Nuclear Waste Disposal: Alternatives to Solidification in Glass Proposed

But glass is still seen as a reasonable solution in the interim

More than a quarter-million cubic meters of liquid radioactive wastes, a volume equivalent to that of about 200 olympic swimming pools, are now being held at government installations awaiting final disposal. More of these highly radioactive wastes will inevitably be generated by nuclear bomb production and possibly by reprocessing of spent fuel from commercial nuclear power plants if President Carter's indefinite ban on reprocessing is ever lifted.

The disposal of radioactive wastes is receiving considerable attention in both political and scientific circles as an important factor in the public acceptability of nuclear power. Waste management is the subject of a study by the President's Interagency Review Group and is being examined during congressional hearings and numerous scientific meetings. The idea that disposal of long-lived, highly radioactive wastes needed only a little engineering to be practical has given way to widespread critical review of the technical problems involved, among them the selection of a suitably stable solid form for the wastes. Although glass, the traditionally favored waste form, has not held up well in recent tests of its durability, most experts still regard it as a reasonable alternative provided that the weaknesses recently pointed up by researchers are taken into consideration in the design of the waste disposal system. Materials scientists are now eager to show that improved waste forms, which by themselves could give confidence in a disposal system, can be developed.

During the past 20 years, the disposal plan of choice has been to incorporate the 40 to 50 radioactive elements dissolved (and suspended) in liquid wastes into blocks of glass, seal the glass in metal canisters, and insert the canisters into deep, geologically stable salt beds. Thus, the chemical form of the waste (the glass), its container, and the geological formation would provide three separate barriers to the release of the wastes until its radioactivity dies away some thousands to hundreds of thousands of years from now, depending on the character of the element.

Over the last few years, some geologists and materials scientists have become concerned that perhaps not enough is known yet about the interaction of waste, container, and salt (or any rock) to have a reasonable assurance that the hazardous wastes will be contained successfully (*Science*, 9 June 1978, p. 1135). Recently, particular attention has been drawn to the idea that ceramics, crystalline materials resembling in many ways natural rocks, may be possible improvements over glass. A recent National Academy of Sciences report was critical of the past emphasis on glass and drew attention to the promise of ceramics (*Science*, 18 August 1978, p. 599). The Department of Energy also wants a closer look at the subject. It has requested an increase in funding for the evaluation of alternatives to glass from the $6.5 million spent in fiscal year 1978 to about $13 million requested in the budget for fiscal year 1980.

Ceramics, if sufficiently stable, might constitute a significant improvement over glass.

Glass has received the most attention in the United States and abroad because it has a number of desirable chemical and physical properties and because the technology for producing massive blocks of it has been readily available from industry. All glasses are amorphous, having no regular order in the arrangement of their atoms; but these atoms (in large part silicon, boron, and oxygen) are strongly bonded to one another in a single, continuous, three-dimensional structure. Having no strict organization on the atomic level, glasses can accommodate a variety of different elements. Doubly and triply charged positive ions (cations) become part of the network itself, and singly charged cations are less securely trapped in the glassy structure. Leaching of radioactive elements from this structure by water has been shown to be low at moderate temperatures. Leaching by water is the primary concern at any disposal site because moving water could carry the wastes beyond the repository before all the radioactivity had decayed. Another advantage of glass is thought to be its inherent resistance to structural damage from radiation and the increased leaching that would likely result.

The biggest advantage of glass at present is the demonstrated practicality of producing large, highly radioactive blocks of it. Workers at Battelle's Pacific Northwest Laboratories (PNL) recently melted calcine, the product of spray-drying liquid wastes, and glass-making materials together to make a cylinder 2.4 meters by 20 centimeters of vitrified commercial reactor wastes, the first to be made on such a scale in this country. The French, at Marcoule, already have a vitrification plant operating on a routine industrial basis, although the wastes there are not as highly radioactive as those in the PNL glass. Waste ceramic processing is still on a small scale in the laboratory.

The suitability of glass under some of the more severe conditions anticipated for waste repositories has been questioned following recent tests of waste glass durability at high temperatures in water. In one set of such tests, Gregory McCarthy and his group at Pennsylvania State University placed a small sample of a borosilicate waste glass, developed at PNL, under 300 atmospheres of pressure at 300°C in distilled water. The glass contained nonradioactive isotopes of waste products. After 1 week under these conditions, the 4-millimeter spheroid had cracked and was discolored in several zones (see figure). At the end of 2 weeks, the sample had broken into several fragments and seemed totally altered. Although 5 percent of the cesium, one of the waste elements of greatest concern, escaped from the glass and re-

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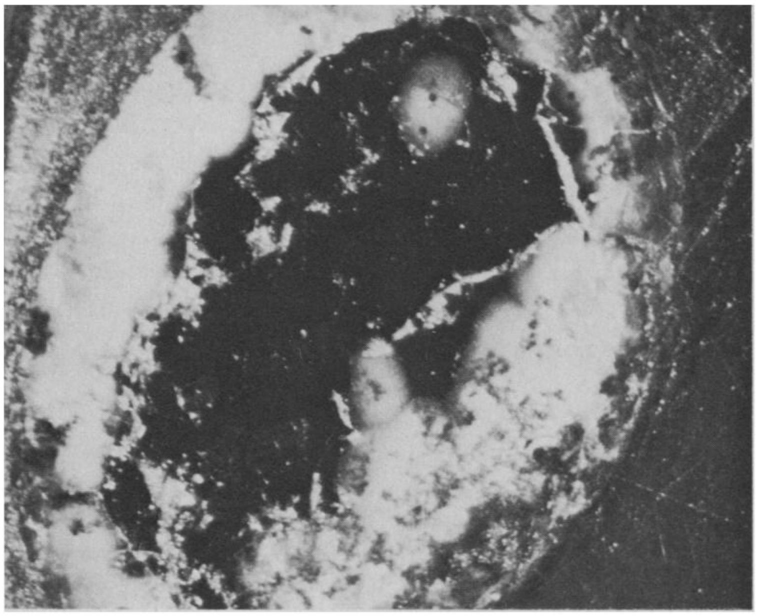

A spheroid (about 2 by 4 millimeters) of borosilicate waste glass treated with water at 300°C and 300 atmospheres for 7 days. The light zone is altered glass and the dark interior zone is apparently unaltered glass. [Source: Materials Research Laboratory, Pennsylvania State University]

mained in solution, it was the only one among the most hazardous elements to remain in substantial quantities, according to McCarthy. When a bittern brine, the kind of solution most likely to contact vitrified wastes in a salt formation, was substituted for the distilled water, large percentages of all the important types of elements went into solution.

This leaching and alteration is much greater than that observed in water at 1 atmosphere between room temperature and 100°C, the conditions of most previous leaching studies. This surprised some people studying waste disposal, but those familiar with the properties of glass anticipated such results. John Mendel of PNL suggests that it has not been a matter of the failure of glass to perform as expected, but rather that more is now expected of a solid waste form.

Proposed waste forms are being subjected to much more severe conditions than in the past, but these conditions may not necessarily be typical of those in an actual repository. Although temperatures in a repository could be higher than 200°C during the first few hundred years because of the heat generated by the wastes, a temperature as low as about 100°C could be chosen. To do this, the wastes could be stored for several decades while their heat output decreased, less waste could be incorporated in each canister, or fewer canisters could be stored per hectare. The presence of some water, even in bedded salt, now appears inevitable, but much more attention is being given to beefing up the canister material's resistance to corrosion. Conceivably, the wastes could be protected from the water, at least during the thermal period. Nonetheless, there is a strong feeling among many materials scientists that glass can and should be improved upon.

The frontrunner as a successor to glass is ceramics, which are nonmetallic crystalline materials formed at high temperature, such as chinaware or natural minerals. An apparent advantage of ceramics is that they already have an ordered atomic structure, whose properties can be tailored to a particular waste element and to conditions of a specific disposal site. So far, not all ceramics have shown improved performance as compared to glasses, but some preliminary results have impressed many materials scientists.

McCarthy's group at Penn State, in cooperation with PNL, has been developing a ceramic tailored for waste disposal that they call supercalcine-ceramic. Before drying the liquid wastes, they add several elements selected to form specific minerals with the waste elements when the dried wastes are simply heated or heated and compressed. In high-temperature leaching experiments involving distilled water, supercalcine-ceramics have exceeded the performance of the PNL glass, allowing about 0.5 percent of the cesium to escape, according to McCarthy. But in a bittern brine, most of the minerals proved as unstable as the glass, releasing large fractions of the waste load into solution. Among the brine-resistant minerals, the Penn State group has suggested that monazite, a phosphate, may be particularly suitable as a host for the actinide elements, which are long-lived and highly toxic components of radioactive wastes.

At the Australian National University, A. E. Ringwood and his group are also following the tailored ceramic approach. They have emphasized that the best minerals for waste solidification may be those that have proved most stable under natural conditions over geologic time. In order to include only these specific minerals, the Australian group limits the proportion of wastes in the ceramic, called synroc (synthetic rock), to about 10 percent. In contrast, the high loadings of supercalcine-ceramic (up to 80 percent) determine to a large extent which minerals are formed.

The first version of synroc consisted of six minerals, compared with the nine of supercalcine-ceramic. Although all the phases withstood 1000 atmospheres at 600°C in water for 24 hours, only three of the minerals survived similar conditions in 1 percent sodium chloride solution, which is generally less corrosive than bittern brines. A second version of synroc, consisting principally of the three stable minerals from the first version (a hollandite, zirconolite, and perovskite) and spiked with three waste elements, suffered no significant alteration or leaching during a 24-hour experiment at 800°C in 10 percent sodium chloride, according to Ringwood. Only at 900°C and 5000 atmospheres did it begin to break down during a 24-hour experiment.

The stability of the cesium in the hollandite crystal structure is probably due to the physical trapping of cesium, Ringwood believes. Cesium is apparently trapped in atomic-scale tunnels formed by linked aluminum and titanium atoms behind plugs of firmly bonded barium atoms. Rustun Roy of Penn State has pointed out that this kind of molecular engineering is a particular advantage of ceramics.

However, ceramics are not without possible disadvantages. Although materials scientists regard the preliminary synroc and supercalcine-ceramic results as encouraging, possible stumbling blocks to the use of such synthetic rocks remain to be investigated. One problem is radiation damage—the disordering of the crystal structure by alpha particles and the recoiling atoms that ejected them. Another is transmutation, which is the substitution of a new chemical element in the structure when its progenitor decays radioactively. Mendel suggests that, on the basis of leaching tests of irradiated waste glasses, radiation does not significantly affect the rate of leaching from glass.

Laboratory experiments on the effects of radiation on proposed ceramic waste forms have not yet been done, but geologic samples may provide some clues. Certain minerals contain radioactive uranium and thorium and suffer damage to their crystal structures over great periods of time. At this time, various interpretations of the geologic record are being made. Ringwood and McCarthy argue that even heavily damaged minerals, or metamicts, can retain their uranium and thorium over millions of years although exposed to severe conditions. Rodney Ewing of the University of New Mexico agrees that natural metamicts may provide good analogs for radiation damage to synthetic rocks, but cautions that a broad survey will be required to sort out the effects of age, composition, crystal structure, and environmental conditions.

It is now obvious that some ceramics are more stable than glass under certain conditions. But how much more stable must ceramics be so as to constitute a significant improvement? An immediate goal of researchers is to compare glasses and ceramics loaded with the same amount of wastes under identical conditions. Then the laboratory results can begin to be incorporated into predictions of waste behavior in a respository. With such predictions, any improved stability due to the form of the wastes can be compared with other ways of achieving reliable long-term containment.

In addition to the chemical and physical properties of the waste forms themselves, researchers are increasingly interested in the form of the wastes after they are exposed to realistic geologic conditions. McCarthy's Penn State group has found that a waste element may be leached into solution only to become part of another solid that is more stable under the prevailing conditions. They exposed basaltic rock and spent nuclear fuel, a possible solid waste form if reprocessing is abandoned, to water under high temperature and pressure. One hundred percent of the cesium left the spent fuel, but 98.8 percent of it did not remain in solution at 200°C because it became tied up with aluminum silicates from the basalt in a new mineral, pollucite. The basalt also prevented any detectable dissolution of uranium, apparently by maintaining reducing conditions that kept the uranium in its highly insoluble reduced form.

Chemical effects of the surrounding rock might also significantly reduce the dissolution of waste elements in the first place. Larry Hench of the University of Florida, working with glass and various rocks in water, reports that the presence of some kinds of rock leads to partial protection of the glass from dissolution. Apparently, certain soluble chemical species from the rock bind to the exposed glass surface, shielding it from the solution. Although waste-rock interactions are only beginning to be investigated, it has become obvious that the solid waste form cannot be considered alone. In fact, positive elements of geologic materials might actually be designed into the repository by surrounding the solidified waste with an "overpack" of crushed rock or clay. This would be only one part of an engineered barrier between the waste form and the surrounding rock.

A sample of the mineral microlite that has been damaged by natural radiation from its own uranium and thorium. Chemical alteration (dark areas) has occurred along microfractures. The area shown is about 1 millimeter across. [*Source: Bryan Chakoumakos, University of New Mexico*]

Originally conceived as a single canister of stainless steel, possible engineered barriers now range from the microscopic to the massive. John Rusin of PNL, M. F. Browning of Battelle Columbus Laboratories, and McCarthy have coated 2-millimeter pellets of supercalcine-ceramic first with a 40-micrometer layer of carbon, to increase leach resistance, and then with a 60-micrometer layer of aluminum oxide, to increase oxidation resistance. After 4 weeks in a bittern brine at 400°C and 300 atmospheres, the coatings remained intact and no detectable cesium entered the solution. For added protection and physical strength, the coated pellets can be encased in copper and enclosed by a stainless steel canister. This apparently high level of protection is achieved, the researchers point out, at the cost of using very complex processing techniques, a problem because solidification of highly radioactive wastes must be handled entirely by remote control.

Another metal-encapsulated ceramic, called cermet, is being developed as a waste form by Scott Aaron, T. C. Quinby, and E. H. Kobish of Oak Ridge National Laboratory. The final product consists of microscopic, crystalline particles of waste oxides, aluminosilicates, and titanates dispersed in an iron-nickel alloy. Cermets are unusual because the alloy is generated from metals in the liquid waste itself and from added metals obtained from stockpiles of contaminated materials. Very preliminary leaching studies indicate that cermets are considerably more resistant at 100°C than a borosilicate waste glass.

The Swedish nuclear industry, faced with a moratorium on nuclear power development until an acceptable waste disposal plan was developed, has proposed a system of engineered barriers that depends more on sheer mass than on sophistication. Vitrified wastes would be encased in layers of stainless steel, lead, and titanium before emplacement in granite. A mixture of quartz sand and bentonite clay, a good adsorber of many wastes, would completely surround the canisters. If spent fuel rods were the final waste form, as is being considered in the United States, they would be encapsulated in lead and placed in a copper canister with 20-centimeter-thick walls.

Researchers are now testing prospective waste forms under the most extreme conditions that might prevail in a waste disposal site. In the case of glass, the objective is not to show that it is unacceptable, but rather to define conditions under which it could not be safely stored. Because the single most critical factor, temperature, can be controlled by simple dilution of wastes or cooling by delayed disposal (as planned in Sweden), there is optimism that glass can still be part of a first generation, multiple barrier disposal system. Some see the goal of studies of ceramics as the development of a second generation waste form that could be considered a dominant barrier, based on carefully controlled laboratory testing. This would, according to these researchers, relieve geologists of the burden of locating ideal sites and would present a convincing case for nuclear waste disposal to the public. Others allow that improvements may be possible in 15 to 20 years, but expect that geologic and engineered barriers will remain vital components of waste disposal systems.

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Additional Readings

1. *Proceedings of the Conference on High-Level Radioactive Solid Waste Forms, 18-21 December 1978, Denver, Colorado* (U.S. Nuclear Regulatory Commission, in press); G. J. McCarthy, Ed., *Scientific Basis for Nuclear Waste Management* (Plenum, New York, in press).