Chapter 1

Introduction
Abstract

Water is a scarce and precious resource. While still considered in many countries and societies as a commodity, water resources are stressed to their maximum all over the globe endangering water and food supply, industry and social life. In the face of current and future challenges for societies like population growth, urbanization and anthropogenic damage to the environment, a sustainable and efficient water supply is therefore a necessity. As new technologies emerge for the treatment of polluted water streams (e.g. for removal of micropollutants and bacteria) or the generation of fresh water out of formerly unusable water sources like sea water or saline aquifers (e.g. desalination techniques like Forward Osmosis), new options are available to fulfill this necessity. For the opening of new water sources, desalination of saline streams is regarded as the option with the largest potential, which is already partly exploited nowadays. Nevertheless, desalination still has to overcome the drawback of a production of a liquid concentrated salt stream as a waste product, which is an unavoidable result of current technologies.
1.1 Background

The question, how water scarcity can be overcome today and how the daily water demand can be met in future, is a crucial question in several regions worldwide. For these regions, the availability of fresh water determines the way of life, public health and economical and social standards. Water is already considered today a valuable resource and is scarce enough to be fought over. The actual scarcity results from multitudes of reasons, which are predominantly of anthropogenic origin. These reasons are most often linked with each other and cannot be addressed individually. First of all, demographic changes play an important role. Current and expected population growth in certain regions like India, China and the Middle East exceeds the available water resources, even under consideration of all currently available technologies. A fact, which enhances this effect, is the migration to coastal areas and the accumulation in urban areas in order to find work and better living standards (1).

A further factor of influence is the growing demand for water in industry and agriculture. Going hand-in-hand with the population growth, the development of several countries to transition countries and industrialized countries and the resulting increase in living standards, water supplies are stressed to an unsustainable degree to support the needs of food production and industrial plants. This results in the depletion of aquifers, the overexploitation of rivers and lakes, the tapping of more remote water sources and the consideration of polluted streams and sea water as new source for fresh water (2).

A third point are global changes in climate and weather. This leads to local diminutions of precipitation, to shifted weather cycles, to a higher frequency of negative weather phenomena and to the loss of fresh water sources. As a direct impact, people tend to leave their original households and regions and to migrate to urban and coastal areas where they emphasize the stress on the present water supply (3).

To provide an additional, reliable fresh water source next to ground water and precipitation, desalination of sea and brackish water is used as method of choice for several decades now. With the introduction of evaporation techniques like Multi-Stage-Flash and later on Multi-Effect Distillation in the 1950’s and 1960’s and Reverse Osmosis as a membrane technique in the 1980’s in the wake of the establishment of membrane technologies, multitudes of technical possibilities for desalination are given nowadays. Therefore, the usage of desalination is considered as one of the most significant tools to deal with the growing demands. Yet, although these technologies have been applied on industrial scale for decades and have undergone modifications and optimizations,
negative aspects like high energy consumption, usage of additional chemicals for scaling and fouling prevention and most prominently treatment and avoidance of brine / waste streams are still neglected to a certain degree and not yet overcome. Especially the treatment of brine streams is a major challenge since it can not be avoided by either evaporation or membrane technologies due to being a result of the respective separation principle (4; 5).

1.2 Why water is a more and more scarce and valuable resource

The reasons for current water problems are complex and cannot be individually addressed and solved. The majority of these reasons are of anthropogenic origin and can only be solved with a global approach. Here, the awareness of the limitation of water supplies and the therefore necessary sustainable usage of this precious resource must be the driving force. Yet, an awareness of an emerging water scarcity on a more global scale is not found in a majority of countries and regions. These countries usually have a surplus of water at the current state or have found exploitable water sources or technologies that satisfy their current water demands. Countries that already suffer due to water scarcity (e.g. Sub-Saharan zone, Sudan, parts of South-East Asia and South and Middle America) frequently neither have the technological or economical possibilities to counter-act these problems nor do they receive major international support to solve them.

1.2.1 Global water resources

Although about 71 % of the surface of the Earth is covered with water, only 2.53 % of the total amount of water is fresh water and thereby directly usable for human needs. The remaining major part of the global water amount is located as salt water in the oceans and not usable without further treatment.

The majority of fresh water is located in the glaciers of Antarctica, Greenland and Arctica (68.7 %), followed by ground water (30.7 %). The remaining two percent are divided between surface water in rivers and lakes, ground ice in permafrost zones and air humidity (cf. Tbl. 1.1) (7).

These fresh water resources are not evenly distributed over the globe and depend on

\footnote{Not all fresh water sources are listed in this table for clarity reasons}
1.2 Why water is a more and more scarce and valuable resource

Table 1.1 Global fresh water distribution (7)

<table>
<thead>
<tr>
<th>Type of water</th>
<th>Volume / $10^3 \cdot km^3$</th>
<th>Fraction / %</th>
<th>Period of renewal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glaciers and snow</td>
<td>24064</td>
<td>68.7</td>
<td>1600 years</td>
</tr>
<tr>
<td>Antarctica</td>
<td>21600</td>
<td>61.7</td>
<td></td>
</tr>
<tr>
<td>Greenland</td>
<td>2340</td>
<td>6.68</td>
<td></td>
</tr>
<tr>
<td>Arctica</td>
<td>83.5</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>Fresh ground water</td>
<td>10530</td>
<td>30.1</td>
<td>1400 years</td>
</tr>
<tr>
<td>Permafrost zones</td>
<td>300</td>
<td>0.86</td>
<td>10000 years</td>
</tr>
<tr>
<td>Surface water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lakes</td>
<td>91</td>
<td>0.26</td>
<td>17 years</td>
</tr>
<tr>
<td>Rivers</td>
<td>2.12</td>
<td>0.01</td>
<td>16 days</td>
</tr>
<tr>
<td>Humidity / Rain</td>
<td>12.9</td>
<td>0.04</td>
<td>8 days</td>
</tr>
<tr>
<td>Total fresh water</td>
<td>35029.2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Total global water</td>
<td>1386000</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

climatic and precipitation patterns as well as geological structures. Due to this distribution, the availability of fresh water is different for every region. Depending on the population strength in one region and the average usage, this can result in an actual water scarcity (cf. Fig. 1.1). As can be seen from this figure, the regions suffering most from water scarcity by 2050 are Northern Africa, the Middle East and the Indian subcontinent. These regions are expected to experience significant population growth in the following decades. This is likely to increase the already pressing water scarcity and the need for a safe and sustainable water supply for everyone (1). Additionally, depletion and overexploitation of renewable water resources like rivers and aquifers have to be taken in consideration in these regions (2; 8).

1.2.2 Demographic changes

The expected growth of the world’s population for the coming decades is about 80 million people per year. This population growth results in an additional water demand of 64 billion $m^3$ per year (9). While till 2050 22 % of the world’s population will be older than 60 years (10 % in 2005), 50 % of the world’s population will be younger than 25 (11). More than 60 % of the world’s population growth between 2008 and 2100 will be in
sub-Saharan Africa and South Asia, which experience already water scarcity right now. Of the 3 billion additional people living on this planet by 2050, 90 % are expected to be born and live in developing countries. These countries and regions already face water scarcity and no access to proper sanitation and drinking water supply is guaranteed. Only a small number of these countries has the resources (financially and industrially) to change these situations and to fight the upcoming problems without international support.

This population growth in combination with economic pressure on the population leads to a migration of people to cities and to an increase of global urbanization. In 2030, 81 % of the urban humanity will consist of people living in cities and towns in developing countries; 60 % of the world’s total population will live in cities. The majority of these cities will be located in coastal areas. This massive urbanization will lead to severe problems in water provision and treatment due to the limited resources water and energy and to the local concentration of habitation and industry. As a consequence, overexploitation, environmental damage and depletion of fresh water sources will occur if no further measures are taken.

As industrialization and economical development further proceed in many countries worldwide, millions of people have the financial possibilities to improve their lifestyle to
1.2  Why water is a more and more scarce and valuable resource

Figure 1.2 | Global and regional population in 2009 (black) and 2050 (grey) (10)

...a higher level. Thereby, their food consumption changes from their traditional diets to more water-intensive products like milk, meat, and bread. To give an example, in 1985 20 kg of meat were consumed per capita in China and will have increased to 50 kg in 2009 (1). This is corresponding to an increase of 390 km$^3$ per year in water demand to provide meat for 1.3 billion Chinese people. Similar trends can be found all over the globe with all of them increasing the substantial pressure on water supplies.

1.2.3 Effects of global warming and climate change

With the effects of a climate change becoming more visible year by year, also the effects on hydrological cycles are recognizable worldwide and will become more severe in the following decades (1). As a direct impact of the climate change, rainfall, wind, and sunshine patterns begin to alter. As a result, changing hydrological cycles are encountered. This leads to a change in quantity as well as quality of available fresh water sources. These patterns shift to extremes causing natural disasters like flooding and extreme drought periods and making the overall climate less predictable. Thereby, also regions, which so far did not suffer from water scarcity, can encounter water problems in extensive dry seasons like the UK (11; 12). Additional water-providing solutions like desalination of sea and brackish water or extended water reuse have to be used to counter these extreme weather scenarios. As direct consequence, climate change can lead to desertification,
flooding, sea-level rise and further environmental damages and changes in the affected areas. Furthermore, migration to secure regions and cities will occur whereby the water stress is further increased in these areas \(1\).

### 1.2.4 Water usage

Agriculture is by a far margin the main user for fresh water. While 70 - 80 % of the available fresh water is used for agriculture, about 20 % are used for industrial purposes and about 10 % for domestic \(2\) \(1\). With the growing population worldwide, also the amount of water for agricultural purposes will rise regardless improvements in fertilizing and irrigation methods. Already now, water-scarce regions like the Middle East cannot provide food on their own and have to rely on imports.

A majority of the withdrawn water worldwide (~ 80 %) result from surface water sources like rivers and lakes. These surface water sources are facing increasing withdrawal rates year by year as well as increasing pollution \(2\). The remaining part comes from groundwater sources, which are partly already depleted or depleting at an alarming rate \(2\ 8\).

\(2\) These numbers vary by region. More industrialized countries have a higher percentage in the industrial sector and a lower one in the agricultural.
1.3 Approaches to minimize water scarcity

The first approach to minimize water scarcity and to prevent future problems is the introduction of a sound, reasonable and sustainable management of the available resources. Here, points like losses due to leakages and unnecessary evaporation, waste of water due to lacking awareness and habitual behavior and the application of non-suitable technologies must be addressed. With agriculture being the main user of fresh water, special focus has to be laid to minimize water losses in this field and to support smart and efficient irrigation methods (e.g. drip irrigation, automatic irrigation systems, collection of humidity for irrigation).

To increase the yield in water usage, waste water and surface water streams, which were untapped so far or left untreated and unused, have to be brought back in the usage cycle. This can happen by advanced treatment of waste water to increase the quality back to drinking water level (4), by usage of not high-end quality water for suitable purposes (like flushing toilet with only partly treated surface water) (5 13) and the reduction in volume and reuse of waste water streams by decentralized sanitation (13-15) or in industry (16 17). Most prominently, the usage of streams, which have not been used as freshwater source so far like low saline streams and aquifers, has to move in the focus of future research and projects (4).

Yet, even with the usage of untapped resources and an improved water management, it is impossible that future water demands can be met just by these two measures. Therefore, desalination of sea water and brackish water is regarded as one possible solution to meet these demands at least partly in the future. With the increased migration to coastal areas and the depletion of local freshwater sources, desalination of sea water represents one of the most promising approaches. Nevertheless, energetically, economically and ecologically sustainable desalination methods have to be found first to realize this.

1.4 Desalination

Desalination is the process of removing excess amounts of salts from an aqueous stream in order to produce fresh water.

The usage of evaporation to separate salts from water to win the salts as value product is known since ancient times (18). The idea to produce drinking water via desalination was used first on ships in the 17th to 19th century, followed by usage on an industrial
scale in 1928 on Curaçao, Netherlands Antilles, and the installation of the first major desalination plant in 1938 in Saudi-Arabia \cite{18,19}. A further boost to desalination and research in desalination occurred during WWII. Here, desalination was used to provide fresh water in remote locations like islands or desert regions and the future potential was acknowledged. Combined with the need to provide fresh water for oil drilling locations in the Middle East, large scale application of thermal evaporation processes started in these regions in the 1950’s. With the introduction of membranes in the late 1950’s by Loeb and Sourirajan, a second viable approach for desalination became available. Yet, it took till the 1980’s till desalination was considered as a serious alternative for drinking water supply worldwide and desalination was applied also for municipal and industrial purposes in regions apart from the Middle East \cite{19}. Nowadays, Reverse Osmosis as a membrane technology has become the predominant desalination technology \cite{20}.

![Figure 1.3](parallel.alt1)

Figure 1.3  \| Development of desalination capacities \cite{25}; solid line represents the global capacity; dashed line represents capacities in the Middle East and North Africa; dashed-dotted line represents capacities in the Arabian Gulf states

The global desalination capacity in 2006 was estimated to be 44.1 million $m^3$ per day \cite{21} with an average growth of 12 \% per year over the past five years \cite{22}. The projected capacities for 2010 are 64 million $m^3$ per day, for 2015 98 million $m^3$ per day \cite{22}. A development of the global desalination capacity from 1950 till 2005 can be found in Figure 1.3. Due to the tremendous increase in capacity, the sustainability and the environmental impact is receiving more and more attention in the last years. Here,
energy demand, usage of chemical agents and the treatment of brine streams have to be addressed and solved in a sustainable way (19; 20; 23; 24).

1.4.1 Desalination technologies

Two desalination technologies are used in over 85 % of the global desalination plants: Reverse Osmosis\(^3\) and Multi-Stage-Flash\(^4\). Here, RO is considered the most promising desalination technology for the next decades due to its efficiency and comparably low energy demand. MSF plants are stagnating in their numbers due to the rising costs for energy, especially fossil fuels (20). Another thermal desalination technology is Multi-Effect Distillation\(^5\) which has its origin in chemical industry and is operated at lower temperature and pressure levels than MSF.

Further technologies like Vapor Compression and Electrodialysis are available for commercial applications. Their main application area is to be found so far on small scale plants and decentral locations (19; 20).

![Diagram of Multi-Stage-Flash Distillation](image)

**Figure 1.4** Multi-Stage-Flash Distillation (26); A - Steam in; B - Seawater in; C - Potable water out; D - Waste out; E - Steam out; F - Heat exchanger; G - Condensation collection; H - Brine heater

\(^3\)In the following abbreviated with RO

\(^4\)In the following abbreviated with MSF

\(^5\)In the following abbreviated with MED
Multi-Stage-Flash Distillation

Due to being a simple and reliable technique, MSF was the first desalination technology used on a commercial base. First plants were built in Saudi-Arabia in the late 1950’s and early 1960’s (19). New installations applying MSF as separation principle are built usually in co-generation with electricity and / or in combination with other desalination technologies like nanofiltration and RO.

A MSF distillation plant is separated in different flash chambers with different pressure levels. Pressurized water (brackish or sea water) flows through pipes in the upper section of the chambers where it exchanges heat with the rising vapor. The water in these pipes is then heated in a steam heater to the necessary temperature by steam or fossil fuels. This high temperature allows in combination with a pressure decrease in the individual chambers a flashing of the liquid phase. The vapor rising from the lower sections of the chambers condenses on the pipes in the upper sections. The condensate itself is gathered in collection trays. The non-evaporated water phase, now concentrated in salt, is removed from the bottom of each chamber and usually diluted in the sea (cf. Fig. 1.4).

MSF plants have a high energy consumption due to the separation effect used, evaporation. Although several improvements in energy recovery and reuse of the energy streams were made, the high energy consumption is the major drawback of this technology. Regarding the rising price of energy, new MSF plants in the future will only be built, where large amounts of cheap or waste energy are available (e.g. co-generation of water and electricity in conventional power plants). Another disadvantage is the low yield of feed water becoming available as fresh water. Due to the nature of the process, appr. 50 % of the feed stream can be used as fresh water, the remaining 50 % are concentrated brine. This brine is usually diluted in the ocean if the plant is located next to the coast. Otherwise, an additional treatment step is necessary if the plant is located in a landlocked position. Nevertheless, dilution in the ocean is in regard of the rising numbers of desalination plants in coastal areas to be considered as a serious problem. The impacts on maritime environment are not fully understood at this moment. Local destruction of fauna and flora next to outlets of such plants has already been described (24, 28, 29). In some countries, brines are considered as a toxic waste and have to be diluted or treated under specific regulations (e.g. USA). A list of the possible

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The heat of evaporation for water is 2270 $kJ \cdot kg^{-1}$ (27). Typical energy demand is between 260 - 350 $MJ \cdot m^{-3}$ (19).
consequences of brine dilution can be found in Table 1.3.

Considered as a positive aspect of MSF is the excellent water quality with a concentration of appr. 50 ppm of salts like most of the other evaporation technologies (20). In general, MSF plants are not sensitive to the salt concentration of the feed streams. Scaling and precipitated salts can accumulate in the chambers and do not precipitate on the heat transfer surfaces in the upper sections of the chambers like usually happening in other evaporation technologies.

Reverse Osmosis

Reverse Osmosis is the most common desalination technology based on membranes. RO uses pressure to overcome the osmotic pressure of a solution. To separate salts and fresh water, membranes are used. These membranes are semi-permeable and reject the salt ions from a transfer while letting the water molecules pass. The materials used for RO membranes are commonly made of cellulose acetate, polyamides and other polymers. Many different combinations of composition, structure (hollow-fiber, mainly spiral-wound) and surface treatment are possible and depend on the feed water composition and the operation parameters of the plant (30).

RO plants are operated at about 50 - 80 bar for sea water desalination and about 10 - 25 bar for brackish water treatment. An energy recovery unit for pressurized streams is considered a necessary asset for these installations. Also the effects of the feed concentration and composition on the amount of usable fresh water have to be mentioned. While a yield of 90 - 95 % for brackish water installations can be achieved, only a value of 35 - 50 % for sea water desalination is reached due to high osmotic pressure (20). Thereby, a large brine stream remains as byproduct of the RO process comparably to MSF and MED. A further drawback is the high amount of TDS in the product stream, which varies between 100 and 600 ppm (30).

These remaining solids mainly consist of small molecules like boric acids, $H_2S$ and silica, which can be removed in a second, expensive RO step or by another technique. In contrast to the evaporation technologies, RO is very sensitive to the feed water composition. Resulting from this, pretreatment steps for removing biological compounds to minimize biofouling, for removing bicarbonates by acid dosing, for dosing anti-scalant agents and solid removal are necessary (30).
1.4.2 Ecological aspects of desalination

By developing to a worldwide applied process with large and growing capacities, desalination more and more has to be discussed critically regarding its ecological impacts. Till the last decade, this point has been neglected and has not been investigated in research and science thoroughly (20; 23; 24; 29; 31). With the developing market, especially for brackish water desalination in non-coastal areas, the awareness of these problems, especially for brine treatment, is growing.

Since all commercially available technologies produce one pure water stream, which can be used as drinking water or irrigation purposes, next to one concentrated stream in a ratio from 0.5...1.5 : 1 (depending on technology used and feed composition), post-treatment of these brine streams present a major problem coming along with growing desalination capacity. These brine streams consist next to the separated salts also of anti-scaling agents, anti-foaming agents, corrosion inhibitors and products as well as biocides (24).

The methods applicable for post-treatment depend on the location of the plant. The most common procedure for sea-sided plants is dilution in the open sea. Here also a mixing with cooling water effluent (for evaporative technologies) or raw sea water before the dilution is possible to minimize the damage on the ecology. Although the dilution
is a simple and effective solution for brine treatment, serious environmental problems appear since increased salinity and disposed agents represent an interference in the local ecosystem. When regarding the oceans with the highest number of desalination plants installed - the Red Sea, the Arabian Gulf and with a high increase of plants in the last years the Mediterranean Sea - one common property is obvious. All three water bodies are closed or semi-closed water bodies with a low water exchange rate. Thereby, an accumulation of chemical agents and salts is possible on a long term (24). Enhancing this effect is the high and still growing population density in some parts of these regions. This results in concentration of desalination plants in these regions to satisfy the water demand. Resulting from this, severe local damage is possible (32).

For land-locked facilities, the possibility of dilution in the ocean is not given. The methods available for the treatment in a land-locked facility are deep well injection, solar ponds and evaporation ponds (33–36). The capacity of all three technologies is comparably small making additional solutions necessary for large-scale desalination (33). Deep well injection is considered the most cost-effective method for land-based plants. The depths of the injection points vary from a few hundred meters to more than 1000 meters depending on the geology in the surrounding of the well (37). Nevertheless, finding a suitable location for the injection and minimizing the danger of a contamination of surrounding ground water are major drawbacks of this technology. Deep well injection in combination with a desalination plant is used among other locations in Florida and
the Netherlands at this moment (38; 39).

The evaporation pond technology requires a high average amount of daily sunlight. Thereby, the application of this method is restricted to arid countries with high amounts of yearly sunshine (Northern Africa, Arabian Peninsula and Middle East, Australia). Additional to that, a large surface area is required in order to evaporate the water in the brine. Low maintenance costs and the simple technology nevertheless offer a feasible option of brine treatment on a small scale (33; 40). Salt gradient solar ponds also use the available sunlight for the evaporation resulting in the same disadvantages and advantages as evaporation ponds. As capacities of these technologies are comparably small, alternative solutions for large-scale desalination are necessary. Here, transport of brine to the ocean or the installation of desalination plants just in coastal areas with a transport of the fresh water back to the land-locked locations are taken into consideration (38).

Ocean dilution and its ecological impacts

Brine streams have a salinity of 6 - 10 %-wt. depending on the technology used and composition of the feed streams. The amount of further components in the brine stream with a negative ecological impact are in the order of magnitude of a few ppm to mg·L$^{-1}$. Yet, these can have serious consequences on fauna and flora when diluted in the ocean (24; 29; 41). The severity of the damage done to the surroundings of dilution outlets depends on the one hand on hydrogeological factors like bathymetry, water depth, waves and currents and on the other hand on the diversity of the biology. Resulting from this, the choice of the actual location is an important step in the design of a desalination plant.

The higher salinity in the surroundings of the outlet has several consequences on fauna and flora. Most of the fauna and flora is not capable of adapting to these new circumstances resulting in an extinction of parts of fauna and flora at these locations (32). Adding up to that, a higher salinity also results in a higher turbidity of the water. This effect constricts the photosynthesis and leads to lower growth rates in the vicinity of the outlet. Due to the higher salinity of brine streams, the density of these streams is higher than that of raw sea water. The denser brine streams tend to sink to the ocean floor and precipitate. Thereby, a salt layer is formed on the ocean floor, which grows due to the continuous brine addition and makes life on the ocean floor impossible (41). Since the number and concentration of desalination plants grows as well as the effects of increased salinity and chemical agents on the ecosystem are still unknown for long-time
periods, special care and research has to be taken for the treatment of the brine streams (24).

Table 1.3 contains several harmful aspects of brine streams as well as a list of components, which can be found in brine streams. The impact of these points on fauna and flora is listed as well.

**Table 1.3** Environmental factors of brine stream dilution (24; 32)

<table>
<thead>
<tr>
<th>Component</th>
<th>Effect</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higher salinity</td>
<td>Higher turbidity, Changed conditions, Higher density</td>
<td>Disruption of photosynthesis, Destruction of fauna and flora, Salt precipitation on ocean floors</td>
</tr>
<tr>
<td>Higher outlet temperature</td>
<td></td>
<td>Change of inhabited fauna and flora</td>
</tr>
<tr>
<td>Biocides / Chlorine</td>
<td></td>
<td>Destruction of plankton / invertebrates, Reaction to toxic residual compounds</td>
</tr>
<tr>
<td>Corrosion products (Cu, Fe, Ni, Cr, Mb)</td>
<td>Accumulation in sediments</td>
<td>Long-term poisoning, Cu toxic for biology</td>
</tr>
<tr>
<td>Anti-scaling agents</td>
<td></td>
<td>Eutrophication phenomena, Oxygen imbalance, Withdrawal of biologically essential trace metal ions due to complex formations</td>
</tr>
<tr>
<td>Anti-foaming agents</td>
<td></td>
<td>Disturbance of intracellular membranes</td>
</tr>
</tbody>
</table>

### 1.5 Supercritical fluids

Supercritical fluids are seen as promising options for the improvement of existing and the development of new chemical and engineering processes like phase separation, particle formation, (oxidation and polymerization) reactions, extraction and heat carrier in power plants. With the important properties like density, heat capacity and viscosity being adjustable by the system parameters temperature and pressure in this state, versatility and flexibility is given thereby for an adjustment of these properties to the needs of any process.

Supercritical water shows significant differences in its behavior in comparison to the
ambient state. While being an excellent solvent for inorganic compounds and salts at these conditions, water turns in its supercritical state into a poor solvent for these compounds. The exceeding amount of salt precipitates and forms a solid phase, which can be separated from the remaining fluid phase. Thereby, an option is available to remove inorganic compounds from aqueous streams without the production of a liquid waste stream.

The application of this phenomenon is base of this thesis. To understand the phase behavior, to be able to predict the conditions in later industrial applications and to solve current precipitation problems in applications with supercritical water, measurements of the phase behavior were necessary as available data are scarce in this field. Furthermore, a comparison of possible fields of applications as well as process options was necessary to evaluate the potential and the advantages. Here, the focus is put on the application of this separation method for the treatment of concentrated salt streams as they can be found as waste product in desalination plants.

An extensive description of supercritical fluids, their properties, their advantages and their possibilities for application can be found in Chapter 2. Here, the fundamentals for a separation process based on the changed solvation behavior are discussed further and examples for applications are given.

1.6 Aim and Outline

The scope of this thesis is the investigation of systems containing inorganic compounds and supercritical water regarding their phase behavior. Resulting from these investigations, an evaluation of process options for an industrial application based on the changed solvation properties of supercritical water is given. Here, emphasis is put on the treatment of brine streams.

Chapter 2 introduces the supercritical state of a compound with its properties and its characteristics. The advantages of supercritical fluids are illustrated by the example of current industrial processes that apply supercritical fluids. To elucidate the main principle of this thesis, the solvation behavior for supercritical water is discussed thoroughly. Fundamental ideas for an application of the introduced separation principle are presented. Furthermore, first ideas and proposals on process options and conditions are evaluated.

Chapter 3 compares several approaches to describe the phase behavior and the solubilities of inorganic compounds in supercritical water. As a base for comparison, literature data is used to evaluate the quality and the relevance of these approaches. To extend
the available literature data, an experimental setup and method for the measurement of solubilities in supercritical water is introduced. This setup and method are validated by the measurements of NaCl in supercritical water, whereby the range of known property data is extended.

Chapter 4 contains the results of the solubility measurements of three alkali nitrates (LiNO$_3$, NaNO$_3$, KNO$_3$) and three alkali chloride salts (LiCl, NaCl, KCl) in supercritical water. A comparison between the solubilities and the properties of the salts is made. The results are correlated with the approach found most applicable for these systems in Chapter 3. The results of the correlation are further discussed regarding a possible relation between the parameters of the correlation and actual properties of the salts. Furthermore, possible side reactions occurring in the system are introduced.

Chapter 5 contains the results for the measurements of the bivalent salts MgCl$_2$ and CaCl$_2$. A comparison between the salts and the correlation parameters is made here in the same manner as in the previous chapters. Precipitates, which were found during the experiments, are investigated regarding their structure and composition as well as their origin and their influence on the system.

Chapter 6 contains the results of the measurements of the bivalent sulfate salts MgSO$_4$ and CaSO$_4$ as well as of the polyvalent phosphate salts Na$_2$HPO$_4$, NaH$_2$PO$_4$ and CaHPO$_4$. The results are compared to each other. A possible influence of pH changes and side reactions on the system is discussed.

Chapter 7 deals with the specifications and advantages of a separation process based on the changed solvation behavior of supercritical water for inorganic compounds. Resulting from the advantages, fields of application and process options are introduced, which benefit from this principle. Here stand-alone applications as well as combined systems with existing technologies are discussed. An evaluation of these process options based on avoidance of liquid waste streams, energy demand and minimization of installation size and costs is done.

Chapter 8 summarizes the current knowledge in the field of inorganic compounds and their behavior in supercritical water including the knowledge gained in this work. Furthermore, it is discussed in how far it is possible to apply this separation principle on an industrial scale. Resulting from this discussion, conclusions are made regarding the applicability of the whole process in regard of further research questions. These questions have to be addressed and solved before a large-scale application can take place.
1.7 References


