improve and validate models for nuclear waste glass corrosion. The paper deals with project planning and initiation, and also presents some early findings on fusion of amphibolite and on the process for joining the granite stones in the hillfort walls.

Keywords: Nuclear, waste, long-lived, glass, anthropogenic, analogue, ageing, leaching, hillfort, hill-fort, rampart, amphibolite, Broborg.

1 Introduction

Protection of health and habitat implies that the environmental impact of nuclear waste, now as well as in the future, be limited to insignificant or at most tolerable levels. The time scale depends on the longevity of the waste, thus ranging from hundreds to thousands of years for short-lived radioactive waste to tens and hundreds of thousand years for long-lived waste. In the various programmes internationally on waste disposal, this is to be achieved by a combination of features: waste form together with technical and natural barriers. A key question in this regard is how to appropriately design the immobilization system, including integrated waste form and repository, in order to achieve assurance regarding the intended long-term behaviour. Any such proof will have to rely heavily on natural and anthropogenic analogues.[1]

In concordance, a number of countries are stabilising their long-lived waste in a glass matrix, utilizing natural and anthropogenic glasses as analogues to prove the long-term durability. Until now, these man-made analogues have included glass in household objects, raw glass ingots, and stained glass windows, but not glass in ancient hillforts where the glass holds pieces of rock together (see below). However, hillfort glasses may offer supplementary or even more similar compositions or other characteristics as compared to glasses utilised as analogues previously.[2] A compositional comparison among different glasses is shown in Figure 1.[3-9]

2 Objectives and scope

The prospect of utilisation of a further category of anthropogenic analogues has prompted the United States Department of Energy (US DOE), through its Office of River Protection (ORP), to initiate a project with the purpose to evaluate such possibilities and to apply the results in performance analyses and environmental impact statements in conjunction with disposal of long-lived radioactive waste.

By necessity, the project will utilize archaeological samples from ancient hillfort sites. Consequently, it has been found pertinent by the US DOE to also include in the objectives to support the understanding of the origin of the samples and their historical context. For instance, there has been a century long debate among historians and archaeologists as to whether the melting of the glass to hold the hillfort rock together was accidental or intentional, and in the latter case whether it was for constructive or destructive purposes.[2,6,10-11]

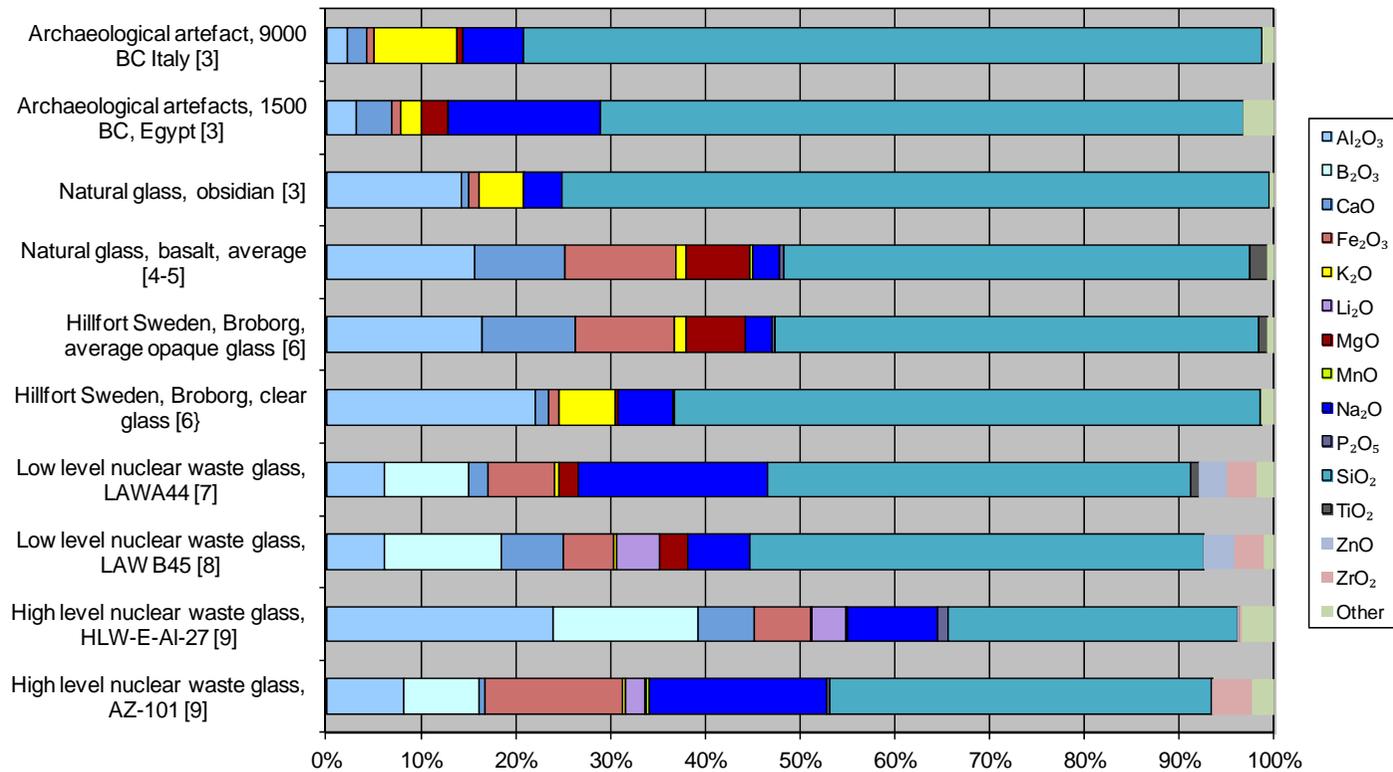


Figure 1: Examples of chemical compositions of glasses figured as oxides. "Other" is uncertain since some of the iron may be in the form of Fe-II, and since all analyses do not include all elements that may be present.

The purpose of the present paper is to present the initiation of the project, including the planning and the first results from sample preparation, information searches and laboratory work.

3 Background

3.1 Nuclear waste and nuclear waste glass

Long-lived radionuclides may be generated by fission as well as neutron activation. Activation of uranium and plutonium in nuclear fuel leads to the creation of transuranic elements which in many cases are long-lived. Operational waste at a nuclear power plant is usually short-lived, especially when there is no fuel damage. However, waste from reprocessing of nuclear fuel as well as legacy waste from research and defence is typically long-lived.

It is only long-lived waste that is considered for vitrification. Typically, glass forming chemicals or a pre-fabricated frit is added to the waste to produce a slurry or melter feed. The melter feed is then transferred to the vitrification process, with or without prior evaporation and calcination, and is converted to a stable glass product or waste form.

The chemistry of the waste stream might be complex, especially in view of the fact that a wide range of elements are formed during the fission of uranium and plutonium. Glass is often the preferred option for the stabilisation of such fission products since suitable compositions of glass can incorporate most of the elements in an efficient manner.

Such efficiency as well as the long-term stability in various environments have been studied for decades, and much of the work carried out until the year 1992 has been summarised in [12]. A recent summary can be found in [13]. It has been found [14-15], see also [2], that there may be at least two main mechanisms that control glass corrosion and thus long-term stability, namely alkali extraction and (congruent) matrix dissolution where the former is favoured by low pH-values and the latter by high. There are also differences between the corrosion of high and low silica glasses.[16]

3.2 Hillforts with vitrified walls

A hillfort is a fortification made of earth and stone, and usually also wood, see Figure 2 for the example of Broborg in Sweden. They date from around 1000 BC to 1400 AD.[18] It has been assessed [18] that there are up to 30000 hillforts in Europe. The number of forts with artificially vitrified walls has been estimated to be approximately 200, about half of them in Scotland, and 17 in Sweden.[19]

Written contemporary records on hillfort utilisation are scarce, but the sources do tell about sieges and sackings.[11] They also unveil frequent engagements away from hillforts, thus indicating that the forts might actually have been much of a refuge of last resort.[11]

Consequently, any understanding of how the vitrification process was performed will have to be based on the artefacts excavated together with various

investigations. Thus, archaeologists have lit huge fires to simulate how people might have made the glass, but with little result in terms of vitrification. This has been criticised in view of the contemporary high level of knowledge regarding iron beneficiation and ability to achieve high temperatures by burning charcoal and utilising forced draft.[10] Quality of heat analyses and calculations in [2] regarding wood and charcoal provide further strong support to the conclusions in [10].

4 Project planning

4.1 The present situation

It is apparent from the previous sections that the objective of utilising ancient glasses as anthropogenic analogues to nuclear waste glasses requires resources from different areas. This refers to the planning of the work as well as its execution.

Consequently, the US DOE through its Office of River Protection has made arrangement for international collaboration in a team of researchers with the following affiliations: US DOE ORP; Pacific Northwest National Laboratory (PNNL); Washington State University (Department of Chemistry; School of Mechanical and Materials Engineering); Environmental Molecular Sciences



Figure 2: Photograph from the Broborg hillfort outside Uppsala in Sweden showing the rampart consisting of stones joined by vitrified rock.

Laboratory (EMSL), US DOE Office of Biological and Environmental Research; Museum Conservation Institute (part of the Smithsonian Institution); The Archaeologists, Geoarchaeological Laboratory, National Historical Museums (SHMM); Luleå University of Technology / Tekedo AB. Most of the organisations mentioned are based in the United States, but the two latter are in Sweden.

One early DOE ORP programmatic objective has been to get access to authentic sample material (previously excavated), and this has already been achieved through the kind support from Peter Kresten [6,10,19] (hillfort samples) and the Geoarchaeological Laboratory (Bloomery furnace samples). Work is in progress at the Archaeologists for the planning of an excavation at Broborg, see Figure 2, with the purpose of obtaining truly pristine samples.

Work is also in progress at the laboratories in the United States to characterize the authentic (previously excavated) samples thus received, and all participants contribute by searching for and evaluating information. Some examples are provided in section 5.

4.2 Some research questions

Appropriate planning of the work relies heavily on the identification of relevant research questions. Of course, the main question is how to best support comparison between glasses in analogues and waste glasses, including how modelling might be as realistic as possible, and how the results might be validated.

As already mentioned, information on the genesis of the hillfort samples is valuable for the understanding of the heritage in Sweden and other countries that have hillforts. But the genesis is probably also important for the analogue perspective, and perhaps even for the compositional and other optimisation of the waste glass manufacturing process.

The geochemical environment is another important aspect with respect to long-term durability. The surfaces of the hillfort glasses have been exposed to local soil pore water conditions for millennia, and in the case of Broborg for around 1600 years. Moreover, these conditions may have varied due to land rise and climate changes. Also, the local chemistry is different at a hillfort as compared to that of a site for disposal of nuclear waste.

Related to this question is the one on alterations of the glass surfaces during and after sampling (see section 5.1). This question is related to that of the mechanisms of alteration of the surfaces on corrosion.

4.3 Testing programme

The following testing programme is being contemplated at present. Please note that commitments to certain activities are made from time to time. Sample preparation is in full progress, see section 5.1.

Data collected from the bulk analyses will be used to develop a deeper understanding of the chemical composition of the glasses, and the surface analyses may provide insight into the chemistry of the alteration layers. Bulk

techniques currently underway or under consideration for use are X-ray Tomography (see details below), μ -X-Ray Fluorescence (elemental composition of the glass), μ -X-Ray Diffraction (to identify glass vs. crystalline phases), magnetic measurements, and a variety of thermal analyses (to determine water content of the glasses and their alteration phases). X-ray tomography has already been employed in the study of a number of the Broborg samples as it is a non-destructive manner by which to identify preferential sampling sites (Figure 3, see section 5.3). Surface characterization methods may include scanning electron microscopy (SEM) with either energy dispersive spectroscopy (EDS) or wavelength dispersive spectroscopy (WDS). SEM will allow for direct visualization of possible alteration layers, and EDS or WDS can provide information regarding their chemistry.

5 Early results

5.1 Ongoing work on sample handling and preparation

Samples taken from the acquired archaeological artefacts are handled and prepared carefully so as to not bias the results of analysis. For this reason, samples are taken without the aid of water or oil cooling during sectioning, and with a new cutting blade. Introduction of water to the sample during preparation is avoided so that water-soluble alteration products are not removed. Use of oil during the sectioning and polishing is also avoided as it would be difficult to remove from the surface and porous interiors of the sample, and could skew any data collected on the carbon content of the alteration layers or exposed surfaces. A new cutting blade is also employed for this reason. When necessary, the samples are polished using a denatured alcohol that has been shown to evaporate without leaving a residue.

Areas of artefacts to be sampled are chosen based on the amount of the glass present, their location relative to an external alteration environment, their location relative to an internal alteration environment, and whether that section has been sampled for previous studies. In general, three representative samplings are made: (1) from glass exposed to the external environment (i.e. from the surface of the artefact), (2) from glass open to but not directly exposed to an external environment (i.e. from an open pore at the surface of the artefact), and (3) from an internal environment (i.e. from a close pore). Once the samplings are complete, each one is analysed by bulk and surface sensitive techniques.

5.2 Information search on amphibolite and its thermal behaviour

One of the first findings in the present project has been that a synthetic mixture of the constituents (except hydrogen) of the Broborg glass (see Figure 1), requires temperatures exceeding 1400 °C in order to melt. Additionally, since the ancient people probably had no possibility to achieve such a high temperature even with charcoal and forced access of air,[13] some other factors must have been involved.

Earlier, Kresten & Ambrosiani [6] had found that Broborg glass melted differently under oxidizing (air) and inert (nitrogen) conditions. In the former case, melting started at around 1130 °C whilst it started already at 1075 °C in the latter. Moreover, visual inspection of the samples clearly indicates that the melting is associated with a substantial evolution of gas phase. Obviously, the vitrification process is considerably more complex than just melting. This observation has prompted an information search and the results are presented in the following.

Kresten & Ambrosiani [6] had observed that the rock that melted was primarily amphibolite. This is a type of rock that is present only occasionally, and actually had to be collected by the ancient people to serve in the ramparts which were erected using mainly gneissic granite.

Amphibole has been described[20] as the "garbage can" or "waste basket" in mineralogy since its chemical composition shows very wide variations. Amphibolites are often formed from dolerite (British English, diabase in the US) as well as from basalt, and gabbro, which all have similar chemical compositions (see Figure 1 for basalt). It should be observed, however that amphibolites are formed only under certain conditions: typically at pressures around 0,3-1,2 GPa and temperatures around 550-750 °C, see e. g. Figure 3.19 in [4], and in the presence of water at lithostatic pressure. Amphibolites that reach the surface through orogenic (uplift) processes are thus only thermodynamically metastable. At a few hundred °C, ion mobility starts to become significant [21], and consequently also various reactions may take place such as oxidation, dehydroxylation and incongruent recrystallisation.

Most of the work on amphibolites has been carried out at high pressures and moderately high temperatures, and are thus not of primary concern for the present work. However, Ghose [21], and references therein, describe a case when crocidolite, $\text{Na}_2\text{Fe}_2^{3+}\text{Fe}_{2,6}^{2+}\text{Mg}_{0,4}\text{Si}_8\text{O}_{22}(\text{OH})_2$, was heated in nitrogen or argon, and in oxygen or air, respectively. For inert atmosphere, dehydroxylation took place at around 500-700 °C, and at about 800 °C, the anhydride decomposed endothermally into acmite, cristobalite, spinel and a liquid. By contrast, in an oxidizing atmosphere, hydrogen ions and electrons were lost already at 300-450 °C to yield oxyamphibole with the formula $\text{Na}_2\text{Fe}_4^{3+}\text{Fe}_{0,6}^{2+}\text{Mg}_{0,4}\text{Si}_8\text{O}_{22}(\text{OH})_2$. This compound decomposed at 600-950 °C to yield acmite, hematite, cristobalite and spinel.

It should be noted that the chemical composition of crocidolite deviates substantially from that of Broborg glass in Figure 1. Nonetheless, the example shows that differences in behaviour are to be expected depending on the atmosphere, and that much information can be obtained by thermal analysis and related techniques. Incidentally, formation of spinel on heating of Broborg amphibolite was confirmed in [6].

Nonetheless, it appears that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio [22] as well as the content of water [23-24] (or hydroxide) may have a profound effect in that they lower the viscosity of a glass melt.

5.3 Imaging

A lot of observations can be made using the naked eye or an inexpensive optical microscope. A drawback in this regard is that only a part of the rock surface will be in focus, wherefore photographs may not be very illuminating in an article. Nonetheless, such observations have been made, and the results are as follows.

Unheated Broborg amphibolite surface has a microcrystalline structure with typical sizes of the crystallites around 0,01 mm. The structures are slightly layered. Heated or (partially) melted amphibolite has less of a crystalline surface

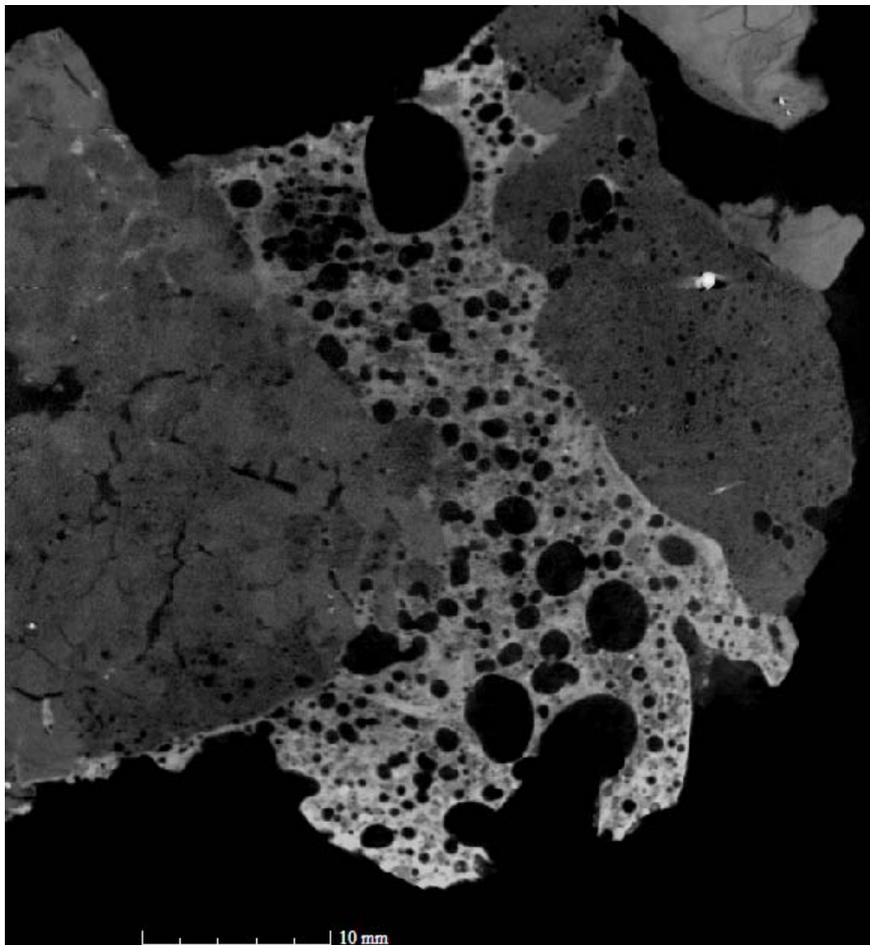


Figure 3: X-ray tomography image of a piece of the Broborg vitrified fort (see Figure 2). Following the tradition in x-ray imaging, light colour refers to high density, and dark colour to low. Details on how the image was obtained can be found in the appendix.

structure. Moreover, layers may have separated to form pores and fissures, and there is also evidence of expansion of the partially melted material.

The best visual illustration of the structure of the rock being held together by a glass in a vitrified fort may well be what might be obtained using x-ray tomography, and such an image is presented in Figure 3. See the appendix for details. The image shows a bubble-filled phase with glass density higher than the surrounding rock (brighter contrast) affixing two pieces of a different rock type which appear also to have seen high temperatures due to some dark areas suggesting phase separation as well as outgassing. It is believed the bubble-filled phase is due to the amphibolite and the rocks being held together are a gneissic granite. Work is in progress to confirm these assertions.

6 Discussion and conclusions with regard to the early results

It is obvious from the results of the information search, as well as of the tests on melting of synthetic material, that the melting of amphibolite at Broborg is a quite complex process which probably is dependent on the redox conditions as well as the water content in the furnace atmosphere.

Depending on the details of the process used, the atmosphere in a charcoal fire may be reducing or oxidizing. If reducing, it may or may not contain water. In the case of a moist reducing atmosphere, water may react with charcoal such that hydrogen is being formed. Water may have the capability to oxidize iron to at least Fe_3O_4 , but hydrogen might reduce it all the way to elementary iron. The information search indicates that reduction of iron and presence of water may facilitate the liquefaction.

Thus, the quality of heat analysis in [2] is probably very relevant for the process of joining the stones, but does not constitute a full explanation. Details on the redox and water vapour conditions are also likely to be highly important.

Obviously, gas is released from amphibolite when it is in a partially molten condition. This, as well as the imaging, confirms the following description by Kresten and Ambrosiani [6]: *"The gas-charged melt penetrated the space between the gneiss boulders, invaded all open fractures in the fire-cracked rock, and served as a flux to initiate melting of the gneiss, thus firmly cementing the whole vitrified mass."*

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Appendix. The x-ray tomography image.

X-ray computed tomography was used to visualize the internal microstructure of the glass. The specimen was scanned with an X-Tek/Metris XTH 320/225 kV high-resolution microfocus tomography (XCT) scanner (Nikon Metrology, Brighton, MI) at 95 kV and 170 μA x-ray power for optimum image quality and contrast. The samples were rotated continuously during the scans with momentary stops to collect each projection (shuttling mode) to minimize ring artefacts. 3142 projections were collected over 360 degrees with 708 millisecond exposure time and 4 frame per projection. Image voxel size was 65 micrometers. The images were reconstructed to get a three-dimensional dataset using CT Pro 3D (Metris XT 2.2, Nikon Metrology). The representative 3D rendering was created using the visualization program VG Studio Max 2.1 (Volume Graphics GmbH, Germany).

The research was performed using EMSL, a DOE Office of Science User Facility sponsored by the Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory under proposal number 49141. The image was provided by Dr. Tamas Varga and Adriana Lynell McKinney (Pacific Northwest National Laboratory).

The image is included as Figure 3 in the report.