

Behavior of Radioactive Metal Surrogates Under Various Waste Combustion Conditions

**Hee-Chul Yang, Jae-Hee Lee, Jung-Guk Kim, Jae-Hyung Yoo,
and Joon-Hyung Kim**

Korea Atomic Energy Research Institute
150 Dukjin-dong, Yusong-gu, Taejon 305-353, Korea
nhcyang@kaeri.re.kr

(Received May 11, 2001)

Abstract

A laboratory investigation of the behavior of radioactive metals under the various waste combustion atmospheres was conducted to predict the parameters that influence their partitioning behavior during waste incineration. Neodymium, samarium, cerium, gadolinium, cesium and cobalt were used as non-radioactive surrogate metals that are representative of uranium, plutonium, americium, curium, radioactive cesium, and radioactive cobalt, respectively. Except for cesium, all of the investigated surrogate metal compounds converted into each of their stable oxides at medium temperatures from 400 to 900°C, under oxygen-deficient and oxygen-sufficient atmospheres (0.001-atm and 0.21-atm O₂). At high temperatures above 1,400°C, cerium, neodymium and samarium in the form of their oxides started to vaporize but the vaporization rates were very slow up to 1500°C. Inorganic chlorine (NaCl) as well as organic chlorine (PVC) did not impact the volatility of investigated Nd₂O₃, CoO and Cs₂O. The results of laboratory investigations suggested that the combustion chamber operating parameters affecting the entrainment of particulate and filtration equipment operating parameters affecting particle collection efficiency be the governing parameters of alpha radionuclides partitioning during waste incineration.

Key Words : radioactive metal, surrogate, combustion, volatility, conversion, partitioning

1. Introduction

On waste incineration, radioactive elements in the incinerator feed stream are partitioned between the bottom ash stream, and the off-gas stream containing entrained fly ash and vapors of

volatile elements or compounds. A further partitioning of the off-gas stream takes place in the particulate emission control devices that efficiently remove large fly ash particles but are less efficient for fine particles. Fine particles easily discharge into the atmosphere through the

exhaust stack and enter the terrestrial and aquatic environments by wet and dry deposition [1]. Therefore, the primary safety concern for radwaste incineration process is the possibility that radionuclides could be emitted to the atmosphere in the off-gas stream [2]. Radioactive elements emitted from the incineration of radioactive waste are regulated using a risk-based approach based on the partitioning behavior of radioactive metals in the process [3].

The partitioning behavior of metals in the incineration process is closely related to the volatility under waste combustion atmosphere [4,5]. Some radioactive metals are volatile and have significant vapor pressure. In the hot, burning environment of the combustion device, a portion of the metals in the waste vaporizes, changing from a liquid state to gas. When the vapors cool, they condense to form very fine particulates less than 1 μ m in diameter, which tend to be difficult to capture in air pollution control equipment. Therefore, the mechanism of particulate formation by volatilization and condensation is of special concern when the inorganic fraction of the waste includes toxic or radioactive metals.

The vaporization process depends on the temperature and on the chemical environment [6,7]. Nonvolatile metals vaporize if the temperature increases or if the metals encounter another species and react to form volatile compounds. If the chlorines are present in the local surroundings, for example, the metals may undergo a chemical reaction and form chlorides, which are typically more volatile than the oxides of the same metal. Those metal chlorides will subsequently vaporize. In this study, laboratory experiments were performed to investigate the conversion and the volatility characteristics of several surrogate metals, which are representative of important radioactive metals. The attention has

been paid to the volatility of surrogate metal compounds under the simulated worst-case conditions. Simulated worst-case conditions are the oxygen-deficient atmosphere and the presence of chlorines. The purpose of this study is to predict the parameters that influence the partitioning behavior of important radionuclides during waste incineration.

2. Experimental

2.1. Surrogate Metals

Using non-radioactive surrogate metals reduces environmental impact during radwaste treatment research. Six non-radioactive surrogate metals representing radionuclides of interest were used in this experimental study. The used surrogate metals were neodymium, samarium, cerium, gadolinium, cesium and cobalt. The surrogates, the radionuclides they represent, and the chemical forms used are summarized in Table 1. The primary criteria for selecting the surrogate metals were their common oxidation states. Metals with common oxidation states identical to those of the radioactive metals of interest were selected based on the literatures [8, 9]. All the chemical compounds were high-purity grade reagents (>99% - >99.99%) supplied by Aldrich Chemical Co.

2.2. Experimental Method

The test program was divided into two series according to the variable investigated. The first series of tests were to investigate the impact of gaseous atmosphere on the behavior of surrogates listed in Table 1 at elevated temperatures. The second series of tests were to investigate the influence of chlorine on the volatility of selected three surrogate metals. The experimental conditions of each test series are summarized in Table 2.

Table 1. Surrogate Metal Compounds Used and Radionuclides Represented

Surrogate metal	Radionuclide represented	Compound investigated
Cerium (Ce)	Am, Pu, Cm, U	Ce(NO ₃) ₃ (6H ₂ O, CeO ₂)
Cesium (Cs)	Cs	Cs ₂ O, CsCl
Cobalt (Co)	Co	Co
Gadolinium (Gd)	Cm	Gd(NO ₃) ₃ (6H ₂ O)
Neodymium (Nd)	U	Nd(NO ₃) ₃ (6H ₂ O, Nd ₂ O ₃ , NdCl ₃)
Samarium (Sm)	Pu	Sm ₂ O ₃

Table 2. Summary of Experimental Conditions of Two Test Series

Test series No.	Variable investigated		Compound investigated	Temperature tested
	O ₂ partial Pressure ¹⁾	Additives		
1	<0.001 atm 0.21 atm	Not used	Ce(NO ₃) ₃ , Cs ₂ O, CsCl, Co, Gd(NO ₃) ₃ · 6H ₂ O Nd(NO ₃) ₃ · 6H ₂ O Nd ₂ O ₃ , NdCl ₃ Sm ₂ O ₃	Room temperature ~1500°C ²⁾
2	0.21 atm	PVC resin or NaCl powder as a chlorine source, and chlorine to metal mole ratio of 0, 5, and 10 for each chlorine source	CoO Cs ₂ O Nd ₂ O ₃	Room temperature ~1000°C ³⁾

1) N₂ Balance

2) Increasing rate of 20 °C/min

3) Increasing rate of 4 °C/min

The first series of tests were the thermogravimetric analyses for all of the surrogate metal compounds listed in Table 1. The used equipment was a commercial thermogravimetric furnace (SDT-2960, TA Instruments). The standard mixed gases of 0.001% and 21% O₂ with remainder consisting of nitrogen were used for simulating oxygen-deficient and oxygen-sufficient atmospheres, respectively. Under each test atmosphere, the sample surrogate metal compound was heated from the room temperature to 1,500°C with a constant heating rate.

The second series of test were conducted using a commercial proximate analyzer (MAC-400, LECO Ltd.). The description and the operating methods of the proximate analyzer are described in detail elsewhere [10]. The temperature of the furnace was heated from the room temperature to 1,000°C. The investigated variable was the mole ratio of chlorine to metal. Polyvinyl chloride (PVC) and sodium chloride (NaCl) were used as the organic and inorganic chlorine sources, respectively. Both chlorine sources were high-purity reagent powders supplied by Aldrich

Table 3. Estimated Conversion of Surrogate Metal Compounds under Oxygen Sufficient and Deficient Atmospheres at Elevated Temperatures

Starting Compound	Conversion	Temperature (°C)	O ₂ Partial Pressure (atm)
Ce(NO ₃) ₃	$Ce(NO_3)_3 \rightarrow CeO_2 + 3/2N_2 + 7/2O_2$	250-500	0.21, <0.001
Co	$2Co + 3/2 O_2 \rightarrow Co_2O_3$ $Co_2O_3 \rightarrow 2CoO + 1/2O_2$	300-600 900-950	0.21
	$Co + 1/2 O_2 \rightarrow CoO$	300-1200	<0.001
Cs ₂ O	$Cs_2O \rightarrow Cs_2(g) + 1/2O_2$	100-800	0.21, <0.001
CsCl	$CsCl \rightarrow CsCl(g)$	> 600	0.21, <0.001
Gd(NO ₃) ₃	$Gd(NO_3)_3 \rightarrow Gd_2O_3 + 3/2N_2 + 3 O_2$	300-500	0.21, <0.001
NdCl ₃	$NdCl_3 + 3/2O_2 \rightarrow NdO_3 + 3/2Cl_2$ $2NdO_3 \rightarrow Nd_2O_3 + 3/2O_2$	700-1000 1000-1300	0.21
	$NdCl_3 \rightarrow Nd + 3/2Cl_2$	750-1350	<0.001
Nd(NO ₃) ₃	$Nd(NO_3)_3 \rightarrow NdO_3 + 3/2N_2 + 3O_2$ $2NdO_3 \rightarrow Nd_2O_3 + 3/2O_2$	300-500 500-800	0.21, <0.001
	$CeO_2 \rightarrow Ce(g) + O_2$ $Nd_2O_3 \rightarrow Nd(g) + 3/2O_2$ $Sm_2O_3 \rightarrow Sm(g) + 3/2O_2$	> 1400	0.21, <0.001

Chemical Co. The tested mole ratios of chlorine to metal were 0, 5 and 10 for each chlorine source.

3. Results and Discussion

3.1. Influence of Oxygen Partial Pressure

The results of thermogravimetric analyses for the pure surrogate metal compounds are shown in Figs. 1-5. From the obtained thermograms, conversions of the surrogate metal compounds at elevated temperatures were estimated and summarized in Table 3. Those estimations were verified by the stoichiometric estimations of thermogravimetric data as well as the available data for the melting, subliming and boiling temperatures, and the vapor pressures of the compounds [11, 12].

3.1.1. Alpha Surrogates

As shown in Figs. 1 and 2, the tested three alpha surrogates in the form of their nitrates and chlorides converted into their stable oxides at low temperatures. Cerium nitrate (Ce(NO₃)₃) and gadolinium nitrate (Gd(NO₃)₃) converted directly into each of their stable oxides (CeO₂ and Gd₂O₃) at low temperatures below 500°C, regardless of the oxygen partial pressure tested. Oxidation of neodymium nitrate quite differs from cerium nitrate and gadolinium nitrate. Neodymium nitrate (Nd(NO₃)₃) first converted into NdO₃ at lower temperatures below 500°C and then it converted into Nd₂O₃ at higher temperatures, regardless of the oxygen partial pressure tested. The oxidation behavior of neodymium chloride (NdCl₃) under oxygen sufficient atmosphere was similar to that of

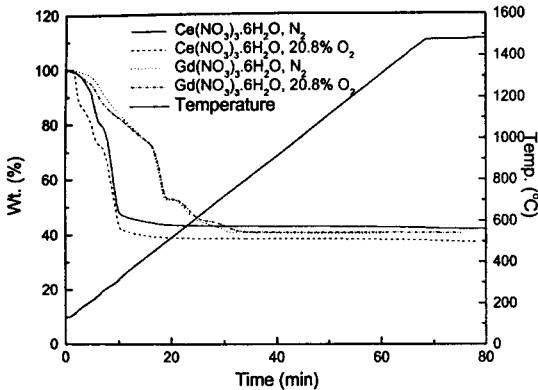


Fig. 1. Thermograms of Cerium nitrate and Gadolinium Nitrate up to 1,500°C under Oxygen-sufficient and Oxygen-deficient Atmospheres

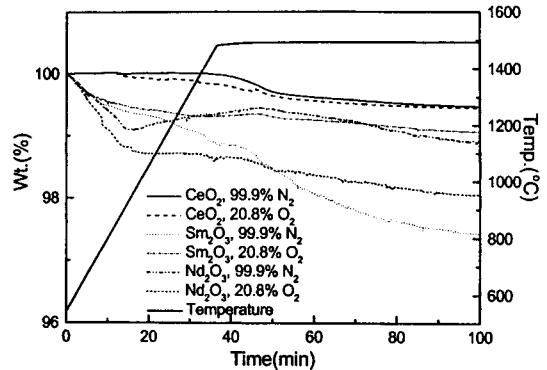


Fig. 3. Thermograms of Cerium Oxide, Samarium Oxide and Neodymium Oxide up to 1,500°C under Oxygen-sufficient and Oxygen-deficient Atmospheres

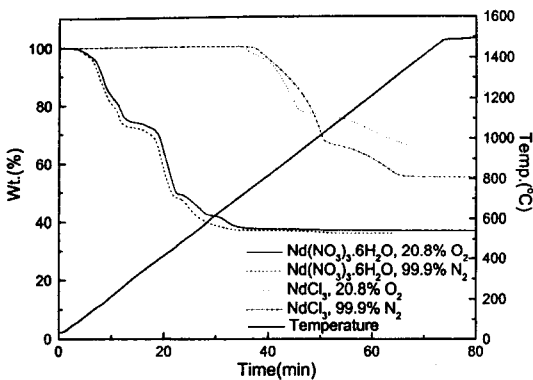


Fig. 2. Thermograms of Neodymium nitrate and Gadolinium Nitrate up to 1,500°C under Oxygen-sufficient and Oxygen-deficient Atmospheres

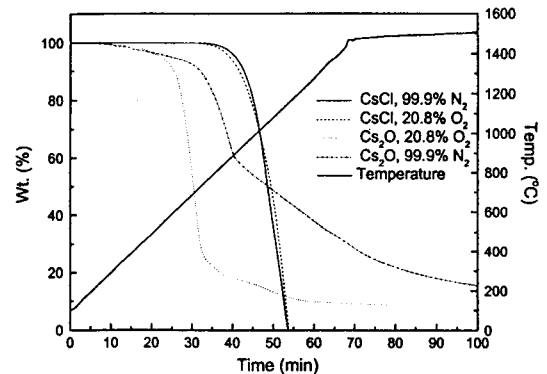


Fig. 4. Thermograms of Cerium Oxide and Cesium Chloride up to 1,500°C under Oxygen-sufficient and Oxygen-deficient Atmospheres

neodymium nitrate. It first converted into NdO_3 at lower temperatures below 800°C and then it converted into Nd_2O_3 at higher temperatures. Under oxygen deficient atmosphere tested (<0.001 atm O_2), neodymium chloride was stable up to about 750°C and then it converted into elemental neodymium emitting chlorines without its oxidation at higher temperatures.

As shown in Fig. 3, the weight of three alpha surrogates in the form of their oxides (CeO_2 ,

Nd_2O_3 and Sm_2O_3) were not much changed at elevated temperatures up to about 1,500°C at both oxygen-sufficient and deficient atmospheres. After volatilization of some impurities before the temperature reached about 1,000°C, three oxides were stable to about 1,400°C. The sample weight of sample oxides then slightly decreased at the temperature above about 1,400°C under both tested conditions. These results suggested that volatile elemental Ce, Nd and Sm were formed by

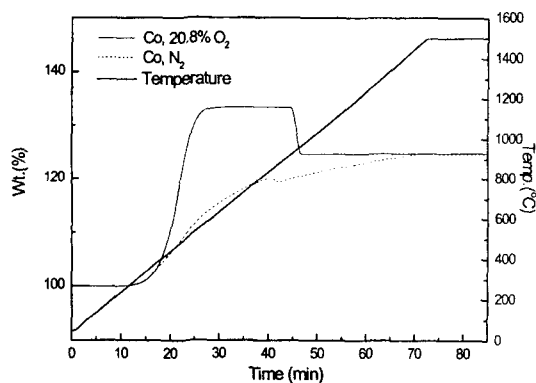


Fig. 5. Thermograms of Cobalt up to 1,500°C under Oxygen-sufficient and Oxygen-deficient Atmospheres

emitting gaseous oxygen molecules at the temperature above 1,400°C, even under oxygen-sufficient atmosphere. The suggested vaporization reactions are shown in Table 3. As shown in Fig. 3, in case of cerium oxide and neodymium oxide, the vaporization rates under both tested conditions were quite similar and extremely low up to 1,500°C. The vaporization rate of samarium oxide under oxygen deficient atmosphere was somewhat faster than that under oxygen sufficient atmosphere. However, its volatilization rates at about 1,500°C are still very low, compared to those of volatile cesium compounds at low temperatures below 1,000°C, which is shown in Fig. 4.

Tested alpha surrogates in the form of their nitrate, chloride and oxide were proven to be low-volatility metals up to 1,500°C. This suggested that alpha radionuclides such as uranium, plutonium, etc. would not easily vaporize under waste combustion conditions. Most of alpha radionuclides may partition in the bottom ash during waste incineration. Some entrained alpha radionuclides in the off-gas may result only from the particulate entrainment and their particle size may be relatively large [5].

3.1.2. Cesium

As shown in Fig. 4, both the oxide and the chloride of cesium examined (Cs_2O and CsCl) started to vaporize with a significant vaporization rate at medium temperatures, regardless of gaseous oxygen concentrations. The smooth thermogram of CsCl suggests that CsCl is chemically stable under tested conditions. The stable CsCl completely vaporized before the furnace temperature reached 1,000°C. A part of unstable Cs_2O started to decompose into elemental cesium (Cs) at the medium temperatures around 500°C, regardless of the oxygen partial pressure. This decomposition product Cs has a significant vapor pressure and it vaporizes with a high vaporization rate. A part of Cs_2O remained up to 10% of the sample loaded. Cs_2O powders that presented in adjacent with the surface of alumina crucible did not vaporize at the temperatures examined (0-1,500°C). These indicate that Cs_2O is preferentially sorbed on alumina matrices but CsCl is not easily sorbed on the adsorption site. In the presence of water vapor, however, cesium chloride can be adsorbed in the aluminosilicate sorbent if it behaves as the other alkali metal chlorides such as sodium chloride (NaCl) does [13, 14].

3.1.3 Cobalt

The conversion of the elemental cobalt (Co) was clearly shown in its thermograms, which is shown in Fig. 5. The behaviors of other available compounds such as the oxides (CoO and CoO_2) and the chloride of cobalt (CoCl_2) were described in the previous work [10]. In the oxygen sufficient atmosphere (0.21-atm O_2), cobalt (Co) started to convert into cobalt (III) oxide (Co_2O_3) at about 300°C. This oxidation reaction in the oxygen-sufficient

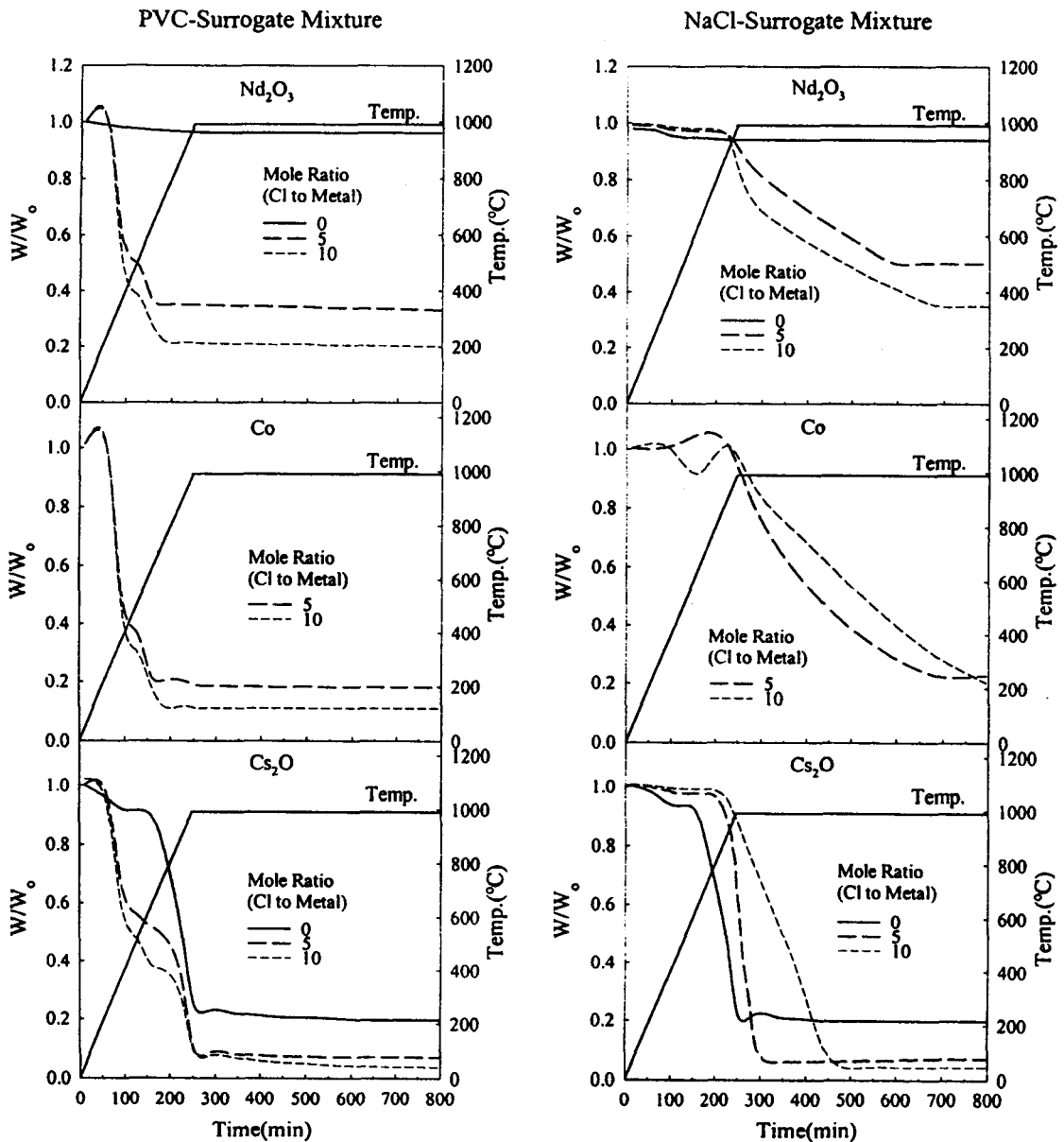


Fig. 6. Thermograms of the Mixture of Chlorine Precursor and Surrogate Metal from Room Temperature to 1,000 $^\circ\text{C}$ Under Atmospheric Air Condition

atmosphere was very fast and finished at about the temperature of 600 $^\circ\text{C}$. A cobalt (III) oxide (Co_2O_3) formed at temperatures between 300 $^\circ\text{C}$ and 600 $^\circ\text{C}$ was stable until the temperature reached 900 $^\circ\text{C}$. At temperatures above 900 $^\circ\text{C}$,

Co_2O_3 converted into CoO , emitting oxygen gas molecules. In the oxygen-deficient atmosphere ($<0.001\text{-atm O}_2$), the oxidation of elemental cobalt (Co) at the temperature from 300 $^\circ\text{C}$ occurred relatively slowly. Its thermogram indicates that

Table 4. Test Conditions and Results of Heating of Surrogate-Chlorine Mixture

Surrogate	Chlorine Source	Mole Ratio (Chlorine to Metal)	Sample Mixture (g)		Surrogate metal element (g)		F_V	
			Chlorine Source	Metal Compound	Q_L	Q_R		
Nd ₂ O ₃	PVC	0	-	0.500	0.43	0.42	0.03	
		5	1	0.500	0.43	0.42	0.01	
		10	2	0.500	0.43	0.43	0.00	
	NaCl	0	-	0.575	0.49	0.48	0.03	
		5	0.5	0.575	0.49	0.47	0.05	
		10	1	0.575	0.49	0.50	-0.01	
Co	PVC	5	1	0.188	0.19	0.17	0.08	
		10	2	0.188	0.19	0.19	-0.01	
	NaCl	5	1	0.200	0.20	0.20	0.01	
		10	2	0.200	0.20	0.35	-0.73	
	Cs ₂ O	PVC	0	-	0.560	0.54	0.11	0.80
			5	1.25	0.560	0.54	0.13	0.76
10			2.50	0.560	0.54	0.10	0.81	
NaCl		0	-	0.603	0.59	0.12	0.80	
		5	1.25	0.603	0.59	0.13	0.75	
		10	2.50	0.603	0.59	0.04	0.93	

most of Co starts to convert directly into CoO at the temperature of 300°C without converting into Co₂O₃.

3.2. Impact of Chlorine on the Volatility

Three surrogates representing the typical radioactive metals in the burnable waste stored in Korea Atomic Energy Research Institute were selected: Nd, Co and Cs for U, Co and Cs, respectively. The effects of the type of the chloride precursor (PVC and NaCl) and mole ratio (Cl to metal) on the volatility of Nd₂O₃, Co, and Cs₂O were examined. Fig. 6 shows the thermograms for the three compounds at the tested range of 0 to 1,000°C. On the basis of the quantity of the surrogate metal loaded (Q_L) and the quantity of the surrogate metal remained (Q_R), the volatilized

fraction (F_V) are defined as follows:

$$F_V = 1 - (Q_R/Q_L) \quad (1)$$

Q_L and Q_R in Eq. (1) are the quantity of surrogate metal element (Nd, Co and Cs) in the sample mixture and that remained ash in the crucible, respectively. The volatilized fractions calculated by Eq. (1) are listed in Table 4. The weights of PVC-surrogate mixtures were greatly reduced before the temperature reached 1,000°C due to the rapid combustion of PVC. Combustion of PVC generates gaseous HCl, Cl₂, CO and H₂O [15]. Neodymium oxide (Nd₂O₃) did not volatilized under this worst-case gaseous atmosphere. Elemental cobalt also did not react with the gaseous products from PVC combustion; rather it reacted with the oxygen in the atmosphere to form CoO that was

very stable at high temperatures. As shown in Table 4, most input neodymium and cobalt remained as stable oxides after the complete combustion of PVC. About 80% of cesium oxide vaporized, regardless of PVC content in the mixtures. A part of cesium oxide remained combining with matrices of alumina crucibles. The weight loss patterns of NaCl-surrogate mixtures were quite similar to those of PVC-surrogate mixtures. Since the vaporization rate of NaCl was quite slow at tested temperature ranges, the weight decrease of NaCl-surrogate sample mixtures continued for relatively long time, compared to that of PVC-surrogate sample mixtures. Most input neodymium and cobalt remained as stable oxides after the complete vaporization of NaCl. Most cesium oxide vaporized with NaCl but it partly remained with combining alumina crucible as in the case of PVC-C₅O mixture.

4. Conclusions

Oxide, chloride and nitrate forms of surrogate metals that represent typical alpha radionuclides such as uranium, plutonium, americium, etc. did not vaporize up to about 1,400°C even under the oxygen-deficient atmosphere tested. In addition, chlorine addition did not increase the volatility of alpha surrogate. This suggested that most of the alpha radionuclides may partition in the bottom ash or the entrained coarse fly ash particles even under the worst-case waste combustion condition such as chlorinated waste combustion. The important parameters that influence the partitioning behavior of alpha radionuclides such as uranium, plutonium, etc. during waste incineration are the parameters that affect the entrainment of particulate in combustion device, such as the propensity to the fragment of the waste matrix and combustion gas velocity and

filtration equipment operating parameters. When the significant quantity of cesium is included in the waste, however, other parameters that effect the formation of fine particles from the volatilized cesium must be considered as important parameters.

Acknowledgement

This project has been carried out under the Nuclear R&D Program by MOST.

References

1. R. D. Vidic, "Removal of Mercury from Stack Gases by Activated Carbon," 21st Annual RREL Research Symposium Abstract Proceedings, EPA/600/R-95/012, 103 (1995).
2. B. B. Ebbinghaus, O. H. Krikorian, and M. G. Adamson, "Vaporization of Actinide Oxides in Thermal Treatment Processes of Mixed Oxides," UCRL-JC-116414, Lawrence Livermore National Laboratory, 2 (1996).
3. H. C. Yang, B. H. Kim, C. H. Kim, W. M. Park and M. S. Jeong, "Radiological safety assessment for KAERI incineration plant on the basis of trial burn results, *J. of the Korean Association for Radiation Protection*, 23 (1998).
4. T. Kady, M. Trichon and J. Feldmann, "Heavy metals in the stacks; where are they?" *Proceedings of 1991 International Incineration Conference*, Knoxville, Tennessee, 597 (1991).
5. R. G. Barton, W. D. Clark, and W. R. Seeker. "Fate of Metals in Waste Combustion System," *Combust. Sci. and Technol.* 74, 327-342 (1990).
6. U.S. EPA, Operational Parameters for Hazardous Waste Combustion Devices,

- EPA/625/R-93/008, 62 (1993).
7. H. L. Goldstein and S. W. Siegmund, "Influence of Heavy Fuel Oil Composition and Boiler Combustion Conditions on Particulate Emissions," *Environ. Sci. & Technol.* 10(12) 1109 (1976).
 8. R. G. Barton, J. S. Lighty and J. Prendergast, "The Behavior of Metals During Thermal Treatment of Mixed Oxide," Proceedings of 1995 *International Incineration Conference*, Bellevue, WA 435 (1995).
 9. D. G. Kolman, Y. Park, M. Stan, R. J. Hanrahan, Jr. D. P. Butt, "An Assessment of the Validity of Cerium Oxide as a Surrogate for Plutonium Oxide Gallium Removal Studies," LA-UR-99-491 (1999).
 10. H. C. Yang, J.-H. Kim, W. Z. Oh, H. S. Park and Y. C. Seo, "The behavior of hazardous and radioactive metals in a laboratory furnace and a demonstration-scale incinerator," *Environmental Engineering Science*, 15, 299 (1998).
 11. C. H. Bamford, *Comprehensive Chemical Kinetics*, Elsevier Scientific Publishing Company, 9 (1975).
 12. O. Kubaschewski, and C. B. Alcock. *Metallurgical Thermochemistry*, 5th Edition, International Series on Material Science and Technology, 379 (1989).
 13. R. L. Davison, D. F. S. Natusch and J. R. Wallace, "Trace Elements in Fly Ash - Dependence of Concentration on Particle Size," *Environ. Sci. & Technol.* 8, 1107 (1993).
 14. M. Uberoi, "The kinetics and mechanism of alkali removal from flue gases by solid sorbents," *Prog. Energy Combust. Sci.* 16, 205-211 (1994).
 15. A. Alajbeg, "Products of non-flaming combustion of poly vinyl chloride," *J. of Analytical and Applied Pyrolysis*, 12, 275 (1985).