Removal of inorganic compounds via supercritical water
Leusbrock, Ingo

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Chapter 8

Outlook and Conclusions
Abstract

This final chapter discusses the status, the available know-how and the future potential of a removal of inorganic compounds from aqueous streams via supercritical water. This is done by summarizing the insights on the phase behavior of the relevant systems, the ideas and evaluations gained for different process options and fields of applications and comparing these insights and ideas to the needs and demands for industrial applications. Furthermore scale-up and research issues are addressed which have to be tackled before this technique can be referred to as a reliable, efficient and mature technology for the sustainable treatment of saline streams without the negative aspect of a liquid waste stream. For future research projects, it is proposed to focus on the construction of small scale units for separation of salts from saline streams that are encountered in industrial applications. Thereby, the so far gathered know-how can be applied and possible bottlenecks and problems can be investigated and solved before a large scale application takes place.
8.1 Conclusions of this thesis

This thesis describes the thermodynamical and physical background and possible applications for Supercritical Removal of Inorganic Compounds (SCR), a promising technology for the treatment of saline streams without the occurrence of a liquid waste stream. This technology can be applied for the treatment for all kinds of saline streams regardless of composition and concentration. To achieve this, the process makes use of the decreased solubility of all inorganic compounds in supercritical water as the driving force for the separation process. Technologies that are considered as state-of-the-art for the treatment of saline streams all produce a liquid waste stream containing the separated salts as a common drawback (cf. Chpt. 1). Supercritical removal on the other side does not have this secondary “waste” product since a solid / liquid separation takes place and not a mere concentration of salts in one part of the feed stream (cf. Chpt. 2 and Chpt. 7).

Since systems containing supercritical water and inorganic compounds were scarcely investigated in research, it was necessary to evaluate available approaches and theories to describe these systems in regard of applicability, quality and ease of use for later work (cf. Chpt. 3). As property data on most of the regularly occurring salts was scarce, experiments were conducted to determine solubilities and phase behavior of these compounds. Combined with data from literature it was possible to compare the solubilities and to correlate the solubilities to properties of the inorganic compounds and to parameters used in the quantitative description (cf. Chpt. 4, Chpt. 5 and Chpt. 6).

For a further evaluation and a comparison with existing technologies, process options were developed that applied the advantages of the separation principle for the benefits of the process (cf. Chpt. 7). Thereby, guidelines for the selection of process conditions were developed to determine the optimal combination of temperature, pressure and solubility in order to have a high efficiency in separation as well as a minimum in energy demand and investment. To get an idea of the mass flows involved and to estimate possible costs, mass and energy balances were established for the most promising process options (cf. Chpt. 7). Here, it was found that SCR has the potential to offer a total separation of salts and water without the production of a waste brine stream - a feature that no other technology can offer at this point - while being energetically less demanding than evaporation technologies applied for desalination.

Since no limitation in concentration is present for SCR, it can be concluded that SCR is an unique technology that can be used to treat highly saline streams as well as brines.
These streams are expected to grow in capacity in the near future as a consequence of the growing desalination capacity and the technologies applied there. At this point, no technology is available, which can treat these streams in a sustainable way.

8.2 Evaluation of the potential of SCR

8.2.1 Application of SCR for treatment of brine streams

As desalination is expected to play a major role to satisfy the growing water demand in future, it is necessary to develop desalination to a more sustainable technology. Among the problems that arise from desalination like the energy demand (cf. Chpt. 1), a solution for a sustainable treatment of the produced brine stream is regarded as the most pressing issue. While dilution in the open ocean can be achieved in a sustainable way without damaging the ecosystem in the vicinity of the plant (e.g. Australian Gold Coast, Perth) or deep-well injection can be the optimal method of choice for brine disposal (1, 2), this is not valid for every location as the surrounding determines the possible options for a brine treatment. In regard of the growing demands and the thereby resulting necessity of tapping so far unused water resources like saline aquifers, brackish water and waste streams, concepts have to be developed for these cases, in particular for land-locked locations where disposal in the ocean is no option at all. Although several Zero Liquid Discharge concepts were proposed to avoid a liquid waste stream, none of these concepts was realized on an industrial scale as either the final costs exceeded the benefits by far or the environmental regulations and laws did not make such a treatment obligatory and allowed other ways to solve this issue (payment of fines, not thoroughly followed regulations, disregard of possible ecological damage).

With the concept of SCR introduced with this thesis, a new approach is given that can be used to tackle this problem in a sustainable way and to provide an applicable process for Zero Liquid Discharge concepts.

8.2.2 Application of SCR for treatment of toxic or high salinity waste streams

Many industrial processes have to deal with the production of unavoidable waste streams that either 1) contain high concentrations of salts (dairy industry), 2) toxic inorganic compounds (e.g. heavy metals from galvanic industry) or 3) precious metal or metal
oxides (catalysts) that cannot be treated by standard technologies or available treatment steps. In these cases, SCR can be used as approach for a batch-wise or small-scale application (cf. Chpt. 7). Thereby, the volume of the occurring toxic compounds can be reduced to its solid part and precious compounds can be recovered resulting in a decrease in costs for disposal and recovery of catalysts.

8.3 Future research

Although numerous experiments on a wide range of compounds, temperatures and pressures were performed in the scope of this thesis, several points still have to be investigated in future research. Most prominently, the investigation of mixed systems containing two or more inorganic compounds is necessary. This includes the investigation of samples from installations where SCR could be applied in future. By this, mutual influence on solubility, crystallization and particle size distribution can be determined like it would occur in all streams that are considered as feed streams for later installations. A further interesting aspect is the fractionized separation of valuable inorganic compounds and salts which could take in supercritical water. As the description of solubilities and phase formation has been conducted in this work in a basic yet efficient way, future research should extend these models and include more sophisticated models and thermodynamical methods like equations of state.

Since the experiments in this work were conducted on a small lab scale, a scale-up is necessary, in which the important aspects of crystallization and separation are more thoroughly analyzed and engineering solutions for an optimal operation can be found. Here, methods to separate the solids and remove them from the pressurized and heated system of significant importance for the operation of the whole process. Furthermore, different ways should be compared, in which a heating and heat exchange is possible which avoids scaling in parts of the installation where the precipitation should not take place or happens in such a way that a normal operation of the setup is not disturbed. This should as well include a proper assignment of an optimal reuse of the heat energies present in the installation. As a result of the harsh conditions of supercritical water, new equipment specified for these conditions has to be developed and / or equipment and know-how used in comparable processes has to be adapted to withstand these conditions and to allow an efficient operation. Here, special attention has to be paid to the choice of working materials to avoid possible corrosion.
8.4 Outlook

SCR offers an unique technique to treat saline streams of any composition and concentration. Therefore, a wide range of industrially relevant applications is possible. As the water demand is going to increase tremendously in the following decades, ways have to be found to guarantee an efficient and sustainable way to provide fresh water without increasing the ecological burden. Here, it is assumed that SCR can be an valuable and important technology that can play a significant role in solving this pressing global problem.

8.5 References
