# Purification of Zirconium cladding using a chloride volatility process

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**ABSTRACT:**

The United States produces a large amount of cladding material from used nuclear fuel, expected to approach 1,000 MT/year for the next 50 year. This requires a technical route to manage this cladding material. Three approaches (mechanical, thermo-mechanical, chemical) were proposed to manage the radioactive cladding. In the mechanical approach, the cladding is compacted and stored with a cement matrix. In the thermo-mechanical method, hot pressing is used for compaction. In the chemical approach, Zr will be recovered so that it can be recycled or disposed of as a low level waste. It was estimated that the reprocessing of Zr would represent a ~50% savings on the geologic waste disposal space requirement. Furthermore, due to the cost of Hf-free Zr, it was estimated that the reprocessing of Zr would represents a material savings of > $40M/y. Different chemical approaches have been proposed for the recovery of Zr: electrorefining, iodination and chlorination methods. In the chlorination method, the Zr cladding reacts with chlorine gas at 350-380 °C to produce $ZrCl_4$. The $ZrCl_4$ product has a relatively low boiling point which enables its separation from the other products. Previous work has shown that Zr can be recovered from the cladding using the chlorination method. However, one of the issues observed was the presence of impurities (Fe, Sn, Cr, Cs, Sb, Nb) in the recovered $ZrCl_4$. From this, further efforts are required to develop a chlorination process that will yield high purity Zr.

The goal of this project is to investigate the thermochemistry of used fuel Zr cladding component chlorides, their activation products and residual radionuclide metal chlorides in order to provide the DOE-NE community with fundamental data that will support the development of a chlorination process for the purification of $ZrCl_4$. The studies will focus on the following elements: Zr, Sn, Fe, Cr, Sb, Nb and Cs. Experimental and theoretical efforts will focus on the characterization, reactivity and volatility of the chloride species present in the $ZrCl_4$ obtained after cladding chlorination . Zircaloy-4, Zircaloy-2 and Zr-Nb alloys ( Zirlo™ and Zr-2.5Nb) are the target claddings of interest.

The goal of the project is in line to the objective of the DOE-NEUP Fuel Cycle Technologies Program (FC-1.4) which states "*Investigate the relative volatility at 300-400 ℃ of used nuclear fuel zirconium cladding component chlorides, including alloying agents and residual radionuclides, such as niobium, iron, antimony, and cesium chloride species that are known to have similar volatility to zirconium tetrachloride.*" The fundamental science of Zr, Nb, Fe, Sn, Cr, Sb and Cs chloride species is directly relevant to reprocessing of Zr cladding by a chlorination process. Understanding of the chemical form of chloride species in $ZrCl_4$ is fundamental to predicting their behavior in a volatilization processes. Understanding the reactivity, volatility and redox chemistry of these chloride species will provide guidance to engineers in the development of a process for the purification of Zr cladding. Finally, training of students in this subject area has direct relevance to DOE-NE needs in fuels cycles technology. This project will provide students with theoretical and experimental knowledge that will allow them to be successful in this and future fuel cycle projects. The project consists of five Tasks:

- **Task 1. Theoretical studies of chloride species.** Modeling and simulation efforts will focus on: (i) the possible chemical and structural forms of the species that are present in $ZrCl_4$ after the chlorination

process, (ii) the behavior of Nb, Sn, Cr, Fe, Sb and Cs chloride species under vacuum, or in the presence of different gases ($Cl_2$, $H_2$, $N_2$, $H_2S$) or reducing agents (Zn and Cd metal), (iii) the possible reactions between $ZrCl_4$ with the various chloride species, indicating whether ternary halides can be produced during the chlorination experiment, and (iv) the relative chemical stability of chloride species during $ZrCl_4$ separation. The modeling and findings can be used to guide and interpret project laboratory experiments.

- **Task 2. Characterization of chloride species.** The chemical form of the chloride species present in $ZrCl_4$ after the chlorination process will be determined by experimental techniques. Characterization will be performed on samples that have been produced from chlorination of: Zr-M alloys (M = Fe, Nb, Sn, Cr and Sb), $Zr/Cs_2O$ mixtures and non-irradiated Zr cladding. After each experiment, products will be characterized by energy dispersive X-ray spectroscopy, scanning electron microscopy, electron probe micro-analysis, powder XRD, X-ray absorption fine structure spectroscopy and ICP-AES, and ICP-MS after nitric acid dissolution.
- **Task 3. Thermochemical behavior of chlorides species and of $ZrCl_4$.** The thermochemical behavior of the chloride species identified in Task 2 and of $ZrCl_4$ will be studied under vacuum as a function of the temperature (200-500 °C), in various gaseous atmospheres ($Cl_2$, $N_2$, $N_2/H_2$ and $H_2S$) and in the presence of metallic reducing agents (Zn, Cd). Thermochemical properties will be initially studied by thermo-gravimetric analysis (TGA). For the TGA experiments, scanning and isothermal measurements will be performed under vacuum, $Cl_2$, $N_2$, $N_2/H_2$ and $H_2S$ gas. The TGA experiments will allow us to determine: the temperatures, chemical and kinetic conditions under which the chloride species will be volatile or not. Following the TGA experiments, the thermochemical behavior of the chloride species and of $ZrCl_4$ will be performed on a larger scale (~10 g). In those experiments, the volatile products and the non-volatile residues will be collected at various time intervals, weighed and characterized by microcopy, diffraction and spectroscopic techniques. Those characterizations will provide data on the nature of species produced during the experiments, their volatility properties and volatilization rates.
- **Task 4. Thermochemical behavior of chlorides species in the presence of $ZrCl_4$.** Building upon the individual compounds examined in Task 3, the thermochemical behavior of the chlorides species in the presence of $ZrCl_4$ will be investigated as a function of the temperature under vacuum, $Cl_2$, $N_2$, $N_2/H_2$, $H_2S$ atmospheres, and in the presence of Zn or Cd metal. In these experiments, $ZrCl_4$ and chloride species will be synthesized, mixed and reacted under the same conditions as the one described in Task 3. During the experiments, the volatile products and non-volatile residue will be collected, weighed and analyzed by microscopy, spectroscopy and diffraction techniques. Those experiments will allow us to determine whether ternary Zr compounds are formed under our experimental conditions; it will also determine separation factors between Zr and the chloride species under different conditions.
- **Task 5. Laboratory scale demonstration of the purification of $ZrCl_4$.** The data obtained in Task 4 will be used to determine the optimal conditions for the separation of $ZrCl_4$/chloride species. The separation process will be tested at the laboratory scale on samples obtained after mixing $ZrCl_4$ with the chloride species and samples obtained after treatment of Zr claddings with $Cl_2$ gas. In the demonstration process, the samples will be treated according the conditions determined for optimal separations. After the experiments, the different products will be characterized and separation factors determined.

The expected project outcomes are: 1) Determination the chemical form of impurity chloride species in $ZrCl_4$ after chlorination of Zr cladding. 2) Acquisition of fundamental data relevant to the thermochemical behavior of $ZrCl_4$ and chloride species under various atmospheres or in the presence of metallic reducing agents. 3) Acquisition of fundamental data relevant to the behavior of $ZrCl_4$ in the presence of other chloride species. 4) Laboratory scale demonstration of the separation of chloride species from $ZrCl_4$.