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Steam Solubilities for Combustion Turbine Steam Cooling[1]

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Steam cooling of combustion turbine parts provides significant advantages over air cooling. Steam potentially carries dissolved salts that can deposit on the cooled parts and cause corrosion. By maintaining the salt concentration below its solubility limit in the steam, deposition of salts may be avoided. A literature survey reveals that only sodium chloride and silica have adequate data for reasonable extrapolation to the steam cooling conditions. Estimates of steam solubility of sodium sulfate and sodium phosphate used liquid–vapor distribution coefficients for a solubility at saturation and sodium chloride as a model compound to extrapolate the solubility to other conditions. Copper oxide data were also insufficient to predict steam solubilities with confidence. The large potential errors in the sodium phosphate and sodium sulfate solubility estimates may add considerable cost to the water treatment system. Accurate experimental values for sodium sulfate and sodium phosphate solubilities in steam are needed.

KEY WORDS: combustion turbine; copper oxide; silica; sodium chloride; sodium sulfate; sodium phosphate; solubility; steam.

1. INTRODUCTION

There is a trend toward enhancing efficiency of combined cycle power plants by optimally using steam from the Rankine (steam turbine) cycle in the Brayton (combustion turbine) cycle. Published combined cycles have shown how steam can be used to cool gas turbine parts effectively while returning reheated steam back to the steam turbine [1].

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Heat capacity, thermal conductivity, and viscosity influence the effectiveness of a gas as a heat transfer medium. Higher heat capacities and thermal conductivities increase effectiveness, while lower viscosities increase effectiveness by reducing both boundary layer thickness and pumping costs. Figure 1 shows the ratio of steam properties at 3 MPa [2] to those of air at similar conditions [3]. At the lower temperatures, the steam values for heat capacity and thermal conductivity vary significantly with pressure but above 1 MPa the trends remain the same as those shown in the figure. Figure 1 shows that both the heat capacity at constant pressure (molar basis) and the thermal conductivity are greater for steam. The steam viscosity is always smaller than that of air. Thus all three parameters concerned with heat transfer effectiveness favor steam. The ready availability of steam at pressures higher than the gas pressure in the combustion turbine and the ease with which the heat may be returned to the steam turbine part of the combined cycle are two additional factors in favor of steam cooling.

Steam conditions in the cooling passages of the combustion turbine are expected to be in the range from 2 to 4 MPa and 600 to 1200 K, including possible hot spots on the metal surface. These pressure conditions are not far removed from those on typical conventional fossil power plant expansion lines, but the temperatures in the combustion turbine are considerably higher. Moreover, it is the lower pressure and temperatures in the steam turbine that govern most of the steam purity recommendations for steam turbines. As the power plant design becomes final, its steam conditions will be known, and final steam purity recommendations will be made available.

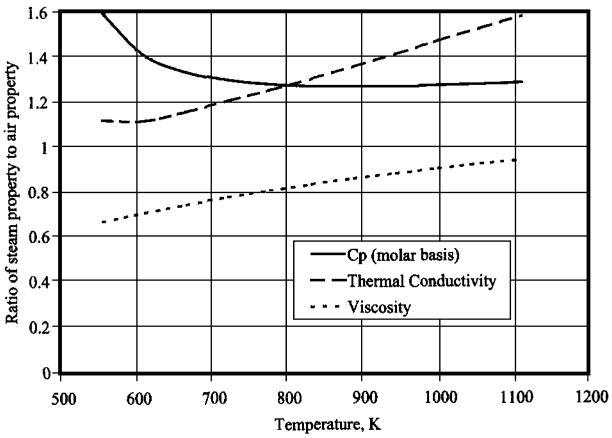

Fig. 1. Ratio of properties of steam at 3 MPa to those of air under similar conditions.

This paper outlines how steam purity recommendations are generated. This process uses estimates of the steam solubilities of contaminants. Satisfactory data exist for only two common contaminants: sodium chloride and silica. For other common steam contaminants, there are minimal data. We report here the highlights of the process we used to fit the available steam solubilities and to estimate the solubilities of those contaminants where inadequate data were available. We concentrate on sodium chloride, silica, copper oxide, sodium phosphate, and sodium sulfate. The remainder of the solubility study may be found elsewhere [4].

2. ISSUES IN DEVELOPMENT OF STEAM PURITY RECOMMENDATIONS

The parts in the hot gas path of combustion turbines are made from various nickel alloys. Sodium sulfate, and possibly sodium phosphate, will cause hot corrosion at the temperatures expected inside the cooling passages. Both of these compounds are commonly found in the steam cycle of current power plants. Indeed, sodium phosphates may be added to the boiler to control the pH and calcium chemistry. Therefore, they must be controlled for the combustion turbine cooling system. Other common contaminants of steam systems are silica, copper oxides, and iron oxide. Iron oxide is adequately insoluble to be treated solely as a particulate [4], but the other materials may have significant solubility in steam.

Steam purity recommendations are constructed by determining the concentration at which materials start to deposit from steam and maintaining the analytical control parameters below these values. Although supersaturation is possible, deposition is usually assumed to occur when the concentration of a material exceeds its solubility in steam since adequate heterogeneous nucleation sites exist on the turbine. Water treatment systems exist that will provide adequately pure water, but the cost increases as the purity increases. Being conservative and requiring excessively pure steam raises the cost of the water treatment plant and its operating costs. An overly conservative manufacturer will price himself out of the market. Being nonconservative and allowing deposition risks corrosion. Development of final steam purity recommendations for a combustion turbine cooling system awaits a completed mechanical design and the results of some deposition testing currently in progress.

3. EVALUATION OF STEAM SOLUBILITIES

Solubility data were gathered from the literature in the temperature range 473 to 1173 K and the pressure range 1 to 6 MPa (with 2 to 4 MPa of primary interest). These conditions correspond to very low steam densities ($<1\ \mathrm{mol\cdot L^{-1}}$) at which few reliable data exist. It was therefore necessary to collect and include in the correlations data at somewhat higher pressures (and therefore higher densities).

We assumed that the solutes remained chemically intact, undergoing no hydrolysis, decomposition, or other chemical reaction. This is not always true. Sodium sulfate is known to undergo hydrolysis. Such reactions were ignored on the grounds that considering them would have made the problem intractable and that the reaction products would likely be at least as soluble as the intact solutes. Thus, the assumptions of no hydrolysis or dissociation provide a conservative estimate for solids deposition calculations.

Also, the work was limited to the equilibrium solubility. Transport of solutes by mechanical carryover in the boiler was not considered. There was no consideration of kinetic aspects of solute deposition. It is possible for situations to arise where the equilibrium favors precipitation, but the kinetics prevent it from happening in the time available. Such considerations are beyond the scope of this study, but assuming precipitation when thermodynamically possible is again a conservative assumption.

All data were entered into a spreadsheet in the units in which they were originally reported. They were then converted to units of temperature in K, pressure in MPa, the density of pure water at that temperature and pressure in $\mathrm{mol\cdot L^{-1}}$, and the solubility in mole fraction. In most cases, the temperature and pressure were reported and the density of water was calculated from the Steam Tables [2]. These data have been tabulated elsewhere [4].

The data were correlated with a reaction model, where the solubility is viewed as a complexation between some number of solvent molecules and a solute molecule. If we consider the solute to be solvated by m solvent molecules, the reaction is written as

$$S(\mathrm{s}) + \mathrm{m}\mathrm{H_2O}(\mathrm{v}) \Leftrightarrow S\cdot \mathrm{m}\mathrm{H_2O}(\mathrm{v}) \tag{1}$$

where S is the solute. To convert the equilibrium constant for this reaction into something usable for a correlation, one replaces the activity of the complex by some direct measure of how much solute is dissolved, such as its mole fraction or partial pressure. It has been found that better correlations are obtained by replacing the activity of water with its density. This leads to equations of the form

$$\ln(x_s) = f(T) + m \ln \rho, \qquad (-\ln P) \tag{2}$$

where x_s is the mole fraction of solute, ρ is the density of the solvent (water), and the last term is included only if partial pressure (rather than mole fraction) is used to express the amount of solute in writing the equilibrium constant. The hydration number m could, in general, be a function of density and/or temperature. In the following sections, we briefly outline the results obtained for the solubilities of the compounds of most importance to the steam purity recommendations.

3.1. Sodium Chloride

Of the compounds considered, NaCl has the most solubility data in the region of interest. Most of the data are in good agreement at densities above 2 $\text{mol} \cdot \text{L}^{-1}$; below that, they diverge considerably. Some data show a continuous steep decrease in solubility with decreasing density, while other data indicate that the solubility levels off or, at least, decreases less rapidly. Shvedov [5] suggested that, at least, some of the latter data, because they were based on measurements of chloride concentration, are artificially high due to the production of HCl by hydrolysis. For this reason, and because it was a more conservative estimate in the context of potential precipitation from steam, we chose to fit the data in this region with the lower solubilities. A good fit was obtained with an equation of the form

$$\ln(x_s) = A + B/T + (m_1 + m_3/T) \ln \rho - \ln P \tag{3}$$

where the coefficients and other details for this and other fits can be found in Harvey and Bellows [4]. Figure 2 shows the fit of the data on the 673 K isotherm, illustrating the data discrepancies at low densities. Due to these discrepancies, our confidence in the calculated solubilities at these low densities is only to within approximately an order of magnitude.

3.2. Silicon Dioxide

For SiO_2, there are abundant solubility data at geological conditions, but the data in lower-pressure steam come primarily from two German dissertations [6, 7]. These two sources disagree by a factor of approximately 3 to 5. Finding no reason to prefer either, we fit an equation similar to Eq. (3) to the combined data. While there is some uncertainty in the resulting solubilities, they were well enough determined for our purposes.

3.3. Sodium Sulfate

While several attempts have been made to measure sodium sulfate solubilities in steam, the data are inconsistent by more than two orders of

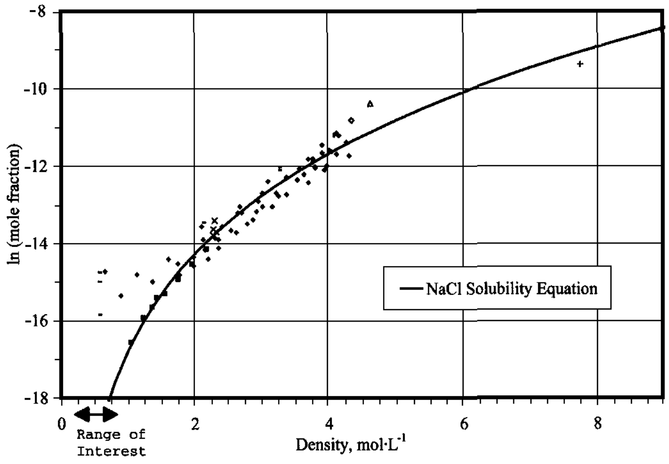

Fig. 2. Calculated and experimental solubilities for CaCl at 673 ± 5 K. Data symbols are defined in Ref. 4.

magnitude. Rather than try to fit these widely scattered data, we adopted a "model solute" approach. In this approach, we began with an estimate for the solubility of Na_2SO_4 in saturated steam at 633 K. We then assumed that the variation in Na_2SO_4 solubility with steam temperature and density was the same as that for NaCl. The solubility in saturated steam was estimated by taking the known solubility in high-temperature liquid water and combining it with data [8] for Na_2SO_4 partitioning between liquid water and steam. Since these partitioning data were not at solid saturation, they had to be extrapolated to higher concentrations.

Figure 3 shows the result of this procedure for the 773 K isotherm. Each data set is represented by a different symbol, and the dashed line is an equation given by Pritchard et al. [9] to represent their data. It is mildly reassuring that the calculated values are in the neighborhood of the scattered data. However, the uncertainties in the "model solute" extrapolation, in the value of the solubility in saturated steam, and in the behavior of the model solute itself combine to produce Na_2SO_4 solubilities that are uncertain by at least two orders of magnitude. An additional complication for Na_2SO_4 is hydrolysis, which is known to occur. For example, it appears that hydrolysis at the conditions of Goodstine's experiments [8] causes sodium bisulfate to be the dominant sulfate species in the vapor phase [10]. Hydrolysis is not taken into account in these calculations but definitely adds to the uncertainty.

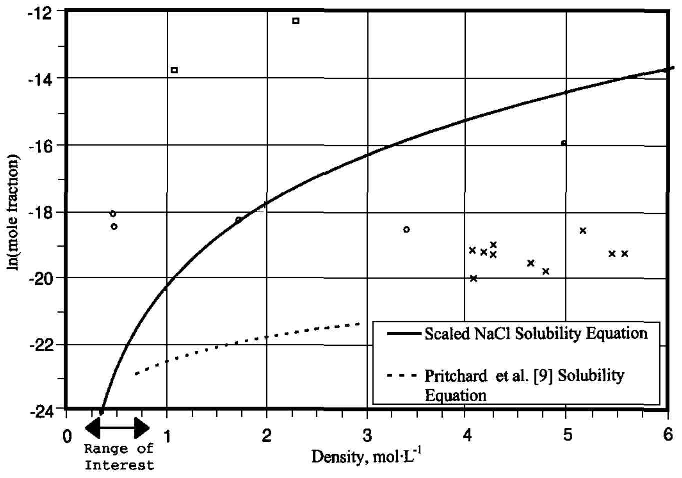

Fig. 3. Calculated and experimental solubilities for Na_2SO_4 at 773 ± 5 K. Data symbols are defined in Ref. 4.

3.4. Sodium Phosphate

For Na_3PO_4, we have not located any steam solubility data. We therefore applied the same "model solute" approach as with sodium sulfate. The lack of data against which to check the calculations makes these estimates even more uncertain than those for sodium sulfate. A further source of uncertainty is the complex chemistry in the sodium phosphate–water system, with the possible formation of nonstoichiometric compounds [11].

3.5. Copper Oxides

The two main data sets for CuO [12, 13] show solubilities that differ by roughly an order of magnitude where they overlap, and show very different density dependences for the solubility. Var'yash [14] has reported some solubilities at somewhat higher densities, but due to the different density dependences of the data in Refs. 12 and 13, his points are consistent with either data set. We used the data of Hearn et al. [13], but recognize that the presence of other, very different data means that, especially when extrapolated to the conditions of interest in this study, the uncertainty in the solubility of CuO is at least two orders of magnitude. For Cu_2O, the only data source is Ref. 12 and it is reasonable to assume that, at least, as

Table I. Calculated Solubilities at Representative Turbine Cooling Conditions

	Solubility (mole fraction) at given conditions				
Compound	600 K, 2 MPa	600 K, 4 MPa	900 K, 3 MPa	1200 K, 2 MPa	1200 K, 4 MPa
NaCl	1.1×10^{-9}	1.6×10^{-8}	9.5×10^{-9}	2.3×10^{-9}	2.6×10^{-8}
SiO_2	1.7×10^{-7}	2.8×10^{-7}	4.9×10^{-6}	7.4×10^{-5}	1.6×10^{-4}
Na_2SO_4	1.6×10^{-12}	2.2×10^{-11}	1.4×10^{-11}	3.3×10^{-12}	3.8×10^{-11}
Na_3PO_4	8.0×10^{-13}	1.1×10^{-11}	6.9×10^{-12}	1.7×10^{-12}	1.9×10^{-11}
CuO	3.3×10^{-9}	3.9×10^{-9}	3.1×10^{-8}	8.1×10^{-8}	9.0×10^{-8}
Cu_2O	3.2×10^{-16}	1.7×10^{-14}	2.6×10^{-15}	1.8×10^{-16}	7.2×10^{-15}

much uncertainty applies to this solute. In addition, it is likely that electrochemical reactions play some role in the solubility of copper and its oxides, further adding to the uncertainty.

3.6. Summary of Solubility Calculations

Table I shows calculated solubilities for the six solutes considered here. The conditions chosen reflect the extremes and midpoint (in temperature–pressure coordinates) of the approximate regime of operation for turbine cooling. The large uncertainties of many of these numbers are discussed above and in Harvey and Bellows [4].

4. IMPLICATIONS FOR STEAM PURITY RECOMMENDATIONS

The allowable steam concentrations of silica and chloride for combustion turbine cooling are greater than the commonly achieved values required by steam turbines. However, if accurate, the steam solubility estimate implies a sodium sulfate concentration below one ppb ($\mu g \cdot kg^{-1}$) in the steam. Achieving such a concentration with current water treatment systems requires excellent operation. In addition, monitoring becomes a necessity. Chloride monitors for the 1-ppb range exist. The only method to monitor sulfate in this range is ion chromatography. Monitoring sodium is not an appropriate approach because the allowable sodium concentration due to sodium chloride is significantly higher. Needlessly maintaining sodium chloride below 1 ppb would present a hardship to operators. Therefore, if the sodium sulfate estimate is low by an order of magnitude, it could have real economic consequences in operation and maintenance costs for the power plants. If the solubility estimate is erroneously high by an order of magnitude, there is a risk of hot corrosion.

The case with the sodium sulfate solubility estimate is better than that for sodium phosphate. Our sodium sulfate model, at least, approaches the data where data exist. In the case of sodium phosphate, there are no known published data. Admittedly, such data are difficult to measure reliably, especially with the potential complication of hydrolysis or other chemistry. However, improved knowledge of the solubility and speciation of sodium sulfate and sodium phosphate could improve operating and maintenance costs.

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