NON-COMBUSTIBLE WASTE VITRIFICATION WITH PLASMA TORCH SYSTEM

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ABSTRACT

Non-combustible radioactive wastes from Nuclear Power Plants (NPPs) are composed of concrete, glass, asbestos, metal, sand, soil, spent filters, etc. The melting tests for concrete, glass, sand, and spent filters were carried out using 60 kW plasma torch system. The surrogate wastes were prepared for the tests and Co & Cs were added to the surrogates in order to simulate the radioactive waste. Several kinds of surrogate were prepared by mixing them or individual waste, and were melted with plasma torch system to produce glassy waste forms. The characteristics of glassy waste forms were examined for the volume reduction factor (VRF) and the leach rate. The VRFs were estimated through measurement of density for surrogate and glassy waste forms, and were turned out to be 1.2 - 2.4. The Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP) was applied to determine the leach resistance for As, Ba, Hg, Pb, Cd, Cr, Se, Co, and Cs, and the leaching index was calculated using the total content in both the waste forms and the leachant for each element. The TCLP tests resulted that the leach rates for all elements except Co and Cs were lower than those of the Universal Treatment Standard (UTS) limits. For Co and Cs, there is no the UTS limits and the leach rate & index for them were around 10 times higher than those of the other elements.

INTRODUCTION

The NPPs generate gaseous, liquid, and solid radioactive wastes during their operation and maintenance, which are termed as low- and intermediate-level radioactive waste (LILW). The solid waste is largely classified as combustibles (e.g. protective clothing, shoes, socks, vinyl sheet, spent ion-exchanger, etc.) and non-combustibles (e.g. sand, concrete, glass, metallic waste, spent filters, etc). The combustibles are put into a 208-liter steel drum and then compressed by a super compactor. Some countries including the U.S.A, Japan, Germany, France, etc. incinerate combustibles excluding spent ion-exchanger since its radioactivity is much higher than one of the others. The spent ion-exchangers are generally solidified with cement or put into a High Integrity Container (HIC) after drying. The non-combustibles are mainly put into 208-liter steel

drum without any treatment, but spent filters is stored in a cement-lined drum(208-liter) because of its high radioactivity (1).

The development of technology for LILW treatment is quickly becoming more necessary because of the high concern for the protection of the environment, the difficulty in disposal site selection, the disposal cost increase, and the current lack of appropriate means for the handling of LILW waste.   Because LILW vitrification, a new technology, can significantly reduce the volume of the waste and provide more stable waste forms of LILW at reasonable costs, this technology is considered the most promising among the new LILW treatment technologies and hence, there has been a world-wide trend to apply it for the treatment of LILW (2,3,4).

Several melters such as plasma torch melter (PTM), cold crucible melter (CCM) heated by direct induction current, etc can be applied to vitrify LILW. This paper describes experiments for noncombustible waste melting with 60 kW plasma torch melter. A plasma torch is a device that converts electrical energy into thermal energy (5,6). The plasma arc creates a "flame" that has temperatures ranging from 4,000 ^{o}C to 7,000 ^{o}C. Thus plasma torches operate at much higher temperatures, higher enthalpies, and at efficiencies much greater than those of fossil-fuel burners. In addition, plasma torches require only about 5% of the gas necessary for fossil fuel burners. Therefore, effluent gases are greatly reduced, and furnace systems can be built that are much more compact than traditional furnaces, at correspondingly reduced capital costs (7).

In this paper, the melting experiments for concrete, glass, sand, and spent filters was performed with 60 kW plasma torch system. In order to examine the vitrification possibility for the mixture of them or individual waste, several surrogates were prepared without any flux addition and then non-radioactive Co and Cs were added to simulate the radioactive waste. The surrogates were put into the plasma torch melter and melted in order to convert into glassy waste forms that were examined to analyze the leaching properties, volume reduction factor, etc. For the examination, specific density and total contents of chemical species measurement, and TCLP tests were performed for the mixtures of waste and the waste forms, respectively.

EXPERIMENTS
Materials and Equipment
The plasma torch melting system is comprised of a 60 kW plasma torch melter, DC power supply, control panel, and off-gas treatment system.   The plasma torch was a solid and straight polarity type, which was largely operated as transferred mode during experiments. In other words, at the startup stage, the startup arcing is taken place between a tungsten solid cathode located at rear of

the torch and a copper anode of the front. The startup arcing ionizes plasma gas, which provides the conducting passage between the cathode of torch and the anode located on melter bottom, and then main plasma is generated. If the main plasma is generated, the startup arcing is automatically disappeared.

The cooling system of torch includes the external cooling jacket whose function is to cool the whole torch body, and the internal cooling loop whose role is to cool the front electrode (Cu anode) of the torch. The tap water was utilized as cooling water without any pre-treatment. The melter is a refractory lined S.S. vessel which was designed to be suit to the batch operation, and whose dimension is I.D 250 mm and effective height of 250 mm. The internal volume of melter was determined to melt the metallic waste of 5 kg.

Several surrogate wastes were prepared as shown in Table I which is a tabulation of the chemical composition of waste and glassy waste forms. The surrogates were made using concrete, glass, sand, and filters, and it was assumed that the filters was composed of S.S., galvanized steel, glass fiber, and polypropylene with ratio of 2:1:1:1. The surrogates, PT1 to PT5 were simulated by the mixing (ratio 3:1) of two material among concrete, sand, and glass, and PT6 to PT9 using individual material including filters. The PT10 was prepared by using equal weight of four materials. The weight of surrogates were 500 g, but the one of PT10 was 600 g. All surrogates were added non-radioactive $Cs(Cs_2CO_3)$ and Co(powder) with ratio of 5g per Kg of waste.

Experimental Procedure
Because the surrogates were non-conductive material, a molten metal should be formed in order to operate the plasma torch as transferred mode. So, carbon steel (4,000g) is put into the melter and melted before the waste feeding. The plasma torch cooling system and the off-gas treatment system have to be started before the torch ignition. The mixture of Ar(18 lpm) and H_2(2 lpm) is injected to the plasma torch as plasma gas, and then the button for start-up arc generation is pushed at control panel. Immediately, non-transferred operation is started, and then the torch operation is automatically switched to the transferred mode. After switching to transferred mode, electrical current rate was constantly adjusted to 500 A through the control of distance between the torch bottom and the metal pool.

The waste is fed onto the molten metal after sufficient melting of the carbon steel on the melter bottom. If the waste is thoroughly melted, the molten waste and metal are separated due to the density difference. The plasma torch operation is stopped and then the molten waste and metal are drained into a mold by tilting of the melter. It takes about 3 minutes for the melting of carbon

steel, 7-8 minutes for waste feeding and melting, and 2 minutes for the drainage of molten material.

RESULTS AND DISCUSSION

Volume Reduction Factor

In order to estimate the volume reduction factor(VRF), the densities were measured for the waste and the glassy waste forms. The measurement for waste was performed through the weighing and the measuring of volume for each waste, and two methods were applied for the waste forms. That is, one was the density after the waste form had been ground to a powder as small as 0.25 - 1.0 mm for prevention of cavity effect within the waste forms. The other is to measure the densities without any pretreatment. We call the densities measured by the former method the intrinsic density and the superficial density for those by the latter method. Table II describes the intrinsic and the superficial densities, and the volume reduction factor, and shows that the VRF of PT9 is the largest because the surrogate waste of PT9 contains polypropylene. The VRFs of PT2 and PT7 have no difference between the intrinsic VRFs and the superficial VRFs, which means that there are no bulky cavities in glassy waste forms.   It is desirable to exclude the bulky cavities from a viewpoint of the volume reduction and the waste form quality. In order to remove the bulky cavities, various techniques such as the flux addition and the optimization of operating parameters (melting temperature, redox potential, etc.) might be adopted.

Composition Analysis on Waste and Glassy Waste Forms

Table I shows the oxides composition of the surrogate wastes and the glassy waste forms (shading values). The composition for surrogates were calculated using the oxides composition of concrete, sand, and glass, and those for 3 raw materials and waste forms were measured with XRF(X-Ray Fluorescence) (model 1700) manufactured by Shimadzu in Japan. Fig. 1 describes the composition of network formers ($SiO_2+Al_2O_3$), network modifiers ($\sum(RO+R_2O)$), and the other oxides. The network formers are elements that can replace silicon. And the network modifiers are elements that do not enter the network, but form ionic bonds with nonbridging oxygen atoms in the structure of silica glass network (8). This figure also shows that nevertheless the compositions for wastes are largely fluctuate, the fluctuation for those of glassy waste forms become smoothly. The composition ranges for network formers, network modifiers, and the others in waste forms are 68 - 77, 9-20, and 12-21, respectively. The ranges are similar to those for waste forms produced by ISV (In-Situ Vitrification) of INEEL soils, which are corresponding to 84.7, 9.8, and 5.5 (8).

Table I. Chemical Composition of Waste and Glassy Waste Forms

Oxides	Composition of Waste and Glassy waste form (wt.%)									
	PT1	PT2	PT3	PT4	PT5	PT6	PT7	PT8	PT9	PT10
SiO_2	50.50	67.27	45.38	51.94	60.33	42.11	75.66	55.22	88.59	59.60
	49.26	57.74	56.65	45.55	61.26	52.68	69.44	62.62	55.56	49.11
Al_2O_3	7.96	2.69	13.75	20.06	17.43	10.59	0.05	23.22	0.09	10.59
	22.06	12.24	11.92	22.02	14.41	20.47	2.39	5.35	21.21	21.17
MnO	0.58	0.41	0.67	0.69	0.61	0.66	0.32	0.70	0.06	0.53
	0.58	0.41	0.41	0.49	0.56	0.92	0.36	0.59	0.56	0.78
CaO	1.96	2.23	3.30	6.25	6.38	1.83	2.36	7.72	0.01	3.72
	1.45	1.08	1.09	5.51	1.20	1.11	3.09	12.45	1.82	1.80
MgO	2.47	2.63	2.11	1.54	1.62	2.39	2.71	1.26	0.02	1.99
	2.35	2.36	2.33	1.82	0.18	2.39	0.23	1.92	2.38	2.38
Na_2O	4.12	5.08	2.97	1.64	2.12	3.64	5.56	0.97	0.53	3.21
	3.26	3.45	3.48	3.93	3.56	3.52	3.22	3.33	3.59	3.99
K_2O	0.51	1.08	0.84	2.07	2.36	0.22	1.37	2.69	0.58	1.37
	1.56	1.73	1.35	2.00	1.95	2.42	2.09	2.08	2.02	2.06
P_2O_5	0.02	0.02	0.02	0.03	0.03	0.02	0.02	0.03	0.00	0.02
	0.07	0.08	0.08	0.00	0.00	0.05	0.01	0.06	0.03	0.02
Fe_2O_3	20.26	14.11	18.81	9.77	7.00	23.33	11.03	5.25	2.35	12.53
	18.59	21.26	22.35	19.36	18.28	18.83	20.02	14.11	15.98	18.99
TiO_2	0.32	0.21	0.35	0.30	0.25	0.37	0.15	0.28	0.04	0.25
	0.33	0.36	0.36	0.35	0.21	0.19	0.24	0.38	0.28	0.27
CaO/SiO_2	0.039	0.033	0.073	0.120	0.106	0.043	0.031	0.140	10^{-4}	0.062
	0.029	0.019	0.019	0.121	0.020	0.021	0.004	0.199	0.033	0.037
$SiO_2 + Al_2O_3$	58.46	69.96	59.13	72.00	77.76	52.70	75.71	78.44	88.68	70.19
	71.32	69.98	68.57	67.57	75.67	73.15	71.83	67.97	76.77	70.28
$\Sigma(RO+R_2O)$	9.64	11.43	9.89	12.19	13.51	8.74	12.32	13.34	1.20	10.82
	9.20	9.03	8.66	13.75	7.45	10.36	8.99	20.37	10.37	11.01
$\Sigma(others)$	31.90	18.61	30.98	15.81	8.73	38.56	11.97	8.22	10.12	18.99
	19.48	20.99	22.77	18.68	16.88	16.49	19.18	11.66	12.86	18.71
Waste Ingredients[*] (wt.%)	C:75 G:25	C:25 G:75	C:75 S:25	C:25 S:75	G:25 S:75	C:100	G:100	S:100	F1:100	C:25 G:25 S:25 F2:25

*C: concrete, G: glass, S: sand, F1(simulated filters): S.S(200g) + galvanized steel(100g) + glass fiber(100g)+polypropylene(100g), F2(simulated filters): S.S(60g) + galvanized steel(30g) + glass fiber(30g) + polypropylene(30g)

As shown in Table I and Fig. 1, alumina contents in waste forms such as PT1, PT2, PT7, and PT9 are higher than those in corresponding wastes, but PT8 shows the reverse phenomenon. These phenomena resulted in the smooth variation of oxide composition in waste forms. Alumina enrichment and reduction in waste forms might be caused by the basicity (CaO/SiO_2) of wastes, which is classified as the acid waste (0.2-0.7), the neutral (0.7-1.2), and the basic waste (1.2-4.0)

according to the value of CaO/SiO_2 (9), and it is thought that the enrichment source of alumina is the alumina refractory of plasma torch melter.

Table II. Densities and Volume Reduction Factors

| I.D. #	Densities (g/cm³)				Volume Reduction Factors	
	Waste(A)	Intrinsic(B)	Superficial(C)	B-C	B/A	C/A
PT1	1.316	3.450	-	-	2.622	-
PT2	1.250	2.990	3.000	-0.010	2.392	2.400
PT3	1.351	2.740	1.680	1.060	2.028	1.243
PT4	1.563	3.330	2.130	1.200	2.131	1.363
PT5	1.563	2.360	2.000	0.360	1.510	1.280
PT6	1.250	3.070	1.720	1.350	2.456	1.376
PT7	1.282	2.180	2.110	0.070	1.700	1.646
PT8	1.429	2.550	1.700	0.850	1.785	1.190
PT9	0.439	3.230	-	-	7.364	-
PT10	0.938	2.440	1.830	0.610	2.603	1.952
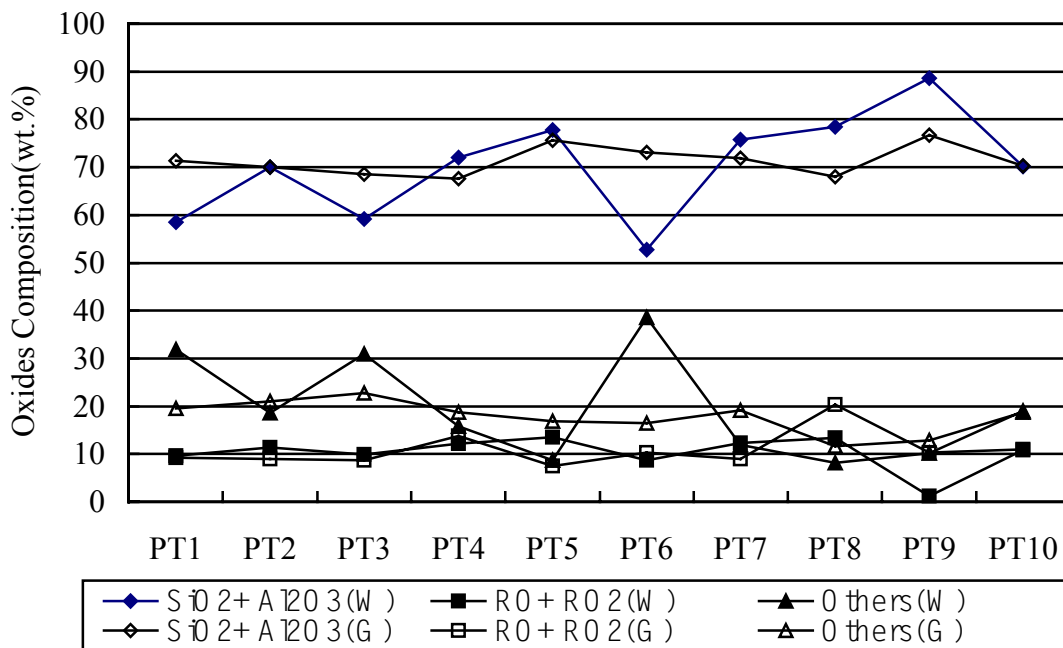
Fig. 1. Oxides composition of the waste and the glassy waste forms
(closed symbols : waste, open symbols : waste forms)

Fig. 2 was examined to find out the relationship between the alumina enrichment amount and the basicity of waste. We can find out that all wastes are nearly acid waste and the wastes having the basicity of about 0.06 and less result in the alumina enrichment in the waste forms. The

enrichment degree increases as decreasing of the basicity. For the basicity more than 0.07, the alumina contents in wastes and waste forms are nearly the same or the contents for waste forms are lower than those for waste.
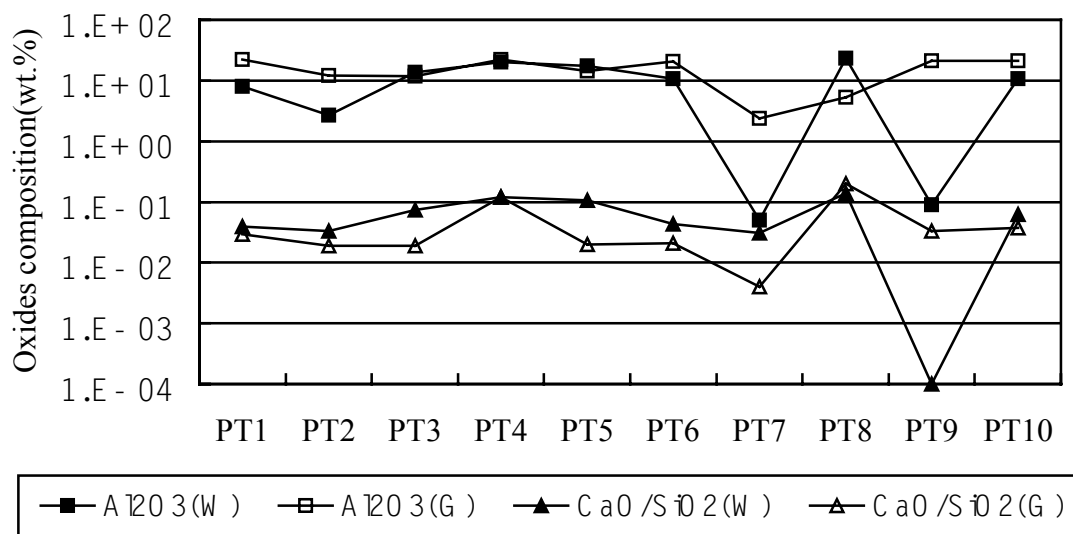

Fig. 2. Variation trends for alumina composition in waste forms with respect to basicity of waste
(closed symbols : waste, open symbols : waste forms)

Leaching Characteristics

The leaching test was carried out in accordance with TCLP established by U.S.A. EPA (10). The Cs content in leachant was analyzed with ICP-MS (Inductively Coupled Plasma - Mass spectrometer (model: VG plasma Quad PQ2 Turbo made by Shimadzu)), and those for the other elements with ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectrometer (model: ICP S-1000 IV, manufacturer: Shimadzu in Japan)).

Fig. 3 shows the results of TCLP test and that all waste forms satisfy TCLP limits of EPA for all elements. We should know that there is no guideline for Cs and Co so that we can not interpret the results. The TCLP tests for the wastes were performed to find out the reasons for high leached amount of Se, which resulted in 0.1 - 0.2 mg/L. The source of Se enrichment in the waste forms might be molten carbon steel in plasma torch melter. The leached amount for Co and Cs is about 10 times more than those for the other elements, and those for Co (2.4 - 67.19 mg/L) are around 2 to 5 times more than those for Cs (0.5-28.84). These results were supposed to be caused by higher contents in waste (5000 ppm) than those for the other elements, and the solubility difference in silica glass (3-5 wt.% for Co and 15-25 wt.% for Cs). The leaching

property for Mercury (Hg) was also examined, but not detected due to the low boiling point (356.9 $^{\circ}$C) and the low solubility in silica glass (< 0.1 wt.%) (8).
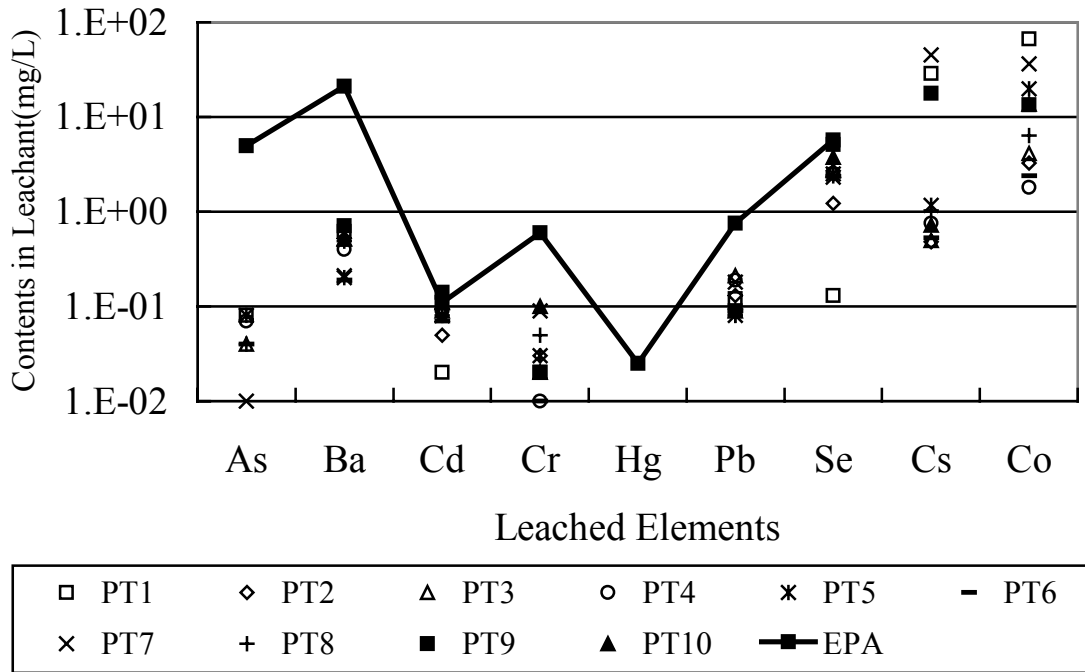

Fig. 3. Elements concentration in leachant with respect to the waste forms

The leached amount for elements may be changed according to the total amount incorporated in waste forms. Therefore the leached fractions (LF) were investigated for the absolute comparison. The leached fraction is defined as follows:

$$LF_i \;=\; \frac{C_{il}}{C_{ig}} \times 20, \qquad\qquad \text{(Eq. 1)}$$

where C_{il} (mg/L) and C_{ig} (mg/Kg) are the concentration in leachant and total concentration in a glassy waste form for element i, respectively. The value, 20 is determined using the weight (g) of sample per unit volume of digestion solution which should be utilized to dissolve thoroughly metal elements in a waste form in the case of Microwave Digestion (MD) analysis.

As shown in Fig. 4, the LF has wide variation according to the type of metal. We can see that the LF of Cr is the smallest (<0.1%), but the one of Co is very high upto 100% for the PT1 waste form. The incorporation ratio for Cs and Co was also investigated and the ratio was turned out to

be 30-80% and 2-25% for Cs and Co, respectively. The result is extraordinary because the volatility of Cs is higher than the one for Co. This phenomenon is supposed to be caused by that the chemical forms of the added Cs and Co are different, which are Cs_2CO_3 and Co powder, respectively. It was known that the Cs_2CO_3 can slightly improve the retention of Cs-137 but the mechanism was not determined (11).
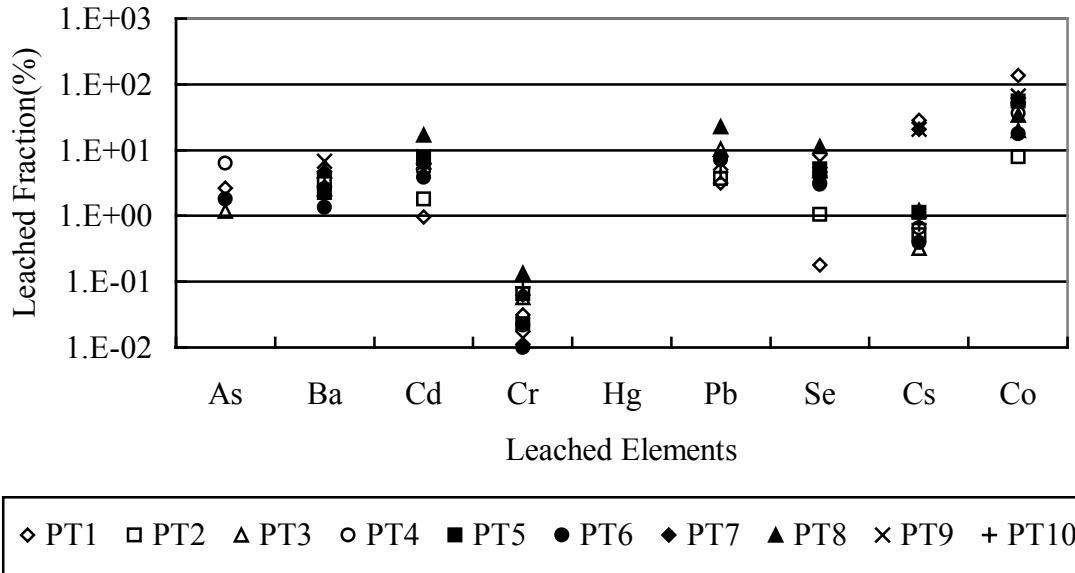
Fig. 4. Leached fraction for 9 elements in waste forms with respect to waste type

CONCLUSION

In order to examine the possibility of vitrification for non-combustible wastes from nuclear power plants, the melting experiments with 60 kW plasma torch system were performed for the waste such as concrete, sand, glass, and simulated filters, and some combined wastes of them. Ten surrogate wastes were prepared and non-radioactive Cs as Cs_2CO_3 and Co powder were added to simulate the radioactive waste. The surrogates were melted with the plasma torch and converted into glassy waste forms. The waste forms were analyzed to find out the best conditions for glass formation.

All waste forms were satisfactory to TCLP test for As, Ba, Cd, Cr, Hg, Se, and Pb compared with UTS limits. However, considering the volume reduction factor and the leaching property for Co, Cs, the best waste form was the one made by the waste of concrete (25 wt.%) and glass (75

wt.%). Its composition was the glass network formers ($SiO_2+Al_2O_3$) of 69.98 wt.%, the network modifiers ($\sum(RO+R_2O)$) of 9.03 wt.%, and the others of 20.99 wt.%. The waste form from the waste of concrete (75 wt.%) and glass (25 wt.%) was turned out to be a poorest one. The other waste forms from the combination of wastes were good as order PT3 (concrete 75 wt.% + sand 25 wt.%), PT4 (concrete 25 wt.% + sand 75 wt.%), and PT5 (glass 25 wt.% + sand 75 wt.%). The waste formers from the combination of wastes had the properties that the range of superficial volume reduction factor was 1.28 - 2.40, and the range of oxides composition was the glass network formers ($SiO_2+Al_2O_3$) of 67.57-75.67 wt.%, the network modifier ($\sum(RO+R_2O)$) of 7.45-13.75 wt.%, and the others of 16.88-22.77 wt.%. Also, it might be concluded that the basicity (CaO/SiO_2) of wastes had better be 0.07 and more in order to prevent the corrosion of alumina refractory.

Among the waste forms PT6 to PT9, which were made by using concrete, glass, sand, and simulated filters each, the PT6 was the best from a viewpoint of the incorporation of Co and Cs, and the PT7 was the best for superficial volume reduction factor.

This works should be studied further for the following items: (1) The melting test and the examination for waste forms made by using the varied mixing ratio of wastes have to be carried out; (2) The chemical forms for Cs and Co had better be changed as CsCl and $CoCl_2$ and the study is necessary to increase the incorporation rate of them with much low concentration.

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