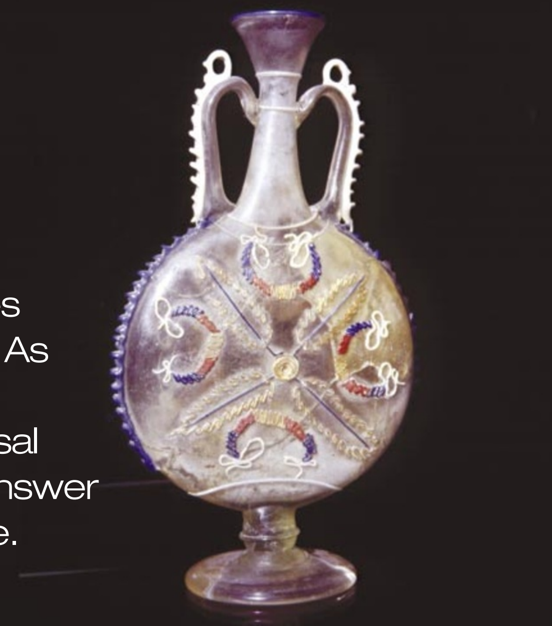
To the heart of glass

How do you run an experiment that takes thousands of years? As scientists studying nuclear-waste disposal are finding out, the answer is to look back in time. Philip Ball reports.



The ravages of time on glass can be assessed by examining ancient artefacts, such as this Roman vase dating from AD 250.

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If you feel that your experiments can take for ever, spare a thought for the scientists studying the disposal of nuclear waste. The half-lives of some radioactive wastes stretch to hundreds of thousands of years. How can the materials used to contain these wastes ever be properly tested?

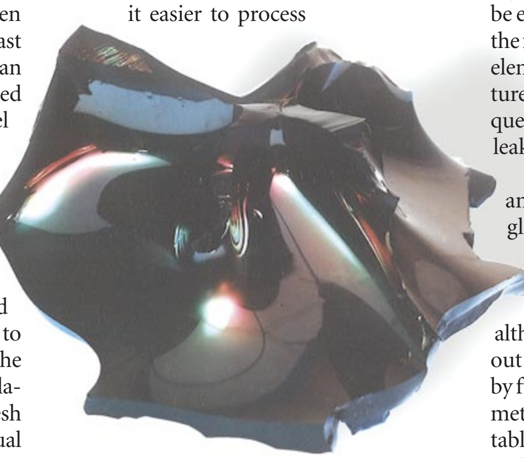
The solution, or at least part of it, is to collaborate with archaeologists. One of the best disposal options is to trap the waste in glass and bury it. So when the civilizations of the Middle East first learnt how to make glass at least 4,500 years ago, they unwittingly launched an experiment on the long-term stability of the favoured material for storing nuclear waste. Archaeologists have since excavated samples of these glasses, and their findings could help materials scientists improve nuclear-waste disposal.

The two communities have actually been courting each other sporadically for at least two decades, but nuclear waste is now an increasingly pressing problem. In the United States alone, 400 million litres of high-level waste — spent fuel from nuclear power plants and the military reactors used to make weapons-grade plutonium — need to be stored. A proposed repository inside Yucca Mountain in Nevada has attracted much controversy (see *Nature* **412,** 850–852; 2001), although it is expected to open early next decade. With the need to test potential storage materials high on the agenda of nuclear-waste researchers, the relationship with archaeologists got off to a fresh start in Boston last December, at the annual meeting of the US Materials Research Society.

Glass is already an established part of the waste-disposal process. Since 1996, a plant at the Savannah River Site, a former nuclear-weapons production facility in South Carolina, has been mixing high-level waste into molten glass and casting it into cylinders about a cubic metre in volume. At Yucca, these would be placed in canisters made of a corrosion-resistant nickel alloy. But water is likely to seep into the underground chambers holding the waste. No one knows for sure if the alloy will hold out over thousands of years, so materials scientists are interested in how water will affect the encased glass over long periods of time.

Waste cocktail

Normal glass consists mainly of a disorderly network of silicon and oxygen atoms. Typically incorporated into this network are small amounts of metals such as sodium and calcium, which are introduced to make it easier to process the glass. Larger metallic elements, including heavy radioactive elements such as caesium and neptunium that are found in nuclear waste, can be caught and held within this silicate network. Stable and robust, glass seems to be an ideal option for storing waste.



Glass is stable, but is it sufficiently robust to store nuclear waste for hundreds of thousands of years?

But over the thousands of years that nuclear waste remains active, glass can undergo significant changes. For relatively short periods of time, a few years say, water barely perturbs silicate glass. But hydrogen ions in water will eventually swap places with the sodium and calcium in the glass, slowly disrupting the network and allowing some of the radioactive elements to escape.

What's more, silicate glass can transform into a crystalline form over hundreds of years, squeezing the radioactive atoms out of the crystal lattice in the process. The glass will also be exposed to high levels of radiation and, for the first few decades, heat from the radioactive elements will create defects in the glass structure that can initiate further damage. The key question is not if nuclear waste will eventually leak out, but when and how fast.

Vital clues could come from studies of ancient glass. The earliest-known artificial glass comes from Mesopotamia, now part of Syria and Iraq, and dates from 2500 BC. The ancient Egyptians also developed considerable expertise in glassmaking, although it remained a luxury item throughout the Middle Ages. These glasses were made by fusing sand with substances that contained metals from groups I and II of the periodic table, such as sodium, found in wood ash.

This is fortunate, as several of the recipes being studied for nuclear-waste glasses also contain high amounts of such metals. Some of

This disc shows how much high-level waste is produced if one person's lifetime electricity needs come from nuclear power.

BNFL

the US waste is currently stored at a former nuclear-weapons facility in Hanford, Washington. Two of the glasses being tested there for low-level waste are HAN-28F and LAWA44, which contain 20–30% sodium oxide.

Moreover, metals such as cobalt and manganese that were added to ancient glass to give it different colours can serve as markers for evaluating how radionuclides in a waste glass might disperse into the surrounding earth. The biggest long-term environmental impact from leaky nuclear waste will come from just a few long-lived and soluble radionuclides, such as technetium-99 and iodine-129. The first of these, for example, has a half-life of about 200,000 years.

But archaeological studies do not provide a perfect guide to the waste-disposal glasses. Unlike ancient glasses, the latter typically contain a relatively large amount of boron or phosphorus. Moreover, the glasses used to store high-level waste do not have the high levels of group I and II metals that archaeological glasses do. "You'll never get a perfect analogue out of an ancient glass," says Pam Vandiver, a materials scientist working on the conservation of ancient artefacts at the Smithsonian Center for Materials Research and Education in Suitland, Maryland.

Despite these drawbacks, materials scientists can still make use of archaeological studies. Ancient glasses provide useful information on how glass corrodes, even if it is not specific to waste-disposal glasses. Experience from archaeological sites suggests that there are many ways in which corrosion occurs, depending on factors such as the composition of the glass, and the acidity and temperature of the soil. Not all degradation is a result of chemical weathering: microbes can also attack the glass.

Window from the past

More importantly, archaeological studies can help researchers to improve their theoretical models and computer simulations of glass corrosion. By adapting these models to the composition of particular archaeological specimens and the environment that they were buried in, researchers can run their models and compare the predictions to real measurements taken on the ancient samples. "A similar mechanism seems to operate for all silicate glasses," says Peter McGrail, a materials scientist at the Pacific Northwest National Laboratory (PNNL) in Richland, Washington. "So the ancient glasses provide a unique validation opportunity that is applicable to all silicate waste glasses."

It is too early to say what the results of this opportunity will show, but nuclear-waste researchers are excited about the possibilities. "Nothing beats a completely independent experiment, and that's what the ancient analogues provide," says Denis Strachan, who studies nuclear-waste materials at PNNL. "If we can verify our models that way, we can show that they are trustworthy."

Further input into the models comes from experiments in which materials scientists bury their samples and dig them up years later. Such tests are being conducted in the United States, Russia, Sweden and Belgium. One of the most exciting field studies for nuclear-waste researchers is one that began partly with archaeological objectives in mind. In 1970, Walter Fletcher of the British Glass Industry Research Association, now part of the Sheffield-based British Glass Manufacturers' Confederation, arranged for a wide variety of different types of glass, including synthetic analogues of Roman and medieval glass, to be buried in limestone soils in a quarry in Ballidon in Derbyshire. Various modern glasses were buried too, to act as reference samples against which the simulated archaeological glasses could be compared. Fletcher intended that some of these samples would be exhumed at set intervals for centuries to come.

The Ballidon project, now overseen by researchers at the University of Sheffield, came to the attention of George Wicks, a materials scientist at the Savannah River Site, in 1985. The following year saw the fifth exhumation, and Wicks took the opportunity to bury some nuclear-waste glasses. These were exhumed last year, and the results so far are encouraging. "We found out that the corrosion of the glass is very low," says Wicks, "and the glass is doing better in the field than in lab leaching tests." The amount of leaching from the samples actually seems to decrease with time.

When he completed the final exhumation, Wicks also buried new samples, including HAN-28F and LAWA44 glasses, which are scheduled to be exhumed in 2, 5, 10 and 16 years' time. McGrail would like to see soil samples collected from the site at the same time.

It was straightforward for Wicks to include his samples in the Ballidon project, but getting materials scientists and archaeologists to work together is not always so easy. McGrail points out that although tracking trace elements is important in studies of nuclear-waste disposal, archaeologists rarely bother to check what might have leaked from their artefacts and entered the soil.

Nuclear-waste researchers, on the other hand, can use and abuse their samples with relative profligacy, but investigations of archaeological glass objects must often use non-destructive methods. Such issues serve as a reminder that, although both communities might be interested in questions such as how glass weathers, they may not always be asking the questions in the same way. The approach and methods of the two communities are almost "mutually exclusive", Vandiver admits.

Despite these differences, materials scientists are in no doubt about the value of the information that archaeological studies can provide. Without such work, they would be left with no long-term data with which to evaluate their models. No one can see a hundred thousand years into the future, but confidence in nuclear-waste glasses would receive a major boost if the predictions work out for the glass of the Pharaohs. ■

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Digging that scene: George Wicks (left) and his colleague test the resilience of glass in the ground.