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Vitrification of the borate waste surrogate using fly ash as an additive

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ABSTRACT

Borate waste is the main waste from nuclear power plants. Glass is an acceptable waste form because of its ability to accept a wide range of components into its network structure. Vitrification of borate waste from nuclear power plants is an attractive approach from the viewpoint of environment and safety. Fly ash is a headache waste generated from the coal combustion power stations. Fly ash contains high contents of SiO_2 and Al_2O_3, which are also the most important glass structure formers. This project takes fly ash as a main additive to vitrify borate waste. Na_2O, the only non-waste additive was added, in order to decrease the melting temperature. The experimental results indicate that glasses with ~ 60 wt% of fly ash, ~ 30 wt% of borate waste, and ~ 10 wt% of Na_2O have good chemical durability and good processability. This approach not only obtained the minimum cost, but also find a treatment method for the industrial waste.

INTRODUCTION

The treatment and disposal of the low level radioactive wastes (LLW) is increasingly becoming a major operating expense to nuclear power plants (NPPs). Volume reduction has become one of the most important issues of radioactive waste management around the world, because the cost of waste storage and disposal has increased very fast. There have been developed many kinds of volume reduction technologies for LLW treatment. Vitrification is considered as an attractive technology because of the large volume reduction, good durability of waste form and the complete destruction of organic compounds.[1] Vitrification has been chosen by the US EPA as the Best Demonstrated Available Technology (BDAT) for the stabilization of high level radioactive wastes (HLW). Thus, vitrification is a logical choice for the stabilization of LLW.[2,3] Korea, stemming from an economical and technical feasibility study, has shown interest in using vitrification as a means of treating LLW produced from her NPPs. [4,5]

Borate waste, arising from the operation of nuclear power plants, is the main wet waste. Yearly volume generation of borate waste in Korean NPPs is $80m^3$ ($2 \times$ 1,000MWe PWR).[4] It is commonly converted to solid state by cementation in many plants. [6] In Korean NPPs, borate waste now is dried and then mixed with paraffin. However, the cement and paraffin solidification are not ideal from the viewpoint of economy (volume increasing) and ecology (low chemical durability). Some research has been focused on the borate waste vitrification, the results show that vitrification is satisfacotory for treatment of boarte waste from NPPs.[6] Korea has decided to use vitrification technology to treat borate waste, which could achieve high volume reduction.

Fly ash is a by-product of coal combustion in electricity generating power stations. It is captured from the exhaust gases of the plants by electrostatic precipitators or bag houses which leave relatively clean air to escape from the smoke stacks. Physically, it is a very fine powder, predominately silica, with particles almost totally spherical in shape. Fly ash would pollute the environment and it is a headache problem in plants. Currently, only a small part of the fly ash is utilized, mainly in the cement industry. The remaining amounts of fly ash are used for landfilling, which is an unsatisfactory solution both from an ecological and economical point of view. Other more efficient uses of flyash have been proposed in the last 40 years, however, the amount of utilized fly ash is still very low and consequently new forms for its utilization as a raw material resource are continually sought. [7]

An innovative vitrification approach known as Minimum Additive Waste Stabilization (MAWS) has been developed since early of 1990s.[8] In the MAWS approach, the waste streams are utilized as resources for the glass-making process, and multiple waste streams are blended to minimize the need for purchased additives. The goal of the MAWS approach is to achieve maximum reduction in waste volume and maximum cost saving by the use of little or no non-waste additives. This is an economical and environmental concept. MAWS is very useful for low- and mid-level radioactive waste vitrification; because such waste usually contains components that are also the main composition of glass, then high waste loading can be achieved. MAWS was developed in order to treat U.S. DOE wastes (e.g., sludge, incinerator ash, soil concentrates), up to 93 wt% of waste loading has been achieved while producing quality glass. Borate waste has high B content, and does not contain suitable glass former. In order to vitrify borate waste, some glass formers such as SiO_2 and Al_2O_3 should be added. Fly ash contain high content of SiO_2 and Al_2O_3, which are best glass formers. It is reasonable to mix this two wastes and produce suitable glass. Korea Atomic Energy Research Institute (KAERI) has studied the application of fly ash to the vitrification of the simulated OREOX (Oxidation and Reduction of Oxide fuel) process wastes. [9] The simulated OREOX wastes include the scrap waste (mainly of U_3O_8) and spent filter. Borosilicate glass containing up to 65 wt% of fly ash had been obtained with the additive of Na_2O and B_2O_3. Using this base glass as a frit could solidify 30 wt% of simulated scrap waste or 30 wt% of spent filter waste and produced preferable leachability glasses.

Development of the glass formulations for a given waste stream is basically a problem in constrained multivariate optimization. The main constraints are economics, processability, and the chemical durability. Waste loading is the major factor that influences the overall economics. In this project, the waste loading is defined as the weight percent of borate waste in final glass. Maximum the waste loading will obtain the largest volume reduction. Generally, the most important requirement for the waste form is the chemical durability, since a major objective of waste solidification is to effectively isolate the radionuclides or other contaminants and to prevent their release into the environment. Viscosity of the melt plays an important role of processability. The glass formulation development is just to optimize the waste loading, viscosity, chemical durability, et al. [6, 8] This project wanted to vitrify borate waste by using fly ash as an additive, and develop glass formulations with suitable ratio of this two wastes.

ADJUSTMENT OF GLASS FORMULATION

The glass structure is usually considered as a random network.[10, 11] The elements are generally classified into three types: (1) Network forming atoms: such as Si, B, P, Ge; (2)

Network modifiers (or glass fluxes): such as Na, K, Li, Ca, Mg; (3) Intermediates: such as Al, Fe, Zn, Ti, Mo, et al. The concept of using glass as a host for radioactive waste is based upon the radionuclides entering into and becoming part of the random network.

There has been much research focus on the composition-durability relationships of glass. A great deal of information is available in simple systems, but, unfortunately, results from one study cannot be compared quantitatively with results from other studies because of the absence of a uniform approach for testing or measuring durability.[10, 12] Much results are qualitative. By the way, some general rules still could be obtained: (1) The components that form the strongest bonds in glasses result in the greatest improvement to glass and waste durability, whereas those that form the weakest bonds prove the greatest detriment to glass and waste glass durability; (2) Adding SiO_2, Al_2O_3, B_2O_3, ZrO_2 may improve durability; (3) Adding alkali metal oxides may decrease the durability; (4) The mole ratio between Na_2O and (Al_2O_3 + B_2O_3) of ~ 0.9 is suitable.

The glass formers are the major constituents of all waste glasses. If the inorganic oxides from the waste have insufficient glass formers to fall within an accepted glass formulation range, additional glass formers must be added through the process. Although the network modifiers (such as alkali metals) may decrease the durability, they are important to control melted glass viscosity (and electrical conductivity, et al.). The addition of fluxes to the glass melt is controlled as increased flux composition decreases glass melting temperature, glass viscosity, and leaching resistance.[13] Of the glass forming oxides, SiO_2 is the most important in glass making and used as the major ingredient in most glasses because of its good chemical durability and cheap price.

B_2O_3 is often used as an additive to silicate glasses; however, glasses composed of large amount of B_2O_3 are not chemical durable. The borate waste from Korean NPPs contains a large amount of boron, and then the waste loading is limited. The most effective glass modifier is Na_2O. It is found that the most suitable glass formulations usually contain ~ 15wt% of Na_2O. The alkali content in fly ash is very low, and in borate waste is not high. Probably some Na_2O should be added in order to obtain suitable viscosity.

FINAL WASTE FORM REQUIREMENTS

Waste loading, chemical durability, and viscosity are the most importnat properties of a waste glass form. According to the system design parameters of vitrification, such properties must meet the requirements which are discussed as follows.

Since disposal of the final stabilized waste form invariably incurs a per-unit-volume disposal cost, the volume change upon vitrification is an important economic factor. Volume reduction should be included as a performance consideration since there is an additional non-economic incentive to minimize the size and number of the disposal facilities that are required to store the treated waste. The larger waste loading results in the higher volume reduction, which will save cost. The waste loading is limited by the waste glass chemical durability and processability as well as by the solubility of the individual inorganic waste components. Viscosity of the melt is mainly dependent on the glass composition, and it also limits the waste loading. Here, the fly ash is looked as the "non-waste" additive. Waste loading of the borate waste ≥ 20 wt% is required.

Chemical durability is the most important property of the waste glass. The chemical durability is influenced by the glass composition and viscosity. In this project, a glass form is acceptable when it has the chemical durability of ML ≤ 10 g/m^2 by using M-PCT leaching test in deionized water at 70 ^oC for 7 days.

Broadly speaking, processability means that when the glass is melted at typical melter temperature (1000-1200 ^oC), its viscosity must be lower enough to extract the melt from the melter. Melting temperature here is defined as that at which the viscosity of melt equals ~ 50 poise. In order to reduce the volatility of some waste components, the melting temperature is usually lower than 1150 ^oC. However, research of HLW vitrification showed that lower melting temperature can lead to the poorer durability of glass form. [10] Viscosity is another very important property from a production viewpoint. To pour satisfactorily a glass should have a viscosity of 20 ~ 100 poise. The viscosity of molten glass would be accepted of < 100 poise at melting temperature in this project.

EXPERIMENTAL

Composition of fly ash and borate waste

The composition of fly ash is a little changable from plants to plants. The typical composition of fly ash in Korean power stations is shown in Table 1. SiO_2 and Al_2O_3 are the main components in fly ash, and they constitute about 90 wt% in fly ash.

Table 1. Typical composition of fly ash in Korean power stations

Oxides	Wt %	Oxides	wt %

SiO_2	63.49	K_2O	1.46
Al_2O_3	26.70	TiO_2	1.22
Fe_2O_3	3.09	MgO	0.88
CaO	1.98	Na_2O	0.74

The composition of borate waste from Korean NPPs is shown in Table 2. Comparing to other countries' borate waste, it has very high B content and relatively low Na content.

Table 2. Typical composition of borate waste from Korean NPPs

Components	concentration, ppm
B	20,016
Na^+	6,177
Ca^{2+}	449
Mg^{2+}	776
Cl^-	808

Glass Manufacture

According to the analysis data, this research used non-radioactive surrogate waste. Weigh and mix the chemical reagent according the designed glass compositions, then melt it in a platinum crucible at 1150 ^oC for 1.5 hours. After pouring, the glass is annealed at 520 ^oC for 1 hour.

Leaching test method

In order to quickly determine the glass chemical durability, M-PCT leaching test method was applied to assess the glass form chemical durability. [14] The glass sample is powdered in a size of 1.0 -2.0 mm. The ratio of glass sample surface to leachant volume (SA/V) is 50 m^{-1}. The material of leaching container is Teflon. Leaching temperature is 70 ^oC; leachant is deionized water, and leaching duration is 7 days. The leachate were analyzed by using inductively couple plasma spectrometry (ICP) for the concentration of several main glass components, such as Si, Na, B, Al, Ca, and Ti. The total mass loss of glass (ML), normalized elemental release rate (NL_i), and pH value of leachate can be obtained. The ML and NL_i are used to monitor the chemical durability of glass form during the glass formulation development.

The ML could be calculated as follows:

$$ML = (m_0 - m_1) / (SA) \qquad ....(1)$$

where ML is the total mass loss, ($g.m^{-2}$); m_0 is the original unleached specimen mass, (g); m_1 is the specimen mass after leaching, (g); and SA is the sample surface area, (m^2). With regard to the elemental concentration in leachate, NL_i was calculated as follows:

$$NL_i = C_i \times V / (SA \times f_i) \qquad ....(2)$$

where NL_i is the element i release rate, ($g.m^{-2}$); C_i is concentration of element i in leachate, (g/m^3); V is the volume of leachant, (m^3); and f_i is the mass fraction of element i in unleached glass.

Viscosity measurement

It is difficult and complex to measure high temperature viscosity of molten glass. Because the accurate viscosity data are not necessary, we only wanted to obtain the glasses which have low viscosity (<100 Poise). A relative method had been used to measure molten glass viscosity. This method first measured the pouring time of different standard viscosity oils from the melter, and then found the relationship between the viscosity and pouring time. According to the pouring time of glass melt, the viscosity could be obtained from the curve fit.

RESULTS

Table 3 provided the test results of some glass forms. The first three glass forms only contained fly ash and borate waste. The increasing of borate waste content would decrease the melt viscosity, and sharply decrease the chemical durability. Because these glass contained very low Na_2O, the pH value of leachate was relatively low. When the borate waste loading was higher than 30 wt%, the chemical durability was very poor. FAB-1 glass has excellent chemical durability, but it is very difficult to melt, the melting temperature is high than 1350 ^oC. From these results, it was found that the borate waste mixed with fly ash does not contain proper ratios of the materials for the formation of a good glass. It was also found that the fly ash content in a glass form should be less than 70 wt% in order to obtain a relatively low melting temperature.

Table 3. Glass formulations and test results

Glass No.	Composition, wt %			Viscosity * (poise)	ML, $g.m^{-2}$	pH
	fly ash	borate waste	Additive (Na_2O)			
FAB-1	70.00	30.00	0	500	2.86	8.6
FAB-2	60.00	40.00	0	100	39.82	8.2

FAB-3	50.00	50.00	0	30	214.2	7.8
FAB-4	60.00	30.00	10.00	30	5.47	9.3
FAB-5	65.00	30.00	5.00	50	5.07	8.9
FAB-6	65.00	25.00	10.00	50	3.37	9.1
FAB-7	75.00	12.00	13.00	100	1.26	9.3

*: viscosity was measured at 1200 ^{o}C.

In order to decrease the melting temperature, Na_2O was added as the only additive. From the test results, it was found that glass forms containing 60-65 wt% of fly ash, 25-30 wt% of borate waste, and 5-10 wt% of Na_2O could have good durability and good processability. Because of the additive of Na_2O, the pH value of leachate was increased.

Fig.1 provides the elemental release rate of glass samples. There has the same tendency of ML and NL_i except that the NL_{Fe} of sample FB-4 is a little high. B and Na are easily released from all samples.

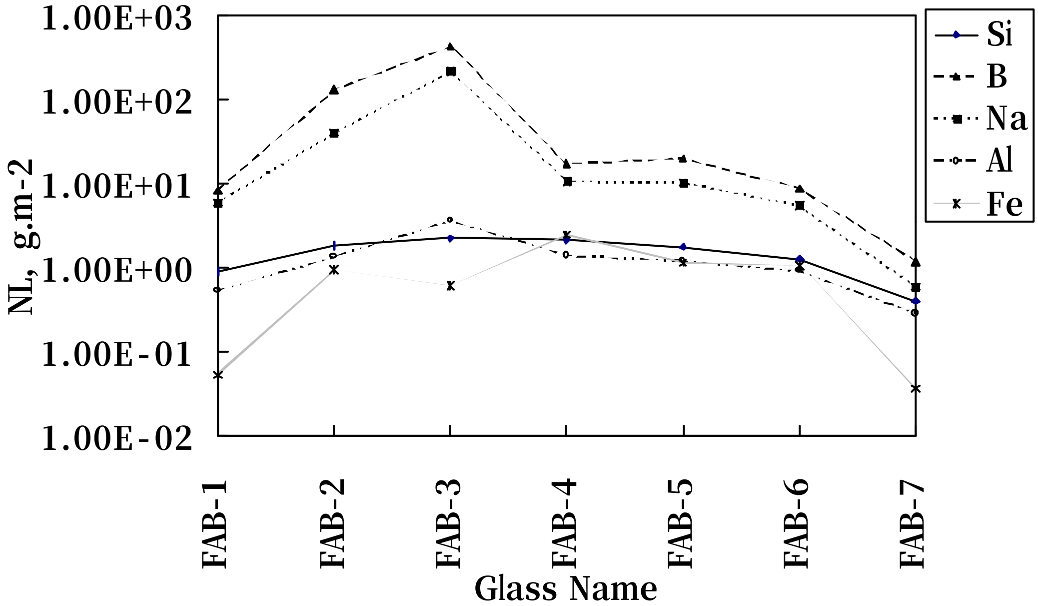

Fig. 1 Elemental release rate.

CONCLUSION

Vitrification of borate waste from NPPs is considered as an attractive approach because of its simplicity processing, large volume reduction and its unique ability to accept a wide variety of waste elements into its network structure. Fly ash is a by-product of coal combustion in electricity generating power stations. Fly ash contains high Si and Al, which are also the main glass network formers. Borate waste has high content of B. By adjusting the ratio of fly ash and borate waste could produce glass form without other additives. However, glasses including 70-50 wt% of fly ash with 30-50 wt% of borate waste could not meet the durability or process requirement. Glasses with high content of fly ash would have high melting temperature; glasses with high content of borate waste had poor chemical durability. Na_2O was added to some glasses in order to improve the glass properties. Glasses with 60-65 wt% of fly ash, 25-30 wt% of borate waste, and 5-10 wt% of Na_2O have good chemical durability and good processability. Tests showed that fly ash could be used as an additive to vitrify borate waste from Korean NPPs.

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