Pyrochemical Electrorefining Experiments with Zr and Nb for CANDU Pressure Tube Decontamination into Low Level Wastes

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1. Introduction

1.1 CANDU Pressure Tube(Zr-2.5Nb)

In Korea, Wolsung unit #1 and Gori unit#1 have been shut-down for retirement. Wolsung unit#1 contains CANDU pressure tubes that correspond to the reactor vessel playing the most important role for operation and safety assurance. The CANDU pressure tube is made of Zr-2.5Nb alloy which can endure corrosion and hydrogen damages under very high pressure, high temperature and high radiation. But, at very high neutron fluence, some of natural niobium (100% Nb-93) and zirconium are transmuted to radioactive isotope Nb-94 which emits beta radiation with very long half-life (20,300 year). Also, a calandria tube surrounding each pressure tube made of Zircaloy-2 makes Nb-94 from the transmutation of Zr-91 and Zr-92. Total waste mass of pressure tube and calandria tube per one CANDU-6 nuclear power plant (NPP), is about 23 tons and 8 tons, respectively. Since there are 4 unit of CANDU-6 NPPs at Wolsung site, 150~180 tons of wastes will be produced. Wolsung unit #1 already emitted Zircaloy wastes from tube replacement after 30 years of operation. The Nb-94 activity of pressure tubes and calandria tubes from Wolsung exceeds the regulatory limit of existing waste repository by several orders of magnitude. Hence they are intermediate level waste that cannot be disposed of at Gyeong-ju LILW repository.

According to tentative national waste disposal plan, the ILW can be disposed of at future High Level Waste (HLW) site that is not yet determined. It is undesirable and costly to store large amount of Zr over long period of time. For this reason, it is proposed that Zr alloys wastes are better be decontaminated into LLW for their disposal at Gyeong-ju repository. But, the radioactivity of pressure tube (Zr-2.5Nb) is very high compared with low level waste limit. For this reason, high performance electrorefining process should be developed by both experiments and modeling to separate niobium from zirconium.

1.2 Decontamination Factor Needs for LLW

To decontaminate Zircaloys, radioactivity of pressure tube has to be confirmed. ORIGEN-2 code is used to calculate radioactivity of pressure tube waste. It is assumed operation duration is 27yr 84.1% operation efficiency by neutron flux. And, radioactivity data of calandria tube(Zircaloy-2) is calculated by other study. [1] By these results, we can get the DF goal to make each Zircaloy LLW. The obtained results are on Table 1.

$$\text{Decontamination Factor(DF)} = \frac{Con.\ of\ decontaminated\ isotopes}{Con.\ of\ initial\ isopotes}$$

Table 1: Specific Activity of Zircaloy wastes from Wolsung uint #1, Gyong-ju LLW Limit and DF goal on Nb-94

Parameters	Pressure Tube	Calandria Tube
Specific Activity (Bq/g)	7.07×10^6	1.94×10^2
LLW Limit on Nb-94 (Bq/g)	1.11×10^2	
DF Requirements for decontamination to LLW	6.37×10^4	1.75

2. Bulk Decontamination by Electrorefining

It is well known that for decontaminating Zircaloy, bulk electrorefining process is most efficient. For this reason, electrorefining process was selected as the process for the decontamination process of CADNU pressure tube. Two competing elctrorefining processes including aqueous process pyrochemical process are compared, for the final down-selection.

2.1 Aqueous Process vs. Pyrochemical Process

To decrease volume, radiotoxicity and decay heat of spent nuclear fuel or other HLW, aqueous (ex. PUREX) or pyrochemical (ex. Pyroprocess) process is being considered now. Since aqueous process is already commercialized, its technical maturity is higher than dry process. Nevertheless, aqueous process has fatal disadvantages regarding degradation of fluid under radioactivity, cost issue with low solubility in typical acid. These issues can be too costly for decontamination of highly active materials like pressure tubes. Whereas, even though pyrochemical process has disadvantages with limited experiences with nuclear materials because of batch process and with lower technical robustness compared with aqueous process, counterpart pyrochemical process is good radiation resistance. This led to the conclusion that pyrochemical process is chosen for pressure tube decontamination process.

2.2 Fluoride vs Chloride Pyrochemical Electrorefining

There are main two methods depend on the type of molten salt, mainly chloride and fluoride. The chloride process have some advantages with low corrosivivity and low process temperature(about 500℃) due to low melting point of chloride salt. But, zirconium in chloride salt, Zr has disproportionate reaction[3], so that process can be complexed. The fluoride process has one-step reduction of Zr(IV) into Zr metal.[16] But, high operating temperature(650℃ ~ 850℃), because of high corrosivity and high melting point of fluoride salt, can be more costlty in decontamination although it is desirable for pure metal production. When large scale processes are done during commercialized, the corrosive issue can be fatal to safety. Therefore, it is make sense that the chloride process was suitable for zirconium decontamination.

3. Experiments

3.1 Materials and Apparatus

To check zirconium and niobium redox behaviors in LiCl-KCl eutectic salt, several cyclic voltametry(CV) experiments were conducted. A glove box was filled and continually purged with inert argon gas of 99.999% by weight purity throughout experiments. Oxygen and moisture concentration was maintained below 0.1ppm and monitored during experiments. The working electrode(WE) and counter electrode(CE) material is 99.99 wt.% purity tungsten wire with 1mm diameter, 40cm length and smooth surface manufactured by Sigma Aldrich. The reference electrode was Ag/AgCl electrode containing 99.999% purity of Ag electrode with 1mm diameter and 1 wt% of AgCl salt manufactured by Sigma Aldrich. The purity of $ZrCl_4$ is 99.99 wt% manufactured by Sigma Aldrich. The purity of $NbCl_5$ is 99.9 wt% manufactured by Alfa Aesar. The molten salt mass for each CV experiment is about 3.0g, and WE and CE area for each CV experiment was about 0.628cm^2. The experiment temperature was 500±1℃.

3.2 Cyclic voltammetry of Zr and Nb in LiCl-KCl

To detect zirconium behaviors in LiCl-KCl, CV experiments were conducted. LiCl-KCl-$ZrCl_4$(1wt%, 0.8wt% of $ZrCl_4$) was prepared and conducted CV experiment.

Figure 1. is the result of LiCl-KCl-$ZrCl_4$ with scan range from -1.3V to 1.0V (vs. 1 wt% Ag/AgCl). It is well known by previous studies that the oxidation peak O_1 about -0.8V (vs. 1 wt% Ag/AgCl) reaction is the Zr metal is transformed to Zr(II) ion or Zr(IV). The reduction peak R_1 about -1.2V (vs. 1 wt% Ag/AgCl) is well know that from Zr(IV), Zr(II) to Zr(0) or Zr(I). It was detected that in the scan range from 0 to 1.0, there are no unusual redox peak was detected. [2][3]

To detect niobium behaviors in LiCl-KCl, CV experiment was conducted. LiCl-KCl-$NbCl_5$(0.32 wt% of $NbCl_5$) was prepared and conducted CV experiment.

Figure 2. is the result of LiCl-KCl-$NbCl_5$ with scan range (-1.3 V ~ 1.0 V). It is also well known that the oxidation peak O_2 about 0.2V (vs. 1 wt% Ag/AgCl) is lowest niobium metal oxidation peak transformed from Nb(0) to Nb(III). And, the reduction peak R_2 about -0.5V (vs. 1 wt% Ag/AgCl) is well know that highest reduction peak from niobium ion (Nb(III)) to niobium metal(Nb(0)).[4][5]

3.3 Cyclic voltammetry of Zr and Nb in LiCl-KCl-$ZrCl_4$-$NbCl_5$

Until now, there have been numerous CV experiments studies on LiCl-KCl salts including Zr salt or Nb salt. But, no experiment involving both Zr and Nb salts has been performed. Since the pressure tube contains both Zr and Nb metal, to confirm unusual redox reaction under Zr ion and Nb ion mixed condition, LiCl-KCl-$ZrCl_4$(1 wt%)-$NbCl_5$(0.1 wt%) salt was prepared and CV experiment was conducted.

Figure 3. is the CV experiment result of LiCl-KCl $ZrCl_4$(1 wt%)-$NbCl_5$(0.1 wt%) salt. From this result, O_1, O_2, R_1, R_2 redox peak was confirmed. Other unusual peak was not detected from this CV result.

3.4 Data Accuracy and Reproducibility Analysis

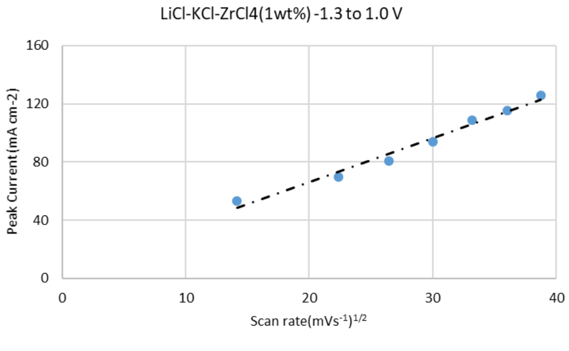

Fig. 4. Peak current at R_1 vs. square root of scan rate on LiCl-KCl-$ZrCl_4$(1 wt% of $ZrCl_4$) with scan range from -1.3V to 1.0V (vs. 1 wt% Ag/AgCl) with W electrodes at 500℃

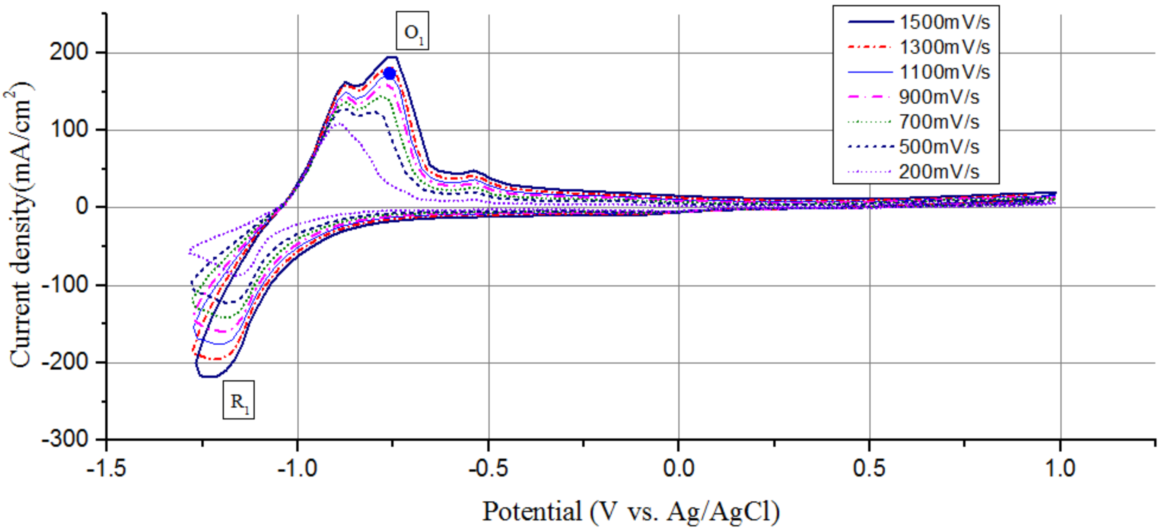

Fig. 1. Cyclic voltammetry result of Zr in LiCl-KCl-$ZrCl_4$ (1 wt.% of $ZrCl_4$) with scan range from -1.3V to 1.0V (vs. 1 wt% Ag/AgCl) with W electrodes at 500℃

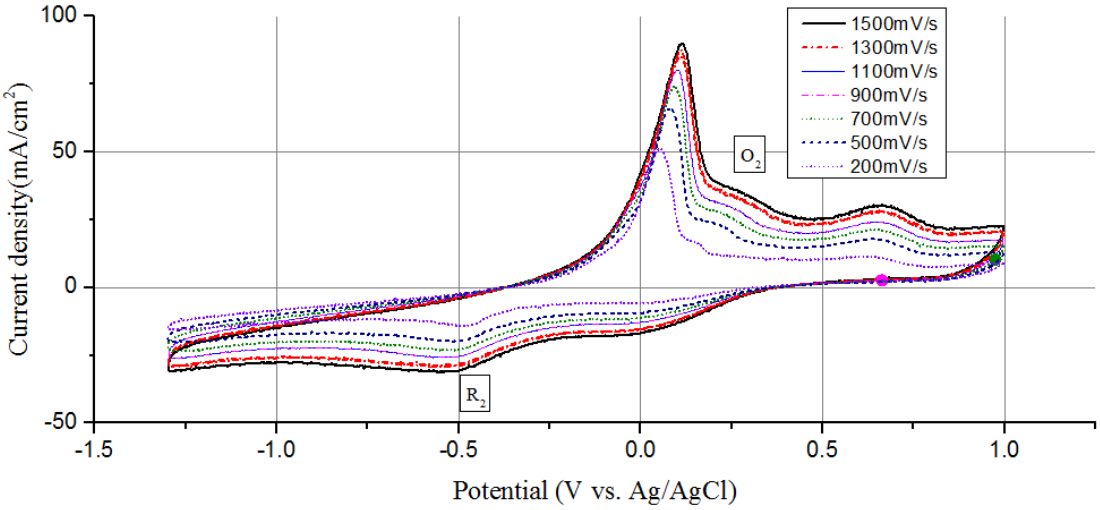

Fig. 2. Cyclic voltammetry result of Nb in LiCl-KCl-$NbCl_5$ (0.32 wt.% of $NbCl_5$) with scan range from -1.3V to 1.0V (vs. 1 wt% Ag/AgCl) with W electrodes at 500℃

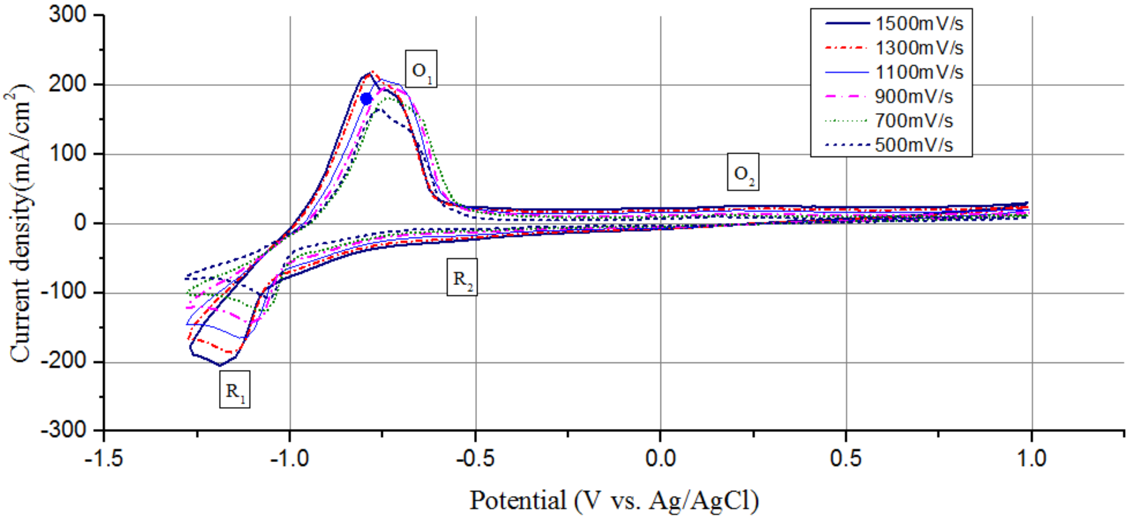

Fig. 3. Cyclic voltammetry result of Zr and Nb in LiCl-KCl-$ZrCl_4$ (1 wt%)-$NbCl_5$(0.1 wt%) with scan range from -1.3V to 1.0V (vs. 1 wt% Ag/AgCl) with W electrodes at 500℃

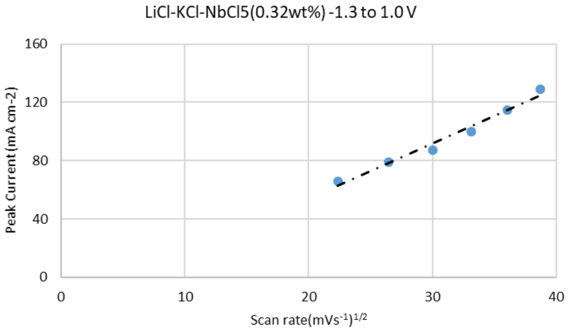

Fig. 5. Peak current at R_2 vs. square root of scan rate on LiCl-KCl-$NbCl_5$(0.32 wt% of $NbCl_5$) with scan range from -1.3V to 1.0V (vs. 1 wt% Ag/AgCl) with W electrodes at 500℃

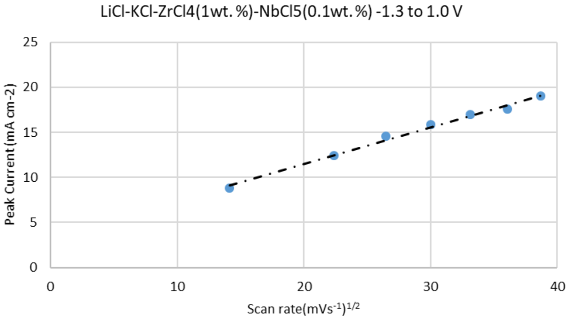

Fig. 6. Peak current at R_1 vs. square root of scan rate on LiCl-KCl-$ZrCl_4$(1 wt%)-$NbCl_5$(0.1 wt%) with scan range from -1.3V to 1.0V (vs. 1 wt% Ag/AgCl) with W electrodes at 500℃

Figs. 4-6 are peak current vs square root of scan rate graph. CV result of each salt shows that peak current is directly proportional to square root of scan rate. From this result, it was confirmed that diffusion coefficient can be obtained from result of this experiment.

4. Reduction of Thermodynamic data

From cyclic voltammetry data, diffusion coefficient and apparent equilibrium potential can be calculated.

4.1. Diffusion Coefficient

It is revealed that Zr(IV) is irreversible during cyclic voltammetry on cathodic reaction R_1.[3] Equation (1) is Delahay equation calculating diffusion coefficient for irreversible reaction. [6]

$$\frac{I_{pc}}{\sqrt{v}} = -0.4958nFSC\sqrt{\frac{n\alpha FD_{ox}}{RT}} \qquad (1)$$

where, I_p is peak current density (A/cm^2), n is the number of electrons participating in the reaction, F is the Faraday's constant (96.485 C/mol), S is surface area of electrode (cm^2), D_{ox} is diffusion coefficient of ion (cm^2/sec), R is the universal gas constant (8.314K/mol/K), v is scan rate (V/sec), α is transfer coefficient, it is generally assumed as 0.5. T is the temperature (K).

Niobium is reverssible on cathodic reaction R_2. Equation (2) is used for reversible reaction. [6]

$$I_{pc} = 0.446(nF)^{3/2}C\sqrt{\frac{Dv}{RT}} \qquad (2)$$

where, I_p is peak current density (A/cm^2), C_{M+} is the concentration of metal ion. Zr and Nb apparent reduction potential data is shown as from Fig. 7 and 8. It is reliable with other previous experiment data.

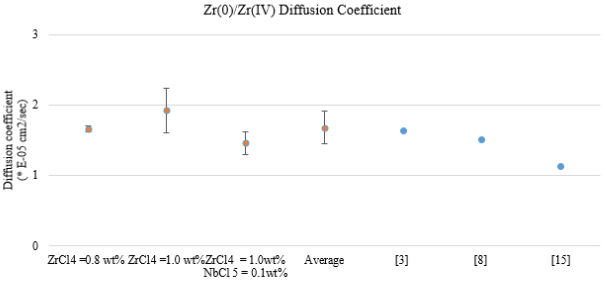

Fig. 7. Zr(IV) ion diffusion coefficient in LiCl-KCl

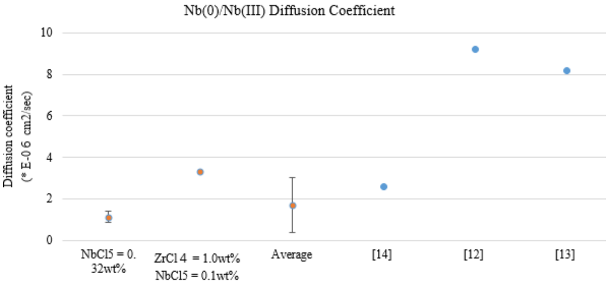

Fig. 8. Nb(III) ion diffusion coefficient in LiCl-KCl

4.2. Apparent Equilibrium Potential

From cyclic voltammetry data, apparent equilibrium potential can be obtained. Zirconium is irreversible during cyclic voltammetry on cathodic reaction R_1. Equation (3) is Delahay equation calculating standard reduction potential for irreversible reaction.

$$E_{pc} = E^{0*} - \frac{RT}{anF}\left[0.78 - \ln k_s + \ln\sqrt{\frac{anFvD_{ox}}{RT}}\right] \qquad (3)$$

where, E_p or E_{pc} is the peak potential. n is the number of electrons participating in the reaction, F is the Faraday's constant (96.485 C/mol), S is surface area of electrode (cm^2), D_{ox} is diffusion coefficient of ion (cm^2/sec), R is the universal gas constant (8.314K/mol/K), v is scan rate (V/sec) , α is transfer coefficient, it is generally assumed as 0.5. T is the temperature (K). $E^{0'}$ is the apparent equilibrium potential,

K_s is the standard rate constant it is generally assumed as $2.6x10^{-4}$.[6]

Niobium is reverssible on cathodic reaction R_2. (4) equation is the equation for reversible equation.

$$E_p = E^{0*} + \frac{RT}{nF}\ln C_{M^{n+}} + 0.8540\frac{RT}{nF} \qquad (4)$$

where, E_p is the peak potential, C_{M+} is the concentration of metal ion.[6] Zr and Nb apparent reduction potential data is shown as from fig. 9, 10. It is reliable with other previous experiment data.

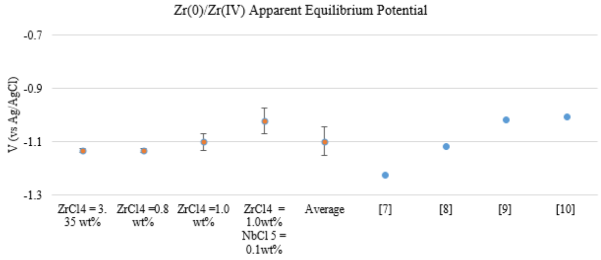

Fig. 9 . Zr(0)/Zr(IV) Apparent Equilibrium Potential

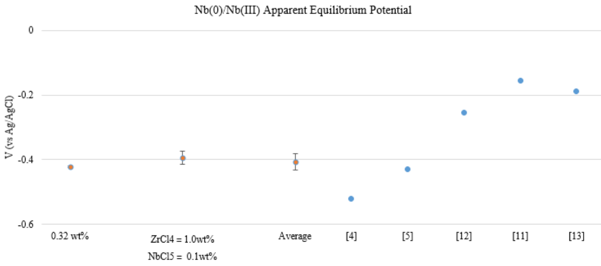

Fig. 10. Nb(0)/Nb(III) Apparent Equilibrium Potential

The apparent potential difference is about 0.7V (vs Ag/AgCl). This result shows the electorefining process is very suitable for zirconium-niobium separation.

5. Conclusion and Future Work

5.1 Conclusion

Firstly, by ORIGEN-2 code, radioactivity of Zr-2.5Nb was calculated, and DF goal of Nb for LLW was obtained. The DF requirement for decontamination to LLW was about 6.37 x 10^4. Secondly, for electrorefining Zr-2.5Nb, CV experiments have been conducted. According to CV, apparent equilibrium potential of Zr was 1.098±0.053V (vs Ag/AgCl) and apparent equilibrium potential of Nb was -0.407±0.026 (vs Ag/AgCl). And diffusion coefficient of Zr was 1.681 ± 0.231 (* E-05 cm^2/sec), and diffusion coefficient of Nb was 1.690 (* E-06 cm^2/sec). Experiment result values are fit with previous studies.

5.2 Future Work

McCARD will be employed to determine activities and their distributions in pressure tubes and caldaria tubes as function of location in CANDU unit 1. This result and previous studies about apparent equilibrium potential of Zr and Nb show that the electorefining process is expected to be very suitable for zirconium-niobium separation. To obtain the verification of the decontamination process, the electrorefining of Zr-2.5Nb metal in the LiCl-KCl molten salt will be carried out on a lab-scale. Then, after developing a pressure tube decontamination method by electrorefining process on pilot scale, post-treatment plan for each element of Zr-2.5Nb wastes should be developed.

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