

EXPIRED

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Solubility of Sodium Sulphate in Superheated Steam

The IAPWS Working Group - Power Cycle Chemistry has examined the published work in the area of the solubility of sodium sulphate in superheated steam, which is of direct relevance to the reliability of electric power plants.

IAPWS recognizes that there is a requirement for work to be pursued in this field and has prepared this document to assist potential investigators obtain sponsorship. Specifically experimental studies are needed to quantify the solubility of sodium sulphate in superheated steam in the thermodynamic temperature range 400-850K and pressure 0.3-30MPa.

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

Issued by the

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

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Background:

Knowledge of thermodynamics of salt solutions is of great importance for the design and operation of power plants. Ever since the birth of the power industry, salts have been a source of trouble. Introduction of desalinated water has eliminated the most grave effects from salts. Over the past 40 years there has been an improvement in the purity of the water. This improvement continues, as long as practical problems can be linked to the presence of contaminating salts. Understanding the thermodynamics of salt solutions gives a tool for diagnosis, prediction and prevention of these problems. Although modern power stations with water having impurities with concentration in the ppb range, it has been established that a considerable amount of salts accumulate at some critical places in the plant. Places of deposition and concentration of deposits are determined by the thermodynamic properties of the system. Also, the release of these deposits is determined by the thermodynamic properties of the system. Knowledge of the thermodynamics is necessary to understand the behavior of the contaminants.

In relation to the power cycle, the thermodynamics of ammonium and sodium salts can be divided into the following areas:

1. Factors of significance for the intrusion of contaminants.

A number of sources of contaminants have been recognized during the history of power generation, and a considerable part of them eliminated in today's power stations. Yet some of them still contribute to the contamination of steam/water cycle either continuously or periodically.

Condenser leaks are the most important source of contamination. Risks in connection with them are dependent on several factors, among them the salinity of cooling water. Condensate Polishing (CP) is the best answer to this problem.

Condensate polishing by ion exchange is the most used technology to eliminate ionic contaminants from condenser leaks and from make up water. However, there is still some contamination after CP. The ion exchangers will continuously give an equilibrium leakage depending on regenerant quality and quantity, as well as periodic leakage of regenerants after every regeneration. An ionic leakage from the CP will also often increase due to kinetic factors, when considerable condenser leaks occur. Ionic leakage



from the CP seems to depend on pH i.e. whether the CP operates on hydrogen or ammonia cycle.

Leakage of organic matter from ion exchangers is also a significant contributor to contamination of the steam/water cycle. Organic compounds can be introduced from raw water passing through the make-up water treatment and CP plants, but more often it is the soluble organic matter from the organic matrix of ion exchangers.

Organic matter entering steam/water cycle decomposes at high temperature and pressures resulting in ionic contaminants such as acetates, formates, carbonates, and even sulphates and chlorides. There are some indications, that on installations where condenser leaks are controlled by means of CP, the predominant part of ionic contamination of the steam/water cycle originates from the decomposition of organic matter.

This situation is paradoxical. The ionic contamination originates from ion exchangers, whose function in the system is to remove the ionic contaminants. It is necessary to minimize organic leachables from ion exchangers.

Knowledge of thermodynamics and kinetics of ion exchange degradation, as well as degradation of their leachables at high temperatures is very limited (1, 2, 3, 4, 5).

Further investigations in this area are needed.

Formation of organic acids can occur by a degradation of other organic compounds than those mentioned above such as organic material from mechanical filters and organic amines added as conditioning agents.

2. Thermodynamic behavior of contaminants during evaporation.

The evaporation process takes place in several places in the steam/water cycle. The most important is in the boiler.

In a drum boiler the evaporation starts in the evaporator tubes and ends in the drum, where the separation of steam and water takes place. Contaminants and conditioning chemicals are distributed between liquid and vapor phases according to their partition coefficients. Partition coefficients for some of the most common sodium salts were estimated nearly 40 years ago (6), but experience from operating plants indicates a significantly higher solubility of salts in saturated steam than these values. Experience indicates, that the presence of ammonia increases the volatility of the anions.



In 1990 an EPRI project started (7) to investigate the volatility of sodium and ammonium salts. Because of its importance, a number of international participants are also sponsoring the project. A part of this project is an Assessment of the Ray Diagram - a double logarithmic diagram of partition coefficients and specific volume of steam. The present plans include investigation of ammonium chloride, ammonium sulphate and sodium sulphate as well as acids and bases involved with these salts. Other salts will be of interest in the future. The discussions are about acetates, formates, and phosphates of sodium and ammonium. From places with high content of potassium in raw water, an investigation of its salts is suggested.

In once-through boilers the situation during evaporation is quite different. Feedwater in subcritical boilers is gradually evaporated during passage through evaporator tubes. The last droplet of water is saturated with low volatility substances, and a deposition on the tube surface or mechanical carry over as solid is expected.

In supercritical boilers the real phenomenon of evaporation does not occur. Water is gradually heated at pressures greater than the critical point pressure to the critical point temperature and higher without any sudden change in volume. Nevertheless changes of many thermodynamic properties such as compressibility, isobaric heat capacity are large in the vicinity of the critical point (8). A drop in solubility of chemically inert components at supercritical conditions has been established, but there are no data available in this region regarding ionized species. A decrease in solubility in this region might be expected also for ionic constituents.

3. Thermodynamic behavior of contaminants in superheated steam.

The first study on solubility of salts in superheated steam was made almost 40 years ago (9). These investigations show a solubility minimum which has to be passed during the expansion of superheated steam in modern power stations. Deposition of salts from steam with higher concentrations of salt can be expected around the solubility minimum. Thus, deposits of sodium sulphate in the first part of the reheater has been observed in a number of countries (10, 11). This qualitative agreement between the mentioned study and practical observations is far from quantitative. The laboratory estimation of the solubility minimum is nearly 10 times higher than the actual sulphate concentration in superheater steam where the deposition of sodium sulphate has been observed. It is of great importance to estimate a more realistic value of solubility minimum and thus establish the target for steam purity.

A later investigation (12) of the current reheater operation region gave considerably lower solubility of sodium sulphate and drew attention to partial



decomposition of sulphate to sulphite at the conditions of the reheater. This reaction even more complicates the understanding of the deposition mechanism.

The importance of this area is supported by the damage to a number of reheaters exclusively due to off load corrosion in the locations with deposits of sodium sulphate. Similar problems have been observed at other places in installations, where the solubility minimum is crossed during steam expansion, e.g. in HP heaters and after the reduction valve of the auxiliary steam pipe. Salt deposits also occur along the steam expansion line in the turbine. The salts may form aggressive brines either during operation or at standstill. Corrosion and efficiency losses are established consequences of this salt deposition.

4. Thermodynamic behavior of contaminants in steam near the saturation line.

Thermodynamic properties of salt solutions in the region near condensation are important because deposition of salt can occur. This is particularly the case just before the Wilson line, where the steam starts to condense(13,14,15,16). Salt initiated fatigue, stress corrosion and off-load corrosion of the LP turbine blades are established consequences of salt deposition.

According to the IAPWS priority list, the following IAPWS Certified Research Need is defined:

Solubility study of sodium sulphate in superheated steam and study of its deposition/release mechanism.

This study should quantify the solubility of sodium sulphate in superheated steam in the range of thermodynamic temperature 400 - 850 K and pressure 0.3 - 30 MPa. Data presently available in the literature are insufficient, because they do not cover the desired range of pressure and temperature, and are also contradictory.

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