Raman Investigation of Nickel Chloride Complexation Under SCWR Coolant Conditions

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Summary

Speciation predictions, *ab initio* calculations, and factor analysis methods are being used to identify aqueous nickel chloride complexes and their equilibrium constants in high temperature water. This is the first step towards determining a transport model for nickel complexes in a supercritical water-cooled reactor (SCWR).

1. Introduction

The SCWR is one of six nuclear reactor concepts selected by the 11 countries in the Gen IV International Forum to fulfill the need for cleaner, more efficient, sustainable energy sources. The SCWR design uses a "direct cycle" that combines the primary coolant and steam generation systems into one circuit. The light water that is pumped directly through the fuel channels is the same water that drives the turbine, before being cooled in the condenser and reinjected into the reactor core. The challenge is to design one coolant chemistry that can be used in both the steam generator and the reactor core.

1.1. SCWR Chemistry Control

The selection of materials and coolant chemistry strategies for the Generation IV supercritical water-cooled reactor (SCWR) concept requires an ability to model the corrosion, transport, and precipitation of nickel oxides in-core. This is a strong function of the sharp drop in the density of water above the critical point ($T_c = 373$ °C, $P_c = 22$ MPa).

The solubility of mixed ferrites is controlled by the reaction:

$$\begin{aligned}&\mathrm{Ni}_{(1-x)}\mathrm{Fe}^{\mathrm{II}}_{x}\mathrm{Fe}^{\mathrm{III}}_{2}\mathrm{O}_4 + \left(6-(1-x)c-(2+x)b\right)\mathrm{H}^+ + \mathrm{H}_2 \rightleftharpoons \\ &\quad (1-x)\mathrm{Ni}(\mathrm{OH})_c^{\,2-c} + (2+x)\mathrm{Fe}^{\mathrm{II}}(\mathrm{OH})_b^{\,2-b} + \left(4-(1-x)c-(2+x)b\right)\mathrm{H_2O}\end{aligned} \tag{1}$$

These solubility equilibria are difficult to measure directly as they often include redox reactions, stepwise hydrolysis reactions and reactions with other competing ligands from corrosion and condenser-leak impurities. Raising the pH to alkaline values causes the solubilities of these oxides to increase with temperature due to the presence of $M(OH)_x^{Z-x}$ species. The reactions are complicated by the presence of Cl^-, HSO_4^-, and amines from ion exchange resins and condenser leaks.

The purpose of this project is to measure the equilibrium speciation of nickel chloride complexes under SCWR conditions in order to better understand and model the transport of metal oxides.

1.2. Nickel Chloride Complexation

Only three aqueous nickel chloride complexes have been reported in the literature [1, 2]:

$$Ni^{2+} + Cl^- \rightleftharpoons NiCl^+ \qquad \beta_{1,1} = \frac{[NiCl^+]}{[Ni^{2+}][Cl^-]} \qquad (2, 3)$$

$$Ni^{2+} + 2Cl^- \rightleftharpoons NiCl_2^0 \qquad \beta_{1,2} = \frac{[NiCl_2]}{[Ni^{2+}][Cl^-]^2} \qquad (4, 5)$$

$$Ni^{2+} + 3Cl^- \rightleftharpoons NiCl_3^- \qquad \beta_{1,3} = \frac{[NiCl_3]}{[Ni^{2+}][Cl^-]^3} \qquad (6, 7)$$

2. Experimental Design

The first step in our experimental design is to establish appropriate solution compositions. Appropriate solution compositions were selected by making chemical equilibrium speciation calculations in MultEQ based on room temperature formation constants by Kennedy and Lister (1966) and high temperature formation constants by Liu et al (2012). The goal is to prepare solutions with predominant concentration of each major species in order to identify peaks in the Raman spectra. Figures 1 and 2 show the predicted distribution of species at 140 and 200 °C for the solution set used in this work.

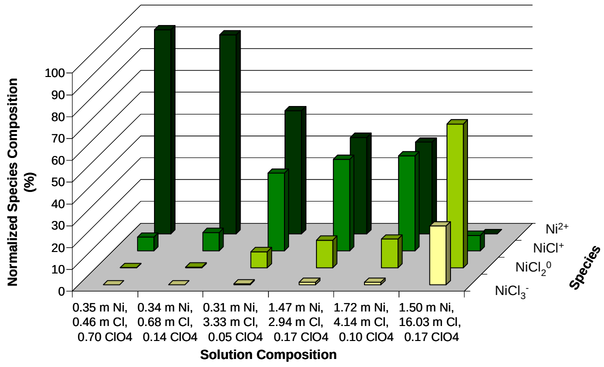

Figure 1: Predicted distribution of species at 25 °C from MULTEQ

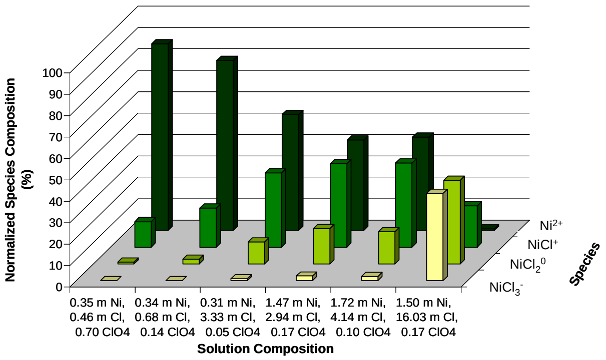

Figure 2: Predicted distribution of species at 200 °C from MULTEQ

2.1. Raman Instrumentation

Isotropic Raman spectra are being measured for solutions of varying concentrations at steam saturation pressures up to temperatures of 200°C using sealed quartz tubes contained in a thermostatted jacket. The measurements are conducted in a large macrochamber which can accommodate high temperature – high pressure cells. The macrochamber is configured to make polarization measurements [3] as depicted in Figure 3. A confocal microscope allows for 180° Raman measurements in a diamond anvil cell (DAC).

Accurate baseline subtraction is needed to resolve contributions by individual species. Polarization techniques yield a nearly perfect baseline based on the physics of light scattering rather than the judgment of the experimentalist.

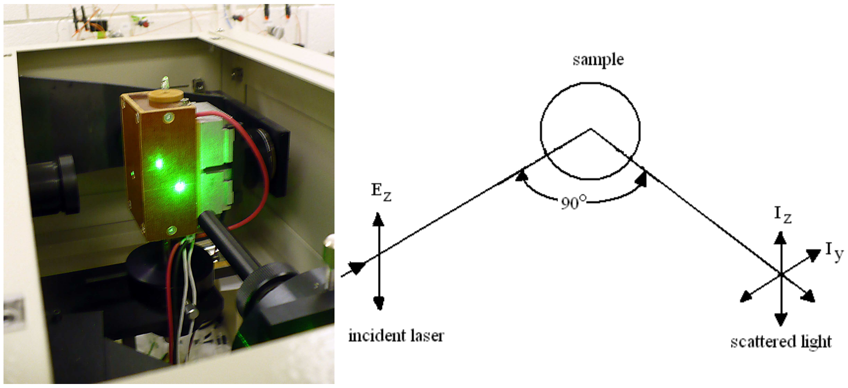

Figure 3: Polarized measurements: (Left) Raman macrochamber set up for polarization measurements (Right) Representation of a 90° geometry Raman experiment for collection of parallel and perpendicular polarizations

2.2. Results and Data Treatment

To date, reduced isotropic Raman spectra were measured and calculated for solutions with concentrations varying from 0.3 to 1.5 mol/kg of Ni^{2+} and 0 – 13 mol/kg of Cl^{-} at steam saturation pressures from 5 to 200 °C in sealed quartz tubes.

We first obtain the isotropic spectrum (Figure 4) by using the following equation:

$$I(\tilde{\nu})_{iso} = I(\tilde{\nu})_{\parallel} - \tfrac{4}{3} I(\tilde{\nu})_{\perp} \tag{8}$$

The next step is to calculate the reduced spectrum as in Figure 5. This equation is used to reduce the intensity contribution at low frequency from thermally excited states [4]:

$$R(\tilde{\nu})_{iso} = I(\tilde{\nu})(\tilde{\nu}_0 - \tilde{\nu})^{-4}\tilde{\nu}B \tag{9}$$

$$B = 1 - \exp(-\frac{h \cdot \tilde{\nu} \cdot c}{kT}) \tag{10}$$

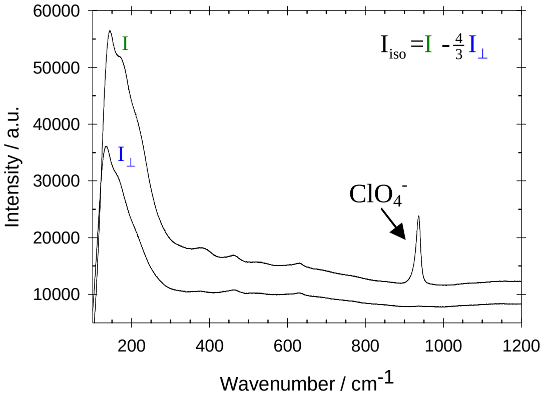

Figure 4: Spectra of the parallel ($I_{\|}$) and perpendicular ($I_{\perp}$) polarizations

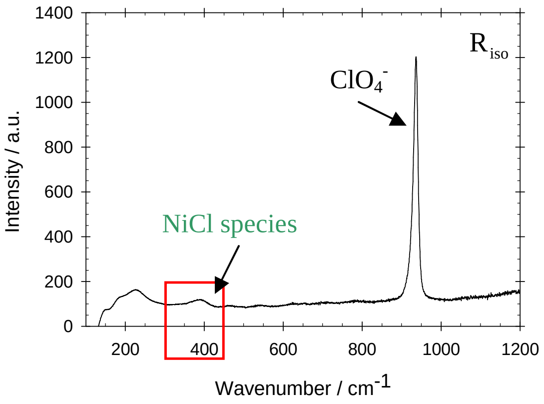

Figure 5: Reduced isotropic spectrum (R_{iso}) of a solution with 0.3 m Ni^{2+}, 0.7 m Cl^- and 0.1 m ClO_4^-

In order to obtain the molality of each species in solution, the deconvoluted nickel peaks must first be normalized to an internal standard [5] as shown in the following equation:

$$m_i = \frac{A_i}{A_{IS}} \cdot \frac{S_{IS}}{S_i} \cdot m_{IS} \qquad (11)$$

where m is molality (kg mol^{-1}), A is the integrated area and S is the Raman scattering coefficient for each species.

Perchloric acid was chosen for the internal standard since it does not interfere with the peaks of interest. We have now determined that ClO_4^- decomposes in solutions with $NiCl_2$ and HCl in Pyrex cells at temperatures as low as 140 °C. This is not the case in quartz cells.

Equilibrium speciation, shown in Figure 6, was determined from least squares and principle component analysis methods.

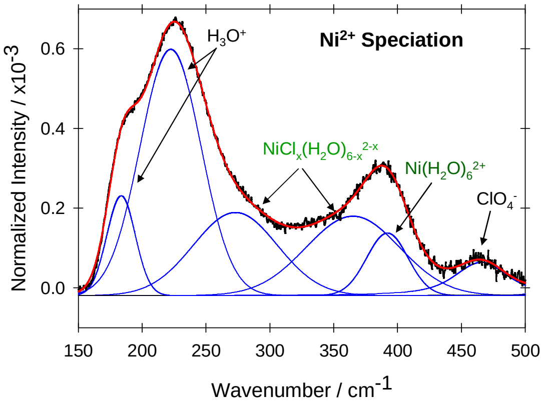

Figure 6: Deconvolution and band assignment of nickel chloride at 25 °C

3. Quantum Mechanical Model

Hartree-Fock calculations with step-wise additions of chloride and water were used to determine the structures and spectra of species $NiCl_n(H_2O)_m^{2-n}$ using the HF/6-31+G* basis set. The results yield the polarized spectrum of each species and their relative intensities which aid in the assignment of peaks in the experimental spectra (Figure 7).

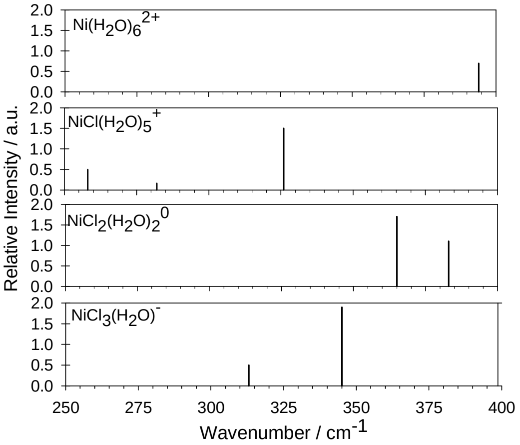

Figure 7: Predicted spectra of Ni species from quantum mechanical models

4. Conclusions and Future Work

Vibrational bands were assigned to the species Ni^{2+}, $NiCl^+$, and $NiCl_2^0$ by comparing the experimental reduced isotropic spectra to the temperature-dependent speciation predicted from the thermodynamic model, and to the relative peak positions predicted by the *ab initio* calculations. Experimental values for the equilibrium speciation were then determined from least squares and principle component analysis methods. These yield the first reported values of scattering coefficients (S) for the symmetric vibrations of the aqueous species Ni^{2+}, $NiCl^+$, and $NiCl_2^0$.

5. References

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