

Study on the Vitrification of Mixed Radioactive Waste by Plasma Arc Melting

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Abstract: Vitrification technologies provide a means for the destruction of hazardous organics, for the immobilization of radioactive waste and heavy metals, and for dealing with difficult mixed wastes. A PAM (Plasma Arc Melter) system is located at the Korean Atomic Energy Research Institute (KAERI), Taejeon, Korea. The melter system was built to demonstrate the applicability of this technology for the treatment of hazardous and low-level radioactive waste from Korean nuclear facilities. To study the treatment of various wastes, including a radioactive low-level waste and a mixed waste, pilot-scale vitrification tests were conducted using a surrogate waste, such as combustible material, solidified resins in cement, inorganic materials, steel, glass, and solidified boric acid cement in a plasma arc melter system. The results of analyses of samples of a vitrified product, using the off-gas collected during the test period, show that a greater part of mixed waste and low-level radioactive waste generated in a nuclear facility can be treated; in addition, it accommodates a wide range of soil and waste types and debris, which eliminates the need for handling, sorting, and size-reduction activities. Conclusively, PAM-200 can treat radioactive and toxic wastes, as well as a mixed form of both; the off-gas can be processed efficiently by operating the system at a negative pressure.

Keywords: vitrification, low-level waste, radionuclide, decontamination, volume reduction, plasma arc melter

Introduction

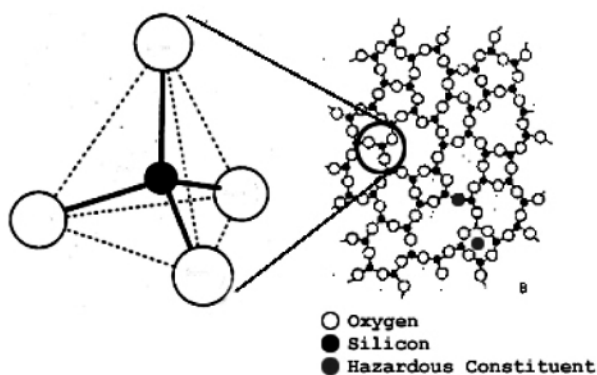
This paper provides the results of a series of Trial Burn Tests conducted on the PAM-200 system. The primary objective was to demonstrate the melter's applicability for treatment of radioactive low-level waste from Korean nuclear power plants. The demonstration program focused on establishing compliance by determining the volume reduction for the low-level waste stream, and establishing the leaching characteristics of the final waste form. This melter design incorporates the results of ca. 20 years of United States government- and industry-sponsored research in the field of radioactive and hazardous waste treatment at the Department of Energy's (DOE) Idaho National Engineering and Environmental Laboratories (INEEL) and other DOE laboratories [1,2].

Vitrification is the process of converting materials into glass or glass-like substances. Glass is a rigid, non-crystalline material of relatively low porosity, often composed primarily of silica, alumina, and oxides of alkali and alkaline earth elements. Thermally formed glasses are produced by fusing or melting crystalline materials and/or amorphous materials at elevated temperatures to produce liquids. These liquids are subsequently cooled to a rigid condition without crystallization. Silicate glasses are composed of three-dimensional networks of silicon-oxygen tetrahedra. Some of the oxygen atoms from the tetrahedra can be shared with other tetrahedra to form organized silicon networks. Hazardous constituents can be immobilized in vitrification processes through two main interactions. Some are immobilized through chemical bonding with silicon or oxygen, such that they become part of the network, and some are immobilized by being surrounded by a layer of vitrified material and encapsulated [3-5]. Figure 1 displays the atomic structure of sili-

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Table 1. Composition of the Two Refractory Used to Line the Crucible of the Arc Melter

	Al ₂ O ₃	SiO ₂	TiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O, K ₂ O
Mortar (%)	8-62	34-38	0.5-1	1-2	trace	trace	1-3
Refractory (%)	93.3				1.4	5.3	

**Figure 1.** Atomic structure of silicon glass and a silicon-oxygen network.

con glass and a silicon-oxygen network [6].

A PAM system uses an electric current to convert contaminated soil and wastes into stable glass and crystalline products. Typical operating temperatures range from 1400 to 1900 °C. Such high melt temperatures result in superior vitrified products. As the molten zone grows it incorporates hazardous inorganic elements, while the high processing temperatures destroy the organic components through pyrolysis. Virtually all types of debris can be accommodated, including drums, scrap metal, concrete, wood, and plastic. The melter system operates by creating a molten pool of a glass constituent in the bottom of a refractory lined container. The melter crucible is a refractory lined chamber that can withstand the high temperature required to melt mineral oxides and metallic-type materials (> 1800 °C). A coat of high-alumina mortar or a ceramic refractory pot lines the crucible to provide better heat and electrical insulation, minimizing heat transfer through the wall. The composition of the two refractory used as crucible insulation is shown in Table 1. Waste is added at the top of the pool, where it is oxidized or thermally decomposed and the inorganic residuals (ashes) are melted into the pool [7,8]. This relatively new concept in waste treatment produces a highly stable final waste form that incorporates most of the hazardous and radioactive metals as oxides in the glass mixture. Gaseous combustion products and incompletely destroyed organics pass out of the melter and into a high-temperature secondary treatment system where complete destruction is assured.

Experimental

Process Description

Figure 2 shows the PAM-200 process flow diagram. The design capacity of PAM-200 is 200 kg/h for non-combustible waste and 100 kg/h for combustible waste. Without pre-treatment, 200-L drums packed with wastes are moved into a shredder by a conveyor, where they are crushed and fed into a melter by a screw feeder. Two tappers for tapping the molten slag and metal are installed on both sides of the melter. The operating temperature ranges from 1400 to 1900 °C. The distance between the two electrodes located on the Psi-section is adjusted by their own transitional and rotational movement. Graphite arc furnaces generate heat by a spark passing from a graphite electrode to either the materials to be melted or another electrode [9]. Gases leaving the melter pass through the Psi-section and enter the thermal oxidizer, which provides complete destruction of gaseous combustion products and incompletely destroyed organics. The off-gas quench/scrub system quenches the thermal oxidizer exhaust gas by contacting the gas directly with a scrubbing solution in the quench chamber. This action cools the gas rapidly to ca. 82 °C, thereby limiting the formation of dioxins and assuring that the temperature rating of the downstream equipment is not exceeded. A scrub solution contacts with the exhaust gas in the quenching chamber, atomizer, and scrubber, thereby scrubbing particulate and soluble gases from the gas stream. The components scrubbed from the oxidizer exhaust are acid gases (HCl, SO₄, HF), solid particulates, and radioisotopes. Particulates conglomerated with water droplets in the scrubber are removed through a Cyclone separator and a Mist Eliminator; finally, they pass through a Filter Bank, which consists of a pre-filter, a HEPA filter, a charcoal filter, and another HEPA filter. The off-gas is emitted through the stack. In the stack, a Continuous Emission Monitor and Radiation Monitor measure the concentrations of hazardous constituents and radionuclides in the off-gas.

Test Information

The primary project objectives of phase 1 were to evaluate the effects of various surrogate hazardous contaminants (including surrogate radionuclides) and different test matrices. The tests in Phase 1 used a simulated waste that included hazardous materials and non-radio-

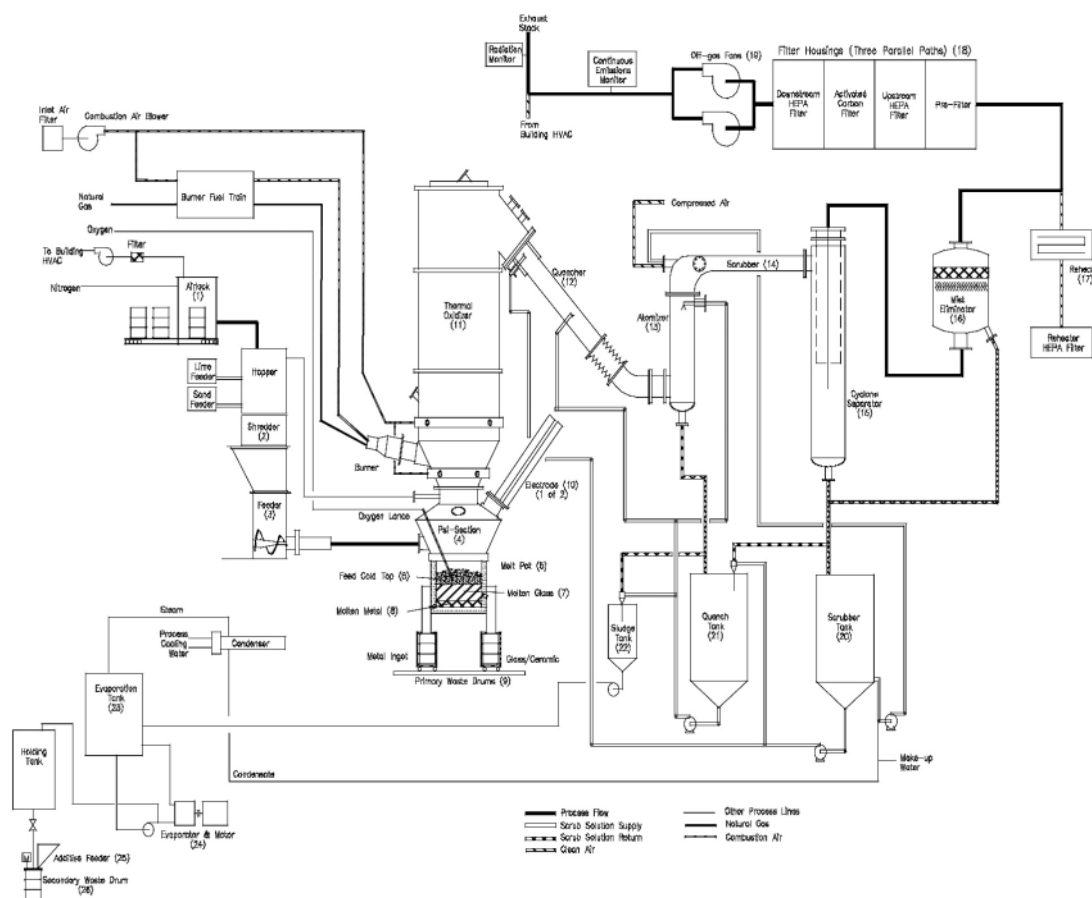


Figure 2. Process flow diagram of PAM-200.

active surrogates. The tests were designed to demonstrate the partitioning of non-radioactive surrogates and hazardous metals and the DRE (Destruction Removal Efficiency) of the system. These tests were performed to evaluate the melter's performance with a mixed waste and radioactive materials in the feed. The phase 1~4 tests were designated as 'campaign' tests, in which a packed bag of each waste type was processed in a pre-determined sequence designed to represent the overall composition of a nuclear power plant's waste. This sequence was developed to ensure that the generated glass-ceramic PWF (Primary Waste Form) had a minimum variation and a very stable composition with the addition of minimal additives. Table 2 shows the test information for Phase 1 in detail.

Process Sample Collection

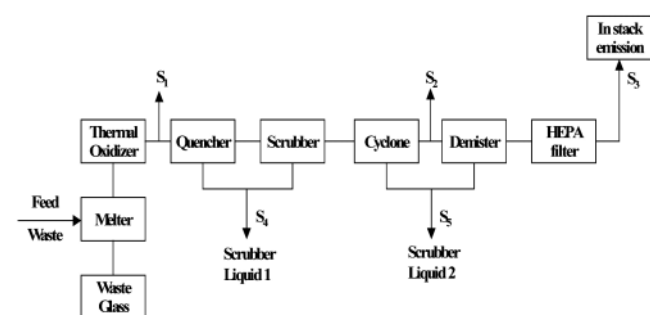
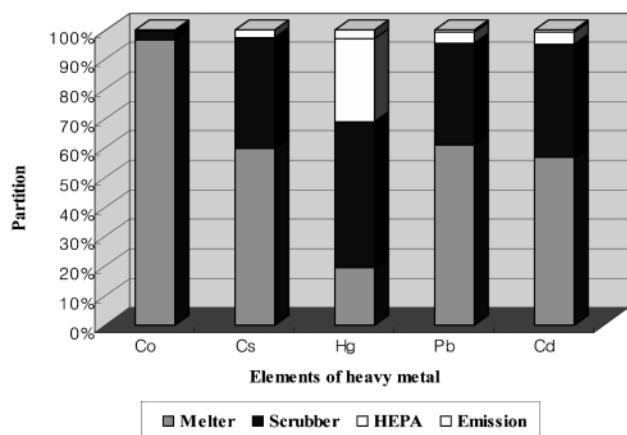
At the completion of each test, samples were taken at the sampling points described in Figure 3. The sampling and analysis activities were necessary to perform a process material mass balance, to determine the product phase partitioning and the fate of the metal and surrogate radioisotope elements in the feed, and to evaluate the physical and chemical properties of the vitrified slag.

Off-gas sampling and device installation were based on the method for measuring a gaseous heavy metal described in the domestic process test method for pollution and multiple metals sampling method by the U.S. EPA (Environmental Protection Agency) [10]. The EPA Multi-Metals Train (MMT) was used to collect the stack gas samples for an analysis of the following metals: cadmium, lead, and mercury. Monitoring for these metals should satisfy the proposed EPA MACT (Most Achievable Control Technology) standards for metals. The sampling train withdrew an isokinetic sample from the source, with particulate emissions collected in the probe and on a heated filter, and gaseous emissions collected in a series of chilled impingers. MMT sampling was conducted isokinetically at the second stack sample port for a minimum of 3 h at a sampling rate of 0.014 ~ 0.028 dscm/min. Stack gas particulate matter samples were collected by using the Method 0050 isokinetic sampling described in the EPA Method 0050 [11]. The method involves the collection of an integrated gas sample extracted from the stack and collecting the particulate material on a particulate filter. The Method 0050 train was positioned at the second stack sample location.

Table 2. Test Information for Phase 1

Test Phase	Waste Composition	Amount of Waste	Spiking Material(g)
P1-1 (Comb.)	PE: 40.6 % PVC: 15.6 % Paper, Cloth: 43.8 %	192 kg	CoO: 2420; CsCl: 1735 PbO: 500; HgCl ₂ : 500 CdO: 500
P1-2 (Non-Comb)	Steel: 2.6 % Concrete: 7.7 % Airfilter: 20.5 % Sand, soil: 35.9 %	360 kg ⁽¹⁾	CoO: 968; CsCl: 694 PbO: 1000; HgCl ₂ : 1000 CdO: 200
P1-3 (Resin)	Cement: 65.5 % Water: 15.0 % Resin: 19.4 %	600 kg	CoO: 968; CsCl: 694 PbO: 200; HgCl ₂ : 200 CdO: 200
P1-4 (Campaigning)	Comb.: 160 kg Non-Comb: 200 kg Resin/Boric ⁽³⁾ : 320 kg	680 kg ⁽²⁾	No spiked

(1) Include additives 200 kg, (2) boric composition (wt%): boric acid 5.4, water 29.5, cement 58.9, limestone 6.2 (3) include additives 240 kg.

**Figure 3.** Sampling locations in the plant.**Figure 4.** Partitioning of heavy metals during phase 1-1.

Results and Discussion

Partition of a Spiked Material

To evaluate the performance for the partitioning characteristics of spiked materials, KAERI analyzed the filter and impinger solution of the off-gas sampling device and

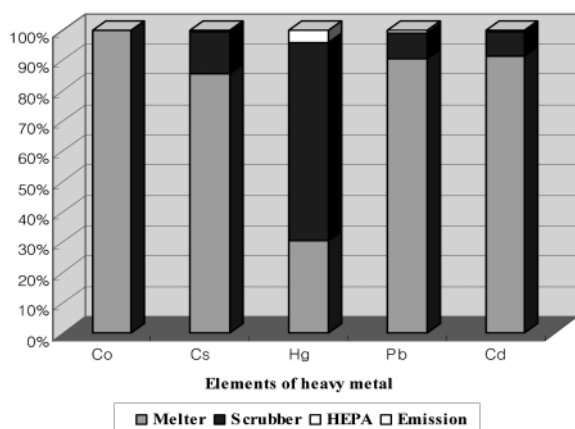
vitrified the specimen sampled during the test period. Figures 3 to 5 show the distribution of Co, Cs, Pb, Cd, and Hg in each unit process. It was revealed that the results in phases 1~2 to 1~4 were similar to those in phase 1-1 (combustible waste). In phase 1-1 (Figure 4), over 96 % of Co in the feed was retained in the glass, but Cs was retained at 56 % in the glass. About 37 % of the Cs was scrubbed. Lead was similar to Cs, with 57 % retained in the glass and 32 % collected in the scrubber. It was surprising that 19 % of the Hg and 57 % of the Cd were retained in the glass. Most of these materials were expected to be volatilized. The scrubber was able to remove most of the rest of the Cd (38 %) and 49 % of the Hg, but much of the Hg was collected in the HEPA filter bank. The charcoal filter, not installed for this run, would have reduced the Hg emissions. The disposition of toxic metals such as Pb, Hg, and Cd, which was included with the radioactive surrogates Co and Cs, was expected to be retained in the glass; Figure 5 shows that 99.9 % was retained in the glass and Cs had 85.4 % retained in the glass. About 13 % of the Cs was scrubbed. Lead was similar to Cs, with 90.6 % retained in the glass and 8.5 % collected in the scrubber. It was surprising that 30 % of the Hg and 91 % of the Cd were retained in the glass. Most of these materials were expected to be volatilized. The scrubber was able to remove most of the rest of the Cd (8 %) and 65 % of the Hg, and 3.8 % of the Hg was collected in the HEPA filter bank. The activated charcoal filter, not installed for this run, would have reduced the Hg emission further. Figure 6 indicates that 99.96 % was retained in the glass; Cs was 76 % retained in the glass. About 23 % of the Cs was scrubbed. Lead was similar to Cs, with 79 % retained in the glass and 20 % collected in the scrubber. About 30 % of the Hg and 91 % of the Cd were retained in the glass. The scrubber was able to

Table 3. Offgas Emission

Classify	Phase 1-1	Phase 1-2	Phase 1-3	US Clean Air Act	MOE/KINS
O ₂ (%)	17.3	17.8	17.8	NA	NA
CO ₂ (%)	2.0	1.7	1.7	NA	NA
CO (ppm)	0.2	0.6	4.2	50-150	600
THC (ppm)	~0.2	~0.2	~0.2		
NO _x (ppm)	37.9	40.2	28.1	150 (180 1 st yr)	200
SO _x (ppm)	0	0	0	30	300 at 12 % O ₂
HCl (ppm)				25	50

Table 4. Overall Decontamination Factors for Spiked Elements for Test Phase 1

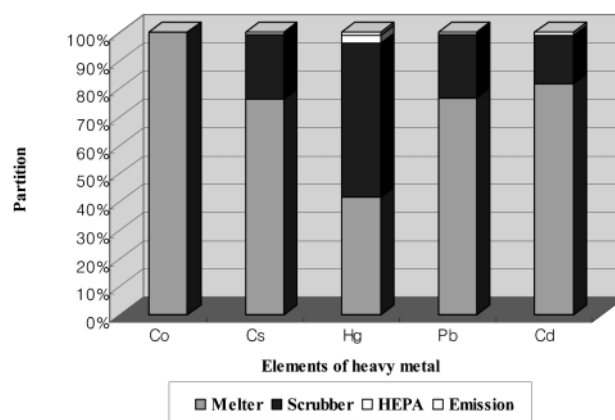
Spiked Material	Co	Cs	Pb	Hg	Hg
Phase 1-1	2.1 E+04	1.7E+04	2.1 E+02	3.4 E+01	1.7 E+02
Phase 1-2	9.1 E+04	1.4 E+03	1.7 E+03	2.9 E+02	1.4 E+03
Phase 1-3	5.0 E+05	9.2 E+03	1.3 E+04	8.8 E+01	3.3 E+04

**Figure 5.** Partitioning of heavy metals during phase 1-2.

remove most of the remaining Cd (17 %) and 55 % of the Hg, and 2.6 % of the Hg was collected in the HEPA filter bank. The activated charcoal filter, not installed for this run, would have reduced the Hg emission further. Each test in the trial burn included sampling of the stack effluent. It was found that, for all tests, the emissions were well within U.S. and Korean emission limits for CO, SO_x, NO_x, and THC. A summary of the gas emissions is given in Table 3.

Decontamination Factor

Based on the results of the analyses of each sample taken at the various sampling points, decontamination factors for the overall and unit process were derived. In Table 4, the decontamination factors for the heavy metals are derived from Phase 1.

**Figure 6.** Partitioning of heavy metals during phase 1-3.

Maximum Concentration of Pollutants in the Waste

On the basis of the test results, the upper limit concentration of each pollutant, particularly radionuclides and hazardous heavy metals, can be calculated as follows:

$$MSC_i = \frac{Q_n \cdot MPC_i}{W \cdot SF} \cdot \pi_i \cdot DF_i \quad (1)$$

where,

MSC_i Maximal Specific Concentration of 'i' contaminant in a waste (g/g or mCi/kg),

MPC_i Maximal Permissible Concentration of 'i' in air (g/m³ or mCi/m³)

Q_n Average flow rate (Nm³/h)

W Waste processing speed (kg/h)

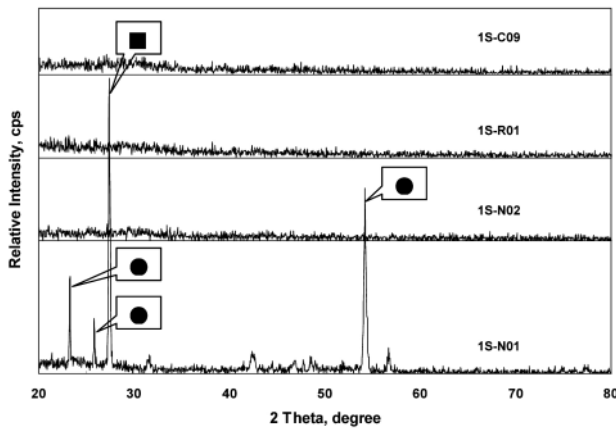
SF Safety Factor

DF_i Overall Decontamination Factor

Table 5 shows the results calculated for the maximum permissible concentration of each pollutant in the wastes by considering the safety factor as 10. The method used was similar to that of the Adjusted Tier 1 approach recommended by EPA, but it did not consider an atmospheric dispersion factor. The waste feeding speed used in these tests will change in a continuous operation, but it will not change the value of MSC_i very much. Even

Table 5. Maximum Concentration of Pollutants in Waste

Contaminant	DF	W (kg/h)	MPC _i (mCi/Nm ³)	MSC _i (mCi/kg)
Co-60	>4.4 E+05	120	3.0 E-06	>4.09
Cs-137	>3.2 E+05	120	5.0 E-07	>0.50
Pb	2.1 E+02	64	5 (mg/m ³)	6.1 (g/kg)
Hg	3.4 E+01	64	5 (mg/m ³)	0.99 (g/kg)
Cd	1.7 E+02	64	1 (mg/m ³)	0.99 (g/kg)

**Figure 7.** XRD analysis of glass samples of phase 1. ● : Na₂Si₃O₇ (Sodium silicate); ■ : (K Na)AlSi₃O₈ (Sanidine).

though this evaluation was sufficiently conservative, it verified that PAM-200 meets the related emission criteria for treating mid- and low-level radioactive wastes and incinerated ashes containing a number of hazardous heavy metals.

XRD Analyses of Glass Samples

The XRD test was performed using a Cu/target with a radiation angle of 20 ~ 80° and a speed of 0.25°/min. The instrument used was a Rigaku model. The top (1S-C09) was for the combustible waste. The XRD analyses of the slag generated are shown in Figure 7. One of the non-combustible materials exhibited some spectral peaks that indicated mineral crystals, or a ceramic phase structure, instead of just glass. The minerals generating the spectral lines were identified as Na₂Si₃O₇ (sodium silicate) and (K Na)AlSi₃O₈ (sanidine).

Micro-Structure and Composition of the Glass Samples

The slag samples were analyzed using an EPMA (Electron Probe Micro X-ray Analyzer) to investigate the microstructures and compositions of the glass samples. The instrument used was a JEOL, JXA-8600. The microstructures of the plate slags generated before the leaching test are shown in Figures 8 ~ 11. The resin (1S-R01), one of the noncombustible (1S-N02), and one of the com-

Table 6. Surface Composition of Glass Samples

Element	N01 (wt%)		N-02 (wt%)	C-09 (wt%)	R-01 (wt%)
	White (A)	Black (B)			
Na	4.86	0.30	5.48	4.21	2.08
K	2.88	0	3.76	1.56	2.13
Si	47.65	40.04	57.52	35.89	35.24
Al	8.88	0	18.50	6.12	7.23
Fe	0	0	0	1.49	1.87
Ti	0.31	0	0.58	0.80	0.57
Mg	1.19	0	3.41	1.79	2.11
Ca	34.22	58.94	8.62	46.55	46.5

combustible (1S-C09) samples formed amorphous materials similar to glass, but 1S-N01 did not. The other non-combustible sample (1S-N01) exhibited a special peak that indicates the formation of mineral crystals, or a ceramic phase structure, instead of just a glass. As previously described, the spectral peaks have been identified as Na₂Si₃O₇ (sodium silicate) and (K Na) AlSi₃O₈ (sanidine). Detailed data for the surface compositions of the glass samples before the leaching test are given in Table 6.

Volume Reduction

One of the most important attributes of a waste treatment system is the volume reduction achieved, because the capital and operating costs for treatment are offset by the reduced cost of disposal. Consequently, the higher the volume reduction ratio, the lower the cost for disposal.

$$\text{Volume Reduction Ratio (VRR)} = \frac{\text{Total Volume Feed In}}{\text{Total Volume PWFout}}$$

The volume reduction of the combustible LLW is potentially very high because of the low ash content. This ash content is largely calcia, so some additive with silica would be necessary to properly melt the ash into glass to obtain a quality PWF. The potential volume reduction of the filters is less because of the concrete liner in the drum. The high silica concentration requires a calcia additive to properly melt it into glass to obtain a quality PWF. On the other hand, The volume reductions of other LLWs (filters, cemented / boric acid, cemented resin, noncombustible) are much lower because of the amount of cement and other additives used for temporary stabilization. The high calcia content requires a silica additive to properly melt it into glass to obtain a quality PWF. The VRR for the Phase 1 tests is shown in Table 7. The VRR for the combustible IWS (Input waste stream) is 52, but this sample includes a pre-charge and other

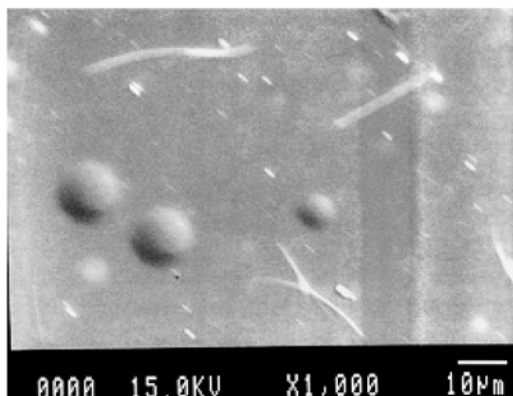


Figure 8. Micro-structure of 1S-R01.

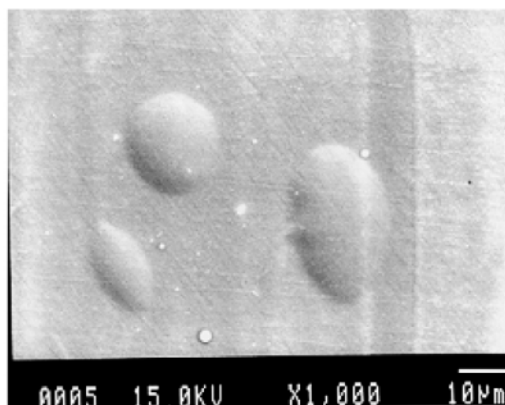


Figure 10. Micro-structure of 1S-NO2.

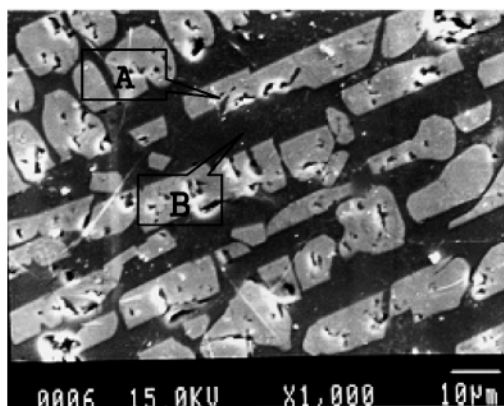


Figure 9. Micro-structure of 1S-NO1.

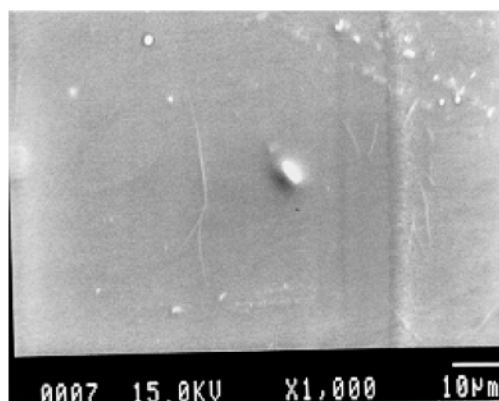


Figure 11. Micro-structure of 1S-C09.

Table 7. Volume Reduction Ratio for Phase 1 Tests

Tests	Waste feed (kg)	Additive (kg)	Total Volume (l)	PWF (l)	VRR
P1-1	192	160	1271	23	52
P1-2	320	200	296	116	1.75
P1-3	230	190	316	100	2.35
P1-4	736*	20	1524	145	10.4

* C-176 kg, NC-200 kg, R-120 kg, BA-240 kg

Waste densities used for these calculations were:

- Combustible-0.16 g/cm³; Resin-1.58 g/cm³; Non-Comb-0.98 g/cm³; Boric acid-1.78 g/cm³; Soil(S)-2.05 g/cm³; Limestone (L)-2.35 g/cm³.

additives. As such, it is not representative of a VRR for a true combustible IWS, which should be ca. 95 with this PAM system. The VRR for the cement resins also includes additives, which reduce its optimum value by ca. 30 ~ 40 %. The phase P1-3 noncombustible waste stream was reduced to a volume of little more than half (Factor 1/2.35) of that of the original waste. This smaller volume reduction arose because the non-combustibles were

shielded by concrete. The purpose of the campaigning test, P1-4, was to mix waste to obtain a good composition for the electrical conductivity and viscosity of the melt and to generate an excellent primary (glass-ceramic) waste form. The FWF (Final Waste Form) campaigning resulted in an overall volume reduction of over 90 % of that of the original waste. If the radioactive waste had not been previously stabilized in cement, the overall volume reduction would be much larger.

Conclusions

Through demonstration tests for PAM-200, the following features were verified: It is possible to control the concentrations of hazardous constituents, heavy metals, and non-radionuclides to below regulatory limits. Metal emissions of Pb, Cd, Co, and Cs were all well within the strict US-proposed MACT limits. The one exception was Hg, for which an activated charcoal filter was not installed to see if it was needed for a Hg retention; it appears that it is required. Another major objective was to demonstrate that the final forms meet the leaching criteria for heavy or toxic metals. Similar glass-ceramic

compositions have exhibited leach resistances equivalent to or better than that of the borosilicate glass used for stabilizing high-level radioactive waste. Another major objective was to demonstrate the volume reduction associated with the vitrification process. While the waste volume reductions were determined for each test, of most importance was the volume reduction for the test P1-4, where the waste was campaigned to form an average glass composition with a minimum of added glass-forming ingredients. In this test, although the feed contained a large fraction of cemented materials and other inorganics, the overall waste volume reduction ratio was ca. 10:1. For a highly combustible material, the volume reduction ratio exceeds 52, i.e., a final waste volume of only ca. 2 % of the input feed. As such, the volume reduction ratios are true measures of the effectiveness of the process in producing a reduced volume waste stream for disposal. During the two tests using a spiked material including non-radioactive cobalt and cesium, gaseous emissions were measured as samples were leaving the stack. All of the spiked material was confined within the system and the primary waste form. Therefore, it can be expected that a greater part of the hazardous waste and LLW generated from a nuclear facility can be treated and that their volumes can be reduced for disposal by a PAM system.

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