Removal of inorganic compounds via supercritical water
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Summary

In the middle of difficulty lies opportunity.

A. Einstein
This thesis introduces the application of supercritical fluids - a highly regarded and emerging technology in process engineering and chemical industry - in a new field: the treatment and purification of aqueous streams. The resulting technology - a new approach to remove inorganic compounds from these streams -, its basics, its options and potential are the tenor of this thesis. New and unique experimental data on behavior and solubility of inorganic compounds in supercritical water are presented and correlated with a semi-empirical approach. Relations between solubility, system parameters, properties of the inorganic compounds and correlation parameters are shown. Process options and concepts are introduced and evaluated regarding their potential, their sustainability and their synergy with other technologies.

The removal of inorganic compounds from aqueous streams via supercritical water is a new and innovative approach to treat water streams with any salt concentration and composition. The separation principle of this approach is based on the changed solvation behavior of supercritical water. While water represents an excellent solvent for inorganic compounds at ambient conditions, it changes to a poor one at supercritical conditions ($T \geq 647 \, K; \, p \geq 22.1 \, MPa$). The resulting decreased solubility of inorganic compounds leads to precipitation and formation of an additional solid phase, which can be removed from the bulk stream. This behavior allows for treatment of saline streams without the production of an aqueous waste stream; an option that current industrial applications like Reverse Osmosis and Multi-Stage-Flash do not offer. Since the technological approach is a new one, fundamental thoughts, fields of applications and possible process options are introduced and discussed. As property data and ways of quantitative and qualitative description are scarce for the systems of interest, special focus is laid on additional property data and methods to interpret and apply this data for later processes.

To underline the necessity of a treatment option for saline streams, Chapter II deals with the current situation of water supplies and water scarcity. It elaborates on the growing water demand in future and its origins. In order to counter the stress on water supplies due to population growth, urbanization, increasing living standards and climate, desalination is considered next to improved water management and increased water reuse as the most probable solution. Desalination is the only way to increase the available global fresh water supply as it uses not drinkable brackish or sea water as feed and produces drinkable fresh water. All other drinking water providing technologies have to use available fresh water sources and purify them. For desalination, membrane technologies like Reverse Osmosis and evaporative technologies like Multi-Stage-Flash are state-of-the-art. While providing drinking water on small as well as on large scale,
both technologies share the common drawback of producing a liquid waste stream with increased salinity. The treatment or disposal of this stream represents a major challenge for the sustainability of a desalination process. As current technology does not provide a satisfying solution for this issue, the usage of supercritical water is proposed as new approach for the treatment of saline streams.

In Chapter 2, the supercritical state of a compound is introduced and its differences to the three common phases solid, liquid and vapor are discussed. Supercritical fluids show a high versatility in their properties since these properties are adjustable by changes in temperature and pressure. The range, in which these properties are adjustable, is the range between the property of the liquid and the vapor phase of a compound. Therefore, the supercritical state is also described as a hybrid state of these two states. This flexibility results in a wide range of applications ranging from analytical methods, particle formation, extraction or medium for oxidation and polymerization reactions. One important aspect of the supercritical state of water is a fundamental change in solvation of inorganic and organic compounds. While being regarded as the solvent for inorganic compounds like salts at ambient conditions, the same is not valid for water in its supercritical state. Here, water is significantly limited in its solvation capability due to changes in its properties and structure. Resulting from this, salts contained in an aqueous stream start to precipitate and to form a solid phase. This solid phase can be removed from the remaining fluid phase. As a consequence of this changed behavior, options for the treatment of saline streams with any composition and concentration are possible while producing a pure water phase and a pure solid phase containing the inorganic compounds.

As a result of the comparably harsh conditions of supercritical water and limited industrial applications with supercritical water at the current moment, property data and studies on crystallization etc. are scarce. Consequently, ways and methods to describe these in a sound thermodynamical way backed up by experimental results are limited and not guaranteeing a valid representation of these systems. Therefore, several approaches to give a quantitative description of solubilities in supercritical water are compared in Chapter 3. As a result of this comparison, one approach based on the semi-empirical description of the phase equilibria is chosen as the most appropriate one for an evaluation of these systems and the comparison of solubilities of different salt species. To extend the property data on systems, which are of interest in later industrial applications, an experimental setup is introduced. This setup allows for the measurement of solubilities till a temperature of 723 K and 25 MPa with a continuous flow method. To validate the
experimental method and setup, measurements were done on the prototype system \( \text{NaCl} - \text{H}_2\text{O} \), which extended successfully the so far available property data from literature.

To increase the knowledge and the available property data in the field of inorganic compounds and their behavior in supercritical water, a systematic investigation of their solubilities was conducted. The first group of compounds, which was investigated, were mono-valent alkali chlorides (\( \text{LiCl}, \text{NaCl}, \text{KCl} \)) and nitrate salts (\( \text{LiNO}_3, \text{NaNO}_3, \text{KNO}_3 \)). Chapter 4 contains the experimental data on these systems. A further aspect introduced in this chapter is the possible occurrence of parallel reactions in supercritical water in form of a hydrolysis. This reaction leads to a transformation of the respective salt to its hydroxide and acid form. While the hydroxide remains in a solid form in the experimental setup, the acid is partly soluble at these conditions leading to a decrease in pH of the effluent. As a further result of these experiments, a relation between the solubilities and the size of the investigated cation was found. Here, a small cation size coincided with a higher solubility due to an easier hydration (\( \text{LiX} > \text{NaX} > \text{KX} \)). Upon application of the quantitative approach, a correlation between the solubilities and the parameters used in the approach was determined, which could be related to the properties of the investigated compound.

In continuation of the systematic investigations, the solubilities of the bivalent salts \( \text{MgCl}_2 \) and \( \text{CaCl}_2 \) were investigated in the scope of Chapter 5. For these systems, a stronger influence of the parallel hydrolysis reaction was found in comparison to previous results. This made it necessary to include a correction of this effect based on the measured pH values in the evaluation of results. Contrary to the experiments on the mono-valent salts, residual solid material was found in the setup after the experiments with \( \text{MgCl}_2 \). This material could be identified as \( \text{Mg(OH)}_2 \). By this observation, a proof for the occurring hydrolysis was found next to the indirect proof by measurement of the pH value.

Chapter 6 describes the results of the experiments on the bivalent sulfate salts \( \text{MgSO}_4 \) and \( \text{CaSO}_4 \) and of the triple-valent phosphate salts \( \text{Na}_2\text{HPO}_4, \text{NaH}_2\text{PO}_4 \) and \( \text{CaHPO}_4 \). Both calcium compounds lead to a clogging of the setup before entering the therefore designated parts of the setup. The experiments on the phosphate salts showed also a dependency between the size of the compound and the actual solubility. Yet, due to the pH dependency of phosphate systems and transformation of one species to another by pH changes, the experimental data needs to be extended. More investigations have to follow for this complex behavior in regard of the relation between pH, species and solubilities in order to guarantee a sound description of these systems comparable
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to the other investigated systems.

With the removal of inorganic compounds via supercritical water being a new approach, numerous innovative options exist to apply this technology. In order to evaluate these options and their future potential, Chapter 7 includes a comparison between this new approach and currently applied technologies. Furthermore, it elaborates on the advantages of Supercritical Removal (SCR) like the treatment of high concentrated salt streams, the avoidance of a liquid waste stream or the possibility to separate different salt fractions from each other. For further evaluation, possible feed streams are discussed regarding their potential. Here, brine streams of desalination units and highly concentrated waste streams from industrial applications show the greatest potential. Since an integration of SCR is possible within existing installations, several concepts for such a combination are presented and discussed. Among these options are the integration of SCR as pre- and post-treatment for the brine of RO / MSF plants and the recycle of the product stream of the SCR unit. To get a first idea of the best conditions in regard of quality and energy demand, the thermodynamics of the system are investigated regarding the energy demand, possible engineering limitations and the quality of the fluid product stream that could be achieved. As a result of this, Chapter 7 contains advices for the choice of these conditions. Calculations of combinations of SCR as a post-treatment for the brine streams of a RO unit show that the output of such a RO unit can be significantly increased. In the meanwhile, the production of a liquid waste stream can be avoided while only the solid salt fraction remains as additional product. Upon comparing SCR to existing Zero Liquid Discharge Concepts like Deep Well Injection and Evaporation Ponds, it becomes obvious that the latter technologies are limited by external factors like the surrounding geology or a high average amount of daily sunshine. SCR on the meanwhile is not limited by these factors and therefore applicable in a broader range of locations and installations.

Chapter 8 discusses the current state of a removal of inorganic compounds via supercritical water. The so far gathered and available knowledge is summarized and a critical outlook on the potential is given. SCR is considered as a very promising approach for a sustainable production of drinking water and can be an interesting asset in combination with other technologies. Since the process is not yet applied on a larger scale and several issues have not been covered so far, possible research topics like the separation of the solids from the fluid and the behavior and solubility of mixtures are to be addressed before an industrial application is feasible. Furthermore, the necessity of a scale-up is highlighted in order to identify and solve bottlenecks and technical limitations.
of the current equipment, to adapt and optimize existing technologies and to test new methods, approaches and ideas.