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by
G. G. Wicks
Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

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

INTRODUCTION

As a result of more than three decades of international research, glass has emerged as the material of choice for immobilization of a wide range of potentially hazardous radioactive and non-radioactive materials. 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.

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].

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, as well as possible immobilization of weapons grade plutonium resulting from disarmament activities. 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 [3].

WASTE GLASS STRUCTURE

For immobilization of HLW, borosilicate glass systems are preferred by most countries. 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 premelted glass or frit prior to waste glass melting operations, which produce solidified radioactive products [4]. 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* [5].

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 [6].

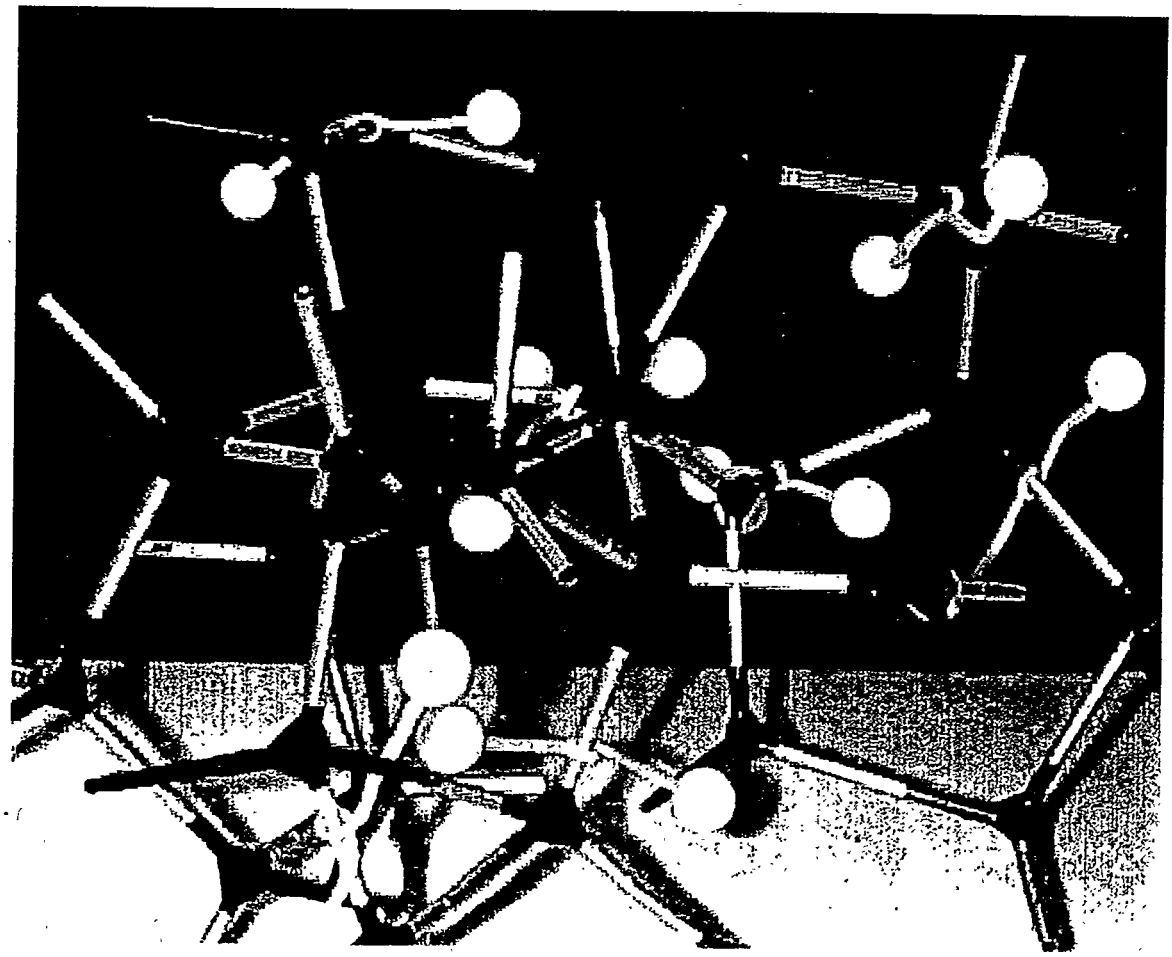

Figure 1. Simplified Random Network Structure of Nuclear Waste Glasses

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. France as been a leader in this area with 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.

• 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]. The glass structure is not only able to incorporate and immobilize the many different species that comprise HLW compositions, but also provides a very forgiving matrix which is able to also accommodate large variations in composition of HLW as well as many other waste streams.

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 [7]. Many different studies have been performed to assess the effects of these structural and chemical changes on the performance of the product [8]. In one series of studies, Savannah River Site waste glass was purposely devitrified [9], 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. This has also been recently shown in other systems, including Pu-based glasses.

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 [10, 11]. 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 [12-14]. 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 as well as Pu glass systems. In HLW experiments performed on Savannah River Site waste glass doped internally with curium-244, an intense alpha emitter considered by many to be the most potentially detrimental radiation effect, only very minor effects were noted [15]. The glass remained intact after being subjected to these extreme conditions and its leaching rate, even with this very high radiation field, was seen to be within a factor two of the undoped glass. The amount of radiation received by the glass sample in these tests was equivalent to the radiation that would be accumulated after more than one million years of storage.

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. No where 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 actually improves 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 [16-21].

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 hypothesis has been confirmed for a special group of borosilicate Pu-glasses known as Loffler compositions. These waste glasses have exhibited more than an order of magnitude improvement in durability compared to HLW glasses [22, 23].

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 [24]. 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 glass forms should be extremely good when subjected to realistic values of these parameters.

There are a number of models that have been developed to explain waste glass leaching behavior. In one approach, a 3-stage corrosion process based on glass structural changes has been postulated for nuclear waste glasses involving interdiffusion, matrix dissolution and surface layer formation [25]. This concept and other detailed models are described elsewhere [26-31].

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 in actual field experiments conducted with simulated HLW glasses buried in Sweden, Belgium, England and the United States.

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