Investigations into the Gas Phase Reactions of Zirconium Tetrachloride ($ZrCl_4$) from UNF Cladding

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INTRODUCTION

Zirconium-based cladding materials that surround used nuclear fuel (UNF) rods represent a significant fraction of the total amount of high level waste that must be disposed of in long term geological repositories. The decontamination, recovery and reuse of these materials would significantly reduce the high level waste associated with light water reactors and could provide a new source of hafnium free zirconium for the fabrication of new nuclear components.

A step in a strategy to recycle zirconium from used cladding materials is the high yield chlorination of Zircaloys to produce zirconium tetrachloride ($ZrCl_4$).[1] The $ZrCl_4$ is contaminated with other metal chloride species that originate from the alloying metals as well as contaminants from oxide layers on the cladding, trace fission products, fuel residues, activation byproducts, and tritium. The properties of these complex mixtures must be better understood before purification protocols can be developed that will allow zirconium chloride to be recycled further.

DESCRIPTION OF WORK

The $ZrCl_4$ product obtained from the direct chlorination of Zircaloys is contaminated with a variety of other metal chlorides including $FeCl_3$, $NbOCl_3$ and $NbCl_5$. One part of our NEUP funded work involves sublimation-based purification protocols to obtain pure $ZrCl_4$ that may either be treated as low level waste or reduced to the metal thereby providing a new stream of nuclear grade zirconium for use in the industry. Early work in the project involved exploring the possibility of chemically modifying the different components of the mixture to aid in their separation from $ZrCl_4$. Adding thionyl chloride ($SOCl_2$) to the inert gas stream during sublimation serves to transform oxide impurities into chlorides. In the particular case of niobium, $NbOCl_3$ is transformed into the pentachloride ($NbCl_5$). This transformation can be incurporated into a purification strategy which involves collecting a sublimation forerun to remove the more volatile $NbCl_5$ before collecting the desired product. Small scale (~10 g) test reactions gave good results with purification factors of 20 or more for niobium removal. Here we report on the results of scale up experiments to determine if these purification factors can be reproduced.

RESULTS

The sublimation protocol that has been developed for purifying $ZrCl_4$ involves two steps (Figure 1). In the first step, thionyl chloride in nitrogen is passed over the impure $ZrCl_4$ for a period of time to transform $NbOCl_3$ into $NbCl_5$ at a temperature below the sublimation temperature of $ZrCl_4$. The temperature is then increased to ~250°C and a forerun of solid material is collected. The reactor is then cooled under nitrogen flow and the condenser with yellow $NbCl_5$ is exchanged for a new one. The reactor is then heated again to ~250°C under a hydrogen atmosphere to reduce Fe(III) to Fe(II) chloride. The final step in the purification is the bulk sublimation of purified $ZrCl_4$ at 350 - 400°C.

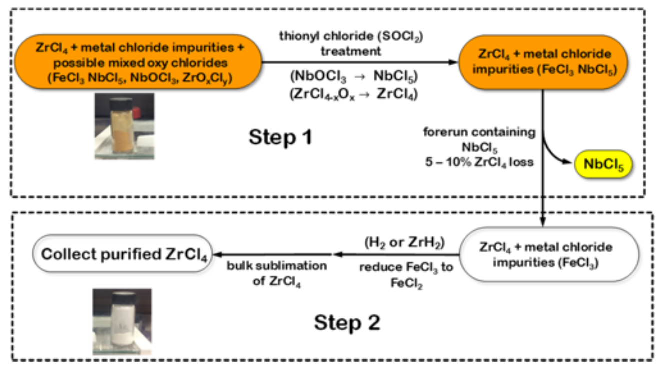

Fig. 1. Purification protocol developed to purify $ZrCl_4$

Results

As summarized in Table I, following protocols developed at small scale, good purification factors (PFs) are obtained for iron and niobium separation. The PFs that are obtained are a sensitive function of the soak times (longer soak times yield higher PFs) used during exposure to $SOCl_2$ in the forerun and hydrogen preceding collection of the product.

Table I. Results of scale up purification runs of $ZrCl_4$

Scale	Mass (g)	Prerun (g)	Residue (g)	Yield (g)	Yield (%)	PF (Nb)	PF (Fe)
20g	20.234	1.531	<0.100	18.745	92.7	9.1	11.7
50g	51.371	2.789	4.113	44.323	86.3	10.3	12.3
75g	73.877	2.852	26.519	44.417	62.8	8.8	10.9
20g	19.998	0.648	<0.100	19.219	96.1	3.2	5.4
70g	71.659	3.137	5.390	63.318	88.4	37.2	17.3

CONCLUSIONS

Sublimation based purification, together with chemical manipulation of the impurity components in the mixture is a viable approach to the production of pure $ZrCl_4$ derived from Zircaloy claddings. Scaleup runs verify that purification factors are roughly the same as observed for small scale experiments.

REFERENCES

[1] E. D. Collins, G. D. DelCul, B. B. Spencer, R. R. Brunson, J. A. Johnson, D. S. Terekhov, N. V. Emmanuel, *Procedia Chemistry* **2012**, *7*, 72-76.