This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

WSRC-MS-2004-00688, Rev. 0
Radioactive waste, hazardous waste, waste minimization, glass, vitrification

GLASS – AN ENVIRONMENTAL PROTECTOR

by

James C. Marra
Carol M. Jantzen
Savannah River National Laboratory
Westinghouse Savannah River Co.
Aiken, SC 29808

A paper proposed for publication in the American Ceramic Society Bulletin
November, 2004

WSRC-MS-2004-00688, Rev. 0

GLASS – AN ENVIRONMENTAL PROTECTOR

James C. Marra and Carol M. Jantzen
Savannah River National Laboratory
Westinghouse Savannah River Co.
Aiken, South Carolina 29808

ABSTRACT

From asbestos abatement to lead paint removal to nuclear waste stabilization and even to heavy metal removal using microorganisms, glass has great potential as a solution to many environmental problems. The ability to accommodate an array of chemical elements within the glass structure has facilitated the use of glass as a medium for the stabilization of numerous hazardous substances. The resulting glasses have proven to be durable enough for direct land disposal. In many cases, the stabilized forms have been deemed suitable for re-use in other applications. As recycling and hazardous material treatment become even more important in the global materials cycle, it is a certainty that glass will assume a prominent role.

THE GLOBAL MATERIALS CYCLE

Raw materials taken from the earth to produce a variety of products and processes must be disposed of safely back into the earth once declared a waste (Figure 1). The only other option is to recycle into new products or new end uses. Technologies have been developed around the world to convert a wide variety of hazardous and/or radioactive wastes to a solid stabilized product via the process of vitrification. The vitrification technology has been shown to render hazardous wastes to be non-hazardous and/or into recyclable products or reusable raw materials.

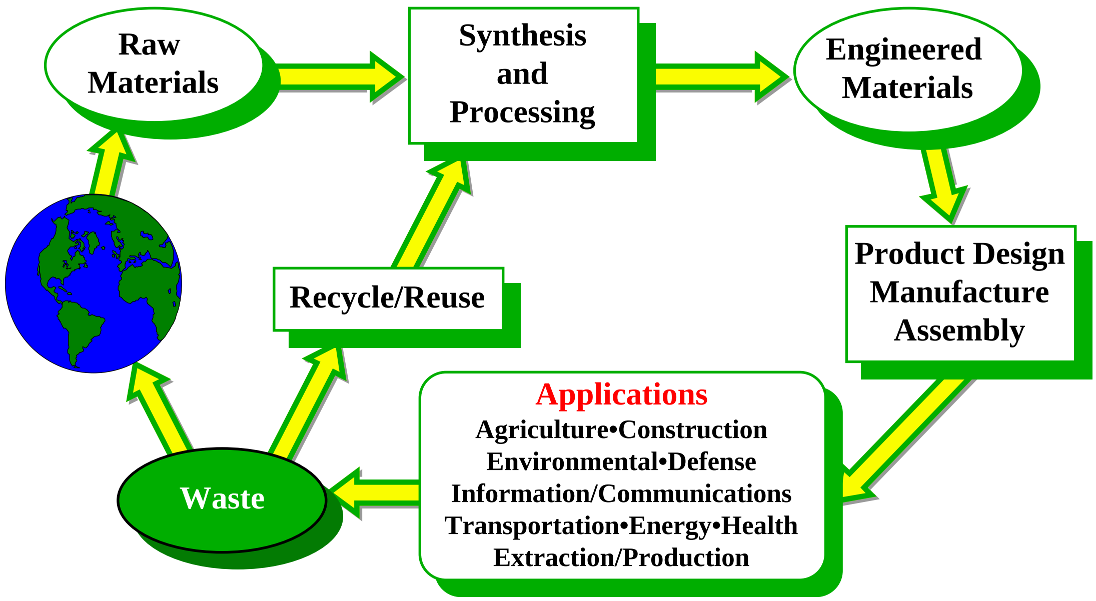


Figure 1. The global materials cycle.

If a waste cannot be recycled due to its hazardous content then it must be safely disposed of back into the earth (Figure 1). Stabilizing such wastes into glass by fusing the waste with glass forming oxides (e.g. SiO_2, B_2O_3, P_2O_5) at elevated temperatures atomistically bonds the hazardous and/or radioactive species in the solid glassy matrix ensuring safe disposal for thousands of years. In addition, large volume reductions (up to 97%) allow for large associated cost savings for such wastes during interim storage, shipping, and/or long term permanent disposal.

An even more exciting prospect is the re-use or recycling of these stabilized hazardous wastes. Re-use or recycling of wastes is an attractive option if it is deemed to be cost effective. In the United States recycling of many materials has not yet become the cost effective alternative. However, as landfill disposal costs rise, recycling and re-use will become more important.

WHY VITRIFY?

Vitrification of hazardous wastes into glass is an attractive option because it atomistically bonds the species in a solid glassy matrix. Glass is also able to accommodate a vast array of elements within the glass structure making vitrification a very flexible technology. Figure 2 depicts waste elements that have been incorporated into glass.

Since hazardous constituents are atomistically bonded within the glass structure, the waste forms produced are very durable and environmentally stable over long time durations. The Environmental Protection Agency (EPA) has declared vitrification the Best Demonstrated Available Technology (BDAT) for high-level radioactive waste (HLW) [1] and produced a Handbook of Vitrification Technologies for Treatment of Hazardous and Radioactive Waste [2].

Vitrification produces large waste volume reductions, e.g. up to 97% [3], using cheap sources of glass former, e.g. sand, soil, crushed scrap fluorescent bulbs, crushed reagent bottles, etc. Figure 3 depicts the volume reduction that would be obtained when nickel plating line wastes were vitrified as opposed to grouted [4-6]. Large reductions in

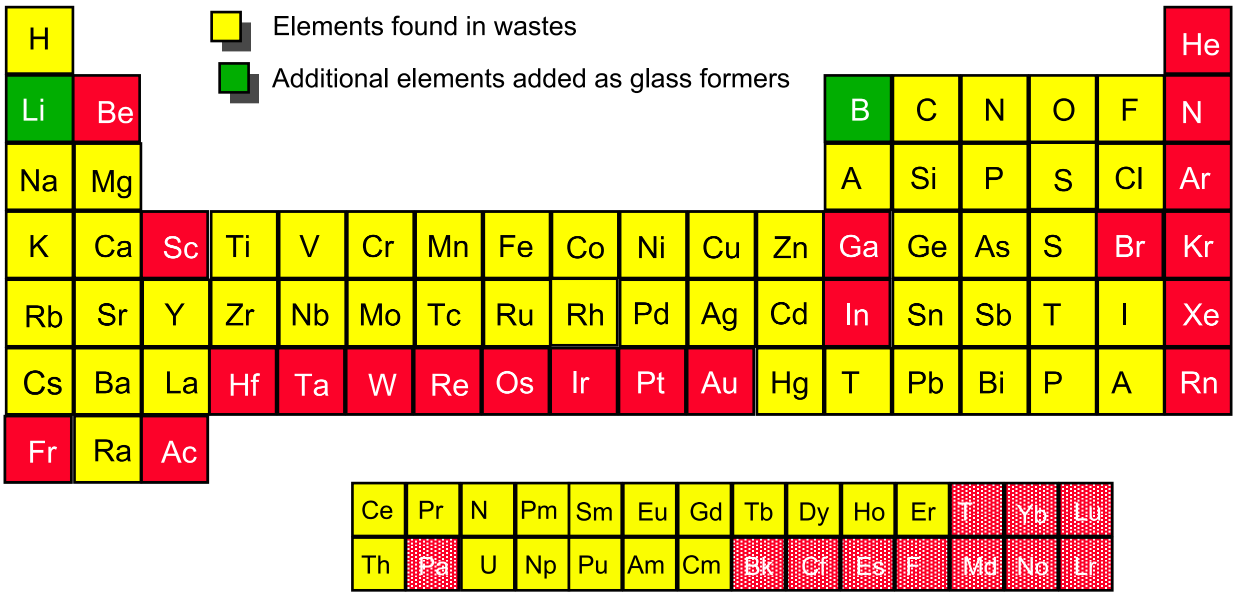
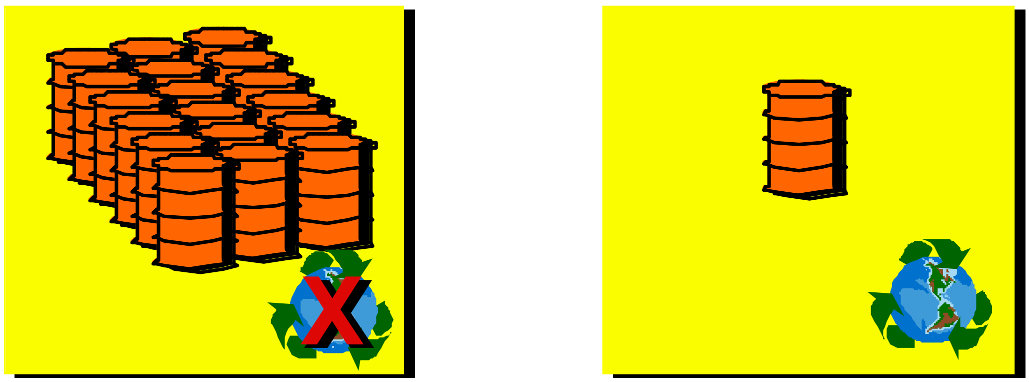


Figure 2. Waste elements that have been accommodated in glass structures.

volume minimize long-term storage/disposal costs if the waste cannot be recycled. Often the alternative stabilization technologies such as cement stabilization cannot produce a waste form that is durable enough, e.g. cement does not thermally decompose the EPA Resource Conservation and Recovery Act (RCRA) hazardous organics and the porosity often allows the RCRA inorganic species to leach at greater than acceptable limits. Therefore, alternative stabilization technologies often cannot produce a waste form that can be recycled (Figure 3).

18 Drums (55 gallon) of cement vs. 1 Drums (55 gallon) of glass



1,440,000 (55 gallon) drums/year cement | **7930 (55 gallon) drums/year glass**

Figure 3. Ninety four percent (94%) volume reduction for nickel plating line wastes vitrified at a conservative waste loading of 35wt% compared to alternative stabilization in cement. Only 1 drum of glass which can be recycled instead of 18 drums of cement which cannot be recycled.

WHAT KIND OF WASTES CAN BE VITRIFIED?

In recent years researchers around the world have looked at the treatment of hazardous and radioactive wastes through vitrification. The following is a sampling of the myriad of wastes where glass has been demonstrated as an effective treatment option:

- industrial wastes
- spent filter aids from waste water treatment
- waste sludges and/or liquid supernates including EPA hazardous sludges from harbors
- mining industry wastes, sludges, and/or mill tailings
- incinerator ash, incinerator off-gas blowdown, or combinations of the two
- cathode ray tube (CRT) recycle
- lead paint
- cement formulations in need of remediation
- ion exchange resins and zeolites
- asbestos containing material (ACM) or inorganic fiber filter media
- radioactive wastes from nuclear fuel processing
- transuranic (TRU), plutonium (Pu), and other actinide materials

The highlighted areas have recently received significant interest and several case studies will be summarized in more detail.

<u>Industrial Wastes</u>

Vitrification of industrial wastes provides an attractive alternative to waste treatment or landfilling. Components in these wastes facilitate the formation of glass and, therefore, allows for high waste loadings. Previous work by Blume and Drummond showed that EPA-listed hazardous wastes composed of foundry sand and electric arc furnace dust could be readily immobilized in glass or glass ceramics [7]. The glass ceramics were especially attractive since the resulting product was primarily spinel with a high Vickers hardness and could be used in high-grade abrasive applications. Approval was granted from the California Environmental Protection's Department of Toxic Substance Control (DTSC) for production of recyclable materials from these wastes [8].

Researchers in Italy have investigated the vitrification of high iron content wastes from metallurgical processes [9]. Two waste streams were examined: sludge from a zinc hydro-metallurgical process; and electric arc furnace dust from steelmaking. By adjusting the Fe^{3+}/Fe^{2+} ratio through the controlled addition of a reductant, the researchers found that the resulting product could be an amporphous glass or a glass ceramic (primarily spinel). This allows for the tailoring the waste form which is especially attractive if recycling is pursued.

Collaborative work by researchers in Italy and Spain has focused on formulating glass and glass ceramics from coal fly ash and incinerator slag. In one of the efforts, the crystallization behavior of formulations in the CaO-Al_2O_3-SiO_2 system derived from fly ash and slag was evaluated [10]. Aluminosilicate and silicate glass-ceramics with were readily obtained through the controlled devitrification of the glasses. In another effort, actual fly ash from a Spanish thermal power plant (As Pontes, Galicia) was used to produce glasses and glass-ceramics [11]. Two families of glass formulations in the CaO-Al_2O_3-SiO_2 system were evaluated for their glass forming and crystallization tendencies. One family (higher CaO content) exhibited more stable devitrification behavior and tended to form wollastonite crystals upon controlled thermal treatment. The second family (higher iron oxide content) tended to form glass ceramics with pyroxene and anorthite crystals.

Researchers in Spain recently demonstrated that recycled glass ceramics could be effectively made and then used for further waste treatment [12]. They fabricated glass ceramic Raschig rings using industrial and urban wastes consisting of glass bottles, pieces of animal bones, diatomite soil waste from the brewing industry and sludge from the pulp and paper industry. Biofilms of microorganisms were then developed on the surface of the Raschig rings. The effectiveness of this product to remove cadmium and lead from an aqueous solution was then evaluated and the results were very promising. The microorganisms were very effective in removing the heavy metals from the solution. Moreover, the glass ceramic performed well as a host for the biofilm but also was found to retain heavy metals by itself.

Cathode Ray Tube (CRT) Recycle

As television and computer technologies continue to improve at a dramatic pace, millions of older televisions and CRT monitors are destined for the trash. The problem has become so large that some states have now put limits on disposal of televisions and CRTs in landfills. Massachusetts, for instance, has completely precluded disposal of these items in state landfills [13]. Residents in Massachusetts must now work with their local municipalities and/or commercial entities to legally dispose of these items. Although a recognized current and future problem, recycling of televisions and CRTs is not yet commonplace in the United States.

The recycling of televisions and CRTs, however, has received some attention in Europe. It was determined that up to 65% of recycled television screen cullet can be applied without quality losses in screen glass tanks [14]. At higher loadings glass fining became problematic since the batch lacked sufficient fining agent (Sb_2O_5). The cullet contained antimony primarily in the +3 oxidation state.

Mining Industry Wastes and Harbor Sludge

Wastes emanating from the mining industry also represent a significant environmental challenge both in the mining and refining operations. Vitrification was evaluated as a means to immobilize waste water treatment sludge and mill tailings from mining operations that failed the U.S. EPA characteristic hazardous leaching limits for cadmium [4]. The use of a cement waste form was the current treatment route. While the cement product passed the characteristic hazardous leaching limit for Cd, little or no volume reduction was obtained by grouting the waste and there was always a legal liability regarding disposal. The soda lime silica glass system was found to readily stabilize the mining waste and rendered it recyclable, thus, eliminating the legal liability associated with disposal. Homogenous glasses were formed with volume reductions up to 93%.

Researchers working jointly in Mexico and Russia evaluated using glass and glass ceramics for the treatment of wastes from ore refining [15]. The targeted wastes were from iron ore and titanic-zircon ore refining with the resulting waste being rich in quartz-feldspar. The high alkali contents in the quartz-feldspar wastes allowed glasses to be melted rapidly. Furthermore, the addition of acidic metallurgy slag rich in iron and phosphorous fertilizer production waste facilitated crystallization and the formation of a glass ceramic product.

Sludge from harbors needs to be routinely dredged to maintain navigability. Routinely, the sludge is dredged and then placed back into the ocean at an off-shore location. Evaluation of dredged New York harbor sludge indicated the presence of hazardous organic substances and heavy metals. Vitrification was found to be a viable means to immobilize the harbor sediment and render it non-hazardous [16]. Sludge loadings of 85 wt % were demonstrated. Furthermore, recycling into products such as fill for asphalt roadways was also examined and deemed practical.

Lead Paint

Red lead primer has been used extensively on many steel structures to control corrosion. The use of lead paint is a widespread problem throughout the world and it has been specifically singled out as an environmental issue within the United States Department of Defense (DOD) [17, 18]. Lead paint has been widely used by DOD on bridges, aircraft hangars, water storage tanks, metal buildings, fire hydrants, and structural steel components. A thermal spray vitrification (TSV) process was patented at the U.S. Army Corps of Engineers –Construction Engineering Laboratory (CERL) to remove and stabilize the lead paint on steel structures. In this process, molten glass is sprayed on the surface using a thermal spray “gun” (Figure 4) [17, 18]. The hot glass vaporized the organics and causes peeling of the paint and the glass from the surface due to thermal stresses upon cooling. The waste is collected and further melted to incorporate the hazardous species into the glass structure to allow for disposal as a non-hazardous waste. One of the key attributes of this technology is the comparatively low worker exposure compared to typical sand blasting techniques. A glass composition was developed for use in the TSV process that accommodated high Pb loadings and resulted in a glass product that passed the characteristically hazardous release limit [17-23]. The glass formulation also effectively stabilized other hazardous constituents potentially present in the paint including chromium and cadmium.

Several field tests and actual treatments have been conducted using the TSV technology. Field tests have been conducted on a bridge (Rock Island Bridge Demonstration, Rock Island Arsenal, IL) and on an aircraft hangar door (Marine Corps Base Kaneohe Bay, HI) [19]. In both cases, all test objectives were met including producing a product that passed EPA regulatory leach limits. Successful demonstrations were also conducted on fire hydrants at Fort Drum Army Base, NY and Tyndall Air Force Base, FL [17, 18]. In these trials, paint removal and lead stabilization were successful and the economics for treating the hydrants were also favorable. In fact, the technology has now been used on over 300 hydrants at Tyndall Air Force base.

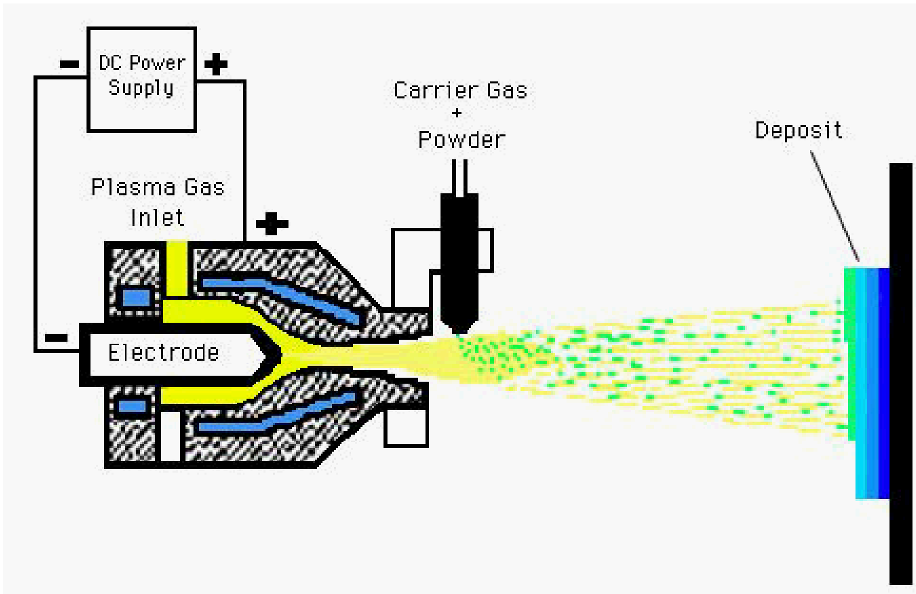


Figure 4. In thermal spray vitrification (TSV) a high temperature plasma carries a mixture of crushed glass powder and a carrier gas in a hot flame. The molten glass impinges on the contaminated or painted metal substrate. The high temperature vaporizes the organics in the paint and atomistically bonds the hazardous species (Pb in the case of paint wastes) in the glass. As the glass cools the thermal mismatch between the glass and the metal substrate causes the glass to crack off the substrate. The glass can then be swept up or vacuumed up for disposal or recycle.

Asbestos Containing Materials

The current practice for disposal of asbestos containing materials (ACM) involves sealing of water wetted asbestos in plastic for safe transportation and disposal in regulated landfills. The "wrap and bury" technology results in large waste volumes and precludes any recycle of the asbestos (or pipe and other framework associated with the asbestos). Glass formulations were developed to stabilize asbestos and filler materials (plaster of paris, gypsum, etc.) associated with ACM wastes [24]. Palex glasses (alkali magnesium silicate glasses) were shown to be tolerant of the high magnesium and calcium contents from the filler materials [24]. Vitrification of ACM destroys the asbestos fibers and renders the asbestos non-hazardous resulting in a glass or glass ceramic suitable for reuse. Further more, a hot caustic bath process was developed and patented to safely remove ACM from metal pipes and structures [24-25] not only facilitating recycle of the asbestos but also of the metallic components.

Radioactive Waste Management

No survey of glass as an environmental treatment medium would be complete without discussing the role of glass in the stabilization of radioactive wastes. As mentioned, glass is the recognized BDAT for the treatment of HLW and vitrification has been employed in the United States, United Kingdom, France, Germany, Belgium, Japan and Russia for the treatment of HLW. Major efforts are ongoing in the United States at the West Valley Demonstration Project (WVDP) (West Valley, NY), Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) (Aiken, SC), and the Waste Treatment Plant (WTP) at the Hanford Site (Richland, WA) to vitrify HLW.

The WVDP performed a vitrification campaign from June 1996 through September 2002 to immobilize HLW resulting from commercial fuel reprocessing activities in the 1960s and 1970s [26]. Over 1.2 million pounds of HLW glass was produced over the six years of radioactive operation. The glass melter was drained and shutdown and final cleanup activities are underway at WVDP.

The DWPF commenced radioactive operations in May 1996 to treat the approximate 34 million gallons of HLW at the SRS [27]. Constant operations have continued through the present with the only extended outage (about six months) occurring in 2003 to replace the Joule heated refractory lined melter. To date over 6 million pounds of HLW glass have been produced.

Construction is underway at WTP with radioactive operations scheduled to begin around the end of the decade. According to the planned flowsheet, the wastes will be separated into high-level and low-activity waste fractions with both fractions slated for treatment by vitrification [28]. Approximately 50 million gallons of waste are slated for treatment at the Hanford Site.

CONCLUSIONS

Glass and glass ceramics are viable options for the treatment and stabilization of many hazardous wastes and have been demonstrated to effectively immobilize radioactive wastes. The potential for recycling and reuse of the waste products makes the use of glass especially attractive. A wide variety of waste types have been successfully stabilized using the robust vitrification technology. Currently, vitrification technology is used extensively in the treatment of certain wastes (e.g. radioactive wastes). As economic drivers make direct disposal of wastes impractical, glass and glass ceramic materials will likely become attractive alternatives. The ability to treat a variety of wastes, incorporate the waste species within the glass structure, and allow for reuse of the waste products truly makes GLASS – AN ENVIRONMENTAL PROTECTOR.

REFERENCES

1. 20. Federal Register, "Land Disposal Restrictions for Third Third Scheduled Wastes, Final Rule," 55 FR22627 (June 1, 1990).

2. U.S. Environmental Protection Agency, "Handbook: Vitrification Technologies for Treatment of Hazardous and Radioactive Waste," EPA/625/R-92/002 (May, 1992).

3. C. M. Jantzen, J. B. Pickett, and W. G. Ramsey, "Reactive Additive Stabilization Process (RASP) for Hazardous and Mixed Waste Vitrification," Proceed. Second Inter. Symp. on Mixed Waste, A.A. Moghissi, R.K. Blauvelt, G.A. Benda, and N.E. Rothermich (Eds.), Am. Soc. Mech. Eng., p.4.2.1 to 4.2.13 (1993).

4. C. M. Jantzen, R. F. Schumacher, and J. B. Pickett, "Mining Industry Waste Remediated for Recycle by Vitrification," Environmental Issues and Waste Management Technologies VI, D.R. Spearing, G.L. Smith, and R.L. Putnam (Eds.), Ceramic Transactions, v.119, 65-74 (2001).

5. C. M. Jantzen, J. B. Pickett, W. G. Ramsey, D. C. and Beam, "Treatability Studies on Mixed (Radioactive and Hazardous) M-Area F006 Waste Sludge: Vitrification Via the Reactive Additive Stabilization Process (RASP)," Proceedings of Spectrum 94 Nuclear and Hazardous Waste Management International Topical Meeting, Am. Nuclear Soc., 737-742 (1994).

6. C. M. Jantzen, J. B. Pickett, and H. L. Martin, "Method for Treating Materials for Solidification (RASP)," U. S. Patent 5,434,333, July, 1995.

7. R. D. Blume and C. H. Drummond III, "High-Grade Abrasive Product Development from Vitrified Industrial Waste," Environmental Issues and Waste Management Technologies II, V. Jain and D. Peeler (Eds.), Ceramic Transactions, v.72, 229-239 (1996).

8. Seiler Pollution Control Systems Inc., "California Environmental Agency Approves Recycling Status for Seiler Vitrification System," Press Release, Dublin, OH, September 25, 1997.

9. A. Karamanov, P. Pisciella, C. Cantalini and M. Pelino, "Influence of Fe^{3+}/Fe^{2+} Ratio on the Crystallization of Iron-Rich Glasses Made with Industrial Wastes," J. Am. Ceram. Soc., 83 [12], 3153-3157 (2000).

10. L. Barbieri, A. M. Ferrari, I. Lancellotti, C. Leonelli, J. Ma. Rincon and M. Romero, "Crystallization of (Na_2O-MgO)-CaO-Al_2O_3-SiO_2 Glassy Systems Formulated from Waste Products," J. Am. Ceram. Soc., 83 [10], 2515-2520 (2000).

11. L. Barbieri, I. Lancellotti, T. Manfredini, G. C. Pellacani, J. Ma. Rincon and M. Romero, "Nucleation and Crystallization of New Glasses from Fly Ash Originating from the Thermal Power Plants," J. Am. Ceram. Soc., 84 [8], 1851-1858 (2001).

12. A. M. Garcia, J. M. Villora, D. A. Moreno, C. Ranninger, P. Callejas and M. F. Barba, "Heavy Metal Bioremediation from Polluted Water by Glass-Ceramic Materials," J. Am. Ceram. Soc., 86 [12], 2200-2202, (2003).

13. "Fact Sheet: Computer Monitors and Televisions Disposal Options for Residents and Small Businesses," Massachusetts Department of Environmental Protection, Boston, MA, September 2003.

14. R. G. C. Beerkens, A. J. Faber and J. G. J. Peelen, "Recycled Cullet – Important Raw Material for Europe,"the GlassResearcher, Vol. 4, No. 1, 1994.

15. A. Gorokhovsky, J. I. Escalente-Garcia, V. Gorokhovsky and D. Mescheryakov, Inorganic Wastes in the Manufacture of Glass and Glass-Ceramics: Quartz-Feldspar Waste of Ore Refining, Metallurgical Slag, Limestone Dust, and Phosphorus Slurry," J. Am. Ceram. Soc., 85 [1], 285-287 (2002).

16. J. C. Marra, "Glass Composition Development for Stabilization of New York Harbor Sediment," WSRC-TR-96-0038, Westinghouse Savannah River Company, Aiken, SC, 1996.

17. R. A. Weber, J. Boy, R Zatorski and A. Kumar, "Demonstration and Validation of Thermal Spray Vitrification of Lead-Containing Paint on Steel Structures," U. S. Army Corps of Engineers Construction Engineering Research Laboratory, CERL TR 99/61 (1999).

18. A. Kumar, R. Zatorski, R. Weber and L. D. Stephenson, "Technology Demonstration of Thermal Spray Vitrification Process at Fort Drum, NY," U. S. Army Corps of Engineers Construction Engineering Research Laboratory, ERDC/CERL TR-03-4, (2003).

19. J. C. Marra, A. Kumar, J. H. Boy, and J. L. Lattimore, "Glass Composition Development for a Thermal Spray Vitrification Process," Environmental Issues and Waste Management Technologies II, V.J. Jain and D.K. Peeler (Eds.), Ceramic Transactions, v.72, 419-426 (1996).

20. C. M. Jantzen, J. C. Marra, J. B. Pickett and C. C. Herman, "Low Melting High Lithia Glass Compositions and Methods (LAMP)", U. S. Patent 6,145,343, November 14, 2000.

21. C. M. Jantzen, J. C. Marra, J. B. Pickett and C. C. Herman, "Methods of Vitrifying Waste with Low Melting High Lithia Glass Compositions (LAMP)" U. S. Patent 6,258,994 B1, July 10, 2001.

22. C. M. Jantzen, J. C. Marra, J. B. Pickett and C. C. Herman, "Low Melting High Lithia Glass Compositions and Methods (LAMP)," U. S. Patent 6,624,103 B2, September 23, 2003.

23. C. M. Jantzen, J. C. Marra, J. B. Pickett and C. C. Herman, "Low Melting High Lithia Glass Compositions and Methods (LAMP)," U. S. Patent 6,630,419, October 7, 2003.

24. C.M. Jantzen and J.B. Pickett, "How to Recycle Asbestos Containing Materials (ACM) by Vitrification," Environmental Issues and Waste Management Technologies VI, D.R. Spearing, G.L. Smith, and R.L. Putnam (Eds.), Ceramic Transactions, v.119, 75-84 (2001).

25. C. M. Jantzen, "Method for Dissolution and Stabilization of Silica-Rich Fibers," U. S. Patent 5,686,365, November, 1997.

26. R. A. Palmer, H. M. Houston and A. J. Misercola, "Completion of the Vitrification Campaign at the West Valley Demonstration Project," Environmental Issues and Waste Management Technologies IX, J. D. Vienna and D. R.L. Spearing (Eds.), Ceramic Transactions, v.155, 179-196 (2004).

27. S. L. Marra, J. T. Gee and J. F. Sproull, "The Defense Waste Processing Facility: Two Years of Radioactive Operation," Environmental Issues and Waste Management Technologies IV, J. C. Marra and G. T. Chandler (Eds.), Ceramic Transactions, v.93, 147-154 (1999).

28. D. B. Blumenkranz, S. Kelly, D. J. Swanberg and C. A. Musick, "Testing to Demonstrate Regulatory Compliance of Glass Waste Forms for Immobilization of Radioactive Wastes at the Hanford Site," Environmental Issues and Waste Management Technologies IX, J. D. Vienna and D. R.L. Spearing (Eds.), Ceramic Transactions, v.155, 227-237 (2004).