

# FORMATION AND SOURCES II –POSTER

## CHARACTERISTICS OF DIOXINS AND METALS EMISSION FROM RADWASTE PLASMA ARC MELTER SYSTEM

Hee-Chul Yang and Joon-Hyung Kim

Nuclear Fuel Cycle R&D Group, Korea Atomic Energy Research Institute, Daejeon 305-353, Korea

### Introduction

High temperature plasma melting process has the potential to offer organics destruction equivalent to incineration with decreased formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). The intense heat of plasma destroys organic contaminants and melts inorganics into a molten ceramic slag. One of the criticisms of a high-temperature melter is that volatile metals are not retained in the slag phase of a melter<sup>1</sup>. In addition, when the chlorinated organics are treated, the formation of PCDD/Fs in the cooled downstream of high-temperature melter is inevitable. This work investigated the emissions of PCDD/Fs, three hazardous metals (Cd, Hg and Pb) and two radioactive metals (Co and Cs) from the radwaste plasma arc melter system. The purpose of this work is to know the emission characteristics of PCDD/Fs under worst-case condition of organics destruction and the partitioning characteristics of hazardous and radioactive metals with respect to the operating condition.

### Plant Description and Trial Burn Methods

The plasma arc melter plant (HJ-200) consists of a graphite-electrode arc melter with a capacity of 200 kg/h for non-combustibles and 100 kg/h for combustibles, a thermal oxidizer, and an off-gas treatment system. The process flow diagram of the plant is shown in Fig. 1. The thermal oxidizer is installed to the top of the melter in order to complete the combustion of products of incomplete combustions (PICs) and the destruction of volatile organic constituents (VOCs). The off-gas quenching system rapidly cools thermal oxidizer exhaust gas to about 80°C, thereby limiting the formation of PCDD/Fs. The scrubber solution contacts the exhaust gas in the quench chamber, atomizer, and scrubber thereby scrubbing particulate and soluble gases from the gas stream. The exhaust gas exiting the mist eliminator passes through a pre-filter and two HEPA filters in series.

Trial burn conditions are summarized in Table 1. Typical kinds of low-level radioactive wastes were simulated as the trial burn surrogate wastes. All kinds of surrogate wastes with simulated real radioactive waste composition were fed for PCDD/Fs emission test (T-1 test). The waste feeding started with the combustibles, followed by non-combustibles and boric acid and cemented resins. A total of 736 kg of waste was treated during T-1 test for 15 h. Three 4-h PCDD/Fs samplings from the off-gas flowing in the stack (S-3 in Fig. 1) for each waste stream were performed using EPA method 23 sampling train<sup>2</sup>. During the metals partitioning tests (T-2, T-3 and T-4 tests), particulate and gaseous metals in the process off-gas streams were sampled using three identical multiple metals sampling trains at three sampling locations (S-1, S-2 and S-3 in Fig. 1)<sup>3</sup>.

# FORMATION AND SOURCES II -POSTER

## Results and Discussions

During PCDD/Fs emission test, minimum operation temperature of each combustion chamber (melter and thermal oxidizer) was maintained to represent the worst-case condition for organics destruction. 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<sup>4</sup>. However, air pollution control equipment (APCE) operation parameters closely associated with the PCDD/Fs production were maintained within normal operating ranges<sup>5</sup>. The flue gas from thermal oxidizer was maintained below 80°C. The inlet temperatures to HEPA filters, which are the available particulate hold-up areas for PCDD/Fs formation, were maintained to be 100-120°C<sup>6</sup>. It was therefore believed that APCE operating conditions were good for limiting the production of PCDD/Fs. In addition, the concentrations of CO and THCs (total hydrocarbons), which are good indicators for the formation PCDD/Fs precursors<sup>7</sup>, were maintained to be below 1 ppm and 65 ppm, respectively. Nevertheless, significant quantities of PCDD/Fs were found in stack emissions, as shown in Fig. 1. When combustible organics, which include 15.6% of PVC by weight, were burned, PCDD/Fs concentration in stack emission was measured to be 0.022 ng/dscm. When non-combustibles, boric acid, and cemented resins were burned, PCDD/Fs concentration remained to be 0.014–0.012 ng/dscm. This result suggested that when the chlorinated organics such as PVC are fed, a significant quantity of PCDD/Fs can be formed in the downstream of high-temperature melter flue gas, even if APCE operating conditions are limiting for PCDD/Fs production. In addition, some chlorines may deposit somewhere in the off-gas system during PVC combustion and they can entrained to form PCDD/Fs when the non-combustibles or non-chlorinated wastes are treated.

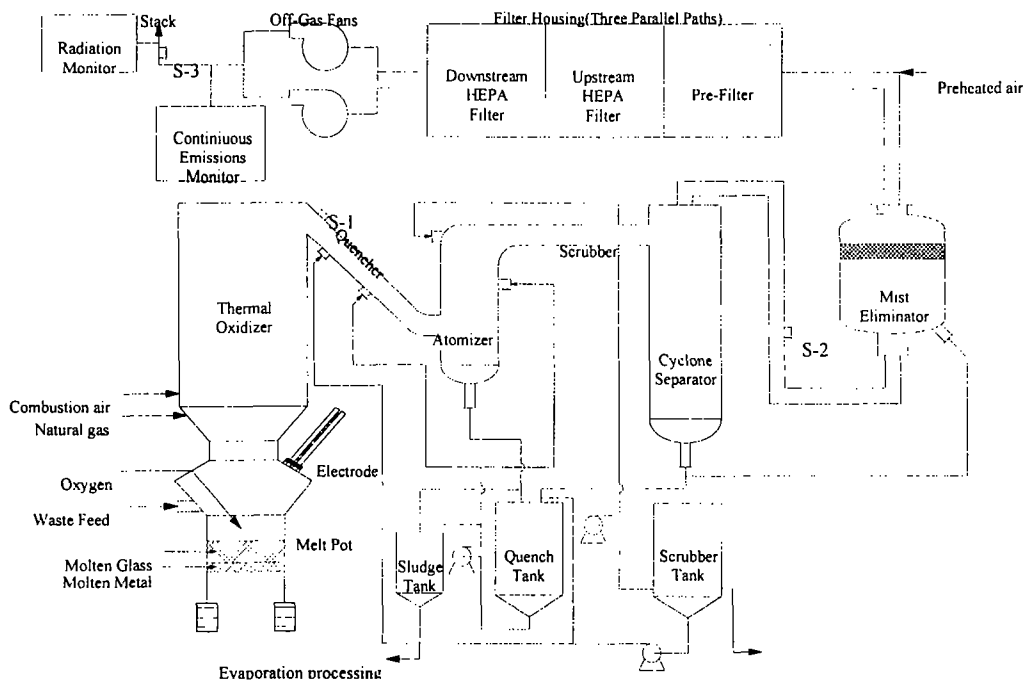


Fig. 1. Process flow diagram of plasma arc melter system

# FORMATION AND SOURCES II -POSTER

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

Test No.	Waste / Feed Quantity (Compositions)	Melter Temp. (°C)	Thermal oxidizer Temp. (°C)	Spiking Materials	Sampling /Analysis	Testing Time (h)
T-1	Combustibles: 176 kg Non-combustibles: 200 kg Cemented Resin: 120 kg Boric Acid: 240 kg	1000 - 1300	900 - 1000	N/A	Emission of PCDD/Fs	15
T-2	Combustibles / 192 kg (PE: 40.6%, PVC: 15.6% Paper and Cloth: 3.8%)	1220 - 1700	1000 - 1160	CoO : 1452g CsCl : 1041g PbO : 300g HgCl <sub>2</sub> : 376g CdO : 300g	Partitioning & Emission of Spiked Metals	17.5
T-3	Non-combustibles / 440 kg (Iron: 2.6%, Concrete: 7.7%, Air filter: 20.5%, Glass: 33.3%, Sand/soil: 35.9%)	1200 - 1600	900 - 1000	CoO : 968g CsCl : 694g PbO : 1000g HgCl <sub>2</sub> : 1254g CdO : 200g	Partitioning & 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 : 968g CsCl : 694g PbO : 200g HgCl <sub>2</sub> : 251g CdO : 200g	Partitioning & Emission of Spiked Metals	12

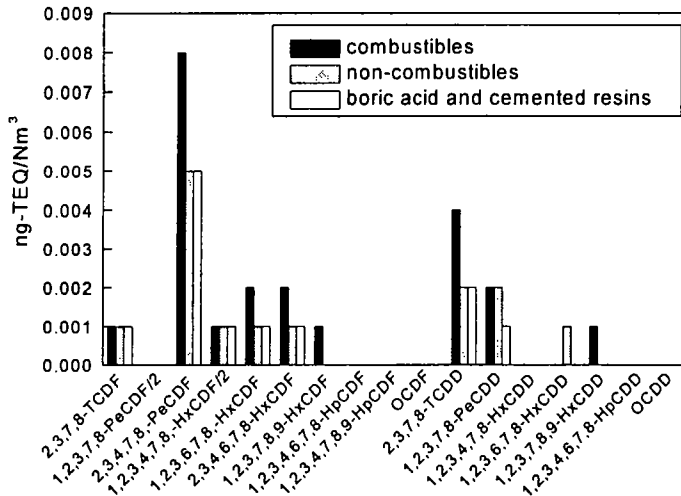


Fig. 2. PCDD/Fs emission concentrations during trial burn test T-1 determined by three 4-h measurements for each waste stream.

## FORMATION AND SOURCES II -POSTER

Based on the analyzed metals concentration in the off gas streams at the sampling locations S-1, S-2 and S-3, which is shown in Fig. 1, the overall partitioning of the metals in different secondary waste streams was calculated to be 100% and the results are shown in Fig. 3. Most of non-volatile cobalt partitioned into glass and the minor fraction entrained was efficiently collected in the off-gas system. The partitioning of volatile cesium varied noticeably with testing condition. Over 50% of the cesium remained in the waste glass during the highest temperature test (T-2). The lower temperature of the tests (T-3 and T-4) resulted in more cesium species remaining in the glass. The most entrained cesium species were collected in the scrubbing system. The partitioning characteristics of cadmium and lead were quite similar. The different partitioning of cadmium and lead in the three tests could thus be explained by the different quantity of chlorine fed, as well as the different melt temperatures. The partitioning of mercury also varied with the testing conditions. Surprisingly the mass balance calculation showed about 20-40% partitioning in the glass. However, 0.4-3% of volatile mercury was emitted during the metals partitioning tests.

The results of these full-scale PCDD/Fs and metals emission tests will be used to improve system design and to limit operating conditions to minimize their emissions. When PVC is fed to high-temperature melter, a significant quantity of PCDD/Fs can be emitted. Wet scrubbing with rapid quenching, as well as low-temperature two-step fine filtration, or both of them together cannot effectively control volatile metal species and PCDD/Fs. Considering that target radioactive waste stream includes 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 activated carbon bed, should be included in the off-gas system for tested plasma arc melter system.

### References

1. Wagner, J. (1997), New and innovative technologies for mixed waste treatment, Prepared under the grant number U-915074-01-0, EPA Office of Solid Waste Permits and State Programs Division, 50.
2. 40 CFR 266, Appendix IX, Determination of PCDDs/PCDFs from stationary sources (Method 23).
3. 40 CFR 266, Appendix IX, Methodology for the determination of metals emission in exhaust gases from hazardous waste incinerator and similar combustion conditions (Method 5).
4. Tuppuanien, K., Halonen, I., Ruokojärvi, P., Tarhanen, J. and Ruuskanen, J (1998), *Chemosphere* 36, 1507.
5. Dickson, L. C., Lenoir, D. and Hutzinger, O. (1992) *Environ. Sci. Technol.* 26, 1822.
6. Stieglitz, L. and Vogg, H. (1987), *Chemosphere* 16, 1917.
7. Gullet, B. K. and Raguhunathan, K. (1997), *Chemosphere* 34, 1027.

# FORMATION AND SOURCES II - POSTER

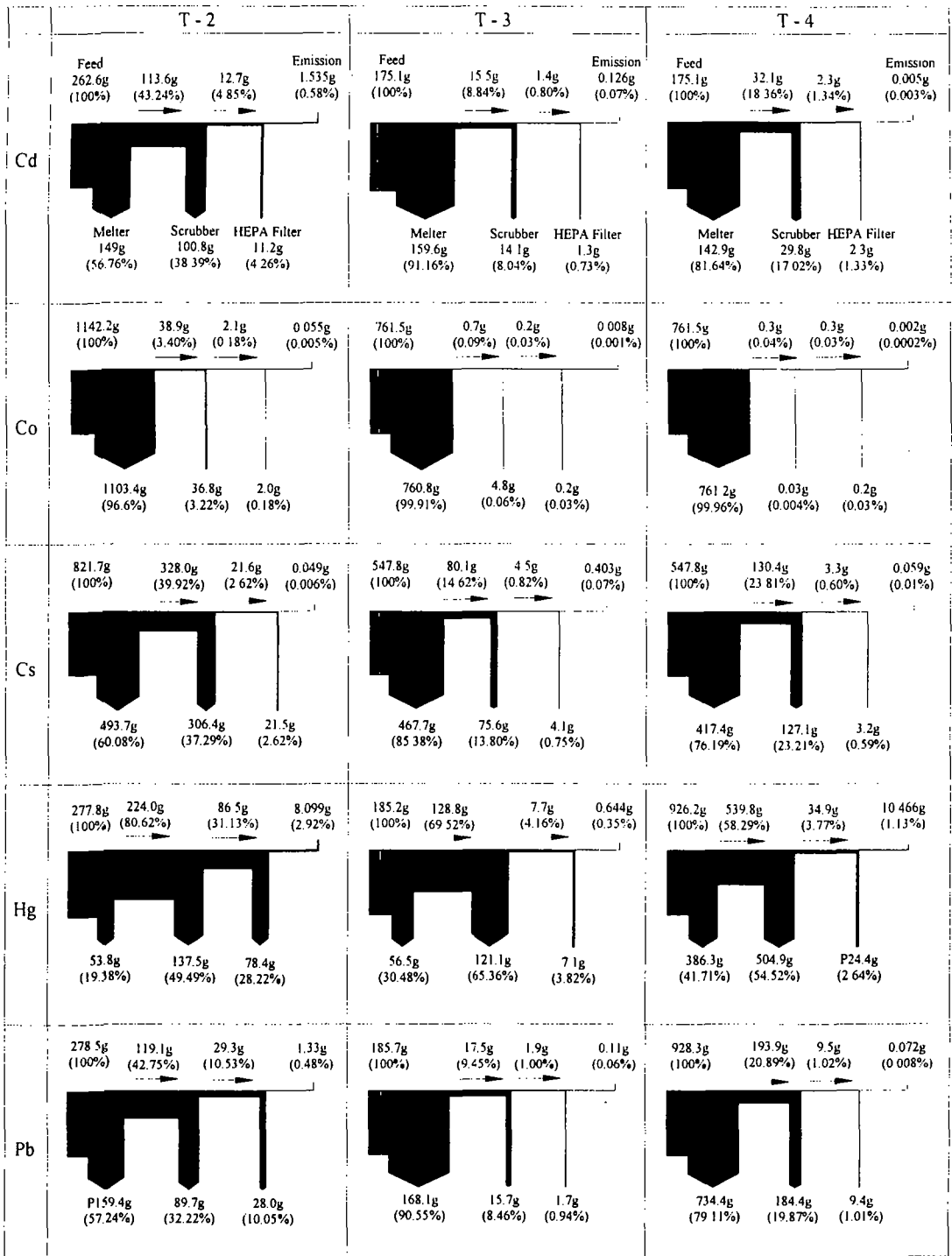


Fig. 3. Partitioning of hazardous metals and radioactive surrogates in the plasma arc melter plant.