

Solubility of sodium sulphate in the vicinity of the critical point

Karol Daucik¹ and Jørgen Peter Jensen²

¹Elsam Engineering A/S, Kraftværksvej 53, DK-7000 Fredericia, Denmark
E-mail: kda@elsam-eng.com

²Energi E2, Teglholmegade 8, DK-2450 Copenhagen SV, Denmark

The solubility of sodium sulphate in steam in the vicinity of the critical point was studied. All experiments were made at a constant pressure slightly above the critical pressure. The temperature was progressively decreased from 425 °C to the critical temperature and the solubility was estimated by ion chromatographic analysis of cooled condensate. Good agreement were achieved with reliable data on the solubility of sodium sulphate in steam at lower densities. A continuity between data on sodium sulphate solubility in superheated steam and liquid solution at high pressure is framed. The results give good basis for interpretation of the deposition of sodium sulphate during expansion of steam.

1. Introduction

Problems with sodium sulphate deposition in superheaters, reheaters and turbines of fossil fired power plants have been known for a long time [1, 2]. Significant amounts of sodium sulphate deposits in reheaters have been observed many times [3, 4]. There is a potential risk of off-load corrosion when having deposits of dry salts [5]. The solubility of sodium sulphate in steam was subject to an extensive investigation in the 1990s [6, 7]. However, due to experimental difficulties the vicinity of the critical point was not included in the investigation in the previous investigations [8-13].

Knowledge of the solubility of salts is of fundamental importance for the understanding of precipitation in certain areas of the steam cycle. It provides a tool for diagnosis, prevention, prediction and solution of processes involving deposition of salts. Improvements of the guidelines for the steam quality can be linked back to the quality of the feed water in supercritical and ultra supercritical units.

In this report, the experiments on measuring the solubility of sodium sulphate in the vicinity of the critical point are described in detail.

2. Experimental

The solubility of the salts was measured by passing a continuous flow of pure steam through a salt bed at controlled temperature and pressure. By having a sufficient residence time of the steam in the salt bed, it is possible to saturate the steam with the salt. The steam sample is cooled and throttled to

atmospheric pressure where it is analysed by online ion chromatography for both anions and cations. This method can be used below the melting point of the salt in question. The melting point for sodium sulphate is 1345 °C. An assumption in this method is that the dissolved salt does not precipitate on the vessel surface within the cool down section. This assumption is based on the fact that the solubility of the salts increases with decreasing temperature at constant pressure. Two effects basically control the solubility of salts, the temperature and - more important - the density.

In the cool down section, the density increases with decreasing temperature and thereby increases the solubility of the salt. Precipitation of the salt onto the surface should therefore be minimal. This technique has been used in several investigations [6, 14].

To avoid formation of a liquid phase that may lead to recrystallization of the salt bed and plugging of the reactor the temperature was decreased during the serie of experiments. All the experiments in this investigation were made at almost constant pressure 22.5–22.7 MPa and the temperature of experiments was stepwise decreased from 425 °C to 375 °C. To ensure the repeatability of measurements, two check measurements were made at the two highest temperatures. In these measurements, the experimental temperature was approached from different sides to establish any tendency to hysteresis.

The whole study was carried through smoothly after initial difficulties with sealing of the rig.

3. Equipment

A schematic diagram of the apparatus used in this study is shown in Fig. 1. A single piston HPLC pump (Eldex Lab., Inc.) was used for pumping deionised water into the system. A relief valve (High Pressure equipment Company) was installed at the exit to the pump, to protect the apparatus from overpressure. A cooler was placed at the inlet to the preheater vessel to prevent any backflow of heat.

A 100 ml preheater vessel (2 inches o.d., 1 inch i.d.) (Autoclave Eng.) - with an internal pre-heat slug with helical grooves on its outside diameter to extend the surface area within the vessel - was used to elevate the temperature of the fluid. A one-zone vertical split design furnace (Autoclave Eng.) was used for the preheater. Thermocouples (type K) were used for control of the temperature of the preheater vessel as well as for over-temperature protection. The tubing (1/4 inch o.d., 1/12 inch i.d.) from the outlet of the preheater to the inlet of the pressure vessel containing the salt-bed was surrounded by a ceramic heater coil in order to maintain the high temperature of the steam. All components in the heated section were made of Hastelloy C276.

Sodium sulphate was placed on top of a 40 mm stainless steel filter in a 500 ml pressure vessel (3 inches o.d., 1 inch i.d.) (Autoclave Eng.). A two-zone vertical split design furnace (Autoclave Eng.) was used for this pressure vessel. One zone covered the lower third of the furnace and the temperature sensor (type K) used for control of the heating was placed just below the filter, inside the pressure vessel.

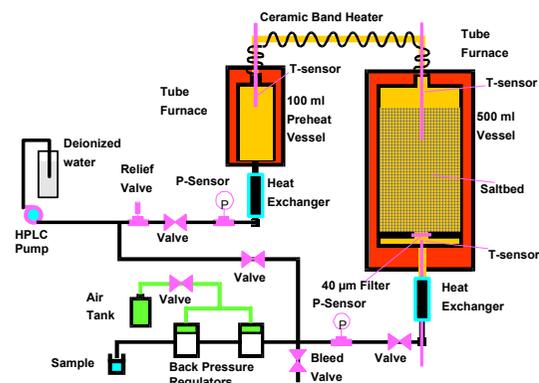


Fig. 1. Schematic diagram of the apparatus for measuring of salt solubility in steam

Table 1. Experimental results of the solubility measurements

Pressure (MPa)	Temp. (°C)	Density ¹⁶ (mol/dm ³)	Sodium (µmol/kg)	Sulphate (µmol/kg)
22.49	426.5	5.78	3.6	0.84
22.66	401.8	7.04	13.8	4.17
22.68	425.0	5.92	4.3	0.89
22.71	390.0	8.21	79.8	17.1
22.60	400.0	7.13	12.6	4.48
22.61	380.0	10.34	564	258
22.61	375.1	23.27	62232	28306

The other temperature sensor used for control of the temperature in the upper zone of the furnace was placed directly in the salt bed approximately 2 cm from the top. Thereby a constant temperature was maintained in the bed. At the exit, the steam was cooled using a shell-and-tube heat exchanger (Autoclave Eng.). Manometers (HBM GMBH) were placed before the preheater and after the 500 ml pressure vessel. The pressure difference never exceeded 0.05 MPa.

Two dome loaded backpressure regulators (Circle Seal) in series were used to maintain a constant pressure in the system. When setting the pressure of the backpressure regulators, the preheater and 500 ml pressure vessel were bypassed using appropriated stainless steel valves (Autoclave Eng.). The exit line of the backpressure regulators was connected to an ion chromatograph (DX-500, Dionex). The samples were analysed for anions where sodium carbonate/sodium bicarbonate was used as eluent, and for cations using sulphuric acid as eluent. Using concentration mode, the detection limit was 0.1 µg/kg for chloride and sodium and 0.2 µg/kg for sulphate.

4. Experimental results and discussion

The results of the investigation are summarized in Table 1. The repeatability of the measurements seems to be quite good compared to the spread of results published earlier. However, the agreement between sulphate concentration and sodium concentration is hardly that good. Particularly at higher temperatures only half of the sulphate is entitled to sodium. At lower temperatures - e.g. in the closest vicinity to the critical point - the agreement is very good.

For the evaluation of the solubility results the below density model is used:

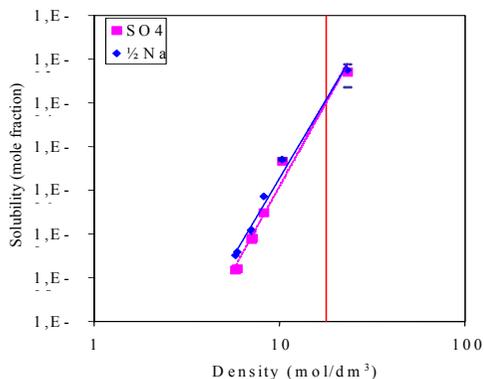


Fig. 2. Solubility of sodium sulphate in steam

$$\log S = F + G * \log \rho_w$$

ρ_w is the density of steam, F is a function of temperature, and G is by some authors interpreted as a constant, while others treat it as a function of temperature and density. According to this model, the experimental results give a straight line in Fig. 2. The red abscise indicates the critical density of pure water. There is a slight disagreement between the lines based on sodium and sulphate.

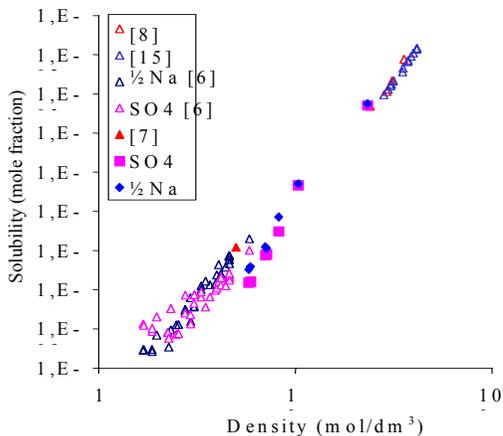


Fig. 3 Comparison of reliable studies of Na_2SO_4 solubility

Figure 3 shows the comparison of the results with data produced in nineteen nineties on superheated steam at lower densities [6, 7]. There seems to be a slight difference in the slope of the regression lines as well as some shift. Lines based on sodium results give the best agreement between the studies. The sodium concentration is slightly

higher than the corresponding sulphate concentration, which indicates that hydrolysis of sodium sulphate, could not be observed in the experiments.

There are data from solubility of sodium sulphate in high pressure and high temperature water [8, 15] with density higher than in the present work. These seem to give good continuity to the results of this work.

The good agreement of the highest density measurement of this study with the solubility measured on pressurised water solutions [8, 15] raises the question what the actual state was in the autoclave at the very last measurement at $375.1\text{ }^\circ\text{C}$ and 22.61 MPa . The critical point of pure water is at $T=373.95\text{ }^\circ\text{C}$, 22.064 MPa and $\rho_w=17.87\text{ mol/dm}^3$. Valyashko et al. [15] estimated the critical end point to $375.05\pm 0.2\text{ }^\circ\text{C}$, where the densities of liquid and vapour solutions in the three-phase equilibrium become identical. They [15] found that the density at the critical end point was not clearly different from that of the critical point for pure water (Fig. 4). Since the pressure in our last measurement is more than 0.5 MPa above the critical pressure of pure water and only one Kelvin above the critical temperature of pure water, it is reasonable to assume that the measured concentration corresponds to a single-phase fluid in equilibrium with a solid phase. Since the pressure is above the critical pressure, the density will be “liquid-like”. The density of pure water at the conditions of our last measurement is 23.27 mol/dm^3 .

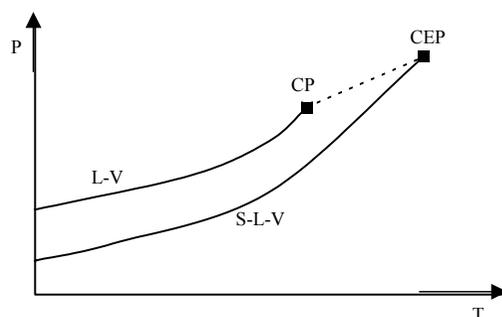


Fig. 4 Schematic saturation line for pure water and saturated Na_2SO_4 solution [15]. The L-V (liquid-vapour) curve is the coexistence curve for pure water. The S-L-V (solid-liquid-vapour) curve is the coexistence curve for salt-saturated solution. CEP is the critical end point – that is the critical point for

the solution saturated with Na₂SO₄. The critical curve - the dashed line - between CP and CEP correspond to critical points for solutions for with salt contents lower than that at CEP.

5. Conclusion

The investigation has generated new data on solubility of sodium sulphate in steam in a range where experimental data were missing - the vicinity of the critical point. A continuity between data on sodium sulphate solubility in superheated steam and liquid solution at high pressure is framed. This knowledge gives background for an understanding of the deposition processes during expansion of steam.

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