

PARTITIONING RATIO OF DEPLETED URANIUM DURING A MELT DECONTAMINATION BY ARC MELTING

BYEONG-YEON MIN, WANG-KYU CHOI, WON-ZIN OH and CHONG-HUN JUNG

Korea Atomic Energy Research Institute

P. O. Box 150, Yusung-Gu Daejeon, 305-600, South Korea

*Corresponding author. E-mail : bymin@kaeri.re.kr

Received December 7, 2007

Accepted for Publication May 30, 2008

In a study of the optimum operational condition for a melting decontamination, the effects of the basicity, slag type and slag composition on the distribution of depleted uranium were investigated for radioactively contaminated metallic wastes of iron-based metals such as stainless steel (SUS 304L) in a direct current graphite arc furnace. Most of the depleted uranium was easily moved into the slag from the radioactive metal waste.

The partitioning ratio of the depleted uranium was influenced by the amount of added slag former and the slag basicity. The composition of the slag former used to capture contaminants such as depleted uranium during the melt decontamination process generally consists of silica (SiO_2), calcium oxide (CaO) and aluminum oxide (Al_2O_3). Furthermore, calcium fluoride (CaF_2), magnesium oxide (MgO), and ferric oxide (Fe_2O_3) were added to increase the slag fluidity and oxidative potential. The partitioning ratio of the depleted uranium was increased as the amount of slag former was increased. Up to 97% of the depleted uranium was captured between the ingot phase and the slag phase. The partitioning ratio of the uranium was considerably dependent on the basicity and composition of the slag. The optimum condition for the removal of the depleted uranium was a basicity level of about 1.5. The partitioning ratio of uranium was high, exceeding 5.5×10^3 . The slag formers containing calcium fluoride (CaF_2) and a high amount of silica proved to be more effective for a melt decontamination of stainless steel wastes contaminated with depleted uranium.

KEYWORDS : Depleted Uranium, Melt Decontamination, Partitioning Ratio

1. INTRODUCTION

During a decommissioning of nuclear plants and facilities, large quantities of slightly contaminated metallic scrap are generated. The contaminated metal can be of two forms: surface contamination or bulk contamination. Bulk contamination usually arises from neutron activation of nuclides during the service life of a component. Surface contamination can be a loose contamination arising from a deposition of nuclides from an interfacing medium; it can also be tightly bound, which tends to happen when the adsorption of deposited nuclides forms an oxide layer on the metal. The removal of deposited radionuclide requires more aggressive decontamination methods, such as a melting. Melting technology is one of the most effective technologies for the volume reduction and recycling of metallic radioactive wastes [1-3]. Melting may provide an essential final step for the release of components with complex geometries; accordingly, the melting process simplifies the procedures for monitoring radioactive

metal characterization. The radionuclides that remain in the molten phase are not only distributed homogeneously but also effectively immobilized; as a result, they reduce and preserve the valuable repository capacity.

According to thermodynamic calculations, such as a free energy calculation, uranium can be completely removed between the ingot phase and the slag phase under an equilibrium condition [4]. Neuschütz et al. [5] studied the equilibrium distributions of uranium by using a program called ChemSag. Their theoretical study indicated that uranium could be concentrated completely in the slag phase. The distribution of uranium during the melting of steel is a complex process that can be influenced by numerous chemical and physical factors. Such factors include the composition of the steel; the solubility of elements in the molten iron; the density of the oxides; the melting temperature; and the melting practices, such as the furnace type and size, the melting time, and the method of carbon adjustment [6, 7]. Heshmatpour and Copeland [8] reported that the partitioning ratio for uranium changes from 7 to 1400 as

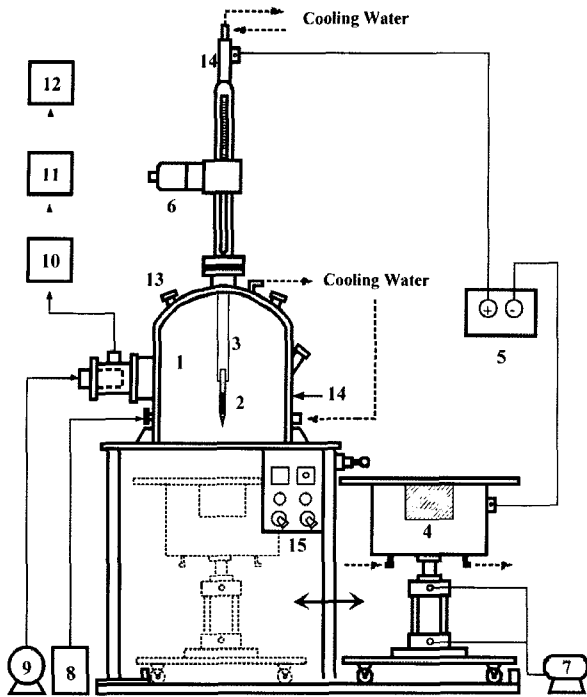


Fig. 1. Schematic of the Electric Arc Furnace

- | | | |
|-------------------|-------------------------|----------------------|
| 1-Chamber | 2-Graphite Electrode | 3-Copper Electrode |
| 4-Copper Crucible | 5-Power Supply | 6-Stepper Motor |
| 7-Air Compressor | 8-Argon Gas | 9-Vacuum Pump |
| 10-Filter Bank | 11-Emission Monitor | 12-Radiation Monitor |
| 13-Viewport | 14-Cooling Water Jacket | 15-Control Box |

a result of the experimental conditions. Abe et al. [9] also reported that the uranium decontamination factor, which was found to be a function of the initial contamination level, varied from about 200 to about 5000. In addition, Joanna et al. [10] reported that the optimum decontamination value was usually obtained near a basicity index of 1.5, and that the decontamination efficiency was further enhanced by the addition of CaF_2 or NiO to a slag. Another researcher reported that the optimum decontamination was achieved with a slag basicity index of 1.1 [11].

The purpose of this study was to use various slag formers such as iron-based metallic waste to obtain the optimal melting decontamination conditions to remove depleted uranium.

2. EXPERIMENT

Electric graphite arc system was selected for melting the metallic radioactive wastes. A lab scale D.C. graphite arc melting system, which is shown in Fig. 1, was fabricated to investigate the characteristics of the metal melting itself and the behavior of the contaminants. The graphite arc furnace consists of one graphite electrode

(with a 20 mm diameter) and a copper crucible (with a 100 mm inner diameter and a depth of 80 mm), which serves as a counter electrode. The cooling water flows in the surroundings of the graphite arc electrode, the copper crucible, and the chamber. The stainless steel contaminated with the depleted uranium was charged in the graphite crucible. Next we mixed 500 g of the simulated stainless steel with the prepared slag former and then melted the mixture under an argon atmosphere for 10 min at a temperature greater than about 1550°C .

The power levels for the test remained for the most part between 10 kW and 20 kW. The current is controlled by the operator, and the voltage depends on the electrical impedance of the arc and melt composition, the electrode tip positions, and the settings of the current and power. After the completion of the melting, the molten metal was poured into a copper mold and left to cool. The ingot of stainless steel was cylindrical for the purpose of quantitative analysis. The slag was easily separated from the ingot. The ingot and slag samples were analyzed with an inductively coupled plasma atomic emission spectroscopy (IRIS DUO, Thermo Elemental Co.) to evaluate the partitioning ratio of the depleted uranium.

Samples of plate-type metal waste (10 mm × 10 mm × 1 mm, stainless steel) were prepared as the feed material for the melting tests and contaminated with the depleted uranium (UO_2). The slag formers were generally based on the constituents of silica (SiO_2), calcium oxide (CaO), and aluminum oxide (Al_2O_3). Borate (B_2O_3), ferric oxide (Fe_2O_3), and calcium fluoride (CaF_2) were added to increase the oxidative potential of the slag [12]. Table 1 summarizes the composition and types used in this study.

The slag former was added to a crucible filled with a metal specimen prior to the beginning of a melting. One of the most important parameters during the melt decontamination of uranium is the basicity of the slag used in the melting of a steel. The basicity is defined as the moles of basic oxide (CaO) divided by the total moles of an acidic oxide ($\text{SiO}_2 + \text{Al}_2\text{O}_3$). In this study, the range of basicity used in the experiment varied from 0.52 to 3.14. Basic oxides have a strong ionization tendency and acidic oxides have strong covalent bond structures and tend to attract ionized oxides. To clarify the effect of the slag basicity on steel decontamination, we examined seven slag compositions.

3. RESULTS AND DISCUSSION

To evaluate the partitioning ratio of stainless steel contaminated with depleted uranium, we analyzed an ingot and slag during a test. The objective was to measure the degree of decontamination and the corresponding partition ratios for the metals intentionally

Table 1. Composition and Types of Slag Former

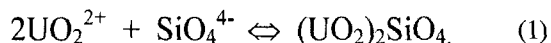
Slag composition (%)				Basicity	Slag (wt%)
SiO ₂	CaO	Al ₂ O ₃	Other		
50	30	20		0.52	10
40	40	20		0.82	10
30	50	20		1.28	10
30	54	16		1.49	10
10	60	30		2.32	10
15	70	15		3.14	10
					5
30	54	16		1.49	7
					12
					15
Al ₂ O ₃ (14.5), B ₂ O ₃ (7.50), CaO(21.8), Fe ₂ O ₃ (0.2), Li ₂ O(0.5) Na ₂ O(0.5), SiO ₂ (55), TiO ₂ (0.5)				-	10
70		30		High silica	10
50		30	CaF ₂ (20)	Fluoride containing	10
30	40	10	Fe ₂ O ₃ (20)	Calcium ferric silicate	10
38.1	41.1	14.1	Fe ₂ O ₃ (2.9), MgO(3.8)	Calcium Magnesium Silicate	10
80	4	2	B ₂ O ₃ (14)	Borosilicate	10
60		20	Fe ₂ O ₃ (20)	Aluminum Ferric Silicate	10
	25	25	CaF ₂ (50)	Fluoride containing	10

contaminated with depleted uranium. Fig. 2 shows the effects of the slag basicity on the partitioning ratio of the depleted uranium. The partitioning ratio is defined as the amount of contaminant in the slag, divided by the amount of contaminant in the melt. The melting tests were conducted with 10 wt% of SiO₂-CaO-Al₂O₃ slag, 500 ppm of depleted uranium (UO₂), and 500 g of stainless steel waste. A melting decontamination process usually adds about 5 wt% to 10 wt% of slag. The basicity of the slag former was varied from 0.52 to 3.14. The depleted uranium on the surface of the metal waste was transferred to the slag phase by up to 97 wt% with a slag basicity of about 1.49. The optimum condition for a melting decontamination of depleted uranium was a slag basicity of 1.49. The partitioning ratio of the depleted uranium was higher than 5.5×10^3 .

The depleted uranium exists in state on the surface of most metal wastes and mostly moves to the slag phase by means of thermodynamics. However, in actual melting

systems, the transfer of the depleted uranium to the slag phase is influenced by various experimental conditions and the chemical composition of the slag [13, 14]. In general, the most suitable slag basicity for steel wastes is from 1.1 to 1.6 when a melting decontamination process is used [9, 11]. In the experiment, the maximum partitioning ratio of the depleted uranium was achieved with a slag basicity of about 1.5. Uda et al. [7] reported that the slag basicity seemed to have an influence on the decontamination mechanism. When a melting decontamination process is used, the basicity of the slag is a crucial variable for removing the uranium because the slag basicity breaks the silicate's chain structure and causes the uranium ion and reaction site to react during the melting of the metal. This phenomenon was attributed to the production of acidic oxide ions, such as SiO₄⁴⁻ or Al₂O₅⁴⁻; these ions combined with UO₂²⁺ ions and were captured in the slag. Uranium is transferred to the slag phase, thereby creating stable inorganic compounds that react with silicate

anions (SiO_4^{4-}) in the slag as follows:



The possible decontamination can be predicted for a very simple melt system. For a real melt decontamination, a more complex system would be much more difficult to predict due to the presence of several elements in the melt. Depleted uranium is removed from the ingot phase by a combination of several variables, such as the thermochemical properties of the slag former, the reaction mechanism between the slag and the melt, and the melting conditions.

Joyce and Lally [15] identified the radioactive partitioning between the metal and slag phases. The basis of their thermodynamic analysis was the removal of transuranic elements from steel by combining them with oxygen and transferring the oxygen to the slag phase. Depending on the chemical potential of the oxygen, the formation of species such as UO_2 , UO_3 , U_4O_9 , and U_3O_8 can be predicted as the valence of uranium changes with the oxygen potential. Under melt decontamination conditions, the uranium in the slag is expected to exist primarily as U^{4+} , though it could exist as UO_3^{2+} , UO^{2+} , or UO_4^{4-} . If the uranium in the slag occurs as U^{4+} or UO^{2+} , the reactions that show basic behavior are as follows:

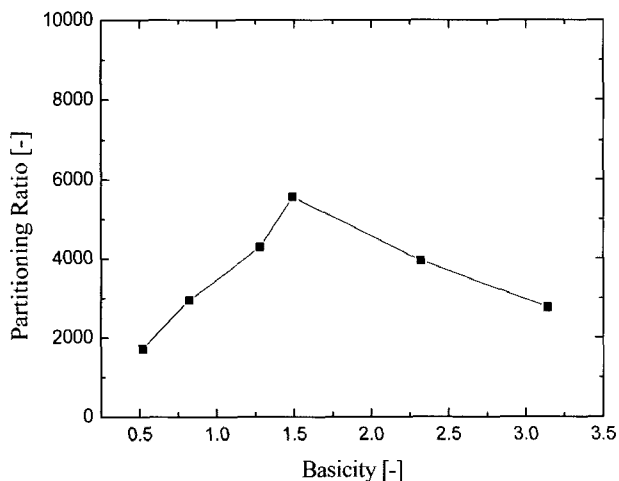
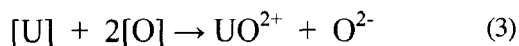
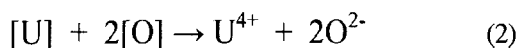


Fig. 2. Effects of the Slag Basicity on the Partitioning Ratio of the Depleted Uranium in the Slag Phase

Such reactions could be driven further to the right by the selection of an acidic slag that accepts O^{2-} ions. If, however, the uranium is of the form UO_3^{2+} or UO_4^{4-} , the acidic behavior results in decreased activity of O^{2-} in the slag. The uranium constituents can be immobilized in the slag 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 when surrounded by a layer of vitrified slag and encapsulate [16].

The relation between the distribution of depleted uranium and the amount of added slag former is shown in Fig. 3. This melting experiment was performed with 500 ppm of depleted uranium (UO_2) and a slag basicity of about 1.49. The partitioning ratio of the depleted uranium increased to 10 wt% of the added slag concentration but there was no major effect after this increase. In this experiment, the optimum condition for the melting decontamination of depleted uranium is a slag concentration greater than 10 wt%. The obtained partitioning ratios of the depleted uranium were 5.5×10^3 , 5.7×10^3 and 5.8×10^3 for a slag concentration of 10 wt%, 12 wt%, and 15 wt%, respectively. Up to 97% of the depleted uranium was removed when the added slag former was increased to 10 wt%.

One of the most important attributes of a melting system is the generated secondary waste. In this case, the secondary waste generated only slag from the segmenting and melting but it comprised only between 2% to 5% of the weight of the melted scrap. The slag former converts materials into a glass-like substance. The slag is rigid noncrystalline material of relatively low porosity. Thermally

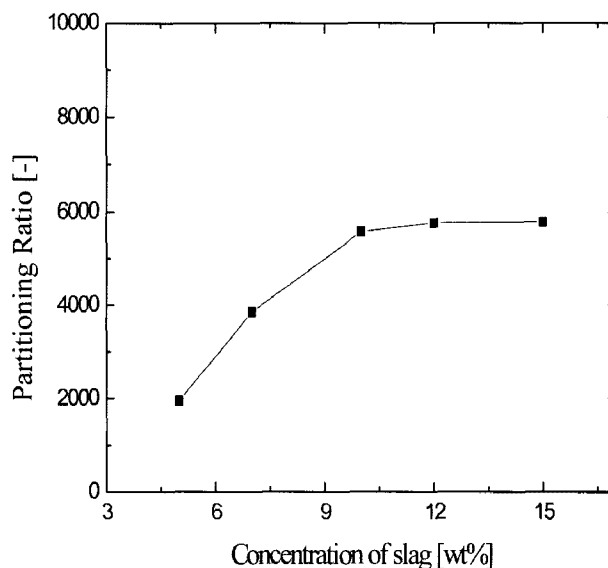


Fig. 3. The Relation between the Amount of Slag Former and the Distribution of Depleted Uranium

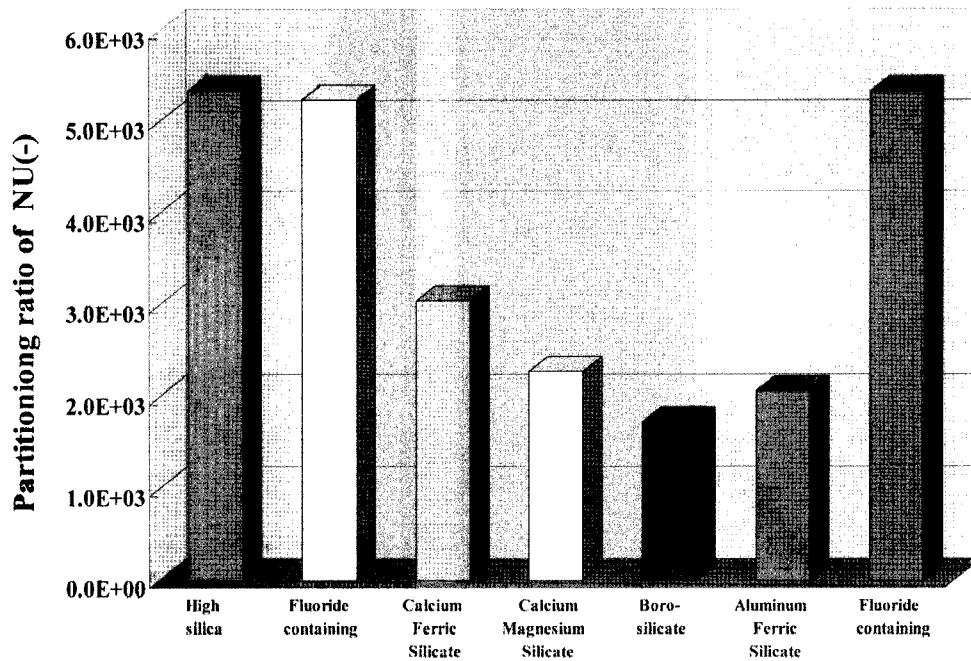


Fig. 4. Effects of Slag Type on the Partitioning Ratio of Depleted Uranium

formed slags are amorphous. Silicate slags are composed of a three-dimensional network of silicon-oxygen tetrahedra.

Fig. 4 shows the partitioning ratio of the depleted uranium in the slag. The tests were performed with 10 wt% of a slag former and 500 ppm of depleted uranium. As shown in Fig. 4, the partitioning ratio of the depleted uranium in the slag depended heavily on the slag composition and type. The partitioning ratio in the tests with the slag that contained high silica and fluoride was higher than 5.0×10^3 . In this experiment, the depleted uranium content in the ingot was less than 0.01 ppm. Note that an additive such as calcium fluoride (CaF_2), nickel oxide (NiO), or ferric oxide (Fe_2O_3) changes the slag properties (fluidity, viscosity, electric conductivity, free-ion movement, and oxygen potential). Furthermore, as mentioned above, fluxes containing CaF_2 were more effective, possibly because the fluoride breaks the bonds of the silicate network present in the slag that contains SiO_2 [17], yielding additional SiO_4^{4-} anions. These additional anions can combine with uranium cations at the slag and metal interface, causing uranium to be captured in the slag. In addition, fluoride elements reacted with uranium elements and changed to a stable gas phase, such as UF_3 . In all the experiments, the depleted uranium content in the ingot was less than 1 ppm. Calcium fluoride generally lowers the melting temperature and the viscosity of the slag by breaking the silicate network. Copeland et al. [18] reported that an effective uranium removal was achieved by using high

silica calcium-aluminum-silicate slags and fluoride containing a basic calcium-aluminum-silicate-ferrite slag. Abe et al. [9] also found that the partitioning ratio for the efficiency of uranium was enhanced by the addition of CaF_2 or NiO . Starkey et al. [19] reported values of 3 ppm U in melt-refined steel scrap with a 6×10^3 partitioning ratio. Borosilicate slag had a lower partitioning ratio than other slags. No effective reaction with UO_2 was observed. However, less than 1 ppm of depleted uranium remained in the ingot phase, and the depleted uranium content was concentrated at about 3,600 ppm in the slag phase. For the melting decontamination of a contaminated metal waste with uranium, a very high partitioning ratio can be obtained by optimizing the basicity and added flux composition.

Fig. 5 shows the relation between the ingot depleted uranium content and the contamination level of a test sample. The distribution of depleted uranium in borosilicate glass (SiO_2 -55%, CaO -21.8%, Al_2O_3 -14.5%, B_2O_3 -7.5%) material was investigated by a means of a gradual saturation method of the melt with depleted uranium up to 4000 ppm. In these experiments, the slag composition and melting time was fixed. In accordance with an increase in the depleted uranium contamination, the total amount of depleted uranium captured within the slag (50 g) was increased linearly as the amount of UO_2 increased. For the characteristics of the distribution of the depleted uranium, it is important to determine the maximum solubility of the components of the depleted uranium in the slag. The solubility of the components in

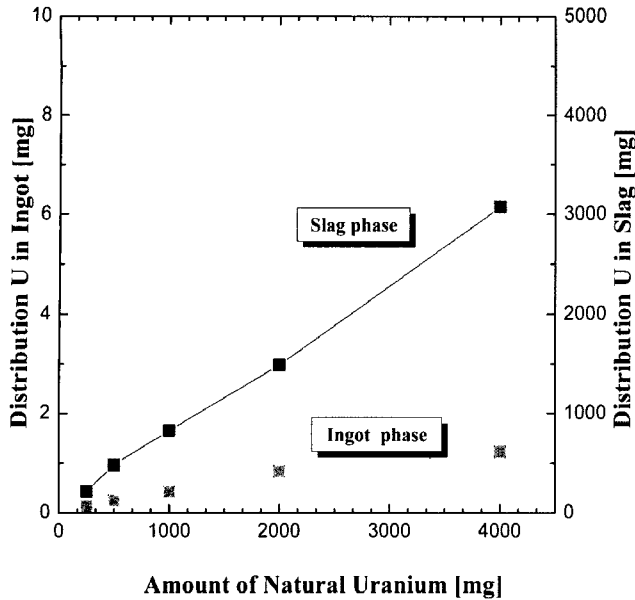


Fig. 5. Amount of Distributed Uranium between an Ingot and Slag

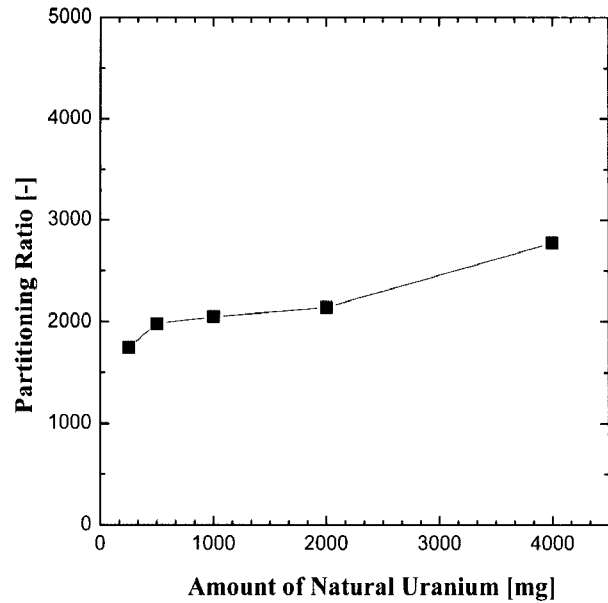


Fig. 6. The Partitioning Ratio of the Slag Phase for an Ingot in Borosilicate Slag

the melt depends on its composition and condition; for variable-valence elements, the oxidizing condition is also important. In general, an increase in the alkalinity of the melt and temperature promotes an increase in solubility.

The high solubility of the depleted uranium in the melt of the same composition under oxidizing conditions is evidently due to the fact that uranium in the form of U(IV) is more easily incorporated into the structural framework of the melt. The results of previous investigations [20, 21] on the valence of uranium in aluminosilicate and borosilicate compositions confirm that uranium is present in the three valence forms of U^{4+} , U^{5+} , and U^{6+} and that the partitioning ratio between them depends on the oxidizing-reducing conditions, the composition of the melt, and the melting temperature. According to previous studies [22], the solubility of uranium dioxide in the slag exceeds 10 wt%.

Fig. 6 shows the partitioning ratio of the slag phase for an ingot in borosilicate slag. The partitioning ratio of the slag phase increased with an increase in the added concentration of uranium. The partitioning ratio of the ingot phase for the slag phase displayed above 10^3 values but the borosilicate showed a partitioning ratio lower than the other slags. The difference of partitioning ratio is due to the low liquidity of the borosilicate. Thus, the effective reaction of the slag and the depleted uranium is limited. Metallic melting decontamination is a complicated process because the partitioning ratio of the radioactivity contaminants is affected by the following factors: the solubility of each element, the density of the oxide, the metal's melting temperature, the melting method, the melt type and size, the melting time, the carbon adjustment method, the chemical property of the slag, and the vacuum pressure of the particles.

Table 2. Results of the Decontamination for the Melting of Stainless Steel Waste from the Uranium Conversion Plant at KAERI

Slag former composition [%]				Remnant of U in the ingot [mg]	Remnant of U in the slag [mg]	Partitioning ratio [-]
SiO ₂	CaO	Al ₂ O ₃	Other			
55	21.8	14.5	B ₂ O ₃ (7.5)	0.207	648	3.13E+3
30	54	16	-	0.128	385	3.01E+3

The depleted uranium contaminated metal waste of stainless steel generated in the uranium conversion plant at Korea Atomic Energy Research Institute (KAERI) was partitioned in an electric arc furnace. The experimental results are summarized in Table 2. The stainless steel waste was contaminated with about 150 ppm of natural uranium. The experiments were performed with about 5 kg of stainless steel waste and two types of slag (alumino-borosilicate and calcium-aluminum-silicate). We found that the trend of the partitioning ratio was very similar to that of a laboratory scale. Most of the surface contaminated depleted uranium was transferred to the slag phase. The depleted uranium remained in the ingot at 0.207 mg (0.0423 ppm) and 0.128 mg (0.0263 ppm). The partitioning ratio agreed well with the experimental value of the laboratory scale before the 10^3 values. The results confirm that we can obtain a decontamination effect through the melting decontamination of a metal waste contaminated with uranium.

4. CONCLUSION

The residual uranium distribution and partitioning ratios were determined for a melt decontamination of various UO_2 contaminated metals. The partitioning ratio of the uranium in the slag phase is dependent on the composition, type, basicity and added amount of slag former. Slag formers that contain calcium fluoride (CaF_2) and a high silica content are more effective for the melt decontamination of stainless steel waste. However, the borosilicate slag is ineffective for treating metallic waste contaminated with uranium. The optimum condition for the melting decontamination of the metal waste contaminated with uranium is a slag basicity of around 1.49 (for the mole ratio of basic oxides/acidic oxides) with $CaO-Al_2O_3-SiO_2$ and a slag concentration greater than 10 wt%. The results confirm that the slag former with calcium fluoride (CaF_2) and a high silica content is more effective.

REFERENCES

- [1] K.L. Hopkinson, A. Bishop, M.T. Cross, J. Harrison and F. Selgas, "Recycling and reuse of radioactive material in the controlled nuclear sector", EUR18041 EN, European Commission (1998).
- [2] D.G. Atteridge, J. Buckentin, J. Carter, H.L. Davis, J. H. Devletian, M.R. Scholl, R.B. Turpin, S.L. Webster, and R.E. Mizia, "Refining technology for the recycling of stainless steel radioactive scrap metals FY 94 Bi-annual report", WINCO-1224 (1994).
- [3] G. Imbard, and S. Rigaud, "Melting of Cs contaminated ferritic steel from G2/G3 reactors, Marcoule", Proceeding of Technical seminar on melting and recycling of metallic waste materials from decommissioning of nuclear installations, European Commission, Germany, 193 (1993).
- [4] R. Anigstein, W.C. Thurber, J.J. Mauro, S.F. Marschke, U.H. Behling, "Potential recycling of scrap metal from nuclear facilities", Technical support document, U.S. Environmental Protection Agency (2001).
- [5] D. Neuschütz, D. Spirin, U. Quade, J. Meier-Kortwig, L. Holappa, M. Hämäläinen, M.A. Heredia Lozano and M.J. Guio Bonany, "Inadvertent melting of radioactive sources in BOF or EAF: Distribution of nuclides, monitoring, prevention, ISIJ International, 45, 288-295 (2005).
- [6] M. Aoyama, Y. Miyamoto, M. Fukumoto, and O. Suto, "Development of melt refining decontamination technology for low level radioactive metal waste contaminated with uranium", *Journal of Physics and Chemistry of Solids*, 66 608-611 (2005).
- [7] T. Uda, H. Iba, and H. Tsuchiya, "Decontamination of uranium contaminated mild steel by melt refining", *Nuclear Technology*, 73 109-115 (1986).
- [8] B. Heshmatpour and G.L. Copeland, "Metallurgical aspects of waste metal decontamination by melt refining", *Nuclear and Chemical Waste Management*, 2 25-31 (1981).
- [9] M. Abe, T. Uda, and H. Iba, "A melt refining method for uranium contaminated steels and copper", In *Waste Management*, Tucson, AZ 375-378 (1985).
- [10] M.R.B. Joanna, B.K. Damkroger, and M.E. Schlienger, "Radioactive scrap metal decontamination technology assessment report", SAND 96-0902 (1996).
- [11] X.W. Ren, U.C. Liu, and Y. Zhang, "Melt refining of uranium contaminated copper, nickel, and mild steel", Proceeding of the international and topical meeting on nuclear and Hazardous waste management, Spectrum 94, Atlanta, August 14-18, ANS (1994).
- [12] P.S. Song, B.Y. Min, W.K. Choi, C.H. Jung, W.Z. Oh, and J.H. Park, "Melting characteristics of metal wastes in an electric arc furnace", *J. Industrial Engineering and Chemistry*, 12, 248-254 (2006).
- [13] S.A. Worcester, L.G. Twidwell, D.J. Paolini, T.A. Weldon, and R.E. Mizia, "Decontamination of metals by melt refining/slagging – An annotated bibliography", WINCO-1138, INEL-DOE (1993).
- [14] M.E. Schlienger, M. Janna, and B.K. Damkroger, "Melt processing of radioactive waste: a technical overview", SAND-97-0811C (1997).
- [15] E.L. Joyce, B.R. Lally, R.J. Fruehan, and B. Ozturk, "Liquid Metal Recycle and Waste Treatment : Liquid Metal Melt-Slag Technology Evaluation for MWIP", LA-UR Report 93-3026. Submitted to DOE-EM50 (1995)
- [16] B.Y. Min, K. Yong, P.S. Song, W.K. Choi, C.H. Jung, and W.Z. Oh, "Study in the vitrification of Mixed Radioactive by Plasma Arc Melting," *J. Ind. Eng. Chem*, 13, 1 57-64 (2007)
- [17] E.T. Turkdogan, *Physical Chemistry of High Temperature Technology*, Academic Press, New York, 140 (190)
- [18] G.L. Copeland, B. Heshmatpour, and R.L. Heestand, "Melting metal waste for volume reduction and decontamination," ORNL/TM-7625, Oak Ridge National Laboratory, March (1981)
- [19] R.H. Starkey, "Health aspects of the commercial melting of uranium-contaminate ferrous metal scrap," *Ind. Hyg. J.* 178 (1960)
- [20] H. Schreiver, G. Balazs, and B. William, "Structural and redox properties of uranium in C-Mg-Al-silicate glass," *Sci. Basis for Nucl. Waste Management*, 3, 109 (1981)
- [21] H. Schreiver and G. Balazs, "The chemistry of uranium in

borosilicate glasses. Part1. Simplest compositions relevant to the immobilization of nuclear waste," *Phys. Chem. Glasses*, 23, 139 (1982)

[22] Y.I. Matyunin and S.V. Yudinsev, "Immobilization of U_3O_8 in borosilicate glass in an induction melter with a cold crucible", *Atomic Energy*, 84 (1998) 173-178.