

Chemistry in the Moisture Transition Region of the Steam Turbine

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The moisture transition region of a turbine, where the steam changes from superheated to moist, is frequently a region of corrosion. The thermodynamics of the region, with the development of concentrated liquid salt solutions from trace concentrations in steam, is reviewed and related to turbine thermodynamics. The situation of volatile impurities is examined. The thermodynamics indicates what is possible, but the development of the solutions is controlled by kinetics. Nucleation of salt solution may be homogeneous in the steam, heterogeneous on particles in the steam, or heterogeneous on the turbine. Rates of nucleation of the various types are examined and the applicability in a region where the steam is moving near or above Mach 1 is discussed. Mass transfer to the nuclei and to the equipment is examined. These processes are related to the corrosion in the region. The approach is to show principles that provide an overview and to include results that can guide one's thinking about the processes in this region.

1. Introduction

The moisture transition region of the steam turbine has received tremendous amounts of research and engineering attention for many years. The interest is driven by the significantly higher frequency corrosion of turbine parts in this region than in the rest of the turbine. For this paper, we will restrict the moisture transition region to the space between the first appearance of salt or other solutions to the point of 1% equilibrium moisture.

Rather than reviewing all the recent work, the approach of this paper is to select significant high points to put the work in perspective. This paper explores the thermodynamics in the region, which indicate what is possible. First will be a short look at the thermodynamics of pure steam and of the expansion of steam through a turbine. Second will be the overlay of sodium chloride solubility on the turbine thermodynamics. After laying the thermodynamic foundation, the paper examines two kinetic phenomena: nucleation and mass transfer. Homogenous nucleation has received much attention. Less attention has been given to heterogeneous nucleation either on particles in the steam or on the surface of the steam turbine. If the nucleation is on the turbine surface, then the rate limiting process in deposit or solution formation will be mass transfer to the surface. The mass transfer of sodium chloride will be examined. Having looked at the problem of getting corrodents to the metal surface, the corrosion process will be briefly examined. The focus will be on conventional fossil turbine conditions, but the principles

and procedures may be used with other cycles, such as nuclear or combined cycle.

2. Thermodynamics

2.1 Pure Steam and Turbine Expansion Lines Steam turbines are designed to extract thermal energy from steam and convert it into rotary work. Turbine thermodynamicists conceive of turbines on an enthalpy-entropy diagram, called a Mollier Chart. The pressure and temperature conditions of the steam at various points in the turbine are shown on this chart and called the expansion line. Fig 1 shows the expansion line for a 160 bar turbine at full and part load (sequential valve). The markers on the lines indicate the boundaries between stages of the turbine. It is important to note that the temperature at a given stage is relatively constant, but the pressure changes significantly as the turbine is operated at part load. It is reasonable to think of the turbine as a constant temperature device where load is varied by pressure.

2.2 Solubility of NaCl in Steam Sodium chloride is the most studied salt in steam systems. Mollier charts with sodium chloride solubility in steam date back at least to 1978 [1] when W. T. Lindsay prepared one. He based his steam solubilities on the data of Sourirajan and Kennedy [2] but there have been further examinations, both experimental [3] and survey [4] since then. In addition, there have been attempts to calculate the solubility of sodium chloride in steam based on statistical mechanics [5]. Fig 2 shows the Mollier chart with

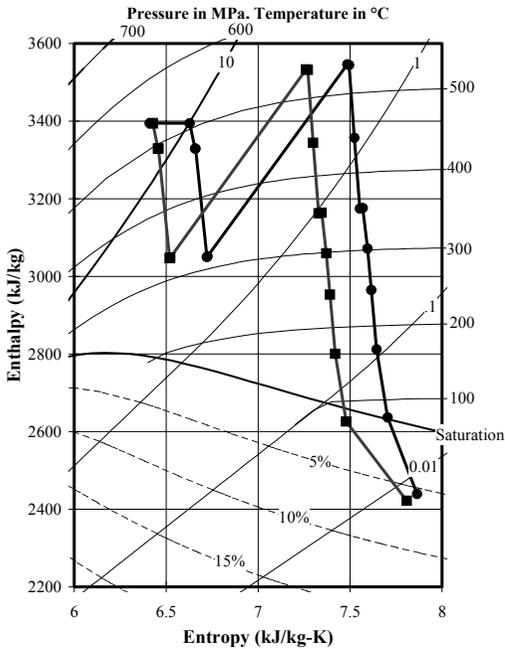


Fig 1. Mollier chart showing turbine expansion lines at full load (squares) and at part load (circles).

the 5 $\mu\text{g}/\text{kg}$ (ppb) solubility of steam according to several sources. It also shows a line for the saturated solution of sodium chloride. This line departs from the pure water saturation line because salts elevate the boiling point of water. Solubility in steam is a strong function of steam density and a weaker function of temperature. On a Mollier chart, solubility increases as the pressure increases (See Fig 3). It is clear that Sourirajan and Kennedy show much higher solubility near the saturation line than do the other two sources. Harvey and Bellows considered not only the data of Galobardes, van Haar and Rogers, but others as well. Their equations are fit to data selected from twelve sources. For the remainder of the discussion we will use their formulation for solubility of sodium chloride in steam.

Fig 3 shows the predicted solubility of sodium chloride. It is clear from the figure that the solubility of sodium chloride in steam at the moisture transition region is below 1 ng/kg (ppt). This means that the solubility of sodium chloride in steam is so low that practical water purification systems cannot produce water with a sodium chloride concentration below the steam solubility. Therefore, the basis of sodium and chloride recommendations for steam purity must be based

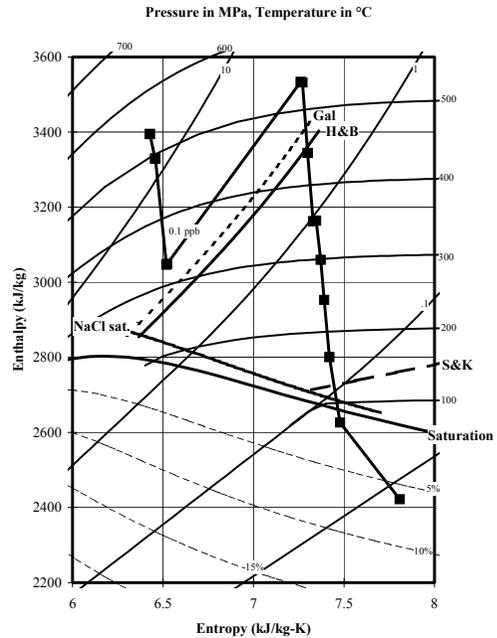


Fig 2 Mollier chart showing turbine expansion line at full load and lines of constant 5 $\mu\text{g}/\text{kg}$ (ppb) sodium chloride solubility in steam according to various formulations (S&R [2], Gal [3], H&B [4]).

on a criterion other than the solubility of the salt in steam.

The moisture transition zone in most conventional fossil cycles occurs near the normal boiling point of water. Most salts will elevate the normal boiling point by, at most, 50 °C. In nuclear turbines and non-reheat turbines, the moisture transition occurs at higher temperature and pressure, but the principles are the same. In contrast to salts, the presence of sodium hydroxide can elevate the boiling point to produce a liquid solution at any location in the turbine. The details of sodium hydroxide will not be explored here but are present in Lindsay's paper [1].

2.3 Volatile impurities in steam Sodium chloride is a typical salt with a very low solubility in steam. Only in the region between the pure water saturation line and the saturated sodium chloride line can sodium chloride be said to partition between the water and steam phases. There other materials that are much more volatile. These materials behave differently in the moisture transition region.

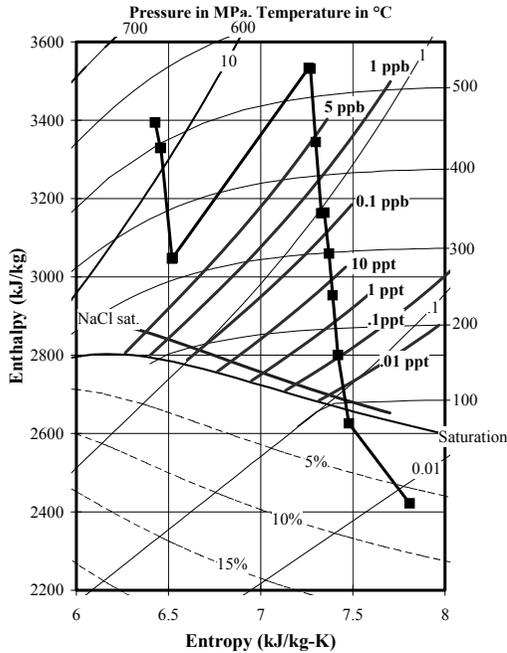


Fig 3. Mollier chart showing turbine expansion line at full load and sodium chloride solubility in steam according to Harvey and Bellows [4].

Acetic acid is a good example of a volatile impurity. Cobble and Lin [6] give a value of 0.36 at 100°C for the distribution coefficient (concentration in vapor divided by concentration in liquid), and 1.12×10^{-5} for the acid dissociation constant. Fig 4 shows the conductivity and pH calculated for a moisture transition (0.1% moisture) at 100°C, typical of a conventional fossil turbine. In order to make comparison easier, the pH is presented as the difference between the pH at the temperature of interest and the neutral pH at that temperature. The acetic acid is varied between 0 and 100 µg/kg, which are not uncommon values in steam systems. The ammonia concentration was maintained constant at 800 µg/kg, which generates a room temperature pH for the sample of 9.3 in the absence of acetic acid (a pH elevation of 2.3). The cation conductivity (conductivity after strong acid cation exchange) of the inlet steam sample (25°C measurement) increases from 0.055 to over 0.6 µS/cm, but the pH of the inlet steam sample (25°C) is not noticeably affected. The situation is different at the moisture transition, where the pH elevation due to ammonia drops from nearly 0.96 to below zero, indicating acidic conditions. The conductivity of the hydrogen, hydroxide and acetate ions is

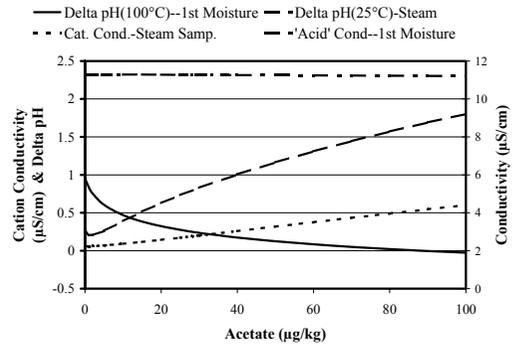


Fig 4. Conductivity and pH for acetate solutions at moisture transition.

called ‘acid’ conductivity in the figure and is similar to a cation conductivity. It starts at 3.05 µS/cm for pure water, and increases to over 9 µS/cm. When the ammonia concentration was raised to 2300 µg/kg, which generates pH 9.6 for the steam sample, the first moisture remained basic, though the pH elevation was very small. A similar study of carbon dioxide, with considerably higher concentrations, showed very little effect on the pH or conductivity of the moisture. [7]

2.4 Oxygen Oxygen may be reasonably treated by Henry’s law calculations in the moisture transition region. That treatment, using data from Cobble and Lin [6] gives 1.4×10^{-3} µg/kg in the 100°C moisture film for a system with 100 µg/kg oxygen in the steam, typical of a system on oxygenated treatment. The same treatment gives 8 mg/kg (ppm) in a 25°C film under air when the turbine vacuum is broken.

Having looked at what is thermodynamically possible in the steam turbine, we consider the kinetic issues. Corrosion requires the metal be in contact with an ionically conducting medium, which takes the form of a water solution in steam turbines. In order to develop that liquid solution several processes must take place. First, moisture must form from superheated steam. This formation requires nucleation, which may be homogeneous in the steam, heterogeneous on particles or ions in the steam, or heterogeneous on the surface of the metal. Then the nuclei must grow, which requires mass transport.

3. Nucleation

3.1 Homogeneous nucleation Homogeneous nucleation has been treated at this conference

before. [8-10] In general, the findings have been that the nucleation is relatively slow, and one must have considerable supersaturation before the nucleation rate is appreciable. This explains the common observation that the moisture line in the turbine is at several percent moisture. Thus the moisture from homogeneous nucleation occurs downstream of the moisture transition zone.

3.2 Heterogeneous nucleation on particles in steam A number of studies of heterogeneous nucleation on particles have appeared in the last few years. There are many small salt and oxide particles traveling in the steam. The work of Stastny and coworkers make is reasonably clear that the nucleation in the moisture transition zone is a blend of homogeneous nucleation and of nucleation on these particles. [11-12] In addition, they find that droplets do not grow, but new droplets are formed. This finding has been confirmed by the work of Petr and Kolovratnik.[13]

3.3 Heterogeneous nucleation on the metal Conventionally processed metals contain numerous microscopic surface irregularities, such as grain boundaries, machining marks, and crystal imperfection. These irregularities may act as nucleating sites. The number is adequate, and they are definitely located at the metal. Either pure water or salt solution may nucleate on such irregularities.

4. Mass Transfer

4.1 Growth of nuclei in vapor Nuclei in the vapor may grow by either of two means. They may grow by adding water molecules or they may grow by aggregation. If they grow by adding water molecules, the composition changes from the initial value to a more dilute solution. This process assuredly occurs as the nuclei travel out of the moisture transition region into the wet steam region and into the condenser. There are many water molecules for each nucleus. In order for an impinging molecule to remain with the developing droplet, the excess energy must be removed by another particle. This energy removal is the rate limiting process for droplet growth by aggregation of water molecules.

If the nuclei grow by aggregation, the composition need not change very much. The only issue is the rate at which nuclei may collide to aggregate. If one considers a steam composition of 5 $\mu\text{g}/\text{kg}$ sodium chloride, the mole fraction of sodium chloride is 1.5×10^{-9} . The waters on the sodium

chloride will not significantly affect the mole fraction, although they do affect the size of the particle in steam. If one does a simple kinetic theory model of sodium chloride clusters using 8 waters (28% NaCl by weight), one finds that the number of collisions of clusters is $2.1 \times 10^{17} \text{ m}^{-3} \cdot \text{s}^{-1}$. A single molecule undergoes about 7 collisions per second. Remembering that the steam in a steam turbine is traveling at more than $472 \text{ m} \cdot \text{s}^{-1}$ through the blade path near the moisture transitions, the collision probability is less than 3×10^{-3} collisions in 20 cm, which is a reasonable value for a steam turbine blade length in this region. While the calculation ignores effects of sonic velocity on the number of collisions, it is probably not wrong by more than an order of magnitude. The conclusion is that clusters cannot grow to macroscopic sizes in the turbine steam. This calculation explains why the heterogeneous nucleation studies [11-13] have found that the nuclei do not grow.

4.2 Growth of films from nucleation on the metal If a salt solution film nucleates on the surface of the turbine, it must grow by mass transfer of salt through the steam and boundary layer. In the moisture transition region, the steam velocities are supersonic, and the author not found studies of mass transfer through boundary layers under supersonic conditions. For this reason, we will treat mass transfer in the superheated zone of the turbine and make the extrapolation that the process is not significantly changed as the first moisture develops.

The mass transfer approach was developed by Bellows [14] based on a suggestion by Lindsay [15]. He was unable to find diffusion coefficients for the species of interest, and so calculated them (incorrectly) from kinetic theory. For sodium chloride [16] and for sodium hydroxide[17], molecular modeling has improved the situation. The sodium chloride modeling results are about 1/3 the values calculated by sophisticated kinetic theory. Other species await modeling.

Fig 5 shows the corrected rate of sodium chloride deposition based on diffusion coefficients correctly calculated by kinetic theory. It is clear that deposition occurs through much of the turbine, but only at the moisture transition region will it be wet. If diffusion coefficients based on molecular modeling were used, the rates would be about 1/3 those shown in Fig 5. The deposition rates indicate that the fraction of salt deposited in a turbine before the steam reaches the condenser is much below 1%.

Some kinetic effects prevent attainment of equilibrium. Others simply affect the rate at which equilibrium is approached. If the rate is slow in the fast-moving steam, the conditions change before equilibrium can be attained. In contrast, the salt concentration in moisture in a crevice can be expected to reach the equilibrium concentration over the course of operation of the turbine. Reaching equilibrium may be accomplished over many months, and it may be accomplished by evaporation of solutions more dilute than the equilibrium.

5. Experimental studies

Although experimental verification of high salt concentrations in the moisture transition region occurred over 25 years ago [18] there is relatively little experimental data on the liquid film. Most of the data comes from the experimental turbine at the Moscow Power Institute [19]. These are difficult experiments and the quantity of moisture present at the sampling point may be difficult to control. The measurements do confirm the concentrated solutions and confirm most of the effects discussed here. Other early condensate schemes usually take a sample from a convenient location, such as the inlet to the low pressure turbine, and process it so that the first condensate is collected [20]. The conditions of processing are not identical to the conditions in the turbine, particularly the non-equilibrium effects. However, such techniques can provide insight into the situation in the turbine.

6. Corrosion

None of the preceding chemistry would be important were it not for the fact that some conditions lead to corrosion. Engelhard, Macdonald and Dooley [21] have outlined a process whereby the corrosion damage passes through several stages, leading to the transition to a corrosion assisted cracking mechanism (stress corrosion or corrosion fatigue):

1. Nucleation of metastable pit
2. Transition from metastable to stable pit
3. Growth of stable pit
4. Transition from pit to corrosion assisted crack
5. Crack growth

The competing process of repassivation can occur instead of process 2 or 4 stopping the process. In order to have transition from pit to corrosion assisted crack, two conditions must be fulfilled. First the pit must be of adequate depth. Second, the

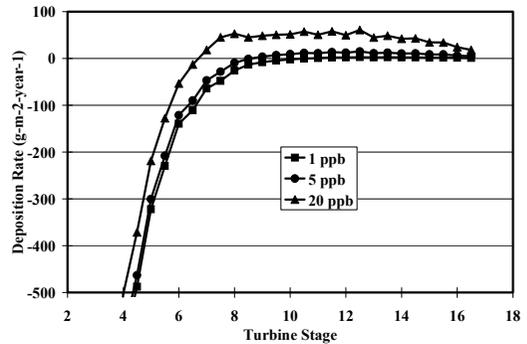


Fig. 5. Deposition of Sodium Chloride in a Turbine.

pit growth rate must be smaller than the crack growth rate. They find that this practically implies that the pit must be inactive to allow transition to cracking.

The implication of this model is that the way to stop damage is to interrupt one of the first three steps. Once the pit has grown deep enough, if the pit growth is stopped, the pit will become a crack. Once the pit has transformed into a crack, the only way to stop the corrosive component of the cracking is to keep the region dry.

In order to nucleate the pit, one must have the corrosive film present with an oxidizing agent at a significant concentration. When the turbine is operating, the oxygen concentration in the first moisture is on the order of a part per trillion. While some corrosion might occur at this concentration, it can be expected to be minimal. However, when the turbine is shut down and the vacuum broken, the concentration of oxygen in the first moisture increases almost 7 orders of magnitude. The lower temperature does not offset the increased oxygen. Unless measures are taken to keep the humidity low, the salt solutions will remain liquid. However, sodium hydroxide will remain in solution at relative humidity above 6% up to 55°C and above 1.8% at higher temperatures [22]. One now has the conditions to allow the pitting to start and pits to grow. When the turbine is restarted, the oxygen concentration drops, and possibly the pit repassivates or it may simply grow at a very slow rate. If the pit is already deep enough, it could transform to a crack. This scenario suggests that the short-term lay-up of a cycling unit, which may be off-line 16 h per day and weekends, will be the critical factor in minimizing corrosion. Minimizing oxygen is during the shutdown, by maintaining vacuum or by breaking vacuum with an inert gas, is

one important means of slowing this corrosion process. Other schemes may also be applicable such as maintaining the turbine at elevated temperatures by insulation or heating.

Summary

Calculations indicate that the solubility of sodium chloride in steam at the moisture transition is significantly below the concentrations attainable with normal water treatment equipment. Equilibrium modeling shows that acetic acid can acidify the first condensate in a steam turbine, though higher bulk steam pH will prevent the acidification. Initial nucleation in the moisture transition can be either on impurities in the steam or on the metal surface. There is inadequate time for nuclei of salt solutions to aggregate before the steam flow sweeps them into the very moist zone. Mass transfer calculations indicate that deposition is a very slow process, and that most of the salt in the steam reaches the condenser. Current understanding of the corrosion mechanisms in turbines suggest that the chemistry in cycling plants must be very carefully controlled because off-line corrosion rates are likely to be much higher than the on-line corrosion rates. In addition the transition to cracking is promoted by the reduction in pit growth rate expected when the turbine starts up. The corrosion mechanism suggests that there is a real need for additional investigation of methods and system designs to prevent off-line turbine corrosion, particularly in cycling plants.

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