Young Scientist IAPWS Fellowship Project

Equilibrium Constants and Speciation of Aqueous Transition Metal Chlorocomplexes over a Wide Range of Temperatures and Pressures

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1. BACKGROUND AND SCOPE

The Supercritiscal Water Cooled Reactor: The "Generation IV" Super-Critical-WaterCooled Reactor ("SCWR") is a concept for a novel, extremely energy-efficient advanced reactor that has been chosen by eleven countries as one of six "best" options to replace the current generation of reactors, after 2025. Design work has not yet begun. This reactor concept would produce supercritical water at temperatures as high as 625°C to generate electricity, hydrogen and district heating. The six competing concepts are listed in:(i) US DOE web-site: http://nuclear.energy.gov/ genIV/documents/gen_iv_roadmap.pdf; (i) Natural Resources Canada Press Release, Feb. 28, 2005. The Canadian conceptual design for a Super-Critical-Water-Cooled reactor is based on a CANDUtype pressure tube reactor one light water loop that carries heat directly from the reactor core to the turbine at super-critical temperatures and pressures (450-625°C, 25 MPa). The other five Gen IV design concepts would produce much higher steam temperatures (800-1000°C, 25 MPa).

The integration of the primary and secondary coolant circuits and higher operating temperatures in the SCWR create a need for thermochemical and kinetic data to model transition metal complexation with chloride, sulfate and organic ligands up to and above the critical point of water.

Hydrogen Co-generation by Thermal Processes: A requirement of all the SCWR concept designs is an ability to co-generate hydrogen from high temperature steam. The proposed project will contribute to research aimed at applying nuclear heat from Canada's Generation IV reactor Super-Critical Water Reactor to the thermochemical production of hydrogen. The nuclear reactor would be separated from the hydrogen production plant, but coupled through an intermediate heat exchanger that supplies heat to the thermochemical cycle. Over 200 processes for thermal hydrogen production have been evaluated by the US Department of Energy and, of these, three "best" processes have been selected for use at at temperatures below 550 °C (Petri *et al.*, 2006). As yet, only one of these, the copper-chloride cycle, has been shown to have promise as a practical process. This part of the "Gen IV" research program aims to optimize heat transfer between the SCWR and the various process loops of the Cu-Cl process. It will identify cycle modifications to maximize heat recovery, minimize heat losses and match the demands of the different thermochemical steps. The Canadian research is led by the University of Ontario Institute of Technology in a collaboration with Atomic Energy of Canada Ltd., Argonne National Laboratory and other Ontario universities.

The copper-chloride cycle, as currently developed by Argonne (Petri *et al.*, 2006), consists of five steps:.

Step 1: $2\ Cu(s) + 2\ HCl(g) \rightarrow CuCl(l) + H_2(g)$, [430 - 470 °C]

Step 2: (a) $4\ CuCl(s) + 4\ Cl^-(aq) \rightarrow 4\ CuCl_2^-(aq)$; [Dissolution + complexation, t < 100 °C]

(b) $4\ CuCl_2^-(aq) \leftrightarrow 2\ Cu(s) + 2\ CuCl_2(aq) + 4Cl^-(aq)$, [Electrolysis; t < 100 °C]

Step 3: $4\ CuCl_2(aq) \rightarrow 2\ CuCl_2(s)$; [Evaporation, t > 100 °C]

Step 4: $2\ CuCl_2(s) + H_2O(g) \rightarrow Cu_2OCl_2(s) + 2\ HCl(g)$, [300-375 °C]

Step 5: $Cu_2OCl_2(s) \rightarrow 2\ CuCl(l) + 1/2\ O_2(g)$ [450 - 530 °C]

The existing Argonne process involves temperatures and pressures of less than 70°C and 2 MPa for the aqueous liquid phase, with HCl concentrations below ~ 6 m, for which the literature is quite complete. The Canadian research program may investigate the use of HCl concentrations up to 13 mol/kg, temperatures up to 130 °C and pressures of 30 MPa, for which copper(I) and copper(II) chloride solubility and complexation constant data are required. For example, a key need for step 3 is for better solubility data for the $CuCl/CuCl_2/HCl/H_2O$ system, up to the maximum saturation temperature, and an ability to model the formation of $Cu_2OCl_2(s)$ in step 4 at temperatures above 300°C, both at steam pressures as high as 0.5 MPa

2. THERMOCHEMICAL DATA FOR COPPER COMPLEXATION.

Existing Data: The steps of the Cu-Cl cycle have been individually demonstrated, but more information is needed on their kinetics and yields as a function of temperature, pressure and reactor feed compositions. The thermochemical properties of the aqueous copper (I) chloride system have been studied at elevated temperatures by several authors, because of its importance to the geochemistry of ore-body formation (Liu *et al.*, 2002; Var'yash, 1992; Xiao *et al.*, 1998). The recent UV-visible study by Brigger *et al.* (2001) provides the only reliable data for the stepwise formation of copper (II) species above room temperature and these extend only to 90 °C. The themodynamic properties of $Cu_2OCl_2(s)$ are also not well known, although recent measurements at Brigham Young University have provided accurate data up to 25 °C (M. Lewis, Pers. Commun.).

"Equations of State" for Standard Partial Molar Properties: Two major methods have been developed to model and extrapolate standard partial molar properties of ions to hydrothermal conditions. These are reviewed by Majer *et al.* (2004) in the recent IAPWS "Atlas" publication. The first approach, which is now widely used, was developed by Helgeson and his co-workers who developed an equation of state based on the Born equation for ionic hydration. (Shock *et al.*, 1992). Briefly, the Helgeson-Kirkham-Flowers (HKF) model consists of expressions for standard partial heat capacity and volume functions, and assumes that the standard molar Gibbs energy and enthalpy of formation of each species at 298.15 K and 0.1 MPa are known properties. Sverjensky *et al.* (1997) have applied this to develop predictive equations for the properties of chloro-complexes, based on the limited high temperature data available. The second approach, which was developed by Sedlbauer, O'Connell and Wood (2000) is based on solution fluctuation theory. The "SOCW"model has had much success in modelling and predicting high temperature data for ions and neutral species, but has not as of yet been applied to transition metal complexes.

3. PROPOSED RESEARCH AND JUSTIFICATION FOR IAPWS SUPPORT

Project Objective: The purpose of the collaborative project with IAPWS is to measure and model stepwise formation constants for the copper(II) chloride complexes at temperatures from 75 to 250°C. The low end of this range will provide thermochemical data needed for process design and optimization of the reactor and heat exchanger. The higher temperature data are of fundamental value for steam generator design, both for the SCWR and more conventional power stations.

Work Plan: This proposal seeks funding from IAPWS to support a visiting young scientist who will supplement the existing scarce experimental results available for these aqueous complexes at high temperature by measuring the stepwise formation constants Cu^{2+}(aq) with Cl^{-}(aq) up to 250°C using UV-VIS spectroscopy. The measurements will be made in solutions of LiCl(aq), to be consistent with the high quality measurements by Liu *et al.* (2002) on copper (I) complexation. A small excess of HCl(aq) will be used to prevent the precipitation of hydroxides. The experimenta work will be carried out in Guelph under the co-supervision of Dr. Tremaine and Dr. Liliana Trevani. The project will make use of the high-temperature UV-visible flow system developed by Trevani *et al.* (2001) which uses titanium or platinum flow cells to measure spectra under oxidizing or reducing conditions, respectively, up to 350 °C and 30 MPa. The upper temperature limit in this work will likely be determined by the precipitation of CuCl2 (s). Because spectra of the complexes overlap one another the interpretation of the UV-visible results require sophisticated statistical techniques (Trevani *et al.*, 2001; Brugger *et al.*, 2001). This part of the work will be done initially at Guelph and, carried on in Liberec if necessary. Subsequently the two teams from the University of Guelph and from the Technical University of Liberec will cooperate on development of models to describe the equilibrium constants and partial molar properties the aqueous complexes of copper(I) and copper(II) using both the Sedlbauer-O'Connell-Wood (SOCW) and the Helgeson-Kirkham-Flowers "equations of state".

Considering the wide range of concentrations, a suitable treatment for the activity coefficients must be included in the model. It might be interesting to test the Mean Spherical Approximation ("MSA") model for this purpose, as the Sedlbauer group has a good deal of experience with its extrapolation abilities, and has found it to require many fewer parameters than Pitzer's virial expansion for ions at high temperatures (Sedlebauer and Wood, 2004). The MSA treatment is computationally more difficult and requires a knowledge of solution densities. The Tremaine group has a high temperature densimeter suitable for such measurements if needed.

Justification for IAPWS Funding: The IAPWS funding will make it possible for a young scientist to spend at the University of Guelph for ten months in a single stay starting in May or September of 2008. Two PhD students have been identified. Ms. Jitka Felcmanova is a PhD student in Dr. Sedlbauer's group and is in the early stages of her program. Ms. Jana Ehlerova would use the project as the final stage in her PhD work. She has experience with the equipment from her previous IAPWS fellowship, and is an expert in statistical methods. Timing of this collaboration is important. In the event that Jitka's participation is not possible or delayed, Jana Ehlerova would come in her place. The funding will allow one of these students to collaborate with Prof. Tremaine and Dr. Trevani on the experimental determinations of the stepwise complexation constants of copper(II) with chloride using UV-visible spectroscopy, and will contribute to the Gen IV

International Forum by providing basic research, student training and collaborative links between the Czech Republic and Canada.

4. BUDGET (in $US)

Subsistence for 10 months: IAPWS Young Scientist Grant..............$14000
Travel (round trip): to be paid by TU Liberec....................................$ 1500
Chemicals, supplies, equipment: to be paid by U. Guelph ....$ 4500
Research Assosiate support, to be paid by U. Guelph ....$ 10000

Total Cost...$30,000
Request from IAPWS: $14,000

5. BIBLIOGRAPHY

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6. Curriculum Vitae

Jitka Felcmanova

Born

1982

Education

2001-2006 Technical University of Liberec, Faculty of Textile Industry, 2006 MSc.

2006- Technical University of Liberec, Faculty of Mechatronics and Interdisciplinary Engineering Studies, programme Science Engineering, Ph.D. study

Employment

2006- TUL, Department of New Technologies and Applied Informatics

Research interests

-thermodynamic properties of aqueous solutions at high temperature conditions
-experimental calorimetry