EXPIRED

ICRN 27

IAPWS Certified Research Need – ICRN

Thermodynamic Properties of Humid Gases and CO_2-Rich Mixtures

The IAPWS Working Groups "Thermophysical Properties of Water and Steam" and “Industrial Requirements and Solutions” have examined the published work and common industrial practice in the area of the thermodynamic and transport properties of humid gases and particularly CO_2-rich gas mixtures as they are common for power-plant concepts with carbon capture and storage (CCS). Severe deficiencies exist, rendering impossible an accurate and consistent description of all relevant states, as it is needed for accurate system design of power plants.

The available information is not sufficiently accurate and comprehensive to permit:

(a) the evaluation of the performance of power plants with CCS now under construction or soon to be constructed

(b) the optimization of the economic performance of these power plant systems including downstream systems for CO_2 drying, purification, compression, transport and storage, and the proper sizing of components

(c) the development and optimization of second-generation power-generation technologies with CCS, including precise comparisons between different technical solutions.

Although encouraging work that aims to overcome these shortcomings, IAPWS is not able under its statutes to provide financial support. The IAPWS contacts can provide any further development information and will liaise between research groups.

Issued by the

International Association for the Properties of Water and Steam

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Background

Power producers and companies building turbomachinery and power plants have realized that there is a need for a substantial reduction of atmospheric CO_2 emissions from power generation. Efforts to further increase the efficiency of power production are supplemented by massive research in the field of CO_2 capture and storage, aiming at future power plants with virtually zero atmospheric CO_2 emissions; for an overview regarding these technologies see, e.g., [1]. For the same reason, a drastically increased use of renewable energy sources (RES) is formulated as long-term goal. Since RES tend to be intermittent, an increased RES penetration results in serious problems regarding grid stability. The development of storage technologies becomes mandatory, if an increased RES penetration is aimed at. Besides pumped water storage, which is geographically very constrained, the most promising storage technologies are diabatic and adiabatic compressed air energy storage.

Though the technical challenges mentioned above (further increasing efficiency, separating and storing CO_2, storing energy) are very different, they have one common feature: Design and simulation of the corresponding processes involve thermodynamic property calculations at states where using the ideal gas thermodynamic property models common in energy technologies becomes questionable and where phase equilibria with water-rich phases have to be considered. This is particularly true for gas-turbine related technologies and for compression, transportation and injection of carbon dioxide separated in power plants. Examples include:

- *Humidified gas turbines:* Intended as a low-investment technology between simple-cycle and combined-cycle gas turbines, the development of humidified gas turbines is believed to result in increased efficiencies in the upper peak-load to lower medium-load range. However, these processes involve states where air at high pressure (2 to 3 MPa) is highly saturated with water vapor.

- *Compressed air energy storage:* Design and simulation of diabatic compressed air energy storage plants is based on thermodynamic property calculations for humid air at pressures far higher than in conventional gas turbines and at temperatures substantially lower. Adiabatic compressed air energy storage additionally involves water–air phase equilibria at elevated pressure.

- *Oxyfuel processes aiming at integrated CO_2 capture*: Design and simulation of oxyfuel processes involves thermodynamic property calculations for mixtures consisting mostly of carbon dioxide and water, which behave much less ideally than air or common combustion gases. Depending on the chosen process, carbon dioxide has to be separated from water by condensation at different pressure levels, whereby the influence of trace gases should be considered.

- *Compression, transportation and injection of separated carbon dioxide:* Carbon dioxide separated in power stations has to be compressed, transported and injected for storage. Compression for pipeline transportation requires calculations for carbon dioxide–water mixtures potentially containing a multitude of trace gases. Phase equilibria, including liquid-liquid equilibria with one water-rich phase, need to be calculated to simulate drying processes or processes in two-phase flows. Ship transportation of carbon dioxide and the simulation of expansion processes in valves and leaks in pipelines require data at states where carbon dioxide and water form liquid-solid equilibria including dry ice and hydrates as solid phases.

The requirements on thermophysical property models resulting from humidified gas turbines and from compressed air energy storage were precisely described in ICRN-14 [2], which focused on the description of humid air and humid combustion gases. Extensive work has been directed towards these topics throughout the last decade; see the closing statement for ICRN-14 [3]. Problems related to CO_2-rich mixtures were already mentioned in ICRN-14. However, the complexity of these topics became more apparent in the meantime (see, e.g., [4]) and was not adequately addressed in ICRN-14. This ICRN addresses phase equilibria with humid gases at high pressures and temperatures, which were already covered by ICRN-14 but which are not yet satisfactorily described, and in particular deficiencies regarding the description of CO_2-rich mixtures.

Requirements resulting from oxyfuel process

In oxyfuel processes, carbon dioxide is separated from a CO_2–H_2O mixture by condensation of water. The pure oxygen required for combustion resulting in a CO_2–H_2O mixture is commonly supplied by an external air separation unit (ASU). In design and analysis of oxyfuel cycles, accurate thermodynamic properties are required for CO_2–H_2O mixtures with varying composition. Combustion of natural gas results in a mixture with ~35% CO_2 and ~65% H_2O,

Table1: Composition, temperature and pressure ranges to be covered by a thermodynamic property model for working fluids of oxyfuel cycles.

Quantity	Min.	–	Max.
Range of (molar) compositions / %			
Carbon dioxide (CO_2)	0	–	100
Water (H_2O)	0	–	100
Nitrogen (N_2)	0	–	25 (100)[a]
Oxygen (O_2)	0	–	10 (100)[a]
Argon (Ar)	0	–	10
Carbon monoxide (CO)	0	–	3
Nitrogen oxides (NO_x)	0	–	0.1
Temperatures and pressures			
Temperature / K	274 (216)[b]	–	2000
Pressure / MPa	0	–	8 (30)[c]
H_2O partial pressure / MPa	0	–	1.5[d]

[a] If the allowable range of compositions is extended for nitrogen and oxygen, the property model can be used for humidified and oxygen-depleted or enriched air as well.

[b] If demands resulting from ship transportation of liquid CO_2 or from an expansion of pipeline CO_2 should be covered, temperatures down to the triple-point temperature of CO_2 and complex phase equilibria have to be considered.

[c] Up to 450 K, the pressure range should be extended to 30 MPa to allow for analysis of pipeline transport and sequestration processes.

[d] For an analysis of humidified processes, saturated states have to be calculated up to a water partial pressure of ~1.5 MPa, corresponding to saturation at ~200 °C.

combustion of coal in far higher CO_2 concentrations. However, since CO_2 is recycled in these processes to control the combustion temperature, no point in the process exactly matches the composition resulting from the chemical reaction of fuel and oxygen. Table 1 summarizes the range of compositions relevant for typical oxyfuel cycles; in this table, strongly process-dependent trace components are not considered.

Requirements resulting from compression, transportation and injection of separated carbon dioxide:

Downstream of the water condenser, the CO_2 is commonly considered almost pure. Depending on the temperature level in the condenser, less than 4% of water remains in the CO_2. During the intercooled compression process, the CO_2 extracted for sequestration is dried even further, resulting in a water content much below 1%. However, since the solubility of water in CO_2 is very small at these liquid or liquid-like states, a second (water-rich) phase may still occur at this point of the process. This second phase needs to be described accurately to assess for example the CO_2 slip of the separation process or the possibility of aqueous-phase corrosion.

Obviously, analysis and design of such a process requires accurate and consistent thermo-physical property data for CO_2–water mixtures including liquid-vapor and liquid-liquid equilibria. The compression process requires calculations at states in the critical region of CO_2-rich mixtures. Depending on the process chosen for separation, these mixtures contain different concentrations of water, nitrogen, and other gases at low concentrations. Though carbon dioxide is the dominant component, the other substances have a strong impact, e.g., on the power required for compression.

If separated carbon dioxide is to be used for enhanced oil recovery in remote oil fields, ship transportation becomes an alternative frequently discussed. Like LNG and LPG, carbon dioxide can be transported in tankers as saturated liquid. Traces of water and certain amounts of non-

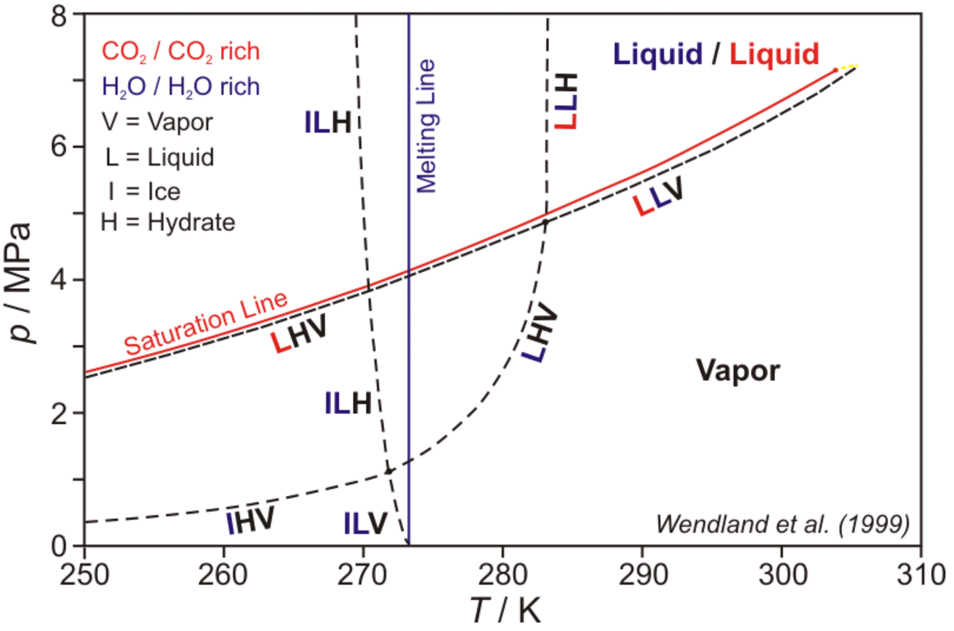

Figure 1: Phase diagram of the system carbon dioxide–water [5].

condensable gases (nitrogen, oxygen, argon, methane) have to be considered. Figure 1 shows the phase diagram of CO_2–water mixtures at low temperatures and elevated pressures. It becomes obvious that ship transportation of carbon dioxide separated from power plants results in complex phase equilibria, including liquid-liquid, vapor-liquid-liquid, hydrate-liquid-liquid and hydrate-liquid-vapor equilibria. Addition of small amounts of non-condensable or acid-forming (SO_2, SO_3 or NO_x) gases can have a strong impact on phase equilibria. Particularly gases like methane, which form hydrates that compete with CO_2 hydrates, make the description of liquid-solid or vapor-solid equilibria difficult.

Similar problems as for ship transport are encountered in safety and operability studies for pipelines and for storage in empty reservoirs. Expansion of CO_2-rich mixtures through leaks or valves results in low-temperature states, at which complex phase equilibria including hydrates and dry ice have to be considered.

Current Activities and Views of IAPWS

Over the last few years, the awareness of the problems described above has increased internationally. Different experimental projects address an improvement of the data situation for relevant properties in single-phase regions or for relevant phase equilibria. Theoretical projects aim at the development of complete data bases for the relevant mixtures. The data situation is scarce for many of the involved binary systems and particularly for multicomponent mixtures. Where data are available, they are frequently old and of doubtful accuracy. An improvement of the experimental data basis is essential for the development of accurate and reliable models. Particularly for systems including trace components like SO_2, SO_3, NO_x or H_2S, the generation of an experimental data base is extremely challenging. In this case, computer simulation based on molecular interaction models or on first principles may turn out to be a powerful tool to supplement the experimental data base. IAPWS strongly encourages work aiming at an improvement of the available data base. Depending on the property, the temperature and pressure range, and the mixture addressed, this work can either be experimental or theoretical.

A multitude of projects and publications deals with equations of state or simple engineering approaches describing CCS-relevant mixtures and phase equilibria. However, most of these approaches address only certain aspects of the complex problem discussed above. Though simple engineering models and other kinds of limited solutions are required at this point in time to assess technological options, these approaches are not suitable to define international standards in the long run. Inconsistencies in the description of different phases or properties will always result in problems in complex simulations addressing the complete process chain of carbon capture and storage. Thus, IAPWS strongly encourages activities aiming at the development of models enabling an accurate and consistent description of all thermodynamic properties for as many phases and relevant mixtures as possible.

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