Supercritical water desalination (SCWD) of multi-component brines

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HIGHLIGHTS

- Phase equilibria measurements of NaCl-KCl and NaCl-Na2SO4 mixtures.
- Visualisation of multi-salt mixtures phase behaviour under supercritical conditions.
- Identification of different phase regions for NaCl-Na2SO4-H2O mixtures.

GRAPHICAL ABSTRACT
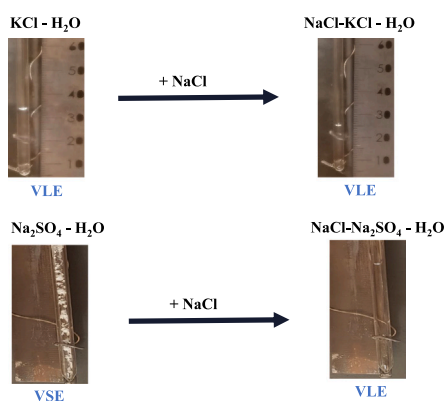
ABSTRACT

The phase behaviour of two model multi-component salt-water mixtures (NaCl-KCl-H_2O and NaCl-Na_2SO_4-H_2O) was investigated for the application of supercritical water desalination (SCWD). The experimental investigation was a two-step procedure starting with qualitative analysis followed by quantitative measurements. The qualitative experiments served as a screening step to visually inspect phase behaviour. The quantitative results for NaCl-KCl-H_2O, showed similarities in phase behaviour between the salts, which led to the assumption that the ternary mixture behaved as an ideal mixture between two binary solutions. The ternary equilibrium concentrations in the SCW phase could therefore be predicted using the binary salt-water models of the respective salts and accounting for the feed concentrations. Based on the quantitative results for NaCl-Na_2SO_4-H_2O, the phase behaviour of the mixture was divided into three regions. The third region was the suitable region for SCWD, as the precipitated salts (Na_2SO_4) dissolved in the hydrothermal brine (NaCl), forming a vapour-liquid equilibrium.

1. Introduction

Around the critical point of water (Temperature > 374 °C, Pressure >

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Nomenclature

AP	Anderko & Pitzer.
BPR	Back pressure regulator.
EoS	Equation of state.
L	Liquid.
LS	Liquid-solid.
SCW	Supercritical water.
SCWD	Supercritical water desalination.
SI	Supporting information.
V	Vapour.
VS	Vapour-solid.
VL	Vapour-liquid.
VLS	Vapour-liquid-solid.
VLE	Vapour – liquid equilibrium.
VSE	Fluid – solid equilibrium.
ZLD	Zero liquid discharge.

22.1 MPa), the properties of water undergo drastic changes, rendering inorganic compounds (*e.g.*, salts) insoluble in water [1]. Based on this phenomenon a method of desalination was developed, in which saline streams are brought to supercritical conditions (above the critical point of water), and drinking quality water, salt and steam are recovered. Supercritical water desalination (SCWD) is based on the formation of a pseudo-vapour-liquid equilibrium (VLE) under supercritical conditions. Above the critical point, salt-water mixture will form a two phase system, which is comparable to a VLE system. The first phase is the supercritical water (SCW) phase, which represents the "vapour" phase. This phase is characterised by a low salt concentration and low density, and behaves as a supercritical fluid. The SCW phase is in equilibrium with the hydrothermal brine phase which represents the "liquid" phase. The hydrothermal brine phase is characterised by a high density and high salt concentrations. The hydrothermal brine is not supercritical, but is in equilibrium with the supercritical water phase. For our proposed process, the SCW is continuously removed (and used for heat integration) and the hydrothermal brine is expanded to retrieve, salt, water and steam (no liquid waste streams) [2,3].

Most of the research (both experimental and model based) on SCWD, has been focussed on model saline streams containing only NaCl [3–5]. However, industrially produced waste brines usually contain multiple salts. Some of these salts directly precipitate from the feed, instead of forming a VLE, required for the application of SCWD [6–10].

Salts can be classified as being either type I or II depending on the phase behaviour of the binary salt-water mixture. The classification is based on the system of Scott and Van Konynenburg [11] for binary mixtures. Type I mixtures (mixtures containing salts such as NaCl, KCl, $MgCl_2$ and $CaCl_2$) form a VLE under supercritical conditions, while type II mixtures (contains salts such as Na_2SO_4, K_2SO_4 and Na_2CO_3) form a fluid-solid equilibrium (VSE) under these conditions [10,12,13]. The phase behaviour of the two types of salt is compared in Fig. 1.

The formation of solids is unwanted, as it will result in plugging and equipment failure. Similar problems are encountered during supercritical water oxidation and gasification [6,13]. As mentioned, a brine waste stream typically contains multiple salts, which also affect the phase behaviour of one another [7,10]. Examples of industries producing brine waste are the desalination industry (production of drinking water), the oil and petrochemical industry (hydraulic fracturing), the dairy industry (production of cheese) and the mining industry. The major salt components for the desalination industry and the oil and gas industry waste are NaCl, $CaCl_2$, $MgCl_2$ (type I) with minor concentrations of $CaSO_4$ and Na_2SO_4 (type II) [15–17]. The concentrations of the streams vary depending on the source. For the dairy industry the major salts present are NaCl, KCl and $CaCl_2$ (type I) [18], while for the mining industry the major salts are NaCl (type I) and Na_2SO_4 (type II) [19,20].

For the mentioned waste streams, the major components in each case were type I salts, with the type II salts being present in smaller quantities. Research on the phase behaviour of multi-component salt mixtures, under supercritical conditions, have shown it is possible to dissolve the precipitated solids of the type II salts in the hydrothermal brine of the type I salt [8,10,12,21–23]. Valyashko [12] reviewed different studies of ternary mixtures (salt-salt-water) containing a type I and II salt, and stated that the mixture will exhibit type I phase behaviour (*i.e.*, the formation of a hydrothermal brine and supercritical water (SCW) phase) if the concentration of the type I salt in the feed is in the majority. The exact concentration of type I salt required is dependent on which salts are present in the mixture. Schubert et al. [7,8] studied the phase behaviour and separation of different ternary mixtures (containing either two type II salts or a type I and II salt) under supercritical conditions. They concluded that if the amount of type I salt is sufficient, the type II salt components will dissolve in the formed hydrothermal brine and the system would exhibit type I phase behaviour. The exact amount of type I salt required is dependent on the salt mixture itself. Schroeder et al. [21] and DiPippo et al. [10] specifically looked at NaCl-Na_2SO$_4$-H_2O mixtures. Schroeder et al. [21] found that for temperatures $\geq$ 350 °C, the solubility of Na_2SO_4 increased with the presence of NaCl in the feed stream (at lower temperatures the solubility decreases with NaCl concentration). DiPippo et al. [10] investigated the phase behaviour at 250 bar for feeds with varying salt concentrations and showed that for higher concentrations of NaCl, the system transitioned from a vapour-liquid-solid (VLS) system to a vapour-liquid (VL) system.

If VLE can be established for the multi-component mixture, SCWD could be applied for the treatment of the liquid waste streams. The treatment of hydraulic fracturing brine waste, using SCWD, has already
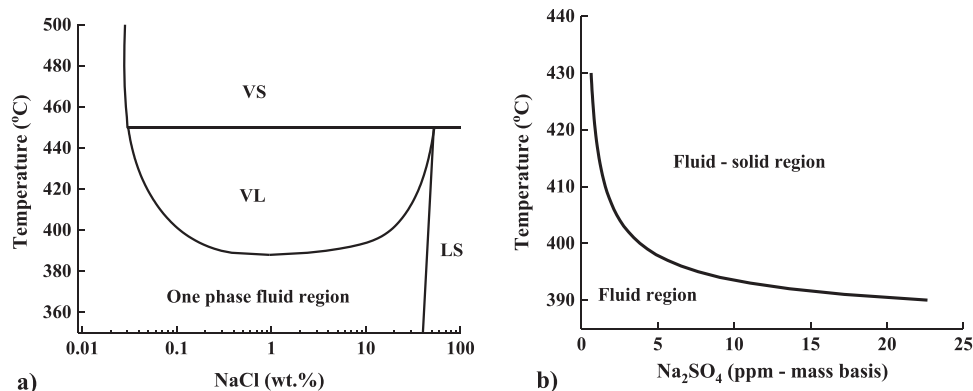
Fig. 1. Phase behaviour comparison of salt-water mixture under supercritical conditions at 250 bar (a) Type I (b) Type II (Drawn using Anderko & Pitzer EoS (parameter reported in [14] used)).

been studied to some extent using either model multi-component solutions or direct source feeds [16,24,25]. From the results it was seen that SCWD could be applied for recovery of a low salinity water that could be recycled back to the process.

The aim of this study was to investigate SCWD for multi-component feeds, using ternary model salt-salt-water solutions. Two model mixtures were investigated namely, (1) NaCl-KCl-H_2O, a type I-I mixture (representative of dairy industry brine) and (2) NaCl-Na_2SO_4-H_2O, a type I-II mixture (representative of mining industry brine). The phase behaviour was investigated both qualitatively and quantitatively. The qualitative analysis was carried out using quartz capillaries and was done as a screening step to ensure that no solids were formed for the chosen conditions before phase equilibria could be measured quantitatively. This was the first time that the phase behaviour of these ternary mixtures was visually observed and captured, under supercritical conditions. The precipitation of Na_2SO_4 and the subsequent dissolving of the solids in the formed hydrothermal brine, was also visually investigated for different feed ratios. Quantitative phase equilibria data for the ternary mixtures of this study have not been extensively measured and reported, and the chosen conditions were typically above or below the conditions applied for SCWD [10,21,23,26]. New phase equilibria data (SCW compositions) was thus measured and reported.

2. Experimental

Two types of salt mixtures were investigated for the application of SCWD. The first was a mixture containing only type I salts, namely NaCl and KCl (representing a dairy industry produced brine waste). The second was a mixture of type I and II salts, namely NaCl and Na_2SO_4 (representing a mining industry produced brine waste). The phase behaviour and separation measurements were done following a two-step approach. Firstly, the phase behaviour of the various mixtures was qualitatively examined using quartz capillaries. This was done as a screening step to ensure that no solids would be formed, under supercritical conditions, which could lead to blockages and equipment failure of the SCWD unit. The second step was to measure the phase equilibria in a continuous small lab-scale SCWD unit (1 mL/min), to obtain quantitative data on the solubility of multi-component feeds in the SCW.

For the saline solutions, pharmaceutical grade NaCl (> 99.0 %; API sodium chloride GMP grade from esco), pure KCl (99 – 100.5 %; ACS from Alfa Aesar) and pure Na_2SO_4 ($\geq$ 99.0 %; ACS reagent from Sigma Aldrich) was used. All solutions were prepared with demineralised water (resistivity of 11.7 MΩ·cm).

2.1. Qualitative experiments

Qualitative experiments were performed using quartz capillaries (Length = 172 mm and inner diameter = 1.92 mm), which were placed in an oven. The capillaries were filled with a saline solution (10 wt% total salt), sealed (using an acetylene flame) and heated inside an oven to supercritical temperatures (T > 374 °C). The oven was equipped with heating elements on the walls to reach the desired temperature, the heating rate was set to 5 °C/min The oven was equipped with a sight glass in the front to enable visual observations, while the light was introduced from the bottom of the oven. The oven was had a TC-I to control the temperature. The ratios of the mixtures were varied from pure NaCl to pure KCl or Na_2SO_4. The experimental set-up is shown in Fig. 2.

The temperature was measured on the wall of the capillary using a standard K-type thermocouple (± 2.2 °C; TI-I). The capillaries were a closed system (isochoric) and the temperature and pressure could not be controlled independently (pressure will increase with temperature). The pressure was regulated by the initial amount of liquid solution inside the capillary. As the capillary was heated the liquid level would increase due to expansion of the liquid with temperature, however once the supercritical region was reached and the mixture transitioned to the VLE
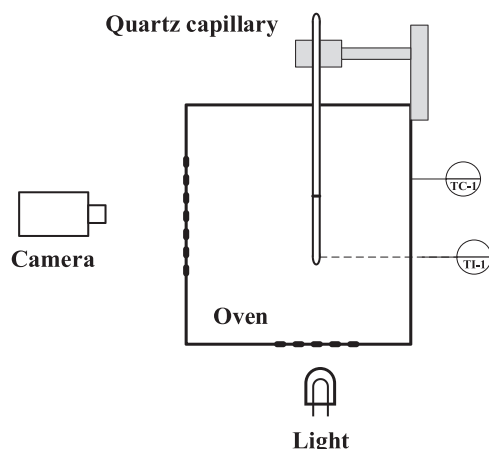

Fig. 2. Quartz capillary set-up for qualitative analysis.

region the liquid level would start to decrease (with respect to the starting liquid level). As the temperature continues to increase the liquid level would continue to drop as the hydrothermal brine becomes more concentrated. Assuming that the vapour phase (SCW) consists only of water, the liquid level drop (with respect to the starting liquid level) in the supercritical region was measured using a stainless steel ruler that was mounted on the capillary holder and the pressure inside the capillary (for a given temperature) was calculated using the steam tables (IAPWS IF-97) and the liquid density calculated from the Anderko & Pitzer EoS (see Section 3) for NaCl-H_2O mixtures [2,27,28].

2.2. Quantitative experiments

The quantitative phase equilibria was measured using a modified version of the set-up described in previous work [2]. The set-up is shown in Fig. 3. The separation took place inside a titanium separator (grade 2 titanium) with inner diameter of 10 mm, length 85 mm and wall thickness of 3.5 mm. The phase equilibrium was measured in a continuous manner by feeding a pressurised pre-heated saline solution to the separator, in which separation between a concentrated hydrothermal brine and low salt concentration SCW phase took place. Prior to each experiment the mass balance closure was checked with demineralised water (closure of $\geq$ 95 %) under supercritical conditions. The saline feed was pumped using a HPLC pump (LabAlliance series 1500, LabAlliance USA) and the pressure was controlled with a back-pressure regulator (BPR) (TESCOM 26–1762–24-S, Tescom Europe GmbH & Co. KG, Germany, Cv = 0.1, accuracy ± 1 % of the central pressure range). The pressures were measured with sputtered thin film type pressure transducers (accuracy was 0.25 % full scale). The temperature was continuously measured on the separator wall and inside the separator (thermocouple placed inside titanium sleeve) using K-type thermocouples (± 2.2 ºC). The fluid temperature (TI-4) and the SCW outlet temperature (TI-1) were similar (differed a maximum of ± 5 °C). The reading of TI-4 was taken as the separation temperature. The top wall temperature (TI-2) was in-line with TI-1 and TI-4, while the bottom wall temperature (TI-3) was lower (± 15 °C), which could be due to uneven heat distribution inside the oven. The standard deviation in the pressure was ± 3 bar and the deviation in temperature was ± 2 °C during the experiments.

The SCW salt concentration was continuously monitored, using an in-house constructed conductivity cell, to ensure that samples were taken at steady state conditions (standard deviation $\leq$ 3 %). Around the critical point, where the system enters the VLE region, the standard deviation was higher (5 %) due to the system being unstable in this region. Once steady state conditions were reached a sample of the SCW was taken and analysed to determine the concentration. For the type I-I mixtures, the cation (Na^+ and K^+) concentration was determined using
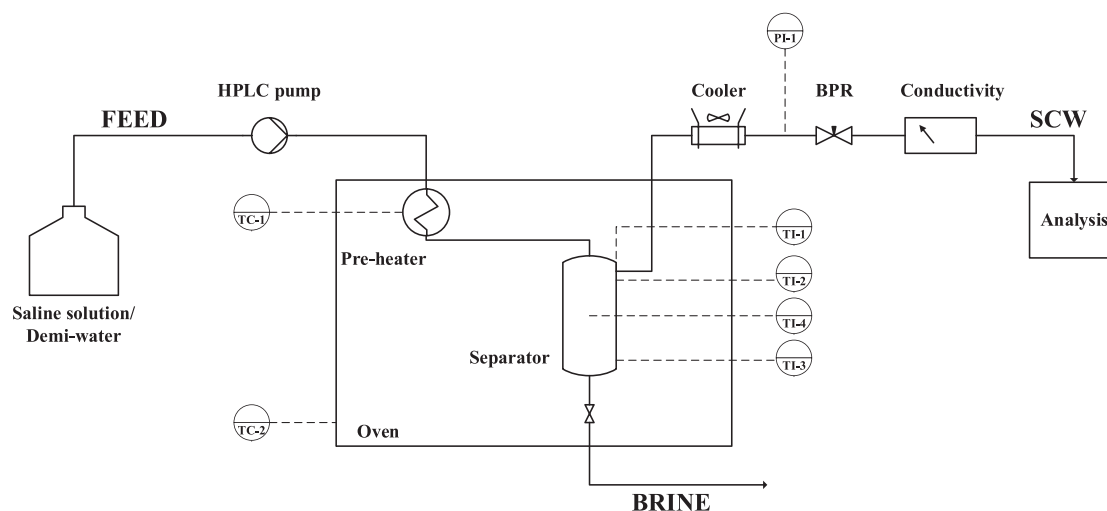
Fig. 3. : Lab-scale set-up for quantitative measurements of phase equilibria.

ion chromatography (IC, Metrosep C6 – 150/4.0 column on a Metrohm 850 Professional IC, mobile phase: 0.1 M HNO_3 + 0.02 M dipicolinic acid solution, column temperature: 20 ± 1 °C, flow rate: 1.0 mL/min). Likewise, the anion (Cl^- and SO_4^{2-}) concentration, for the type I-II mixtures, was determined using the IC (Metrosep A Supp – 150/4.0 column on a Metrohm 850 Professional IC, mobile phase: 0.1 M KOH + 0.1 M Na_2CO_3 solution, column temperature: 45 ± 1 °C, flow rate: 0.8 mL/min). The error in the SCW salt concentration was taken as the standard error in the calibration curve for the respective anions and cations. The standard error was < 1 % for all components. The concentration of the brine was calculated by performing a mass balance over the separator. The system has been validated in a previous work for $NaCl-H_2O$ and $KCl-H_2O$ mixtures [2,29].

Isobaric experiments (250, 270 and 300 bar) were performed for a temperature range of 370–450 °C. The total salt concentration of the feed solution was 1 wt%, with the ratio of salts in the feed varying. For the type I-I mixtures the mass ratio was varied from 9:1 (NaCl:KCl) to 1:9 (NaCl:KCl) since VLE was established for all mixtures (see Section 4.1). Experiments for $KCl-H_2O$ mixtures at 250 and 300 bar were also performed. Only the mass ratios 9:1, 8:2 and 7:3 (NaCl:Na$_2$SO$_4$) were investigated for the type I-II mixtures. For higher ratios of Na$_2$SO$_4$, the solids (formed by Na$_2$SO$_4$) no longer fully dissolved in the hydrothermal brine (formed by NaCl), which would lead to plugging and equipment failure (see Section 4.1).

3. Thermodynamic modelling of binary salt-water phase equilibria

The Anderko & Pitzer equation of state (AP EoS) was used to model the high-pressure, high-temperature salt water mixtures. A full description of the AP EoS can be found in the paper of Anderko & Pitzer [28] and detailed description of the calculations and validations for $NaCl-H_2O$ mixtures can be found in previous work [4].

In our previous work [29], a simple algorithm was developed to determine the phase region of a binary salt-water mixture under high pressures and temperatures or supercritical conditions. During the research the AP EoS transformation parameters were also fitted for $KCl-H_2O$ and $Na_2SO_4-H_2O$ mixtures using SCW equilibrium concentrations. The developed algorithm and transformed AP EoS for the respective binary salt-water mixtures, will be used in subsequent sections to determine the phase region and calculate the equilibrium concentrations.

4. Results and discussion

4.1. Experimental qualitative results

The qualitative phase behaviour for different feed ratios of NaCl to KCl (total salt concentration 10 wt%) as well as the single salt mixtures are shown in Fig. 4:

From the first image it is seen that all solutions start as a homogenous mixture, with no solids present. The following pictures show different $NaCl-KCl-H_2O$ solutions for pressures and temperatures above the critical point, where the mixtures are in the VLE region (according to the phase algorithm developed in our previous work [29]). Under supercritical conditions the liquid level dropped as the temperature increased and the level was measured (meniscus is indicated on images with an ellipse) to estimate the pressure inside the capillary.

From the results it is seen that for all mixtures VLE was achieved at a temperature of ~ 420 °C. The meniscus is visible for all the mixtures and no solid disposition is seen at the bottom the capillary (see Fig. 5 for reference of solid deposition). The liquid level dropped (compared to the starting liquid level, not shown in Fig. 4) indicating that more vapour (SCW) is being produced and a more concentrated brine (liquid phase) is formed. The observed phase behaviour for the different conditions and mixtures is summarised in Table S.1 in the Supporting information (SI). In all cases VLE was observed (no solids formation) and all the mixtures can be quantitatively investigated for SCWD without the risk of solid formation and equipment plugging.

The phase behaviour for different ratios of NaCl to Na$_2$SO$_4$ (total salt concentration 10 wt%) is shown in Fig. 5.

The first image of the starting solution once more shows that before the experiments started, the solutions were homogenous mixtures. From the results it is seen that for mixtures where NaCl was in the majority (mass ratio greater than 7:3 (NaCl:Na$_2$SO$_4$)), no solids were present. For these mixtures the Na$_2$SO$_4$ (type II) dissolved in the hydrothermal brine formed by the NaCl (type I). However, as the concentration of Na$_2$SO$_4$ (with respect to NaCl) increased, it no longer fully dissolved in the hydrothermal brine. This was already observed for a mixture of 6:4, with solids present at the bottom of the capillary (indicated with the arrow). For a feed ratio of 2:8 the phase is indicated as VLS even though the meniscus is not indicated. Due to the low NaCl concentration in the feed the hydrothermal brine phase is small and not clearly visible in the photo. For Na$_2$SO$_4$-H_2O mixtures, a VSE was formed and there was no hydrothermal brine present. For mass ratios of 9:1–7:3 (NaCl:Na$_2$SO$_4$), VLE was achieved and the mixtures can be quantitatively investigated. However, for ratios of 6:4 and higher (with respect to Na$_2$SO$_4$) precipitation will occur, which in turn will cause plugging and equipment

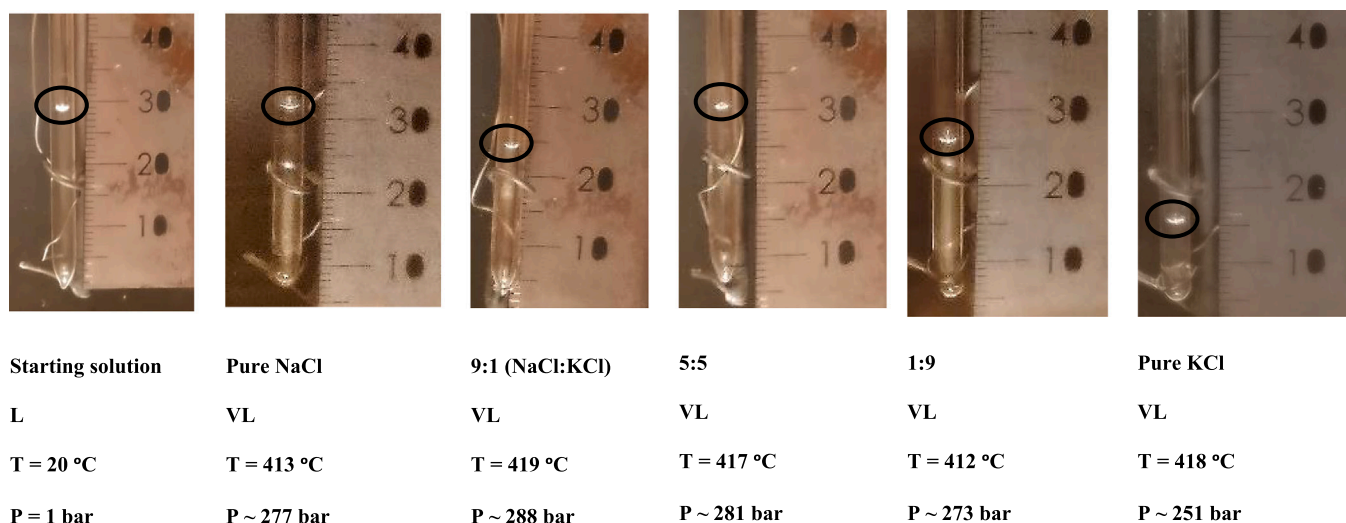| Starting solution	Pure NaCl	9:1 (NaCl:KCl)	5:5	1:9	Pure KCl
L	VL	VL	VL	VL	VL
T = 20 °C	T = 413 °C	T = 419 °C	T = 417 °C	T = 412 °C	T = 418 °C
P = 1 bar	P ~ 277 bar	P ~ 288 bar	P ~ 281 bar	P ~ 273 bar	P ~ 251 bar

Fig. 4. Phase behaviour of NaCl-KCl-H_2O mixture for different feed ratios (mass basis) of NaCl:KCl (ellipse indicates meniscus). Starting concentration of solution is 10 wt%.
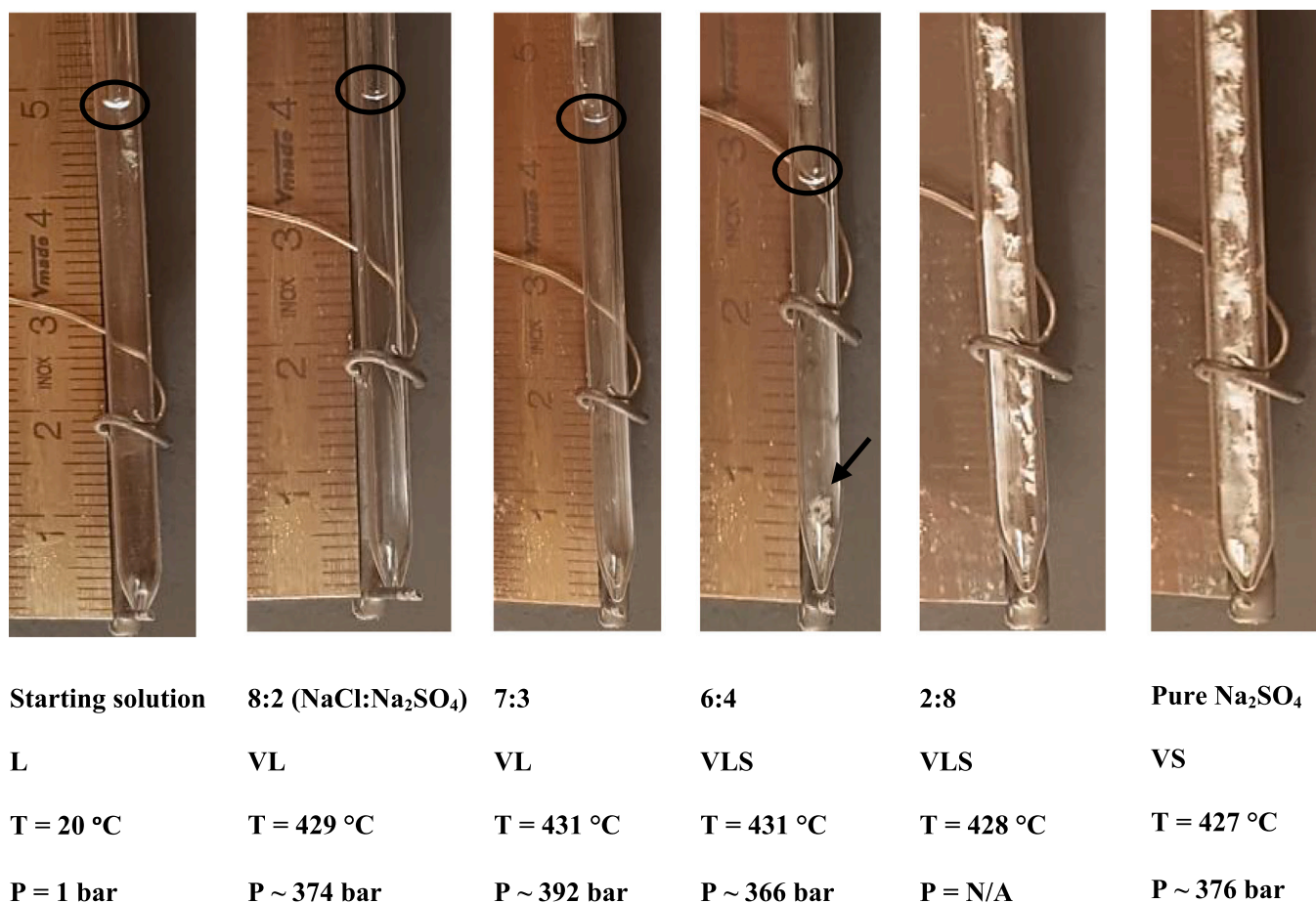

Starting solution	8:2 (NaCl:Na$_2$SO$_4$)	7:3	6:4	2:8	Pure Na$_2$SO$_4$
L	VL	VL	VLS	VLS	VS
T = 20 °C	T = 429 °C	T = 431 °C	T = 431 °C	T = 428 °C	T = 427 °C
P = 1 bar	P ~ 374 bar	P ~ 392 bar	P ~ 366 bar	P = N/A	P ~ 376 bar

Fig. 5. Phase behaviour of NaCl-Na_2SO_4-H_2O mixture for different feed ratios (mass basis) of NaCl:Na_2SO_4 (ellipse indicates meniscus; arrow indicates solids). Starting concentration of solution is 10 wt%.

failure. Studies done by Armellini & Tester [30] and DiPippo et al. [10], have stated that as the concentration of NaCl increases, the precipitation of Na_2SO_4 becomes less. These experiments were performed using a high-pressure, high-temperature optical cell, but not images with regards to the solutions at different conditions were provided. The results of DiPippo et al. [10], showed that the transition from

Na_2SO_4(s)-Liquid-Vapour to VLE usually occurred for a NaCl:Na_2SO_4 ratio of 7:3 (mass basis), corresponding with the results above. Earlier studies done by Schroeder et al. [21] and Ravich et al. (reference in [30]), have also stated that the solubility of Na_2SO_4 increases with increased concentration of NaCl. To our knowledge, this is the first time that this phenomenon has been visually shown. A summary of the phase

behaviour for the different mixtures and conditions is given in the SI (see Table S.2).

4.2. Experimental quantitative results

4.2.1. Type I - I mixture (NaCl – KCl – H₂O)

The salt concentrations in the outlet stream (top outlet stream of the separator - see Fig. 3) are shown in Fig. 6, for a feed mass ratio of 7:3 (NaCl:KCl) and for separation pressures of 250 and 300 bar. The graphs for the remaining feed ratios and pressures are given in the SI, as well as the tabulated results (Table S.3).

The transition from the subcritical to supercritical region is indicated by the separation between the SCW and hydrothermal brine phase (mixture enters the VLE region, see Fig. 1a). In Fig. 6, the outlet concentrations measured at the top outlet of the separator (see Fig. 3) are given. In the subcritical region (one phase fluid region, see Fig. 1a), no phase separation occurs and the outlet concentration is equal to the inlet feed concentration. In the supercritical region, separation occurs as both NaCl and KCl are type I salts and the outlet concentrations decrease as the SCW phase, which exists at the top of the separator, has a low salt concentration. The hydrothermal brine, which accumulates at the bottom of the separator, has a high salt concentration. The concentration of the hydrothermal brine is not indicated in Fig. 6. The separation between the SCW and hydrothermal brine phase (and transition from subcritical to supercritical) was indicated by the decrease in the experimentally measured concentrations of NaCl in the outlet stream (start of the SCW phase), *i.e.*, for 250 bar separation starts at 390 °C and for 300 bar separation starts at 400 °C. NaCl was selected to indicate transition as it was the main component in most mixtures. For the case where KCl was the main component in the feed (see Figure S.3b) the transition was indicated by the decrease in the KCl concentration.

Using the phase algorithm along with the adapted AP EoS for KCl-H₂O mixtures from our previous work [29], the outlet concentrations were calculated at 5 °C intervals for binary KCl-H₂O and NaCl-H₂O mixtures and compared with the ternary mixture composition measured at 10 °C intervals. It is important to note that the calculated concentrations presented in Fig. 6 are for pure binary mixtures and were not corrected for the feed concentration of ternary mixtures, as will be done in the sections below. By comparing the binary calculated results (solid lines) for the two salts, it is seen that the temperature at which separation between the SCW and hydrothermal brine phase starts (mixture enters the VLE region) was within 5 °C for both mixtures. The separation temperature (mixture enters VLE) at 250 bar was similar (within 5 °C for NaCl and < 5 °C for KCl) for both the binary calculated and ternary measured mixtures. For 300 bar, the calculated temperature (using the binary AP EoS) was ~10 °C higher than the measured temperature for the ternary mixture, which could be attributed to the instability in concentration measurements experienced around the critical point as the mixture transitions (see Section 2.2).

The results show that for 250 bar the concentration of NaCl in the SCW stream (410 – 440 °C) was close (maximum deviation of 13 %) to the concentrations calculated by the binary AP EoS for NaCl-H₂O. This indicates that, for high feed concentrations of NaCl (relative to KCl), the NaCl phase behaviour was not greatly affected by the presence of KCl. The total salt concentration of the outlet stream was also close to the binary NaCl-H₂O concentration. The KCl concentration for both 250 and 300 bar, was lower in comparison to the equilibrium concentration calculated by the binary AP EoS for KCl-H₂O.

Furthermore, as shown in Fig. 6a&b, the calculated equilibrium concentrations of the salts NaCl and KCl in the SCW (in some cases referred to as the solubility) were similar. Leusbrock et al. [31] also measured the solubilities of different alkali and alkaline compounds and showed that the alkali compounds (NaCl and KCl) have an almost equal solubility in SCW, while the alkaline compounds (MgCl₂ and CaCl₂) have a slightly lower solubility. The recovery of SCW was high (97–99 %), which was due to the low concentration of total salt in the feed (1 wt

%). The SCW total salt concentration ranged from 500 ppm (high separation temperature) to 8000 ppm (lower separation temperature close to the pseudocritical point [1]).

From Fig. 6, it is seen that the binary AP EoS for NaCl and KCl, respectively, is able to predict the concentration of the ternary mixture to some extent, but generally tends to overestimate the concentrations. According to the Gibbs phase rule the degrees of freedom is three, for the ternary mixture NaCl-KCl-H₂O in the VLE region (three components and two phases). In this case the temperature, pressure and feed concentrations are known and set for the calculations, instead of just the temperature and pressure as done for the binary mixtures (degrees of freedom is two).

The extended Anderko & Pitzer [32] model for NaCl-KCl-H₂O was originally used for the equilibrium calculations. In their work the NaCl-H₂O model was adapted to calculate the phase equilibria of KCl-H₂O mixtures, after which the parameters of binary KCl-H₂O and NaCl-H₂O mixtures were used to calculate the properties of the ternary mixtures (NaCl-KCl-H₂O). For the extended model, only two temperature-independent binary interaction parameters for NaCl-KCl were added. Hovey et al. [33] also developed a correlation to determine the pressure of the three-component system, which mainly consisted of binary mixture (salt-water) parameters and one cross term for NaCl and KCl, which could be taken as the mean of two pure component parameters. For the extended model of Anderko & Pitzer [32], the fitted parameters were close to one and the remaining parameters were set to one, which is expected as the properties of NaCl and KCl are similar as shown in Fig. 6. The similarity in the phase behaviour of NaCl and KCl mixtures, was also seen in our previous work [29] when the transformation parameters were fitted for the binary KCl-H₂O mixtures, using the NaCl-H₂O parameters as a basis. The fitted parameters were close to one, indicating that the phase behaviour and properties are similar for the two salts. The similarity in the phase behaviour of the two mixtures were also noted in other studies [31,34,35]. The extended AP model could not be verified with comprehensive VLE data, but could be verified using the concentration ratio of NaCl and KCl in the SCW phase, by assuming that the ratio of NaCl to KCl in the brine is equal to the ratio in the feed. Trends were verified, but there were deviations in the quantitative concentration values [32]. For this work, the model was also not able to accurately determine the concentrations of the NaCl and KCl in the SCW phase, resulting in overestimation of the equilibrium concentrations.

Due to the similarities in properties and phase behaviour of NaCl and KCl, the mixture of the two binary solutions can be viewed as an approximate ideal mixture of two regular solutions [33,36]. Based on previous studies using the binary mixture parameters to model the ternary mixture properties and that the mixture can be seen as ideal, the ternary equilibrium concentrations of the respective salts in the SCW phase were calculated using the calculated binary mixture concentrations and multiplying it with the respective feed concentrations (mol basis). In Fig. 7, the NaCl, KCl and total salt experimental concentrations in the SCW are compared with the binary calculated concentrations, for a pressure of 300 bar and temperature of 430 °C, for the different molar ratios of KCl to total salt in the feed.

The measured concentrations of NaCl, KCl and total salt in the SCW stream (conditions are for the supercritical region) are presented as a function of the molar fraction of KCl to the total salt in the feed.

From the experimental results it is seen that the equilibrium concentrations of the respective salts in SCW increased with the increase in the salt feed concentration. Thus, as the fraction of KCl of the salt mix in the feed increased, the concentration of the KCl in the SCW stream also

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[1] The pseudocritical temperature (T_{pc}) is defined as a temperature above the critical temperature ($T_{pc} > T_c$) which corresponds to the maximum in the specific heat capacity of the fluid, for a given pressure, above the critical pressure ($P > P_c$) of the pure solvent [40].
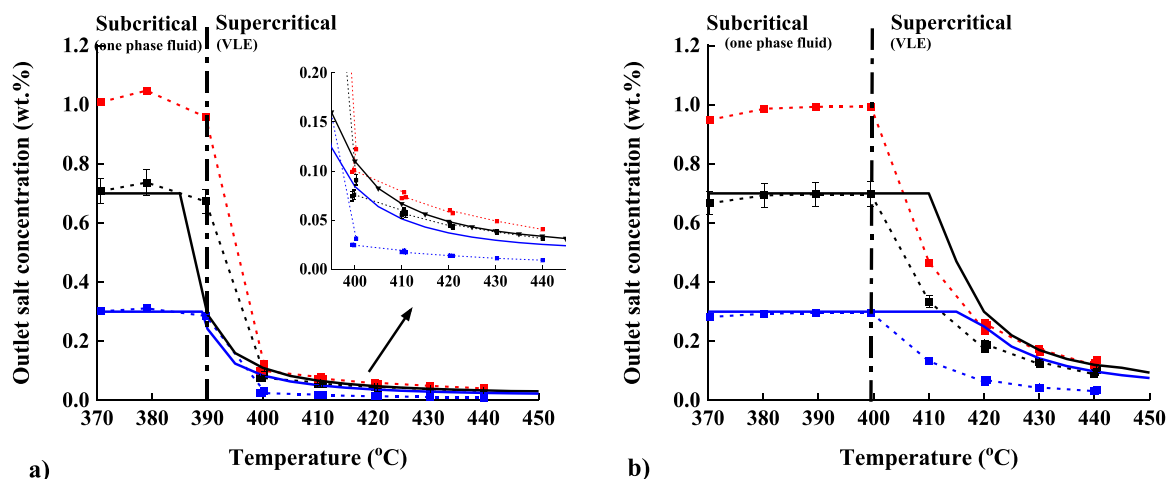
Fig. 6. NaCl and KCl concentration in the outlet stream for a feed mass ratio of 7:3 (NaCl: KCl) and total salt concentration of 1 wt%, (a) 250 (b) 300 bar (■ Experimental NaCl; ■ Experimental KCl; ■ Experimental total salt (dashed lines help to guide the eye for the experimental points); — Calculated NaCl from binary AP EoS; — Calculated KCl from binary AP EoS). Phase regions in brackets, correspond to the phase regions depicted in Fig. 1a.
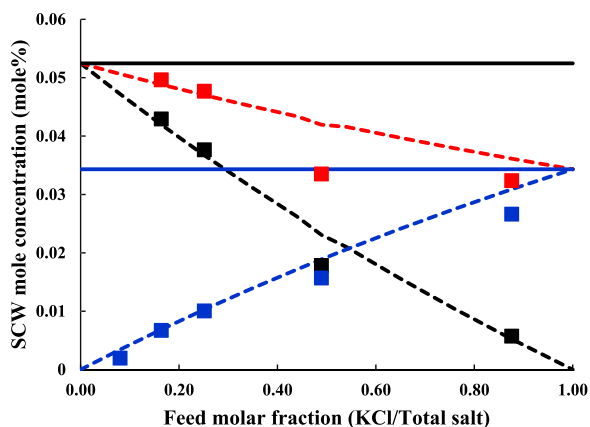

Fig. 7. : NaCl and KCl concentration in the SCW stream at 300 bar and 430 °C as a function of molar ratio of KCl to Total salt in the feed (■ Experimental NaCl; ■ Experimental KCl; ■ Experimental total salt; — Calculated NaCl binary mixture; — Calculated KCl binary mixture; — — Calculated NaCl adjusted for feed conc.; — — Calculated KCl adjusted for feed conc.; — — Calculated total salt concentration). Total feed concentration of 1 wt% salt.

increased. Furthermore, the total salt concentration in the SCW stream becomes equal to the binary calculated concentration of the majority salt in the feed. The calculated concentrations for the binary mixtures (solid lines in Fig. 7) remained constant, as the equilibrium concentration is only dependent on the temperature and pressure and not on the feed concentration. For low concentrations of KCl in the feed (left-hand side of Fig. 7), the total salt concentration was close to 0.052 mol%, which was the binary calculated concentration of NaCl in the SCW phase for a pressure and temperature of 300 bar and 430 °C, respectively. As the concentration of KCl in the feed increased (move towards the right-hand side of Fig. 7), the total salt concentration decreased to 0.034 mol. %, which was the calculated equilibrium concentration for KCl-H$_2$O in the SCW phase.

From Fig. 7, it is thus seen that for this case the equilibrium concentrations in the SCW phase could be predicted using the binary EoS for NaCl-H$_2$O and KCl-H$_2$O respectively and adjusting for the feed composition on mol fraction basis. The feed concentrations of both salts were low (total salt concentration was 1 wt%) and the properties and phase behaviour of NaCl and KCl in SCW is quite similar as seen in this work and previous work [29], which led to the mixture exhibiting ideal behaviour.

In order to verify if the mixture retains ideal behaviour and if the approach of calculating the equilibrium concentrations is still viable for higher feed concentration of NaCl and KCl, where the interactions between the salts become more prominent, further study is required. For other type I-I salt mixtures (*e.g.*, NaCl-CaCl$_2$), this approach may not be valid due to differences in the properties and structure of the salts.

In Fig. 8 the mass ratio of NaCl to KCl in the outlet stream is presented for 250 and 300 bar.

It can be seen that some partitioning occurred between NaCl and KCl once the mixture entered the VLE region, which is due to the different partition coefficients of the salts in the liquid and vapour phase as seen in Fig. 7. The ratio (NaCl$_{SCW}$/KCl$_{SCW}$) increased slightly, with the SCW phase becoming more concentrated in NaCl. This would mean that the hydrothermal brine phase would become slightly more concentrated with KCl. It is furthermore seen that the ratio did not continue to increase with temperature, but stabilised once the VLE region was entered. The ratios and trends could be predicted using the binary AP EoS for the respective salt-water mixtures and adjusting the calculated equilibrium concentration for the feed composition based on mole fraction.

The phase behaviour of ternary NaCl-KCl-H$_2$O mixtures, under supercritical conditions, has not been extensively investigated, with most studies conducted for geothermal conditions where liquid-solid (LS) and vapour-solid (VS) equilibria were investigated and modelled [34,35, 37–39]. Sublett et al. [39] investigated the partitioning of Na$^+$ and K$^+$ in the VLE region for temperatures of 600 – 800 °C and 500–1000 bar for different feed ratios. From the results, it was also seen that the Na$^+$ concentration increased slightly in the SCW (vapour) – phase, while the K$^+$ concentration increased in the hydrothermal brine (liquid) – phase, which is in-line with the results of this study.

Lastly, it is seen that the ratio (NaCl$_{SCW}$/KCl$_{SCW}$) decreases for higher pressures (compare Fig. 8a & b). This is due to the degree of solubility increase – of KCl in SCW – with pressure being greater in comparison to the solubility increase of NaCl. Pressure thus has a greater influence on the solubility of KCl than that of NaCl. For example, for NaCl the mass concentration in SCW will increase with a factor of six (from 0.049 to 0.3 wt%) from 250 to 300 bar at 420 °C. For KCl, the mass concentration will increase with a factor of seven (from 0.037 to 0.25 wt%) and therefore the ratio of NaCl to KCl in the SCW phase will decrease with increased pressure. The mass concentrations were based on the calculated values of AP EoS for respective binary mixtures.

4.2.2. Type I – II mixture (NaCl – Na$_2$SO$_4$ – H$_2$O)

The outlet stream salt concentrations of NaCl and Na$_2$SO$_4$ for a feed mass ratio of 7:3 (total salt feed concentration of 1 wt%) at 250 and
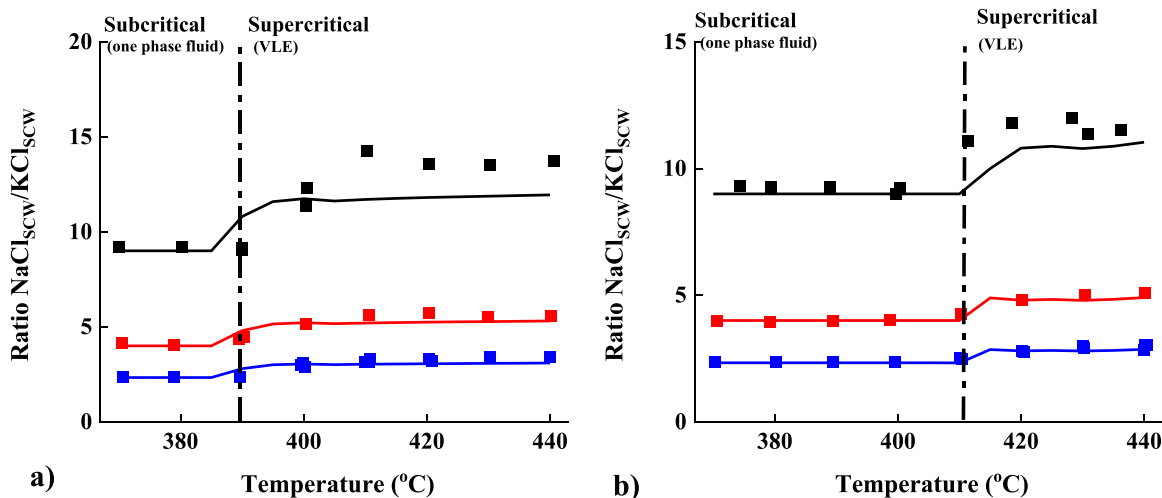
Fig. 8. : Mass ratio between NaCl and KCl concentration in the high-pressure, high-temperature or SCW stream (a) 250 bar (b) 300 bar (■ Experimental ratio for 9:1 (NaCl:KCl) feed ratio; ■ Experimental ratio for 8:2 feed ratio; ■ Experimental ratio for 7:3 feed ratio; — Calculated ratio for 9:1 feed ratio; — Calculated ratio for 8:2 feed ratio; — Calculated ratio for 7:3 feed ratio). Phase regions in brackets, correspond to the phase regions depicted in Fig. 1a.

300 bar, are given in Fig. 9 below. The results for the other feed ratios and pressures can be found in the SI, as well as the tabulated results (Table S.4).

As with the NaCl-KCl mixtures, the transition from the subcritical to supercritical region is indicated by the separation between the SCW and hydrothermal brine phase for NaCl (mixture enters the VLE region, see Fig. 1a). In Fig. 9, the outlet concentrations measured at the top outlet of the separator (see Fig. 3) are given. In the subcritical region, the concentration of NaCl remains constant and equal to the feed concentration as NaCl is still in the one phase fluid region (see Fig. 1a). The concentration of Na_2SO_4 in the outlet stream starts to decrease above a certain temperature as Na_2SO_4 starts to precipitate in the separator, which is due to the solubility of Na_2SO_4 decreasing with an increase in temperature (see Fig. 1b). The mixture is thus still in the fluid region, however, now solid Na_2SO_4 remains in the separator. The mixture enters the supercritical state once the NaCl concentration starts to decrease, which indicates the separation between SCW and hydrothermal brine, with the SCW (low salt) concentration being measured at the top. The hydrothermal brine, which accumulates at the bottom of the separator, has a high salt concentration and is not indicated in Fig. 9. The concentration of Na_2SO_4 (now in the SCW) also continues to decrease once the supercritical state is entered. As shown in Fig. 9, the subcritical state is

subdivided into region 1 and 2, while the supercritical state is marked as region 3. An in-depth explanation of the regions is given below.

The outlet concentrations for the binary mixtures were determined using the phase region algorithm and the adapted AP EoS for a Na_2SO_4-H_2O mixture from our previous work [29]. The transition from the subcritical to the supercritical region (the separation between the SCW phase and the hydrothermal brine phase – VLE region) was indicated by the decrease in the NaCl experimental concentration. By comparing the experimental and binary calculated concentrations for NaCl, it is seen that the temperature where the separation starts could be predicted within ± 10 °C. The model predicted concentrations of NaCl in the SCW phase that were comparable with the experimentally measured concentrations.

For the Na_2SO_4 at 250 bar, the measured concentrations were higher than the calculated concentrations for the region of 380–400 °C. Once the mixture entered the VLE region (region 3 in Fig. 9) the calculated and measured concentrations were comparable. This was also seen for other feed ratios of 9:1 and 8:2 for 250 bar (see the SI). For 270 and 300 bar the calculated and measured concentrations were comparable for the entire temperature range. Note that the calculated concentrations were not adjusted for the feed composition of the salt mixture.

Based on the experimental observations made for the NaCl-Na_2SO_4-

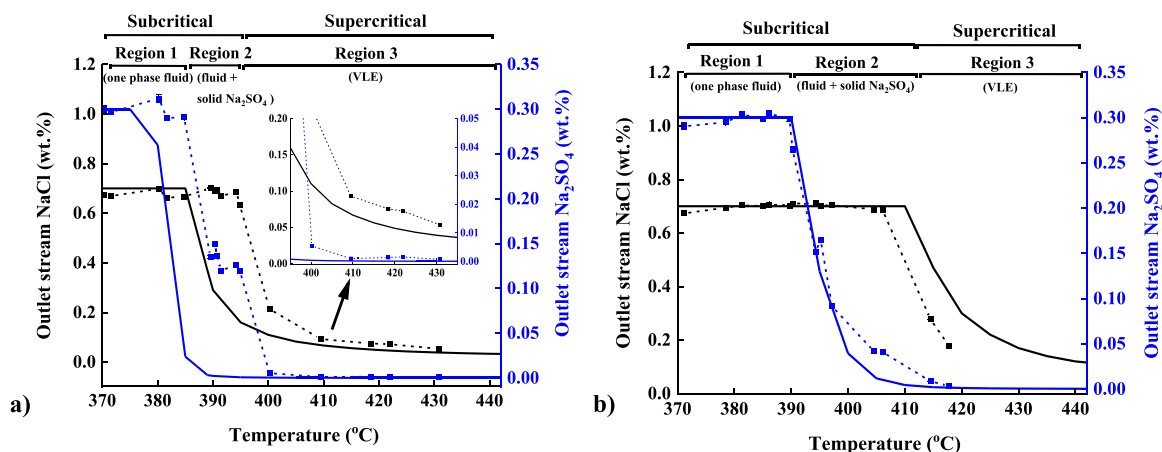**Fig. 9.** : NaCl and Na_2SO_4 concentration in the outlet stream for a feed mass ratio of 7:3 (NaCl: Na_2SO_4) and total salt concentration of 1 wt%, a) 250 b) 300 bar (■ Experimental NaCl; ■ Experimental Na_2SO_4; (dashed lines help to guide the eye for the experimental points); — Calculated NaCl from binary AP EoS; — Calculated Na_2SO_4 from binary AP EoS).

H_2O mixtures, the phase behaviour was divided into three regions. The regions are indicated in Fig. 9. For Fig. 9a the first region (370 to ≈ 385 °C), the salt concentrations of the high-pressure, high-temperature outlet stream were equal to the feed concentrations and no separation occurred. In the second region (385 to ≈ 400 °C) the concentration of Na_2SO_4 in the high-pressure, high-temperature outlet stream decreased, while the NaCl concentration remained the same as the feed concentration. In this region, the concentration of Na_2SO_4 in the outlet stream was greater or equal to the calculated equilibrium concentration for the binary mixture. The decrease of Na_2SO_4 concentration indicates that there was precipitation of Na_2SO_4 inside the separator, as Na_2SO_4 is a type II salt which does not form a hydrothermal brine (see Fig. 1). In region two there was no separation between a hydrothermal brine and the SCW phase, as the system had not yet entered the VLE region (indicated by the NaCl outlet concentration remaining constant). The precipitated Na_2SO_4 could not be dissolved in the hydrothermal brine and most probably solids were present and deposited in the separator. The binary AP EoS for NaCl and Na_2SO_4 respectively, predicted phase separation in this region, which indicates that the presence of Na_2SO_4 affects the phase behaviour of NaCl. For the Na_2SO_4 at 250 bar it appeared as if a plateau formed in region two where the concentration of Na_2SO_4 stabilised at ± 0.11 wt%. The plateau region was also seen for a feed ratio of 8:2 at 250 bar (see the SI) and by Voisin et al. [23], who stated that the concentration of Na_2SO_4 remains constant as it starts to partly dissolve in the hydrothermal brine formed by the NaCl. However, as stated no hydrothermal brine was present yet and thus for this study it was concluded that the Na_2SO_4 precipitated in this region. The plateau was also not observed for a pressure of 270 and 300 bar (see the SI), where the Na_2SO_4 concentration gradually decreased. For a mixture of 9:1 at 250 bar (see Figure S.4) the plateau region was also not observed, most likely due to the low concentration of Na_2SO_4 in the feed mixture.
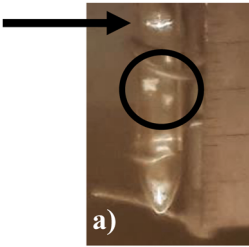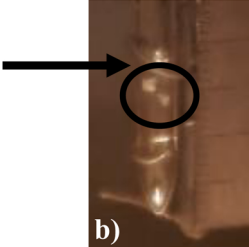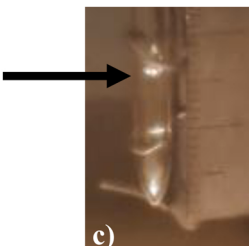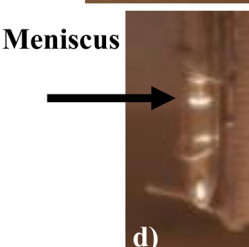
For the third region (T > 400 °C – Fig. 9a), separation between the SCW and the hydrothermal brine occurred (VLE region) as the NaCl concentration in the SCW decreased along with the Na_2SO_4 concentration. In this region, the solid Na_2SO_4 dissolved (fully or partially) in the hydrothermal brine present in the separator, as evident from the qualitative results shown in Fig. 5 (Section 4.1). Fig. 9b can be divided into similar regions, with the precipitation of Na_2SO_4 occurring between 392 and 410 °C.

The recovery of SCW (third phase region) was once again high (97 – 99 %) due to the low salt feed concentration (1 wt% total salt). The total salt concentration of the SCW was 500–1900 ppm and mainly consisted of NaCl, with trace amounts of Na_2SO_4.

The three phase regions were also visually investigated further to see if the precipitation of Na_2SO_4 (in region 2) and the subsequent dissolving (in region 3) could be observed. Qualitative capillary experimental were performed for a feed ratio of 6:4 (NaCl:Na_2SO_4), with the total salt concentration being 10 wt%. The concentrations reported were calculated by solving the VLE and VSE using the AP EoS for NaCl-H_2O and Na_2SO_4-H_2O mixtures, respectively. For Figure a (in Table 1), the concentration of Na_2SO_4 in the liquid phase was estimated based on the results reported by DiPippo et al. [10] for 10 wt% NaCl/Na_2SO_4 aqueous solution at 200 bar. For Figure b, the solubility of Na_2SO_4 in the hydrothermal brine for the given conditions is not known and thus only the vapour (SCW) concentration of Na_2SO_4, based on the binary equilibrium calculations is given. The Na_2SO_4 brine concentration for region 3 (fully dissolved), was calculated by performing a mass balance. The hydrothermal brine flow rate was calculated from the NaCl-H_2O AP EoS. Results of the capillary experiments are given in Table 1.

For Figure a, the mixture is in region 2, as the conditions are just above the critical point of water. The precipitation of Na_2SO_4 is visible. As the mixture is heated further (Figure b) it transitions to region 3, where there is a phase separation between the SCW phase and the hydrothermal phase. This is indicated by the slight decrease in the meniscus (indicated by the arrow). The Na_2SO_4 precipitation is still visible in this stage, indicating that it is partially dissolved in the

Table 1
Results of capillary experiments for a feed ratio of 6:4 (NaCl: Na_2SO_4). The arrow indicate the meniscus.

Capillary	Conditions	Predicted results[b]
a)	Feed ratio: 6:4 (NaCl:Na_2SO_4) Total salt: 10 wt% Temperature: 375 °C Pressure ~ 220 bar VLS	Region: 2 (Na_2SO_4 deposition in separator) $x_{L, NaCl}$: 6 wt% $x_{L, Na2SO4} \approx 2.5$ wt%[b] $x_{V, Na2SO4}$: 0.0019 wt%
b)	Feed ratio: 6:4 (NaCl:Na_2SO_4) Total salt: 10 wt% Temperature: 392 °C Pressure ~ 225 bar VLS	Region: 3 (Na_2SO_4 partially dissolved in brine and partly deposited in separator) $x_{L,Brine, NaCl}$: 20 wt% $x_{V, SCW,NaCl}$: 0.048 wt% $x_{V,SCW,Na2SO4}$: 0.00014 wt%
c)	Feed ratio: 6:4 (NaCl:Na_2SO_4) Total salt: 10 wt% Temperature: 398 °C Pressure ~ 236 bar VL	Region: 3 (Na_2SO_4 fully dissolved in brine) $x_{L,Brine, NaCl}$: 22 wt% $x_{V,SCW,NaCl}$: 0.061 wt% $x_{LBrine, Na2SO4}$: 15 wt%[a] $x_{V,SCW,Na2SO4}$: 0.00017 wt%
Meniscus **d)**	Feed ratio: 6:4 (NaCl:Na_2SO_4) Total salt: 10 wt% Temperature: 408 °C Pressure ~ 248 bar VL	Region: 3 (Na_2SO_4 fully dissolved in brine) $x_{L,Brine, NaCl}$: 27 wt% $x_{V,SCW,NaCl}$: 0.067 wt% $x_{L,Brine, Na2SO4}$: 18 wt%[a] $x_{V,SCW,Na2SO4}$: 0.00016 wt%

[a] $x_{Brine,Na_2SO_4} = \dfrac{x_{Feed,Na_2SO_4} m_{Feed} - x_{SCW,Na_2SO_4} \quad m_{SCW}}{m_{Brine}}$

[b] Concentration based on the results of DiPippo et al. [10]

hydrothermal brine. As the temperature is further increased (Figure c and d), the brine becomes more concentrated (indicated by a decrease in the height of the meniscus) and the precipitated Na_2SO_4 dissolves completely to once again form a VL mixture. Conversely, for Fig. 5 (mixture 6:4), precipitated Na_2SO_4 was still visible, which was due to the mixture just transitioning to region 3. For the given conditions, the brine concentration was estimated to be ~ 6.4 wt% which is close to the feed concentration of NaCl, indicating that phase separation was barely established [29]. For the NaCl-Na_2SO_4-H_2O mixture this would mean that there is not a sufficient amount of hydrothermal brine to completely dissolve the precipitated Na_2SO_4, which was similar for the phase behaviour seen for Figure b from Table 1.

With regards to predicting the equilibrium concentrations in the SCW phase, the method used for NaCl-KCl-H_2O mixtures could not be applied for NaCl-Na_2SO_4-H_2O mixtures. The properties and phase behaviour of Na_2SO_4 and NaCl differ significantly as Na_2SO_4 is a type II salt and NaCl in a type I salt. The mixture of the two salts can thus not be regarded as an ideal mixture, as the presence of NaCl affects the phase behaviour of Na_2SO_4 (fully or partially dissolves the precipitated salts).

In order to predict equilibrium concentrations, the interaction parameters of NaCl and Na_2SO_4 would need to be fitted/known, in order to predict the solubility of Na_2SO_4 in the hydrothermal brine.

5. Summary and conclusion

The phase behaviour of two model ternary salt-salt-water mixtures (NaCl-KCl-H_2O and NaCl-Na_2SO_4-H_2O) was investigated for the application of SCWD. The study was carried out in a two-step procedure, namely a qualitative analysis to visually inspect the phase behaviour and a quantitative analysis to measure the equilibrium concentrations.

The qualitative investigation of the NaCl-KCl-H_2O showed that VLE was established for different ratios, with no risk of solid formation. The results for the NaCl-Na_2SO_4-H_2O showed that for mixtures containing mostly NaCl (70 wt% or greater on a total salt basis) the hydrothermal brine would be sufficient to completely dissolve the precipitated Na_2SO_4. For a mixture of 6:4 (NaCl to Na_2SO_4 – mass basis), the Na_2SO_4 will firstly precipitate, and consequently redissolve once the concentrated NaCl hydrothermal brine is formed. For lower concentrations of NaCl, the Na_2SO_4 was only partially dissolved and solids were present.

From the quantitative results for NaCl-KCl-H_2O mixtures, it was concluded that SCWD could be applied for the recovery of freshwater from the mixed feed. The phase behaviour and equilibrium concentrations in the SCW phase were similar for both salts, meaning that the salts could not be separated using SCWD and the resulting solid product (after flashing the brine) would be a mixture of KCl and NaCl. Due to the similar properties of NaCl and KCl, the mixture of the two binary solutions (NaCl-H_2O and KCl-H_2O) could be seen as an approximate ideal mixture of two regular solutions. For this reason, the equilibrium concentration of the SCW phase for the ternary mixture could be predicted using the respective binary salt-water concentrations (AP EoS) and correcting for the feed composition on molar fraction basis.

From the quantitative analysis of NaCl-Na_2SO_4-H_2O mixtures, the phase behaviour of the mixture could be divided into three regions for the temperature range investigated in this study. In the first region no separation occurred, followed by the second region, where Na_2SO_4 precipitated from the mixture, while the NaCl remained in solution. SCWD could be applied for the treatment of these NaCl-Na_2SO_4-H_2O mixtures, provided that the process was operated in the third phase region, where separation occurs between the SCW and hydrothermal brine phase (pseudo-VLE). The precipitated Na_2SO_4 would dissolve in the hydrothermal brine, allowing the conditions for VLE, as required by the SCWD process.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.supflu.2022.105687.

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