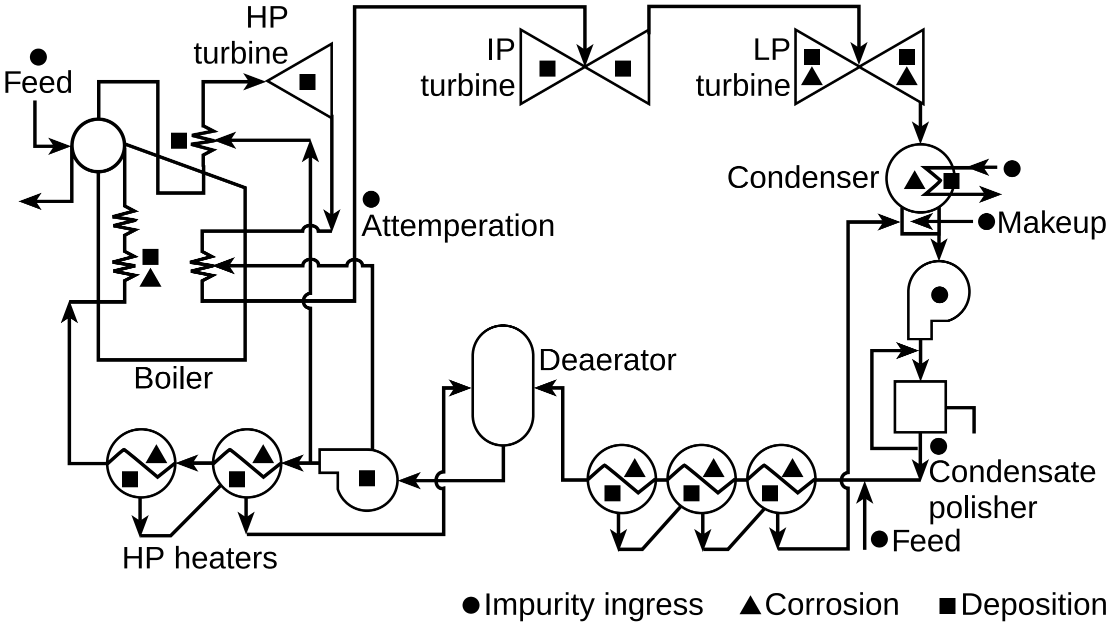
The Volatility of Impurities in Water/Steam Cycles

Technical Report



The Volatility of Impurities in Water/Steam Cycles

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Final Report, September 2001

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REPORT SUMMARY

The quality of water and steam is central to ensuring power plant component availability and reliability. A key part of developing cycle chemistry guidelines is an understanding of the impurity distribution between water and steam. This report summarizes EPRI work conducted over the last ten years to understand this partitioning process.

Background

Impurities in turbine steam and subsequent deposition and corrosion are due primarily to mechanical and vaporous carryover of boiler water impurities. Detailed monitoring of plant conditions has shown that serious discrepancies exist between field data and the historical representation (ray diagram) of the expected carryover of impurities into steam. A rigorous new approach was needed to calculate steam and early condensate compositions from a knowledge of the boiler water composition, and vice versa.

Objectives

- To summarize detailed partitioning constants for typical impurity compounds and related species that have been measured in EPRI work.
- To provide a qualitative understanding of the ramifications in a fossil plant.

Approach

The EPRI team first developed partitioning diagrams for NH_4Cl, NH_3, HCl, NH_4HSO_4, Na_2SO_4, $NaHSO_4$, NaOH, H_2SO_4, organic acids (acetic and formic), $Cu(OH)_2$, H_3PO_4, Na H_2 PO_4, and Na_2 HPO_4 from previous EPRI work (EPRI reports TR-102377, TR-105801, TR-112359, TR-113089, and 1000455). The team next delineated an understanding of how each compound partitions from boiler water into steam. They then used a model, containing partitioning constants and hydrolysis reactions, to predict steam and early condensate compositions for a range of boiler water chemistries ranging from normal guidelines to upset conditions.

Results

The predictions are generally in agreement with field and model turbine measurements. Chloride is much more volatile than sulfate. Chloride is transported as hydrochloric acid and sulfate as sulfuric acid, although ammonium and sodium bisulfates also play a role. Caustic treatment, equilibrium phosphate treatment, and phosphate treatment reduce the amount of chloride transported to steam by vaporous carryover, but increase the amount of sodium in steam. Initial simulations clearly indicate that even small amounts of mechanical carryover produce more impurities in steam under most conditions than vaporous carryover.

EPRI Perspective

Results from this 10-year EPRI study are now starting to provide a more detailed picture of how salts and impurities partition between boiler water and steam. The overall approach needs to be verified by detailed plant measurements. During the next phase, the model will be refined and used to revise EPRI treatment guidelines. In particular, new target values for sodium, chloride, sulfate, and the corresponding cation conductivity in boiler water will have to be derived for each drum boiler. The model will be incorporated into EPRI's ChemExpert to provide instantaneous guideline values that will be dependent on chemical parameters as well as unit conditions.

Keywords

Water chemistry
Steam
Boiler water
Turbine blades
Salts

ABSTRACT

Knowledge about the concentration of impurities in boiler water and steam is critical to the operation, availability and performance of fossil plants. Information on how the impurities partition from the boiler water to steam is also the key step in deriving and customizing operating chemical limits for drum boilers. The carryover of boiler water impurities into steam can occur as a result of vaporous and mechanical carryover. For almost 50 years the ray diagram has been used to express vaporous carryover, more recently this has been found by analysis in plant to be incorrect for some key compounds by orders of magnitude. This initiated a series of EPRI sponsored research projects to rigorously measure experimentally the partitioning constants for most of the important compounds, which can be present in boiler water and steam. Over the last ten years, work has addressed the following compounds and related species: NH_4Cl, NH_3, HCl, NH_4HSO_4, Na_2SO_4, $NaHSO_4$, NaOH, H_2SO_4, organic acids (acetic and formic), $Cu(OH)_2$, H_3PO_4, NaH_2PO_4, and Na_2HPO_4. The results have been reported in EPRI reports.

This report summarizes all this prior work and provides a qualitative understanding of the ramifications. The report also describes the first step in developing a computer model which incorporates the partitioning constants and the hydrolysis reactions at high temperature. These are required to predict pH and conductivity of the early condensate from the boiler water composition. These initial and qualitative simulations have shown that the concentrations of impurities in steam can reach ppb levels and those in the early condensate, ppm levels. These predictions are generally in agreement with field and model turbine measurements. Chloride is much more volatile than sulfate, again as seen in early condensate measurements. Chloride is transported as hydrochloric acid, and sulfate as sulfuric acid, although ammonium and sodium bisulfates can also play a role.

Caustic treament (CT), equilibrium phosphate treatment (EPT), and phosphate treatment (PT) reduce the amount of chloride transported to the steam by vaporous carryover, but increase the amount of sodium in the steam. The simulations clearly indicate that even a small amount of mechanical carryover produces more impurities in steam under most conditions than vaporous carryover.

During the next phase, the model will be refined and used to revise the EPRI treatment guidelines. In particular, new target values for sodium, chloride, sulfate and the corresponding cation conductivity in boiler water will have to be derived for each drum boiler.

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BACKGROUND AND HISTORICAL PERSPECTIVE

1.1 Introduction

The concentrations of impurities in power plant boiler water/steam cycles have to be carefully controlled to prevent corrosion in the boiler and carryover into the steam, where they might lead to deposition and corrosion in the superheaters, reheaters and turbines. Failures of turbines due to stress corrosion cracking and corrosion fatigue are particular problems costing many millions of dollars per year.

The transport of boiler water impurities and conditioning chemicals into steam can occur due to mechanical and vaporous carryover. Mechanical carryover in drum boilers can be significant; for example at a pressure of 2400 psi (16.5 MPa), it may be as high as 0.2%[1] (see Figure 3-4). Thus it is important that mechanical carryover is measured and known for each boiler. Vaporous carryover occurs due to the inherent volatility of the compounds present in the boiler water. Some compounds, for example ammonia, are deliberately added to the water/steam circuit as conditioning chemicals, because they are volatile and can protect various parts of the boiler water/steam circuit during operation and off-load conditions. With once-through boilers, all of the impurities in the feedwater either deposit in the boiler or continue into the steam.

A quantitative description of the partitioning of solutes between liquid and vapor phases is needed to determine the composition of working fluids (water and steam) at all points in the steam cycle. The low concentrations of solutes typically found in well-operated plants may increase significantly upon condensation of steam to water in the phase-transition zone (PTZ) and early condensates in low pressure turbines.

The concepts of carryover were included in the derivation of boiler water chemistry guidelines from the steam limits[1]. In order to apply these concepts to a variety of individual systems with widely differing chemical and physical environments (e.g. water chemistry, boiling and condensation temperatures), it is necessary to quantify the extent of partitioning of various solutes between water and steam under phase change conditions (boiling and condensation).

Jonas pointed out discrepancies between partitioning data obtained from operating plants and the values predicted from the ray diagram[2] (Figure 1-1)[7]. In particular, the plant measurements of distribution coefficients for chloride and sulfate were higher by orders of magnitude than those given by the ray diagram for NaCl and Na_2SO_4. This observation led to the conclusion that both the experimental and theoretical basis for the ray diagram should be investigated in some detail, to include those solutes for which no experimental partitioning data were available, and to develop a more rigorous treatment of solute partitioning between liquid water and steam.

This new model for solute carryover could then be applied to the wide range of operating conditions and water chemistry found in fossil-fired plants worldwide.

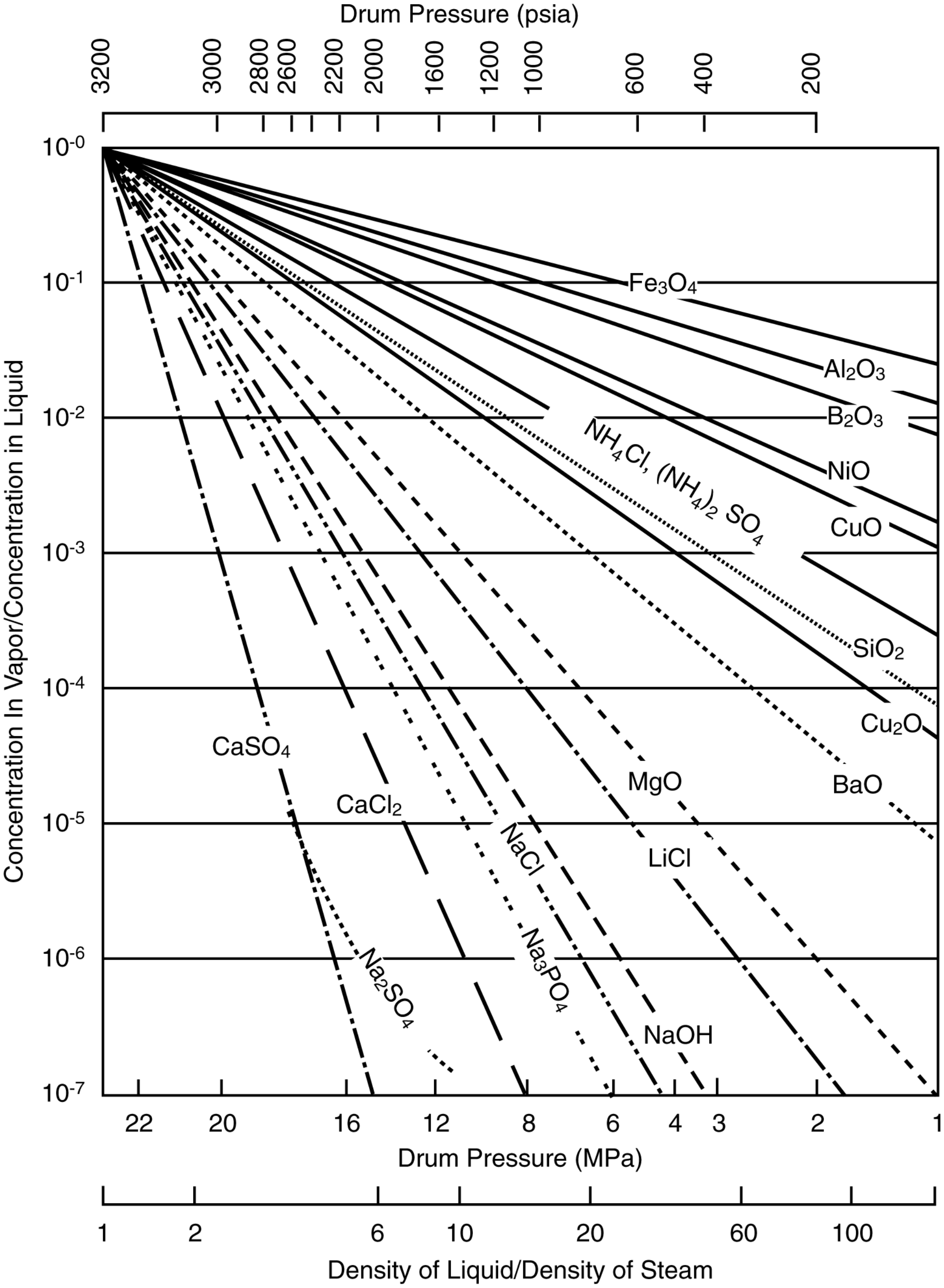

Figure 1-1
The Ray Diagram[7]

1.2 Experimental Approach

In assessing the need for new information on the volatility of salts, it was found that no data were available for some salts of interest (e.g. NH_4Cl) and that it was difficult or impossible to judge the reliability of data for other compounds as the original experimental results were essentially unavailable. EPRI's systematic investigation of the volatility of acids, bases and salts, which are of central importance in reliable calculations of the steam transport of contaminants through the steam cycle, was begun at Oak Ridge National Laboratory in order to address the need for new data. There are advantages to sampling coexisting liquid and steam phases in a dynamic (flowing) system, in that a flowing system represents an approximation to plant conditions and large samples of dilute solutions (steam condensate) can be obtained for analysis. However, it can be difficult to ensure equilibrium between liquid and steam in a flowing system, and it is also challenging to assemble a system with the chemical inertness (corrosion resistance) required for volatility experiments on corrosive solutions. Therefore, all the volatility experiments described below were carried out in a static apparatus. In this equipment, a platinum-alloy liner and sample lines were encased in a commercial high pressure autoclave. Vapor condensate samples were obtained at very low sampling rates (usually less than 1 ml per hour) in order to avoid disturbing the liquid-vapor equilibrium or entraining liquid droplets in steam. Analyses of liquid and vapor-condensate samples were carried out using analytical techniques appropriate for the solute under investigation. The apparatus used for these measurements is not described further here, but the reader is referenced to the extensive EPRI reports[3-6].

1.3 Modeling Approach

The first systematic description of the effect of temperature on the compositions of coexisting liquid and steam was through the development of the ray diagram as illustrated in Figure 1-1[7]. The most widely used version of the ray diagram represents the ratio of the solute concentration in steam to that in liquid water as a function of the ratio of the density of steam to liquid water. This representation, which in logarithmic form produces linear plots with an intercept of zero at the solvent critical point (where concentrations of all species are equal in liquid and steam), is conceptually simple and is easy to use in generating estimates of solute carryover in steam. However, this approach cannot account for the partitioning of hydrolysis products to steam. For example, HCl and NaOH partition to varying extents from NaCl solutions, depending on solution pH at the boiling temperature. This distribution of hydrolysis products may contribute the majority of a particular ion (e.g. chloride) found in steam due to the relatively higher volatility of acids compared with salts.

The ray diagram was subjected to a detailed assessment of its usefulness and theoretical justification; this found that the rays for many electrolytes were based on data from a restricted concentration range, and that the partitioning ratios in the ray diagram were not independent of solute concentration and pH[8]. A new approach to predicting volatilities of compounds in steam cycles was needed to give more reliable predictions than those obtained from the ray diagram. The new approach needed to be applicable to mixtures of solutes and to account for the partitioning of acids formed by hydrolysis in the boiler water.

An alternative theoretical description of electrolyte volatility was developed based on the thermodynamic equilibrium of solutes in water and steam, including the effects of solute non-ideality (activity coefficients) in the liquid. In order to develop this approach, information was required on the volatility of the salts and their corresponding acids and bases likely to be present in boiler water. Some early EPRI data were available for sodium chloride, hydrochloric acid, sodium hydroxide and ammonia[3], but in order to produce a rigorous thermodynamic approach, additional data were required on the volatility of ammonium chloride, sulfuric acid, sodium hydroxide, sodium and ammonium sulfates and bisulfates; phosphoric acid and sodium phosphate; copper and its oxides and hydroxides; and organic acids and salts. The data required were measured over the range of temperatures of interest, or derived from existing data[3-6, 9 , 10].

The information obtained on the various compounds and related species can be used to model the chemistry around the water/steam circuit under various chemical regimes at any temperature, pH or composition of the boiler water. This model makes it possible to represent the contributions of compounds in the liquid to the total concentration of solutes in steam. The treatment is applied in a number of examples to experimental data on the equilibrium compositions of liquid and steam, (Section 2), to extract thermodynamic partitioning constants for particular solutes. This approach then forms the basis for subsequent calculations of solute transport on boiling and partial condensation in the practical examples described in Section 3.

2

SUMMARY OF DATA

2.1 Introduction

The results obtained using the new thermodynamic approach are expressed as partitioning constants (i.e. the concentration in the steam over the activities of the constituent ions in the water) and can be illustrated on a partitioning diagram by plotting the logarithm of the partitioning constant against reciprocal absolute temperature (in Kelvin). Separate curves have been derived for each compound and related species: NH_4Cl, NH_3, HCl, NH_4HSO_4, Na_2SO_4, $NaHSO_4$, NaOH, H_2SO_4, organic acids, $Cu(OH)_2$, H_3PO_4, NaH_2PO_4 and Na_2HPO_4. Some species, NH_3, SO_2, organic acids, $Cu(OH)_2$ and H_3PO_4 are neutral, others are 1:1 ionic compounds, NH_4Cl, HCl, NaOH, NaCl, $NaHSO_4$, NH_4HSO_4 and NaH_2PO_4, while Na_2SO_4 and Na_2HPO_4 are 1:2 ionic compounds.

The partitioning constants for the neutral species are shown in Figure 2-1, the 1:1 compounds in Figure 2-2 and the 1:2 species in Figure 2-3. Sulfuric acid can be classed as a 1:1 compound, because under the conditions of the experiments, it only ionises one stage to H^+ and HSO_4^-. The relative volatilities of each type of species can be compared directly on each graph, but because of the different ways in which 1:1 or 1:2 electrolytes dissociate and the fact that the partitioning constants have different units, neutral compounds can not be compared with 1:1 compounds, or 1:1 compounds with 1:2 compounds. However, it is clear from the graphs that the volatilities of all the ionic solutes increase with temperature.

The equations for the partitioning constants in these three figures are provided in the Appendix.

2.2 Ammonium Chloride, Ammonia and Hydrochloric Acid

The overall partitioning between liquid and vapor phases depends on the distribution of ammonium ions, hydrochloric acid and ammonia in the liquid, the ionization of ammonium ions and water, and the partitioning reactions for these species between the liquid and the vapor. Chloride may undergo volatile transport to the vapor phase as both HCl and NH_4Cl, the ratio of which depends largely on the pH of the liquid. Therefore, the chloride concentration in the vapor phase cannot be predicted on the basis of the chloride concentration in the liquid phase alone (i.e. not from a single line on the ray diagram). The results for NH_3 (neutral) can be expressed as partitioning constants, between vapor and liquid, as shown in Figure 2-1, and those for HCl (1:1) and NH_4Cl (1:1) in Figure 2-2.

Whereas the dominant species for NH_4Cl solutions in both the high and low temperature liquid phase are NH_4^+ and Cl^-, the species transported to the vapor are predominantly HCl and NH_3.

At low ammonia concentrations, the major source of chloride in the vapor is partitioning of HCl from the liquid. At 350°C (662°F), in addition to the sharp increase in HCl volatility with temperature, even the hydrogen ion concentration in pure water makes HCl an important contribution to chloride transport.

On the other hand, the primary contribution of HCl partitioning to the chloride content in the vapor phase does not imply that the subsequent appearance of chloride, in early or first condensate, will be as HCl. Under equilibrium conditions, the enhancement of chloride in early condensate is due mainly to the steep decrease in the partitioning constant for NH_4Cl with decreasing temperature (Figure 2-2).

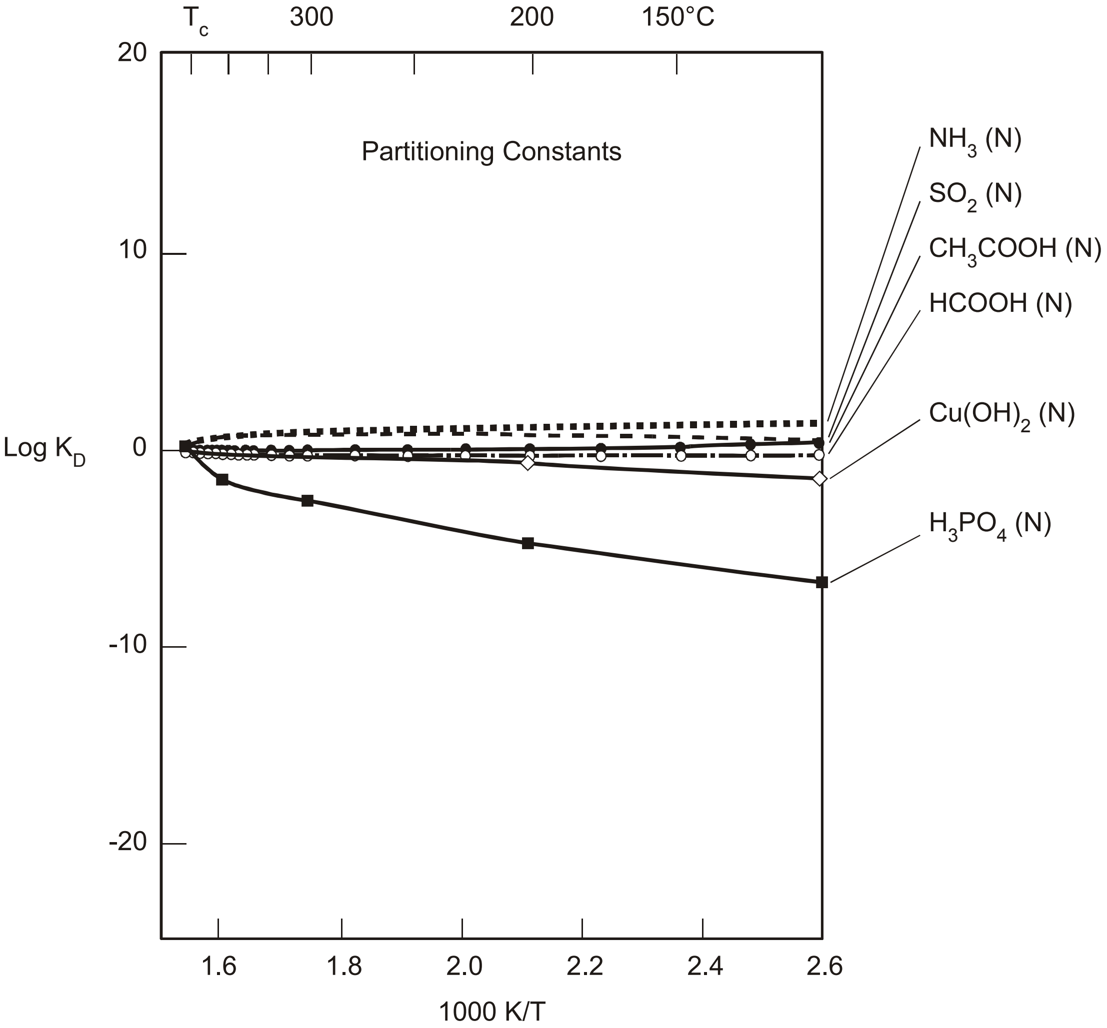

Figure 2-1
Partitioning Constants – Neutral Species

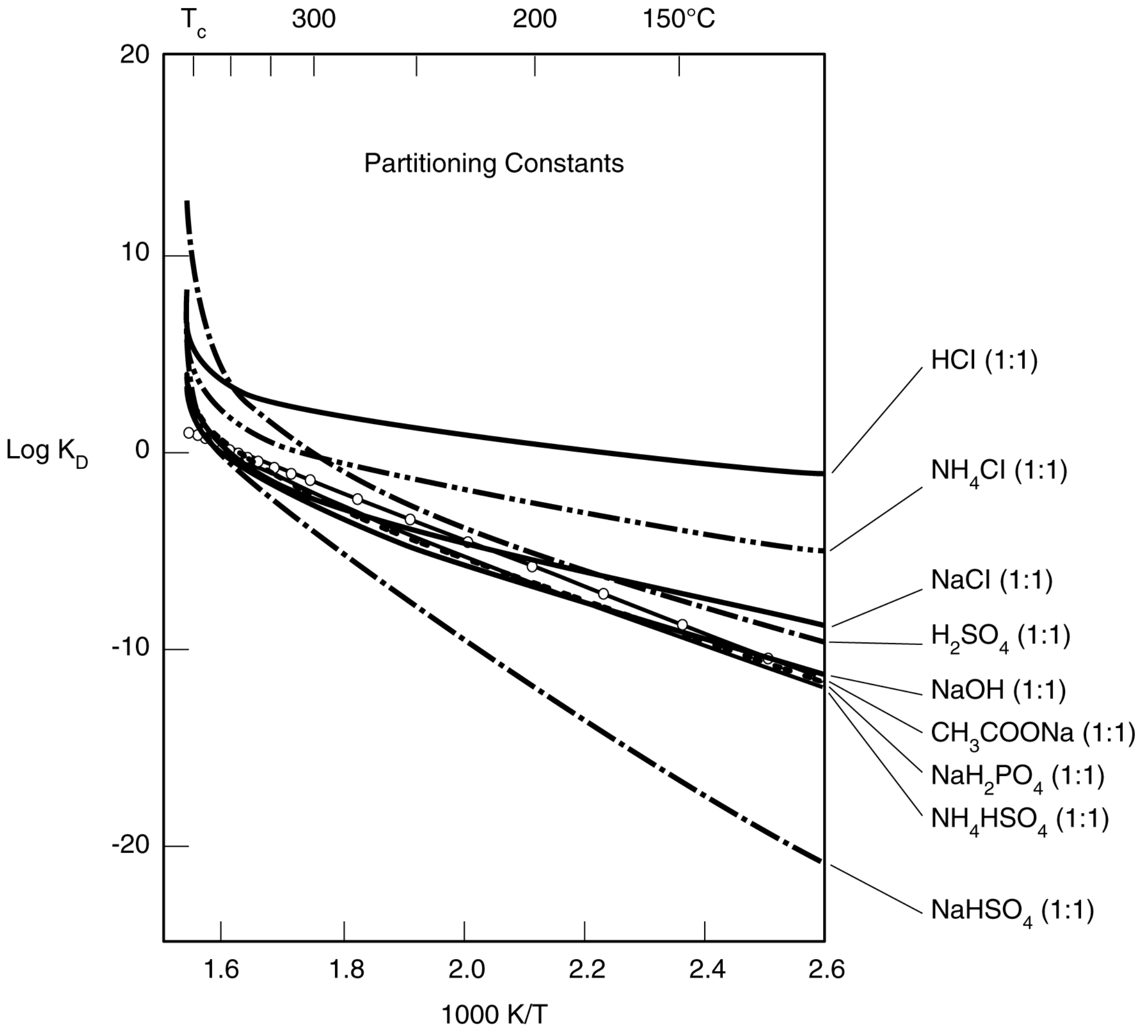

Figure 2-2
Partitioning Constants – 1:1 Compounds

For the volatility and speciation in ammonium chloride solutions, it is important to remember that the solute transports to the vapor phase as mixtures of HCl, NH_3 and NH_4Cl, the relative proportions being dependent on temperature, total chloride, solution pH and the presence of other cations (e.g. Na^+). The difference in pH and the increasing volatility of HCl, accounts for the increased importance of chloride as HCl at high temperatures. Moreover, under AVT conditions the high volatility of NH_3 (coupled with the low volatility of ammonium salts formed by neutralization of acidic contaminants) may lead to lower boiler water pH values than predicted, and hence an increase in the carryover of chloride as HCl.

Further information on the volatility and transport of ammonium chloride and hydrochloric acid is given in the EPRI report[3].

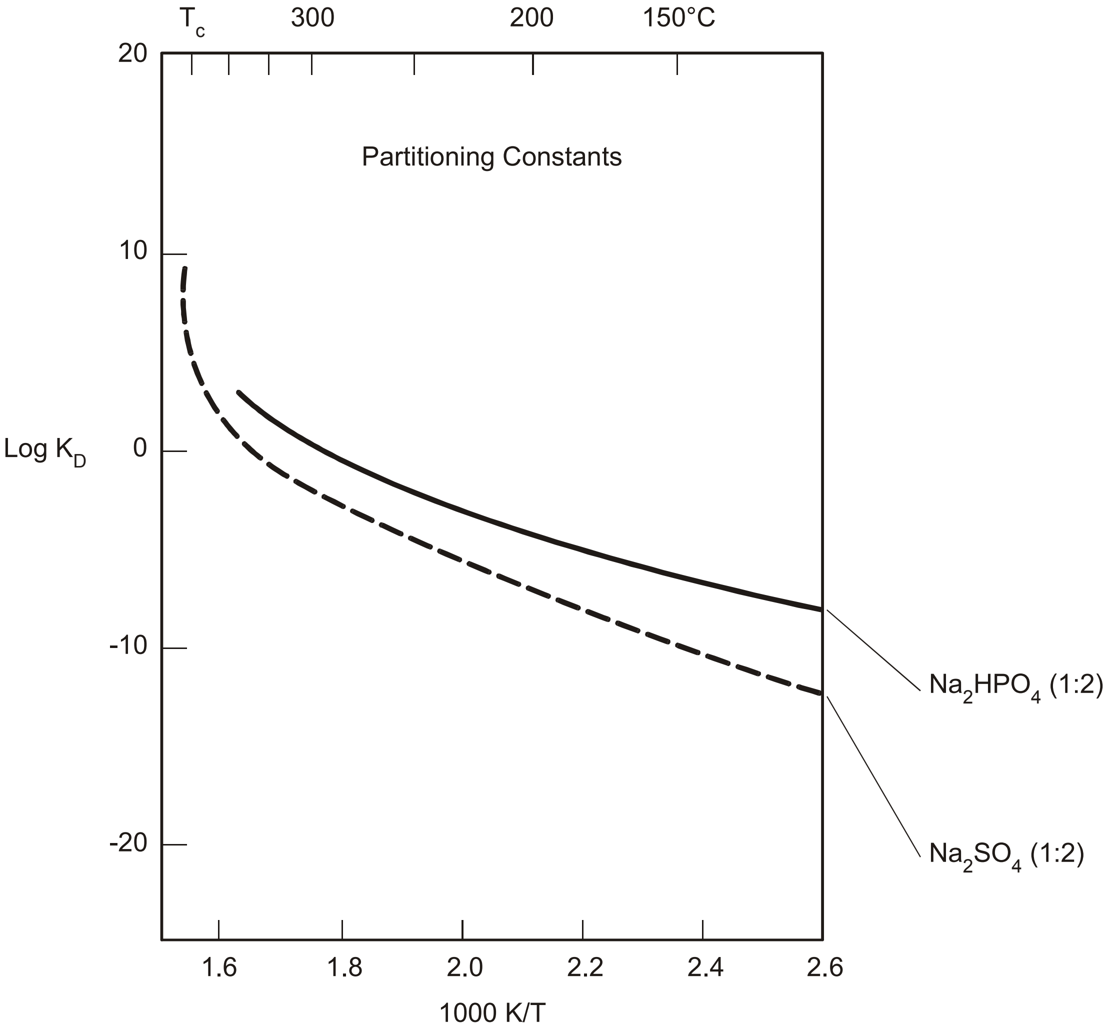

Figure 2-3
Partitioning Constants – 1:2 Compounds

2.3 Sodium Chloride and Sodium Hydroxide

Information on the volatility of NaCl was already available and, as Figure 2-2 shows, it is relatively non-volatile and nowhere near as volatile as NH_4Cl or HCl (all 1:1 compounds). Sodium hydroxide is important for several reasons. It is formed from hydrolysis of sodium phosphate and can be used in its own right as a boiler conditioning chemical. It is also associated with the formation of sodium sulfate, sodium phosphate and sodium chloride, and, therefore, can have an influence on the carryover of sodium. The partitioning data for NaOH were in good agreement with previous results obtained in various flow-through systems.

Sodium hydroxide has a volatility similar to that of NaCl and both are potentially dangerous, since, if they are present in excess in steam, they can concentrate and could cause stress corrosion cracking of austenitic components in superheaters, and of turbine materials.

Further information on the volatility of sodium hydroxide is given in the EPRI report[4].

2.4 Sulfuric Acid and Sulfur Dioxide

The situation with sulfuric acid is more complex than for hydrochloric acid, because it is divalent and can dissociate in two steps, forming bisulfates, as well as sulfates. It is also less volatile than hydrochloric acid, so that a rather different approach was required. The relationships of sulfuric acid volatility were considered in the context of other constituents, including sodium sulfate and bisulfate. Practical measurements were made on sulfuric acid alone and as a member of two series: sulfuric acid/ammonium bisulfate/ammonium sulfate, and sulfuric acid/sodium bisulfate/sodium sulfate.

Although H_2SO_4 can be considered as a 1:1 compound or a 1:2 compound, at high temperatures, it behaves more as a 1:1 compound (and, therefore, is included in Figure 2-2). Sulfuric acid was found to be the dominant form of sulphur (VI) species in steam under most conditions and is the principal transporting medium for the vaporous carryover of sulfate in steam.

Reduced sulphur species (SO_2) were observed in all vapor samples taken over sulfuric acid solutions. The partitioning coefficients for SO_2 obtained from the sulfuric acid volatility data, showed that with increasing pH, the hydrolysis of the weaker sulfurous acid becomes significant and the level of sulfite decreases in the vapor phase. Sulphur dioxide is a neutral species and is very volatile (see Figure 2-1). Reduced sulphur species may provide an important route for the transport of sulfate and sulfite to the steam. The carryover of sulfate should be significantly reduced for plants with oxygenated treatment by eliminating SO_2 transport.

Further information on the volatility and transport of sulfuric acid is given in the EPRI report[5].

2.5 Sodium and Ammonium Sulfates and Bisulfates

Sodium bisulfate and ammonium bisulfate are both 1:1 compounds and their partitioning information is included in Figure 2-2, where they can be compared directly with sulfuric acid. Sodium sulfate is a 1:2 compound and, therefore, is included in Figure 2-3. The curve for Na_2SO_4 (1:2 electrolyte) in Figure 2-3 is higher than that for $NaHSO_4$ (1:1 electrolyte) in Figure 2-2, despite Na_2SO_4 being much less volatile, but for the reasons explained in Section 2.1, the two curves can not be compared directly.

There is a close connection between the volatility of ammonium sulfate and sulfuric acid. Ammonium bisulfate is an important form of sulfate present in steam at high pH under AVT conditions. Sodium bisulfate is also significant with high levels of sodium in the boiler water, whereas ammonium sulfate and sodium sulfate are not significant in steam under any operating conditions, although sodium sulfate can be the dominating species in the boiler water.

The relative volatilities decrease in the order $H_2SO_4 >> NaHSO_4 \cong NaOH > Na_2SO_4$.

Further information on the volatility and transport of sulfates is given in the EPRI reports[4, 5].

2.6 Sodium Phosphate and Phosphoric Acid

Phosphoric acid is classed as a neutral compound, because it is hardly ionized at the temperatures of interest. It could represent a mechanism for transporting phosphates to the steam, but it is less volatile than most of the other neutral compounds investigated (see Figure 2-1). NaH_2PO_4 behaves as a 1:1 compound and is included in Figure 2-2. Na_2HPO_4 behaves as a 1:2 compound and is included in Figure 2-3. NaH_2PO_4 and Na_2HPO_4 have low volatilities and no phosphate at all was detected in the vapor in contact with trisodium phosphate solutions, in the presence of sodium hydroxide.

The relative volatilities decrease in the order $H_3PO_4 > NaH_2PO_4 > Na_2HPO_4 > Na_3PO_4$.

Unless it is a very high pressure/temperature plant (above 2700 psi, 18.6 MPa), or the boiler water pH is abnormally low, it is unlikely that significant amounts of phosphate get into the steam, except by mechanical carryover.

Further information on the partitioning of phosphates is given in the EPRI report[9].

2.7 Copper, Copper Oxides and Hydroxides

Copper can be transported from the copper alloys used in the feedwater heaters to the HP heaters, boiler waterwalls, drums and superheaters, where it can accumulate. It can then be transferred to the turbine, where it can rapidly reduce the output capability of the high pressure section of the turbine. Cupric hydroxide ($Cu(OH)_2$) is a neutral species and is very volatile (see Figure 2-1). It is important to note the high volatility of $Cu(OH)_2$ right across the temperature/pressure range; this means that $Cu(OH)_2$ can partition into steam during early startup periods[11]. This gives a route for the transport of oxidized copper compounds in the boiler water to the steam, where they can deposit in the superheaters and high pressure turbine.

Corrosion of copper alloys in the feedwater heaters is increased by operation under positive oxidizing/reducing (ORP) potentials, and the corrosion products formed on copper alloys, in the presence of oxygen, are prone to supersaturation. Cuprous oxide is the more protective oxide formed on copper alloys, but is easily converted to cupric oxide. Although the solubilities of copper oxides in the boiler water are low, cupric hydroxide is carried over into the steam, because it is very volatile. The solubility of copper hydroxide in steam is dependent on temperature and pressure, but is only a few ppb. This means that copper oxides will deposit from the vapor at pressures below about 2400 psi (16.5 MPa), and then be re-entrained at higher pressures, providing a mechanism for the continued transport of copper. The process can be reduced by minimizing the amount of cupric and cuprous oxides in the boiler water.

The reader is referenced to the new EPRI Copper Guidelines for a full explanation of copper around a fossil plant[11].

Further information on the volatility of copper compounds will be given in the EPRI report; early results are included in reference 10.

2.8 Organic Acids and Salts

As would be expected, organic acids, such as formic and acetic acids ($HCOOH$ and CH_3COOH) form neutral species under the conditions of interest and are included in Figure 2-1. These molecules are very volatile and represent the dominant route for transporting organic compounds to the steam. Sodium acetate (CH_3COONa) is a 1:1 compound and has a low volatility, moreover, at high temperatures the acid forms are stabilized in boiler water relative to the formate and acetate anions, so vaporous carryover is high. Organic acids and their decomposition products, e.g. CO_2, can lead to a reduction in pH.

Further information on the volatility of organic compounds is given in the EPRI report[6].

2.9 Relative Volatilities

As explained in Section 2.1, the partitioning constants for neutral, 1:1 and 1:2 electrolytes cannot be compared directly. The neutral species NH_3, SO_2 and the organic acids are extremely volatile and are almost completely carried over into the steam. Cupric hydroxide is also very volatile. Phosphoric acid is less volatile, but is probably the most significant phosphate species in the steam leaving the boiler as a result of vaporous carryover. Of the 1:1 compounds, HCl is very volatile, NH_4Cl is significantly less volatile, while NaCl, H_2SO_4, NaOH and NH_4HSO_4 are all less volatile, and $NaHSO_4$ the least volatile. Sodium sulfate (1:2) and Na_2HPO_4 (1:2) may be considered as being non-volatile. Trisodium phosphate could not be detected in steam in any of the laboratory studies.

2.10 Oxidizing Versus Reducing Conditions

Oxygenated treatment (OT) should suppress the formation of SO_2 and sulfite from sulfate in the boiler water and hence reduce the overall transport of sulfur containing species to the steam. But the lower pH values allowed for OT, 9.0-9.2 (for drum units)[12, 13], compared with 9.2-9.6 for AVT[14], could lead to increased carryover of chloride as HCl and sulfate as H_2SO_4. Oxidizing conditions will have a profound effect on copper compounds in the boiler water, since copper metal will be oxidized to cupric oxide and supersaturated solutions are readily formed, and $Cu(OH)_2$ will provide a route for transport to the steam[10].

2.11 Speciation in Water and Steam

As a general rule, salts and bases tend to be ionized and remain in boiler water, although the degree of ionization always decreases with increasing temperature. Neutral, non-ionized species are highly favored in the steam phase, so that, if neutral species can be formed, they represent the major route for vaporous carryover of compounds from the boiler water into the steam.

2.12 Conclusions

Some limitations were found when the ray diagram was used in estimating the vaporous carryover of impurities and conditioning chemicals into steam from drum boilers. Measurements have been made on the volatility of salts, and associated acids and bases, likely to be present in boiler water. The results have been used in a new thermodynamic approach, involving the temperature dependence of partitioning constants. The relative volatilities of the various species present can be compared on graphs of partitioning constants plotted against temperature. The results show that acids, such as hydrochloric, sulfuric, acetic and formic, are volatile and provide routes for the transport of salts. Under reducing conditions, sulfite carryover as SO_2 is also very significant. Other substances, e.g. cupric hydroxide, were found to be very volatile, but phosphates have a low volatility.

3

THE MODEL, PREDICTIONS AND EXAMPLES

3.1 Introduction

Before describing the model, it is appropriate first to consider the mechanisms affecting the carryover of impurities from the boiler water to the steam.

First is the pressure versus saturation temperature relationship. This curve, prepared from the steam tables, is shown in Figure 3-1. For each pressure, there is a corresponding equilibrium temperature.

The vaporous carryover of almost all constituents increases with temperature. But vaporous carryover not only depends on the temperature for the species of interest, but also on the conditions, and the presence and interactions between species. While a single line can be drawn for a single species under a single set of conditions, a continuous set of curves would be required for each component for each set of conditions, which becomes impracticable. For illustrative purposes only, Figure 3-2 shows the trend curves for sodium, chloride and sulfate concentrations in steam for an example of boiler water conditions with all-volatile treatment.

Mechanical carryover depends on the boiler drum steam separation system and drum level.
The performance for steam separation reduces as the pressure increases, because the difference between the density of the steam and that of the water, decreases. Figure 3-3 shows the densities of water and steam, and their ratios, up to the critical pressure.

Mechanical carryover is a function of the ratio of the densities and reaches 100% at the critical pressure. EPRI[12 - 15] derived a practical relationship for mechanical carryover versus pressure for use in developing guideline limits. It should be noted that this curve includes a safety factor of 2 (see Figure 3-4), and that actual values should be derived for each drum boiler. This curve is used in all EPRI guidelines, together with the predictions for vaporous carryover (previously from the ray diagram), to calculate the limits for impurities in the boiler water, to prevent the impurities in steam from exceeding the permitted concentrations.

Examples using the new approach described in this report are included later in this section to illustrate the effects of temperature and pressure on vaporous and mechanical carryover for all-volatile treatments (AVT/OT), phosphate treatment (PT), equilibrium phosphate treatment (EPT) and caustic treatment (CT), for normal and upset conditions, such as condenser leaks, acid and caustic ingress.

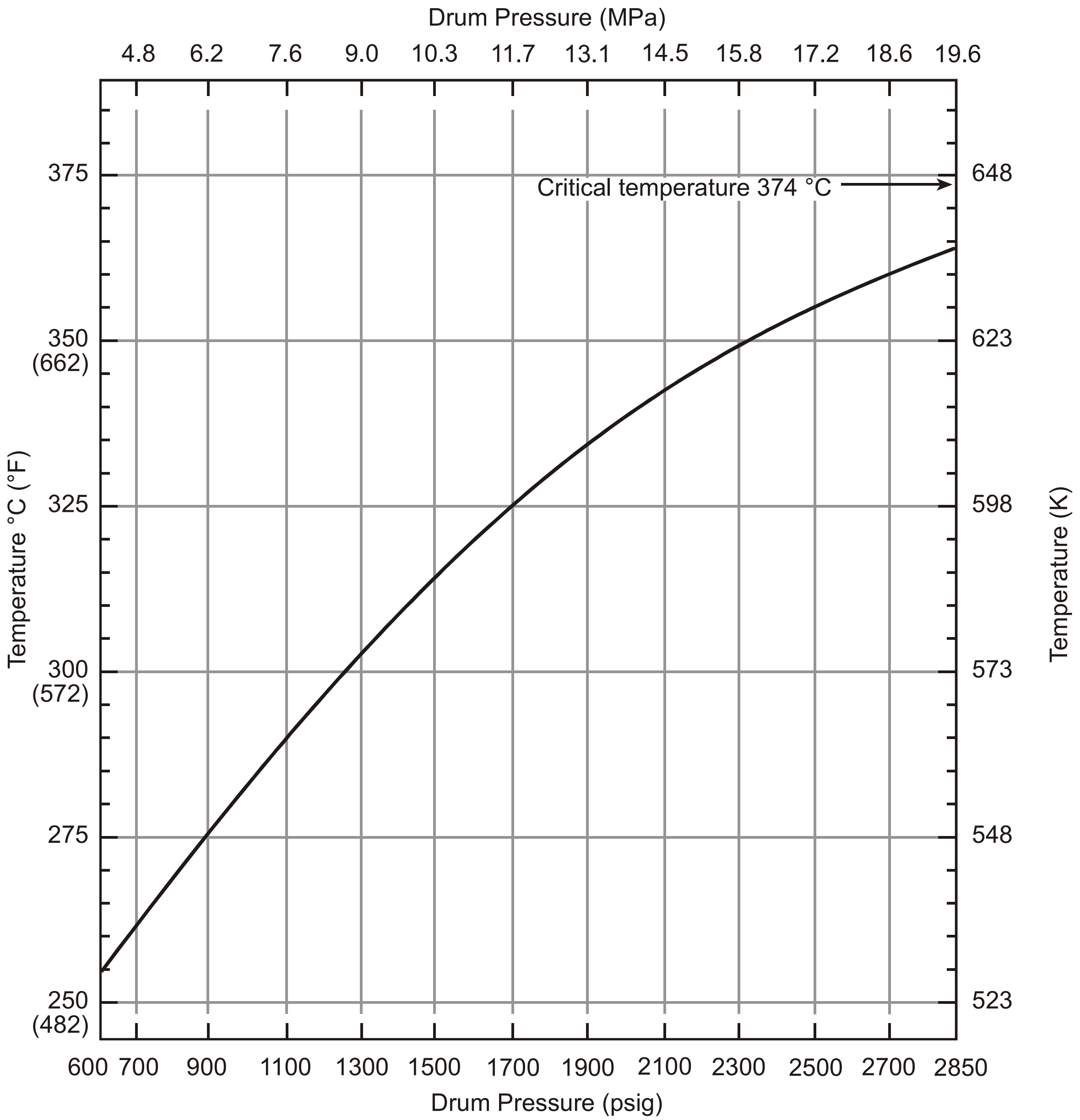

Figure 3-1
Pressure vs Steam Saturation Temperature

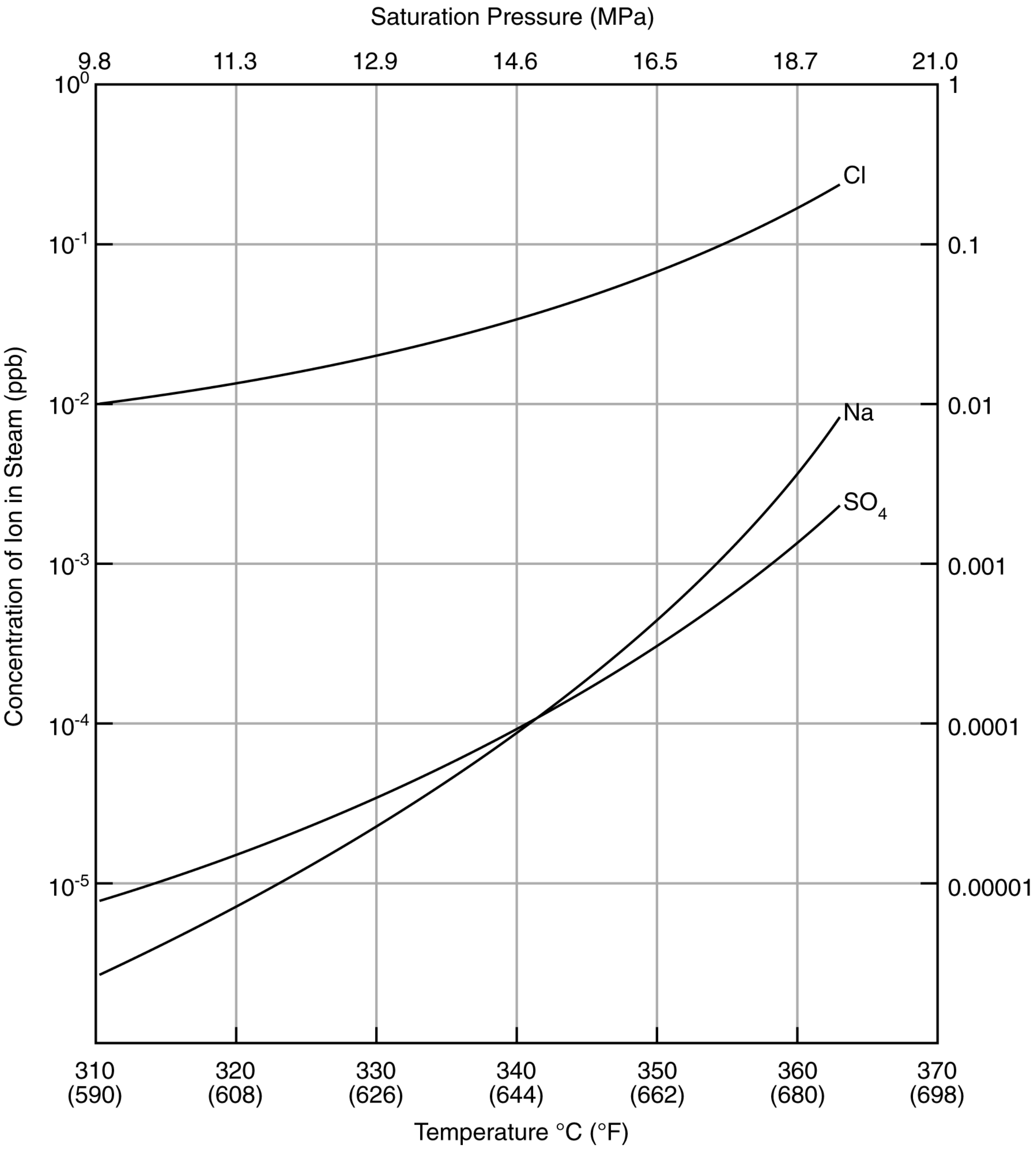

Figure 3-2
An Example of Vaporous Carryover vs Temperature for All-Volatile Treatment (Trends)

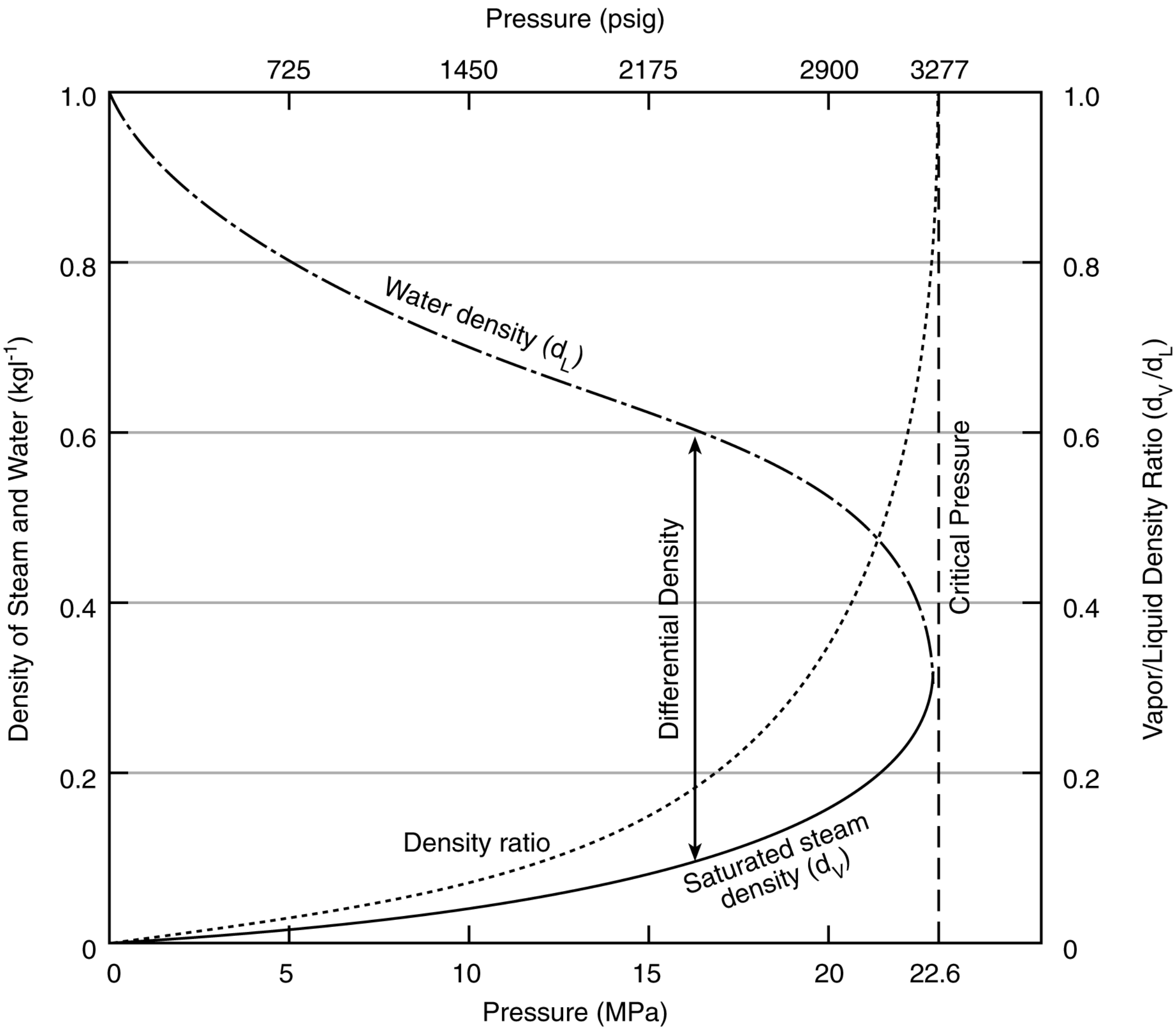

Figure 3-3
Water and Steam Densities and Ratios vs Pressure

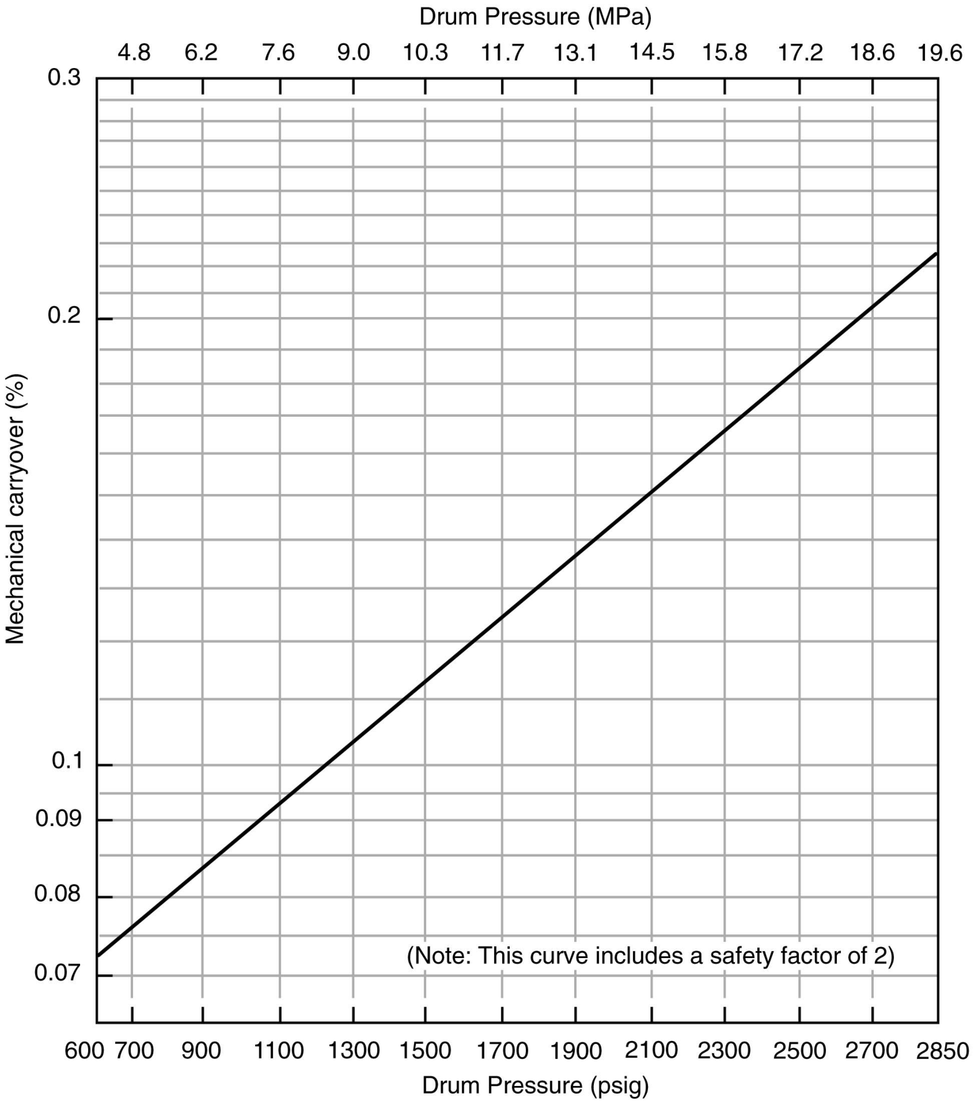

Figure 3-4
Mechanical Carryover vs Pressure [1, 12 - 15]

3.2 The Model

The aim was to incorporate the partitioning constants of the substances commonly found in water/steam circuits (provided in Appendix) and the related liquid phase equilibria, into a computer code. This allows predictions to be made of the composition of the boiler water, steam and condensate in utility water/steam circuits. The exact calculations depend on the type of plant, e.g. drum or once-through. For this report, some initial preliminary examples are described for drum units in Section 3.3. Over the next year, when all the partitioning data are incorporated into the code more comprehensive examples will be developed. These results will then be tested against actual plant data. The approach will also be used to modify the EPRI Treatment Guidelines for optimum plant operation and predict the consequences of abnormal water chemistries and the use of attemperation.

The code incorporates the partitioning constants of the compounds, the hydrolysis reactions at high temperatures and hence the information required to calculate pH, and finally an activity coefficient model to deal with the thermodynamics of more concentrated solutions, e.g. the early condensate formed in the LP turbine. Mass and charge balances are used to ensure the consistency of the values obtained. The first step is to calculate the composition of the boiler water at a given temperature, usually 25°C (77°F) and establish the mass and charge balances by adjusting the pH or concentration of a given compound. Second, the concentration at the appropriate boiler temperature is calculated. Third, the composition of the steam in equilibrium with the boiler water at the boiler temperature is determined from the partitioning constants. The next step is to calculate the composition of the steam when cooled to condensate temperature. Calculation of the composition of early condensate in equilibrium with the steam is more complicated due to large changes in liquid composition that occur with varying degrees of condensation. It is an iterative process involving estimating the molalities and activity coefficients of the various constituents, using the partitioning and ionization constants, and the charge and mass balance equations. Once convergence is obtained, the composition and pH can be calculated. The specific and cation conductivities of the condensate can also be estimated.

Equilibrium conditions are assumed to apply all around the water/steam circuit with no precipitation or adsorption effects being considered. Moreover, by assuming that equilibrium conditions apply, the amount of vaporous carryover represents the maximum vaporous carryover that is expected to occur. In a real plant, this might be overwhelmed by mechanical carryover. The effects of mechanical carryover and attemperation sprays are also included in the program. It should also not be forgotten that in a turbine, the phase transition zone does not represent equilibrium conditions.

The model can predict the vaporous carryover alone, which is valuable in determining the extent of this effect in the absence of mechanical carryover, and with various degrees of mechanical carryover. Note that in power plant boilers, vaporous carryover is always accompanied to some degree by mechanical carryover and further impurities can reach the steam via attemperation sprays. The program includes AVT and OT, PT, EPT and CT, but at this stage does not discriminate between oxidizing and reducing conditions. Therefore, it does not take into account the specific effects of reducing conditions with AVT or oxidizing conditions with OT, although the latter case is more closely represented in the predictions of the code.

3.3 Results from applying the Model to Case Studies

Where chloride and sulfates are contaminant anions and sodium is present, solute species partitioning between phases could include a large number of components, eg. NH_3, NH_4Cl, NH_4HSO_4, $(NH_4)_2SO_4$, NaCl, $NaHSO_4$, Na_2SO_4, HCl, H_2SO_4, H_3PO_4 NaH_2PO_4, Na_2HPO_4 and NaOH. The relative amounts of each will depend on the temperature, pH and composition of the solution, and the volatility of the individual compounds. Wide variations in both the composition and pH of early condensate liquids may be found, depending on the particular conditions of boiling and condensation. The composition of early condensate will also depend strongly on the extent of condensation. Clearly, if the steam is taken completely to liquid, the bulk composition of the liquid will reflect that of the steam from which it was formed. However, the decrease in distribution constant values with decreasing temperature for most solutes (excepting NH_3 in these examples) enhances the concentration of relatively non-volatile solutes in early condensate as compared with their concentration in steam.

Predictions using the Model

Predictions were made for AVT/OT, CT, EPT and PT for drum boilers operating at 2400 psi (16.5 MPa) and 2800 psi (19.3 MPa), over a range of boiler water pH conditions, simulating sea water, sulfuric acid and sodium hydroxide ingresses, with purely vaporous carryover and with various degrees of mechanical carryover. Results were also derived for the concentration of impurities in the steam at boiler temperature and in early condensate (using 0.1% condensation in the examples) at 25°C (77°F). Examples of the results obtained for a 2400 psi (16.5 MPa) boiler under normal and "upset" conditions are given in Tables 3-1 to 3-4 for the various methods of chemical treatments. "Normal" conditions refer to a unit operating within the normal EPRI guideline range. "Upset" conditions refer to seawater ingress to the boiler water as defined on the tables.

It should be noted that these examples may not be applicable to all operating conditions. For example, the results for sulfuric acid and sodium hydroxide ingress, and 2800 psi (19.3MPa) are not included in these tables.

Table 3-1
All-Volatile Treatment, 16.5 MPa (2400 psi) Pressure, Boiler Water pH 9.2

Part A: No Mechanical Carryover (All-Ferrous Feedwater Heaters)

	Boiler Water		Steam		Early Condensate 25°C (0.1% moisture)	
	Normal	Upset*	Normal	Upset*	Normal	Upset*
pH (at 25°C)	9.2	9.2	9.43	9.43	8.93	8.77
Ammonia (ppb)	530	540	1210	1230	230	300
Sodium (ppb)	28	750	<0.1	<0.1	<0.1	10
Chloride (ppb)	25	1025	<0.1	0.3	12	260
Sulfate (ppb)	25	180	<0.1	<0.1	0.1	1.9
SC (μS/cm)	4.53	8.50	7.43	7.49	2.38	2.72
CC (μS/cm)	0.53	13.8	0.055	0.056	0.16	3.10

Part B: As Above, with 0.05% Mechanical Carryover

	Boiler Water		Steam		Early Condensate 25°C (0.1% moisture)	
	Normal	Upset*	Normal	Upset*	Normal	Upset*
pH (at 25°C)	9.2	9.2	9.43	9.43	8.93	8.77
Ammonia (ppb)	530	540	1210	1230	230	300
Sodium (ppb)	28	750	<0.1	0.4	14	390
Chloride (ppb)	25	1025	<0.1	0.8	25	770
Sulfate (ppb)	25	180	<0.1	0.1	13	91
SC (μS/cm)	4.53	8.50	7.43	7.49	2.46	4.78
CC (μS/cm)	0.53	13.8	0.055	0.059	0.41	10.0

Upset* conditions equivalent to seawater ingress of 1 ppm chloride, added as 1.65 ppm NaCl and 0.226 ppm Na_2SO_4 to the boiler water. (1 ppm ≡ 1 mg/kg; 1 ppb ≡ 1 μg/kg).
SC = Specific Conductivity, CC = Cation Conductivity

Table 3-2
Caustic Treatment, 16.5 MPa (2400 psi) Pressure, Boiler Water pH 9.4

Part A: No Mechanical Carryover (All-Ferrous Feedwater Heaters)

	Boiler Water		Steam		Early Condensate 25°C (0.1% moisture)	
	Normal	**Upset***	**Normal**	**Upset***	**Normal**	**Upset***
pH (at 25°C)	9.4	9.4	8.55	8.61	8.30	8.30
Ammonia (ppb)	32	38	74	87	38	45
Sodium (ppb)	820	1550	<0.1	<0.1	6	30
Chloride (ppb)	200	1200	<0.1	0.1	7	56
Sulfate (ppb)	250	400	<0.1	<0.1	1.3	3.9
SC (μS/cm)	7.75	11.7	0.97	1.12	0.57	0.76
CC (μS/cm)	4.62	17.9	0.055	0.055	0.115	0.71

Part B: As Above, with 0.05% Mechanical Carryover

	Boiler Water		Steam		Early Condensate 25°C (0.1% moisture)	
	Normal	**Upset***	**Normal**	**Upset***	**Normal**	**Upset***
pH (at 25°C)	9.4	9.4	8.55	8.61	9.10	9.09
Ammonia (ppb)	32	38	74	87	11	13
Sodium (ppb)	820	1550	0.4	0.8	420	800
Chloride (ppb)	200	1200	0.1	0.7	110	660
Sulfate (ppb)	250	400	0.1	0.2	130	210
SC (μS/cm)	7.75	11.7	0.98	1.12	3.91	5.99
CC (μS/cm)	4.62	17.9	0.056	0.059	2.40	9.67

Upset* conditions equivalent to seawater ingress of 1 ppm chloride, added as 1.65 ppm NaCl and 0.226 ppm Na_2SO_4 to the boiler water. (1 ppm ≡ 1 mg/kg; 1 ppb ≡ 1 μg/kg).
SC = Specific Conductivity, CC = Cation Conductivity

Table 3-3
Equilibrium Phosphate Treatment, 16.5 MPa (2400 psi) Pressure, Boiler Water pH 9.4

Part A: No Mechanical Carryover (All-Ferrous Feedwater Heaters)

	Boiler Water		Steam		Early Condensate 25°C (0.1% moisture)	
	Normal	**Upset***	**Normal**	**Upset***	**Normal**	**Upset***
pH (at 25°C)	9.4	9.4	9.05	9.06	8.29	8.26
Ammonia (ppb)	140	145	320	330	120	120
Sodium (ppb)	1010	1730	<0.1	<0.1	15	46
Chloride (ppb)	25	1025	<0.1	<0.1	0.9	48
Sulfate (ppb)	25	180	<0.1	<0.1	0.1	1.7
Phosphate (ppb)	950	950	0.2	0.3	240	260
SC (µS/cm)	8.24	12.2	3.08	3.15	1.03	1.22
CC (µS/cm)	4.35	17.6	0.055	0.056	0.99	1.65

Part B: As Above, with 0.05% Mechanical Carryover

	Boiler Water		Steam		Early Condensate 25°C (0.1% moisture)	
	Normal	**Upset***	**Normal**	**Upset***	**Normal**	**Upset***
pH (at 25°C)	9.4	9.4	9.05	9.06	8.94	8.92
Ammonia (ppb)	140	145	320	330	48	51
Sodium (ppb)	1010	1730	0.5	0.9	520	910
Chloride (ppb)	25	1025	<0.1	0.6	13	560
Sulfate (ppb)	25	180	<0.1	0.1	13	91
Phosphate (ppb)	950	950	0.7	0.7	710	730
SC (µS/cm)	8.24	12.2	3.08	3.08	3.54	5.64
CC (µS/cm)	4.35	17.6	0.056	0.056	3.15	10.5

Upset* conditions equivalent to seawater ingress of 1 ppm chloride, added as 1.65 ppm NaCl and 0.226 ppm Na_2SO_4 to the boiler water. (1 ppm ≡ 1 mg/kg; 1 ppb ≡ 1 µg/kg).
SC = Specific Conductivity, CC = Cation Conductivity

Table 3-4
Phosphate Treatment, 16.5 MPa (2400 psi) Pressure, Boiler Water pH 9.4

Part A: No Mechanical Carryover (All-Ferrous Feedwater Heaters)

	Boiler Water		Steam		Early Condensate 25°C (0.1% moisture)	
	Normal	**Upset***	**Normal**	**Upset***	**Normal**	**Upset***
PH (at 25°C)	9.4	9.4	9.20	9.20	8.08	8.01
Ammonia (ppb)	230	230	530	530	170	180
Sodium (ppb)	2380	3100	0.1	0.2	88	150
Chloride (ppb)	500	1500	<0.1	0.1	27	100
Sulfate (ppb)	800	950	<0.1	<0.1	8	12
Phosphate (ppb)	2470	2470	0.6	0.6	560	620
SC (μS/cm)	14.7	18.6	4.34	4.38	1.57	1.88
CC (μS/cm)	22.9	36.1	0.056	0.056	2.68	3.82

Part B: As Above, with 0.05% Mechanical Carryover

	Boiler Water		Steam		Early Condensate 25°C (0.1% moisture)	
	Normal	**Upset***	**Normal**	**Upset***	**Normal**	**Upset***
PH (at 25°C)	9.4	9.4	9.20	9.20	8.71	8.68
Ammonia (ppb)	230	230	530	530	78	80
Sodium (ppb)	2380	3100	1.3	1.7	1280	1700
Chloride (ppb)	500	1500	0.3	0.8	280	850
Sulfate (ppb)	800	950	0.4	0.5	410	490
Phosphate (ppb)	2470	2470	1.8	1.9	1800	1860
SC (μS/cm)	14.7	18.6	4.34	4.39	6.52	8.74
CC (μS/cm)	22.9	36.1	0.061	0.065	14.1	21.9

Upset* conditions equivalent to seawater ingress of 1 ppm chloride, added as 1.65 ppm NaCl and 0.226 ppm Na_2SO_4 to the boiler water. (1 ppm ≡ 1 mg/kg; 1 ppb ≡ 1 μg/kg).
SC = Specific Conductivity, CC = Cation Conductivity

3.4 Discussion of Results

All-Volatile Treatment (AVT/OT)

For AVT a second example of modelling has been included in Tables 3-5 to 3-7 to illustrate the effect of varying boiler water pH (8.5, 9.2, and 9.6). It should be noted that the conditions in these tables are slightly different to those used in Table 3-1. Unlike Table 3-1, the concentrations in the steam and early condensate are not rounded off to the nearest 0.1 ppb to illustrate the effects of varying boiler water pH.

- the sodium concentration of the boiler water is set at slightly in excess of the stoichiometric equivalents of chloride and sulfate.
- The upset conditions are less severe than in Table 3-1.
- The mechanical carryover in Tables 3-5 to 3-7 is set at 0.1% compared with 0.05% in Table 3-1.

Table 3-5
All-Volatile Treatment, 16.5 MPa (2400 psi), Boiler Water pH 8.5

Part A: No Mechanical Carryover (All Ferrous Feedwater Heaters)

	Boiler Water		**Steam**		**Early Condensate 25°C (0.1% moisture)**	
	Normal Target	**Minor Upset**	**Normal Target**	**Minor Upset**	**Normal Target**	**Minor Upset**
pH (at 25°C)	8.5	8.5			8.33	8.29
Ammonia (ppb)	41	41	94	94	45	48
Sodium (ppb)	55	140	<0.001	<0.001	0.038	0.28
Chloride (ppb)	25	100	0.007	0.021	7.1	21
Sulfate (ppb)	25	100	<0.001	<0.001	0.054	0.27
SC (μS/cm)	1.00	1.47			0.62	0.63
CC (μS/cm)	0.53	2.09			0.108	0.26

Part B: As Above with 0.1% Mechanical Carryover

	Boiler Water		**Steam**		**Early Condensate 25°C (0.1% moisture)**	
	Normal Target	**Minor Upset**	**Normal Target**	**Minor Upset**	**Normal Target**	**Minor Upset**
pH (at 25°C)	8.5	8.5			8.45	8.41
Ammonia (ppb)	41	41	94	94	37	39
Sodium (ppb)	55	140	0.055	0.14	55	140
Chloride (ppb)	25	100	0.032	0.12	32	121
Sulfate (ppb)	25	100	0.025	0.10	25	100
SC (μS/cm)	1.00	1.47			0.93	1.39
CC (μS/cm)	0.53	2.09			0.61	2.34

SC = Specific Conductivity, CC = Cation Conductivity

Table 3-6
All-Volatile Treatment, 16.5 MPa (2400 psi), Boiler Water pH 9.2

Part A: No Mechanical Carryover (All Ferrous Feedwater Heaters)

	Boiler Water		**Steam**		**Early Condensate 25°C (0.1% moisture)**	
	Normal Target	**Minor Upset**	**Normal Target**	**Minor Upset**	**Normal Target**	**Minor Upset**
pH (at 25°C)	9.2	9.2			8.92	8.91
Ammonia (ppb)	495	495	1130	1130	220	220
Sodium (ppb)	55	140	<0.001	<0.001	0.039	0.28
Chloride (ppb)	25	100	0.007	0.021	6.8	21
Sulfate (ppb)	25	100	<0.001	<0.001	0.062	0.30
SC (μS/cm)	4.50	4.97			2.30	2.30
CC (μS/cm)	0.53	2.09			0.106	0.26

Part B As Above, with 0.1% Mechanical Carryover

	Boiler Water		**Steam**		**Early Condensate 25°C (0.1% moisture)**	
	Normal Target	**Minor Upset**	**Normal Target**	**Minor Upset**	**Normal Target**	**Minor Upset**
pH (at 25°C)	9.2	9.2			8.92	8.94
Ammonia (ppb)	495	495	1130	1130	210	210
Sodium (ppb)	55	140	0.055	0.14	55	140
Chloride (ppb)	25	100	0.032	0.12	32	120
Sulfate (ppb)	25	100	0.025	0.10	25	100
SC (μS/cm)	4.50	4.97			2.59	3.06
CC (μS/cm)	0.53	2.09			0.61	2.34

SC = Specific Conductivity, CC = Cation Conductivity

Table 3-7
All-Volatile Treatment, 16.5 MPa (2400 psi), Boiler Water pH 9.6

Part A: No Mechanical Carryover (All Ferrous Feedwater Heaters)

	Boiler Water		Steam		Early Condensate 25°C (0.1% moisture)	
	Normal Target	Minor Upset	Normal Target	Minor Upset	Normal Target	Minor Upset
pH (at 25°C)	9.6	9.6			9.26	9.25
Ammonia (ppb)	2260	2260	5170	5175	660	665
Sodium (ppb)	55	140	<0.001	<0.001	0.042	0.28
Chloride (ppb)	25	100	0.006	0.020	6.3	20
Sulfate (ppb)	25	100	<0.001	<0.001	0.089	0.39
SC (μS/cm)	11.2	11.6			5.03	5.04
CC (μS/cm)	0.53	2.09			0.101	0.26

Part B: As Above with 0.1% Mechanical Carryover

	Boiler Water		Steam		Early Condensate 25°C (0.1% moisture)	
	Normal Target	Minor Upset	Normal Target	Minor Upset	Normal Target	Minor Upset
pH (at 25°C)	9.6	9.6			9.27	9.27
Ammonia (ppb)	2260	2260	5165	5170	650	655
Sodium (ppb)	55	140	0.055	0.14	55	140
Chloride (ppb)	25	100	0.031	0.12	31	120
Sulfate (ppb)	25	100	0.025	0.10	25	100
SC (μS/cm)	11.2	11.6			5.32	5.80
CC (μS/cm)	0.53	2.09			0.60	2.33

SC = Specific Conductivity, CC = Cation Conductivity

The results show that chloride is by far the most volatile inorganic anion. There is a slight pH effect, where increasing the boiler water pH reduces the amount of chloride carried over into the steam by vaporous carryover.

Increasing the chloride and sulfate content of the boiler water to simulate sea water ingress, increases the chloride content of the steam and early condensate, but less than in proportion to the increase in the boiler water (Table 3-1). Simulating the ingress of sulfuric acid by adding ammonium sulfate to the boiler water, not only increases the amounts of sulfate in the steam and early condensate, but also the chloride concentrations. Simulating sodium hydroxide ingress increases the vaporous carryover of sodium but reduces the chloride content of the steam and early condensate.

Chloride is much more volatile than sulfate and sodium. Chloride is transported largely as hydrochloric acid, with ammonium chloride playing only a minor role, and sodium chloride hardly any role at all. Sulfate is normally transported as sulfuric acid, with ammonium bisulfate and sodium bisulfate playing significant roles under certain conditions. Sodium sulfate plays no measurable role.

The chloride contents of the steam and early condensate from vaporous carryover are doubled by relatively small amounts of mechanical carryover (e.g. 0.05%) (Table 3-1). Because the volatilities of sodium and sulfate are much lower than chloride, the concentrations of these constituents can be doubled by even smaller amounts of mechanical carryover.

Caustic Treatment (CT)

Compared with AVT, the addition of sodium hydroxide to the boiler water significantly reduces the amount of chloride carried over into the steam by vaporous carryover. It also counteracts the effects of sulfuric acid ingress better than AVT. However, there is a need to strictly limit the amount of mechanical carryover (e.g. <0.1%) to reduce the risk of exceeding the limits for sodium in steam (see Table 3-2). The pH at boiler operating temperatures is considerably higher under CT compared to AVT, because of hydrolysis of ammonia at high temperatures.

Equilibrium Phosphate Treatment (EPT)

The vaporous carryover of chloride is significantly lower with EPT than for AVT (compare Tables 3-1 and 3-3). EPT deals much better with sulfuric acid ingress than AVT, particularly in suppressing chloride vaporous carryover.

The vaporous carryover of sodium (and phosphate) are higher than with AVT and, surprisingly, sodium carryover is higher than with CT. Disproportionate amounts of phosphate, compared to sodium, in the boiler water, are carried over into the steam and reach the early condensate. This high level of phosphate in the early condensate is also counter to measurements of early condensate and liquid films in the model turbine(16). As with CT, there is a need to carefully restrict the amount of mechanical carryover to limit the concentration of sodium in steam.

Phosphate Treatment (PT)

As with CT and EPT, the vaporous carryover of chloride with PT is also relatively lower than with AVT (compare Tables 3-1 and 3-4). Sulfuric acid ingress considerably increases the vaporous carryover of sulfate and, to a lesser degree, chloride. Sodium hydroxide ingress increases the carryover of sodium and, to a lesser extent, chloride. There are always disproportionately larger amounts of phosphate than sodium in the steam and early condensate, than in the boiler water. Again the high levels of phosphate in the early condensate are counter to the measurements in the model turbine(16).

Because the concentrations in the boiler water are much higher than for EPT, the concentrations of sodium and phosphate in steam and early condensate are higher due to both vaporous and mechanical carryover. A relatively small amount of mechanical carryover (e.g. 0.02%) can more than double the amount of chloride already present in the steam due to vaporous carryover. Strict limits for mechanical carryover need to be applied for sodium (and phosphate) to prevent exceeding the limits for steam.

General Findings

The concentrations of impurities in the steam due to carryover can reach ppb levels and those in early condensate (0.1% condensation), ppm levels. Unless the boiler water is very pure, even small amounts of mechanical carryover are likely to produce more impurities in the steam and early condensate than vaporous carryover. However, in all cases simulated for this report the steam composition remains within EPRI guidelines(12 - 15).

Increasing the operating pressure from 16.5 MPa to 19.3 MPa (2400 psi to 2800 psi) increases the saturation temperature from 350°C to 363°C and the vaporous carryover by a factor of two. Increasing the operating pressure also increases the amount of mechanical carryover by about 50%, so that increasing the operating pressure considerably increases the concentrations of impurities in the steam and early condensate.

3.5 Conclusions

The equilibrium-based computer model allows predictions to be made of the composition of the steam and early condensate from the composition of the boiler water, for various forms of chemical conditioning and operating conditions. The initial qualitative simulations have shown that the concentrations of impurities in steam can reach ppb levels and those in early condensate, ppm levels; much in agreement with field measurements. Chloride is much more volatile than sulfate as seen in all early condensate sampling. Chloride is transported mainly as hydrochloric acid and sulfate as sulfuric acid, though ammonium and sodium bisulfates can also play a role.

Caustic treatment, equilibrium phosphate treatment and phosphate treatment reduce the amount of chloride transported to the steam by vaporous carryover, but increase the amount of sodium (and phosphate) in the steam. With phosphate treatment, it is predicted that a disproportionate amount of phosphate, compared to sodium, will be carried over into the steam by vaporous carryover. Even a small amount of mechanical carryover produces significantly more impurities in steam compared to vaporous carryover under most conditions, unless the boiler water is very pure.

The measurement of total carryover from a drum to saturated steam has always been an integral part of the derivation of EPRI guideline limits. These results demonstrate clearly again the importance of measuring and controlling mechanical carryover. Future revisions of EPRI guidelines will include guidance on drum boiler carryover and the necessary testing to verify compliance. Drum level control will be a key part of this overall control.

During the next stage of this study, the remaining partitioning constants will be incorporated into the model, and then more comprehensive simulations can be performed. These will include two stage boiler contamination which might involve: (a) ingress of sea water followed by the introduction of caustic or phosphate, or (b) adjustment of ammonia levels during high caustic excursions. The effects of organic acids on the early condensate (and liquid film) compositions will be included. The effect of attemperation will also need to be considered.

Although a very early version of this code is incorporated into EPRI's ChemExpert, the final version will become an inherent feature of later ChemExpert software.

4
REFERENCES

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EQUATIONS FOR PARTITIONING CONSTANTS

The temperature dependence of the partitioning constants, as illustrated in Figures 2-1, 2-2 and 2-3, are given by the following equations:

Hydrochloric acid (1:1) - $\log K_D(HCl) = -13.4944 - \frac{934.466}{T} - 11.0029\log\rho_l + 5.4847\log T$

Ammonium bisulfate (1:1) -

$$\log K_D(NH_4HSO_4) = 2.612 - \frac{3355}{T} - 2.2632\times\frac{10^5}{T^2} + 3.984\times\frac{10^7}{T^3} + \left(-13.957 + \frac{1262.3}{T} - 8.5641\times\frac{10^5}{T^2}\right)\log\rho_l$$

Ammonium chloride (1:1) - $\log K_D(NH_4Cl) = -1.875 - \frac{1248.65}{T} - 23.401\log\rho_l$

Ammonia (N) - $\log K_D(NH_3) = -0.056 + \frac{458.71}{T} + 1.3267\log\rho_l$

Sulfuric acid (1:1) - $\log K_D(H_2SO_4) = -1.81 - \frac{7317}{T} - 6.203\log\rho_l$

Sulfur dioxide (N) - $\log K_D(SO_2) = -1.175(\frac{1}{T_r} - 1) + 2.840\log\rho_r$

Sodium hydroxide (1:1) - $\log K_D(NaOH) = 4.713 - \frac{11077}{T} - \log K_w(H_2O)$

Sodium sulfate (1:2) - $\log K_D(Na_2SO_4) = -3.762 - \frac{9298}{T} - \log K_w(H_2O) - \log K_{12}(NaHSO_4)$

Sodium bisulfate (1:1) - $\log K_D(NaHSO_4) = 19.62 - \frac{20208}{T} - \log K_w(H_2O)$

Acetic acid (N) - $\log K_D(CH_3COOH) = -\frac{85.15}{T_C}\left(\frac{1}{T_r} - 1\right) - 0.01647\log\rho_r$

Formic acid (N) - $$\log K_D(HCOOH) = -\frac{0.1380}{T_C}\left(\frac{1}{T_r}-1\right) - 0.6340\log\rho_r$$

Cupric hydroxide (N) - $$\log K_D(Cu(OH)_2) \approx 0$$

Phosphoric acid (N) - $$\log K_D(H_3PO_4) = -\frac{3868.89}{T_C}\left(\frac{1}{T_r}-1\right) - 5.817\log\rho_r$$

Sodium dihydrogen phosphate (1:1) - $$\log K_D(NaH_2PO_4) = 6 + \frac{283.20}{T_C}\left(\frac{1}{T_r}-1\right) - 24.00\log\rho_r$$

Disodium hydrogen phosphate (1:2) - $$\log K_D(Na_2HPO_4) = 11 + \frac{1269.84}{T_C}\left(\frac{1}{T_r}-1\right) - 30.98\log\rho_r$$

Where:

(N) represents neutral species and (1:1) and (1:2) the ionic dissociated species,

$\log K_D$ is the logarithm of the ratio of the concentration in the vapor and the activities of the ions in the liquid phases,

T is the temperature in Kelvin,

ρ_l is the density of the liquid phase,

T_r is the reduced temperature (T/T_C, where T_C = 647K),

ρ_r is the reduced density of water (ρ_l/ρ_C, where ρ_C = 0.322g/cm^3),

$K_{12}(NaHSO_4)$ is the acid dissociation constant of bisulfate ion, and

K_W is the dissociation constant for water.

Targets:

Rights-of-Way Environmental Issues in Siting, Development, and Management

Boiler and Turbine Steam and Cycle Chemistry

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