

IAPWS Certified Research Need - ICRN

Thermophysical Properties Associated with Ultra-supercritical Coal-fired Steam Generators

The IAPWS Working Groups – Physical Chemistry of Aqueous Systems and Power Cycle Chemistry have examined the published work in the area of thermophysical properties associated with ultra-supercritical coal-fired steam generators that are of direct relevance to the future reliability of electric power plants.

IAPWS recognizes that there is a requirement for work to be pursued in this field and has prepared this document to assist potential investigators in obtaining sponsorship. Specifically computer simulations together with complementary experimental studies are needed to assess ionic dissociation of steam and thermodynamic information on electrolytes that may be present as control chemicals up to 800 °C and 50 MPa.

Although encouraging this work, IAPWS is not able under its statutes to provide financial support. The IAPWS contact can provide any further development information and will act as a liaison between research groups.

**Issued by the
International Association for the Properties of Water and Steam**

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Target: 800 °C (1472 °F) and 50 MPa (7250 psi)

Background

The relevant chemical issues in future ultra-supercritical (USC) fossil-fired units will depend primarily on the properties of water and water plus additives/impurities under these extreme conditions, as well as the stability of the metal oxide layer formed on the walls of the containment alloy and its interfacial interactions with super-heated steam (*i.e.*, its mechanical and chemical stability, and the effect of solutes on the interface). The chemistry will most likely be very different from that experienced in existing supercritical (SC) units, and there are virtually no supporting experimental data on the properties of pure water or solutions in steam at these conditions. Even the stability of common alkalizing agents and the effect of impurities are uncertain. Due to the obvious breadth of these topics, we will confine the scope of this ICRN to those issues related directly to the aqueous medium without consideration of the solid – liquid interface.

The proposed ultra-supercritical (USC) power cycles will operate to considerably higher temperatures and pressures than the existing conventional supercritical (SC) once-through units, maybe as high as 800 °C with pressures approaching 50 MPa. This relatively high-pressure limit leads to unusually high steam densities, a few examples of which are shown in Table 1 as calculated by means of the IAPWS 1995 formulation.

Table 1: Steam properties at projected USC and existing SC conditions, and at a possible economizer inlet condition.

Temperature °C	Pressure MPa	Specific Volume m ³ /kg	Specific Density kg/m ³	Molar Density mol/dm ³
760	38	0.01153	86.7	4.8
760	40	0.01091	91.9	5.1
582	29	0.01144	87.4	4.9
600	24.5	0.01446	69.2	3.8
350	38	0.00149	671	37.3

The higher temperature and pressure regime corresponding to USC conditions imposes severe limitations on the currently known materials that can be considered for constructing USC units. A means of calculating these properties of water directly or by extrapolation must be considered, and ultimately the more difficult task of measuring these fundamental properties must also be contemplated. The behavior of chemicals dissolved in this medium is also difficult to predict as it is outside the experience of most chemists and chemical engineers, mainly because the solvent density is also significantly higher than experienced in SC units or in supercritical water oxidation (SCWO) applications.

A) Physical Properties and Thermodynamic Properties of the Solutions

For some thermophysical properties of pure water, existing data-based formulations are adequate for the conditions of interest here. The thermodynamic properties are correlated to 1000 °C by the IAPWS-95 formulation. The viscosity is correlated to 900 °C at the pressures of interest here by the formulation adopted in 2008. The thermal conductivity can be calculated to 800 °C according to the revised release adopted by IAPWS in 2008. The vapor-liquid surface tension can be calculated from the triple point to the critical point according to the 1994 release. See www.iapws.org for more information on these formulations.

However, for other important properties there are gaps in the knowledge:

- The dielectric constant is known at present to 500 °C and 73 to 800 kg/m³ [see the IAPWS release of 1997 and Fernández *et al.* (1997)], and there are estimates of this quantity up to 2227 °C (200 to 1000 kg/m³) using simulation techniques (Mountain and Wallqvist, 1996). Neumann (1995) also reported the results of computer simulations of water and its dielectric constant in the same range 227 to 2227 °C (200 to 1000 kg/m³).
- The ion product of water can be calculated up to 800 °C from the 2007 IAPWS release (see also Bandura and Lvov, 2006), but at high temperatures and low densities the formulation is based on very limited data and on interpolation to the known ideal-gas limit.

Knowledge of the dielectric constant of steam over a range of conditions which include the conditions of USC plant operation is important, especially for ionic species, because the behavior of dissolved impurities and treatment chemicals will depend strongly on the value of the dielectric constant. From Table 1 it can be seen that reliable measurements and/or calculations are needed for the dielectric constant of water to 760 °C and 40 MPa. Computer simulations may provide the most promising path for estimating the dielectric constant at these extreme conditions.

A point to be considered is the range/reliability of existing formulations, especially when ions are involved and the problem of extrapolation of available formulations to higher temperature and higher density of water may be very important. The hydration of ions at the conditions of operation is in need of further study.

Consideration of the properties of solutions would be linked to such phenomena as: pH, ionic association of solutes, solubilities of impurities, e.g., Cl⁻, SO₄²⁻, Na⁺, SiO₂, Ca²⁺, CO₂, metal-containing species from the feedwater train and boiler, organic acids (although these would likely be decomposed to give principally CH₄/CO₂), corrosion products and possible additives (NH₃, MOH, O₂). Should ammonia be an unacceptable pH buffer, one could consider using alkali metal hydroxides, and hence their solubilities and ion association properties would be important. Here again simulation studies would be the appropriate starting point to estimate the extent of ion association of MOH solutes.

B) Transport properties of the solutions

The diffusion of electrolytes and neutral species including O₂ is an important factor affecting corrosion. Very little information is presently available regarding diffusion coefficients at USC conditions. NMR (Nakahara and Yoshimoto, 1995) could be used to determine diffusion coefficients in bench-scale experiments, and diffusion of neutral species and ion pairs can also be studied by computer simulation (Harvey and Mountain, 2003). The diffusion of O₂ and other neutral species to the walls of the tubes should be especially considered given the flow of steam that is possibly moving at supersonic velocities. It may be possible to carry out laboratory scale measurements of the transport properties of additives and prototype solutes in the heat-transporting fluid by means of cells fitted with microelectrodes.

One important tool with prospects for a breakthrough in experimental capabilities is electrical conductivity. Recent high-precision work has been reported at relatively low densities using a flow-cell

design at ORNL (Ho and Palmer, 1997) which was pioneered at the University of Delaware (e.g., Gruskiewicz and Wood, 1997). Currently, these techniques are limited to about 450 °C, but they can operate to remarkably low concentrations, below 10^{-5} molarity of the solute (Wood claims that his measurements are effective to solute concentrations of 3×10^{-7} molar and in theory to densities well below the current limit of 300 kg/m³). Conductance data at extremely low concentrations allow for direct determination of ionic mobilities (limiting values of conductance) without the need for a tenuous extrapolation. Elimination of one variable in the conductance model, coupled with the use of specialized cells for low-density steam measurements, would lead to an unprecedented improvement in accuracy. Analysis of the uncertainty inherent in the existing low-density conductance data indicates that the high-temperature, high-dilution flow technique can provide a radical improvement in the values of solute dissociation constants.

Moreover, as these cells offer vastly improved sensitivity at lower pressures and concentrations over the original static design of Franck and Marshall (Franck *et al.*, 1962) that was capable of reaching the extreme conditions of 800 °C and 400 MPa, it is anticipated that the flow-through cell configuration can be readily adopted to reach 760 °C and 40 MPa (Chialvo *et al.*, 2009). In addition to providing accurate data for modeling ultra-supercritical cycle chemistry, experience with the design of the high-temperature, low-density conductance technique could lead to future development of new power plant chemistry control instruments for monitoring directly the purity of superheated steam.

C) Priority Issues for Investigation

C-1) *Computer Simulations.*

Many simulation problems can be addressed with available knowledge and computing facilities. Molecular simulations, *via* isothermal-isochoric and isothermal-isobaric molecular dynamics, can provide a variety of thermophysical properties for realistic descriptions of aqueous electrolyte systems at high dilution and within a wide range of state conditions. In addition to the configurational internal energy (enthalpy) and pressure (density) for the chosen temperature-density (pressure) conditions, simulations can provide the corresponding dielectric constant, diffusivity/mobility (electric conductance), solvent microstructure around species in solution, ion-pair association constants, and Henry's constant. To tackle these simulations a collection of force-fields for non-electrolyte solutes, ions, and models for water are currently available in the literature; care must be exercised to choose models that are physically realistic for USC conditions rather than being optimized for liquid water.

Simulation studies can also be used to investigate the equilibrium properties of electrolytes under the USC conditions to try and establish the fraction of free ions for (1:1) electrolytes and determine the hydration number of ions. This may also be relevant to adsorption of metal ions onto the oxide layer covering the alloy surfaces. These simulations would also include the determination of the dielectric constant of water under conditions that are beyond the present range of the IAPWS formulations. Simulations should also be used to analyze hydration of possible reaction products in the fluid.

There is also a need to determine hydration and diffusion of some neutral species that could be relevant to the chemistry operating in ultra supercritical power plants: O₂, H₂, N₂, NH₃, *etc.*

Finally, molecular simulation can also provide valuable insights into the solid/fluid interfacial - electric double layer - phenomena toward realistic macroscopic modeling.

C-2) *Complementary Experimental Investigations.*

Conductivity measurements under the proposed USC conditions would provide direct and unique information on the degree of ionic dissociation of steam as well as providing the same thermodynamic information on electrolytes that may be present as control chemicals or impurities. As mentioned above, this endeavor requires the further development of the technology of flow-through conductivity cells (Gruskiewicz and Wood, 1997). However, these cells offer vastly improved sensitivity at lower

pressures and concentrations than the original static design of Franck and Marshall (Franck *et al.*, 1962) that were capable of reaching the extreme conditions of 800 °C and 400 MPa, which would suggest that the flow-through cell configuration can be readily adopted to reach 760 °C and 40 MPa (Chialvo *et al.*, 2009).

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