

Computational Studies of Gas Phase Reactions of Zirconium Tetrachloride (ZrCl<sub>4</sub>) and Metal Chloride ImpuritiesMichael Orick,<sup>a</sup> Craig Barnes,<sup>a</sup> Guillermo (Bill) Daniel DelCul,<sup>b</sup> David F. McLaughlin<sup>c</sup><sup>a</sup>Dept. of Chemistry; University of Tennessee; Knoxville, TN 37996-1600<sup>b</sup>Oak Ridge National Laboratory; 1 Bethel Valley Road, Oak Ridge, TN 37831-6243<sup>c</sup>Westinghouse Electric Company LLC; 1332 Beulah Rd., 301-205E; Pittsburgh, PA 15235-5083

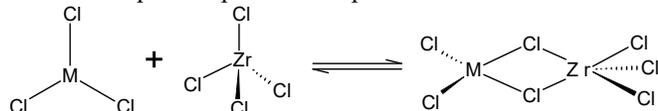
## INTRODUCTION

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 [1].

One element of the strategy to recycle zirconium from used cladding materials involves developing a computational modeling (DFT/WFT) protocol to understand the chemical reactions that occur between ZrCl<sub>4</sub> and metal chloride impurities under sublimation conditions and determine how they may impact purification strategies to obtain pure ZrCl<sub>4</sub>. Several of the metal chloride species present are known to form Lewis acid/base adducts in the gas phase and purification protocols require investigation into the properties of these potential ZrCl<sub>4</sub> contaminants.

## DESCRIPTION OF WORK

Through the use of quantum-based computational modeling, a Density Functional Theory (DFT) protocol was developed to calculate the thermodynamic properties and stability of ZrCl<sub>4</sub> relative to potential Lewis acid-base adducts (e.g. FeCl<sub>3</sub>) with ZrCl<sub>4</sub> derived from Zircaloy digestions as illustrated in Scheme 1. The gas phase equilibria leading to the formation of poly-nuclear adducts was studied and their impact on purification protocols assessed.

Scheme 1. Potential Lewis acid-base adduct with ZrCl<sub>4</sub>.

Current work involves moving from DFT based quantum modeling to wavefunction-based coupled cluster perturbation theory (WFT). WFT should reduce benchmarking errors significantly but are computationally costly.

## RESULTS

Computational models were developed using DFT/WFT based quantum models for reactions (Scheme 1) occurring in the gas phase. Several functionals and basis sets were investigated to determine convergence criteria and to benchmark against literature values for reactions similar to the ones under study here. At the DFT level, the Truhlar functional M06-2X gave acceptable benchmarking results and convergence was achieved at the triple Zeta level of the Def2 basis set yielding an average absolute error from literature values of  $\pm 2.88$  kcal mol<sup>-1</sup>. Coupled cluster wavefunction

theory was used to verify the accuracy of the benchmarking protocol. Preliminary results gave an average absolute error from literature values of  $\pm 1.52$  kcal mol<sup>-1</sup> with the CCSD(T)/aug-cc-pVTZ functional/basis set combination. Table 1 summarizes the DFT/WFT computationally derived free energy ( $\Delta G$ ) for possible adducts that may form with ZrCl<sub>4</sub> at sublimation conditions. The results indicate that the formation of the Lewis acid-base adducts is unfavorable for all species listed, except for the homodimerization of FeCl<sub>3</sub>.

Table I. DFT/WFT computational modeling results of possible heterometallic chloride species present at sublimation conditions of ZrCl<sub>4</sub> (All values: kcal mol<sup>-1</sup>, 600K, 1 bar). \*\* In progress


	DFT	WFT
	M06-2X Def2-TZVP	CCSD(T) aug-cc-pVTZ
	$\Delta G$	$\Delta G$
Zr <sub>2</sub> Cl <sub>8</sub>	12.69	8.94
ZrFeCl <sub>7</sub>	5.20	4.25
Fe <sub>2</sub> Cl <sub>6</sub>	<b>-12.37</b>	<b>-11.22</b>
ZrNbCl <sub>9</sub>	9.95	**
Nb <sub>2</sub> Cl <sub>10</sub>	16.00	9.79
ZrNbOCl <sub>7</sub>	16.95	**
Nb <sub>2</sub> O <sub>2</sub> Cl <sub>6</sub>	13.38	**
ZrSbCl <sub>9</sub>	13.52	9.17
Sb <sub>2</sub> Cl <sub>10</sub>	21.35	19.50

Furthermore, free energies at temperatures between 300 and 600K reflect the effect of the negative entropy term for these reactions causing them to switch from being favored at low temperature to disfavored at high temperature.

## CONCLUSIONS

A major conclusion that can be derived from our computational analyses to date is that the formation of mixed metal adducts involving ZrCl<sub>4</sub> and metal chloride impurities in the gas phase at equilibrium is highly temperature dependent. At low temperatures (298 K), several heterometallic adducts are favored, but at sublimation conditions (600 K), all adducts are disfavored due to the high entropic penalty associated with these reactions. Therefore, sublimation protocols need only consider simple gaseous species.

## REFERENCES

- Collins, E. D.; Spencer, B. B.; DelCul, G. D.; Brunson, R. R.; Johnson, J. A. *Roadmap for Zirconium Recovery/Recycle Process Development*; ORNL: 2012.