WSRC-MS-99-000082

NUCLEAR WASTE GLASSES- Suitability, Surface Studies and Stability

George G. Wicks
Senior Advisory Scientist
Westinghouse Savannah River Technology Center
Aiken, SC USA

ABSTRACT

Every major country involved with long-term management of high-level radioactive waste (HLW) has either selected or is considering glass as the matrix of choice for immobilizing and ultimately, disposing of the potentially hazardous, high-level radioactive material. There are many reasons why glass is preferred. Among the most important considerations are the ability of glass structures to accommodate and immobilize the many different types of radionuclides present in HLW, and to produce a product that not only has excellent technical properties, but also possesses good processing features [1]. Good processability allows the glass to be fabricated with relative ease even under difficult remote-handling conditions necessary for vitrification of highly radioactive material. The single most important property of the waste glass produced is its ability to retain hazardous species within the glass structure and

this is reflected by its excellent chemical durability and corrosion resistance to a wide range of environmental conditions [1, 2].

INTRODUCTION

In addition to immobilization of HLW, glass matrices are also being considered for isolation of many other types of hazardous materials, both radioactive as well as non-radioactive. This includes vitrification of various actinides resulting from clean-up operations and the legacy of the cold war. Other types of wastes being considered for immobilization into glasses include transuranic wastes, mixed wastes, contaminated soils, asbestos, incinerator ashes, medical wastes, electronic circuitry, weapons parts, and a variety of other potential hazardous materials or components. The ability of glass structures to incorporate and then immobilize many different elements into durable, high integrity, waste glass products is a direct function of the unique random network structure of the glassy state.

WASTE DISPOSAL STRATEGY

The strategy that has been adopted for long term management of HLW involves removing the waste from temporary storage facilities, chemically processing the waste to reduce volume when appropriate, and then immobilizing the potentially hazardous radionuclides into a solid, non dispersible form-borosilicate glass. The waste glass forms produced can then be temporarily stored on-site at the vitrification facility, but eventually, will be shipped off-site to carefully selected geologic repositories. Once at the geologic site, the forms will be placed in deep burial as one element of a multibarrier isolation system directed at permanently disposing of the radioactive material. It is important that the glass systems chosen have the ability to incorporate and immobilize HLW constituents and that the waste glass produced will perform well during fabrication, interim storage, transportation, and final geologic disposal.

WASTE GLASS STRUCTURE

For immobilization of HLW, borosilicate glass systems are preferred world-wide. In the case of Savannah River Site (SRS) defense HLW, waste glass forms are produced from approximately 70% glass forming chemicals added to about 30% waste constituents. The glass components are generally added to the liquid waste stream in the form of a multi-component pre-melted glass or frit prior to waste glass melting operations, which produce solidified radioactive products [3]. Although there are many individual elements that are found in nuclear waste glass systems, these components can play only one of three basic roles in the glass structure; *network formers*, *intermediates* or *modifiers* [4].

Constituents such as silica and boric oxide are generally added to the waste stream as major components of the glass frit. The silicon and boron atoms are NETWORK FORMERS and are located in the center of oxygen polyhedra in the configuration of tetrahedra or triangles. These polyhedra are then tied together by sharing corners, generally in accordance with Zachariasen's rules, which then make up the 'framework or skeleton' of the random network structure of the solidified waste glass form. Another structural role that both glass frit and waste elements can play is that of INTERMEDIATES, which is exemplified by major components found in the waste such as alumina. These components can replace the network formers and still retain the framework structure of the glass. Other cations can move to the singly-bonded oxygen ions that are created, for charge neutrality. The final role that components can play is the most prevalent, that of MODIFIERS. In this case, important waste components such as cesium and strontium, along with alkali and alkali earth constituents, are located within the holes of the random network structure, and can also be associated with nearby singly-bonded oxygen ions. In Figure 1, a model depicting a simplified waste glass random network structure is shown. An important point to note is that both glass and waste components become an integral part of the random network structure of the glass. Components are incorporated by primary and/or secondary bonding which helps explain why glass is able to retain radionuclides so well during leaching and why different elements can leach at different rates [5].

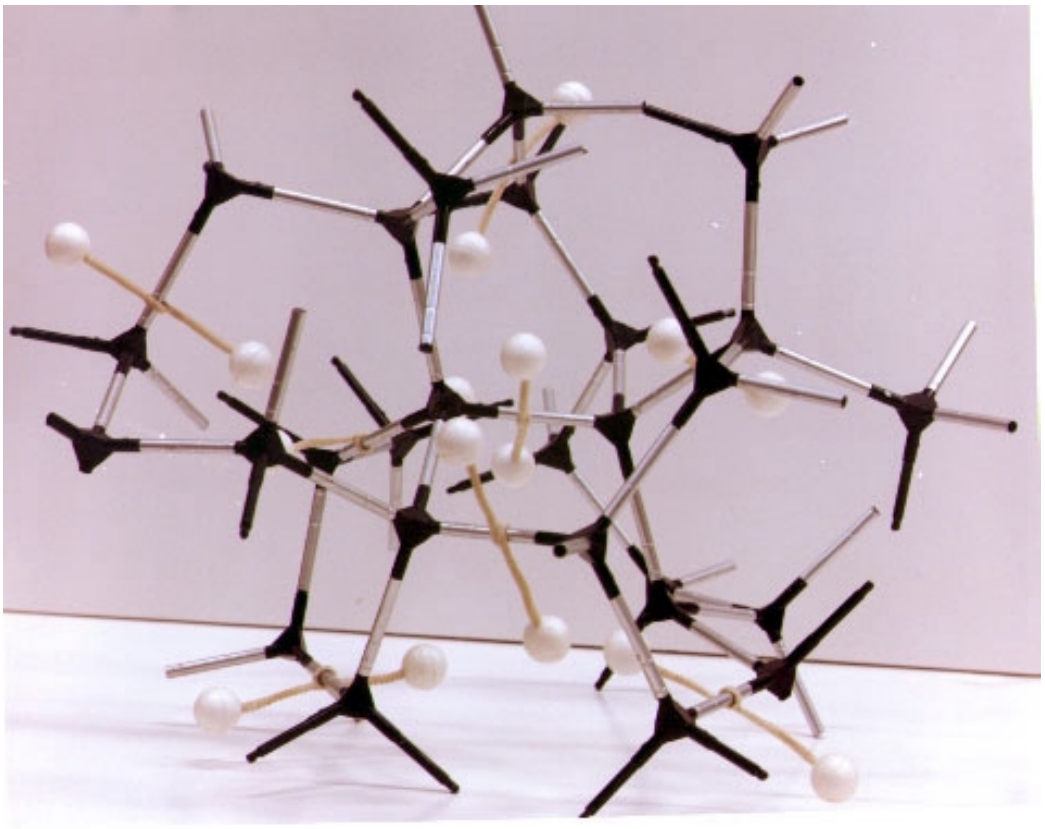

Figure 1. Simplified Random Network Structure of Nuclear Waste Glasses

GLASS SUITABILITY FACTORS

There are a variety of factors which contribute to the suitability of glasses for immobilization of hazardous materials. These considerations generally fall into two major technical categories. First, involves PROCESSING CONSIDERATIONS, which include the ease of being able to produce waste forms even under difficult remote conditions, and second, TECHNICAL PERFORMANCE FEATURES, which can be related to the structure and composition of the vitrified waste forms. Technical performance features are in five major areas of interest; (a) flexibility/ waste compatibility (b) mechanical integrity, (c) thermal stability, (d) radiation effects and (e) chemical durability. Chemical durability is generally considered the most important technical property of the final waste glass form, but there are also other important considerations of a less technical nature. Consideration of all factors

are essential in the development of high integrity, cost-effective waste forms and subsequent systems, designed to permanently manage or dispose of hazardous materials. Following is a brief description of glass suitability factors for immobilization of potentially hazardous materials, with an emphasis on SRS high level waste glasses:

• Processing Considerations

Vitrification Facilities & Practical Operating Experience. The only HLW immobilization facilities in the world are glass-making or vitrification operations. This includes France and their successful production facilities at Marcoule and LaHague. Other vitrification plants in production world-wide include facilities located in Belgium, England as well as the United States, along with additional vitrification plants located or being planned in other countries. In the United States, the first major waste vitrification plant is the almost one billion dollar Defense Waste Processing Facility located in Aiken, South Carolina, which is currently in production vitrifying hazardous constituents in more than 30 million gallons of HLW.

• Technical Performance

Flexibility. Glass has demonstrated the ability to accommodate not only the 40 or more different elements that are found in HLW waste streams, but also large variations in waste composition. The reason for this feature is a result of the relatively open random network structure that characterizes glass systems and its ability to accommodate elements or radionuclides of different sizes, charge, and characteristics, as well as differing amounts of these constituents [1].

Thermal Stability. Waste glass products possess good thermal stability. Upon cooling from the melt or from self-heating due to radionuclide decay, waste glasses can phase separate or crystallize [6]. Many different studies have been performed to assess the effects of these structural and chemical changes on the performance of the product [7]. In one series of studies, Savannah River Site waste glass was purposely devitrified [8], even though extensive devitrification is not expected for this system. From the resulting time-temperature-transformation [TTT] curves, the phases formed were identified and leaching tests showed that even in this 'worst-case' scenario, the effects of the crystalline phases that formed on chemical durability were not significant.

Mechanical Integrity. Waste glass products also possess good mechanical integrity. Glasses are relatively brittle materials and cracking can occur due to stresses induced during fabrication or from accident scenarios during handling, transportation or storage operations. A variety of mechanical tests have been performed ranging from laboratory-scale studies to drop tests of full-size canisters containing simulated waste glass, at speeds up to 80 mph [9,10]. In

one set of drop tests performed by Battelle Pacific Northwest Laboratory on SRS canisters filled with simulated waste glass, several interesting observations were noted. First, glass forms fracture into relatively large chunks inside the canisters and fracture was generally localized to the area of impact. Second, the amount of increased surface area produced was low along with the amount of resulting fines or small particles. The waste glass product possessed more than adequate mechanical stability under anticipated as well as accident conditions.

Radiation Stability. As radionuclides are incorporated into glass structures, a significant radiation field can be produced. The glass can be irradiated by alpha and beta particles, gamma rays and neutrons that result from decaying radionuclides. The effects that these components have on important properties of waste forms have been assessed for a variety of parameters, including chemical and mechanical integrity, stored energy, helium accumulation, density changes and radiolysis [11,12]. Based on all existing data, waste glass forms perform very well under all of the radiation conditions expected during all stages of solidification and isolation of the HLW. In experiments performed on Savannah River Site waste glass doped internally with curium-244, an intense alpha emitter considered by many to be the most detrimental radiation effect, only very minor effects were noted [13]. The glass remained intact after being subjected to these extreme conditions (simulating more than one million years of storage) and its leaching rate, even with this very high radiation field, was seen to be within a factor two of the undoped glass.

Chemical Durability. The most important and most studied property of solidified waste glass forms is its chemical durability. This provides a measure of how well the waste glass will retain radionuclides under anticipated as well as accident scenarios. Nowhere is this more important than in the final resting place of the waste, the geologic repository. The two most important observations made after evaluating the chemical durability of a variety of waste glass systems under many different repository conditions is that 1) *leaching of glass is very low when subjected to realistic scenarios and conditions* and 2) *not only is the chemical durability of the waste glass systems good, but durability can actually improve with time.* These observations are consistent with our understanding of how and why glass structures incorporate and immobilize hazardous components, and the subsequent behavior these systems exhibit when subjected to extreme conditions. These data have been observed not only in laboratory studies and repository interactions testing, but have also been confirmed in actual field or in-situ testing of the simulated HLW waste forms in various geological settings [14-19].

Actinides and especially plutonium, also incorporate very well into glass structures. Due to this effect, as well as other important considerations, Pu-glasses are expected to have even better chemical durability than the already

internationally accepted HLW glasses. Recently, this has been confirmed for a special group of borosilicate Pu-glasses known as Löffler compositions [20].

In order to assess, understand and ultimately, predict the long term reliability of waste glass systems, chemical durability has been assessed as a function of many important parameters that would be encountered during each stage of the solidification, transportation, interim and permanent disposal scenarios [21]. The parameters are related to the chemistry and structure of the glass systems studied. These important variables affecting the chemical durability of waste glasses include time, temperature, solution pH, Eh, composition (waste, glass, leachate and homogeneity), devitrification, waste loading, surface area of sample to leachant ratio [SA/V], flowrate, pressure, surface finish, glass cracking and fines, radiation effects, geology, hydrology, and package components [canister metal, possible overpack, potential backfills]. Based on all data currently available, the chemical durability of waste glasses should be extremely good when subjected to realistic values of these parameters.

SURFACE STUDIES AND STABILITY OF NUCLEAR WASTE GLASSES

• Integrated Study Approach

A typical approach for assessing glass durability is to immerse a glass in a corrosive medium under defined conditions and then to either measure weight loss or analyze the solution, to detect elements leached from the glass. Weight loss measurements are often the simplest to perform while solution analysis provides additional information on the leaching behavior of specific elements of interest. These techniques are very useful and continue to be used effectively in many studies today. However, this approach has limitations, since possible alteration products or back reactions forming on glass surfaces are generally not detected. This can be especially relevant for more complex glass systems, which is what characterizes nuclear waste glasses. These reactions and the products that may form can have significant effects on measurements and subsequent interpretation of data.

In the 1960's and 1970's, investigators such as Hench and Clark of the University of Florida began routinely combining solution analysis with bulk and surface studies of leached waste glasses, to obtain a more complete picture of the leaching process [22]. Over recent years, new and more sophisticated surface analytical tools have been developed along with more accurate solution analyses. Recognizing that the analytical tools used to study nuclear glass systems all have limitations along with advantages, an integrated study approach was used which combined and overlapped each of these techniques. This provides important information on the chemistry and structure of species of interest on and in leached surface layers and therefore, provides a more complete picture of the leaching process and corrosion mechanisms involved.

The integrated study approach and the various analytical tools used to characterize surface layers and interfaces in nuclear glasses are depicted schematically in Figure 2, along with their sampling depths [22,23].

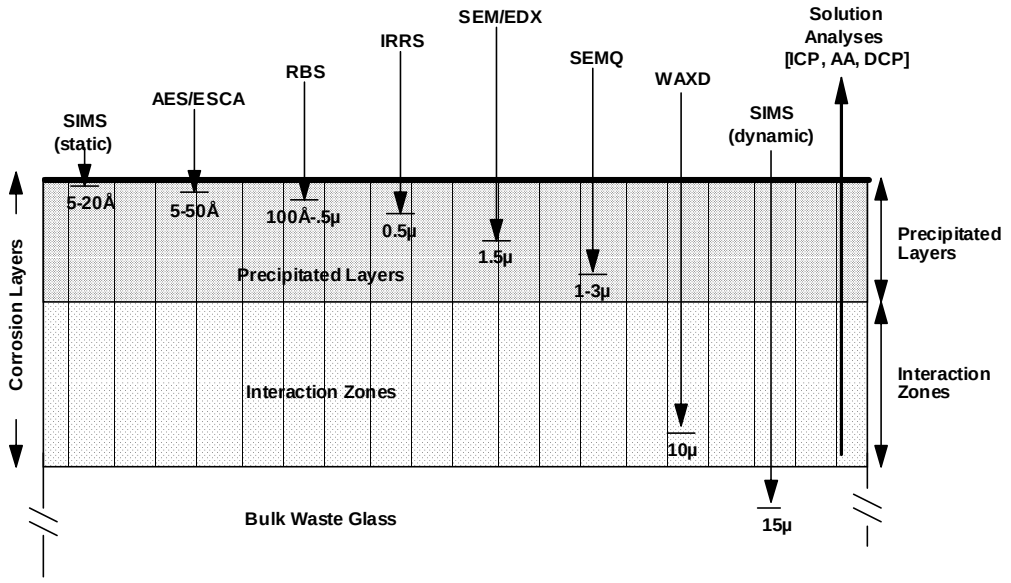

Figure 2. Analytical Tools Used for Integrated Study Approach of Leached Glasses

• Nuclear Waste Glass Surface Layers and Stability

As a result of the numerous surface studies performed by the nuclear waste management community on U.S. and international waste glasses, surface layers have been observed on a wide array of nuclear glass systems and under a wide range of conditions. These layers are generally complex and often, contain a variety of crystalline and non-crystalline phases as well as a series of sublayers, which can be characterized and more fully understood using the integrated study approach. The chemistry, morphology, density and general characteristics of the layers are a strong function of the chemistry of the glass and leaching conditions. The leached glass surface layers can be very important as protective layers, resulting is an already durable glass product exhibiting improved durability with time. While some systems exhibit significant benefits of protective surface layers under specific conditions, other systems and other conditions can produce surface layers that provide much less protection to the glass underneath and in some cases, no protection at all. Surface layers

observed in various nuclear waste glass systems all fall within the 5 cases as defined and described by Hench [24].

An example of layers formed and elemental distributions for simulated SRS HLW, after being leached under various conditions and leachants, is shown in Figure 3. An interesting feature of these layers is that for this system, they are generally enriched in major waste components (ex. Fe) while being deficient in major frit components (ex. Si) that are added to the waste to produce the glass forms. Surface layers, with similar as well as unique features, have also been observed and characterized for this same system leached not only in deionized water, but also in tuff, granite, shale, salt and basalt groundwaters. Leached layers and improved glass behavior have also been observed for leaching of the glass in the presence of lead, while deleterious effects have been noted for leaching in the presence of carbon steel, a potential package component.

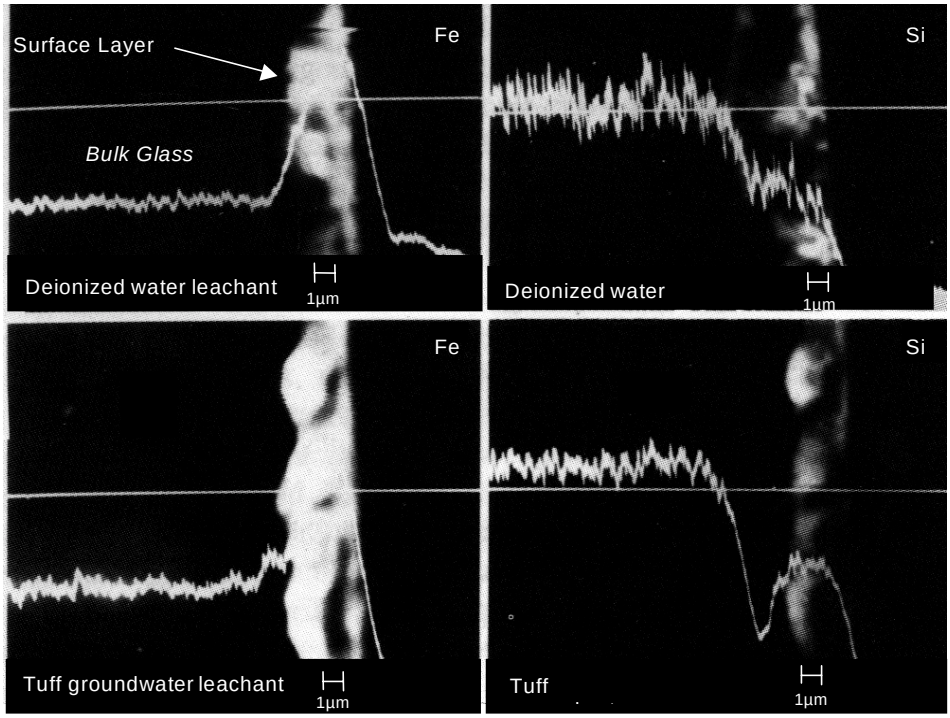

Figure 3. Leached Layers on SRS Waste Glass

Based on these and many other studies that have been performed over the past 30 years, both qualitative and quantitative glass leaching models have been developed to explain the observed leaching behavior and the effects of the surface interactions that have been characterized. In one approach, a simplified 3-stage corrosion process based on glass structural changes has been postulated for nuclear waste glasses involving interdiffusion, matrix dissolution and the

effects of surface layer formation [25]. This concept and other modeling efforts are described in detail elsewhere [26-30].

SUMMARY

The random network structure of glass provides a unique matrix that is particularly suited for incorporation and subsequent immobilization of potentially hazardous radioactive and non-radioactive materials. Based on all data currently available, the performance of a wide variety of waste glass systems and their ability to retain hazardous species is excellent, when tested under realistic conditions, as determined by many studies performed by many different investigators in many different countries. In addition to possessing outstanding chemical durability, the durability of nuclear waste glasses generally improves with increasing time. This behavior has been observed not only in laboratory tests, but also in actual field experiments conducted with simulated HLW glasses buried in Sweden, Belgium, England, and the United States.

REFERENCES

1 Wicks, G.G., "Nuclear Waste Glasses", in Treatise in Materials Science and Technology- GLASS IV, (M. Tomozawa and R.H. Doremus ed) Vol. 26, pp. 57-118, (1985).

2 Wicks, G.G., "Nuclear Waste Glasses: Corrosion Behavior and Field Tests, in Corrosion of Glass, Ceramics and Ceramic Superconductors, ed. by D.E. Clark and B.K. Zoitos, pp. 218-268 (1992).

3 Wicks, G.G. and Bickford, D.F., "Doing Something About High Level Nuclear Waste", MIT Technology Review, p. 51 Nov/Dec (1989).

4 Kingery, W.D., Bowen, H.K. and Uhlmann, D.R., Introduction to Ceramics, 2nd ed., (1976).

5 Wicks, G.G., "Structure of Glasses", in Encyclopedia of Materials Science and Engineering, Vol. 3, p. 2020, Pergamon (1986)

6 Tomozawa, M., Singer, G.M, Oka, Y., and Warden, J.T., in Ceramics in Nuclear Waste Management (T.D. Chikalla and J.E. Mendel, ed.) CONF-790420, p. 193 (1979).

7 Turcotte, R.P. and Wald, J.W. in Scientific Basis for Nuclear Waste Management (C. Northrup ed.), Vol. 2, p. 141 (1980).

8 Bickford, D.F. and Jantzen, C.M., in Scientific Basis for Nuclear Waste Management VII (G.L. McVay ed.), Vol. 26, p. 557 (1984).

9 Smith, T.H and Ross, W.A., "Impact Testing of Simulated HLW in Canisters", BNWL-1903, Pacific Northwest Laboratory (1975).

10 Perez, J.M. and Westsik, J.H. "Effects of Cracks on Glass Leaching", ORNL Conference on Leachability of Radioactive Solids, p. 35 (1980).

11 Weber, W.J. and Roberts, F.P., Nucl. Tech. 60: p. 178 (1983).

12 Matzke, Hj. and vanGeel, J., in Disposal of Weapon Plutonium (E.R. Merz and C.E. Walter, NATO Series1: Disarmament Technologies, 4, p.93 (1996).
13 Bibler, N.E., in Scientific Basis for Nuclear Waste Management (S.V. Topp ed.), Vol. 6, p. 681 (1982).
14 T. McMenamin ed., Testing of HLW Forms Under Repository Conditions, Commission of European Communities, EUR 12 017 EN (1989).
15 T. McMenamin ed., In-Situ Testing of Radioactive Waste Forms and Engineered Barriers, Commission of European Communities, (1992).
16 Wicks, G.G. and Molecke, M.A., in Advances in Ceramics (G.B. Mellinger ed.), Vol. 39, p. 383, Am. Cer. Soc. (1994).
17 Williams, J.P., Wicks, G.G., Clark D.E., and Lodding, A.R., in Ceramic Transactions, Nuclear Waste Management IV, (G.G. Wicks, D.F. Bickford and L.R. Bunnell, eds.), Vol. 23, pp. 663-674 (1991).
18 Namboodri, C.G. Jr., S.L. Namboodri, Wicks, G.G., Lodding, A.R., Hench, L.L., Clark D.E., and Newton, R.G., in Ceramic Transactions, Nuclear Waste Management IV, (G.G. Wicks, D.F. Bickford and L.R. Bunnell, eds.), Vol. 23, pp. 653-662 (1991).
19 Schulz, R.L., Clark, D.E., Wicks, G.G., Lodding, A.R. and Van Iseghem, P., to be published in Advances in Ceramics (1998).
20 Wicks, G.G., McKibben, J.M., Plodinec, M.J. and Ramsey, W.G., in Disposal of Weapon Plutonium (E.R. Merz and C.E. Walter, NATO Series 1: Disarmament Technologies, Vol. 4, p.93 (1996).
21 Vernaz, E.Y., in "Glass as a Waste Form and Vitrification Technology", National Research Council Workshop, p. E26 (1996).
22 Clark, D.E., Pantano, C.G., and Hench, L.L., Corrosion of Glass, Books for Industry (1979).
23 Wicks, G.G., "Nuclear Waste Glasses: Corrosion Behavior and Field Tests", in Corrosion of Glass, Ceramics and Ceramic Superconductors (D.E. Clark and B.K Zoitos, eds.), p.218 (1992).
24 Hench, L.L., G.G., "Surface Modificaton of Bioactive Glasses and Ceramics", in Corrosion of Glass, Ceramics and Ceramic Superconductors (D.E. Clark and B.K Zoitos, eds.), p.298 (1992).
25 Wicks, G.G. and Wallace, R.M., in Scientific Basis for Nuclear Waste Management VI (D.C. Brookins ed.), Vol. 15, p. 23 (1983).
26 Pescatore, C. and Machiels, A.J., in Advances in Ceramics (G.G. Wicks and W.A. Ross ed.), Vol. 8, p. 508, Am. Cer. Soc. (1984).
27 Chamber, P.L., Kang, C.H., Dim, C.L. and Pigford, T.H., in Scientific Basis for Nuclear Waste Management XI (M.J. Apted and R.E. Westerman ed.), Vol. 112, p. 285 (1987).
28 Grambow, B., Lutze, W., Ewing, R.C. and Werme, L.O., in Scientific Basis for Nuclear Waste Management XI (M.J. Apted and R.E. Westerman ed.), Vol. 112, p. 531 (1987).

29 Plodinec, M.J., Jantzen, C.M. and Wicks, G.G., in Advances in Ceramics (G.G. Wicks and W.A. Ross ed.), Vol. 8, p. 491, Am. Cer. Soc. (1984).
30 Bourcier, W.L., in "Glass as a Waste Form and Vitrification Technology", National Research Council Workshop, p. E26 (1996).