

# Demonstration of Zr Recovery from 50 g Scale Zircaloy-4 Cladding Hulls using a Chlorination Method

## 50 g 규모의 Zircaloy-4 피복관으로부터 염소화 방법을 이용한 Zr 회수 거동 연구

Min Ku Jeon<sup>\*</sup>, Chang Hwa Lee, You Lee Lee, Yong Taek Choi, Kweon Ho Kang and Geun Il Park  
*Korea Atomic Energy Research Institute, 989-111 Daedeokdaero, Yuseong-gu, Daejeon, Korea*

전민구<sup>\*</sup>, 이창화, 이유리, 최용택, 강권호, 박근일  
*한국원자력연구원, 대전광역시 유성구 대덕대로 989-111*

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The recovery of Zr from Zircaloy-4 (Zry-4) cladding hulls using a chlorination method was demonstrated for complete conversion of Zr into  $ZrCl_4$ . A chlorination reaction was performed by reacting Zry-4 hulls for 8 h under a 70 cc/min  $Cl_2$  + 70 cc/min Ar flow at 380°C. The initial weight of the reactant (51.7 g) decreased to 0.49 g after 8 h of operation, which is only 0.95wt% of the initial weight. The weight of the total reaction products was 121.7 g with a high Zr purity of 99.80wt%. Fe and Sn were identified as major (0.18wt%) and minor (0.02wt%) impurities of the reaction products, respectively. It was also shown that Zr exhibited a high recovery ratio of 96.95wt% with a relatively small experimental loss of 2.34wt%. Observation of the reaction residues revealed that the chlorination reaction was dominant along the longitudinal direction, and surface oxide layers remained as reaction residues. The high purity and recovery ratio of Zr proposed the feasibility of the chlorination technique as an effective hull waste treatment method.

**Key words:** Chlorination reaction, Hull waste, Zr recovery, Spent nuclear fuel, Pyro-processing

본 논문에서는 염소화 반응을 통해 Zircaloy-4 (Zry-4) 피복관으로부터 Zr의 회수 연구를 수행하였다. 피복관의 Zr을 전부  $ZrCl_4$ 로 전환시키기 위해, Zry-4 피복관을 380도에서 70 cc/min  $Cl_2$  + 70 cc/min Ar 기체를 이용하여 8시간 동안 반응시켰다. 피복관의 초기 무게는 51.7 g이었으나, 8 시간 반응 후에는 0.49 g만이 잔류물로 남아있는 것을 확인하였는데 이는 초기 무게의 0.95wt%에 해당하는 값이다. 반응 생성물의 무게는 121.7 g이었으며, Zr의 순도는 99.80wt%였다. 주요 불순물로는 Fe (0.18wt%)와 Sn (0.02wt%)를 확인할 수 있었다. 실험 결과를 통해 확인한 Zr의 회수율은 96.95wt%였으며, 실험상 손실은 2.34wt%로 확인되었다. 반응 잔류물의 관찰을 통해 염소화 반응이 길이 방향으로 주로 일어나며, 표면의 산화층이 반응 잔류물로 남는다는 것을 확인할 수 있었다. 본 연구를 통해 확인된 Zr의 높은 순도와 회수율은 염소화 공정이 폐 피복관 처리 방법으로 매우 유망한 기술임을 의미한다고 볼 수 있다.

중심단어: 염소화 반응, 폐 피복관, Zr 회수, 사용후핵연료, 파이로프로세스

<sup>\*</sup>Corresponding Author . E-mail: [minku@kaeri.re.kr](mailto:minku@kaeri.re.kr), Tel: +82.42.868.2435

## 1. Introduction

It is widely known that a cladding hull waste is produced after reprocessing of Spent Nuclear Fuels (SNFs), whether a wet or dry reprocessing technique is employed. The importance of the cladding hull waste cannot be underestimated owing to its large portion (about 25% of nuclear material) and high radioactivity. Previous works suggest that cladding hull waste should be treated as a GTCC (Greater Than Class C) or HLW (high level waste) [1, 2]. In the case of pyro-processing, which employs electrochemical reactions to recover nuclear materials from the SNF, the cladding hulls are separated from nuclear materials using an oxidative decladding process [3-6]. Even after the oxidative decladding, a little amount of SNF stuck on the inner surface of the hulls cannot be removed completely. In addition, some of the fission products penetrate into the hulls [2] and the radioactivation of the hulls also produces various radioactive nuclides inside the hulls [7]. These various impurities make it difficult to decontaminate the cladding hull waste to treat it as an intermediate- or low-level waste.

At the Korea Atomic Energy Research Institute (KAERI), two options of chlorination and electro-refining processes are under investigation for the treatment of cladding hull waste. These techniques are aimed at the selective recovery of Zr from the cladding hull waste because cladding materials employed in light water reactors in Korea contain about 98wt% of Zr. In the electro-refining process, Zr is selectively deposited on a cathode electrode by applying the appropriate current/potential in a molten salt bath [8]. The electro-refining method is beneficial for integrated operation with the pyro-processing because it employs similar operation conditions with those of pyro-processing unit operations. However, slow reaction kinetics and difficulty in scale-up are major obstacles to be solved before the electro-refining technique is commercialized. On the other hand, the chlorination technique has merits of fast reaction kinetics and a relatively easy scale-up, although the high toxicity of chlorine gas should be considered before integration. In the chlorination technique, metallic Zr reacts with chlorine gas to produce volatile Zr tetrachloride, which is gaseous at over 331°C. The low sublimation temperature

of  $ZrCl_4$  enables easy separation of the reaction product from the other radioactive nuclides including the residual SNF. There have been a few papers that have performed the chlorination process using cladding hulls [9-12]. Yasuike et al. [9] reported that they could recover Zr from Zircaloy-2 hulls even in the presence of Co,  $UO_2$ , Ni, and Cs. Our group previously demonstrated that highly pure Zr can be achieved using a quartz reactor designed for the chlorination reaction of cladding hulls [10, 11], and it was also shown that oxidation of the hulls prior to the chlorination reaction suppresses the chlorination process [11]. However, these experiments were performed at the 10 g scale, and partial chlorination of the hulls was performed. In theoretical calculations, it was suggested that oxides of Zr, Sn, Fe, and Cr might not react with chlorine gas, while chlorides of Sn and Fe produced from metallic Sn and Fe might be co-recovered with  $ZrCl_4$  owing to their lower boiling point than that of  $ZrCl_4$  [10, 13, 14].

In the present study, a complete recovery of Zr from Zry-4 hulls was demonstrated at the 50 g scale using a quartz reactor system previously introduced by our group [10]. Based on the scale of PRIDE (PyRoprocess Integrated inactive DEMonstration facility), 10 MTHM of SNF per year, the chlorination process should treat up to 13 kg of cladding hulls per day based on 200 days operation. To achieve this goal, many aspects should be considered including effect of operation conditions on the recovery ratio and purity of Zr. Because it was previously reported by Yasuike et al. [9] that reactor temperature suddenly increased at the start-up of the process due to release of reaction heat. The control of reactor temperature might cause different Zr product purity due to formation of volatile impurities such as  $CrCl_4$ . In the present study, a preliminary test was performed to verify the recovery ratio and purity of Zr in 50 g scale of Zry-4 cladding hulls when a complete chlorination is carried out. An analysis of the reaction products and residues was performed based on the composition analysis results.

## 2. Experimental

A quartz reactor designed for the chlorination reaction of cladding hulls, which was introduced in our previous work [10], was also employed for this study. The quartz reactor

has a quartz frit in the middle to support cladding hulls in the reaction zone and to separate vaporized  $ZrCl_4$  from the cladding hulls and reaction residues. When  $Cl_2/Ar$  gas is fed from the top of the reactor,  $Cl_2$  reacts with Zr to produce gaseous  $ZrCl_4$ .  $ZrCl_4$  gas goes through the quartz frit with an Ar flow and reaches a collection zone where the temperature is kept at room temperature such that  $ZrCl_4$  is collected. The chlorination reaction was performed at 380 °C for 4 h flowing 70 cc/min Ar + 70 cc/min  $Cl_2$  gas, and this experiment was repeated twice for a complete recovery of Zr.

The fresh Zry-4 hulls employed in this study as a surrogate material were oxidized at 500 °C for 10 h under air, before performing the chlorination reaction. The hulls were cut into 5 cm long pieces before the oxidation process. A composition analysis of the reaction products, mainly  $ZrCl_4$ , was performed by an Inductively Coupled Plasma - Atomic Energy Spectroscopy (ICP-AES) system, except  $Cl^-$ , which was analyzed using an Ion Chromatography (IC) technique. The composition of the reaction residue was analyzed using a Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM-EDS) system.

### 3. Results and discussion

Fig. 1 shows pictures of the reaction reactants, products,

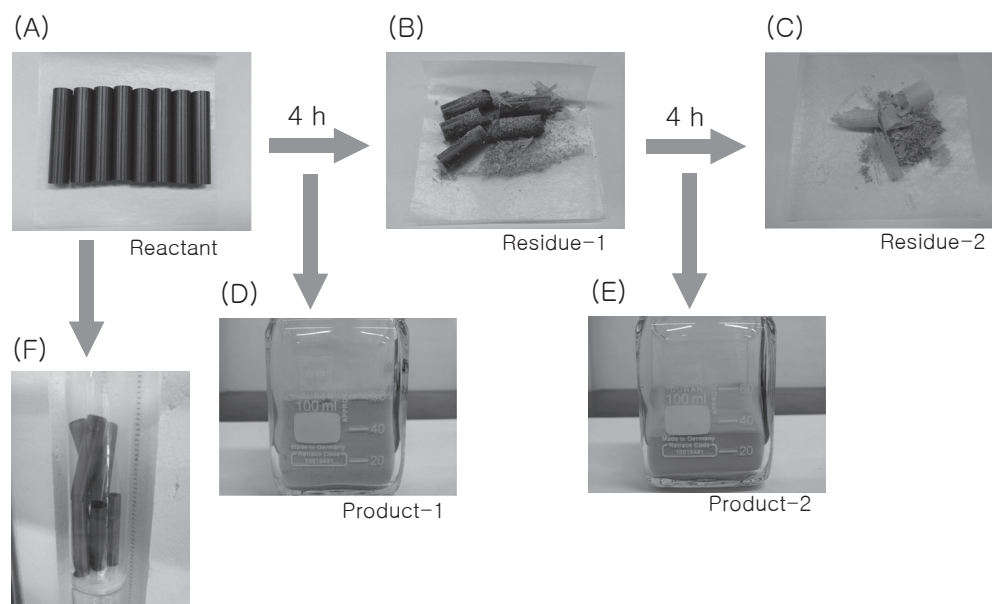


Fig. 1. The pictures of (A) reactants (eight Zry-4 hulls oxidized at 500 °C under air for 10 h), (B) Residue-1, (C) Residue-2, (D) Product-1, (E) Product-2, and (F) reactants loaded in the quartz reactor.

and residues. The weight of the Zry-4 hulls (8 pieces) decreased from 51.7 to 16.8 g after 4 h of the chlorination process. The amount of reaction product collected during the first operation was 83.5 g. The reaction residue of the first operation (Residue-1, Fig. 1(B)) was further chlorinated through a second operation, and the weight of the final residue was 0.49 g, which is only 0.95wt% of the initial weight. This result is very promising from a recovery point of view, because a loss of Zr caused by the decladding oxidation might be within a range of 1wt%, suggesting that the mass of HLW can be reduced up to this level. A close look of Residue-1 reveals an interesting point: the number of hulls decreased from 8 to 5. This result suggests that 3 hulls were completely already converted into  $ZrCl_4$ , and the picture of the hulls stacked inside the reactor, shown in Fig. 1(F), provides a hint of this result. Among the 8 hulls, 5 hulls were stacked on the quartz frit of the reactor, while 3 hulls were put over the five hulls. Recalling that  $Cl_2$  is fed from the top of the reactor, it is strongly suggested that the hulls first contacted with  $Cl_2$  (3 hulls on the upper level) were converted into  $ZrCl_4$  prior to the five hulls stacked below the 3 hulls. The final reaction residue (Fig. 1(C), Residue-2) also shows an interesting feature. Residue-2 exhibits two features of powdery and thin-film forms. Based on the picture of Residue-1 and its shape, it is suggested that the film type residues are originated from the outer surface of the

cladding hulls, and they were partially destroyed into powdery form because of the gas stream pressure. It should also be noted that the hulls of Residue-1 clearly show the direction of the reaction progress within the hulls. In all 5 cases, the edges of the hulls were significantly removed by the chlorination reaction, while only small holes were observed on the side walls. This behavior suggests that the chlorination reaction might proceed from both the edges and side walls, leaving the outermost oxide layer as shown in Fig. 1(C), although the chlorination reaction along the edges might be a dominant process. A significant difference between the two reaction products was observed, as shown in Fig. 1(D) and 1(E). It was clearly shown that the color of Product-1 (Fig. 1(D)) exhibits a more whitish color than that of Product-2 (Fig. 1(E)). In addition, the dark-orange color observed in both products is clearly different from the previous results of our group [10], where a white colored powder was achieved after a weight loss of 65.8% with a Zr purity of higher than 99.97wt%. The difference in the color of the reaction products was further discussed using the composition analysis results.

Table 1 lists the composition analysis results of the reactant, products and Residue-2. It should be noted that the amount of oxygen incorporated during the oxidation process (0.16wt%) was not considered in the composition calculation. As shown in the table, the mass ratios of Zr among metals were 99.90 and 99.59wt% for Product-1 and Product-2, respectively, which are lower than 99.97wt% from our previous study [10], where an incomplete chlorination process was performed. On the other hand, the metal ratio of Fe was 0.10 and 0.36wt% for Product-1 and -2, respectively, suggesting that the color change in the reaction products might have come from different Fe concentration in the products. In addition, the results of reduced Zr purity and increased Fe concentration are in good agreement with our theoretical calculation result [10], which suggests that the chlorination reaction preference follows an order of  $Zr > Cr > Sn > Fe$ . Although the purity of Zr was slightly decreased in Product-2, the purity of Zr based on the total products still exhibited a high value of 99.80wt% with Fe and Sn as impurities. Here, it should be commented that no Cr was observed in the reaction products, which looks natural when low vapor pressure of  $CrCl_3$  (less than 0.01

Torr at 380 °C) is considered [15]. In addition, this result also shows that a formation of volatile  $CrCl_4$  [15] was not significant in the conditions of the present study.

The composition analysis results of the reaction residue shown in Table 1 shows a relatively low Zr purity of 74.05wt%, which looks natural when recalling the high Zr purities of Product-1 and -2. Iron was not observed in the residue, suggesting that most of the Fe chloride was recovered with  $ZrCl_4$ . However, low concentration values of Sn in the reaction products are questionable because the concentration of Sn was still low in Residue-2. Using the total amount of recovered materials, the recovery ratio of each metal was calculated, the values of which were 96.95, 0.95, 82.69, and 0.00wt% for Zr, Sn, Fe, and Cr. A high recovery ratio of Zr was achieved, although the weight of oxygen incorporated during the oxidation process was not considered. These results clearly prove that the chlorination technique is promising as an effective Zr recovery method from Zry-4 hulls. Vapor pressures of  $ZrCl_4$ ,  $SnCl_4$ ,  $SnCl_2$ ,  $Fe_2Cl_6$ , and  $CrCl_3$  are shown in Fig. 2 by employing data of the HSC chemistry code [16] expect for  $Fe_2Cl_6$  [17]. The data of  $Fe_2Cl_6$  is valid only in a range of 422-575 K, but the data was employed in this study because the temperature range of interest is similar to this region. In the figure, it is suggested that  $SnCl_4$ ,  $Fe_2Cl_6$  ( $FeCl_3$ ), and  $ZrCl_4$  might be collected as products, while only a small content of Sn was observed in the experimental results. Experimental losses

Table 1. The composition analysis results of the chlorination reaction reactant, products and residue. The analysis was performed using the ICP-AES and IC (for Cl) systems except for Residue-2, which was performed using the SEM-EDS system

	Zr	Sn	Fe	Cr	Cl
Inlet (wt%)	98.09	1.60	0.21	0.10	-
Inlet (g)	50.71	0.83	0.11	0.05	-
Product-1 (wt%)	40.46	0.00	0.04	0.00	59.50
Product-1 (g)	33.78	0.00	0.03	0.00	49.68
Metal ratio of Product-1 (wt%)	99.90	0.00	0.10	0.00	-
Product-2 (wt%)	40.26	0.02	0.14	0.00	59.57
Product-2 (g)	15.38	0.01	0.06	0.00	22.76
Metal ratio of Product-2 (wt%)	99.59	0.05	0.36	0.00	-
Product total (g)	49.16	0.01	0.09	0.00	72.44
Metal ratio of product (total, wt%)	99.80	0.02	0.18	0.00	-
Residue-2 (wt%)	74.05	1.28	0.00	1.61	Cl: 5.06 O: 18.17
Residue-2 (g)	0.36	0.01	0.00	0.01	Cl: 0.02 O: 0.09

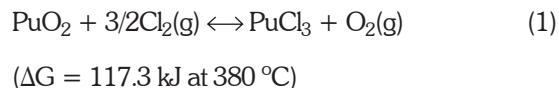
were calculated for each element, especially because of Sn and Cr, which exhibited a low concentration in the products and residue, and the calculation results for Zr, Sn, Fe, and Cr were 2.34, 98.29, 17.31, and 84.74wt%, respectively. The high losses observed for Sn and Cr might have come from measurement limitations of the residue samples due to their low contents. Especially for the case of Sn, a possibility of flow-away of fine chloride powders along with the Ar gas stream should be considered. Further investigation is necessary to clarify the high loss ratios of Sn and Cr.

In a real case of the chlorination process, the cladding hulls are mixed with residual SNF, and it is well known that ZrCl<sub>4</sub> can chlorinate other oxides such as UO<sub>2</sub>. Therefore, before scaling up the chlorination process, it might be helpful to investigate the reactivity of ZrCl<sub>4</sub> with U oxides which are the main components of the residual SNF. Table 2 lists calculated thermodynamic values calculated using the HSC chemistry code [16] for the reactions of ZrCl<sub>4</sub> with UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub>. The Table shows that UO<sub>2</sub> can produce U chlorides by reacting with ZrCl<sub>4</sub>, while only UO<sub>2</sub>Cl<sub>2</sub> formation reaction is feasible for U<sub>3</sub>O<sub>8</sub>. The effect of residual SNF was further investigated by calculating equilibrium compositions of Zry-4, UO<sub>2</sub>, U<sub>3</sub>O<sub>8</sub>, PuO<sub>2</sub> and Cl<sub>2</sub> using the HSC chemistry code. The calculation results are listed in Table 3, where only major reaction products are shown. In the calculation results, it is well known that metallic Zry-4 components can be converted into their chloride forms (ZrCl<sub>4</sub>(g), SnCl<sub>4</sub>(g),

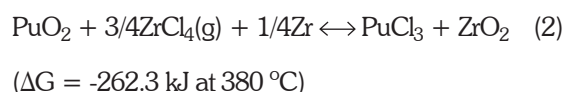
Table 2. Theoretical calculation results for the reactivity of ZrCl<sub>4</sub> with UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub> at 380 °C performed using the HSC chemistry code

	ΔH (kJ)	ΔS (J/K)	ΔG (kJ)	Log(K)
ZrCl <sub>4</sub> (g) + UO <sub>2</sub> ↔ ZrO <sub>2</sub> + UCl <sub>4</sub>	-158.78	-183.49	-38.93	3.11
ZrCl <sub>4</sub> (g) + UO <sub>2</sub> + 1/2Cl <sub>2</sub> (g) ↔ ZrO <sub>2</sub> + UCl <sub>5</sub>	-139.12	-182.40	-19.98	1.60
ZrCl <sub>4</sub> (g) + UO <sub>2</sub> + Cl <sub>2</sub> (g) ↔ ZrO <sub>2</sub> + UCl <sub>6</sub>	-172.78	-246.26	-11.93	0.954
ZrCl <sub>4</sub> (g) + 1/3U <sub>3</sub> O <sub>8</sub> ↔ ZrO <sub>2</sub> + UCl <sub>4</sub> + 1/3O <sub>2</sub> (g)	-54.48	-137.38	35.25	-2.82
ZrCl <sub>4</sub> (g) + 1/3U <sub>3</sub> O <sub>8</sub> + 2Cl <sub>2</sub> (g) ↔ ZrO <sub>2</sub> + UCl <sub>5</sub> + 1/3O <sub>2</sub> (g)	-34.82	-136.29	54.20	-4.34
ZrCl <sub>4</sub> (g) + 1/3U <sub>3</sub> O <sub>8</sub> + Cl <sub>2</sub> (g) ↔ ZrO <sub>2</sub> + UCl <sub>6</sub> + 1/3O <sub>2</sub> (g)	-68.48	-200.15	62.24	-4.98
ZrCl <sub>4</sub> (g) + U <sub>3</sub> O <sub>8</sub> + Cl <sub>2</sub> (g) ↔ ZrO <sub>2</sub> + 3UO <sub>2</sub> Cl <sub>2</sub>	-383.2	-363.7	-145.6	11.6

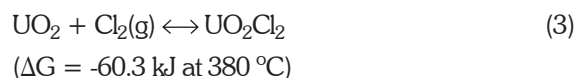
CrCl<sub>3</sub>, Fe<sub>2</sub>Cl<sub>6</sub>(g), and FeCl<sub>3</sub>(g)), while U and Pu cases need an explanation. In the case of Pu, reaction of PuO<sub>2</sub> with chlorine gas (reaction (1)) at 380 °C is not favored owing to positive ΔG value of this reaction as shown below.



Therefore, the formation of PuCl<sub>3</sub> in Table 3 might have come from a different route such as a reaction of PuO<sub>2</sub> with ZrCl<sub>4</sub> as reaction (2).



In the case of U, direct reaction of UO<sub>2</sub> with chlorine gas to produce UO<sub>2</sub>Cl<sub>2</sub> is thermodynamically feasible as reaction (3), while U<sub>3</sub>O<sub>8</sub> is not reactive with chlorine gas [13]. But as mentioned above, U<sub>3</sub>O<sub>8</sub> can be converted into UO<sub>2</sub>Cl<sub>2</sub> in the presence of ZrCl<sub>4</sub> and the amount of UO<sub>2</sub>Cl<sub>2</sub> in Table 3 (0.0031 kmol) suggest that both UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub> contributed to the formation of UO<sub>2</sub>Cl<sub>2</sub>.



The other reaction product of U, UOCl<sub>3</sub>, also can be

Table 3. The equilibrium composition calculation results performed using the HSC chemistry code. Temperature of the calculation was set as 380 °C. Only major products are shown

Reactant		Product	
Chemicals	Amount (kmol)	Chemicals	Amount (kmol)
Zr	0.9825	Cl <sub>2</sub> (g)	3.0015
Sn	0.0123	ZrCl <sub>4</sub> (g)	0.9793
Fe	0.0034	SnCl <sub>4</sub> (g)	0.0123
Cr	0.0018	UO <sub>2</sub> Cl <sub>2</sub>	0.0031
UO <sub>2</sub>	0.0010	ZrO <sub>2</sub>	0.0021
U <sub>3</sub> O <sub>8</sub>	0.0010	CrCl <sub>3</sub>	0.0017
PuO <sub>2</sub>	0.0010	Fe <sub>2</sub> Cl <sub>6</sub> (g)	0.0014
Cl <sub>2</sub> (g)	5.0000	PuCl <sub>3</sub>	0.0010
		UOCl <sub>3</sub>	0.0007
		FeCl <sub>3</sub> (g)	0.0006

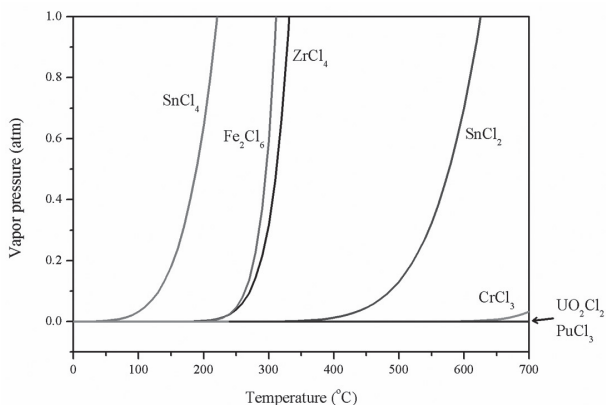
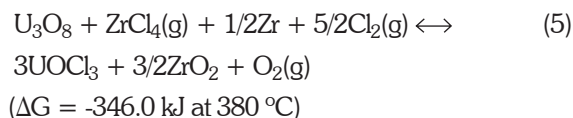
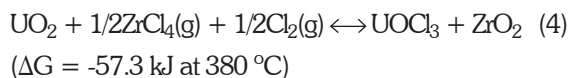


Fig. 2. The temperature – vapor pressure plots of ZrCl<sub>4</sub>, SnCl<sub>4</sub>, SnCl<sub>2</sub>, Fe<sub>2</sub>Cl<sub>6</sub>, CrCl<sub>3</sub>, UO<sub>2</sub>Cl<sub>2</sub>, and PuCl<sub>3</sub> drawn using the data of HSC chemistry code expect Fe<sub>2</sub>Cl<sub>6</sub> which referenced a previous report [17].

produced from both of UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub> through reactions (4) and (5).



The goal of the chlorination process is to separate Zr from other hull waste constituents so that it can be treated as a low- or intermediate level waste. Therefore, evaporation of alpha-emitting nuclides such as U and Pu is an important issue. Vapor pressures of PuCl<sub>3</sub> and UO<sub>2</sub>Cl<sub>2</sub> are also shown in Fig. 2 for comparison purpose, and it is clearly shown that vapor pressure of PuCl<sub>3</sub> and UO<sub>2</sub>Cl<sub>2</sub> are negligible up to 700 °C. Vapor pressure of UOCl<sub>3</sub> was not included in Fig. 2 due to lack of data. Therefore, it can be mentioned that the formation of PuCl<sub>3</sub>, UO<sub>2</sub>Cl<sub>2</sub> and UOCl<sub>3</sub> might happen during the chlorination process, but co-evaporation with ZrCl<sub>4</sub> might be negligible at the operation temperature range of the chlorination process.

#### 4. Conclusions

A complete recovery of Zr from Zry-4 cladding hulls was successfully demonstrated at a 50 g scale using a quartz reactor system. After 8 h of the chlorination process, highly

pure Zr (99.80wt%) was achieved with a high recovery ratio of 96.95wt%, showing that the chlorination method is a quick and simple technique to recover Zr from cladding hull wastes. It was also shown that Fe is recovered with ZrCl<sub>4</sub> as a major impurity (0.18wt%). The amount of the final reaction residue was 0.95wt% of the initial weight, proving that the chlorination technique is an effective method to minimize the amount of HLW generated during the pyro-processing.

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