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Characterization of Glass-Like Fragments from the 3714 Building

EC Buck

February 2010

Pacific Northwest
NATIONAL LABORATORY

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Abstract

This report describes characterization of a sample obtained from the 3714 building in the 300 Area. Characterization of this unknown material was required for the demolition activities in the 300 Area. The object of the study was to determine the nature of the material, composition, possible structure, and evidence for any hazards components. The material consisted of pebble-sized translucent green fragments. The green material was determined to be sodium alumino-silicate glass from scanning electron microscopy (SEM) combined with x-ray energy dispersive spectroscopy (EDS). Images of the fragments that exhibited sharp edges suggested a glass-like structure. Raman analysis was attempted but did not yield useful data. Further analysis with infrared did not indicate the presence of any organics.

Acronyms and Abbreviations

EDS	x-ray energy dispersive spectroscopy
keV	kilo-electron volt
PNNL	Pacific Northwest National Laboratory
SEM	scanning electron microscopy
TEM	transmission electron microscopy
wt%	weight percent
μm	micrometer
XRD	X-ray diffraction

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Introduction

This report describes characterization of a sample obtained from the 3714 building in the 300 Area.[(a)] Characterization of this unknown material was required for the demolition activities in the 300 Area. The object of the study was to determine the nature of the material, composition, possible structure, and evidence for hazards components.

Electron microscopy is a versatile technique for investigating the nature of materials with a combination of imaging and compositional analysis at high resolution (Bertsch, et al., 1994, Buck and Bates 1999, Utsunomiya et al., 2002). The scanning electron microscopy (SEM) investigation used low voltage imaging that highlights the surface of the particles and reduced the effects of charging. X-ray energy dispersive spectroscopy (EDS) which was used for compositional analysis has a spatial resolution of about $1\mu m^3$ and is unable to detect any elements lighter than carbon. In general, elements below 1 wt% in any analyzed region cannot be detected. All the electron-beam and x-ray techniques described herein are unable to confirm the presence of organic phases. The presence of organics in the 3714 waste material would be important to know. Raman spectroscopy and infrared spectroscopy were used to investigate the occurrence of any organic material.

([a]) Hanford's 300 Area is a Manhattan Project and Cold War era legacy on the south end of the Hanford Site that is comprised of aging facilities, mostly built in the 1950s.

Figure 1.1 Photograph of as-received material in a can in Building 3714.

1.0 Experimental Procedure

The micro-characterization work was performed in full compliance with PNNL Integrated Safety Management System requirements. The PNNL ISMS was approved by DOE in 1998. Technical or operating procedure (RPL-EMO-1) utilized by this project were reviewed and approved by the Radiochemical Processing Laboratory (RPL) Independent Review Committee (IRC) and appropriate laboratory safety organizations. This process outlines the specific hazards and appropriate mitigating and emergency actions to be followed.

1.1 Micro-structural Analysis of Samples

For SEM, a small quantity of the solid material was placed on a sticky carbon tape mounted on an aluminum SEM stub. The SEM sample was examined in a FEI™ Quanta250FEG equipped with a backscattered detector and EDAX™ Genesis x-ray energy dispersive spectrometer (EDS) system in the 325 Building. A conductive carbon coat was not used for sample preparation.

1.2 Magnification Scale

Most of the SEM images were obtained with a 1 keV electron beam to enable the surface to view clearly and to reduce charging effects. As the sample was not a polished flat section, it is unreliable to extract quantitative data from the EDS analyses.

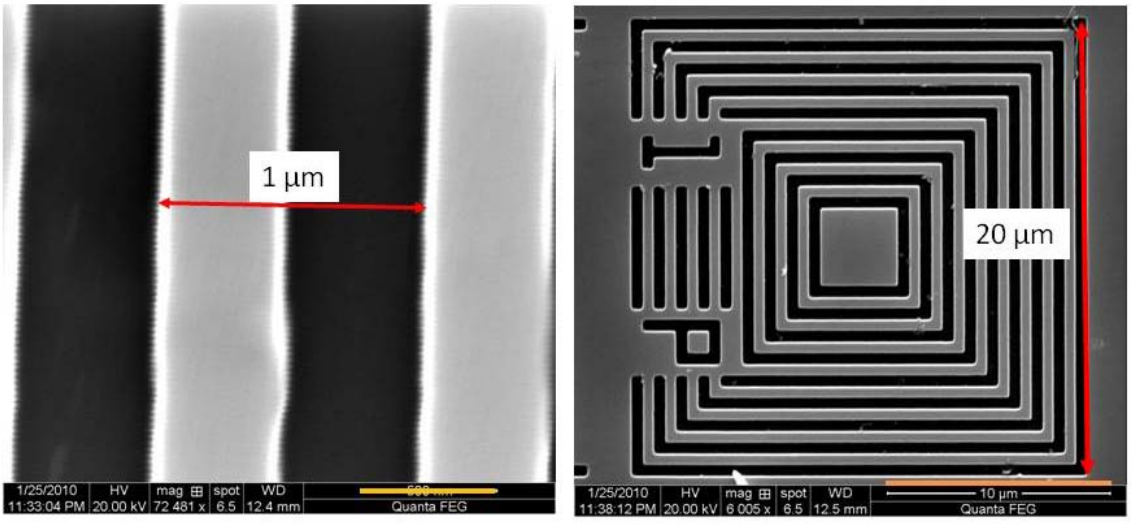

Figure 1.1 SEM images of the Magnification Standard showing calibration checked distances

The SEM magnification scale was calibrated with a National Institute for Science and Technology (NIST) traceable standard. The SEM images of this measurement standard are shown in Figure 2.1. The instrument indicated magnification was within 1% of the expected value. The energy scale was checked by looking at high and low energy x-rays from known materials.

1.3 X-ray energy dispersive spectroscopy

The calibrated scale of the EDS system was checked against known compounds. The energy positions of peaks measured on the EDS system were compared to literature values. The agreement between literature and experimental values was excellent, demonstrating that the system is calibrated correctly for analyzing characteristic x-rays at both low and high energies. The error in the peak energy assignments was estimated to be <1%.

2.0 Results

The solid material exhibited a strong translucent green color. Some fragments were had a much darker green and there was a lot of dust or just general dirt within the collected sample. As the material been left out in the open for an indefinite period this is not surprising. A random sample of 1-2 grams of the material was extracted from the tin can shown in Figure 1.1 and put into a clean plastic vial. Several fragments were removed from the collection vial and were examined with the SEM. Under the naked eye, the material looked liked glass shards and fragments. The edges of the fragments were sharp like fractured glass. In Figure 3.1, a kink-like structure of the glass is visible as horizontal lines across the image. This type of structure was consistent with a glass. The EDS analysis of the fragments indicated that the material was a sodium alumino-silicate (see Figure 3.2). As analyses were repeated through the sample, variations in the composition were observed. Some particles contained iron and copper, and there were variable amounts of sulfur, sodium, potassium, and calcium. The distinctive green color could not be related to any particular element. It is possible that a trace component that was not detectable with EDS caused the coloration.

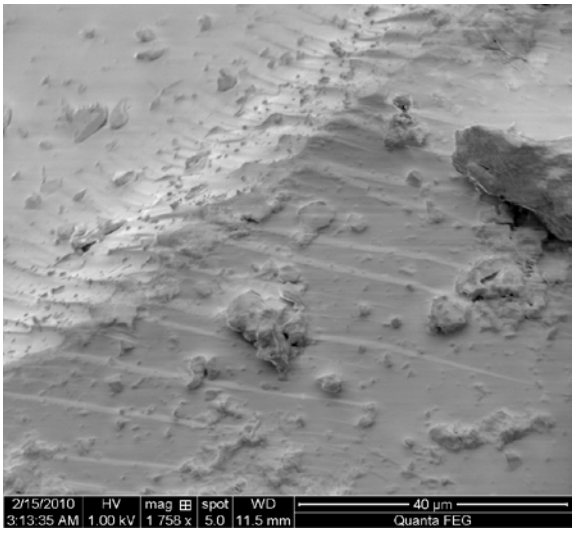

Figure 2.1 Low Voltage Image of Glass Surface.

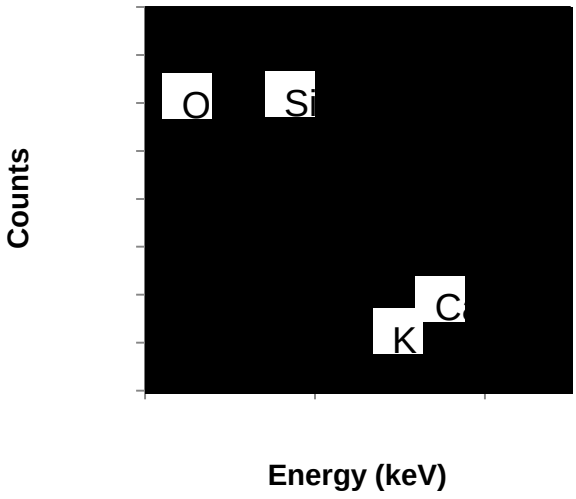

Figure 2.2 X-ray energy dispersive analysis of glass

Additional images showing the structure and the presence of other types of deposits are shown in Figures 3.3 and 3.4.

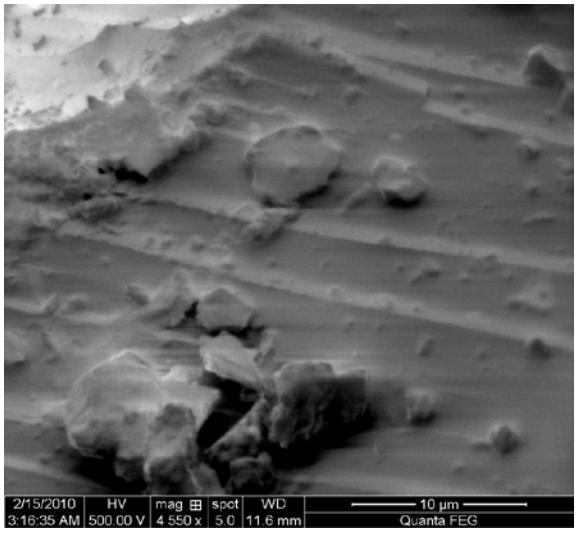

Figure 2.3 Image of Glass Surface.

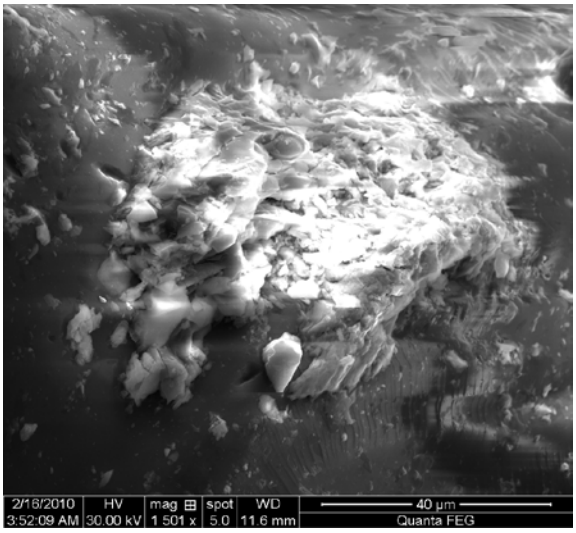

Figure 2.4 Image showing higher average atomic number material (white) on the glass surface

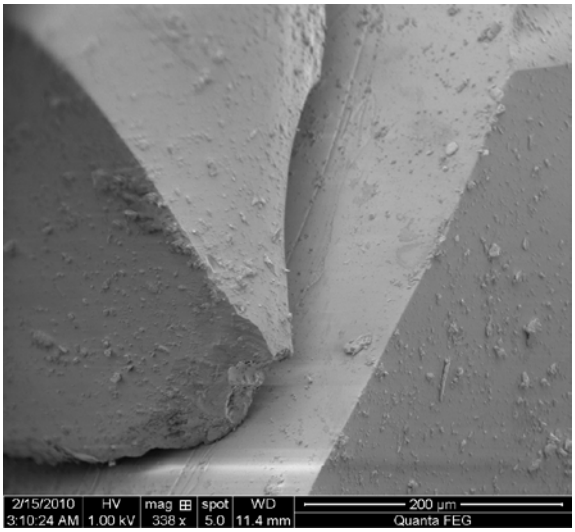

Figure 2.5 The sharp edges and fractured surface exhibited in this image are typical of a glassy material

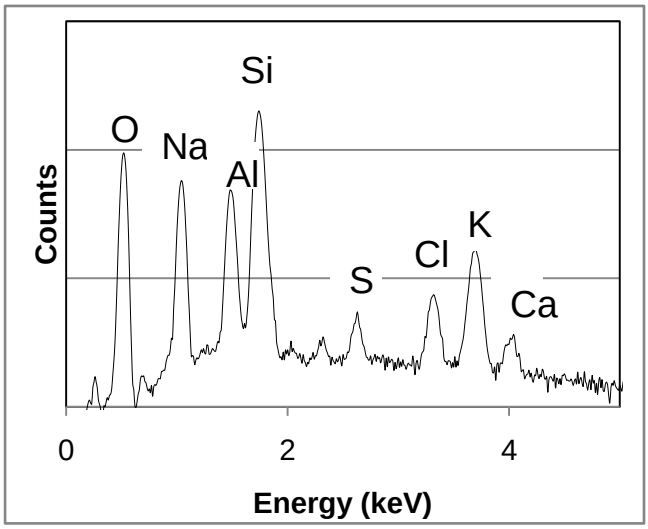

Figure 2.6 EDS analysis (log scale) showing only weak peaks from iron.

With low voltage imaging, the sharp edges in the material can be seen. Figure 3.5 illustrates the nature of the sharp edges in the glass. Using a log-scale, there is little evidence of trace elements in the glass. The peaks visible could be assigned to O, Na, Al, Si, S, Cl, K, Ca and a small

amount of Fe. Additional images showing the nature of the glass are shown in Figures 3.7 and 3.8. Figure 3.8 was obtained with a higher voltage which resulted in some charging. Most EDS analyses were obtained with the high voltage so that all elements of interest could be detected, if present.

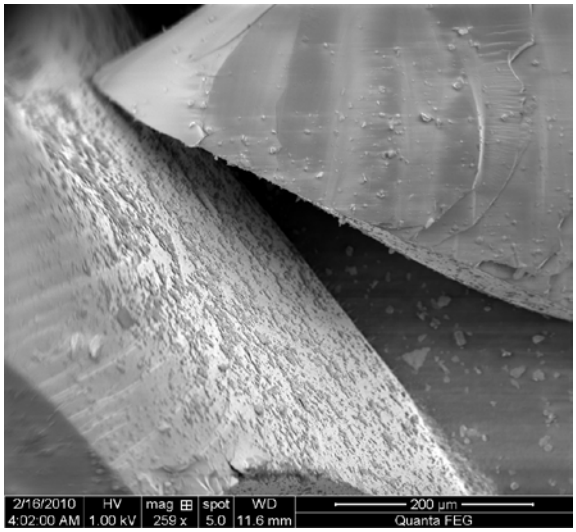

Figure 2.7 Image showing the various types of smooth and rough surfaces in the material

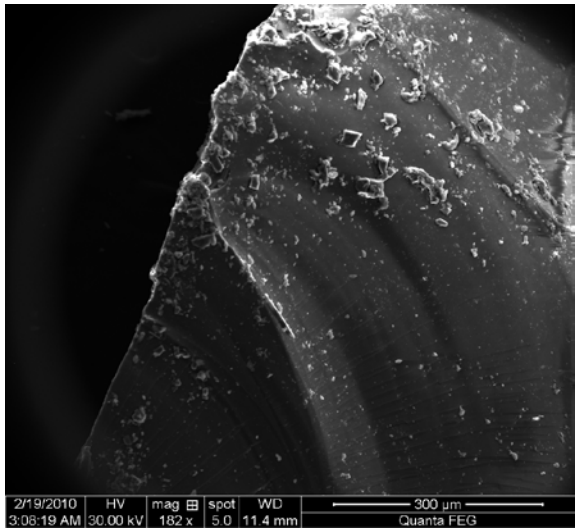

Figure 2.8 High voltage SEM image showing particles on the surface of the glass

2.1 Infrared and Raman Spectroscopy

Raman spectroscopy of the solid was attempted. The sample was strongly fluorescent and this swamped any other signals. Infrared spectroscopic analysis did not reveal any features that would be consistent with organics (see Figure 2.9). The infrared absorption spectra of sodium silicate glasses contain several characteristic features (Julien et al., 1989; El-Egili, 2003), including, a very sharp absorption band at 460–480 $cm^{-1}$and at 775–800 cm^{-1}. There are absorption bands at1050 cm^{-1} and at 1120 cm^{-1}. Another sharp absorption band is observed at 1640 cm^{-1}, and an absorption band with at around 3420–3430 cm^{-1}. The spectrum recorded in this study shows very little structure; however, the broad band at 1200 cm^{-1} may be due to SiO_2 vibrations which can be shifted to higher frequencies with the addition of alkalis.

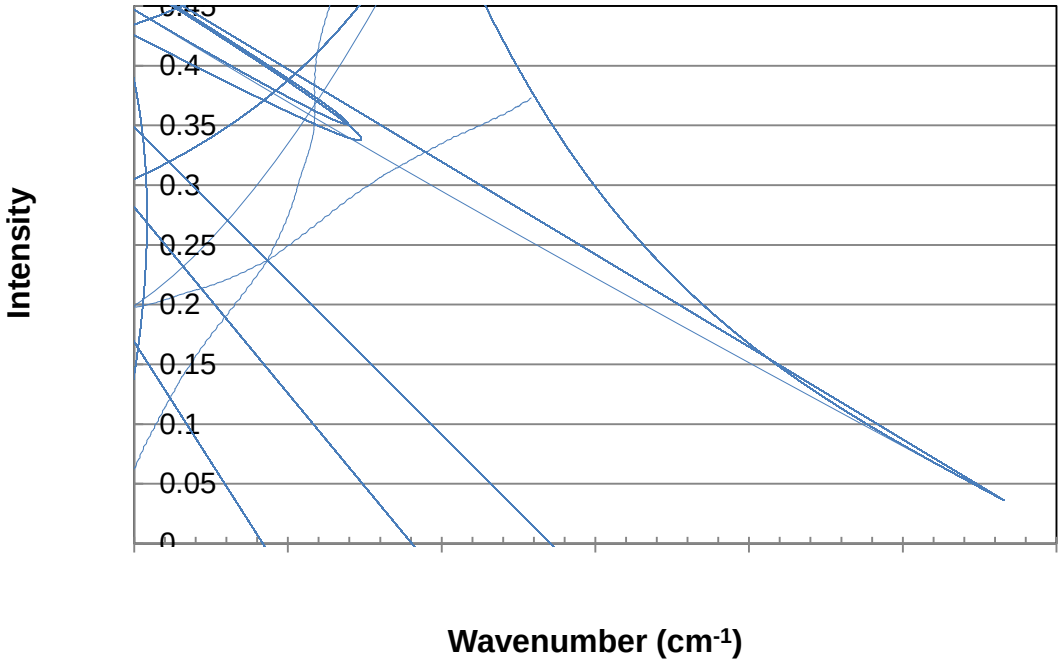

Figure 2.9 Infrared spectrum of the green glass material

3.0 Conclusions

The green material is a sodium alumino-silicate glass. This conclusion is based on the composition provided by SEM-EDS, and the images that suggest a glass-like morphology. No useful information was obtained with Raman as the sample exhibited strong fluorescence and no useful signal could be obtained. Further analysis with infrared also confirmed that organics were not present.

4.0 References

Bertsch, P. M., Hunter, D. B., Sutton, S. R., Bajt, S. and Rivers, M. L. (1994). *Environ. Sci. Technol.* **28**: 980-984.

Buck, E. C. and Bates, J. K. (1999). *Appl. Geochem.* **14**: 635-653.

El-Egili, K. (2003). Physica B325, 340-348.

Julien, C., Massot, M., Balkanski, M., Krol, A., and Nazarewicz, W. (1989). *Mater. Sci. Eng.* **B3**, 307-312.

Utsunomiya, S., Jensen, K. A., Keeler, G. J. and Ewing, R. C. (2002) *Environ. Sci. Technol.* **36**: 4943-4947.

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