

## Computational Analysis on Electrefining Process for Zirconium Recovery from PWR Spent Zircaloy-4 Cladding

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### 1. Introduction

Zircaloy cladding from Pressurized Water Reactors (PWR) spent nuclear fuel is classified as high level waste because used clads contain activation products such as Co-60 and Zr-93 and actinides and fission products penetrating from fuel pellets into cladding [1]. The irradiated Zircaloy-4 cladding still includes a large amount of zirconium while containing only a small amount of radioactive isotopes. With a suitable decontamination process, recycled zirconium could be treated as low level waste and reused at least for nuclear industry [2]. Recycling used Zircaloy-4 cladding, which is approximately 16wt% of PWR spent nuclear fuel, can result in additional volume reduction of high level waste and possible cost save for nuclear fuel fabrication.

We have studied a preliminary one-dimensional computational analysis of zirconium recovery from PWR spent Zircaloy-4 cladding with electrefining process. Contaminated zircaloy cladding is loaded at anode; decontaminated zirconium metal is recovered at cathode. One-dimensional transient electrochemical reaction code, REFIN, was used for this assessment. Radioactivity of Co and U for deposited zirconium alloy at cathode was investigated according to different initial concentration of Co and U in molten salt and diffusion boundary layer thickness. Radioactivity and materials composition of irradiated Zircaloy-4 cladding loaded at anode were obtained from ORIGEN-2 calculation.

### 2. Methods and Results

#### 2.1 Composition and radioactivity of used Zircaloy clad.

Zircaloy-4 cladding is initially composed of 98wt% Zr, 1.5wt% Sn 0.21wt% Fe, 0.1wt% Cr and a very small amount of Al, B, C, Co, Cu, Hf, Mn, Ni, Si, Ti and W [3]. After three years of irradiation under average PWR neutron flux ( $4.5E+13 \text{ \#/cm}^2\text{s}$ ) and 3 years of post-cooling, activation products are accumulated. According to the prediction with ORIGEN-2, Co-60 and Sb-125 are dominant radionuclides among the activation products of Zircaloy-4 as represented in Table I.

Table I: Radioactivity of activation products of Zircaloy-4 cladding for 3 years irradiation and 3 years post-cooling.

	Sb-125	Co-60	Others	Total
Radioactivity [Bq/g-Zircaloy-4]	1.7E+07	8.8E+06	1.3E+07	3.9E+07

On the other hand, the concentration of actinides and fission products penetrated and diffused into Zircaloy-4 cladding was determined by literature survey since the penetration of those products cannot be considered in ORIGEN-2. According to In-Ha Jung et al. (2006), approximately 1.1g of uranium and 14mg of plutonium could exist in 1kg of irradiated Zircaloy-4 hull [4].

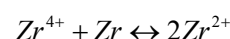
#### 2.2 Numerical analysis on zirconium electrefining

Both time-dependent behavior of electrefining for zirconium recovery and composition of final zirconium metal products were investigated. Because no specific reference electrefiner for zirconium recovery was determined yet, anode and cathode area and molten salt volume were simply assumed as shown in Table II. To reduce the complexity of modeling, only Co and U were considered as representative materials of activation products and actinides in the computational analysis with major constituent elements of zircaloy-4 as represented in Table II. Several operating conditions with different initial concentrations and diffusion boundary layer thicknesses were applied to evaluate the effect of these parameters on the decontamination factor and radioactivity of deposited alloy on the cathode. The applied current was set as 1A which is lower than limiting current for whole cases.

Table II: Modeling conditions for REFIN simulation.

Molten salt	LiCl(44.2wt%)-KCl(55.8wt%)
Temperature [K]	773
Elements loaded at anode	Zr, Sn, Fe, Cr, Co, U
Anode and cathode area [ $\text{cm}^2$ ]	10
Molten salt volume [ $\text{cm}^3$ ]	10
Diffusion boundary layer thickness [cm]	$10^{-4} \sim 10^{-1}$
Initial concentration of total dissolved elements in molten salt [wt%]	10 (99wt% Zr)
Initial concentration of Co in molten salt [wt%]	$10^{-9} \sim 10^{-1}$

In LiCl-KCl molten salt, zirconium possibly has two stable ion states that are both divalent and tetravalent states, although divalent ion exists only a small amount. These two zirconium ionic states were related by disproportionate reaction with zirconium metal [2].  $\text{Zr}^{4+}$  can be reduced to  $\text{Zr}^{2+}$  by the following equation:



This reaction might be dissolved deposited zirconium metal from cathode, reducing recovery ratio. However, this reaction was slow because several experiments were observed only a very small  $Zr^{2+}$ . In this analysis, disproportionate reaction was ignored; all electrochemical reactions were assumed as one-step reactions [5].

To determine the termination time of electrorefining, it was assumed that the electrorefining is stopped when the anode potential is suddenly changed because of depletion of zirconium in anode. At the initial stage of electrorefining, the Cr divalent ion in molten salt is deposited on the cathode with zirconium until the ion is depleted in molten salt. Then only zirconium is dissolved from anode and deposited on cathode up to the last few hours of electrorefining. At the final stage of electrorefining, Sn, Cr, Fe, Co and U are dissolved from anode as Zr is exhausted and Sn, Cr and Co are deposited with Zr. Until the end of electrorefining, uranium analytically was not deposited on cathode surface. On this account, the radioactivity was evaluated for only Co-60. Fig. 1 shows radioactivity of Co-60 deposited on cathode surface according to diffusion boundary layer thickness and initial concentration of cobalt. Co-60 is 1.06wt% of overall cobalt element.

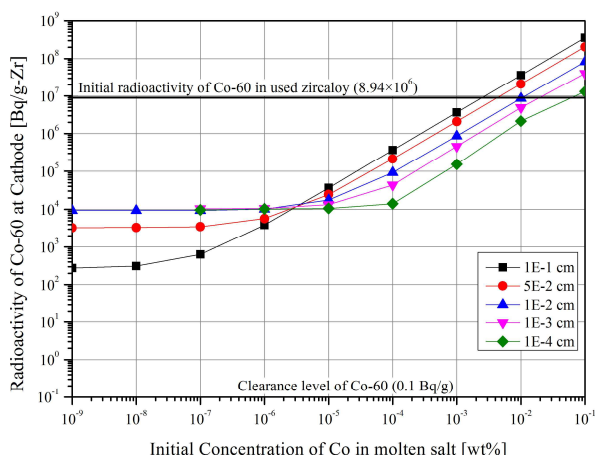


Fig. 1. Radioactivity of Co-60 at cathode according to diffusion boundary layer thickness and initial concentration of Co element in molten salt.

For cases that initial concentration of cobalt in molten salt is higher than approximately 3E-6wt%, the case which has thinner boundary layer shows smaller amount of cobalt deposition on the cathode. Because cobalt is more reductive than other metals, the cobalt ion which existed in initial molten salt can be thermodynamically reduced while simultaneously oxidizing metals at anode from at the initial stage of electrorefining. More cobalt ion might be transported to anode with thinner boundary layer thickness; as a result, less amount of cobalt surface could be deposited on the cathode.

In contrast to the high concentration cases, with cobalt concentration lower than 3E-6wt%, thinner diffusion boundary layer cases cause lower cobalt

contamination. This trend is because thinner diffusion boundary layer increases ion transfer from anode to cathode. Cobalt might be dissolved when zirconium at anode is depleted at the last stage. If mass transfer is fast near the electrode, cobalt ion which is dissolved at the end of electrorefining could reach cathode.

### 3. Conclusion

The parametric studies for electrorefining process to recover zirconium from PWR spent Zircaloy-4 cladding was simulated with different diffusion boundary layer thickness and initial concentration of cobalt. A little uranium, which had been penetrated to cladding from fuel, was co-deposited at cathode with zirconium. The trend of Co-60 deposition largely depends on initial cobalt concentration and diffusion boundary layer thickness. If initial cobalt contamination in molten salt is extremely low, thinner diffusion boundary layer might be preferred for higher purity of recovered zirconium. However, since it is hard to secure high throughput under thin boundary layer thickness condition, future investigation with both experiment and simulation is required to optimize operating conditions.

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### REFERENCES

- [1] Tracy S. Rudisill, Decontamination of Zircaloy cladding hulls from spent nuclear fuel, *Journal of Nuclear Materials*, Vol. 385, pp. 193-195, 2009.
- [2] Reiko Fujita et al., Development of Zirconium Recovery Process for Zircaloy Cladding and Channel Boxes from Boiling Water Reactors by Electrorefining in Molten Salts, *Proceedings of ICAPP05*, Seoul, Korea, May 15-19, 2005.
- [3] M. Ahmad et al., Role of Solute Segregation on Microstructure and Mechanical Properties of Zircaloy-4, *Journal of Materials engineering and Performance*, Vol. 12, pp179-182, 2003.
- [4] In-Ha Jung et al., Investigation of PWR Hull with a View to Downgrade, *Separation Science and Technology*, Vol. 41, pp. 2097-2109, 2006.
- [5] Yoshiharu Sakamura, Zirconium Behavior in Molten LiCl-KCl Eutectic, *Journal of the Electrochemical Society*, Vol. 151, pp. C187-C193, 2004.