

An Evaluation of Cathode Ray Tube Leaded Glass as a Feedstock for Vitrifying Radioactive Waste

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ABSTRACT

The disposal of cathode ray tubes (CRT) is a serious, costly, and growing problem. One alternative to disposal is the use of CRT glass as part of the feedstock for vitrifying radioactive waste. Experiments have been conducted on representative samples of CRT glass cullet to determine (1) the composition and viscosity and (2) partitioning and waste loading capacity of the glass. The preliminary experimental results show (1) it is possible to modify the viscosity of CRT glass to a proper range at melter temperatures and (2) some containment of radioactive surrogate material is possible.

INTRODUCTION

Cathode ray tubes (CRTs) are used in computer monitors, televisions, and some electronic monitoring devices or instruments. CRTs contain up to 25 percent lead by weight (5 pounds) of the monitor to shield users from the radiation required to produce the visual display image. CRTs also contain phosphorous, cadmium, and other hazardous materials. When CRT glass is crushed in a trash-compacting facility, the lead-bearing particles may become an airborne hazard. When CRT glass is broken during landfill disposal, the hazardous materials may leach and find their way into the public water supply. These noxious substances, especially the lead, can be an imminent, dynamic health hazard if they are inhaled or ingested in appreciable quantities. Used CRTs are classified as hazardous waste due to the lead content.

The disposal of outdated or broken CRTs is a serious and costly problem. In 1992, the Environmental Protection Agency (EPA) banned the landfill disposal of CRTs. And in 1993, the EPA began targeting companies that sent large quantities of CRTs to landfill or incineration facilities. In addition, many states and local regulatory agencies are now monitoring the disposal of CRTs and other computer equipment. It has been predicted that the total number of computer monitors being scrapped in the world will rise to 30 million units per year by the year 2005.

Because of the concerns mentioned, alternatives to the disposal of CRT glass are examined. This paper reports the results of an evaluation of the CRT glass as part of the feedstock for vitrifying radioactive waste. To accomplish that evaluation, a project—upon which this report was based—was commissioned to analyze a representative sample of recycled CRT glass and to compare the analytical results with key parameters for glass matrix vitrification feedstock.

Vitrification takes an inherently mobile and voluminous liquid or solid waste form—which could conceivably be easily dispersed to the environment—and compacts it into a leach resistant glass form. The idea of immobilizing

radioactive waste in glass first garnered serious attention in the 1950's by researchers in the United States, England, and France. The first glass systems studied for waste immobilization were based on the CaO–Al₂O₃–SiO₂ systems. The addition of boron oxide reduced processing temperatures to 1300°C and increased the solubility of many waste constituents without having detrimental effects on the thermal and mechanical durability of the glass while having only minimal effects on chemical durability of the glass.

Borosilicate glass (BSG) has been deemed to be the most suitable glass matrix for radioactive waste immobilization and has been accepted as the reference waste form in the United States, United Kingdom, Belgium, Germany, France, Sweden, Sweden, and Japan. The selection of BSG as the reference waste form is based on several parameters including its low processing temperatures (thereby reducing volatilization of radionuclides), low melt corrosivity (due in part to its lower processing temperatures), compatibility with a variety of processing technologies, and its high waste solubilities (an indicator of the quantity of waste the matrix is capable of containing) over broad composition ranges.

Processing requirements of the glass matrix ultimately define the properties of the final waste form. Glass properties that dictate processing parameters include its liquidus temperature, viscosity, redox state, phase separation and crystallization, durability, and waste loading capacity. This work focused on the analysis of representative samples of CRT glass cullet to determine (1) the composition and viscosity and (2) partitioning and waste loading capacity of the glass.

SAMPLE PREPARATION

Representative samples of CRT glass cullet were obtained from 5R Processors, Ltd, Glen Fora, Wisconsin. Three different types of waste glasses were supplied by the company, consisting of: color glass (color); TV glass (TV), and black/white glass (BTW). The samples came in the form of small broken pieces. Sample preparation was straightforward. First, the glass pieces were crushed, ground into powder form, and well mixed in a hammer mill. To ensure homogeneity, each type of glass sample was hammer milled at least twice. The ground glass powder was then screened to recover the following particle size range:

Coarse, with the particle size of >75m
 Medium, with the particle size of 63~74m (used in viscosity measurements)
 Fine, with the particle size of <63m (used in partitioning study)

The glass powder samples were then dried at 450°C in an electric furnace for more than 12 hours, then sealed in Ziploc bags, and placed in a dry place for later use. The prepared glass samples were considered representative samples of the color, TV, and BTW glass respectively.

COMPOSITION AND VISCOSITY OF CRT GLASS CULLET

To identify the compositions of these three different types of glass, Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used to do full scan on solutions prepared from digested measured amounts of the samples. The results are listed in Table I.

As shown in Table I, both color and TV glasses contain SiO₂, PbO, K₂O, and Na₂O as major compounds, and Al₂O₃, BaO, CaO, and SrO as minor ones. The results indicate that PbO is present in color and TV glass at about 17.0%. However, BTW glass contains only minor amount of PbO. BTW contains SiO₂, BaO, K₂O, and Na₂O as major compounds.

Table I – Composition Of Studied Glasses

Glass Type	Weight Percentage, %																
	Al ₂ O ₃	Sb ₂ O ₃	BaO	B ₂ O ₃	CaO	CuO	Fe ₂ O ₃	PbO	Li ₂ O	MgO	K ₂ O	SiO ₂	Na ₂ O	SrO	TiO ₂	ZnO	Balance
Color	3.0	0.2	2.2	0.1	3.1	0.2	1.2	16.8	0.0	1.2	6.9	52.4	6.0	1.7	0.1	0.2	4.8
TV	2.7	0.2	1.4	0.2	3.0	0.3	1.4	17.0	0.0	1.3	6.6	52.2	6.2	1.8	0.1	0.2	5.4
BTW	2.8	0.1	10.8	0.0	0.4	0.3	1.1	3.4	0.8	0.1	6.3	64.8	7.2	1.3	0.1	0.0	0.5

Viscosity of the glass matrix melt is a function of melt chemistry and temperature and must be maintained within certain limits. Too high of a viscosity reduces melting rates, leads to difficulty in pouring, and decreases glass homogeneity; too low of a viscosity increases the melt's rate of attack of melter walls and promotes volatilization of some radionuclides. Viscosity has very important practical as well as theoretical implications and is one of the most important mechanical properties of glass materials. Knowledge of viscosity is essential to deal with fluid flow behavior and understand the kinetics of reactions. However, to our knowledge, experimental data on viscosity measurement of CRT glass are very limited.

A rotating cylinder method was employed for viscosity measurements. The viscosity measurement system consisted of a Brookfield LVDV-II+ programmable viscometer apparatus and a Linberg crucible furnace with a programmable temperature controller.

The initial viscosity measurements were done on color glass at the temperature range of 1223°K to 1393°K. To roughly identify the softening temperature ranges of the studied glasses, three exploratory experiments were carried out. It was observed that the softening temperature of color glass fell between 1023°K to 1073°K. However, even at 1373°K, the measured viscosity of color glass was very high (100~110 Pa.s). Apparently, the fluidity of color glass at this temperature is poor. To improve the fluidity and thus decrease the viscosity of the glass melt, 5% CaF₂ was added to the original glass. As expected, the viscosity of 5% CaF₂ amended color glass was significantly decreased. The viscosity of a color glass with an additive of 2.5% CaF₂ was also measured. Under the same measurement conditions, at least two individual tests were performed to check the reliability of the measurements. Good agreement between different measurements was obtained.

According to our observation, viscosity data obtained as a function of spindle rotation speed display only minimal variations. As seen in the measurements, the viscosity of liquid color glass is almost independent of the rotation speed within the temperature range studied. Therefore, at a specific temperature point, an average value of a measured viscosity was simply taken from those measured values with different spindle rotation speeds. Table II and Fig. 1(a) summarize the measured results for color glass. Plotted in Fig. 1(a) are the measured viscosities versus temperatures. The results measured from three different compositions, namely, without additive, with 2.5% CaF₂, and with 5.0% CaF₂, are compared in this figure. Apparently, the viscosity of color glass is highly temperature dependent. Viscosity differences among these three different compositions were bigger under low temperature. Yet, with the glass melt temperature increasing, the difference became narrower. The addition of CaF₂ significantly decreases the viscosity of the glass melt. As seen in Table II, at 1373°K, the measured viscosity is 106 Pa.s; with 2.5% CaF₂ added to same glass, the viscosity decreases to 58.5 Pa.s; and with 5.0% CaF₂ in the glass, the viscosity is almost decreased 70% of original value. Overall, the viscosity of the color glass without CaF₂ is 1.6 to 1.8 times that of the color glass melt with 2.5% CaF₂, and the viscosity of the color glass without CaF₂ is almost 3 times that of the glass melt with 5.0% CaF₂. The addition of CaF₂ greatly improves the fluidity of the color glass melt.

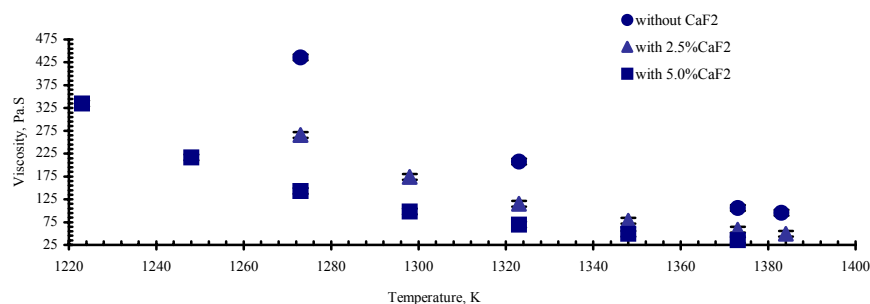


Fig. 1(a) A comparison of measure viscosity data on color glass (error. 6.286Pa.s)

Table II – Comparison of Measured Viscosities on Color Glass

Temperature K	Viscosity in Pa.S		
	NO CaF ₂	2.5% CaF ₂	5.0% CaF ₂
1384		49.283	
1383	95.866		
1373	106.043	58.540	35.461
1348		78.332	49.606
1323	207.765	115.128	69.819
1298		174.131	98.236
1273	435.552	265.731	143.185
1248			217.043
1223			335.022

When the logarithm of the viscosity, η , is plotted against the inverse absolute temperature, a linear trend is found. This can be seen in Fig. 1(b). The fits are very good. Based on our measurement results, it can be concluded that the logarithm of the viscosity η depends linearly on $1/T$. This observation supports the view that the variation of viscosity with temperature follows Arrhenius behavior. The measured percentage torque versus the rotation speed in rpm is plotted in Fig. 1(c). The data shown is from the results of color glass with 5.0% CaF₂. As is evident in this figure, within experimental scatter, the torque response may be reasonably well expressed by a linear dependence on spindle rotation speed.

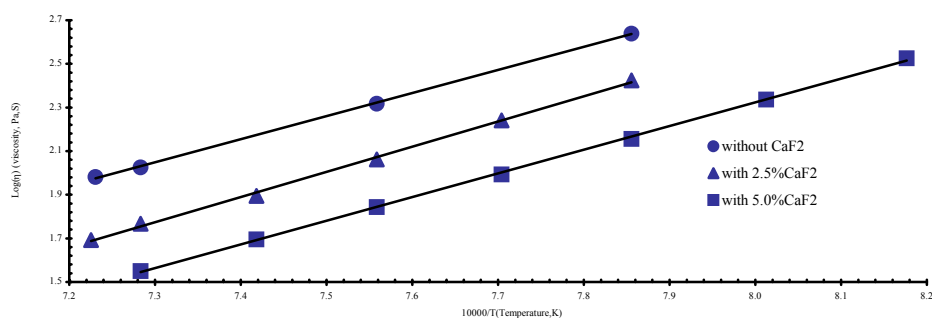


Fig. 1(b) A comparison of the viscosity data on color glass

The viscosity measurements were also done on TV glass. The method and procedure are the same as those of color glass. Measurements were conducted on three different compositions of TV glasses. The viscosity of color glass and that of TV glass is very close to each other at same temperature. This is not surprising since the composition of color glass and that of TV glass are almost the same.

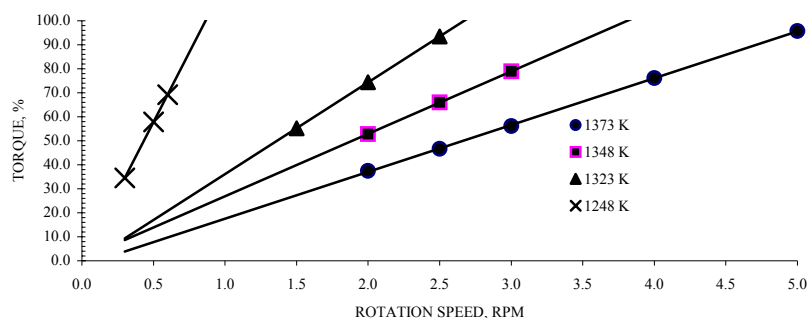


Fig. 1(c) Measured torque(%) vs rotation speed for color glass with 5.0% CaF₂ at different temperatures

PARTITIONING AND WASTE LOADING OF CRT GLASS

Glass is used for immobilization of radioactive and hazardous wastes because of its durability and ability to accept a variety of waste constituents into its network structure. CRT glass poses a potential processing and environmental problem due to its lead content. Very limited information is available on the vaporization of lead and partitioning of heavy and radioactive metals from CRT glass melts. The question of whether this partitioning behavior could be controlled—by modifying the glass formulation and processing conditions in order to stabilize the materials into the final waste form—needed to be answered experimentally.

To avoid the stringent requirements for radiological work and a significant investment in equipment, surrogates were chosen to mimic the partition behavior of actual radioactive elements. Guided by other research work, we performed a simple match of element physical and chemical properties, and identified the following surrogates in our experiments (Table III).

Table III. Selected Surrogates

Waste	MP (C)	BP (C)	Temp. (C) at Vapor Pressure of 1 atm	Reason for Substitution	Surrogate	MP (C)	BP (C)	Temp. (C) at Vapor Pressure of 1 atm
Cs	28	678	690		Cs			
Pd	1552	3140	3140	Expense	Ni	1453	2732	2730
Pu	641	3232		NNI*	Ce	798	3257	
Rb	39	688	700	Expense	K	64	774	770
Rh	1966	3900	3760	Expense	Co	1495	2870	2870
Ru	2310	3900		Expense	Fe	1535	2750	2750
Sr	769	1384	1380		Sr			
Tc	2172	4877		NNI*	Mo	2617	4612	4830
U	1132	3818	3800	NNI*	Mn	1244	1962	2100

* No Non-radioactive Isotope

It was decided that Ce, Sr, Co, Ni should be chosen as simulants to spike into the base glasses for the exploratory tests. The amount of each surrogate added into the glass was:

2.5% NiO
1.5% CoO
5.0% SrO
3.0% CeO₂

A CRESS Model C1228K electric furnace with series 945 digital LED display temperature controller and a 28mL porcelain crucible was used in the partitioning study. Partitioning data was collected at a furnace temperature of 1273°K, 1373°K, 1473°K, and 1517°K.

Elemental analysis was done on several elements to study the volatile behavior of these elements under different fusion temperature. The normalized weight loss data are given in Table IV.

SAMPLES	TIME HOUR	TEMP. K	Table IV-- WEIGHT LOSS OF SOME COMPOUNDS, IN %									
			Al ₂ O ₃	BaO	CeO ₂	CoO	Fe ₂ O ₃	PbO ₂	NiO	SiO ₂	Na ₂ O	SrO
#C020103A	3	1517	*no loss	2.0	*no loss	0.5	0.5	1.8	*no loss	5.0	2.8	*no loss
#T020103B	3	1517	*no loss	2.0	*no loss	0.5	28.6	*	*no loss	*	*	*no loss
#B020103C	3	1517	*no loss	0.0	*no loss	0.2	34.3	*	*no loss	4.5	*	*no loss
#C020107	3	1373	*no loss	0.7	7.9	32.4	5.5	*	10.7	2.7	0.8	*
#T020107	3	1373	*no loss	*	10.4	29.6	33.1	4.3	12.7	2.7	4.7	9.2
#C020102B	3	1517	*no loss	3.7	2.5	32.7	2.2	1.3	22.9	3.5	0.2	10.5
#T020102A	3	1517	*no loss	4.3	9.7	32.9	*	5.7	23.2	*	7.0	10.5

annotation: samples marked with "C" are color glasses, "T" are TV glasses, and "B" are black/white glasses

Although the results presented in Table IV are limited, the data provides some interesting information. As can be seen, among those spiked chemicals, CoO (the Rh surrogate) has the highest volatility followed by NiO (the Pd surrogate). SrO and CeO₂ (the Pu surrogate) have relatively lower volatility. Temperature plays a major role in the vaporization of glass compounds. Higher temperature leads to higher volatility. This is evident from the following figures. Figure 3 gives the total weight loss of three different types of glasses without spiking with the surrogate elements. Overall, color glass has the highest weight loss of 0.54% over the tested temperature range, followed by TV glass. Black/white glass has very low weight loss, which is 0.20% even at 1517°K. When spiked with 2.5% NiO; 1.5% CoO; 5.0% SrO; and 3.0% CeO₂, the total weight loss increases significantly after fusion. This can be found from Fig. 4. Comparing Fig. 3 with Fig. 4, one may find that the total weight loss is nearly tripled with spiked samples. This also indicates that the spiked elements have relatively high volatility. Shown in Figs. 5 and 6, CoO has a volatility fraction of more than 30% from 1373°K to 1517°K, and NiO has 10% volatility fraction at 1373°K and 23% volatility fraction at 1517°K. Both CeO₂ and SrO have around 10% weight loss over the experimental temperature range. Based on present observation, it seems that Co and Ni are more volatile than Ce and Sr. No significant volatility on Si, Al, and Pb was observed under these conditions.

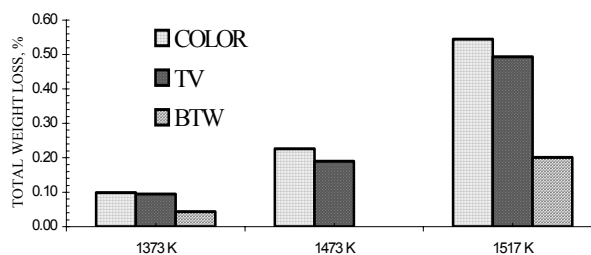


FIGURE 3. VOLATILITY OF GLASSES AT DIFFERENT TEMPERATURES (WITHOUT ADDITIVES, FUSION TIME: 3 HOURS)

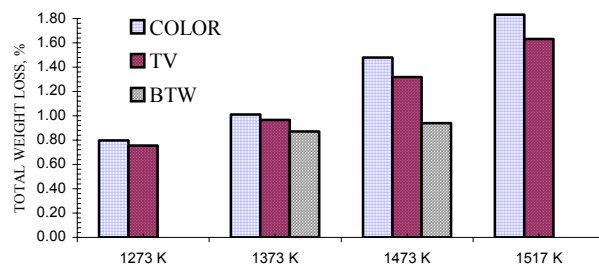


FIGURE 4. VOLATILITY OF GLASSES AT DIFFERENT TEMPERATURES (WITH ADDITIVES, FUSION TIME: 3 HOURS)

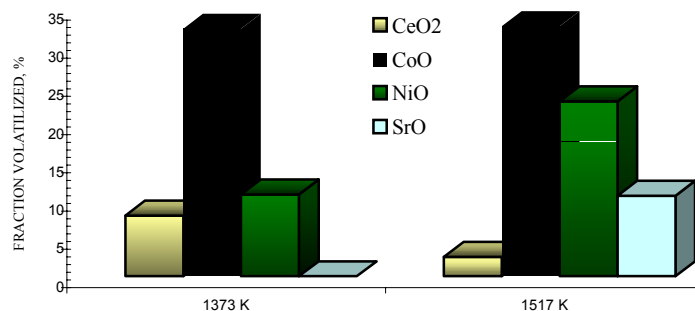


FIGURE 5. VOLATILITY OF COLOR GLASS COMPONENT AT DIFFERENT TEMPERATURES (SPIKED WITH Co, Ni,Ce,Sr, FUSION TIME: 3 HOURS)

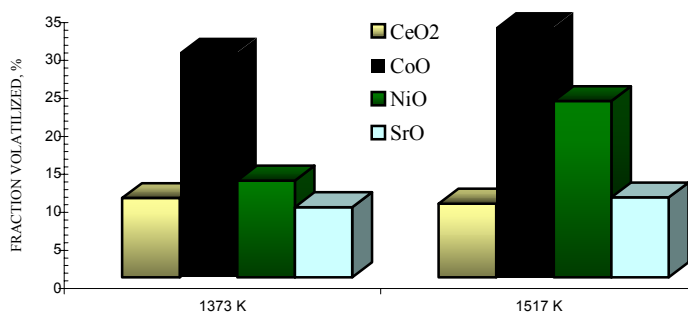


FIGURE 6. VOLATILITY OF TV GLASS COMPONENT AT DIFFERENT TEMPERATURES (SPIKED WITH Co, Ni,Ce,Sr, FUSION TIME: 3 HOURS)

SUMMARY AND CONCLUSIONS

Preliminary experiments have shown that it is possible to modify the viscosity of CRT glass to acceptable values in the right temperature range for vitrification through the addition of small amounts of fluorspar, CaF_2 . Specifically, the tests have shown that the addition of CaF_2 can reduce the viscosity from over 400 Pa.S to less than 150 Pa.S at 1273°K with 5% CaF_2 additions. This is important in that without fluidity, melter operation is not possible. It is also possible that the addition of waste material will be beneficial in reducing the viscosity; this should be evaluated.

Tests show that the CRT glass is capable of containing moderate amounts of radioactive surrogate materials. The present results are limited and preliminary. Yet, the data provides some interesting information. As was reported, among those spiked chemicals, CoO has the highest volatility followed by NiO. SrO and CeO_2 which have

relatively lower volatility. Temperature plays a major role in the vaporization of glass compounds. Higher temperature leads to higher volatility. For the un-spiked samples, color glass has the highest weight loss of 0.54% over the tested temperature range, followed by TV glass. Black/white glass has very low weight loss, which is 0.20% even at 1517°K. When spiked with 2.5%NiO; 1.5%CoO; 5.0%SrO; and 3.0%CeO₂, the total weight loss increases significantly after fusion. One finds that the total weight loss is nearly tripled with spiked samples. This also indicates that the spiked elements have relatively high volatility. CoO has a volatility fraction of more than 30% from 1373°K to 1517°K, and NiO has 10% volatility fraction at 1373°K and 23% volatility fraction at 1517°K. Both CeO₂ and SrO have around 10% weight loss over the experimental temperature range. Based on present observation, it seems that Co and Ni are more volatile than Ce and Sr. No significant volatility on Si, Al, and Pb was observed under these conditions. The minor oxides that are present in the glass (Cu, Sb) were not tracked, due to their low level. The other elements (Ba, K, and Sr) are expected to be retained to a fairly high level as they are basic constituents in an acid slag as was indicated by the results for Sr in the spiked samples.