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Characteristics of dioxins and metals emission from radwaste plasma arc melter system[☆]

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Abstract

This study investigated the emission characteristics of PCDD/Fs and the partitioning of three heavy metals (Cd, Hg and Pb) and two radioactive metal surrogates (Co and Cs) in a radwaste plasma arc melter system. Typical mixtures of low-level radioactive wastes were simulated as the trial burn surrogate wastes. The emission of PCDD/Fs and the partitioning of the metals were strongly influenced by the feed waste stream and melter operating temperature, respectively. The emissions of PCDD/Fs, cadmium and lead were greatly enhanced when the polyvinyl chloride was included in the feed waste stream. Most of the nonvolatile cobalt partitioned into the glass. A significant quantity of cesium, cadmium and lead was vaporized during the highest melter temperature test. A lower melter temperature resulted in more cesium, cadmium and lead species remaining in the glass. The results of this study suggest that wet scrubbing as well as a low-temperature two-step fine filtration, or both of them together could not effectively capture the gas-phase or fine particle phase PCDD/Fs and mercury species. In order to effectively treat low-level radioactive waste streams, the tested high-temperature melter should include an adsorption system, which could collect the gas-phase PCDD/Fs and mercury species.

Keywords: Plasma arc melter; PCDD/F; Hazardous metal; Radioactive metal; Emission; Partitioning

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1. Introduction

Nuclear industries usually have to deal with the problems of radioactive waste for disposal. Because of space limitations, maximum volume reduction is desired and a stable, leach resistant final waste form is needed. Plasma arc melter systems have been shown to be capable of processing radioactive waste materials, providing those attributes. In addition, a high temperature plasma melting process has the potential of offering a hazardous organics destruction alternative to incineration with a decreased formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). The intense heat of the plasma destroys organic contaminants and melts the inorganics into a molten ceramic slag (Wagner, 1997).

One of the criticisms of a high-temperature melter is that volatile metals are not retained in the slag phase of a melter. Other important criticism is the formation of PCDD/Fs during the cooling of high-temperature melter

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flue gas. The hazardous metals in the plasma arc melter feed stream are partitioned between the bottom slag stream, and a flue gas stream containing the suspended fly ash and the vapors of volatile elements or compounds. A further partitioning of the flue gas stream takes place in the particulate emission control devices that effectively capture larger fly ash particles but are less efficient for the vapor-phase or fine particle phase metals and PCDD/Fs (Barton et al., 1990).

The public has become increasingly concerned with the mobilization of radioactive or hazardous metals to the environment from the radwaste treatment system. For the successful application of the plasma arc melter system to the radioactive waste, a system capable of treating waste materials from the nuclear industry including polyvinyl chloride (PVC), inorganic and organic resins, cement, and steel, etc. is needed. This work investigated the emission characteristics of PCDD/Fs, and three hazardous metals (Cd, Hg and Pb) and two radioactive metals (Co and Cs) from a pilot-scale plasma arc melter system, which was developed for the treatment of radioactive waste from nuclear power plants. Trial burn tests using a simulated radioactive waste stream were performed to obtain the emission characteristics of PCDD/Fs and the partitioning characteristics of hazardous or radioactive metals with respect to the operating condition. The primary purpose of this work is to improve the system design and to optimize the operating conditions to minimize the PCDD/Fs and hazardous/radioactive metal emissions.

2. Test and data analysis

2.1. Plant description

The process flow diagram of the tested plasma arc melter plant is shown in Fig. 1. The plasma arc melter plant (HJ-200) consists of a graphite-electrode arc melter with a capacity of about 200 kg/h for inorganic materials and about 100 kg/h for combustible organics, a thermal oxidizer, and an off-gas treatment system (Quapp et al., 1999). The thermal oxidizer is installed on the top of the melter in order to complete the combustion of the products of an incomplete combustion and the destruction of volatile organic constituents. The off-gas quenching system rapidly cools the thermal oxidizer exhaust gas to about 80 °C. A scrubber solution contacts with the exhaust gas in the quench chamber, atomizer, and scrubber thereby scrubbing the particulate and soluble gases from the gas stream. The exhaust gas exiting the mist eliminator is heated to about 120 °C in order to avoid water vapor condensation. Cleaned flue gas finally passes through a pre-filter and two HEPA (high efficiency particulate air) filters in series.

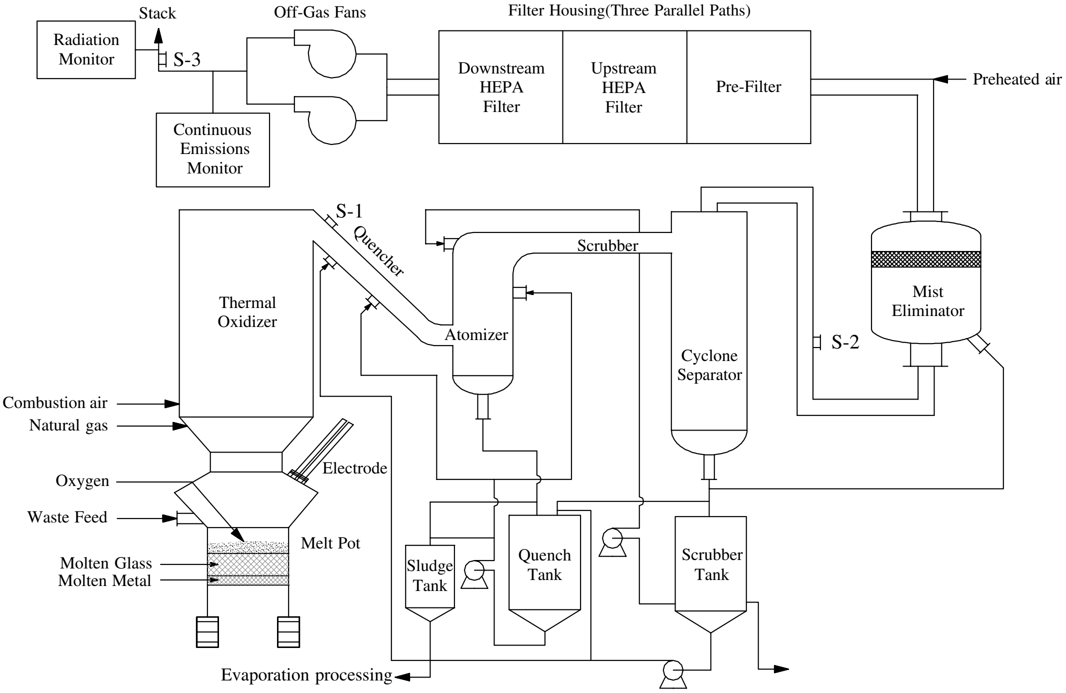

Fig. 1. Process flow diagram of tested plasma arc melter system.

2.2. Trial burn test methods

2.2.1. Model waste

Trial burn test conditions are summarized in Table 1. Typical kinds of low-level radioactive wastes from nuclear power plants were used as the trial burn surrogate wastes. The wastes were categorized into combustibles, noncombustible, and cemented resin. Combustibles were composed of PVC (15.6%), polyethylene (40.6%), and cellulose materials (43.8%), such as paper and rubber. Noncombustibles were composed of iron (2.6%), concrete (7.7%), air filter (20.5%), glass (33.3%) and soil (35.9%). Cemented resin was composed of cement (65.6%), water (15.0%) and organic ion-exchange resin (19.4%).

2.2.2. PCDD/Fs emission test

As shown in Table 1, all kinds of surrogate wastes with the simulated real radioactive waste composition were fed for the PCDD/Fs emission test (T-1 test). The waste feeding started with the combustibles, followed by the noncombustibles, and cemented resins. A total of 736 kg of waste was treated during the T-1 test for 15 h. The averaged concentrations of PCDD/Fs in the stack emission were measured during the treatment of each typical waste stream.

2.2.3. Metal partitioning test and analysis

Inactive cobalt (Co-59) and cesium (Cs-133) were used as surrogates for radioactive Co-60 and Cs-137, respectively. Cadmium, lead and mercury were used as important hazardous metals. Chemical formulae of the used sample metal compounds are shown in Table 1. Powdered samples of the metal compounds were spiked into the feed waste streams. Sampling locations for the metal partitioning tests are shown in Fig. 2. During the metal partitioning tests (T-2, T-3 and T-4 tests in Table 1), particulate and gaseous metals in the process of the off-gas streams were sampled using three identical EPA-type multiple metal sampling trains at three sampling locations (S_1, S_2 and S_3). From the measured concentration of each metal species at each sampling location, metal partitioning into the waste glass, the scrubber liquid and the HEPA filter were determined as

$$M_{WG} = M_T - M_{S1} \quad (1)$$

$$M_{SL} = M_{S1} - M_{S2} \quad (2)$$

$$M_{HF} = M_{S2} - M_{S3} \quad (3)$$

where M_T is the total mass of the spiked metal, M_{WG}, M_{SL}, M_{HF} are the quantities of the metal remaining in the waste glass, that was collected by the scrubber

Table 1
Test conditions for PCDD/Fs emission and metals partitioning in the plasma arc melter plant

Test no.	Waste/feed quantity (compositions)	Melter temperature (°C)	Thermal oxidizer temperature (°C)	Spiking materials	Sampling/ analysis	Testing time (h)
T-1	Combustibles/176 kg (noncombustibles: 200 kg, cemented resin: 120 kg)	1000–1300	900–1000		Emission of PCDD/Fs	15
T-2	Combustibles/192 kg (PE: 40.6%, PVC: 15.6%, Paper and Cloth: 43.8%)	1220–1700	1000–1600	CoO: 1452 g CsCl: 1041 g PbO: 300 g $HgCl_2$: 376 g CdO: 300 g	Partitioning and emission of spiked metals	17.5
T-3	Noncombustibles/440 kg (Iron: 2.6%, Concrete: 7.7%, Air filter: 20.5%, Glass: 33.3%, Sand/soil: 35.9%)	1200–1600	900–1000	CoO: 968 g CsCl: 694 g PbO: 1000 g $HgCl_2$: 1254 g CdO: 200 g	Partitioning and emission of spiked metals	16
T-4	Cemented ion-exchange resin/530 kg (Cement: 65.6%, Water: 15.0%, Resin: 19.4%)	1000–1300	900–1000	CoO: 968 g CsCl: 694 g PbO: 200 g $HgCl_2$: 251 g CdO: 200 g	Partitioning and emission of spiked metals	12

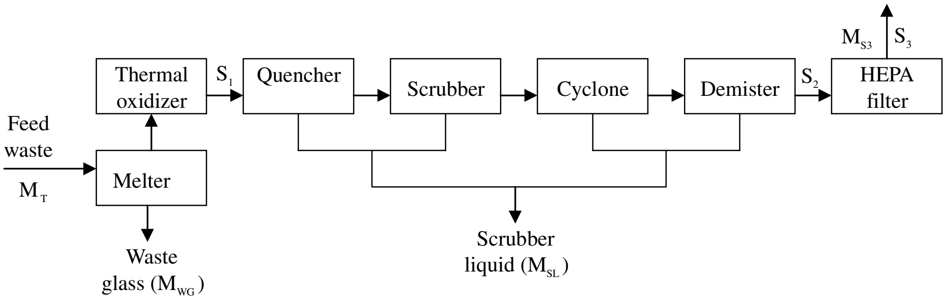

Fig. 2. Sampling locations for flue gas (S_1, S_2 and S_3) for determination of metals partitioning in the waste glass (M_{WG}), scrubber liquid (M_{SL}) and emission (M_{S3}) in the tested plasma arc melter system.

system and the HEPA filter system, respectively, and M_{S1}, M_{S2}, M_{S3} are the total masses of the metal in the flue at the sampling locations S_1, S_2 and S_3, respectively.

3. Results and discussion

3.1. PCDD/Fs emission

Measured PCDD/Fs concentrations are shown in Table 2. The total emissions of PCDD/Fs were in the range of 0.45–0.20 ng TEQ/Nm^3. These concentrations are temporarily satisfactory because they are below the regulated emission limit of PCDD/Fs in Korea (5 ng TEQ/Nm^3), considering that the tested condition could be considered as the worst-case conditions for chlorinated organics emission. The operating temperatures of the melter are very wide and in the range of about 1000–1700 °C, at which temperatures the melter can destroy organics and melt inorganics. During the PCDD/Fs emission test, the operation temperature of the melter was maintained at relatively low temperature ranges (1000–1300 °C), which could represent the worst-case condition for the organics destruction and the chlorinated organics emission. The operating temperatures of the thermal oxidizer are also in the low temperature range of 900–1000 °C, at which temperatures the destruction of unburned hydrocarbon in the flue gas is relatively inefficient. In addition, rubbers such as gloves and shoes were removed from the feed waste stream, since they include a significant quantity of sulfur, which is known as a PCDD/Fs inhibitor (Tuppuanien et al., 1998). Among three waste mixtures, combustibles were considered as the worst-case mixtures for PCDD/Fs emission, since they includes the largest amount of organic chlorines.

The measured PCDD/Fs concentrations for worst-case conditions were in the range within 10% of the current regulated emission standard in Korea. However, there have been some arguments as to whether the measured PCDD/Fs emission values are satisfactory or not. One criticism is that the tested condition could not represent the worst-case condition. Although the temperature of each combustion chamber could represent the worst-case scenario of the organics destruction and the chlorinated organic emission, other operating parameters could not represent the worst-case condition of organic destruction. Air pollution control equipment (APCE) operation parameters closely associated with the PCDD/Fs production (Dickson et al., 1992) were maintained within the normal operating ranges. The flue gas from the thermal oxidizer at about 1000 °C was rapidly cooled to below 200 °C by quenching. The inlet temperatures for the HEPA filters, which are the available particulate hold-up areas for PCDD/Fs formation (Stieglitz et al., 1991; Gullet and Raguhunathan, 1997), were maintained to be about 120 °C. Since the formation of PCDD/Fs has been confirmed experimentally in the temperature range 250–450 °C (Tuppuanien et al., 1998), it was believed that APCE operating conditions during the PCDD/Fs emission tests were good for limiting the production of PCDD/Fs. This was the reason why the tested condition could not represent the worst-case scenario of PCDD/Fs emission. The other criticism is that 10% of the current emission standard is not enough for the developing thermal plant, since the PCDD/Fs emission standard will become severe in Korea. It is generally recommended in Korea that the developing thermal plants should satisfy the proposed future emission limit of 0.1 ng TEQ/Nm^3 (Yoon, 2003). These critical discussions suggest that the developed radwaste plasma plant of this study should include some additional off-gas system equipment. As described in the section of the plant description, the off-gas system includes a quenching and wet scrubbing system, and a two-step fine HEPA filtration system. It was suggested that wet scrubbing and a low-temperature two-step fine filtration, or both of them together could not effectively collect the gas-phase PCDD/Fs generated from the high-temperature plasma arc melter. It was therefore concluded that another type of APCE such as an adsorption system, which could col-

Table 2
Measured real dioxin emission concentrations (12% O_2 basis)

	Emission concentration (ng TEQ/Nm^3)-12% O_2 basis		
	Combustibles[a]	Noncombustibles[b]	Cemented resin[c]
PCDF			
2,3,7,8-TCDF	0.012	0.007	0.008
1,2,3,7,8-PeCDF	0.010	0.006	0.007
2,3,4,7,8-PeCDF	0.015	0.010	0.010
1,2,3,4,7,8-HxCDF	0.010	0.006	0.007
1,2,3,6,7,8-HxCDF	0.017	0.009	0.009
2,3,4,6,7,8-HxCDF	0.025	0.013	0.011
1,2,3,7,8,9-HxCDF	0.006	0.000	0.000
1,2,3,4,6,7,8-HpCDF	0.000	0.000	0.000
1,2,3,4,7,8,9-HpCDF	0.012	0.006	0.006
OCDF	0.134	0.045	0.042
PCDD			
2,3,7,8-TCDD	0.004	0.002	0.002
1,2,3,7,8-PeCDD	0.004	0.004	0.003
1,2,3,4,7,8-HxCDD	0.003	0.004	0.002
1,2,3,6,7,8-HxCDD	0.005	0.006	0.003
1,2,3,7,8,9-HxCDD	0.006	0.004	0.001
1,2,3,4,6,7,8-HpCDD	0.038	0.018	0.020
OCDD	0.146	0.059	0.071
Total PCDFs	0.241	0.102	0.099
Total PCDDs	0.206	0.097	0.101
Total (PCDDs + PCDFs)	0.447	0.199	0.200

[a] Combustibles (PE: 40.6%, PVC: 15.6%, Cellulose: 43.8%).

[b] Noncombustibles (Iron: 2.6%, Concrete: 7.7%, Air filter: 20.5%, Glass: 33.3%, Sand/soil: 35.9%).

[c] Cemented ion-exchange resin (Cement: 65.6%, Water: 15.0%, Organic resin: 19.4%).

lect gaseous contaminants, should be installed to reduce the emissions of PCDD/Fs under the proposed future emission limit of 0.1 ng TEQ/Nm^3.

The emission concentrations of PCDD/Fs with respect to the feed waste stream are compared in Fig. 3. When combustible organics, which include 15.6% of the PVC by weight, were test-burned, averaged PCDD/Fs concentration in the stack emission was measured to be 0. 022 ng TEQ/Nm^3. This result suggests that when the chlorinated organics such as PVC are fed, a significant quantity of PCDD/Fs could be formed in the downstream of a high-temperature melter flue gas, even if the APCE operating conditions are limiting for PCDD/Fs production. When noncombustibles and cemented resins were melted, PCDD/Fs emission concentrations remained at 0.012 and 0.014 ng TEQ/Nm^3, respectively. Although noncombustibles and cemented resins do not include chlorines as a major constituent, the emissions of PCDD/Fs for those waste streams were not much lower than that for the combustibles including PVC. This suggests that some chlorines might deposit somewhere in the off-gas system during PVC combustion and they can be re-entrained to form gas-phase or fine particle phase PCDD/Fs when the noncombustibles or nonchlorinated wastes are treated.

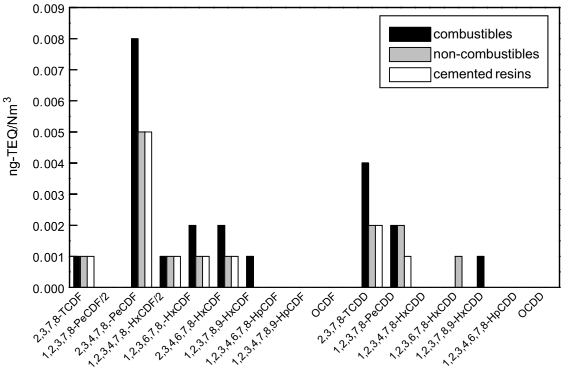

Fig. 3. PCDD/Fs emissions from simulated samples of the typical feed waste stream from nuclear power plant.

3.2. Metal emission

Based on the analyzed metal concentration at each sampling location, the overall partitioning of the metals in different secondary waste steams was calculated to be 100% by Eqs. (1)–(3) and the results are shown in Fig. 4.

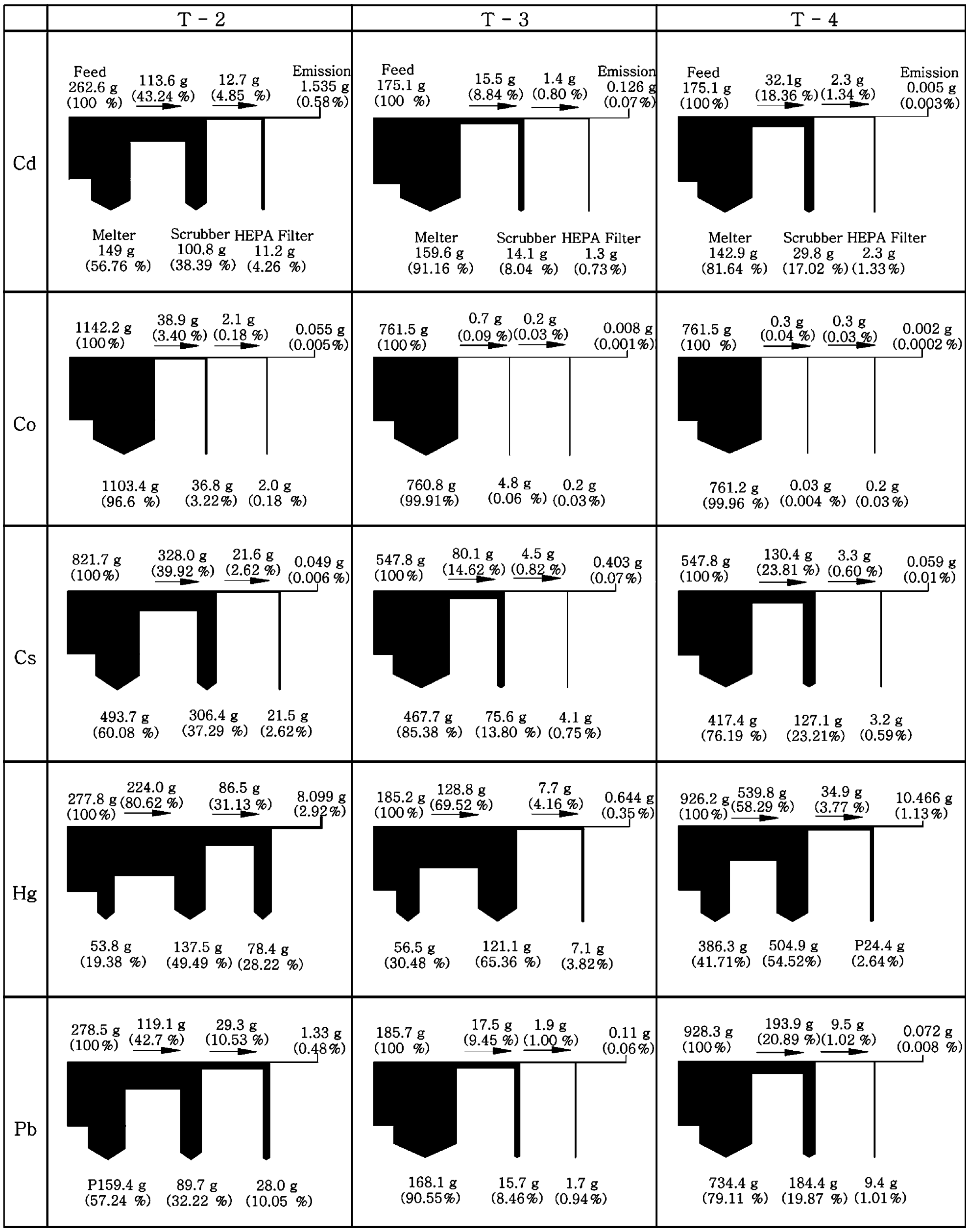

Fig. 4. Partitioning of hazardous metals and radioactive metal surrogates in the plasma arc melter plant.

3.2.1. Radioactive metal

Most of the cobalt partitioned into the glass and the minor fraction entrained was efficiently collected in the off-gas system. Cobalt oxide (CoO) is known as a stable oxide in the presence of chlorine at the high temperatures tested (Yang et al., 1998). It is therefore suggested that the entrained fraction of cobalt was the particulate entrainment. It can also be stated that the difference in the entrained fraction of the particulate cobalt with respect to the operating condition resulted mainly from the difference in the gas turbulence due to the differences in the organics feed rates.

The partitioning of cesium varied noticeably with the testing condition. As shown in Fig. 4 over 50% of the cesium fed remained in the waste glass during the high-temperature metal test (T-2). The lower temperatures of the tests (T-3 and T-4) resulted in more cesium species remaining in the glass. The collection of entrained cesium species by the wet off-gas system (quencher, hydrosonic scrubber, cyclone and demister in series) was about 95% and that by the HEPA filter (high efficiency particulate air) was about 96%. As in the case of three tested hazardous metals, the collection of the condensed fine cesium species by the scrubber system and HEPA filter system was not effective.

3.2.2. Hazardous metals

As shown in Fig. 4, the partitioning characteristics of cadmium in the same trial burn conditions were quite similar to that of lead. As shown in Table 1, cadmium and lead were fed in the form of their stable oxides (PbO and CdO). These stable oxides can easily be transformed into their relatively more volatile chlorides ($PbCl_2$ and $CdCl_2$) in the presence of chlorine. The retention of cadmium and lead in the melter was greatest for the T-3 test. Less than 10% of the spiked cadmium and lead remained during the T-3 test. Considering that the melter-operating temperatures were relatively high (1200–1600 °C), it was suggested that this higher retention in the melter resulted from the interaction between the spiked metals and fed sand or soil. Interaction between the oxides of lead and cadmium and the aluminum silicates in the sand or soil could form stable metal–mineral complexes such as $PbAl_2Si_2O_8$ and $CdAl_2Si_2O_8$, which are known as extremely low-volatility metal–mineral compounds (Linak and Wendt, 1993). Over 40% of the spiked cadmium and lead species were entrained in the off-gas system during the T-2 test. This lower retention of the cadmium and lead species could be explained by the chlorination of the cadmium and lead species. The feed waste stream for the T-2 test contained 15.6% PVC by mass. The interaction between the HCl or free chlorine (Cl_2) first released in the PVC and the spiked cadmium and lead oxides could produce cadmium and lead chlorides ($PbCl_2$ and $CdCl_2$), which are much more volatile than their oxides (Yang et al., 1998).

The collection of the entrained cadmium and lead species by the scrubber system and the HEPA filter system did not significantly vary with the test condition. The averaged collection efficiency of the scrubber system and the HEPA filter system for the entrained cadmium and lead species was about 90% and 95%, respectively. This shows that the collection of the HEPA filter system and the scrubber system for condensed fine particulate cadmium and lead species is not effective.

The partitioning of mercury varied significantly with the testing conditions, as shown in Fig. 4. Surprisingly the mass balance of mercury based on the off-gas samples showed that about 20–40% of mercury retaining in the glass. However, only a trace quantity of mercury was found in the waste glass sample. Anyway, the overall mercury collection efficiency was about 97–99.6%. Wet scrubbing, as well as low-temperature fine filtration, or even both of them together could not effectively capture the volatilized mercury species.

4. Conclusion

The results of PCDD/Fs and metals emission tests for a radwaste plasma arc melter system will be used to improve the system design and limit the operating conditions to minimize their emissions. When PVC was fed into the high-temperature melter, a significant quantity of PCDD/Fs, cadmium and lead was emitted. Wet scrubbing with rapid quenching, as well as a low-temperature two-step fine filtration, or both of them together cannot effectively control the volatile metal species and gas-phase PCDD/Fs. Considering that radioactive waste streams include volatile trace metals and radionuclides as well as organic and inorganic chlorines, an appropriate adsorption system for the collection of volatile trace metals and PCDD/Fs, such as an activated carbon bed, should be installed into the off-gas system for the tested plasma arc melter system. The removal of PVC from the feed waste stream must also be effective to reduce the emissions of the PCDD/Fs, cadmium and lead species. However, since the volatility of the cesium and mercury is great in the absence of feed chlorines, an appropriate absorption system should be installed to reduce the emission of the cesium and mercury species.

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