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Ancient Glass Studies: Potential Low-Activity Waste Disposal at Hanford

D. M. Strachan

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Prepared for the U.S. Department of Energy
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Summary

When developing a performance assessment model for the long-term disposal of Hanford low-activity waste glass, it is desirable to determine the durability of glass forms over very long periods of time. However, testing is limited to short time spans, so experiments are performed under conditions that accelerate the chemical phenomena being investigated. Verification that models can be used reliably to calculate the behavior of stored waste is needed, so we are looking for a way to apply a performance assessment model to the results from a completely independent experiment. Buried ancient glasses represent a potential independent experiment. Archaeological digs are being investigated at which ancient glass artifacts have been found or are likely to be found. These glass artifacts are manmade, they contain alkali concentrations approaching 20 mass% (similar to Hanford low-activity waste glasses), and they have been buried for times approximating the period of regulatory concern.

In this phase of the Ancient Glass Task, we have identified several potential archaeological sites where glasses have been found and that are currently active. These are still potential sites—we have not yet talked with site archaeologists nor made any arrangements to recover glass artifacts or soils. Following is a partial list of sites that have been identified for further investigation. Most of these sites are located in the Eastern Mediterranean because that is where glass was developed as long ago as 4500 years before present.

Tell Ahmar (Syria). The site has been inhabited from the 5th millennium BC to the present. Its greatest influence was during the Iron Age when the city was captured and occupied by the Assyrians. Since 1988, staff members from the University of Melbourne have been conducting yearly excavations at and in the vicinity of the site.

Tell Brak (Syria). Brak is the largest tell in North Mesopotamia and Syria. It was occupied from at least as early as 6000 BC to the early Iron Age. A "Gateway City," Brak lies on one of the major roads leading from the Tigris Valley north to the metal sources in Anatolia and west to the Euphrates and the Mediterranean.

Caesarea Maritima (Israel). Caesarea Maritima, founded by King Herod between 22 and 10 BC, served as the main port and administrative capital of his kingdom. It served as the headquarters of the Roman administration of Judaea, later to become Palestine. The site converted from paganism to Christianity and then was brought under Muslim rule. It was later conquered by Crusaders and then brought back again under the rule of Islam. Caesarea thus embodies the great transitions that marked the history of the Old World during and just after the first millennium A.D. Glass artifacts have been found here.

Khirbet Cana (Israel). Khirbet Cana appears to be the location of the biblical town of Cana mentioned in John 2:1-11. In 1998, glass was the major focus of archaeologist Alysa Fischer (University of Puget Sound). Soil samples were also obtained. Soil and glass samples were sent to the University of Arizona for analysis.

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1.0 Introduction

Performance assessments for Hanford low-activity waste glass are based for the most part on results from laboratory experiments and models of the behavior of the glass and radionuclides. These experiments are necessarily short-term by comparison to the storage times over which performance must be calculated. Because they are short-term, most experiments are performed under conditions that accelerate the chemical phenomena being investigated, such as the dissolution of the glass or the transport of the radionuclides in the soil. Even lysimeter tests, which are set up to mimic as close as possible the actual storage conditions, are performed under accelerated conditions. Verification that models can be used reliably to calculate the behavior of the stored waste is needed (McGrail, Bacon et al. 2000). One method to verify that a performance assessment model is valid is to apply the model to the results from a completely independent experiment, i.e., one for which the results have not been used in developing the model. To address this need, we are investigating the use of archaeological digs at which ancient glass artifacts have been found or are likely to be found. Although these "experiments" are less constrained than those run in the laboratory or in controlled field tests (Meyer, McGrail et al. 2001), they meet the criterion of independence, and the sites are usually well characterized. The advantage of this approach is that ancient glasses are manmade, are found to contain alkali concentrations approaching 20 mass%, and have been buried for times approximating the period of regulatory concern. What is typically not done during the recovery of these glass artifacts is to recover the soil surrounding the artifact so that the migration of the glass components can be mapped. We propose to address this need in this task.

In this phase of the Ancient Glass Task, we have worked with archaeologists to identify several potential archaeological sites where glasses have been found and are currently active. The latter is particularly important, since we would eventually like to work with the site archaeologist to participate in the recovery of a glass artifact and, more importantly, recover soil samples around the artifact. It should be emphasized that these are potential sites; we have not talked with the site archaeologists nor made any arrangements to recover glass artifacts or soils.

Because the period of regulatory concern is thousands of years, it would be beneficial to find ancient glasses that approach this age. However, the oldest glass artifacts are about 4000 years before present and are extremely rare. Glass artifacts from the Roman times or slightly earlier are more common. These are approximately 3000 years old. Another group of glasses that have high alkali are the medieval window glasses that date from about 1500 years before present. The more ancient glasses are to be found at sites surrounding the Mediterranean, such as Italy, Turkey, Iran, Israel, Egypt, Syria, and Greece. The medieval glasses are to be found in central Europe. We have not investigated potential sites in Asia.

2.0 Potential Sites

What follows are brief descriptions of some potential sites. The text was largely adapted from the web site for each archaeological dig. Some notes have been added that were obtained from archaeologists, in particular those who participated in the Materials Research Society meeting session on Archaeology and Waste Management (Boston 2002).

2.1 Middle Eastern Sites

Figure 2.1. Map of Syria Showing the Location of Potential Archaeological Sites: 1) Tell Ahmar and 2) Tell Brak.

Tell Ahmar (Syria)[Figure 2.1]. Since 1988, staff members from the University of Melbourne have been conducting yearly excavations in northern Syria on and around a Tell (mound or hill) named Tell Ahmar. It is the site of an ancient Assyrian city known in antiquity as Til Barsib. There is evidence of habitation at the site dating from the 5th millennium BC through to the present, but the period when it ascended to its greatest affluence was during the Iron Age when the city was captured and then occupied by the Assyrians. Assyria consisted of a number of river plains, each dominated by a major city such as Assur, Nimrud, Nineveh, and Khorsabad. In the Neo-Assyrian period, which lasted from 1000 to 612 BC, the Assyrians governed an empire that extended from Egypt to Turkey and from the Mediterranean to the Persian Gulf. From 1929 to 1931, a French team of archaeologists excavated at the site and discovered the Assyrian palace (an initial sounding was made in 1928), but for the last 50 or so years no other work has proceeded at the site. In the mid-1980s, the Syrian government announced plans to build the Tishrin Dam in the region of the upper Euphrates. The initial completion date for the dam was forecast for 1995, but construction was delayed, and the dam was not finished until 1997. It appears that the Syrians began operating the dam in 2001 and, so most, if not all, of the site may be submerged.

Tell Brak (Syria)[Figure 2.1]. Brak is the largest tell in North Mesopotamia and Syria, over 40 m in height, 800 × 600 m in area. In the Northern Middle Uruk period (c. 3500 BC) Brak occupied an area of over 110 ha, including a corona of smaller tells surrounding the main mound. The tell was occupied from at least as early as 6000 BC to the early Iron Age. A "Gateway City," Brak lies on one of the major roads leading from the Tigris Valley north to the metal sources in Anatolia and west to the Euphrates and the Mediterranean. Its ancient name, Nagar, appears in the 3rd millennium Ebla texts as the most important city in northeastern Syria. Well-stratified material has been recovered from private houses of the 4th to the 2nd millennium BC. Large casemate walls and a unique city gate dating to the early 4th millennium are among the most recent discoveries. The latest occupation at the site consists of a Roman village and castellum (fortress), situated to the north and east of the main tell.

Caesarea Maritima (Israel)[Figure 2.2]. Caesarea Maritima, founded by King Herod between 22 and 10 B.C., served as the main port and administrative capital of his kingdom. It served as the headquarters of the Roman administration of Judaea, later to become Palestine. Eventually, in the 4th century A.D., the

site converted from paganism to Christianity and became a major center of the Christian Roman Empire. The Islamic conquest of the Holy Land in the 7th century brought Muslim rule. Much reduced in size and population, the city remained a prosperous agricultural town. The Crusaders conquered this town in 1101 and occupied it, with some interruptions, until 1265, when the Muslims captured Caesarea. Shortly thereafter, the Mamluk sultan of Egypt ordered Caesarea demolished to prevent it from ever again becoming an entry point for Western invaders. Caesarea thus embodies the great transitions that marked the history of the Old World during and just after the first millennium A.D. Glass artifacts have been found here.

Khirbet Cana (Israel)[Figure 2.2]. Khirbet (ruin of) Cana is a site in the Galilee, 8 miles northwest of Nazareth and 12 miles west of the Sea of Galilee, which seems the most likely "candidate" in the quest for the true location of Cana. Recent archaeological evidence points to it as the location of the biblical town mentioned in the Gospel of John (John 2: 1-11). Approximately 25% of the plentiful pottery uncovered here stems from the late Hellenistic and early Roman, and 50% from the Byzantine Period.

In 1998, glass was the major focus of archaeologist Alysa Fischer (University of Puget Sound). She, along with Greg Smith, collected glass and soil samples for a preliminary analysis of the relationship between the weathering layers found on glass objects and their deposition environment. The glass samples found *in situ* were sent to the University of Arizona where the soil and glass were to be divided and each analyzed separately in a Scanning Electron Microscope with Wavelength Dispersive Spectrometer. There was to be a comparison between the glass found here and that found at Sepphoris (see above) so that they could determine trade routes. Second, they were to examine both the core of the glass that was unaffected by the surrounding soil and the weathering layers on the surface of the glass in order to determine the differences between the two. With these data and the soil pH data, they hoped to get a relative indicator of the amount of water that has passed through the area around the glass.

Sepphoris (Israel)[Figure 2.2]. At the crossroads of two major ancient roads, the north/south Via Maris and the east/west Acre-Tiberias road, was the once great city of Sepphoris. Known as *Zippori* in Hebrew, it was the capital city of Galilee throughout many periods. For a time, Herod Antipas made it his capital after inheriting the territory at his father's (Herod the Great) death in 4 B.C. As the city was greatly destroyed by the Romans after a riot in the city only a couple of years earlier, Herod Antipas began an ambitious and extensive building program.

The first archaeological dig at Sepphoris was done in 1930 by a team from the University of Michigan under the direction of Leroy Waterman. After that, nothing was done until 1983, when James Strange from the University of South Florida resumed excavations at the site. Later, in 1985, a joint team from Duke University and Hebrew University under the direction of Eric Myers and Ehud Netzer also began extensive work here. Continuous work has been done since then by these and other

Figure 2.2. Map of Israel Showing the Location of Potential Archaeological Sites: 1) Caesarea Maritima, 2) Khirbet Cana, and 3) Sepphoris.

groups. Through the years, the size of the dig has expanded, uncovering more and more of the city. In University of South Florida excavations since 1983, they have excavated a Jewish villa first excavated by the University of Michigan in 1931, a bathing establishment, and an enormous market building or basilica with stunning mosaics. They have recovered thousands of sherds, hundreds of coins, many fragments of glass, and other traces of the material culture of the city.

Aghia Kyriaki (Greece)[Figure 2.3]. The most spectacular feature of Aghia Kyriaki is the existence of abundant quantities of coarse pottery in the form of amphorae, pithoi, and lekanae dating, from the Late Hellenistic to the Early Roman period, approximately 200 BC to 200 AD. Large numbers of vessels, many in collapsed stacks as well as *in situ* within a relatively small settlement, points to commercial and perhaps industrial activities. Their presence may be related to the exploitation of mineral resources. In common with other Greek islands, Melos was noted in antiquity as a source of these "earths," natural materials such as kaolin, bentonite, alum, and sulfur, all of which had diverse applications. There are about 150 archaeological features, including stairs, walls, and pottery.

Figure 2.3. Map of Greece Showing the Location of the Potential Archaeological Site at Aghia Kyriaki on the Island of Milos (orange square)

Tell El-Amarna (Egypt)[Figure 2.4]. Tell El-Amarna was formally known as Akhetaten. The new name came from a local village called El-Till. The word Amarna came from the Bedouin tribe that settled in this village. Even though the word Tell, in Arabic, means a mound or a small hill, interestingly enough, Tel El-Amarna is a flat piece of land beside the Nile Valley. The ancient name, Akhetaten, means the horizon of the solar disk. It is very similar to the meaning of Amun Dwelt at Thebes, Ptah at Memphis, and other gods at their favored places. King Akhenaten offered this place to be the home for his god Aton. The area is a plain field, separated from the Nile Valley by a strip of palm trees. It stretches 12 kilometers from north to south. The area is covered mostly with sand and outlined with ruins of temples, palaces, and houses that archeologists discovered. Reportedly, glass cullet, beads, vessels, and (probably) furnaces have been found at the site.

Figure 2.4. Map of Egypt Showing the Location of the Potential Archaeological Site at Akhetaten (square near Asyut)

Upper Tigres Archaeological Research Project (Turkey)[Figure 2.5]. Upper Tigres Archaeological Research Project (UTARP) is a multiyear archaeological excavation and survey project to define the ancient imperialism, colonialism, and cultural contact correlations in an area that bordered

Mesopotamia. The sites included in this study are Boztepe, Talavash Tepe, and Kenan Tepe in southeastern Turkey. Habitation predates the Bronze Age (ca 2500 B.C.).

Figure 2.5. Map of Turkey Showing the Location of Potential Archaeological Sites: 1) Upper Archaeological Research Project and 2) Amuq Valley Regional Projects and Tel Atchana

Amuq Valley Regional Projects (Turkey)[Figure 2.5]. Situated at the northeastern corner of the Mediterranean Sea, the Amuq Valley or the Plain of Antioch is located in a region known as *The Hatay* in what is today Turkey. Surrounded by mountains on all sides, the Amuq is a rich and fertile valley well watered by the Orontes and Karasu Rivers. While the Amuq is perhaps best known for having been home to the classical city of Antioch, one of the largest cities in the Roman Empire, the valley has been densely occupied since at least 6000 BC to the present day. The unusual concentration of ancient sites in such a small area makes the region ideal for archaeological investigation. As such, the Amuq was targeted for several important and formative archaeological projects as early as the 1930s. In 1995, the Amuq Valley Project was started by the staff of the Oriental Institute of the University of Chicago.

Alalakh (Tell Atchana) (Part of the Amuq Valley Regional Projects)[Figure 2.5]. Historically, the city of Alalakh was the capital of the Mukish kingdom, a vassal to the kingdoms of Yamhad (today Aleppo) during the 18th through 16th centuries B.C. and to Mitanni during the 15th through 14th centuries B.C.; it was later incorporated into the Hittite empire (Anatolia). The rise of large territorial states in the Late Bronze Age marks an important transformation in the Near East. According to reports, glass artifacts have been found here.

2.2 European Sites

Poggio Colla (Italy). Poggio Colla is important because it has undisturbed habitation layers that span much of Etruscan (Florentine) history. The site seems to have been inhabited by the Etruscans at least as early as the 7th century and was abandoned or destroyed in the late 3rd century B.C. Excavations to date have revealed well-defined fortification walls, an extensive necropolis area, and the rare remains of an archaic monumental building, probably a temple. Poggio Colla was inhabited at least as early as the 7th century B.C. and had monumental architecture on its northeastern flank, probably a temple, by the early 6th century. The site suffered a violent destruction and was then rebuilt during the Hellenistic period. Remains of the Hellenistic fortifications can still be seen on the three sides of the Poggio today. Glass artifacts have been reported at the Materials Research Society Annual Meeting in 2001.

Germany. There are several sites in Germany from which medieval window glasses might be obtained. The names of these sites were unavailable at the time this report was written. However, we have been in contact with Dr. Hannelore Römich at the Fraunhofer Institüt für Silicatforschung. She has samples of these glasses and of simulated medieval window glass that she is currently testing. We will be able to establish a sound collaboration with her.

United Kingdom. We have been in contact with several archaeologists in the UK. Although we have not received communications from them, there appear to be several appropriate projects that are active through the University of Glasgow, Cambridge, Oxford University, Nottingham University, and York Archaeology.

2.3 United States

While there are no ancient sites in the United States, several staff members from various universities are working or leading projects at some of the sites listed above. The universities include the University of South Florida, the University of South California, Duke, MIT, the University of Michigan, and the University of South Dakota. Of particular interest is James Strange from the University of South Florida. He has published several articles on the glass from Sepphoris.

3.0 Conclusion

We will be talking with several archaeologists to identify additional sites. We will then narrow the field of potential sites by determining where it is possible to get access to the information that is vital to our study. We will continue to explore the collaborative studies with Hannelore Römich to see if it is possible to participate more fully in her controlled burial experiments. She is also one of our best contacts for obtaining access to sites where medieval glasses are buried. The other archaeologists with potential for identifying sites and site access are James Strange (University of South Florida), Julian Henderson (University of Nottingham), and Pamela Vandiver (Smithsonian Center for Materials Research and Education). The investigations by Alysia Fischer (University of Puget Sound) appear to be very appropriate to our studies. We will be in contact with her.

Since most of these sites are in the Middle East, activities at these sites may be suspended because of local political instabilities. This will also be a factor in site selection.

4.0 References

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