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# **Influence of multiphasic systems on salt(s) solubility in supercritical water: the case of NaCl and NaCl-Na<sub>2</sub>SO<sub>4</sub>**

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## **Abstract**

Supercritical water oxidation processes (SCWO) have been developed as an alternative technology to treat toxic and/or complex chemical wastes with a very good efficiency. However, one main limitation of the SCWO process comes from the precipitation of inorganic compounds. When dealing with supercritical water conditions ( $T \geq 374^\circ\text{C}$ ,  $p \geq 22.1 \text{ MPa}$ ), the polarity of water drops and inorganics, such as salts, are no longer soluble. This precipitation phenomenon results in a solid salt deposition in the reactor, which can lead to clogging and interruption of the continuous process. Considering a specific salt, beside its intrinsic solubility in supercritical water, the presence of other salts or other compounds in the media can modify its precipitation behaviour. With the use of a specific experimental set-up, we propose in the present work to study the solubility of NaCl (type I salt) in supercritical water, and the influence of its phase diagram on its precipitation behaviour as well as on the solubility of a second salt, Na<sub>2</sub>SO<sub>4</sub> (type II salt). The complex and dynamic aspect of NaCl precipitation has been studied through the use of a continuous solubility measurement set-up, revealing unexpected results.

**Keywords:** SCWO, supercritical water, salt precipitation, multiphasic systems, solubility

## **Introduction**

Research regarding Supercritical Water Oxidation (SCWO) process has become an important field of development over the past 30 years [1–5]. With high degradation rates and efficiencies for the treatment of industrial wastewater and chemical wastes, SCWO processes are part of the technologies bringing environmental waste treatment alternatives [1,6]. However, supercritical water ( $T \geq 374^\circ\text{C}$ ,  $p \geq 22.1 \text{ MPa}$ ) exhibits particular properties among which a very low polarity, leading to the capacity to dissolve organics compounds, with the drawback of precipitation of inorganic compounds. This precipitation phenomenon is one of the main limitation regarding SCWO industrialization as a continuous process [7–9]. As precipitation occurs, inorganic compounds are deposited on the reactor wall, leading to the formation of clogs and interruption of the process.

Although this limitation is well-known, a limited amount of data is available in the literature concerning the solubility limits for inorganic compounds in supercritical water, especially for salts present in most of the real wastewater to be treated [10]. Few research works studied the salt solubility in supercritical water, and fewer the solubility of salt mixtures [10–15]. Indeed, SCWO processes rarely deal with simple water/salt wastes, but most of the time with complex mixtures of several compounds including organics, inorganics, water and oxidizing agent (air,  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ...). Mixture of different salts can influence the solubility of each salt and some research works have been conducted regarding the change in solubility with salt mixtures [12–15]. We also have to mention the important work of classification performed by Valyashko *et al.* regarding the types of salt and their behaviour according to it [16]. Different interaction phenomena can take place with salt mixtures, and influence the solubility of each salt. One effect frequently mentioned in the literature is the common ion effect. If two salts share a common ion, then the less soluble salt sees a decrease of its solubility. In addition, it is

mentioned that mixing a type I salt with a type II salt (less soluble in supercritical water than the type I salt) increases the solubility of the type II [16,17]. Thus, considering a type I salt such as NaCl, and a type II salt like Na<sub>2</sub>SO<sub>4</sub>, with the sodium as a common ion, it is difficult to predict if the Na<sub>2</sub>SO<sub>4</sub> solubility is increased or decreased. Very few research works achieved a quantitative study of the changes in solubility due to a mixture of different salts [10]. The present work intends to study on one hand, the solubility of a common type I salt, sodium chloride (NaCl), and its influence on the solubility of a type II salt, sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), when they are mixed together in sub- and supercritical water.

Regarding the study of the NaCl solubility in supercritical water, the literature data are restricted to two research works [18,19] which used an experimental method consisting in dissolving NaCl salt crystals into supercritical water and then measuring the salt concentration. We decided to use a reverse method, consisting in injecting a salted water solution in a continuous reactor to precipitate the salt and measuring the remaining salt concentration in water. The benefits of such process are double. First, working in continuous enables a fast screening of NaCl solubility in large temperature domains. Second, continuous measurements can give access to new information on the dynamic of salt precipitation in supercritical water conditions.

## **Materials and methods**

To perform the solubility measurements of NaCl and of the mixture NaCl-Na<sub>2</sub>SO<sub>4</sub>, a continuous conductivity analysis set-up was used, coupled with Inductively Coupled Plasma (ICP) analysis.

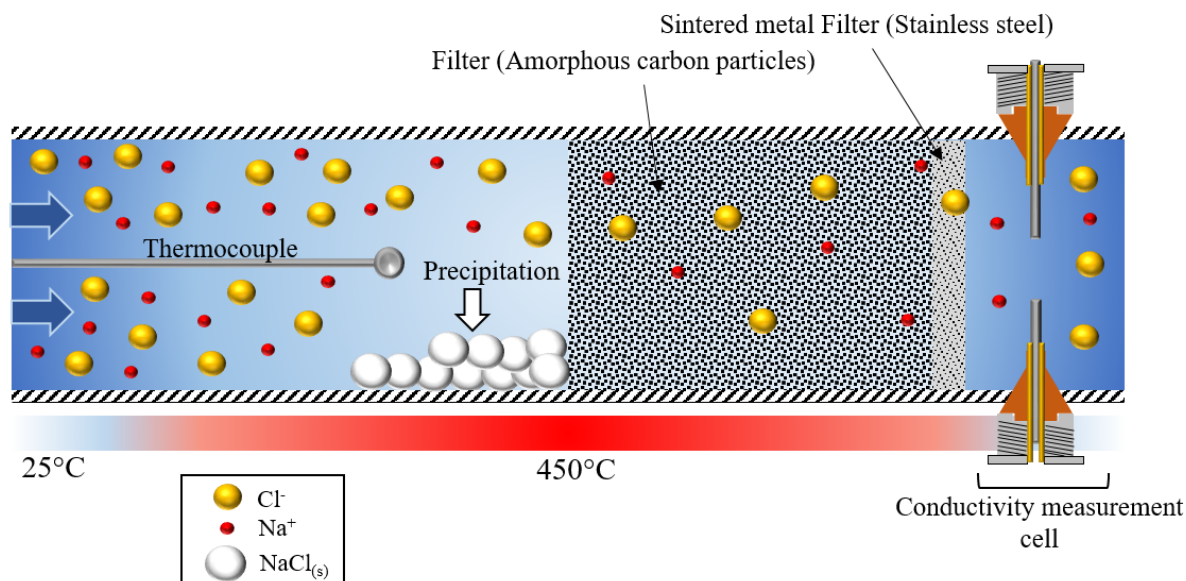


Figure 1: Scheme of the principle of the experimental set-up and the continuous conductivity measurement used for the salt solubility analyses. Illustration with NaCl.

The set-up used for the solubility measurements has been described in details elsewhere [20]. It is composed of a 600 mm long Inconel 625 reactor, heated with two heating cartridges inserted in a brass support, with a large filter inside the second half part of the reactor. The filter is composed of amorphous carbon particles, to sustain supercritical water conditions and insure that salt particles are not pulled along the reactor with water, but remain in the hot part (c.f. Figure 1). The water flow is then cooled down with the remaining salt ions and is analysed in an in-flow conductivity cell. Samples are also recovered at the outlet to perform ICP measurement. When studying one pure salt in water, conductivity can be used to measure the salt solubility in a continuous way. However, for salt mixture, conductivity only indicates when precipitation occurs but cannot be used for a quantitative analysis. This is why ICP analysis was mainly performed for the NaCl- Na<sub>2</sub>SO<sub>4</sub> mixture, through the quantification of the sulfur and sodium content. Sulfur content will then be used to determine Na<sub>2</sub>SO<sub>4</sub> concentration, whereas the remaining sodium content will give the NaCl concentration. Salted solutions have been prepared with ultra-pure water, NaCl powder (ALFA AESAR, crystalline powder, PDV, 99+%) and Na<sub>2</sub>SO<sub>4</sub> powder (SIGMA-ALDRICH, ACS reagent, ≥99.0%, anhydrous, granular).

Regarding the NaCl- Na<sub>2</sub>SO<sub>4</sub> mixture, initial concentrations of the two salts are equal to 0.01 mol/L.

NaCl solubility measurement using conductivity is performed according to the same methodology described in our previous work [20]. A power law is used to fit the molar conductivity of NaCl (c.f. Figure 2) [21]. This empirical law is then combined with the expression of the conductivity  $\sigma$  to result in a polynomial equation. Solving this polynomial expression gives access to the NaCl concentration.

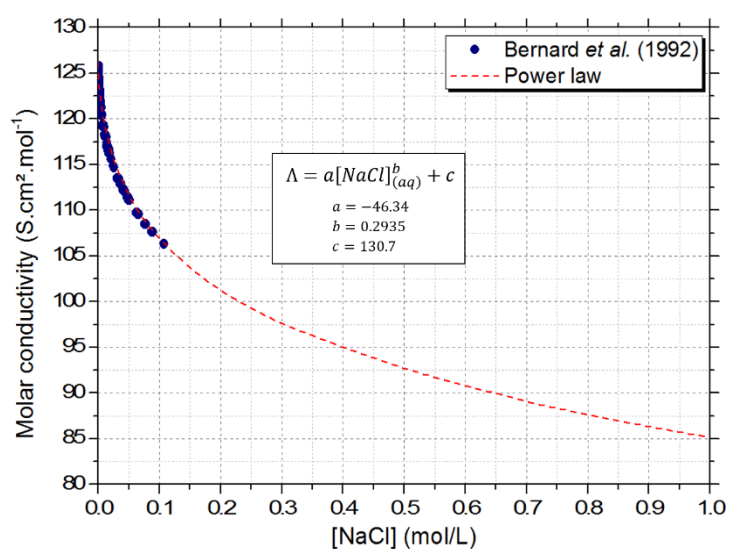


Figure 2: Molar conductivity data for NaCl at 25 °C from the literature and empirical power law used to fit the data .

## Results and discussion

This result section is composed of two different subsections. First is presented the solubility study of NaCl, in order to know the reference system and then proceed to the second section, dedicated to the study of the NaCl-Na<sub>2</sub>SO<sub>4</sub> system.

## 1. Solubility of sodium chloride

Several previous research works studied the NaCl solubility in water at high temperatures, but few in supercritical water conditions at 25 MPa [10,18,19]. However, the NaCl-H<sub>2</sub>O binary diagram has been determined in these conditions (c.f. Figure 3) [22,23], and one should know that a liquid-vapor diphasic domain appears, beginning at about 390°C and ending at 450°C. This diphasic domain means that instead of a solid precipitation, two phases are first formed. One “vapor” phase consists in a low-density water phase, with a low salt concentration, and one “liquid” phase which corresponds to a high-density brine with a higher salt concentration.

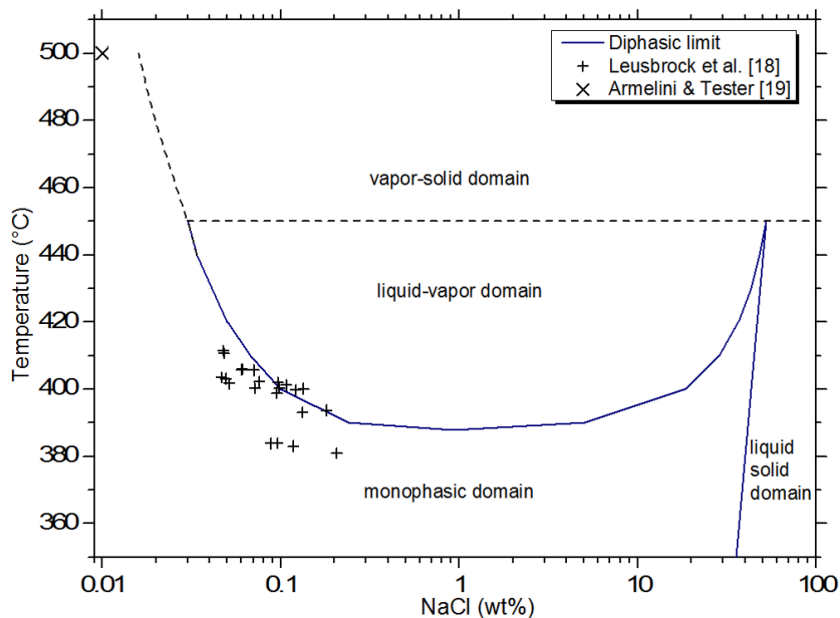


Figure 3: NaCl-H<sub>2</sub>O binary diagram, with solubility data from the literature, at 25 MPa.

As temperature increases, the salt concentration in the vapor phase decreases whereas the liquid phase becomes more and more concentrated, but also less dense. One should notice that the only NaCl solubility data available at 25 MPa, presented in Figure 3, have been determined using a salt dissolution process, meaning salt crystals deposited in a reactor filled with supercritical water and progressively dissolved up to the saturation [19,18]. Therefore, the dynamic of the NaCl precipitation cannot be evidenced.

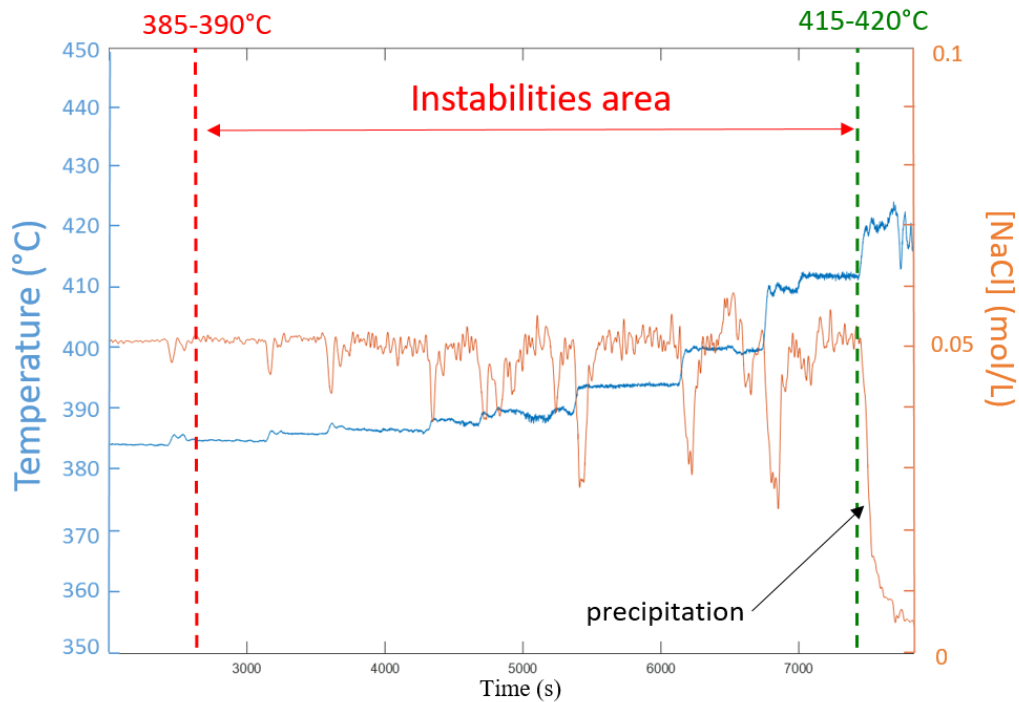


Figure 4: Example of the detection of instabilities between 385 and 415°C, before precipitation of NaCl, for an initial concentration of 0.05 mol/L.

The first interesting result obtained from our continuous set-up for the NaCl concentration measurement, is due to the impact of the diphasic domain on the solubility of the system. Indeed, as the liquid-vapor equilibrium is formed, instabilities in temperature and concentration (conductivity) are detected in the system (c.f. Figure 4), thanks to a K-type thermocouple placed inside the reactor (c.f. Figure 1) and the continuous conductivity measurement cell. One can then determine the beginning and ending temperature of these instabilities and report them on the H<sub>2</sub>O-NaCl binary diagram for different initial concentrations (c.f. Figure 5).

At first glance, one would think that instabilities begin with the appearance of the new phase, as described by the binary diagram. Although the detection of the first instabilities well matches with the lower limit of the liquid-vapor domain (around 390°C), the upper limit is lower than the one which could be expected from the diagram. As it can be seen from Figure 5, the



detection of the first instabilities corresponds to the lower limit of the diphasic domain, at about 390°C.

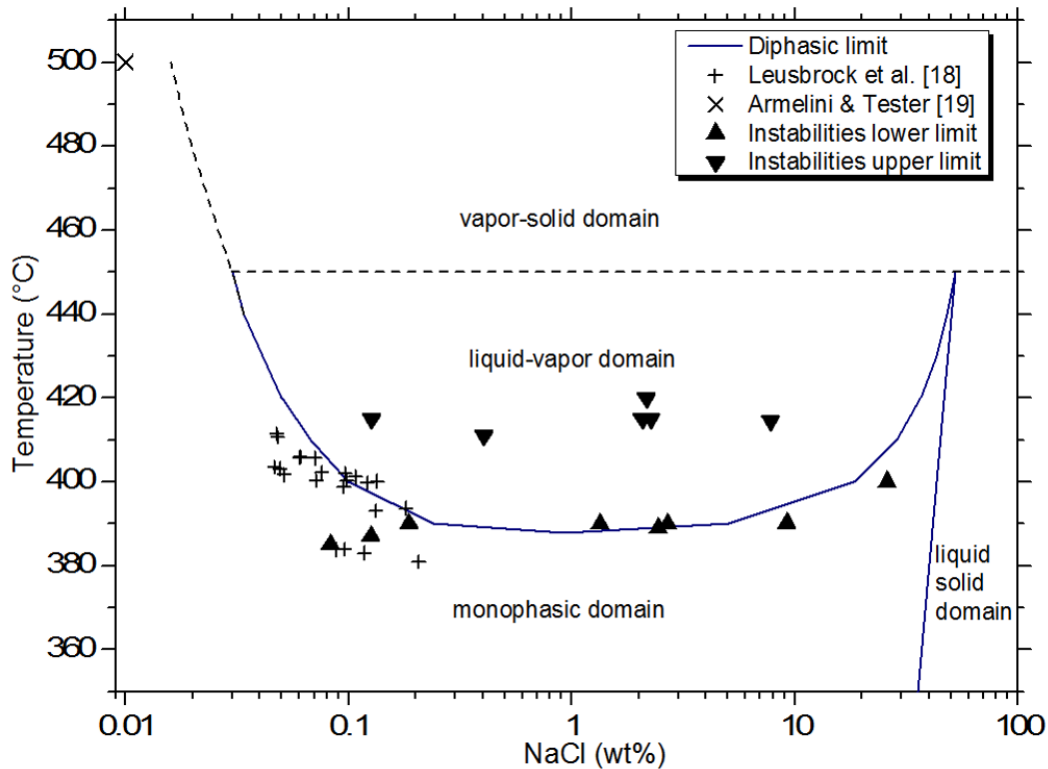


Figure 5: Representation of the beginning and ending temperatures of instabilities on the phase diagram of NaCl-H<sub>2</sub>O, for different NaCl initial concentrations.

A more unexpected result is related to the end of these instabilities. While the NaCl-H<sub>2</sub>O binary diagram predicts the end of the liquid-vapor domain at a temperature of 450°C, experimentally the instabilities disappear around 415-420°C, with an abrupt decrease in NaCl concentration, indicating the precipitation of the salt (c.f. Figure 4).

However, it appears that between the upper limit of instabilities (415°C) and the end of the diphasic domain (450°C), the measured NaCl concentrations vary, for a given temperature, depending on the initial concentration (c.f. Figure 6). This unexpected behaviour suggests that the system is still located in its diphasic domain, as predicted, and the measured concentrations are then influenced by the proportions between the liquid phase and the vapor phase. As this proportion may depend on the initial concentration, it would explain the different concentration values obtained for a given temperature. Consequently, the measured concentrations

(performed at room temperature by conductivity measurement) in this domain correspond to an average between the salt concentration in the vapor phase and the brine phase. It is only when reaching 450°C that the measured concentrations converge towards a unique value and independently from the initial concentration. This concentration corresponds to the NaCl solubility in water at 450°C and 25 MPa, in good agreement with the proposed phase diagram of H<sub>2</sub>O-NaCl.

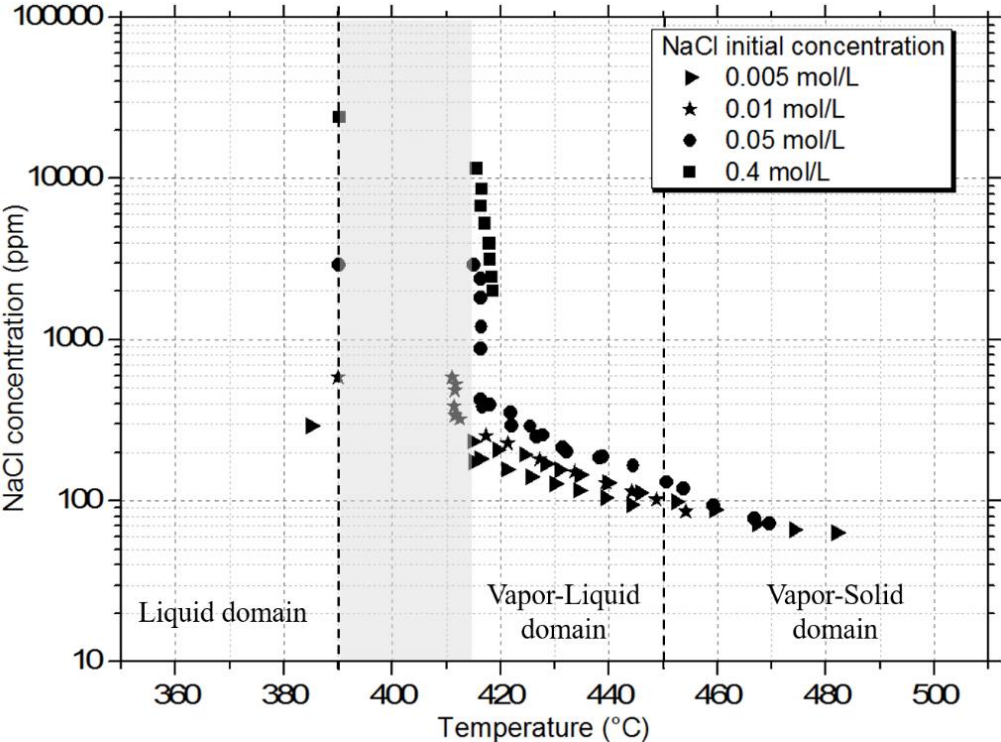


Figure 6: NaCl concentrations as a function of temperature, at 25 MPa. The grey area represents the instabilities domain.

These results clearly show how the existence of this high temperature diphasic domain, between NaCl and water, makes more complex the determination of the NaCl solubility in this temperature range. The results suggest that a first diphasic limit exists between 390°C and about 415-420°C, then an event occurs at 420°C, which may be due to a significant change in the phase proportions, and also to the precipitation of the first NaCl crystals. A triphasic domain would then prevail between 420°C and 450°C (as illustrated in Fig. 7). Above 450°C, a standard diphasic equilibrium between water and solid salt is present. The solid precipitation occurring

between 420 and 450°C has never been predicted before, especially by the reported binary H<sub>2</sub>O-NaCl diagram.

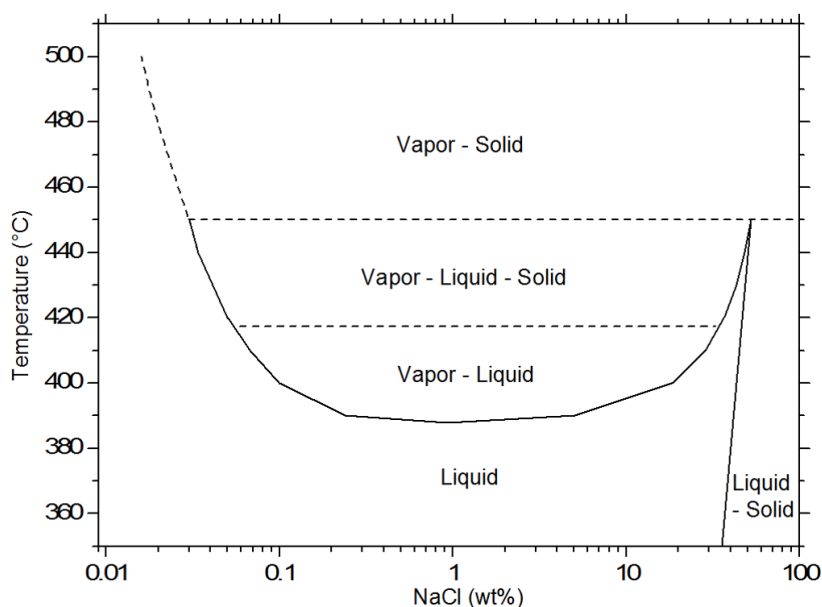


Figure 7: Schematic illustration of the proposed H<sub>2</sub>O-NaCl diagram

As a type I salt, NaCl behaviour in supercritical water conditions differs from Type II salt such as Na<sub>2</sub>SO<sub>4</sub>. With the existence of a diphasic domain at high temperatures, the determination of the solubility becomes difficult. Complex behaviours occur in this domain, with the coexistence of dense brine and a low density vapor phase. As this diphasic domain influences the NaCl solubility in water, it is now interesting to investigate the influence of this multiphasic domain on the solubility of other salt(s), such as Na<sub>2</sub>SO<sub>4</sub> in the H<sub>2</sub>O-NaCl-Na<sub>2</sub>SO<sub>4</sub> system.

## 2. H<sub>2</sub>O-NaCl-Na<sub>2</sub>SO<sub>4</sub> system

The Figure 8 presents the values of solubility of Na<sub>2</sub>SO<sub>4</sub> in SCW [20]. The experimental data were obtained using the same experimental set-up used in the present study.

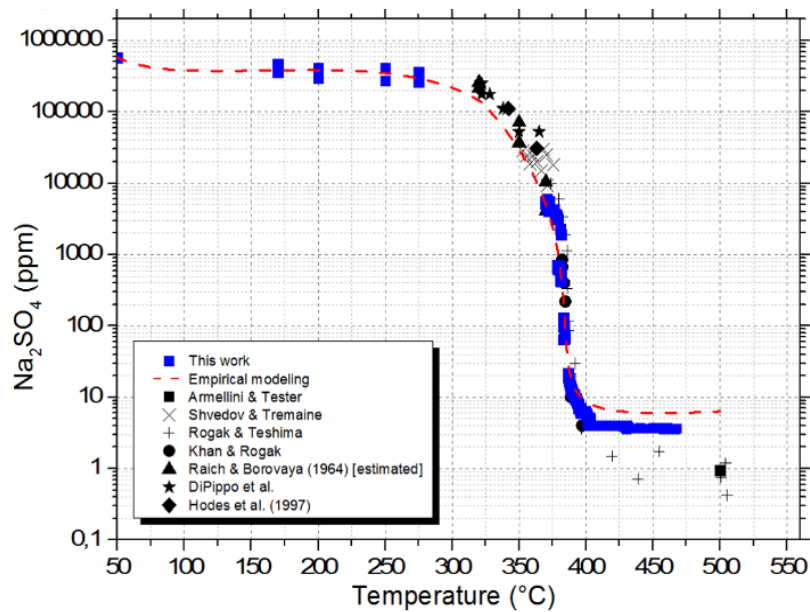


Figure 8:  $\text{Na}_2\text{SO}_4$  solubility measurement in SCW as a function of temperature at 25 MPa (reprinted with permission from Voisin et al. [17]. Copyright © (2017) Elsevier)

Results of the concentration evolutions for  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  obtained from the ICP analyses are presented in Figure 9. Different phenomena can be observed from these evolutions, particularly three temperature domains I, II and III.

The first domain concerns the temperature from 370°C to 380°C (area I in Figure 9). Regarding the  $\text{Na}_2\text{SO}_4$  concentration evolution, it can be seen that the precipitation occurs at a lower temperature compared with the solubility of pure  $\text{Na}_2\text{SO}_4$  (dashed curved in Figure 9, from [20]). This difference can be explained by the common ion effect. Indeed, as the two salts have in common the sodium ion  $\text{Na}^+$ , the precipitation of  $\text{Na}_2\text{SO}_4$  is favoured due to the larger quantity of sodium ions.

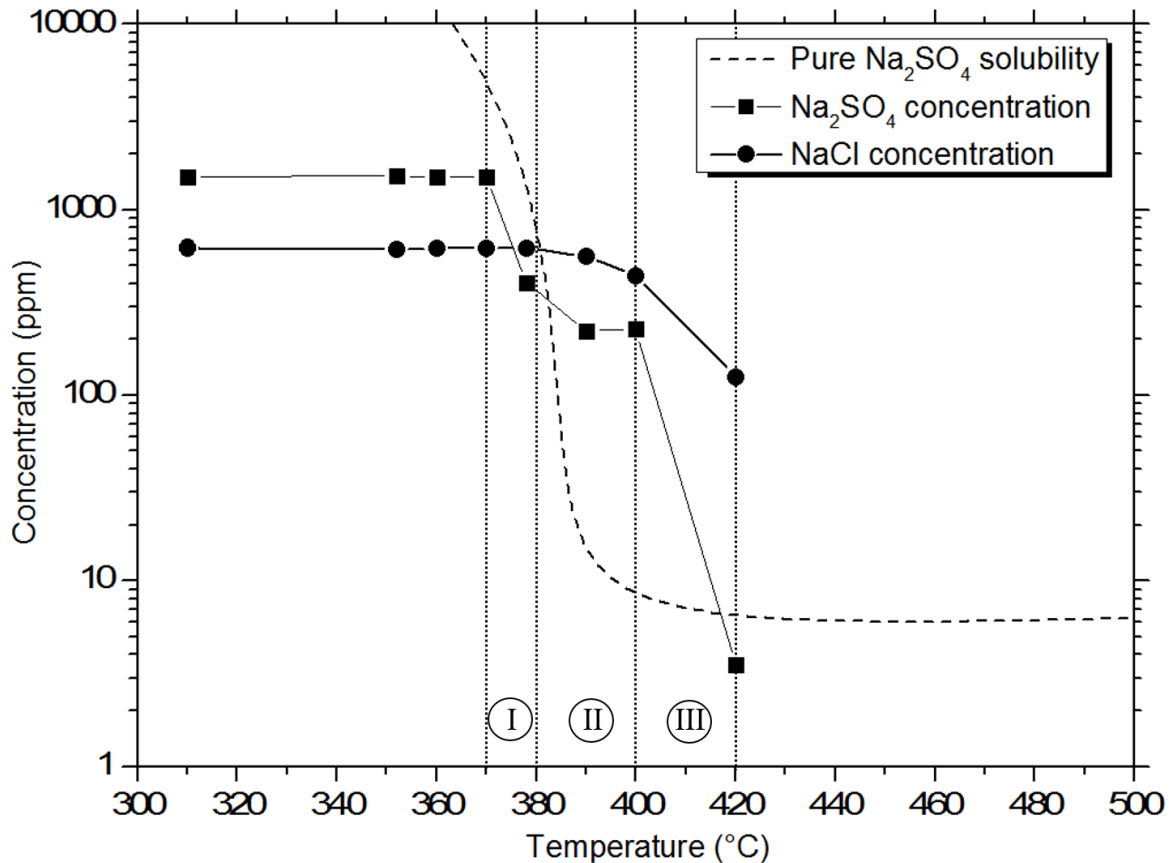


Figure 9: Concentration results for NaCl (dots) and Na<sub>2</sub>SO<sub>4</sub> (squares) from ICP analysis. Comparison with the solubility curve of Na<sub>2</sub>SO<sub>4</sub>

The second observation is related to the temperature domain between 380°C and 400°C (area II on Figure 9). It can clearly be seen that the Na<sub>2</sub>SO<sub>4</sub> concentration is stabilized to a value ten times higher than the solubility of pure Na<sub>2</sub>SO<sub>4</sub>. This temperature domain also corresponds to the beginning of the NaCl diphasic domain with water, meaning that a dense brine phase appears in the system. This dense phase could probably dissolve a part of the Na<sub>2</sub>SO<sub>4</sub> solid crystals, preventing the complete precipitation. This explain why the sodium sulfate concentration remains so high compared to its solubility at these temperatures for pure Na<sub>2</sub>SO<sub>4</sub>.

The last result is located in the third temperature domain above 400°C (area III on Figure 9). At this point, both concentration of NaCl and Na<sub>2</sub>SO<sub>4</sub> get back to their “normal” solubility values. Yet, NaCl concentration begins to decrease around 400°C, instead of 415-420 °C as previously exposed. This premature precipitation can be explained by the fact that, as sodium sulfate is dissolved by the NaCl brine, the saturation concentration in the brine is reached for

lower temperatures as if it was pure NaCl. Instead of reaching saturation for temperatures around 415-420 °C, the sodium sulfate saturates the dense phase around 400°C. Thus, NaCl precipitation occurs at a lower temperature than for pure NaCl, and as soon as the brine phase disappears, Na<sub>2</sub>SO<sub>4</sub> get back to its solubility for pure Na<sub>2</sub>SO<sub>4</sub>.

These results evidence the influence of the dense brine phase from NaCl, on the solubility of a second salt with a lower solubility, such as Na<sub>2</sub>SO<sub>4</sub>. However, the presence of sodium sulfate has also influenced the precipitation of NaCl, as the dissolution of sodium sulfate in the brine phase decreases the temperature at which NaCl precipitates. Despite the small impact of the common ion effect between two salts, the main mixture effect comes from the dense phase. This phenomenon brings quantitative evidences of the impact of a type I salt (NaCl) on the solubility of a type II salt (Na<sub>2</sub>SO<sub>4</sub>), as it was predicted by Valyashko and his classification.

## **Conclusion**

Understanding the precipitation behaviour of a salt in supercritical water is of main interest for SCWO processes and hydrothermal applications. But the salt solubility can be influenced by numerous parameters, especially when mixing several salts together. From the common ion effect, to the influence of a type I salt on a type II salt, it is not always easy to determine the global effect on the solubility. This work showed, through the extensive study of the NaCl precipitation, its complex diphasic behaviour and the study of the NaCl-Na<sub>2</sub>SO<sub>4</sub> system, that one decisive parameter on the solubility of salts is the intervention of a dense phase. Indeed, as seen on the example of the NaCl-Na<sub>2</sub>SO<sub>4</sub> system, the main effect on the solubility of sodium sulfate is the formation of the dense brine phase by NaCl. Due to the high concentration in NaCl in the water brine phase, a high polarity is maintained and enables to dissolve sodium sulfate among it. This leads to a visible increase in sodium sulfate solubility. Despite the small decrease in solubility which can be explained by the common ion effect, it is mainly the dissolution by

the NaCl brine which impacts the sodium sulfate precipitation. This supports the statement according to which a type I salt increase the solubility of type II salt.

This work also exposes the interest in using continuous quantification measurements as it reveals dynamic aspects which can otherwise be missed. Regarding SCWO investigations, it is of great interest to perform studies in conditions as close as possible to the process reality.

Considering the high temperature and high pressure of the supercritical water, any existence of a dense phase in these conditions is often synonym of a high polarity, leading to the dissolution of salt and influencing the solubility. It is likely that other type I salt with the existence of a diphasic domain, like NaCl, would influence the solubility of other salts. For a better understanding of these diphasic behaviours, and to obtain accurate solubility measurements within this temperature domain, one should try to look closely into the chemical/physical explanation of this brine phase formation.

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