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Corrosion Assessment of Refractory Materials for High Temperature Waste Vitrification (U)

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CORROSION ASSESSMENT OF REFRACTORY MATERIALS FOR WASTE VITRIFICATION

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ABSTRACT

A variety of vitrification technologies are being evaluated to immobilize radioactive and hazardous wastes following years of nuclear materials production throughout the Department of Energy (DOE) complex. The compositions and physical forms of these wastes are diverse ranging from inorganic sludges to organic liquids to heterogeneous debris. Melt and off-gas products can be very corrosive at the high temperatures required to melt many of these waste streams. Ensuring material durability is required to develop viable treatment processes. Corrosion testing of materials in some of the anticipated severe environments is an important aspect of the materials identification and selection process. Corrosion coupon tests on typical materials used in Joule heated melters were completed using glass compositions with high salt contents. The presence of chloride in the melts caused the most severe attack. In the metal alloys, oxidation was the predominant corrosion mechanism, while in the tested refractory material enhanced dissolution of the refractory into the glass was observed. Corrosion testing of numerous different refractory materials was performed in a plasma vitrification system using a surrogate heterogeneous debris waste. Extensive corrosion was observed in all tested materials.

INTRODUCTION

Glass is attractive for immobilization of radioactive and hazardous wastes due to its ability to accept a wide variety of components into its network structure. The resulting glass product is very stable and highly durable. Vitrification has been designated as the Best Demonstrated Available Technology (BDAT) by the Environmental Protection Agency (EPA) for the treatment of radioactive liquid high level wastes [1]. Technologies are currently being developed by the U. S. Department of Energy's (DOE) nuclear sites to immobilize low-level radioactive and hazardous wastes (low-level mixed wastes) for permanent or long term disposal. Vitrification is an attractive alternative for treatment of these compositionally varied wastes. An extensive amount of process knowledge can be leveraged from the many years of high level waste vitrification research and development. Significant volume reductions (up to 97 volume percent) for radioactive wastes have been realized utilizing vitrification [1]. The resulting glass waste form has exceptional durability and has be found to be as much as 10,000 times more durable than other waste forms, such as cement [2]. If the durability of a mixed waste can be certified to the extent that it satisfactorily stabilizes the hazardous constituents, the treated waste can be "delisted". Once delisted, a treated mixed waste is classified only as a low-level radioactive waste and subsequent disposal costs are greatly reduced.

The low-level mixed wastes currently being stored at the various sites across the DOE complex can be classified in the following categories with corresponding percentages by volume: aqueous liquids (39%); inorganic sludges and particulates (33%); debris (13%); organic wastes (3%); soils (2%); and "other" wastes (10%). The physical and chemical make-up of these waste streams can vary dramatically ranging from relatively well characterized chemical processing sludges to drummed heterogeneous debris (protective clothing, tools, construction materials, refuse, etc.). Vitrification of these varied wastes will require a broad range of technologies since no one present technology is well suited to all wastes. Technologies currently being considered include: Joule heated melters; platinum "bushing" melters; plasma melters; induction melters, graphite arc melters and microwave systems.

No matter what vitrification technology is utilized, an assessment of materials of construction issues is paramount to eventual successful waste stabilization. A number of processing conditions must be considered in this assessment of materials durability. The relatively high temperatures associated with many of these technologies can accelerate corrosion rates and cause extreme temperature gradients and subsequent thermal stresses. Elevated concentrations of many salt species are present in these wastes. Molten salts are highly corrosive and can cause rapid degradation of many pure metals, alloys and ceramics [3-6]. The presence of molten metals can also cause corrosion or dissolution of many materials. Corrosive gas species driven off from the melt can rapidly degrade off-gas system and superstructure components. Finally, the redox state of the melt, influenced by the presence of carbon, metals and molten oxides, can lead to attack of melter components.

The proper selection of materials to withstand the possible extreme environmental conditions associated with vitrifying these wastes is an important aspect of system design. There is obviously no one material which can resist all severe environments. A list of candidate materials is shown in Table I. The use of a combination of materials, replaceable components and innovative designs are all aspects which must be considered.

Table I - Candidate Materials for Waste Vitrification Systems

Ceramics	Refractory Metals	Metal Alloys
Oxides	Molybdenum	Nickel-based
Carbides	Chromium	Cobalt-based
Nitrides	Tungsten	Steels
Borides	Tantalum	Titanium-based
Castable refractories	Platinum	
Fused-cast refractories	Niobium	
Fired refractories		
Cements		

Since materials selection is sometimes overlooked and often deemed as a secondary element in system design, the assessment of candidate materials for use in vitrification systems must be done expeditiously. Examination of the literature from comparable processes is a first step in assessing materials performance. Small-scale laboratory coupon corrosion tests under anticipated conditions can be beneficial for comparisons of specific materials and roughly assessing the corrosion behavior. Exposure of coupons in actual vitrification systems provides more detailed information regarding actual in-use performance. Although often difficult (especially in radioactive operations), routine examination of materials in use in operating systems can provide the most useful information on materials performance. The following two sections discuss results from laboratory scale coupon tests and coupon exposures in an operating plasma system. The lab-scale coupon tests were performed to examine the corrosion behavior of candidate Joule heated melter electrode and refractory materials to glass melts containing high salt concentrations. In the plasma vitrification trials, a wide variety of refractory materials were exposed to a surrogate heterogeneous debris waste melt to assess corrosion behavior.

CORROSION COUPON TESTS IN HIGH SALT CONTENT GLASS MELTS

Joule heated waste glass melters have been developed in the U. S., Europe and Japan for the conversion of high-level radioactive wastes (HLW) to borosilicate glass for permanent disposal [7]. These melters typically consist of a refractory lined vessel with metal electrodes which conduct electricity directly through the melt. These melters typically operate in a slurry fed mode and are, thus, very applicable to waste water treatment sludges. Since the majority of current Joule heated waste glass melters are geared to high-level waste treatment, remotability and durability are important design issues. These systems are designed to typically operate maintenance free for two to four years. Many of these melters, including the largest scaled system (the Defense Waste Processing Facility (DWPF) at DOE's Savannah River Site), are limited to a maximum operating temperature of 1150° C. These lower operating temperatures result from the use of nickel-based alloy electrode materials (historically Inconel® 690[a]). Although these electrode materials limit maximum process temperatures, the durability of these materials is typically excellent. Several HLW melters using Inconel® 690 electrodes have operated continuously for over 4 years [7].

Based on this wealth of experience, Joule heated glass melters are attractive for the treatment of several low-level mixed waste streams including sludges, ash wastes and liquid waste solutions. However, many common salts found in LLMWs, (e.g. sulfates, chlorides, phosphates and chromates) offer several vitrification processing challenges. These salts have typically low solubilities in glass and can hinder melt pouring and degrade product quality. Furthermore, the presence of salt species in the melt combined with the relatively high processing temperatures can lead to extensive corrosion of melter and superstructure components.

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[a] Inco Alloys International, Huntington, WV

Laboratory scale tests were performed to examine the performance of candidate melter materials exposed to glass melts containing various salt concentrations. In these tests, two nickel based alloys (Inconel® 690 and Inconel® MA-758) and a high chromium content refractory (Carborundum Monofrax® K-3 [b]) were exposed to glasses containing elevated salt contents. Melter electrodes, as well as many off-gas components, are routinely fabricated from Inconel 690®. Inconel® MA-758 is a mechanically alloyed nickel based alloy with enhanced grain boundary attack resistance. Carborundum K-3 is a high chromium content refractory used extensively in waste glass melters. Since in service these materials may be exposed to varying environments, efforts were made to have sample exposure in the melt, at the melt/vapor interface, and in the vapor space (Figure 1). The glass composition was a typical borosilicate waste glass formulation. Salts were added to the base glass composition at four levels (Table II). Coupons were exposed at 1100 and 1300° C for 72 hours. Corrosion rates were estimated by dimensional measurements before and after exposure. Scanning electron microscopy (SEM) coupled with energy dispersive electron spectroscopy (EDS) was utilized to gain insight into corrosion mechanisms.

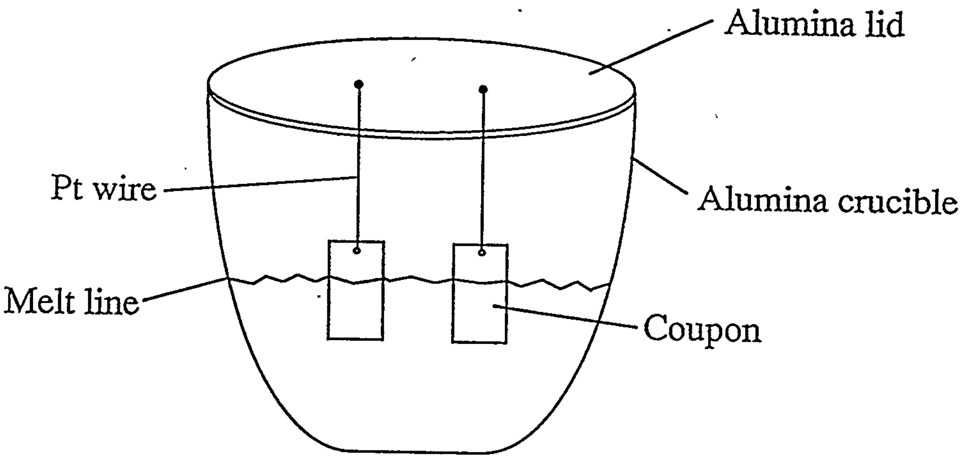

Figure 1. Schematic diagram of test configuration for coupon exposure tests.

[b] Carborundum Company, Falconer, NY

Table II. Salt Concentrations for Coupon Exposure Tests

Sample Code	(Wt % in feed) Sulfate	Chloride	Phosphate	Chromate
S3	0.7	-	-	-
C1	-	0.5	-	-
C3	-	1.5	-	-
AH	0.7	1.5	4.5	0.6

Typically little attack occurred to coupons exposed to sulfate only glass compositions. In the three other compositions studied, attack was evident on all coupons following exposure. The greatest amount of corrosion was seen at the melt line (interface between the melt and vapor space) as anticipated. Estimated corrosion rates for the various materials and sample locations are shown in Tables III and IV. No significant differences in performance was detected between the nickel based alloys. Samples exposed to the chloride containing melts typically exhibited the most rapid corrosion. Corrosion rates showed a dramatic increase with increasing temperature. The corrosion rates at 1300° C were typically at least two times faster than the rates at 1100° C. In the refractory samples, the increases in corrosion with increasing temperature were the most dramatic with greater than an order of magnitude increase observed in some instances.

Scanning electron microscopy coupled with energy dispersive spectroscopy was used to examine the corrosion surfaces in detail and gain insight into corrosion mechanisms. It is hypothesized that in the metal alloys, degradation occurred by chloride breaking down the protective oxide film allowing subsequent oxidation of the base metal. A chromium oxide layer (devoid of nickel and iron) was seen consistently in the corrosion regions of all areas of the coupons (Figure 2). In the refractory samples, attack occurred by the dissolution of refractory constituents into the glass. A "dissolution layer" was observed in all exposed areas of the coupons (Figure 4). Although only trace amounts of salts were observed in the dissolution layer, it is thought that the salts may enhance refractory dissolution, thus, explaining the relatively rapid corrosion rates.

Table III. Corrosion Rates for 1100° C Exposure

Corrosion Rate (in/yr)

Material	S3	C1	C3	AH	Location
Inconel 690	0.14	0.39	0.41	*	Vapor space
	0.37	2.53	2.11	*	Melt line
	0.42	0.64	0.34	0.15	In glass
Inconel MA-758	0.54	0.33	0.10	*	Vapor space
	0.22	2.00	2.17	*	Melt line
	0.11	0.10	0.44	0.67	In glass
Refractory	0.47	0.83	0.16	0.81	Vapor space
	1.05	2.30	3.14	0.73	Melt line
	0.75	0.00	1.61	0.67	In glass

* Pt wire corroded and samples fell into melt, so data unavailable.

Table IV. Corrosion Rates for 1300° C Exposure

Corrosion Rate (in/yr)

Material	S3	C1	C3	AH	Location
Inconel 690	0.72	0.60	1.43	0.89	Vapor space
	0.97	3.82	4.31	2.57	Melt line
	0.00	0.95	0.72	0.66	In glass
Inconel MA-758	0.47	1.43	0.95	0.95	Vapor space
	0.85	4.31	3.59	2.39	Melt line
	0.24	0.83	0.72	1.19	In glass
Refractory	4.28	4.90	2.71	1.83	Vapor space
	6.19	10.17	7.51	7.58	Melt line
	0.21	#	#	1.35	In glass

Samples were not located intact in solidified melt, so data unavailable.

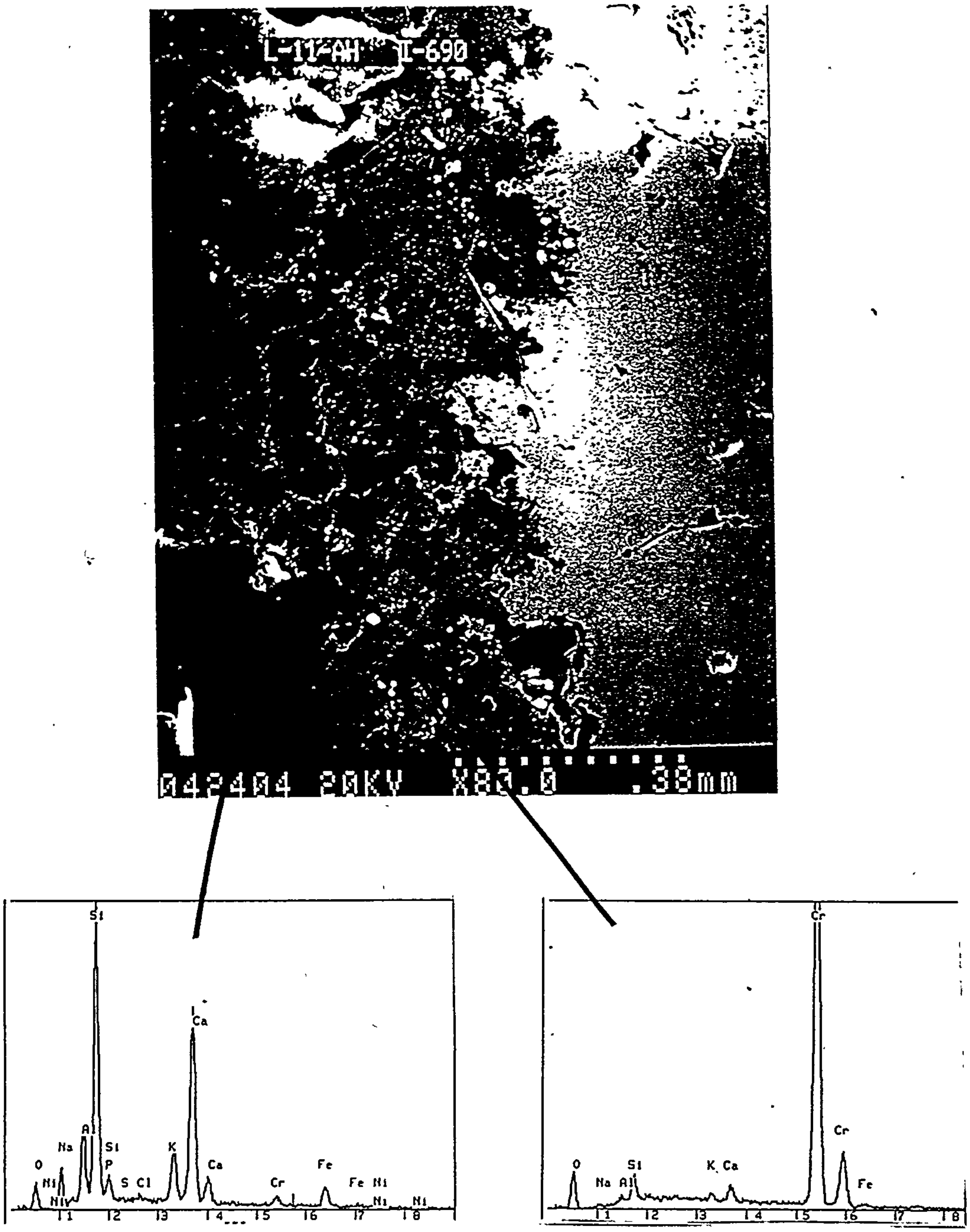

Figure 2. Inconel 690 coupon following exposure to the AH composition at 1300° C. Note the chromium oxide layer.

Figure 3. Refractory sample following exposure to AH composition at 1300° C. Note dissolution layer between glass and base refractory.

CORROSION COUPON TESTS IN PLASMA MELTER SYSTEM

Plasma arc melters are good candidates for the treatment of low-level radioactive debris wastes, metal wastes and asbestos [7]. In this treatment technology, the plasma torch operates as a very intense heater transferring heat to the melt via impingement of the arc or by thermal radiation. However, due to the extremely high torch temperatures, elevated melt temperatures and volatility of constituents from the melt are likely. Several issues must be addressed to ensure successful application of this technology to radioactive waste treatment. Demonstration of refractory life, control of melt pouring, control of volatilization and entrainiment of radioactive species, and maintenance of plasma torches in a radioactive environment are all issues currently being considered.

Refractory corrosion scoping tests were performed at the Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Mississippi State University. A 250 kW plasma torch attached to a gimbal mount to allow for complete x, y, z mobility served as the heat source for the tests. The feed material consisted of briquettes with a composition reflecting a "typical" LLMW heterogenous debris waste (Table V). Two tests were conducted to assess the refractory materials performance in the plasma torch system: 1) a multiple cycle test and 2) a continuous operation test.

Table V. Heterogeneous Debris Waste Composition

Bulk Component	Wt %	RCRA Simulant	Wt %
Pecan shell flour	10.8	Lead chloride	0.25
PVC granules	10.8	Chromic chloride	0.25
Glass beads	10.8	Cadmium chloride	0.25
Perlite	10.8	Nickel chloride	0.25
Iron powder	10.8	Cesium chloride *	0.25
Alumina	7.8	Cerium chloride *	0.25
Activated carbon	4.9		
Silica sand	4.3	Hamaco Starch	5.9
Portland cement	4.3	Water	15.7
Aluminum powder	1.6		

* Radioactive simulant

The heterogeneous debris waste is likely the most challenging waste stream to be treated due to its varied composition. Refractory materials used to line the plasma vitrification furnace must be resistant to corrosion from molten metals, molten oxides, molten salts, water vapor, hot acids, carbon, carbon monoxide and temperatures up to 1700° C. In the selection of candidate materials for testing, corrosion resistance was deemed to be most important. Good thermal shock resistance was also considered essential. Materials ranging from typical glass contact refractories to exotic, developmental ceramic materials were considered. Even though it would likely be cost prohibitive to use some of these expensive developmental materials in a melt vessel, knowledge into their corrosion behavior was felt to be valuable in assessing corrosion issues for a plasma system. Furthermore for extremely corrosion sensitive areas of a system, the use of these materials may well be justified. A total of 33 different materials were identified and obtained from manufacturers for testing (Table VI). A graphite crucible held different test materials (Figure 4). Since many of these samples were odd-shaped, the walls and bottom of the crucible were notched to accommodate the samples and minimize sample movement during the tests. Sample location and identity were carefully mapped to assist in the analysis following testing.

TABLE VI. Material Tested in Plasma Vitrification Trials

Oxides:	Alumina - high purity, fiber board
	Zirconia - fiber board, castable, stabilized
	Mullite
Nitrides:	Silicon nitride - reaction-bonded, pressureless sintered
	Aluminum nitride - varying sintering additive levels
	Boron nitride - pyrolytic, hot pressed
	Sialon
Carbides:	Silicon carbide - hot pressed, sintered
Borides:	Titanium diboride - sintered
Fused Cast Refractories:	Very high chromium - alumina
	High Chromium - alumina
	Magnesia - alumina
Graphite:	Pyrolytic graphite
Composites:	Aluminum nitride + silicon carbide whiskers
	Zirconia toughened alumina
	Zirconia + alumina
	Boron nitride + titanium diboride

Multiple Cycle Test

Within hours of initiation of the test most of the samples had fallen into the melt. The graphite crucible was heavily oxidized, so it was difficult to ascertain if the samples had corroded into the melt or fell in because they were left

Figure 4. Test samples in graphite crucible before testing.

unsupported. The test was run for 4 hours and the melt was allowed to solidify. Initial examination of the melt indicated that significant corrosion was occurring to the samples at the melt line. A combination of excessive heat from the torch "dancing" along the surface of the melt and the severe chemical reactions occurring in this region likely caused the excessive degradation. The solidified melt was re-melted and the run was continued for approximately another 1 hour. The corrosion was again excessive so the test was stopped to ensure that at least some samples remained intact for analysis. The resulting solidified melt appeared inhomogeneous and consisted of a mixture of slag and glassy material. The intact coupons were severely corroded at the melt line and were covered by deposited salts (Figure 5). The aluminum nitride, high chromium fused cast refractories and one silicon nitride material appeared to perform the best in this trial. Oxide samples, silicon carbide samples and fused cast refractory samples showed evidence of thermal shock. High surface area materials (i.e. fiber boards and castables) were completely consumed during the tests. Corrosion of samples in the vapor space was relatively insignificant in comparison to the melt line corrosion. Initial observation of samples in the melt implied a vertical

Figure 5. Test samples following multiple cycling test.

temperature gradient existed in the melt. Corrosion in samples at and near the bottom of the crucible was much less than near the surface of the melt.

Continuous Operation Test

Based on the results of the cycling test, only the best performing materials were exposed in the continuous operation test. Three aluminum nitride samples, three fused cast refractory samples and 1 reaction bonded silicon nitride sample were installed in a graphite crucible. This test was run for four hours at which time the test was discontinued due to excessive corrosion to most of the samples. Essentially only the very high chromium refractory and the aluminum nitride sample with 0.25 wt % yttria additive remained intact. In this test the feeding rate of the surrogate waste was increased in an attempt to keep a uniform melt height. This likely caused the increase in corrosion rates as compared to the cycling tests.

Pending funding allowances, a detailed analysis will be performed on the materials in an effort to identify corrosion mechanisms and better quantify corrosion rates. A review of the initial results, however, indicate a number of design and processing considerations must be considered for viable use of a plasma system to vitrify these wastes. The scaling of the melt vessel appears to be the most important issue due to the potential extreme temperatures and severe chemical reactions occurring at the surface of the melt. The vessel must be made large enough to ensure wall temperatures are kept to an allowable minimum. A skull melting process may be another alternative to alleviate this problem. It may also be prudent for some pre-characterization and segregation of the waste streams to remove the most corrosive constituents from the wastes.

CONCLUSIONS

The wide range of waste streams being considered for remediation by vitrification offer many opportunities for existing and new vitrification technologies. The variety in waste compositions and presence of many reactive species, however, offer many processing challenges. Selection of materials for melter systems is an important aspect of system design. The best performing materials must be selected for each application and creative design strategies must be employed to ensure effective waste processing. The presence of salts in the waste streams can significantly enhance the corrosion of materials in Joule heated melter systems. Heterogeneous debris wastes are likely the most challenging waste streams to treat. A plasma system may be an appropriate technology to treat these wastes. The choice of refractory materials and design of a melt vessel must be carefully considered in these treatment systems due to the severe temperatures and corresponding chemical reactions occurring at the surface of the melt.

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