Glasses: archaeological and historical

Description: Archaeological and historical glasses have been studied many times to elucidate dissolution/degradation mechanisms and alteration rates as analogues of borosilicate glassform in a similar way as various types of natural glasses (see glasses: natural).

Glass has been produced for approximately 3,500 years, firstly in Egypt and the Iraq areas. Glass was luxury material and was often used as a substitute for precious stones. Glass has become inexpensive since the discovery of glassblowing (approximately 50 - 0 B.C.) and many glassworks appeared throughout of Europe and Mediterranean area. A soda-lime glass was produced until around 1000 A.D. when potassium-lime glass started to be produced in Northern and Western Europe (Kaplan, 1980).

The first comprehensive study of alteration of archaeological glasses was performed by Kaplan (1979). Four ancient materials were assessed: Egyptian blue, enamels, faience, and glazes. Unfortunately, Egyptian blue and Egyptian faience have quite different chemical compositions in comparison with radioactive waste glass. Enamels are predominantly Pb glasses and their durability is low. Glazes (particularly Chinese) were evaluated as durable, but they are covered by coatings (Kaplan, 1980). Five decomposition processes were identified in archaeological glasses (Kaplan, 1979; Kaplan, 1980) that are rather descriptive coming from archaeological language:

- weeping - the sweating of droplets of water when excavating glasses come into contact with moisture in the air,
- crizzling - the formation of networks of tiny cracks all over an object's surface,
- pitting - formation of pit-like scars by abrasive action or chemical dissolution leaving holes filled with weathering products,
- layering - development of a filmy iridescent surface formed of multiply layers of mica-like minerals,
- crusting - development of powdery, amorphous and opaque residues by the leaching of species out of the glass in a way that alters the object's structural stability.

Macquet and Thomassin (1992) studied archaeological glasses (from 10th century), which have been collected in the same archaeological site (Saint-Denis, northwest of Paris), they have thus been exposed to the same environmental conditions (soil, climate), and they have been altered over the same length of time. The glass items were collected and stored under identical conditions, particularly with regards to humidity, luminosity and soil structure. The various characterisation methods revealed that these samples, which had very different compositions, show very different alteration patterns, both macroscopically and microscopically. The thickness of altered layer is around 10-30 µm.

Like similar complementary and interlinked experiments and analyses on natural and artificial glasses, the development of altered layers were also studied on archaeological glasses after burial along with laboratory experiments on glasses with identical composition or on the same archaeological glasses with removed altered layers. Cooper and Cox (1994) assessed 31 glass samples from 5 sites from Great Britain originating from 3 terrestrial (soil conditions) and 2 marine sites. The samples were from 230 to 1,700 years old. Corrosion rates could not been measured because original sample thickness were not known. However, the glasses were either from windows or vessels and are likely to have been less than 5 mm thick. A lower limit for the corrosion rate was estimated from the crust thickness - an approximate upper limit was given by: [(5 mm - thickness of pristine glass) / 2 (burial time)].

The alteration rates were estimated to be in the range 1,400 - 3,400 µm/1000 y, although the actual rate was probably at the lower end of this range. All analysed corrosion crusts were multi-layered, porous silica containing secondary precipitates. The density of the silica gel was about 28% of the original glass (originally contained around 46 wt. %). Accompanying laboratory experiments using flow-through leach test are presented in Cooper and Cox (1994). It was found that corrosion in infinitely dilute water is slower than the corrosion in damp soil, which can be explained by environmental factors.

Roemich et al. (2003) also compared alteration progress of 3 archaeological glasses (at different degradation stages - local corrosion along cracks, fragments with local plugs and severely damaged) with laboratory leaching experiments on model glasses simulating condition in soil.

Manichev et al. (2004) studied colourless, blue and greenish glass items from Olbiya ancient city (current Parutino, Ukraine) that were dated to the first century B.C. The size of pieces varied in the range of 1 - 6 cm; 3 samples were studied in detail. Altered layers were depleted by Na, Ca and partially Si and relatively enriched by Al. These layers were characterized by pronounced lamellar and lamellar-porous structure. The thickness of the alteration layer is in the range from several tens to hundreds µm. Surface part of alteration layers contains various crystalline phases detected by X-ray diffractography (hydromica, smectite, Ca-bearing zeolite). Organic matter was also detected in surface layers which role is not clear.

A special category of material represents uranium glass that was has been produced in the second half of 19th century. Famous kinds of yellow and green colours were produced in Bohemia. It is estimated that throughout the 19th century more than 15,000 t of uranium glass was produced that served for manufacturing of various items (vases, tumblers, ashtrays, etc.). The uranium glass is characteristic by fluorescence in UV spectra due to the presence of $(UO_2)^{2+}$. The content of uranium is in the range of tenths up to 5 wt.%. The samples excavated from the landfill of the former glasswork were studied by Laciok et al. (2004). Thicker alteration zones (100 - 500 µm) were identified as being depleted in K and Na (partially also by U) with relative enrichment in silica (Figure 1). The estimated apparent alteration rate is 1,250 - 6,250 µm/1000 y. PIXE and RBS measurements indicate approximately 10 fold enrichment of U in superficial altered layers (0.5 – 2.3 µm) in comparison with the glass matrix.

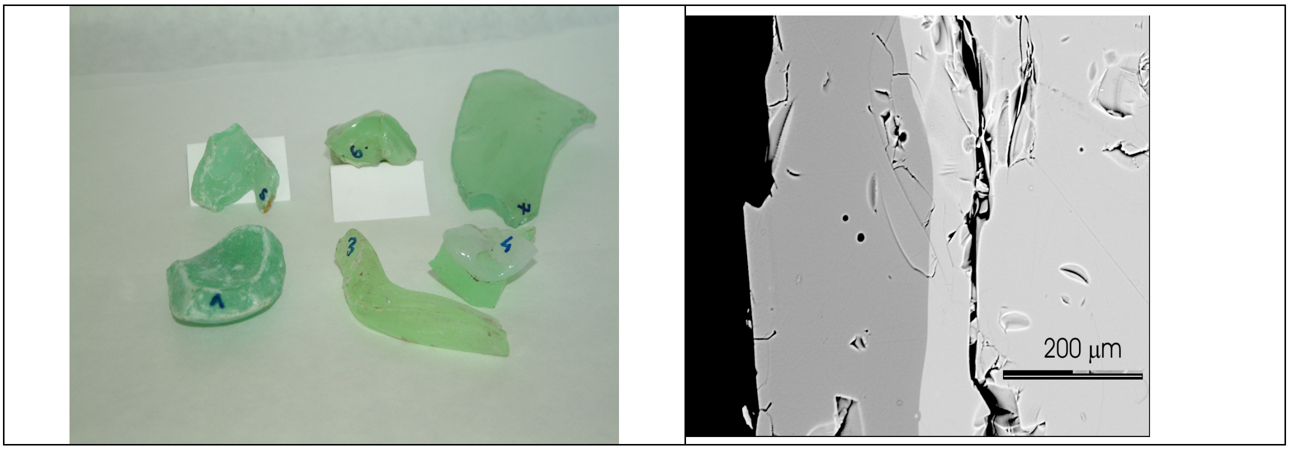

Figure 1: Samples of uranium glass from the Czech Republic and cross-section of altered layer

Many studies on the stability of ancient glasses have been undertaken by archaeologists without any mention of their use as natural analogues to radioactive waste glass - such documents and reports can be checked for their relevance and interpreted for the specific conditions of disposal of radioactive waste.

Relevance: Glass is a most frequent waste form used for high-level waste (used universally for the solidification of liquid HLW from reprocessing of spent nuclear fuel) and is also sometimes proposed for solidification of low-level and mixed waste. Mainly borosilicate glass is utilised. Reliable information on degradation of glass (rate, mechanisms) is therefore highly desirable for performance assessment support.

Position(s) in the matrix tables: (Near-field) Concerning waste form (glass) and demonstration of many near-field processes: barrier containment (physical and chemical integrity), RN release (dissolution and leaching), RN movement (diffusion) and RN retardation (precipitation of priority elements in surface layers).

Limitations: Differences in the geochemical conditions of deposition of items are usual - more severe conditions represent near-surface environment in comparison with deep disposal conditions concerning water circulation, oxygenated conditions, occurrence of organic complexants and microorganisms, etc. A critical factor for such studies is the storage conditions of individual items – and the use of museum samples for such purposes can be questionable. Archaeological glasses have relatively low ages (max. 3,500 years old, but generally much less) compared with long-term degradation processes of radioactive waste glassforms. Radiation effects have not been studied to date.

Quantitative information: Apparent alteration rates of glass materials were derived, but such numbers includes relatively great uncertainties.

Uncertainties: Derived data on alteration rates and mechanisms are generally higher compared with results from naturally corroded basaltic samples reflecting different chemical composition (mainly soda-lime and potash-lime glasses) and differences in geochemical conditions of deposition of archaeological items. Applicability of alteration rates to performance assessment is lower (lower confidence, higher uncertainties) comparing with the data resulted from studies on natural glasses.

Time-scale: Generally, archaeological samples are some hundreds of years old and historical samples only some tens of years old.

PA/safety case applications: Analogues of archaeological and historical glasses provide mainly qualitative information concerning reliable alteration rates of nuclear waste glass for the purpose of performance assessment. No direct use of such data in performance assessment is known.

Communication applications: Archaeological glasses are mentioned when it is needed to demonstrate relative durability of glass waste forms.

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Added value comments: The long-term radiation effects have not been studied so far on anthropogenic glasses. There are probably only 2 possibilities for realization of such studies: uranium glasses produced in Central Europe, and the shock glasses resulting as a consequence of nuclear detonations that can contain both fission products and actinides (re-melted basic rocks would be preferred).

Potential follow-up work: Uranium glass degradation and corrosion processes are studied in the Czech Republic (financed by RAWRA). Unfortunately, the effects of ionizing radiation have not been covered - this subject is proposed to be covered in a new project in the Czech Republic.

Keywords: glass, dissolution, waste form

Reviewers and dates: Ales Laciok, NRI (August, 2004), John Dalton (January 2005)