Purification of Zirconium Tetrachloride ($ZrCl_4$) from UNF Cladding

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ABSTRACT:

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 and/or recovery and reuse of these materials would significantly reduce the amount of high level waste associated with light water nuclear energy 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 direct, high yield chlorination reaction that produces zirconium tetrachloride ($ZrCl_4$). The $ZrCl_4$ is contaminated with other metal chloride species that originate from the alloying metals present initially 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.

In the proposed research we seek to investigate and better understand the properties of contaminated chlorination product mixtures and, from this understanding, demonstrate a viable process or sequence of processes for the purification of $ZrCl_4$ that will allow it to be reduced to metal and recycled.

Zirconium tetrachloride does not form a liquid phase except at high pressures not well suited for industrial scale processes. For this reason we propose to develop sublimation-based experimental protocols for the purification of $ZrCl_4$ at or near atmospheric pressure.

While preliminary chlorination studies have shown that the $ZrCl_4$ product is contaminated, the exact identities of these contaminants are still not known. Furthermore the contaminant profiles in the chlorinated product will vary significantly based on a number of factors:

1. The type of cladding (Zircaloy-2, Zircaloy-4, High-Nb Zr alloys) and its use history
2. The decladding procedures used and pretreatment protocols used before chlorination
3. The direct chlorination protocols used to make the $ZrCl_4$ feed which requires purification.

In Phase 1 of the proposed research we will investigate the properties of a variety of simulant mixtures for $ZrCl_4$ feeds from the direct chlorination reaction from virgin Zircaloy materials. The properties of interest are: 1) the relative volatilities of contaminant metal chlorides (e.g. $SnCl_4$, $NiCl_2$, $NbCl_5$, $NbOCl_3$, $FeCl_3$, $CrCl_3$, $SbCl_3$, etc.) and nonradioactive isotopomers of possible radiologically active contaminant chlorides; 2) potential gas phase reactions that form mixed metal species during sublimation that will impact their separation from $ZrCl_4$, and 3) kinetic factors that could cause the sublimation not to proceed under equilibrium conditions. In Phase 1 of this work, a sublimator will be constructed which will be interfaced with an atmospheric sampling mass spectrometer to monitor the composition and identify the species in the gas phase as a function of the time course of the sublimation. Simultaneously with these experimental efforts, thermodynamic models for the species in the gas phase during the sublimation process will be developed using open source data bases and commercially available modeling software. It is of particular

interest in the investigations proposed here to study the significance of mixed metal species that form under the conditions of sublimation because of their predicted effects on separating $ZrCl_4$ from the mixture. The results of modeling and experimental investigations will be compared to obtain a 1st order understanding of the sublimation characteristics of these mixtures.

In Phase 2 of the project, a number of different strategies are proposed to enhance the separation of $ZrCl_4$ from contaminants via sublimation near room pressure. Three chemical strategies will be investigated:

1. The effect of selective reductants such as hydrogen, zinc, tin, sacrificial zirconium, and zirconium hydrides will be studied. Selective reduction of impurity chloride species should significantly lower their vapor pressures relative to $ZrCl_4$ and therefore lead to more effective purification via sublimation.
2. The effect will be investigated of added chloride salts (Li, Na, K, Cs, Mg, Ca) which are known to form molten salt mixtures with Lewis acidic metal chlorides such as $FeCl_3$ and $NbCl_5$. The formation of binary salts such as $NaFeCl_4$ and $NaNbCl_6$ that have much lower volatilities than their respective neutral chlorides should make sublimation purification strategies more effective.
3. Oxide, hydroxide and oxychloride species are expected to be present in contaminated $ZrCl_4$ feeds. $NbOCl_3$, in particular, is of concern because of similar volatility characteristics to $ZrCl_4$ as well as being less reactive with added chloride salts or reductants. A general procedure to transform oxygen containing complexes into pure chloride complexes is reaction with thionyl chloride ($SOCl_2$). Exposing mixtures to $SOCl_2$ prior to sublimation will be investigated to transform all oxygen-containing contaminants into homoleptic chloride complexes that can then be dealt with using the strategies described in (1) and (2) above.

The objectives of Phase 2 are to investigate and understand the effects that various additives have on the sublimation characteristics of $ZrCl_4$ feeds with contaminant profiles that will be encountered from the different types of Zircaloy claddings on UNF rods.

The major objective of Phase 3 is to transfer the knowledge and protocols developed in the first two phases of this program to the laboratories of our collaborator Dr. G. D. (Bill) DelCul at ORNL and demonstrate purification of actual contaminated $ZrCl_4$ samples on a ~1 kg bench scale. Tests with samples derived for used (radiologically active) claddings will be performed if authorized to do so and time and resources permit. The successful demonstration of a suite of purification protocols that can be adjusted depending on the factors listed above, would fulfill the objective of the Advance Waste Forms program (1.4) of the NEUP program.

In addition to the PI, one National Laboratory Collaborator (Dr. Bill DelCul) and one Industrial Collaborator (Dr. David McLaughlin; Westinghouse Electric Co.) will participate and be supported (partially) on this project. DelCul has been a lead scientist investigating the direct chlorination reaction of Zircaloy claddings for the DOE. He has an intimate knowledge of the experimental protocols associated with this step in the Zr-recycling program and thus can inform and advise the PI about protocol changes and variations in the contaminant profiles. The close proximity of DelCul's laboratories at ORNL and the PIs research program at the University of Tennessee (UTK) (40 min. by car) will allow researchers at UTK to work closely with DelCul and regularly visit with him as required. Dr. McLaughlin is a Fellow Engineer at Westinghouse with over 30 years' experience in a number of areas associated with nuclear materials and specifically with the development of zirconium recycling technologies. He has collaborated with DelCul in the recent past on topics related to the properties of contaminated $ZrCl_4$ feeds and is an expert in modeling their properties and in the design of industrial purification processes for $ZrCl_4$ mixtures. He will visit with DelCul and researchers at UTK at least once a year and be available for consultation via email and video conferencing to balance out his committed time to the project.