NEW METHODS FOR RECOVERY OF INORGANIC SALTS FROM WASTE WATER IN THE PETROLEUM INDUSTRY

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New Methods for Recovery of Inorganic Salts from Waste Water in the Petroleum Industry

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ABSTRACT

In this study three novel methods for the removal/recovery of inorganic salts from aqueous solution were explored to make a contribution to ongoing efforts by the petroleum industry to upgrade waste water for reuse by immobilising and removing inorganic substances from such contaminated water.

These methods were targeted precipitation, supercritical treatment and eutectic freeze crystallisation. The feasibility of these methods for waste water treatment was investigated by using both simple laboratory prepared solutions and complex real-world waste water samples (TRO and EDR brine) from the petroleum industry. Different analytical techniques, including simple and complexometric titrations ($AgNO_3$, EDTA), ICP-MS and IC were utilised to analyse original solutions and filtrates collected after precipitation by the different methods for several key anions/cations typically found in the waste water of a petroleum industry.

The method of targeted precipitation entailed an adjustment of the molar ratio of species in laboratory and industrial solutions to effect precipitation of a target compound having a favourable stoichiometry to remove large amounts of anions/cations from solution. It was successful for the removal of sulfate ion from both simple synthetic solutions (> 85%) and complex real-world solutions (50% for TRO and 75% for EDR). The optimum chloride ion removal from synthetic solutions (60%) was obtained by using a slightly different molar ratio than planned, but from the industrial brines disappointingly low chloride ion removal (25% for TRO, 12% for EDR) was achieved.

The second method required laboratory and industrial solutions to be subjected to conditions (typically 218 atm and 400^0C) at which water is a supercritical fluid. The polar character, hydrogen bonding and ion solvating capability of water are destroyed under such conditions, so that ionic species are forced out of solution. The removal of sulfate ion from synthetic solutions was just as successful (80%) as targeted precipitation, though redissolution occurred over time as a result of competition with other ions for hydrating water molecules. A vast amount of sulfate (1000 mg/L or 28% for TRO and 3500 mg/L or 35% for EDR) was removed under supercritical water conditions, and large amounts of sodium (450 mg/L or 31% for TRO, 1 300 mg/L or 41% for EDR) and calcium (450 mg/L or 85% for TRO, 600 mg/L or 90% for EDR) precipitated in addition to sulfate. Chloride ion removal was disappointingly low and never exceeded 15% for synthetic and 8% for real-world solutions.

Eutectic freeze crystallisation was used in successive fractionations to remove substantial amounts of simple inorganic salts, such as Na_2SO_4 (67%) and Na_2CO_3 (31%), from preprepared eutectic solutions. Application of the technique to industrial waste water samples in seven successive fractionations led to collective removal of 20% of sulfate and 18% of chloride content of TRO and 60% of sulfate and 15% of chloride content of EDR waste water samples. The reliability of the operation to precipitate and collect ice-salt mixtures in several successive fractionations was proven by a proper mass balance enabled by analysis of the original solution, the filtrates after each collection and the residual mother liquid.

The study rendered a modest contribution to the treatment of industrial waste water for the sake of mineral recovery and water restoration. It identified, applied and evaluated novel methods of waste water treatment in order to expand knowledge in this field and to broaden the capability of industry to help conserve water as a scarce resource. The inclusion of a method related to supercritical technology demonstrated its applicability to industrial processes and its relevance to green chemistry by utilising environmentally friendly supercritical fluids.

OPSOMMING

In hierdie studie is drie minder bekende metodes vir die verwydering/herwinning van anorganiese soute uit waterige oplossing ondersoek ten einde ’n bydrae te lewer tot voortgesette pogings van die petroleumnywerheid om afvalwater vir hergebruik op te gradeer deur anorganiese stowwe in sulke gekontamineerde water te immobiliseer en te verwyder.

Hierdie metodes was doelgerigte presipitasie, superkritieke behandeling en eutektiese vrieskristallisasie. Die uitvoerbaarheid van hierdie metodes vir afvalwaterbehandeling is ondersoek deur van sowel eenvoudige laboratorium bereide oplossings en komplekse reële-wêreld-afvalwatermonsters (TRO en EDR pekel) afkomstig van die petroleumnywerheid gebruik te maak. Verskillende analitiese tegnieke, waaronder eenvoudige en kompleksiometriese titrasies ($AgNO_3$, EDTA), ICP-MS en IC, is gebruik om die oorspronklike oplossings, en die filtrate wat na afloop van presipitasie met die verskillende metodes verkry is, te analiseer vir verskeie belangrike anione/katione wat tipies in die afvalwater van ’n petroleumnywerheid voorkom.

Die metode van doelgerigte presipitasie was daarop gebaseer dat die molêre verhouding van stowwe in laboratorium- en nywerheidsoplossings aangepas word om presipitasie van ’n teikenverbinding met ’n gunstige stoïgiometrie vir die verwydering van groot hoeveelhede anione/katione uit oplossing te bewerkstellig. Dit was suksesvol vir die verwydering van sulfaatioon uit sowel eenvoudige sintetiese oplossings (> 85%) as komplekse reële-wêreld-monsters (50% vir TRO en 75% vir EDR). Die optimum verwydering van chloriedioon uit sintetiese oplossings (60%) is verkry deur ’n effens anders as beplande molêre verhouding te gebruik, maar die chloriedverwydering uit die industriële pekeloplossings was teleurstellend laag (25% vir TRO, 12% vir EDR).

Die tweede metode het vereis dat laboratorium- en nywerheidsoplossings onderwerp word aan kondisies (tipies 218 atm and 400^0C) waarby water ’n superkritieke fluïed is. Die polêre karakter, waterstofbinding en ioonsolveringsvermoë van water is by dié kondisies opgehef, sodat ioniese entiteite uit oplossing gedwing word. Die verwydering van sulfaatioon uit sintetiese oplossings was met hierdie metode net so suksesvol (80%) as met doelgerigte presipitasie, maar van die gepresipiteerde sulfaat het met tyd weer opgelos as gevolg van wedywering met ander ione om deur watermolekule gehidrateer te word. 'n Groot hoeveelheid sulfaat (1000 mg/L of 28% vir TRO en 3500 mg/L of 35% vir EDR) is by die kondisies vir superkritieke water verwyder, en groot hoeveelhede natrium (450 mg/L of 31% vir TRO, 1300 mg/L of 41% vir EDR) en kalsium (450 mg/L of 85% vir TRO, 600 mg/L of 90% vir EDR) het benewens die sulfaat uitgesak. Die verwydering van chloriedioon was teleurstellend laag en het nooit 15% vir sintetiese en 8% vir reële-wêreld-monsters oorskry nie.

Eutektriese vrieskristallisasie is in opeenvolgende fraksionerings gebruik om merkbare hoeveelhede van eenvoudige anorganiese soute soos Na_2SO_4 (67%) en Na_2CO_3 (31%) uit vooraf bereide eutektiese oplossings te presipiteer. Die toepassing van die tegniek op industriële afvalwatermonsters in sewe opeenvolgende fraksionerings het tot 'n gesamentlike verwydering van 20% van die sulfaat- en 18% van die chloriedinhoud van TRO en tot 60% van die sulfaat- en 15% van die chloriedinhoud van EDR afvalwatermonsters gelei. Die betroubaarheid van die werkswyse om ys-sout-mengsels in verskeie opeenvolgende fraksionerings te presipiteer en te isoleer, is aangetoon met behulp van 'n massabalans wat moontlik gemaak is deur die oorspronklike oplossing, die filtrate na elke presipitaatverwydering en die oorblywende moederloog te analiseer.

Die studie het 'n beskeie bydrae gelewer tot die behandeling van industriële afvalwater in die belang van mineraalherwinning en watersuiwering. In die studie is nuwe metodes vir afvalwaterbehandeling geïdentifiseer, toegepas en geëvalueer ten einde kennis in die betrokke veld uit te brei en die vermoë van die nywerheid te verbeter om water as 'n skaars hulpbron te help bewaar. Die insluiting van 'n metode wat op superkritieke tegnologie gebaseer is, het die toepaslikheid daarvan in nywerheidsprosesse en die relevantheid daarvan vir groen chemie op grond van die gebruik van omgewingsvriendelike superkritieke fluïede gedemonstreer.

CHAPTER 0

MOTIVATION

Be curious always, for knowledge will not acquire you; you must acquire it.
Sudie Back

There is a considerable amount of waste water in a typical petroleum industry. This water contains substantial concentrations of organic and inorganic compounds. The inorganic wastes result from salts already present in the reaction water from coal leaching (particularly from ash after gasification and steam production), from regeneration of ion-exchange resins and from salts present in other water sources (e.g. mine water). These salts accumulate during processes at the plant and lead to all kinds of problems along the processing line. It is estimated that about 200 tons of salts accumulate in the local petroleum industry per day.

Techniques, like precipitation, adsorption, ion-exchange, membrane technology (nanofiltration), sedimentation, flotation, coagulation, flocculation, air stripping and aeration [1] are available for removal of inorganic and organic materials from waste water streams. The selection of a suitable technique is based on factors such as metal concentration, pH and operational efficiency [2].

There is a continuous demand from government to reduce the pollutants generated and discharged by the petroleum industry [3]. This is the main motivation for the reuse and recycling of waste water. The petroleum industry therefore constantly seeks new, alternative methods for recycling waste water and for immobilising and/or recovering inorganic salts.

Separation Science and Technology (SST) at the North-West University (Potchefstroom) in collaboration with Sasol (Secunda) initiated this research project to explore novel methods for the removal/separation and/or immobilisation of inorganic salts in waste water and simultaneous upgrade of the water for reuse.

The specific objectives of this project were

- to identify, study and evaluate new, alternative methods of separation and/or immobilisation of inorganic salts in waste water, viz. targeted precipitation [4-6], supercritical water assisted recovery [7,8] and eutectic freeze crystallisation [9,10];
- to investigate the different methods by virtue of both simple synthetically prepared and complex real-world waste water samples from the petroleum industry;
- to apply different analytical techniques to analyse waste water samples before and after treatment;
- to compare the results obtained with the different methods and to evaluate the advantages and disadvantages of each method.

Apart from these specific objectives, a contribution to a number of general objectives was envisaged, viz.

- to improve synergy between a petroleum industry and a tertiary institution for more effective research and development;
- to emphasise the importance of "clean" technology for a "greener" chemical industry and supercritical water technology as a potential method to help achieve that;
- to contribute to supercritical fluid technology in particular and to convince industry to employ this method regardless of the negative perceptions about the use of extreme conditions;
- to make a contribution towards the conservation of relatively scarce water resources in South Africa;
- to expand theoretical knowledge of waste water recovery and methods used in accomplishing this.

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CHAPTER 1

PROBLEM AND STRATEGY

Global fresh water consumption rose sixfold between 1900 and 1995 - more than twice the rate of population growth. About one third of the world's population already lives in countries considered to be "water stressed" - that is where consumption exceeds 10% of total supply. If present trends continue, two out of every three people on earth will live in that condition by 2025.

Kofi Annan, in We The Peoples, 2000.

1.1 The Significance of Water

The world population puts increasing stress on the environment [1]. Water-related problems have been recognised as the most immediate and serious threat to mankind [2]. Water will continue to be a major factor for the survival of humans and human activities. In many populated areas of the world it is an increasingly scarce resource.

Water is essential for satisfying human needs, protecting health and ensuring food production, generation of energy and restoration of ecosystems. It is also indispensable for social and economic development. For sustainable water resources, i.e. adequate amounts of quality water for living on earth, the management of water is vital. In many parts of the world people are already facing a water crisis. Unlike the energy crisis, the water crisis is life-threatening, and it is the most immediate and serious environmental, social and economic problem facing over a billion people in the world today [2].

If water management remains as inadequate as it currently is, the water crisis will become a catastrophe that will prevent sustainable development in many parts of the world. In global water consumption, agricultural water use accounts for about 75%, mainly through crop irrigation, while industrial use accounts for about 20%, and domestic operations for the remaining 5%. Of the ca. 20% of global fresh water withdrawals, 30 - 40% is used for industrial processes. In Africa alone, it is estimated that 25 countries will experience water stress (below 1 700 m^3 per capita per year) by 2025. At present, 450 million people in 29 countries suffer from water shortages. Many African countries, with a total population of nearly 200 million people, are facing serious water shortages. By the year 2025 it is estimated that nearly 230 million Africans will suffer from water scarcity and 460 million people around the globe will live in water stressed countries [2].

Under the conditions of natural supply shortage, water demand to satisfy domestic and industrial consumption stimulated various forms of effluent reuse by means of treatment processes [3]. This is especially true in the industrialised areas of the world. Though water quality regulations regarding waste water discharges have helped to reduce industrial water demands, industrial water needs are increasing in line with the rate of manufacture and production. Almost every manufactured commodity requires water for processing, washing, cooling, and other phases of production. In many instances, industry has to pretreat public supply water to reach required manufacturing purity levels, such as for boiler feed.

Most industries obtain water directly from wells, rivers, lakes and estuaries and may supplement resources by purchasing water from a public supply. As fresh water resources continue to become scarce and costs for waste disposal rise, there is growing interest within the industrial sector in the benefits of industrial treatment and reuse of process water. Many manufacturers have begun to recycle water within their plants to reduce the cost of waste water treatment and disposal as required by the Clean Water Act, and to control process water consumption effectively [4].

Water is required in processes such as gasification, coal mining activities, regeneration of resins and cooling processes where enormous cooling towers are used. All of these processes produce a large amount of waste water which can be classified as stripped gas liquor from gasification, reaction water from catalytic reactors, mine water from coal mining and storm water consisting of washwater, rainwater, etc. All of these mentioned categories of water are combined in a central system from where some of the water is reused in cooling processes and the rest is treated for disposal in a proper manner.

1.2 Advantages of Recycled Waste Water

Waste water reuse has environmental benefits, as it decreases discharge of pollutants into the environment and contributes to higher quality water acquired from ground and surface aquifers. The recovered pollutants can be of economical value as these can be reused or sold to other industries. However, the economical value of recovered inorganic salts – mainly complex compounds such as sulfates – is very low due to a saturated industrial market. A possible application of such inorganic salts is in the manufacture of concrete and concrete products for the building industry.

Different waste waters from a typical petroleum industry are highly contaminated with organic and inorganic materials, which can be harmful to the environment and human life. The combined pressure of increasing water and waste water costs and the regulatory requirements of discharged waste water force the petroleum industry to recycle waste water, to recover or immobilise inorganic materials and to treat organic substances. There are many known processes to achieve this, but a major challenge to the petroleum industry is the reuse of recovered materials. A plausible approach is to involve chemists to assist in achieving this. "This role for chemistry is not generally recognised by government or the public. In fact, chemicals, chemistry and chemists are actually seen by many as the cause of the problems" [5].

This new approach, which has become known as "green" chemistry, intends to eliminate intrinsic hazard itself rather than focusing on reduced risk by minimising exposure. Twelve principles for "green" chemistry have emerged from a diverse set of practices and research endeavours. These can be viewed as imperatives or directives that address alternative starting and target materials, alternative reagents, solvents and catalysts, and improved processes and process control.

Some of these principles prevent waste by reuse of pollutants and recovery of inorganic materials, or by maximising incorporation of materials into the final product. Others develop synthetic methodologies to generate substances with limited toxicity to human health and the environment, renew raw material of feedstock, avoid unnecessary derivatisation or develop analytical methodology for real-time process monitoring and control prior to formation of hazardous substances. Lastly, some minimise the potential for chemical accidents, hazardous releases, explosions and fires [5].

Some waste water treatment (recycling for industrial purposes) requires technologically advanced membrane processes (micro-, ultra- and nanofiltration and reverse osmosis) combined with chemical-physical processes (sand or activated carbon filtration, ozonation) or biological processes. The sophisticated equipment used in these processes are expensive, and industry is therefore constantly seeking for alternative processing methods.

Waste water recycling enables industries to diminish costs for decontamination processes and for fresh water availability [3]. In view of this, alternative methods were explored and evaluated in this study to remove/immobilise inorganic materials in the waste water of a petroleum industry and to simultaneously purify the water. The emphasis was on novel, innovative or less known methods which such an industry could consider in future as alternatives for or improvements over existing methodology. These methods are disclosed in the next section.

1.3 Alternative Methods Pursued in This Study

1.3.1 Targeted precipitation

One of the first methods considered in this study was targeted precipitation. This entailed precipitation of specific or target compounds which have a relatively comprehensive stoichiometric composition and thus cause removal of several elements, anions/cations or functional groups from solution in specific mol ratios. The principal requirement is that the concentration of the species to be isolated from solution should be adjusted to the required stoichiometric ratio to facilitate precipitation of the target compound.

Two targeted precipitation strategies were pursued, namely (1) removal of sulfate ion as calcium sulfoaluminate from water by the addition of aluminium ion [6] and (2) removal of chloride ion as calcium chloroaluminate from water using the ultra-high lime with aluminium (UHLA) process [7].

1.3.2 Supercritical water technology

Another method studied was supercritical water technology, where the properties of subcritical and supercritical water were utilised to effect mineral recovery. Supercritical fluids are increasingly used in industry, largely because of their tunable solvent strengths. Supercritical water can be defined as water heated to above its critical temperature (374°C) and compressed to above its critical pressure (22.1 MPa). At the critical point, the fluid phase boundary between the liquid and gaseous phases disappears, and the properties of the new single supercritical phase are best described as a combination of those of the liquid and gaseous phases [8].

Water is a good solvent for salts at ambient conditions because of its high relative dielectric constant of 78.5 at a high density of 997 kg m^{-3}. At near-critical conditions, the relative dielectric constant approaches 10 (this is nearly the relative dielectric constant of methylene chloride under standard conditions) and further decreases with increasing temperature. Hence, supercritical water (sc-H_2O) is considered a "non-polar" solvent in which the solubility of ionic species, like inorganic salts, is poor. In fact, literature sources [9] denote the dramatic decrease in solubility of inorganic compounds near the critical point as the most striking property of sc-H_2O. Moreover, the extensive hydrogen bonding of water is disrupted in the supercritical state, causing its solvation/hydration capability to diminish significantly.

The ionic product can be some orders of magnitude higher in supercritical than in ambient water (10^{-11} instead of 10^{-14}). Under such conditions, water may play the role of an acid or base catalyst because of the high concentration of H_3O^+ and OH^- ions. Moreover, in aqueous solutions containing other anions/cations, the increased concentration of OH^- could result in the precipitation of hydroxides of which the solubility products are generally smaller than those of other compounds (typically 10^{-15} - 10^{-18}) [10].

The complete miscibility with sc-H_2O makes it possible to carry out an oxidation in which the non-polar solvent (H_2O), non-polar oxidising agent (O_2) and non-polar organic compound (hydrocarbon) are brought into intimate contact with one another. In this process, known as supercritcal water oxidation (SCWO), harmful organic compounds contained in aqueous waste effluents can be rapidly and efficiently oxidised to CO_2 and H_2O. Organic bound nitrogen forms N_2 and small amounts of N_2O, without toxic and/or undesirable by-products such as NO_x. Typical operating conditions for commercial systems result in reactor residence times of 1 min or less for complete organic destruction. The heteroatoms chlorine, sulfur and phosphor present in organic waste are transformed into the mineral acids HCl, H_2SO_4 and H_3PO_3, respectively. These acidic solutions cause corrosion of the SCWO equipment and is often reduced by injecting neutralising bases into the system. Many inorganic salts form upon neutralisation with the added bases and consequently precipitate as solid phases [11]. Other salts may be present in the waste stream itself. Oxides, such as aluminium oxide, generally have low solubility at subcritical and supercritical conditions [12].

Research is presently done worldwide on this promising subject. One of the companies with more than 10 years experience in the development and field demonstration of SCWO technology is General Atomics for Advanced Process Systems. As the technology advances, a multitude of general purpose applications are envisaged, including waste treatment, resource recovery and power generation using low grade fuels. SCWO has a role in a wide range of industrial applications and environmental solutions. Advantages include high destruction efficiencies, low NOx and SOx, smoke-free stacks, compact equipment and competitive cost [13].

1.3.3 Eutectic freeze crystallisation

A third method investigated in this study to treat waste water was eutectic freeze crystallisation (EFC). Compared to evaporative crystallisation, which is a conventional technique to separate well-soluble salts from solution, EFC requires less energy [14]. Theoretically, the conversion of water at 0°C into ice at 0°C takes only one seventh of the energy required to convert water at 100°C into steam at 100°C. The separation of salt and water by means of freezing thus requires much less energy than evaporation does [15].

Eutectic freeze crystallisation is a physical process to separate most aqueous solutions of well-soluble salts into ice crystals and solidified solutes at the eutectic point. Ice is a solid consisting of a crystallographic arrangement of water molecules. These water molecules are bound together by the positive dipole of one molecule in contact with the negative dipole of another. This purely electrostatic attraction is strong and plays a major role in organising the structure of the ice crystal. Because of this strong attraction, other molecules or particles are rejected and cannot become part of the ice crystal lattice. Similarly, when sludge is frozen, solids are rejected by a growing ice crystal in favour of water molecules. This displacement gathers the solids into larger particles apart from the ice crystals. When freezing is complete, the sludge has been converted from a suspension of fine particles in water to a matrix of ice crystals and aggregated solid particles [14]. A typical phase diagram of a binary water-salt system is depicted in Figure 1.1.

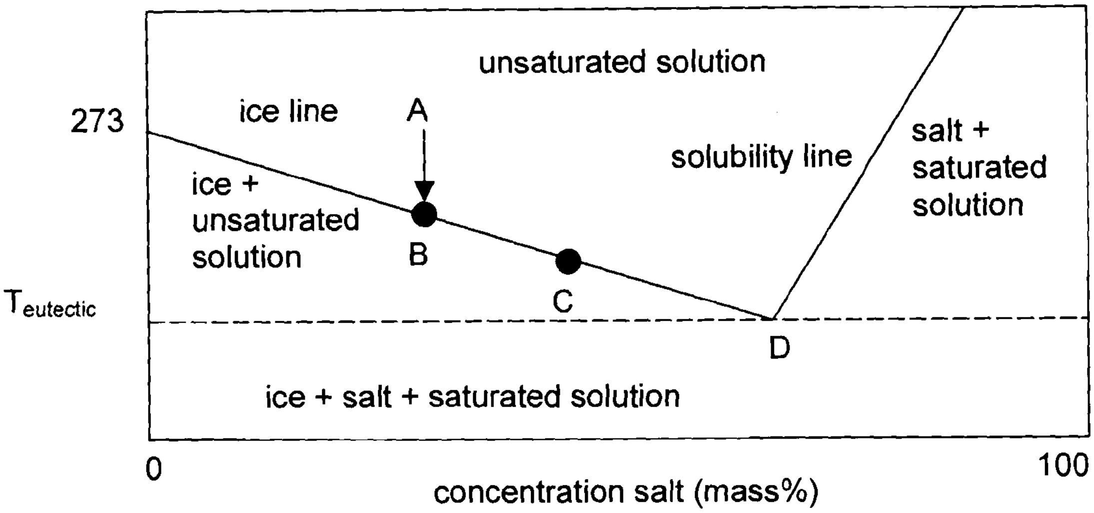

Figure 1.1 Phase diagram of a binary water-salt system

D is the eutectic point. Cooling a solution with composition A causes the temperature to decrease until B is reached. At B, ice is formed, and the salt concentration of the liquid phase increases. The system follows the line B-C, which enlarges the amount of ice and further concentrates the liquid phase. At D the ice line intersects the solubility line of the salt and its saturation concentration is reached. Further cooling results in the simultaneous formation of ice and salt. These two solid phases are completely separated: no solid solution and no inclusions are formed when the growth process is controlled carefully. Furthermore, the density difference of ice and salt is typically in the order of 1000 kg/m^3, which makes the separation of these solids by gravity feasible.

EFC is a separation technique that can be applied to most aqueous solutions of well-soluble salts. Cooling crystallisation, which is a comparable conventional technique, is limited by the solubility of salts at low temperature, whereas with EFC in principle a 100% separation into ice and salt can be achieved.

Since salts of all kinds are widely present in both waste and process streams in industry, applications of EFC are numerous. One application is the extraction of potassium salts from waste water in the potato processing industry. The technique can be used to separate industrial effluent into water and salt streams and thus help to reduce environmental damage [15]. Current research focuses on the recovery of valuable salts and pure water from process streams in the fertiliser, salt mining and chemical industries.

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CHAPTER 2
WATER TREATMENT PROCESSES

Selection of a water treatment process is a complex task. Circumstances are likely to be different for each water utility and different for each source used at a given utility. Selection is influenced by the necessity to meet regulatory quality goals, to satisfy other water goals (such as aesthetics), and to provide a water service at a reasonable cost. Other factors to be considered include contaminant removal, reliability of the process, existing processes at the plant, process flexibility, environmental compatibility and water distribution system. The choice of water treatment methods is expanding. New processes are being developed and implemented, and existing methods are refined and improved. The availability of more options complicates decision making and forces one to make choices wisely [1].

The most common water treatment processes known are described briefly in the following sections:

2.1 Chemical Precipitation

Chemical precipitation is one of the most common techniques used for treatment of metal salt contaminated waters and waste waters in industry. Owing to past successes, chemical precipitation is often selected to remediate hazardous and toxic waste sites [2].

Chemical precipitation is a separation method based on the difference in solubility of compounds present in a mixture. Soluble compounds are converted to relatively insoluble compounds by addition of a precipitating agent. Most often, an alkaline reagent is used to raise the solution pH to lower the solubility of the metallic constituent to effect precipitation and to allow crystal growth to a size sufficiently large for separation by physical methods [3]. An example is the use of caustic soda to raise the pH and to act as precipitating agent to lower the solubility of nickel by forming nickel hydroxide:

$$Ni^{2+} + 2NaOH \longrightarrow 2Na^{+} + Ni(OH)_2\,(s)\quad(1)$$

The precipitate, which may be colloidal, is either coagulated, flocculated, settled or filtered out of solution to leave a lower metal ion concentration in solution [2].

Chemical precipitation is both a physical and chemical process. The physical part comprises nucleation and crystal growth.

Nucleation begins with a supersaturated solution (i.e. a solution that contains a larger concentration of dissolved ions than can exist under equilibrium conditions). Under such conditions a condensation of ions occurs to form very small particles. The extent of supersaturation required for nucleation varies. The process can be enhanced by introducing preformed nuclei.

Crystal growth follows nucleation as ions diffuse from the surrounding solution to the surface of the solid particles. This process continues until the condition of supersaturation has been relieved and equilibrium is established. When equilibrium is achieved, a saturated solution has been formed [4].

Efficient chemical precipitation depends on several variables, including a suitable pH, adequate settling time, sufficient excess of precipitating agent to drive the precipitation reaction to completion, and effective removal of precipitated solids.

2.1.1 Solubility equilibrium

Solubility equilibrium may be attained either by formation of a precipitate from the solution phase or from partial dissolution of a solid phase.

Precipitation is effected when the concentration of ions of a soluble compound is increased beyond saturation. Such a process is described by the reaction

$$A^+ + B^- \rightleftharpoons AB(s) \quad (2)$$

where (s) denotes the solid phase.

No compound is totally insoluble and every compound forms a saturated solution. When a dissolution reaction occurs in an aqueous suspension of a sparingly soluble salt, the molecule dissociates into a cation and anion

$$AB(s) \rightleftharpoons A^+ + B^- \quad (3)$$

with

$$K_{sp} = [A^+][B^-] \quad (4)$$

the classical solubility product of the slightly soluble compound. The brackets denote molar concentration, which may be used instead of activity without introducing significant error in calculations. The more general form of the solubility product expression is derived from the dissolution reaction

$$A_xB_y(s) \rightleftharpoons xA^{y+} + yB^{x-} \quad (5)$$

and has the form

$$K_{sp} = [A^{y+}]^x[B^{x-}]^y \quad (6)$$

The value of the solubility product gives an indication of the solubility of a particular compound. A highly insoluble compound has a very small solubility product. When the ion product ($[A^{y+}]^x[B^{x-}]^y$) of the concentrations of the ions in solution is less than the K_{sp} value, no precipitation will occur and any quantitative information derived from equation (6) will apply only if equilibrium conditions exist. If, on the other hand, the ion product of the concentrations of the ions in solution is larger than the K_{sp} value, precipitation will occur.

2.1.2 Common ion effect

When ions of soluble salts are present in solution in defined concentration, a given ion can be precipitated by another ion, common to the salt, when the concentration of that ion is increased to the point that the ion product exceeds the solubility product. This is called the common ion effect. Precipitation of different compounds is possible if they share a common ion of which the concentration is increased to above the solubility product of the soluble salts. This type of precipitation is normally possible when the K_{sp} values of the compounds do not differ significantly.

The common ion effect is an example of Le Chatelier's principle, which states that if the equilibrium of a system is perturbed, the system will counteract the change to restore equilibrium under a new set of equilibrium conditions. For example, if a salt containing the cation A (e.g. AC) is added to a saturated solution of AB, AB(s) would precipitate until the ion product $[A^+][B^-]$ has a value equal to the solubility product. The new equilibrium concentration of A^+, however, would be larger than its previous value, while the new equilibrium concentration of B^- would be lower than its previous value [1]. The solubility of a salt is thus reduced by the presence of a common ion in accordance with Le Chatelier's principle [5].

2.1.3 Water softening

Hardness of water is the property of forming curds when used with soap and is caused by the presence of polyvalent metallic cations. Principal cations causing hardness are listed in Table 2.1. Since the most common of these species are the divalent cations calcium and magnesium, total hardness is typically defined as the sum of the concentration of these two elements and is usually expressed in terms of mg/L of $CaCO_3$.

TABLE 2.1 Principal cations causing hardness of water

Principal Cations	*Associated Anions*
Ca^{2+}	HCO_3^-
Mg^{2+}	SO_4^{2-}
Sr^{2+}	Cl^-
Fe^{2+}	NO_3^-
Mn^{2+}	SiO_3^{2-}

Softening implies removal of calcium as $CaCO_3(s)$, while magnesium is removed as $Mg(OH)_2(s)$. The concentrations of the various carbonic species and pH play important roles in the precipitation of these two solids. Carbonate hardness is removed by adding hydroxide ion and elevating the solution pH to above 10, so that hydrogen carbonate ion is converted into the carbonate form. The increase in carbonate concentration causes the ion product $[Ca^{2+}][CO_3^{2-}]$ to exceed the solubility product of $CaCO_3(s)$ and precipitation to occur. The result is that the concentration of calcium ion is significantly reduced. The remaining calcium is not removed by simple pH adjustment, but precipitated by added sodium carbonate from an external source. Carbonate and non-carbonate magnesium hardness are removed by increasing the hydroxide ion concentration until the ion product $[Mg^{2+}][OH^-]^2$ exceeds the solubility product of $Mg(OH)_2(s)$ and precipitation occurs.

2.1.4 Contaminant removal

The focus in the previous section was on removal of calcium and magnesium, but organic contaminants, heavy metals and radionuclides may also be removed from water by utilising chemical precipitation. The most popular method of removing toxic heavy metals from water is precipitation of the metal hydroxide. This process normally involves addition of caustic soda or lime to adjust the solution pH to the point of maximum insolubility. A few typical examples are listed in Table 2.2.

TABLE 2.2 Effectiveness of chemical coagulation and lime softening processes for inorganic contaminant removal

Contaminant	**Method**	**% Removal**
Arsenic		
As^{3+}	Oxidation to As^{5+} required	>90
As^{5+}	Ferric sulfate coagulation, pH 6–8	>90
	Alum coagulation, pH 6–7	>90
	Lime softening, pH 11	>90
Barium	Lime softening, pH 10–11	>80
Cadmium*	Ferric sulfate coagulation, pH >8	>90
	Lime softening, pH >8.5	>95
Chromium*		
Cr^{3+}	Ferric sulfate coagulation, pH 6–9	>95
	Alum coagulation, pH 7–9	>90
	Lime softening, pH >10.5	>95
Cr^{6+}	Ferrous sulfate coagulation, pH 6.5–9 (pH may have to be adjusted after coagulation to allow reduction to Cr^{3+})	>95
Lead*	Ferric sulfate coagulation, pH 6–9	>95
	Alum coagulation, pH 6–9	>95
	Lime softening, pH 7–8.5	>95
Mercury*	Ferric sulfate coagulation, pH 7–8	>60
Selenium* Se^{4+}	Ferric sulfate coagulation, pH 6–7	70–80
Silver*	Ferric sulfate coagulation, pH 7–9	70–80
	Alum coagulation, pH 6–8	70–80
	Lime softening, pH 7–9	70–90

* No full-scale experience

2.2 Membrane Technology

Membranes allow new processes for water treatment, and their tremendous potential results from their separation capabilities and competitive cost [1]. There are very few water contaminants that cannot be removed economically by membrane processes.

A membrane is a permselective barrier between two homogeneous phases, and transport through the membrane takes place when a driving force is applied to the components in solution. For most membrane processes the driving force is a pressure difference or a concentration gradient across the membrane [6]. Water contaminants removed by membrane technology include biological, inorganic and organic contaminants, as well as radionuclides and particulates.

Membrane processes with the largest application to water treatment include reverse osmosis (RO), nanofiltration (NF), microfiltration (MF), ultrafiltration (UF), and electrodialysis (ED).

2.2.1 Pressure driven membrane processes

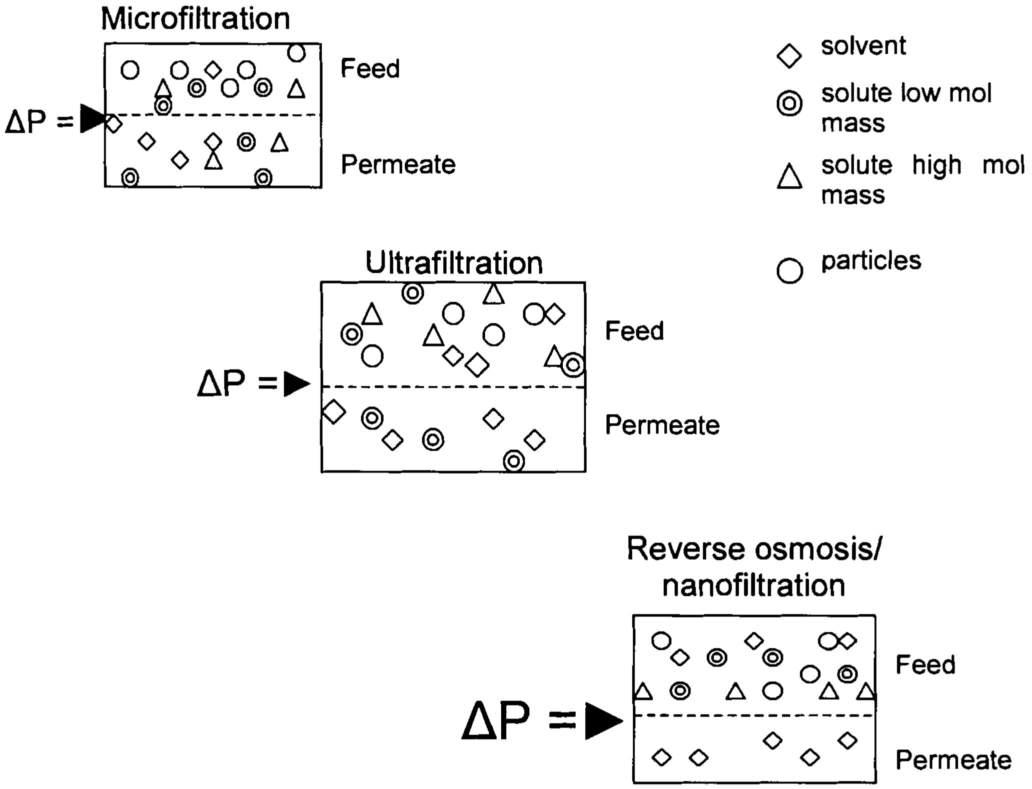

Figure 2.1 Schematic representation of microfiltration, ultrafiltration, nanofiltration and reverse osmosis

Pressure driven membrane processes are used to concentrate or purify dilute solutions. In these processes the solvent is the continuous phase and the concentration of the solute is relatively low. The particle or molecular size and chemical properties of the solute determine the pore size distribution of the membrane employed. These membrane processes are microfiltration, ultrafiltration, nanofiltration and reverse osmosis. The principle of the four processes is illustrated in Figure 2.1.

As a result of applied pressure as driving force, the solvent and solute molecules permeate through the membrane, whereas other molecules or particles are rejected, depending on the structure of the membrane. The pore size of the membrane decreases as one moves from microfiltration to ultrafiltration to nanofiltration to reverse osmosis, which implies that the resistance of the membrane to mass transfer increases and the applied pressure needs to be increased to maintain the same flux. However, no sharp distinction can be drawn among the various processes.

2.2.1.1 Microfiltration

This membrane process closely resembles conventional coarse filtration. The pore size of microfiltration membranes ranges from 10 - 0.05 µm, making the process suitable for suspensions and emulsions. Main industrial applications include sterilisation and clarification of all kinds of beverages and pharmaceuticals and removal of particles on processing ultrapure water in the semiconductor industry.

A major problem encountered with microfiltration is flux decline caused by concentration polarisation and fouling (the latter being the deposition of solutes inside the pores of the membrane). To reduce fouling, careful control is exercised over the mode of process operation. Two process modes exist, viz. dead-end and cross-flow filtration. In dead-end filtration the feed flow is perpendicular to the membrane surface so that the retained particles accumulate and form a layer of cake at the membrane surface. In cross-flow filtration the feed flow is along the membrane surface so that part of the retained solutes accumulate.

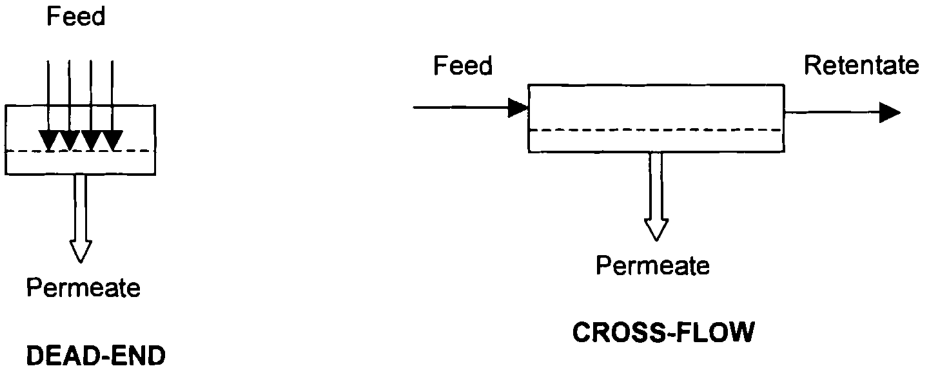

Figure 2.2 Schematic representation of dead-end and cross-flow microfiltration

2.2.1.2 Ultrafiltration

Ultrafiltration slots in between nanofiltration and microfiltration with membrane pore sizes ranging from 0.05 µm to 1 nm. It is used to retain macromolecules and colloids from solution and to remove turbidity, pathogens and particles from fresh water. The method is applied to concentrate macromolecular solutions where large molecules have to be retained while small molecules permeate freely. Various applications include the concentration of milk and cheese products, recovery of whey proteins and clarification of fruit juices and alcoholic beverages.

2.2.1.3 Reverse osmosis and nanofiltration

Nanofiltration and reverse osmosis are used to separate low mol mass solutes, such as inorganic salts, from solution. The basic principles of the two processes are the same. Dense membranes with high hydrodynamic resistance are required to force the solvent through the membrane, which is permeable to the solvent but not to the solute.

Reverse osmosis can be used in solvent purification (where the permeate is the product) and solute concentration (where the concentrate is the product). Most of the applications are in the purification of water, mainly the desalination of brackish and seawater, to produce potable water. Nanofiltration, the most recently developed membrane process, is used to soften fresh water and to remove disinfected by-product precursors.

2.2.2 Electrically driven membrane processes

In this type of membrane process an electrical potential difference is applied as driving force to a salt solution to allow positive ions to migrate to the negative electrode and negative ions to the positive electrode in order to separate them mutually from their uncharged counterparts. Two types of membranes can be distinguished: cation-exchange membranes allowing the passage of positively charged cations and anion-exchange membranes allowing the passage of negatively charged anions.

Electrodialysis (ED) and electrodialysis reversal (EDR) are capable of removing contaminant ions as small as 0.1 nm. A number of cation- and anion-exchange membranes are placed in an alternating pattern between a cathode and an anode. When an ionic feed solution (e.g. sodium chloride solution) is pumped through the cell pairs, the positively charged sodium ions migrate to the cathode and the negatively charged chloride ions migrate to the anode. The chloride ions cannot pass the negatively charged membrane and the cations cannot pass the positively charged membrane. The overall effect is that ionic concentration increases in alternating compartments and simultaneously decreases in the other compartments. Electrolysis occurs at the electrodes, with hydrogen and hydroxyl ions being produced at the negative electrode and chlorine, oxygen and hydrogen ions being produced at the positive electrode.

Important applications of elctrodialysis are the production of potable water from brackish water, demineralisation of seawater and softening of fresh water.

There is an increasing number of industrial applications where ions have to be removed from a process stream such as the production of boiler feed water.

2.3 Ion-Exchange

Cations such as calcium, magnesium, barium, strontium and radium, and anions such as fluoride, nitrate, arsenate, selenate and chromate, can be removed from water by passing through ion-exchange resins or by adsorption onto hydrous metal oxides such as activated alumina granules. In these water treatment processes a presaturant ion on the adsorbent is exchanged for an unwanted ion in the water. Source water is continually passed through the bed until the adsorbent is exhausted, as evidenced by the appearance (breakthrough) of the unwanted contaminant at unacceptable concentration levels in the effluent. Most ion-exchange reactions are reversible and the exhausted bed is regenerated using an excess of the presaturant ion. For these reversible reactions the bed is reused many times before it is replaced as a result of irreversible fouling.

In carrying out cation- or anion-exchange reactions, ions in addition to the target ion are removed by the resin. All ions are concentrated, in order of preference, in bands in the resin column. The most preferred species are last to exit the column, and their effluent concentrations never exceed their influent concentrations. The species exit the column in reverse preferential order, with the less preferred ions leaving first. The less preferred species will be concentrated in the column and will exit the column in concentrations exceeding their influent concentrations.

The major application of ion-exchange technology is the softening of water by exchanging sodium for calcium and magnesium using a strong acid cation resin. Softening by ion-exchange can supplement excess lime-soda ash softening (Section 2.1.3) because of better economics and fewer precipitation problems. Another important application is ion-exchange of chloride for nitrate. This is currently the simplest and lowest cost method for removing nitrate from contaminated groundwater for drinking. Other examples of ion-exchange include removal of fluoride by packed beds of activated alumina for the defluoriation of water supplies, and the removal of chromate from water, especially groundwater, by anion-exchange with synthetic resins to produce drinking water.

2.4 Adsorption and Desorption

Adsorption involves accumulation at the interface between two phases, such as a liquid and a solid or a gas and a solid. The substance that adsorbs at the interface is called the adsorbate, and the solid on which adsorption occurs, is the adsorbent. Adsorption of many compounds is reversible. Desorption may be caused by displacement by other compounds or by a decrease in influent concentration. Both phenomena may occur in some situations.

Adsorbents of interest in water treatment include activated carbon, ion-exchange resins, adsorbent resins, metal oxides and activated alumina. Removal of organic compounds causing taste, odour, toxicity and natural organic matter (NOM) by adsorption on activated carbon is important in water purification. Calcium carbonate and magnesium hydroxide solids formed in the lime softening process also have adsorption capabilities.

Granular activated carbon (GAC) is an alternative to powdered activated carbon (PAC) commonly used. GAC in columns permits higher adsorption capacity and easier process control for many undesirable substances and can be removed from the columns for reactivation.

Activated carbon in water treatment may inadvertently contact oxidants such as oxygen, aqueous chlorine, chlorine dioxide, and permanganate and react with these. Reactions of free chlorine with activated carbon may result in the production of organic byproducts.

A number of ions can be removed from water by GAC, but the capacity for most substances is quite low. The gold cyanide complex is adsorbed on GAC to recover gold in the mining industry. The removal of cadmium(II) at high pH can be increased slightly by complexation with chelating agents before adsorption. The removal of chromium involves adsorption of Cr(III) or Cr(VI), and under some conditions Cr(VI) is chemically reduced to Cr(III) by activated carbon.

2.5 Sedimentation and Flotation

Sedimentation and flotation are solid-liquid separation processes used to lower the concentration of solids on granular filters. As a result, filters can be operated more easily and cost effectively to produce filtered water.

Settling or sedimentation is simply a gravity process that removes flocculated particles from water [7]. The term settling is used to describe all types of particles falling through a liquid under gravity. The various regimes of settling of particles are commonly referred to as Types 1 to 4.

Type 1:	Settling of discrete particles in low concentration, with flocculation and other interparticle effects being negligible.
Type 2:	Settling of particles in low concentration but with flocculation. As flocculation occurs, particle mass increases and particles settle more rapidly.
Type 3:	Hindered, or zone, settling in which particle concentration causes interparticle effects, which might include flocculation, to the extent that the rate of settling is a function of concentration of the solids present.
Type 4:	Compression settling or subsidence, which develops under the layers of zone settling. The rate of compression is dependent on time and the pressure caused by the mass of overhead solids.

With horizontal-flow tanks, untreated water flows in at one end and treated water flows out at the other end. The inlet flow is managed to maximise settling of particles. If flocculation is carried out to increase particle size, the flow at the inlet should not disrupt the flocculant. Sludge should be removed regularly and allowance should be made to the tank depth for sludge accumulation so that the sedimentation efficiency remains unaffected.

Flotation is a gravity based separation process in which gas bubbles attached to solid particles cause the density of the bubble-solid agglomerates to be less than that of water, thereby allowing the agglomerate to float to the surface. Different methods of producing gas bubbles give rise to different types of flotation processes. These include electrolytic flotation, dispersed-air flotation and dissolved-air flotation.

Electrolytic Flotation

The basis of electrolytic flotation is the generation of bubbles of hydrogen and oxygen in a dilute aqueous solution by passing a DC current between two electrodes. The bubble size generated is very small, and the surface loading is therefore restricted to less than 4 m^3/h.

Dispersed-Air Flotation

Dispersed-air flotation is generally unsuitable for water treatment as the bubble size tends to be large and either high turbulence or undesirable chemicals are used to produce the air bubbles required for flotation.

Dissolved-Air Flotation (DAF)

In dissolved-air flotation, bubbles are produced by the reduction in pressure of a water stream saturated with air. Particles in the water should be flocculated and coagulated effectively prior to introduction of the microbubbles to form bubble-flocculant aggregates. The three main types of DAF are vacuum flotation, microflotation and pressure flotation. In pressure flotation, air is dissolved in water under pressure. The pressurised water is introduced into the flotation tank through a pressure-release device and mixed with the flocculated water, and the resulting aggregates float to the surface. The floated material (the float) is removed from the surface, and the clear water is taken from the bottom of the flotation tank.

2.6 Air Stripping and Aeration

The most common types of air stripping and aeration employed are diffused-air, surface aeration, spray aeration and packed-tower systems.

Diffused-air aeration

This process entails contact between gas bubbles and water with the purpose of removing volatile contaminants from water by stripping. The diffuser consists of a matrix of perforated tubes (or membranes) or porous plates arranged near the bottom of the tank to provide maximum gas-to-water contact.

Surface aeration

Surface aeration is used for oxygen absorption and stripping of gases and volatile contaminants. Surface aeration devices consist of several brushes attached to a rotary drum, which is half-submerged in water in the center of the tank. As the drum rotates, it disperses the water into the surrounding air, providing contact between the air and water for mass transfer to take place.

Spray aerators

Spray aerators have been used in water treatment for many years to oxygenate groundwater for the purpose of iron and manganese removal and for air stripping of gases (e.g. carbon dioxide, hydrogen sulphide) and VOC's. Spray aerator systems consist of a series of fixed nozzles on a pipe grid. Pressurised nozzles disperse fine water droplets into the surrounding air, creating a large air-water surface for mass transfer.

Packed towers

Water is pumped to the top of a tower and through a liquid distributor where it is allowed to flow by gravity over the packing material. At the same time, a blower is used to introduce fresh air into the bottom of the tower, and the air flows countercurrent to the water upward through the void spaces between the wetted packing material. The latter provides a large air-water interfacial area, resulting in efficient transfer of the volatile contaminant from the water to the air. The contaminant-free air-stripped water leaves the bottom of the tower, while the air containing the contaminant exits the top of the tower for further treatment or exhaustion to the atmosphere.

Water treatment applications of the systems described above include the absorption of reactive gases for water stabilisation and disinfection, precipitation of inorganic contaminants and air stripping of volatile organic compounds (VOC's) and dissolved gases. The diffused-aeration systems are primarily used for the absorption of reactive gases, such as oxygen (O_2), ozone (O_3), and chlorine (Cl_2). Surface-aeration systems are primarily used to remove VOC's, and packed tower and spray nozzle systems are utilised for removal of NH_3, CO_2, H_2S, and VOC's.

2.7 Coagulation and Flocculation

Natural and waste waters may contain small suspended particulates or colloids. The particles carry the same charge and repulsion prevents them from combining into larger particulates to settle. Thus, some chemical or physical techniques are applied to help these particles to settle [8]. Coagulation is such a technique. It is an essential component of water treatment which, in combination with sedimentation, filtration and disinfection, is employed to clear water and to remove microbiological contaminants such as bacteria.

In water treatment, coagulation comprises three separate and sequential steps: coagulant formation, particle destabilisation and interparticle collisions. The salt $Al_2(SO_4)_3 \cdot 14H_2O$, for instance, forms a variety of chemical species (aluminium hydrolysis products) in aqueous solution which cause coagulation. The small, highly positive aluminium ions form such strong bonds with the oxygen atoms of six surrounding water molecules that the oxygen-hydrogen atom association with the water molecules is weakened. This destabilisation increases the tendency of particles in the suspension to attach to one another or to aggregate.

The water treatment literature sometimes makes a distinction between the terms "coagulant" and "flocculant." When this distinction is made, a coagulant is a chemical used to initially destabilise a suspension. In most cases, a flocculant is used after the addition of a coagulant. Its purpose is to enhance particle formation and to combine small particles into larger particles, which settle as sediment and are removed in subsequent separation processes such as sedimentation, flotation and coarse bed filtration. It is sometimes called a "coagulant aid".

Rapid, or flash, mixing is a high-intensity mixing step used before flocculation to disperse the coagulant(s) and to initiate the particle aggregation process. This is also the start of the flocculation process. By adding coagulant, the particles become destabilised and the high-intensity mixing leads to rapid aggregation.

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CHAPTER 3

TECHNICAL ASPECTS

This chapter describes the experimental aspects of the investigation. It covers the sample preparation, treatment and analysis procedures applicable to synthetic and real-world waste water samples used in the different recovery/purification methods studied in this investigation.

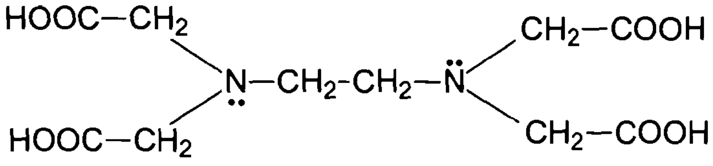
3.1 Analytical Techniques

An important component of this study was the analytical techniques used for determining the concentrations of the different ions involved. Mainly three techniques were used, viz. titrimetric analysis, inductively coupled plasma mass spectrometry (ICP-MS) and ion-exchange chromatography (IC).

3.1.1 Titrimetric analysis

Titrimetric methods based on complex formation (also called complexometric titrations) have been used for more than a century and are based upon coordination compounds or chelates. An example of a complexation reaction is titration of a cyanide solution with silver nitrate ($2CN^- + Ag^+ \rightleftharpoons [Ag(CN)_2]^-$) or titration of a chloride solution with mercury(II) nitrate ($2Cl^- + Hg^{2+} \rightleftharpoons HgCl_2$) [1].

EDTA (Ethylenediaminetetra-acetic acid) is an important reagent for complex formation titrations as it is a powerful complexing agent. It is a hexadentate ligand having six sites for bonding to a metal ion (four carboxyl groups and two amino groups) as shown on the next page [2].



EDTA forms chelates with all cations, giving rise to a cage-like structure in which the cation is effectively surrounded and isolated from solvent molecules. It combines with metal ions in a 1:1 ratio regardless of the charge on the cation.

There are three types of titration employing EDTA:

Direct titrations

The determination of calcium is by direct titration. The calcium containing solution is buffered to the desired pH and titrated directly with a standard EDTA solution.

Back-titrations

Back-titrations determine cations which form stable EDTA complexes and for which a satisfactory indicator is not available, or for cations that react slowly with EDTA. An excess of standard EDTA solution is added to the analyte solution. After the reaction is judged complete, the excess EDTA is back-titrated with a standard magnesium or zinc ion solution as these form EDTA complexes that are less stable than the corresponding analyte complex. Back-titration is also useful for analysing anion solutions that form sparingly soluble precipitates with the analyte. The excess EDTA prevents precipitation under such conditions.

Displacement titrations

In displacement titrations, an unmeasured excess of a solution containing a magnesium or zinc complex of EDTA is introduced into the analyte solution. If the analyte forms a more stable complex than that of magnesium or zinc, the following displacement reaction occurs:

$$MgY^{2-} + M^{2+} \rightarrow MY^{2-} + Mg^{2+}$$

The liberated cation is then titrated with standard EDTA solution [2].

Indicators for EDTA titrations are organic dyes that form coloured chelates with metal ions. These complexes are discernible to the eye at concentrations in the range of 10^{-6} to 10^{-7} mol/L. Solochrome Black T [sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate(II)] is a typical metal ion indicator used in titrations of several cations [2].

3.1.2 Inductively coupled plasma mass spectrometry

The technique used to analyse the cation concentrations in real-world samples was inductively coupled plasma mass spectrometry (ICP-MS). Titrimetric analysis failed to provide reliable information on the different ions in real-world water samples as the composition of these samples was too complex and the different ions influenced each other during titration. ICP-MS has grown to be one of the most important techniques for elemental analysis because of its low detection limits for most elements, its high degree of selectivity and its reasonably good precision and accuracy.

An inductively coupled plasma (ICP), consisting of ions, electrons and neutral particles and formed from argon at 7000 K, is used to atomise and ionise elements in the sample. Liquid samples are introduced by conventional or ultrasonic nebulisers, whereas a spark, laser ablation or a glow discharge are employed for solids. The positively charged metal ions produced in the ICP torch are sampled and extracted into a quadrupole mass spectrometer for analysis [3]. A schematic representation of an ICP-MS is shown in Figure 3.1.

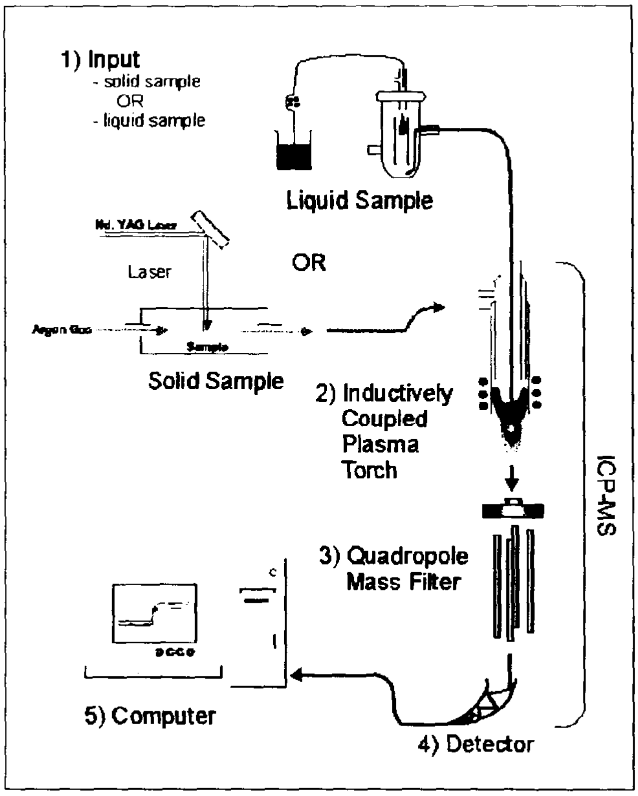


Figure 3.1 A schematic representation of an ICP-MS

The obtained spectra consist of a series of isotope peaks for each element. The isotopes of the elements are identified by their mass-to-charge ratio (*m/e*), and the intensity of a specific peak in the mass spectrum is proportional to the abundance of that isotope (element) in the original sample. These spectra are used for qualitative and quantitative analysis of the elements present in the sample [4].

3.1.3 Ion-exchange chromatography

IC refers to a modern and efficient method of separation and determination of ion mixtures on HPLC columns, based upon ion-exchange resins [4]. IC was developed especially for the separation of closely related rare earth cations with cation-exchange resins. These resins consist of small porous beads of styrene and divinylbenzene with chemically bonded acidic or basic functional groups. Ion-exchange process is based upon exchange equilibria between ions in solution and ions of like sign on the surface of the resin.

3.2 Sample Preparation and Treatment Procedures

The procedures outlined in this section apply to the three different recovery/purification methods considered in this study, viz. targeted precipitation, supercritical water treatment and eutectic freeze crystallisation. For each of these methods, distinction is made between the procedures for synthetically prepared and collected real-world water samples.

3.2.1 Targeted precipitation

The attempt with this approach, as outlined previously, was to precipitate a target compound by adjusting the composition (molar ratio) of a given water sample (synthetically prepared or industry collected) in such a way as to effect chemical precipitation of a target compound consisting of elements, anions/cations or functional groups which are to be removed/recovered from solution.

3.2.1.1 Synthetic samples

Removal of sulfate ion from synthetic water samples by targeted precipitation was approached as follows:

A synthetic solution with a Al:SO_4:Ca molar ratio of 2:3:6 was prepared by dissolving 0.4205 g $Al(SO_4)_3 \cdot 18H_2O$ in 100 mL distilled water in a 250 mL beaker [5]. The pH, measured with a Metrohm 691 pH-meter equipped with a glass electrode, was raised to 11.9 by addition of concentrated NaOH with continuous stirring. Following this, 0.2805 g $Ca(OH)_2$ was added and stirred until the pH stabilised (after ± 30 minutes). The final volume was 110 mL. After two hours, the formed precipitate was filtered off on a Buchner funnel and washed with a small amount of water. The wash water was not added to the filtrate. The precipitate was air-dried and weighed. The filtrate was analysed for aluminium, calcium and sulfate content by EDTA titrations. The procedure was repeated four times.

Determination of Calcium

2 mL of 1 mol/L NaOH was added to 50 mL of the filtrate and 3 to 6 droplets of saturated aqueous murexide (indicator) were added. The titration was performed immediately with standardised 0.1 mol/L EDTA to prevent $CaCO_3$ precipitation. The end point was indicated by a colour change from red to blue [2].

Determination of Aluminium

25 mL of the filtrate was pipetted into a conical flask and an excess of 0.01 mol/L EDTA was run in from a burette. The pH was adjusted to between 7 and 8 by addition of ammonia. The solution was boiled for a few minutes to ensure complete complexation of aluminium with EDTA. The solution was cooled to room temperature and the pH was adjusted again to between 7 and 8. 50 mg of a mixture of Solochrome Black and KNO_3 was added as indicator and the solution was titrated immediately with 0.01 mol/L zinc sulfate solution until the colour changed from blue to wine red [2].

Determination of Sulfate

In this determination 25 mL of the filtrate was pipetted into a 250 mL beaker and diluted to 50 mL with deionised water. The pH was adjusted to 1 with 2 mol/L HCl. The solution was heated to near boiling and 15 mL of 0.05 mol/L of near boiling $BaCl_2$ was added rapidly and with vigorous stirring. This solution was heated on a steam bath for 1 hour. The precipitate was filtered with suction through a filter paper (Whatman No. 42) supported on a porcelain filter disc. The precipitate was washed thoroughly with cold water. The filter paper and precipitate were transferred quantitatively to the original beaker and 35.0 mL 0.05 mol/L EDTA solution and 5 mL of concentrated ammonia were added and the mixture boiled gently for 15 to 20 minutes. A further 2 mL of concentrated ammonia was added to facilitate dissolution of the precipitate. The resulting clear solution was cooled to room temperature and 10 mL of a buffer solution (pH = 10) and a few drops of Solochrome Black indicator were added to the solution. The excess EDTA was titrated with magnesium chloride to a clear red colour [2].

The removal of chloride ion from synthetic water samples using the ultra-high lime with aluminium (UHLA) process was studied as follows:

Equilibrium experiments to evaluate calcium chloroaluminate precipitation were conducted by adding dry lime and dry sodium aluminate to a NaCl solution [6]. Seven different molar ratios (1:1:4, 1:1:2, 1:1.6:4, 1:1.6:3, 1:2:4, 1:2:3 and 1:1.3:3) were prepared and sealed in glass bottles. These were shaken at room temperature on a shake platform (Labcon 1086 K, 152 rpm) for seven days. The precipitate was then filtered off on a Buchner funnel and the filtrate analysed for calcium and aluminium by EDTA titrations as outlined earlier in this section. Chloride was determined by a non-complexometric titration with silver nitrate to form insoluble silver chloride as described below.

Determination of Chloride

The filtrate, to which 2-3 drops of saturated potassium chromate were added, was titrated with 0.1 mol/L silver nitrate from a burette until a faint blood-red tinge was produced [2]. The colour change, which signifies the endpoint of the titration, originates from the formation of red silver chromate through reaction of silver chloride with the added excess of potassium chromate according to

$$2AgCl + K_2CrO_4 \longrightarrow Ag_2CrO_4 + 2KCl$$

3.2.1.2 Real-world samples

In this project two types of real-world waste water samples were obtained from the petroleum industry, viz. TRO and EDR brines. The TRO brine originated from water treated in a tubular reverse osmosis plant, and the EDR brine resulted from water treated in an electrodialysis reversal plant. Figure 3.1 shows typical TRO and EDR plants.

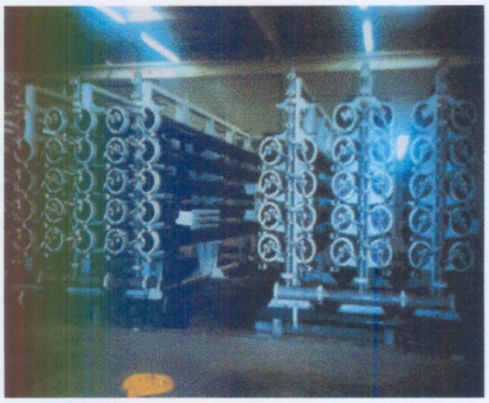



Figure 3.1 Typical TRO and EDR plants [7,8].

Table 3.1. Concentration of different ions in TRO and EDR brine waste water samples

[Ion] (mg/L)	TRO Brine	EDR Brine
Na	1 400	3 200
Mg	39	420
K	130	35
Ca	500	660
Sr	42	31
SO_4	10 148	3 576
NO_3	13	60
Cl	731	1 183
F	5	8

The removal of sulfate ion from real-world TRO and EDR brine samples by targeted precipitation proceeded as follows:

To 100 mL of TRO brine waste water in a 250 mL beaker 0.6936 g $Al(OH)_3$ and 1.2398 g $Ca(OH)_3$ were added, and to 100 mL EDR brine waste water in a 250 mL beaker 1.9652 g $Al(OH)_2$ and 3.6547 g $Ca(OH)_2$ were added. The pH was raised to 12.55 and 12.44 for the TRO and EDR brine waste water samples, respectively. The formed precipitates were filtered off on a Buchner funnel and washed with a small amount of water. The wash water was not added to the filtrates. The filtrates were analysed for the cations sodium, magnesium, potassium, strontium, aluminium and calcium by ICP-MS and for the anions sulphate, nitrate, fluoride and chloride by IC at Eco-Analytica, an on-campus analytical facility.

The removal of chloride ion from the real-world samples was undertaken by selecting two Cl:Al:Ca molar ratios based on the results obtained for the synthetic samples, viz. 1:1.6:3 and 1:1.6:4.

For the TRO brine, 1.1098 g dry aluminium hydroxide and 1.1473 g dry lime were added to 200 mL of the solution to attain a Cl:Al:Ca molar ratio of 1:1.6:3. For a Cl:Al:Ca molar ratio of 1:1.6:4, 1.1098 g dry aluminium hydroxide and 1.7765 g dry lime were added to another 200 mL sample.

For the EDR brine, 0.6936 g dry aluminium hydroxide and 0.5885 g dry lime were added to a 200 mL sample to obtain a Cl:Al:Ca molar ratio of 1:1.6:3. For a Cl:Al:Ca molar ratio of 1:1.6:4, 0.6936 g dry aluminium hydroxide and 1.1103 g dry lime were added to another 200 mL sample.

The mixtures were sealed in glass bottles and shaken for seven days at room temperature on a shake platform (Labcon 1086 K, 152 rpm). The precipitate was filtered off on a Buchner funnel and the filtrate was analysed in the same way as for the synthetic samples as outlined above.

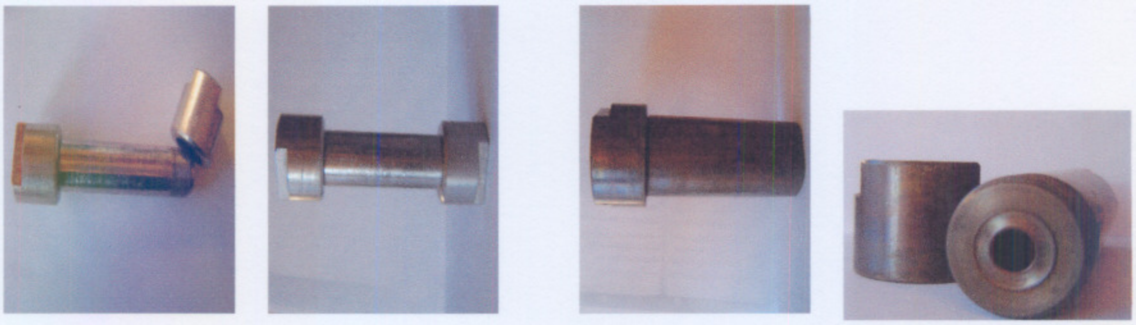
3.2.2 Supercritical water technology

The idea behind utilisation of supercritical technology was to subject water samples (freshly prepared laboratory solutions and waste water brine from industry) to conditions of subcritical (4.8 atm, 150^0C) and supercritical water (218 atm, 400^0C) to desolvate anions/cations as a result of the changes in polarity and hydrogen bonding of water under these extreme conditions.

3.2.2.1 Synthetic samples

The procedures followed for targeted precipitation in the previous section were slighty adapted to suit the experiments at subcritical and supercritical water conditions in terms of equipment and methodology. The objective was to remove sulfate and chloride ion by precipitating target compounds on subjecting solutions with an appropriate molar ratio to subcritical and supercritical water conditions.

Two different sample vessels were used to withstand subcritical and supercritical water conditions and to allow concentration-time runs to be performed safely under these conditions. The vessels are shown in Figure 3.2, followed by a short description of the design of each.



(a) (b)

Figure 3.2 Sample vessel for experiments at (a) subcritical and (b) supercritical water conditions.

Sample vessel (a) was manufactured of stainless steel with screw-on caps on both ends. Copper gaskets fit into the end caps to ensure a proper seal, and copper slip was spread over the threading to prevent lock-up. The dimensions of the cell were as follows: total length: 110 mm; inner diameter: 14 mm; outer diameter: 20 mm; volume: 16 mL; threading: 17 mm at 8 threads/cm. Based on water-steam tables, the pressure in the vessel would be 4.8 atm at 150 ºC.

Sample vessel (b) was designed and manufactured in-house, specifically to withstand the temperatures and pressures of supercritical water (218 atm and 400^{0}C). It was submitted to a testing authority to acquire a safety certificate for use at the stringent conditions mentioned. The dimensions were as follows: total length: 158 mm; depth of inner cylinder: 130 mm; inner diameter: 11 mm; outer diameter: 34 mm; volume: 15 mL; threading: 24 mm with a pitch of 2 mm. The cell was made to seal by placing a thin copper washer into grooves on the top of the cell. When the lid is screwed on tightly, the copper compresses to form the seal. Copper slip was applied to the threading of the cell. The copper washers could be re-used upon annealation, i.e. heating over a flame followed by rapid cooling in water.

The removal of sulfate ion was investigated by preparing the solution described below, for each individual run in duplicate, and subjecting it in the two different sample vessels for concentration-time runs at subcritical and supercritical water conditions, respectively.

A synthetic solution with a Al:SO_4:Ca molar ratio of 2:3:6 was prepared by dissolving 0.0631 g $Al(SO_4)_3 \cdot 18H_2O$ in 15 mL distilled water. The pH was raised to 11.9 with concentrated NaOH. Following this, 0.0421 g $Ca(OH)_2$ was added. The sample vessel filled with this solution was then placed in a preheated muffle oven (Naber) at either 150^0C (subcritical conditions) or 400^0C (supercritical conditions) for time intervals ranging from 10 to 90 minutes. After each heating time interval, the sample vessel was removed from the oven and cooled down under running cold water to ambient temperature. The formed precipitate was removed from the sample vessel and washed with a small amount of water. The wash water was not added to the filtrate. The filtrate was analysed by EDTA titrations for aluminium, calcium and sulfate as described in Par. 3.2.1.1.

Chloride ion removal by treatment at subcritical and supercritical water conditions was investigated by using solutions with a Cl:Al:Ca molar ratio of 1:1.6:3 since the best reduction in the concentration of calcium, aluminium and especially chloride was found for such a solution by targeted precipitation. The solution was prepared as follows:

0.0999 g dry lime and 0.05904 g dry sodium aluminate was added to 0.0263 g sodium chloride dissolved in 15 mL deionised water in either of the two sample vessels described above. The vessel with its contents was heated at the appropriate temperature (150°C or 400^0C) for time intervals ranging from 15 to 90 minutes in a muffle oven (Naber). After heating, the sample vessel was cooled down under running cold water to ambient temperature. The formed precipitate was filtered off and washed with a small amount of water. The wash water was not added to the filtrate. The filtrate was analysed by EDTA titration for aluminium and calcium content and by silver nitrate titration for chloride content as described previously.

3.2.2.2 Real-world samples

The TRO and EDR brine waste water samples referred to previously (Section 3.2.1.2) were used in these experiments without adding any chemicals. Samples of both types of waste water were placed into either of the sample vessels, depending on the conditions (subcritical or supercritical), and heated at the appropriate temperature (150^0C or 400^0C) for time intervals ranging from 10 to 90 minutes. After the elapsed time, the sample vessel was cooled down under running cold water. The solution was filtered with Whatman No. 1 filter paper to ensure a clear solution for analysis and to collect any precipitate that might have formed under the conditions concerned. The latter was air-dried and analysed by scanning electron microscopy (SEM). The filtrates from the TRO and EDR brines were analysed for the cations sodium, magnesium, potassium, strontium, aluminium and calcium by ICP-MS and the anions sulfate, nitrate, fluoride and chloride by IC in exactly the same manner as outlined previously (Section 3.2.1.2).

3.2.3 Eutectic freeze crystallisation

The effect of cooling on solubility and eventual precipitation of substances at the eutectic point of simple synthetically prepared mixtures and of complicated real-world samples were the basis of studying this third recovery/purification method.

3.2.3.1 Synthetic samples

Two inorganic salts, viz. sodium carbonate and sodium sulfate, were identified to be used in this part of the investigation on account of their eutectic point, their relevance to the petroleum industry and their availability [9]. Aqueous solutions of these salts were prepared according to the description below and such that the required amount of salt for an eutectic solution was met.

Table 3.2 Eutectic point and required mass percentage of selected inorganic salts

Inorganic salt	Eutectic point (^{0}C)	Required mass %
Sodium carbonate	-2.1	5.9
Sodium sulfate	-3.6	12.7

59 g anhydrous sodium carbonate was dissolved in 941 g deionised water in a 1 L volumetric flask. Of this solution, 830.99 g (approximately 800 mL) was transferred into a 1 L beaker and placed in a cooling bath (Haake B) with 10 L capacity. The solution was cooled down to reach the eutectic point. To maintain temperatures below 0°C a mixture of water and isopropanol (the cooling agent) was prepared by mixing 6 L of isopropanol with 4 L of water.

At the eutectic point an ice-salt mixture formed. The solids were removed by filtration and the mother liquid returned to the solution in the cooling bath. The solution was cooled further and several ice-salt mixtures were collected. These were allowed to melt and then weighed, dried in an oven at 100^{0}C to remove any crystal water and reweighed. The procedure of drying and weighing was repeated until a constant mass was obtained.

The same procedure was followed with anhydrous sodium sulfate, of which 127 g was dissolved in 873 g of deionised water, and 874.94 g of this solution was placed in the cooling bath.

3.2.3.2 Real-world samples

The TRO and EDR brine waste water samples used in the previous methods were also used for this application (Section 3.2.1.2.).

1113.19 g of TRO or 1170.10 g of EDR brine waste water was weighed in a 1 L beaker and placed in a cooling bath (Haake B). At the eutectic point of the water sample (which was at a temperature below 0^0C) an ice-salt mixture formed. It was separated from the solution by filtration and the mother liquid was returned to the solution for further cooling. A total of seven ice-salt precipitates were collected in this way, and each of these were allowed to melt before being analysed for sodium, magnesium, potassium, strontium, aluminium and calcium by ICP-MS and for sulfate and chloride by IC as outlined in Par 3.2.1.2. The solution remaining after the seven fractionations was also analysed for the same anionic and cationic species as the melted precipitates.

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CHAPTER 4

RESULTS: TARGETED PRECIPITATION

This chapter presents the results obtained for sulfate and chloride ion removal from synthetically prepared and industrial water samples by precipitating target compounds through a change in the composition of the water samples to obtain the required stoichiometry in solution.

4.1 Removal of Sulfate Ion

The removal of sulfate ion was based on the targeted precipitation of calcium sulfoaluminate ($Ca_6Al_2(SO_4)_3(OH)_{12}$) in which the Al:$SO_4$:Ca ratio is 2:3:6 [1].

4.1.1 Synthetic samples

The titrimetric data obtained for the filtrates of synthetically prepared water samples after precipitation are presented in Table 4.1.

Table 4.1 Titration figures of EDTA (0.01 mol/L) titrations of filtrates

Ion →	**Aluminium**		**Sulfate**	**Calcium**
↓Sample	**V_{EDTA} (mL)**	**V_{ZnSO_4} (mL)**	**V_{MgCl_2} (mL)**	**V_{EDTA} (mL)**
1	13.0	3.4	29.9	0.30
2	30.0	19.3	30.1	0.29
3	30.0	21.2	30.5	0.31
4	30.0	19.1	30.8	0.36

The titration figures in Table 4.1 were used to calculate the Al, SO_4 and Ca content in Table 4.2 of the synthetically prepared samples and of the filtrates collected after precipitation. A representative example of how the values in that table were calculated, is presented below:

Aluminium:

The amount of Al^{3+} present in solution before precipitation was calculated as follows:

$$\text{mol } Al_2(SO_4)_3 \cdot 18H_2O = 0.4207 \text{ g} \;/\; 666.45 \text{ g/mol}$$
$$= 6.313 \times 10^{-4} \text{ mol}$$

$$\text{mol } Al^{3+} = 2 \times (6.3126 \times 10^{-4} \text{ mol})$$
$$= 1.263 \times 10^{-3} \text{ mol}$$

$$\text{mass } Al^{3+} = 1.2625 \times 10^{-3} \text{ mol} \times 27 \text{ g/mol} \times 1000 \text{ mg/g}$$
$$= 34.09 \text{ mg}$$

The amount of Al^{3+} present in the filtrate after precipitation was calculated as follows:

$V_{EDTA} - V_{ZnSO4} = (13.0 - 3.4) \text{ mL} = 9.6 \text{ mL}$

1 mL 0.01 mol/L EDTA = 0.2698 mg Al^{3+} [2]

mass Al^{3+} present = 9.6 x 0.2698 = 2.59 mg

Sulfate:

The amount of SO_4^{2-} in solution before precipitation was calculated as follows:

$$\text{mol } Al_2(SO_4)_3 \cdot 18H_2O = 0.421 \text{ g} \;/\; 666.45 \text{ g/mol}$$
$$= 6.313 \times 10^{-4} \text{ mol}$$

$$\text{mol } SO_4^{2-} = 3 \times (6.3126 \times 10^{-4}) = 1.893 \times 10^{-3} \text{ mol}$$

$$\text{mass } SO_4^{2-} = 1.2625 \times 10^{-3} \text{ mol} \times 96 \text{ g/mol} \times 1000 \text{ mg/g}$$
$$= 181.8 \text{ mg}$$

The amount of SO_4^{2-} present in the filtrate after precipitation was calculated as follows:

mol EDTA available = 0.05 mol/L x 0.035 L = 1.75×10^{-3} mol

mol $MgCl_2$ used = 0.05 mol/L x 0.0299 L = 1.495×10^{-3} mol

mol EDTA used = 1.495×10^{-3} mol

mol EDTA excess = mol EDTA available - mol EDTA used

= $(1.75 \times 10^{-3} - 1.495 \times 10^{-3})$ mol

= 2.550×10^{-4} mol

mol SO_4^{2-} = 2.550×10^{-4} mol

mass SO_4^{2-} = 2.550×10^{-4} mol x 96 g/mol x 1000 mg/g

= 24.48 mg

Calcium:

The amount of Ca^{2+} before precipitation was calculated as follows:

mol $Ca(OH)_2$ = 0.2805 g / 74.02 g/mol

= 3.790×10^{-3} mol

mol Ca^{2+} = 3.790×10^{-3} mol

mass Ca^{2+}= 3.790×10^{-3} mol x 40.0 g/mol x 1000 mg/g

= 151.581 mg

The amount of Ca^{2+} present in the filtrate after precipitation was calculated as follows:

mass Ca^{2+} = 0.30 mL x (0.48008 mg / 0.01 mol/L EDTA) = 12.024 mg [2]

Table 4.2 Mass of ions in solution before and after precipitation

Ion →	**Al (mg)**	**SO_4 (mg)**	**Ca (mg)**
Before precipitation	34.1	181.8	151.6
After precipitation			
Sample 1	2.59	24.5	12.0
Sample 2	2.89	23.5	11.6
Sample 3	2.43	21.6	12.4
Sample 4	2.92	20.2	14.4

The calculation below of the percentage decrease of Al^{3+} in solution serves as a representative example of the calculation of percentage decrease of all ions present in solution. These values are listed in Table 4.3.

Aluminium:

% Al^{3+} in the filtrate was
(2.6 mg / 34.1 mg) x 100% = 7.6%
% decrease is
(100 - 7.6)% = 92.4%.

Table 4.3 Percentage decrease due to precipitation

Sample	%Al decrease	%SO_4 decrease	%Ca decrease
1	92.4	86.5	92.0
2	91.5	87.0	92.3
3	93.0	88.1	91.8
4	91.5	88.9	90.5

As shown in Table 4.3, sulfate ion was successfully removed from solution by addition of aluminium and calcium to form calcium sulfoaluminate ($Ca_6Al_2(SO_4)_3(OH)_{12}$) at high pH. It was found that the ideal molar ratio for Al:SO_4:Ca should be 2:3:6, in agreement with the stoichiometric composition of this compound. The maintainment of this ratio was important, especially the Ca:Al ratio, to effect optimum precipitation. When the Ca:Al ratio shifts away from 6:2, sulfate ion removal decreases as a result of the limited amount of aluminium and/or calcium.

4.1.2 Real-world samples

The removal of sulfate ion from real-world waste water samples was also based on targeted precipitation of calcium sulfoaluminate in which the Al:SO_4:Ca ratio is 2:3:6 [1]. Filtrates were collected twice after precipitation, viz. (1) 30 minutes after initialising precipitation by addition of compounds needed to adjust the

Al:SO_4:Ca ratio to the required value, and (2) 7 days after precipitation occurred. The ICP-MS, IC and pH values of the initial water samples and of the collected filtrates are given in Table 4.4.

Table 4.4 ICP-MS, IC (values in mg/L) and pH results for ions in filtrates

↓Ion	TRO brine waste water			EDR brine waste water		
Time→	**Initial**	**30 min**	**7 days**	**Initial**	**30 min**	**7 days**
Ca	7 200	560	87	20 400	280	34
Mg	39	1.6	0.01	420	0.84	0.0008
K	130	130	24	35	35	9.8
Na	1 400	1400	180	3 200	3 200	380
Sr	42	10	7.8	31	5.9	3.3
Al	2 400	0.259	0.189	6 800	0.324	0.218
SO_4	3 576	1 675	2 713	10 148	2 585	5 486
Cl	1 183	662	1 049	731	343	668
Time→	**Initial**	**30 min**	**7 days**	**Initial**	**30 min**	**7 days**
pH→	5.73	12.6	8.70	8.17	12.5	8.53

The results show that removal of sodium and potassium ion was zero at 30 minutes after precipitation had been initiated, but that removal was much higher after the filtrate had been allowed to stand for 7 days and then analysed. A possible reason for this is that after 30 minutes these ions were still solvated/hydrated by water molecules, whereas after 7 days, while being in the presence of hydroxide ion (high pH), insoluble sodium hydroxide and potassium hydroxide probably formed and precipitated out of solution. The decrease in pH (12.5 → 8.5) supports this assumption. This could also explain the increase in percentage of sulfate ion present in the filtrate after 7 days. The sodium and potassium ions were no longer solvated/hydrated by water molecules as they precipitated out of solution over time, thus leaving solvational space for the sulfate ions to be solvated/hydrated by water molecules.

Table 4.5 Percentage decrease for ions in solution

↓Ion	TRO brine waste water		EDR brine waste water	
Time→	**30 min**	**7 days**	**30 min**	**7 days**
Ca	92.2	99.8	98.6	98.8
Mg	95.9	99.9	99.8	99.9
K	0	81.5	0	72.0
Na	0	87.1	0	88.1
Sr	76.2	81.4	81.0	89.4
Al	99.8	99.9	99.8	99.8
SO_4	53.2	24.1	74.5	45.9
Cl	44.1	11.3	53.1	8.5

The percentage decrease for ions in solution in Table 4.5 shows that sulfate removal with targeted precipitation was much lower from the real-world samples than from the synthetic samples. The real-world samples are much more complex due to the presence of many different ions. For the purpose of this study, only ions present in relatively high concentration in the waste water were analysed and included in Tables 4.4 and 4.5. The Al:SO_4:Ca ratio was initially 2:3:6 in order to facilitate formation of calcium sulfoaluminate as target compound, but from the results in Table 4.4 it could be calculated that the final Al:SO_4:Ca ratio was 3:1:6 for both TRO and EDR brine waste water samples after 30 minutes as well as after 7 days. A representative example of how the Al:SO_4:Ca ratio was calculated, is presented below. The Al:Ca ratio of 1:2 instead of 1:3 points to a calcium limitation, which explains the lower than expected sulfate ion removal. The Ca limitation could have been caused by calcium aluminate ($CaAl_2O_4$) formation.

Calcium:

[Ca^{2+}] in EDR precipitate = (initial [Ca^{2+}] - [Ca^{2+}] after 30 minutes)
= (20 400 - 280) mg/L
= 20 120 mg/L

$$\begin{aligned} \text{mass } Ca^{2+} &= (100 \text{ mL} / 1000 \text{ mL}) \times 20\ 120 \text{ mg} \\ &= 2\ 012 \text{ mg} \\ &= 2.012 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{mol } Ca^{2+} &= 2.012 \text{ g} / 40.01 \text{ g/mol} \\ &= 0.0503 \text{ mol} \end{aligned}$$

The mol of Al^{3+} and SO_4^{2-} were calculated similarly and was found to be 0.025 mol and 0.008 mol respectively.

The mol ratio was calculated as

$$\begin{array}{ccccc} Al & : & SO_4 & : & Ca \\ (0.025/0.008) & & (0.008/0.008) & & (0.0503/0.008) \\ 3 & : & 1 & : & 6 \end{array}$$

4.2 Chloride Ion Removal

The intention with the ultra-high lime with aluminium (UHLA) method [3] was primarily to remove chloride ion from water. The formation of calcium chloroaluminate with a Cl:Al:Ca ratio of 1:1:2 formed the basis of this targeted precipitation to separate chloride ion from solution.

4.2.1 Synthetic samples

Seven solutions of different Cl:Al:Ca molar ratios (1:1:4, 1:1:2, 1:1.6:4, 1:1.6:3, 1:2:4, 1:2:3 and 1:1.3:3) were prepared by adding dry lime and dry sodium aluminate to a NaCl solution. These solutions were shaken for 7 days in sealed glass bottles, the precipitate filtered off on a Buchner funnel and the filtrate analysed for chloride, aluminium and calcium content. The experimental procedures are found in Section 3.2.1, and the results are given in Table 4.6.

Table 4.6 Percentage decrease for different mol ratios

Sample ↓	Mol ratio	Initial mass (mg) per 200 mL	Mass (mg) per 200 mL after 7 days	% Decrease
Ratio →	Cl:Al:Ca	Cl:Al:Ca	Cl:Al:Ca	Cl:Al:Ca
1	1:1:4	213:162:959	160:142:436	25:12:55
2*	1:1:2	213:162:479	153:52:116	28:68:76
3	1:1.6:4	213:259:959	99:122:292	54:53:70
4*	1:1.6:3	213:259:719	85:87:96	60:66:87
5	1:2:4	213:324:959	92:92:204	57:72:79
6	1:2:3	213:324:719	90:129:28	58:60:96
7	1:1.3:3	213:211:719	87:67:96	59:68:87

Chloride ion removal was targeted for by precipitation of calcium chloroaluminate ($Ca_4Al_2Cl_2(OH)_{12}$) with a Cl:Al:Ca ratio of 1:1:2 [3] marked with * in Table 4.6. However, the stoichiometry after equilibrium of 7 days was typically different from that expected, the deviation probably being the result of the formation of another compound, such as calcium hydroxyaluminate ($Ca_4Al_2(OH)_{14}$), through substitution of Cl^- in $Ca_4Al_2Cl_2(OH)_{12}$ by OH^- as suggested by the better chloride removal for Cl:Al ratio of 1:2 instead of 1:1. A fairly high percentage of chloride removal (~60%) could be achieved for reasonable ranges of aluminium and lime dose as shown by the last 5 entries in Table 4.6.

4.2.2 Real-world samples

Two molar ratios were selected for the real-world samples on account of the results obtained for the synthetically prepared solutions in the previous section, viz. Cl:Al:Ca =1:1.6:3 (best result) and 1:1.6:4 (literature recommended). The analytical data for these two molar ratios are given in Table 4.7 and the corresponding percentage decrease for the ions in solution in Table 4.8.

Table 4.7 ICP-MS and IC results (values in mg/L) for ions in filtrate

↓Ion	TRO brine waste water		EDR brine waste water	
Ratio→	**1:1.6:3**	**1:1.6:4**	**1:1.6:3**	**1:1.6:4**
Ca	95	99	39	58
Mg	0.072	0.120	0.150	0.140
K	17	18	4.1	4.1
Na	170	170	370	380
Sr	7.9	8.2	3.9	3.6
Al	2.8	1.2	0.69	0.96
SO_4	2 175	2 144	5 204	3 902
Cl	896	864	662	632

Table 4.8 Percentage decrease for ions in solution

↓Ion	TRO brine waste water		EDR brine waste water	
Ratio→	**1:1.6:3**	**1:1.6:4**	**1:1.6:3**	**1:1.6:4**
Ca	97.4	97.9	98.3	98.1
Mg	99.8	99.7	99.9	99.9
K	86.9	86.2	88.2	88.2
Na	87.9	87.9	88.4	88.1
Sr	81.2	80.5	87.4	88.4
Al	99.9	99.9	99.9	99.9
SO_4	39.2	40.1	48.7	61.5
Cl	24.2	26.9	9.4	13.5

The chloride ion removal from the real-world samples was poor in comparison to that obtained for the synthetic samples. It follows from the results that the final Al:Cl ratio was 1:1.2 for experiments done with a targeted Cl:Al:Ca ratio of 1:1.6:3 and 1:2 for a targeted ratio of 1:1.6:4. This suggests the formation of $Ca_4Al_2(OH)_{14}$, possibly through substitution of Cl^- ion by OH^- ion, explaining the low chloride ion removal.

The removal of sulfate ion when the Al:Ca ratio is 1:2, on the other hand, was high in relation to chloride ion removal. When there is sufficient calcium ion available in solution at high pH, it is probable that the removal of sulfate ion proceeds via $Ca_6Al_2(SO_4)_3(OH)_{12}$ as shown in the previous method.

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CHAPTER 5

RESULTS: SUPERCRITICAL WATER TECHNOLOGY

The strategy with this part of the investigation was to utilise the significant decrease in polarity, dielectric constant, hydrogen bonding and solvating capability of water on shifting from ambient to subcritical to supercritical conditions to force ions out of solution, similarly as addition of a common ion would decrease the solubility of a given ion and cause its precipitation from solution.

5.1 Synthetic Samples

The removal of sulfate ion at subcritical and supercritical water conditions was studied with the same synthetically prepared solutions as those employed for the targeted precipitation of calcium sulfoaluminate ($Al:SO_4:Ca = 2:3:6$) [1] in the previous chapter, since it was argued that the formation of this compound could most likely occur as a result of lower solubility or less solvation of ionic species in subcritical and supercritical water.

The $\Delta\%$-*versus*-time profiles in Figure 5.1 indicate that at subcritical water conditions only Ca^{2+} precipitated completely (and almost instantaneously), and that eventually (after 150 minutes of treatment) more than 80% of Al^{3+} and at the utmost (after 40 minutes of treatment) 75% of SO_4^{2-} could be recovered from solution. It is thus unlikely that precipitation of exclusively the target compound $Ca_6Al_2(SO_4)_3(OH)_{12}$ occurred. However, the $Al:SO_4:Ca$ molar ratio after ca. 90 minutes of treatment turned out to be 2:2:7, which approaches the range 2:2-3:5-7 considered in the literature [1] to be indicative of precipitation of a compound similar to $Ca_6Al_2(SO_4)_3(OH)_{12}$.

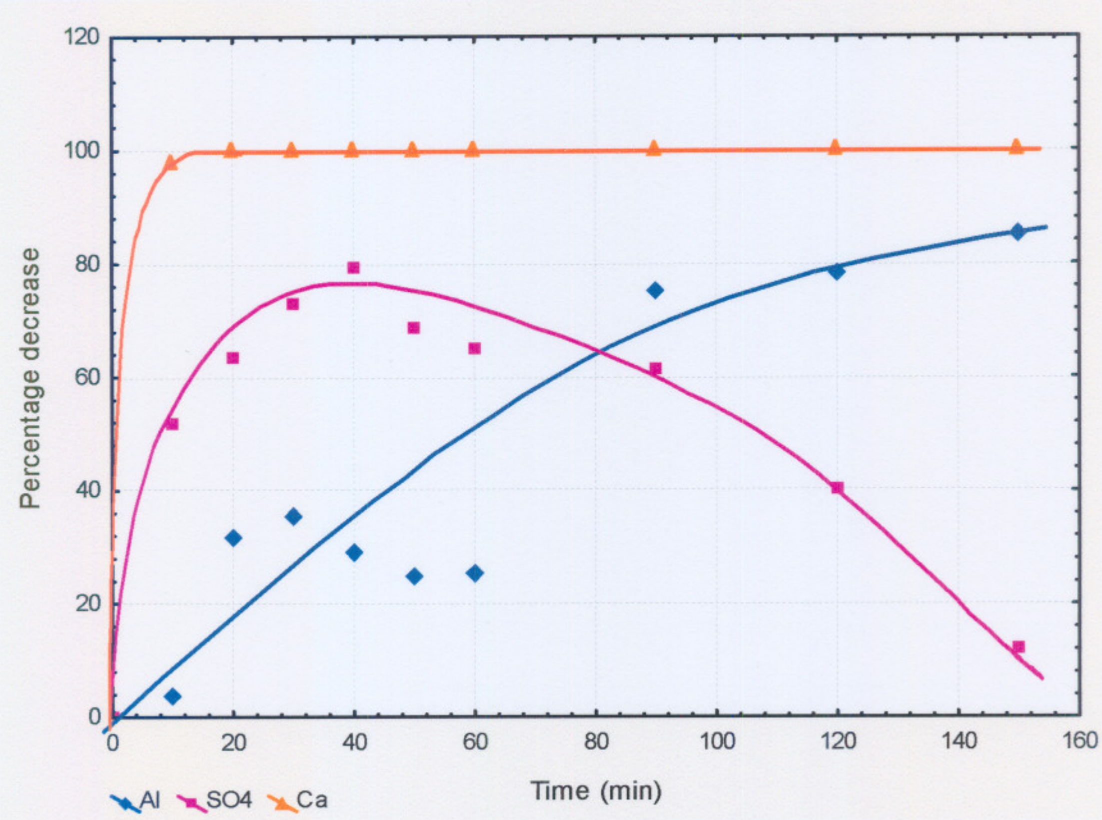

Figure 5.1 Δ%-*versus*-time profile for aluminium, sulfate and calcium ion at subcritical water conditions (p = 4.8 atm, T = 150^{0}C)

The decrease in concentration of all three ions can be attributed to the decrease in polarity of water and to partial disruption of hydrogen bonding on approaching subcritical water conditions. After instant precipitation of all Ca^{2+} and certain percentages of the two other ions in solution, the remaining Al^{3+} and SO_4^{2-} are expected to compete for solvation by the available water molecules. The smaller and higher charged Al^{3+} may be solvated more effectively than the bulky and lower charged SO_4^{2-}, resulting in higher sulfate removal initially. However, calculation of the final number of moles present in the filtrate showed a Al:SO_4 ratio not much different from the initial ratio of 2:3, indicating that the decrease in recovered sulfate and simultaneous increase in recovered aluminium observed for longer treatment times resulted from the competition between the two ions for solvating water molecules [2].

The Δ%-*versus*-time profiles in Figure 5.2 were obtained at supercritical water conditions. The results echoed those obtained under subcritical water conditions, with comparable to slightly higher yields of recovery of aluminium and sulfate after a treatment time of 60 min. The recovery of the ionic species can be attributed to the non-polar character of supercritical water and the depleted hydrogen bond structure under supercritical conditions [3].

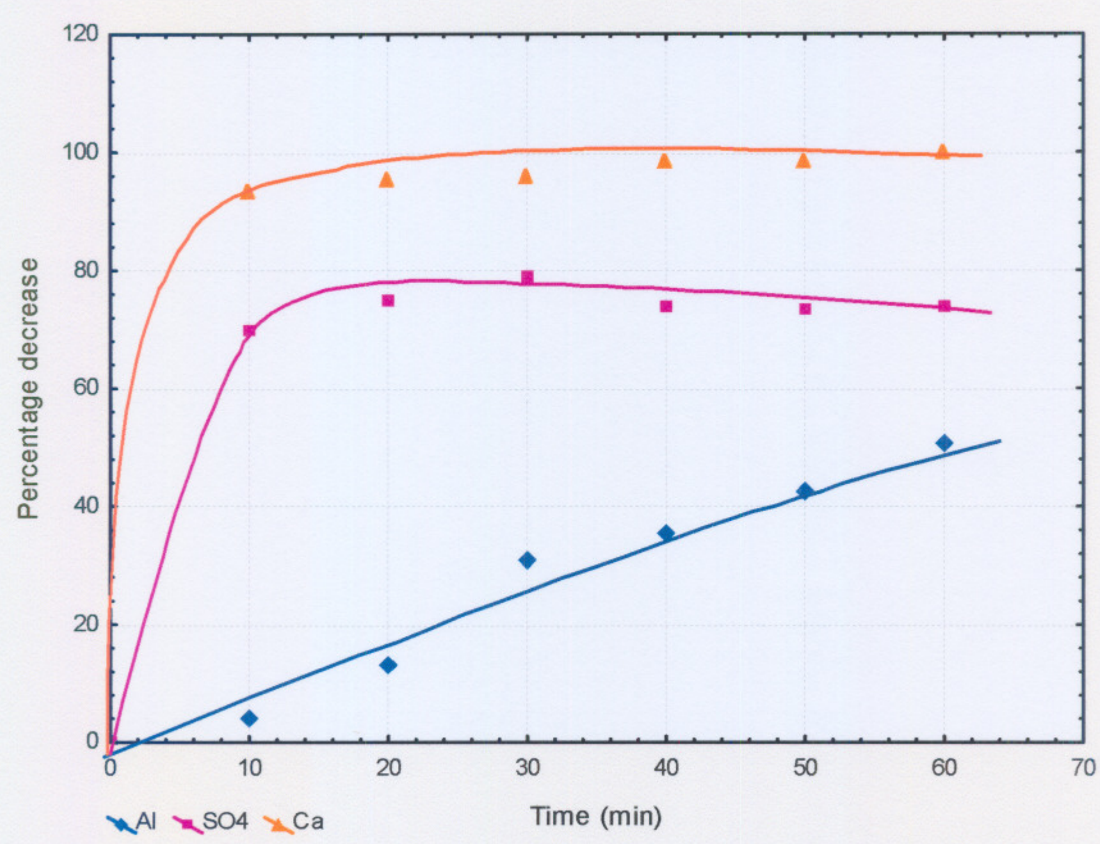

Figure 5.2 Δ%-*versus*-time profiles for aluminium, sulfate and calcium ion at supercritical water conditions (p = 218 atm, T = 400^{0}C)

The intention with the ultra-high lime with aluminium (UHLA) method [4] was, as in the previous chapter, to remove chloride ion from water. The formation of calcium chloroaluminate with a specific Cl:Al:Ca ratio formed the basis of the envisaged precipitation under subcritical and supercritical water conditions.

Table 5.1 Percentage decrease of aluminium, chloride and calcium ion on subjection to subcritical water conditions (p = 4.8 atm, T = 150^{0}C)

Time	%Al decrease	%Cl decrease	%Ca decrease
15	76.4	16.8	99.7
30	77.2	-	96.9
45	77.6	-	97.2
60	77.4	16.8	98.2
75	77.5	16.8	98.4
90	77.4	22.4	98.8

Table 5.2 Percentage decrease of aluminium, chloride and calcium ion on subjection to supercritical water conditions (p = 218 atm, T = 400^{0}C)

Time	%Al decrease	%Cl decrease	%Ca decrease
10	74.8	11.2	98.7
15	73.7	11.2	97.0
20	74.7	-	97.3
30	79.5	-	99.6
45	78.0	-	99.6
60	76.5	-	99.9
75	75.8	-	99.6
90	75.9	-	99.4

Treatment at both subcritical and supercritical water conditions failed to remove chloride ion to any significant level. The Al:Ca molar ratio of 1:2 suggests formation of $Ca_4Al_2(OH)_{14}$ when chloride ion in $Ca_4Al_2Cl_2(OH)_{12}$ is replaced by hydroxide ion. The availability of hydroxide ion at the prevailing conditions (highly basic solution, critical point of water) is the result of a larger than ambient ionic product of water ($K_w = 10^{-11}$ instead of $K_w = 10^{-14}$) [3] and the generally lower solubility products of hydroxide compounds (typically 10^{-16}) compared to other, e.g. chloride, compounds [5].

5.2 Real-World Samples

TRO and EDR brine waste water samples were subjected to subcritical and supercritical water conditions to establish any change in concentration of the ions in solution as a result of precipitation. The results are listed in Table 5.3 (TRO, subcritical), Table 5.4 (EDR, subcritical), Table 5.5 (TRO, supercritical) and Table 5.6 (EDR, supercritical), and presented by Δ%-*versus*-time profiles in Figure 5.3 (TRO, subcritical), Figure 5.5 (EDR, subcritical), Figure 5.7 (TRO, supercritical) and Figure 5.8 (EDR, supercritical). The bulk of precipitation occurred within the first 10 minutes of treatment at subcritical/supercritical water conditions, and the data in the tables largely reflect the scenario after this time interval. However, a comprehensive time dependence study was undertaken and the resulting Δ%-*versus*-time profiles were used to determine more accurately the change in concentration Δ[A] and the percentage decrease Δ% for each ion reported in the tables. Figures 5.4 and 5.6 show representative examples of Δ%-*versus*-time profiles exhibiting the extent of scatter in the data of all profiles due to several different error sources (conditions, filtration, analysis) and how, by establishing a mean data error by virtue of duplicate runs, smooth curves could be drawn through the standard deviation error limits.

Table 5.3 ICP-MS and IC results for TRO brine waste water treated at subcritical water conditions ($p = 4.8$ atm, $T = 150^0C$)

Ion	**$[A]_0$**	**$[A]_t$**	**Δ[A]**	**Δ%***
Na	1 400	1 000	400	28
Mg	39	26	13	33
K	130	100	30	23
Ca	500	420	80	16
Sr	42	33	9	20
SO_4	3 576	3 446	130	3
NO_3	60	54	6	8
Cl	1 183	1 139	44	3
F	7	7	0	0

A = concentration (mg/L)

* derived from Δ%-*versus*-time profiles in Figure 5.3

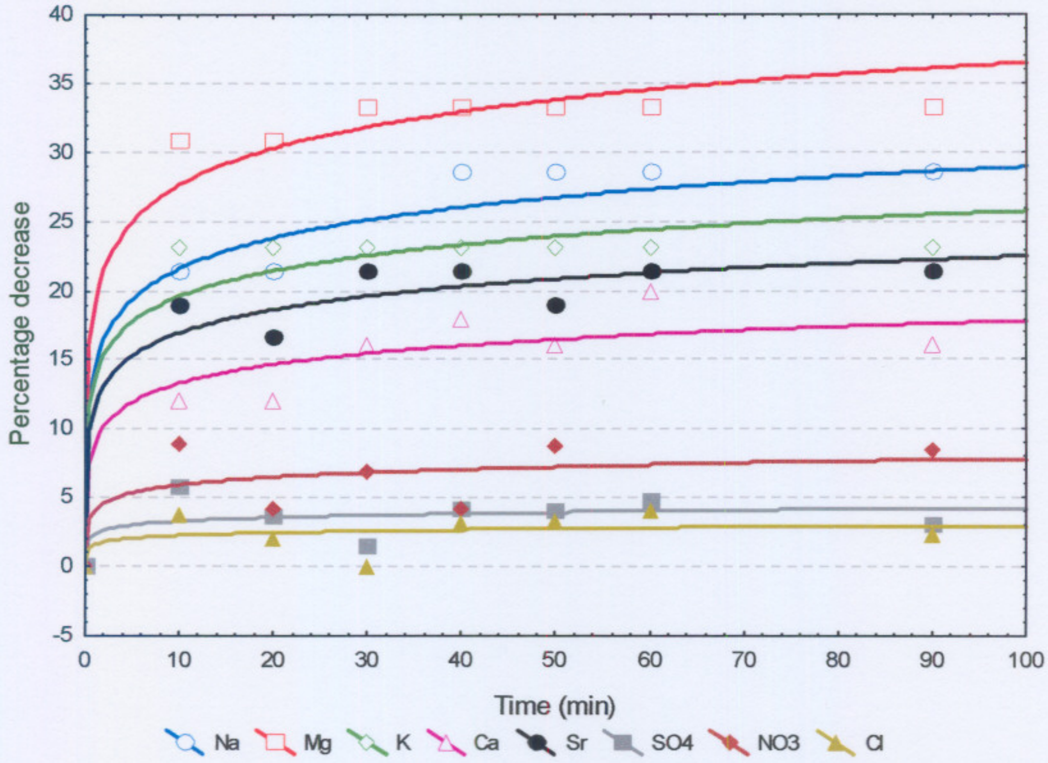

Figure 5.3 Δ%-*versus*-time profiles for ions in TRO brine waste water at subcritical water conditions (p = 4.8 atm, T = 150^{0}C)

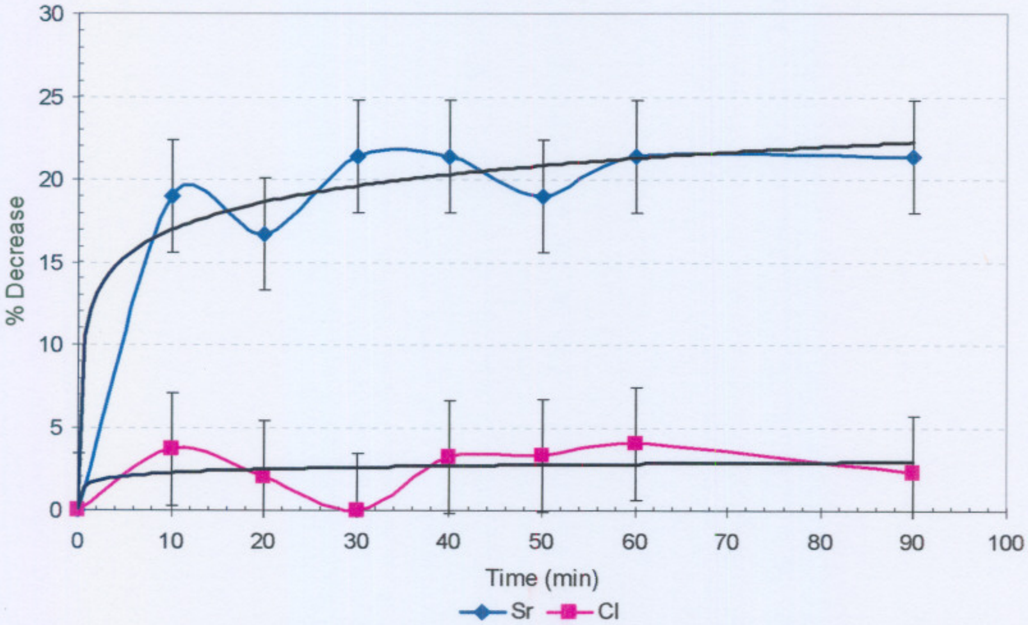

Figure 5.4 Representative Δ%-versus-time profiles showing typical data scatter and curve-smoothing (TRO brine waste water, subcritical water conditions)

Table 5.4 ICP-MS and IC results for EDR brine waste water samples at subcritical water conditions (p = 4.8 atm, T = 150^{0}C)

Ion	**$[A]_0$**	**$[A]_t$**	**Δ[A]**	**Δ%***
Na	3 200	2 300	900	27
Mg	420	310	110	26
K	35	22	13	40
Ca	660	640	20	3
Sr	31	24	7	25
SO_4	10 148	10 108	40	1
NO_3	13	9	4	34
Cl	731	731	0	0
F	5	4	1	22

A = concentration (mg/L)

* derived from Δ%-*versus*-time profiles in Figure 5.5

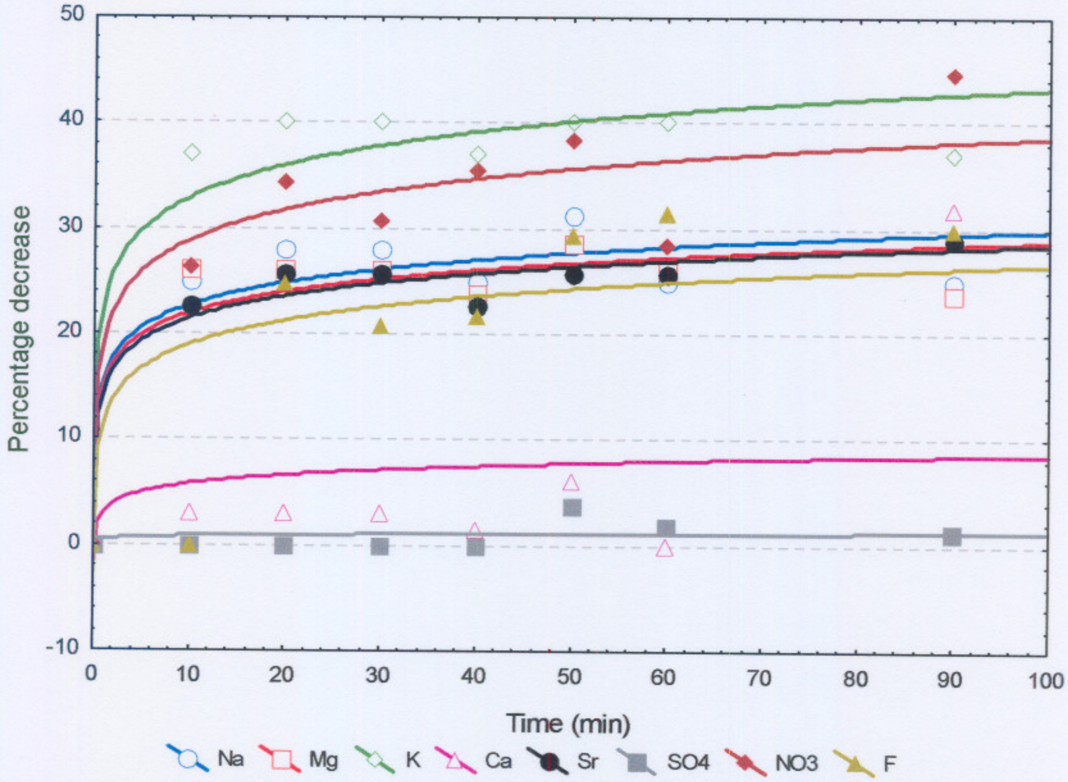

Figure 5.5 Δ%-versus-time profiles for ions in EDR brine waste water at subcritical water conditions (p = 4.8 atm, T = 150^{0}C)

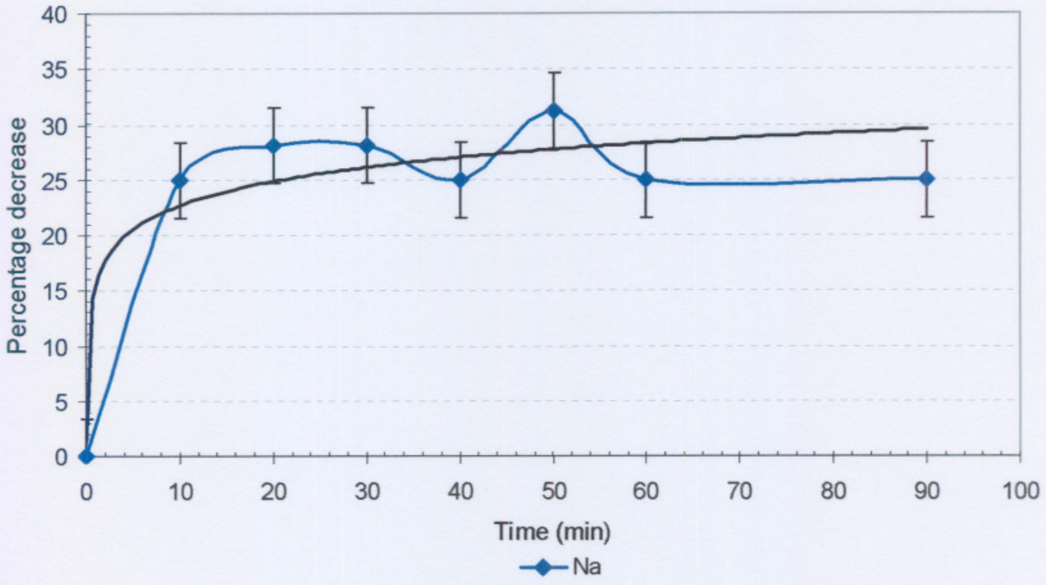

Figure 5.6 Representative Δ%-*versus*-time profiles showing typical data scatter and curve-smoothing (EDR brine waste water, subcritical water conditions)

Table 5.5 ICP-MS and IC results for TRO brine waste water at supercritical water conditions (p = 218 atm, T = 400^{0}C)

Ion	$[A]_0$	$[A]_t$	Δ[A]	Δ%*
Na	1 400	950	450	31
Mg	39	22	17	40
K	130	94	36	24
Ca	500	58	442	85
Sr	42	5	37	85
SO_4	3 576	2 569	1007	28
NO_3	60	50	10	20
Cl	1 183	1 112	71	6
F	7	5	2	20

A = concentration (mg/L)

* derived from Δ%-*versus*-time profiles in Figure 5.7

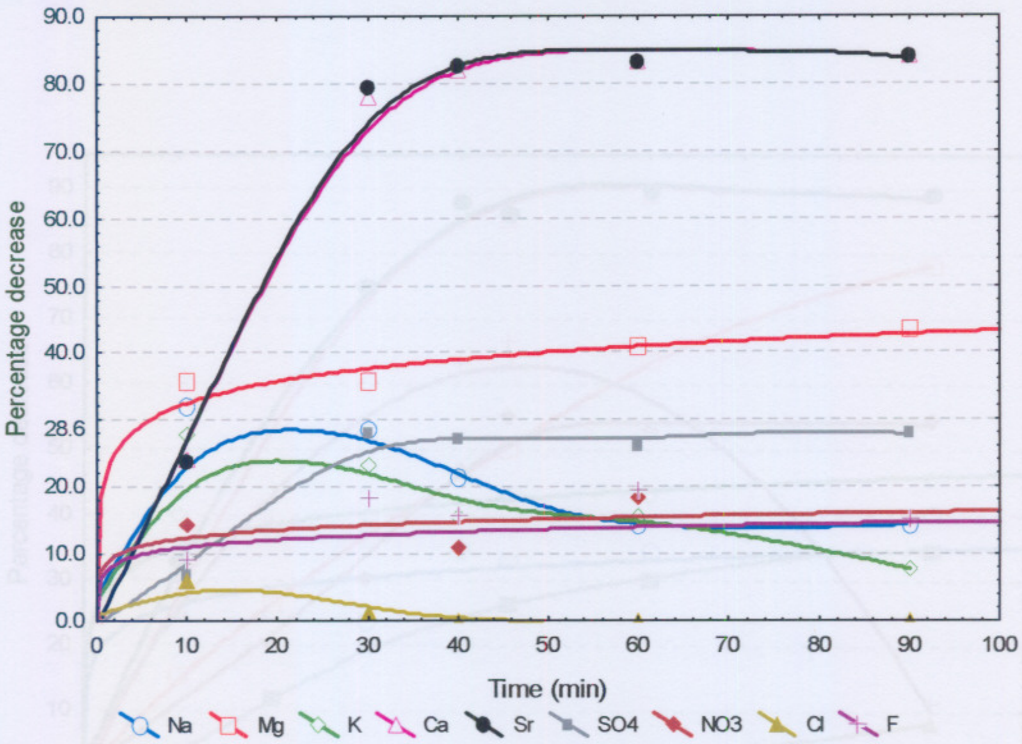

Figure 5.7 Δ%-*versus*-time profiles for ions in TRO brine waste water at supercritical water conditions (p = 218 atm, T = 400^{0}C)

Table 5.6 ICP-MS and IC results for EDR brine waste water at supercritical water conditions (p = 218 atm, T = 400^{0}C)

Ion	$[A]_0$	$[A]_t$	Δ[A]	Δ%*
Na	3 200	1 900	1 300	41
Mg	420	92	328	90
K	35	19	16	46
Ca	660	72	588	89
Sr	31	3	28	90
SO_4	10 148	6 636	3 512	35
NO_3	13	6	7	55
Cl	731	671	60	8
F	5	2	3	63

A = concentration (mg/L)

* derived from Δ%-*versus*-time profiles in Figure 5.8

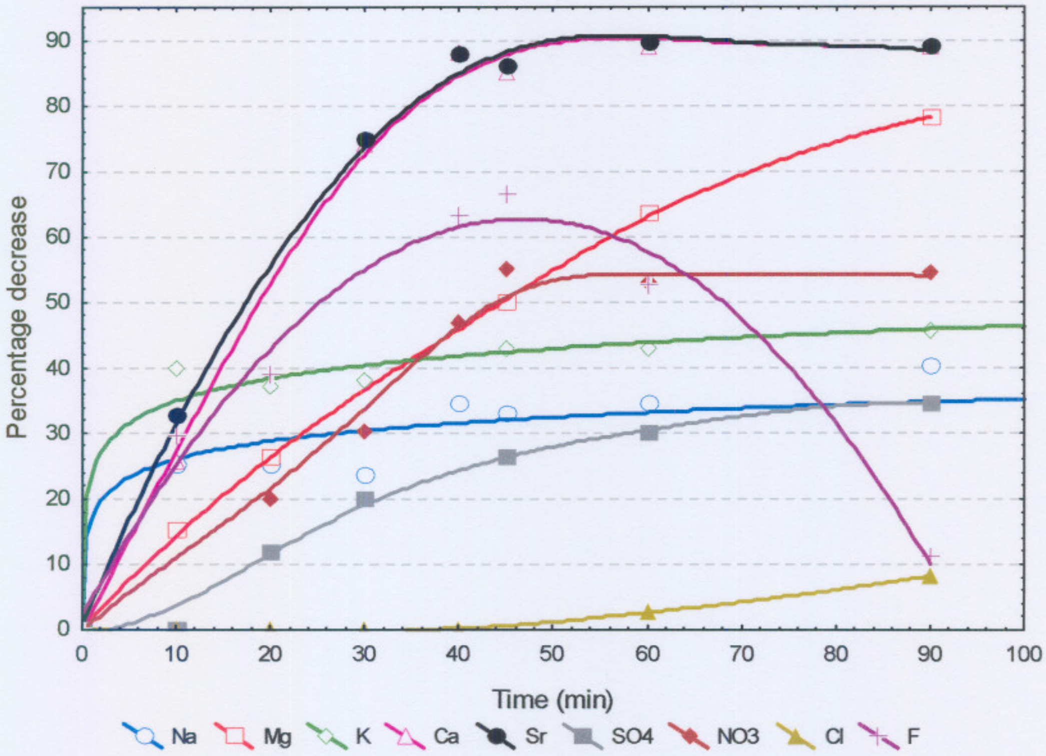

Figure 5.8 Δ%-*versus*-time profiles for ions in EDR brine waste water at supercritical water conditions (p = 218 atm, T = 400ºC)

The data in Table 5.7 were collected from the previous four tables to summarise the extent to which a few prominent ions could be removed from real-water samples by treatment at subcritical and supercritical water conditions.

Table 5.7 Element removal from real-world water samples by treatment at subcritical and supercritical water conditions

Ion	**TRO brine waste water sample**		**EDR brine waste water sample**	
	subcritical	**supercritical**	**subcritical**	**supercritical**
Na	400 mg/L (28%)	450 mg/L (31%)	900 mg/L (27%)	1500 mg/L (41%)
K	30 mg/L (23%)	36 mg/L (24%)	13 mg/L (40%)	16 mg/L (46%)
Cl	44 mg/L (3%)	71 mg/L (6%)	0 mg/L (0%)	60 mg/L (8%)
Mg	13 mg/L (33%)	17 mg/L (40%)	110 mg/L (26%)	328 mg/L (90%)
Ca	80 mg/L (16%)	442 mg/L (85%)	20 mg/L (3%)	588 mg/L (89%)
Sr	9 mg/L (20%)	37 mg/L (85%)	7 mg/L (25%)	28 mg/L (90%)
SO_4	130 mg/L (3%)	1007 mg/L (28%)	40 mg/L (1%)	3512 mg/L (35%)

From this table the following conclusions can be drawn regarding subjection of real-world TRO and EDR brines to subcritical and supercritical water conditions as a means of removing/precipitating ions present in these waste water samples:

The removal of chloride and sulfate, which are two of the major undesirable components of the TRO and EDR brine waste waters turned out to be reasonable for Cl ion (60-70 mg/L, 6-8%) and quite satisfactory for SO_4 ion (1000-3500 mg/L, 28-35%) at supercritical water conditions in comparison to the recovery of other ions. Two other frequently encountered ions in the industrial waste water which could be removed by supercritical water treatment were Na^+ (450 mg/L or 31% for TRO, 1 300 mg/L or 41% for EDR) and Ca^{2+} (450 mg/L or 85% for TRO, 600 mg/L or 90% for EDR). These cations are known for their strong ion-dipole interaction with ambient water (polar), explaining their loss of hydration in and consequent precipitation from supercritical water (non-polar). The availability of appropriate equipment in an industrial plant to subject waste water to supercritical conditions could result in partial recovery of chloride, sulfate, sodium and calcium in this novel way.

For the monovalent anions/cations (Cl^-, Na^+, K^+) the difference in recovery at subcritical and supercritical water conditions is not that large, but for the divalent species (SO_4^{2-}, Mg^{2+}, Ca^{2+}, Sr^{2+}) a vast difference in the yield of recovery was observed. The divalent ions have larger (more negative) enthalpies of hydration (-1 922 kJ/mol for Mg^{2+}, -1 592 kJ/mol for Ca^{2+} and -1 445 kJ/mol for Sr^{2+}) than the monovalent ions (-405 kJ/mol for Na^+, -363 kJ/mol for Cl^- and -321 kJ/mol for K^+), and are therefore better hydrated in ambient water than the monovalent species [5, 6]. However, due to loss of the unique properties of water (polarity, hydrogen bonding) under supercritical conditions, the situation is reversed and the divalent ions are less solvated or better recovered/precipitated than the monovalent species (typically 85-90% for Mg^{2+}, Ca^{2+} and Sr^{2+} compared to typically 25-45% for Na^+ and K^+).

The lowest percentage decrease was observed for chloride ion, and this can be attributed to two possible factors. Firstly, the quoted enthalpies of hydration are directly dependent on the size of the ion charge and inversely dependent on the radius of the ion (i.e. the distance between the ion and the solvating water molecule) [5]. Chloride ion is large with a relatively small charge of -1, which enables interaction even with less polar water molecules at supercritical water conditions to prevent precipitation to occur readily. Secondly, chloride ion may be replaced in precipitates by hydroxide ion, the presence of which relates to the several orders of magnitude larger ionic product in supercritical than in ambient water [3].

The solubility of fluoride is larger in acidic than in basic solution. At high pH the solubility decreases to the point that precipitation occurs [7]. This explains the higher percentage of recovery of fluoride for EDR brine waste water (pH > 8) than for TRO brine waste water (pH < 6).

A principal feature of precipitation of various ions from real-world waste water samples is the competition among ions for solvation/hydration by the available solvent molecules. Figures 5.7 and 5.8, which both relate to supercritical water conditions, bear witness of this feature as outlined below:

Figure 5.7 for TRO brine waste water shows that calcium, strontium and sulfate ion gradually precipitate before reaching a maximum after 30-40 minutes of treatment, whereas sodium, potassium and chloride ion precipitate almost completely instantaneously but show a decrease in yield after 30-40 minutes of treatment. This indicates that calcium, strontium and sulfate ion compete with sodium, potassium and chloride ion for the available water molecules for hydration, causing the last-mentioned three to redissolve once the first-mentioned three are sufficiently removed from solution. The ions Ca^{2+}, Sr^{2+} and SO_4^{2-} have a larger charge than that of Na^+, K^+ and Cl^- and are thus less hydrated in (or better precipitated by) supercritical water.

Figure 5.8 for EDR brine waste water similarly illustrates that fluoride ion removal reached a maximum after 45 minutes of treatment but, as it competes with chloride and magnesium ion for available water molecules for hydration, started to redissolve with an accompanying increase in precipitation of chloride and magnesium ion.

5.3 SEM Micrographs

SEM micrographs of precipitates obtained from (a) TRO and (b) EDR brine waste water after treatment at supercritical water conditions (p = 218 atm and T = 400^{0}C) are shown in Figure 5.9. These precipitates were not analysed, as identification of the precipitates of the different methods was not considered to be an objective of this study. A comprehensive analysis using techniques such as powder and/or X-ray diffraction, SEM, XRF, laser ablation, and other, could be undertaken in future to complement the results of this investigation.

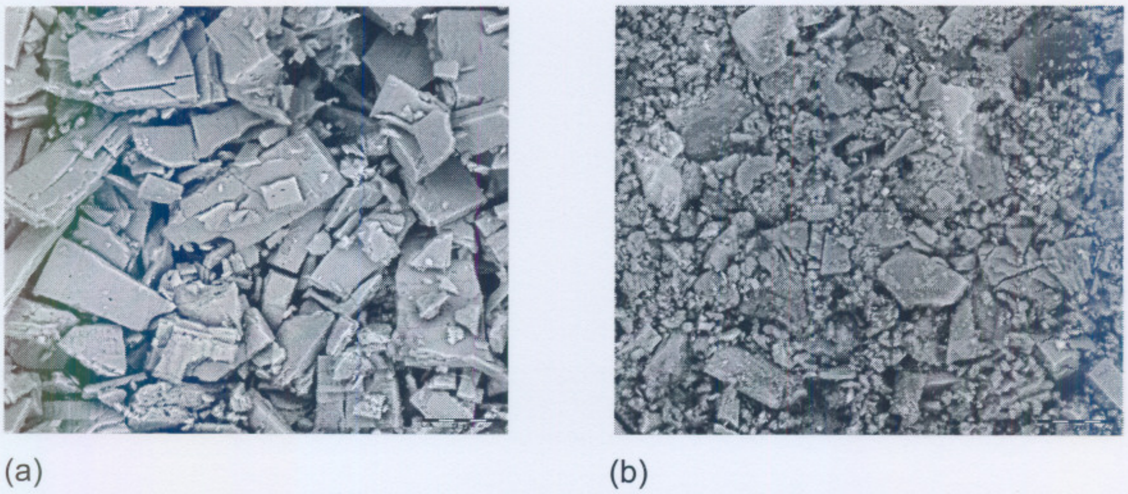
(a) (b)

Figure 5.9 SEM micrographs of precipitates from (a) TRO and (b) EDR brine

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CHAPTER 6

RESULTS: EUTECTIC FREEZE CRYSTALLISATION

This chapter deals with the effect of cooling on solubility and eventual precipitation of substances at the eutectic point of simple synthetically prepared mixtures and of complicated real-world waste water samples.

6.1 Synthetic Samples

Eutectic solutions of two selected inorganic salts, viz. sodium sulfate and sodium carbonate, were prepared as outlined in Section 3.2.3 by dissolving 59 g Na_2CO_3 in 941 g H_2O and 127 g Na_2SO_4 in 873 g H_2O, respectively. These solutions were then cooled down to their respective eutectic points, and the resulting ice-salt mixtures were oven-dried and weighed. In both cases precipitate was collected successively as different fractions and the masses of these added to determine the total mass and % removal of the particular inorganic salt as shown in Table 6.1.

The tabled results show that sodium sulfate and sodium carbonate could be partly removed from solution. A slow decrease in freezing point was observed for both eutectic solutions on successive removal of precipitate as the mother solution became more concentrated after each fraction [1, 2].

Table 6.1 Experimental results for inorganic salts removed at eutectic point

Salt →	**Sodium carbonate**		**Sodium sulfate**	
↓ Fraction	**Temp (°C)**	**Mass (g)**	**Temp (°C)**	**Mass (g)**
1	-1.8	0.493	2.5	73.0
2	-3.0	1.81	-3.1	9.08
3	-3.0	4.04	-3.5	1.59
4	-3.0	0.735	-3.5	0.783
5	-3.1	2.01	-3.5	0.733
6	-3.2	1.54	**total mass →**	85.2
7	-3.5	1.17	**% removal →**	67.1
8	-4.0	0.905		
9	-4.2	2.43		
10	-5.3	3.39		
	total mass →	18.5		
	% removal →	31.4		

6.2 Real-World Samples

In view of the results obtained with the synthetically prepared samples in the previous section, it was decided to investigate the removal of inorganic salts from the real-world TRO and EDR brine waste water samples obtained from industry. A stock solution of each of the two samples was subjected to cooling, and seven successive fractions of precipitated solid were collected, weighed and analysed on melting as described in Section 3.2.3. It was found, as for the synthetically prepared samples, that the freezing point of both waste water types decreased after each fraction as the mother solution became more concentrated [1, 2].

Table 6.2 ICP-MS and IC results (values in mg/L) for seven ice-salt mixtures removed from real-world water samples

Fraction →	**1**	**2**	**3**	**4**	**5**	**6**	**7**
TRO brine waste water							
↓Ion Mass (g)→	44.0	73.4	33.1	68.4	61.1	48.7	37.8
Na	923	846	923	923	1 000	1 154	1 308
Mg	16.9	15.4	19.2	17.7	18.5	21.5	23.1
K	23.3	10.8	13.1	12.3	13.9	15.4	16.9
Ca	231	208	238	231	254	285	292
Sr	16.9	15.4	17.7	16.9	18.5	20.8	20.8
SO_4	1 966	1 810	1 996	1 970	2 344	2 456	2 586
Cl	637	582	640	631	458	786	825
EDR brine waste water							
↓Ion Mass (g)→	58.7	55.7	62.0	82.3	50.2	57.9	45.7
Na	2 538	2 231	2 308	2 538	2 692	3 923	3 692
Mg	246	215	221	246	262	377	354
K	3.15	2.92	3.00	3.77	3.38	4.92	4.62
Ca	346	315	323	308	338	585	538
Sr	13.1	11.5	11.5	12.3	13.1	21.5	20.0
SO_4	5 269	5 257	5 762	6 623	6 386	7 527	7 670
Cl	376	378	414	476	764	541	551

Table 6.3 Actual mass of ions present in TRO brine ice-salt mixtures

Ion	**Initial mass (mg)**	**Fraction mass (mg)**							**Final mass (mg)**	
		1	**2**	**3**	**4**	**5**	**6**	**7**	**Total 1-7**	**Residual**
Na	1 558	40.6 *	62.1	30.6	63.2	61.1	56.2	49.4	363	1 068
Mg	43.4	0.743	1.13	0.637	1.21	1.13	1.05	0.872	6.77	18.9
K	145	1.02	0.791	0.433	0.842	0.846	0.748	0.639	5.32	13.9
Ca	557	10.1	15.2	7.90	15.8	15.5	13.8	11.0	89.5	185
Sr	46.8	0.744	1.13	0.586	1.16	1.13	1.01	0.784	6.54	13.5
SO_4	3 981	86.4	133	66.1	135	143	120	97.7	781	2 020
Cl	1 317	28.0	42.7	21.2	43.2	28.0	38.3	31.1	232	637
Total	7 648 **	168	256	127	260	251	231	192	1 484 **	3 958 **

* Mass calculated from Table 6.2 and shown here as a representative example of values for all ions reported in this table:

mass Na = (44.0 g/1000 g) x 923 mg = 40.6 mg

** Mass balance (7 648 mg versus 1 484 mg + 3 958 mg = 5 442 mg) reflects relative accuracy with which seven successive fractions of precipitate were acquired, collected and analysed

Table 6.4 Actual mass of ions present in EDR brine ice-salt mixtures

Ions	Initial mass (mg)	Fraction mass (mg)							Final mass (mg)	
		1	2	3	4	5	6	7	Total 1-7	Residual
Na	3 744	149 *	124	143	209	135	227	169	1 156	2 730
Mg	491	14.5	12.0	13.7	20.3	13.1	21.8	16.2	112	241
K	41.0	0.185	0.163	0.186	0.310	0.170	0.285	0.211	1.51	3.22
Ca	772	20.3	17.6	20.0	25.3	17.0	33.8	24.6	159	147
Sr	36.3	0.768	0.642	0.715	1.01	0.656	1.25	0.913	5.95	8.40
SO_4	4 184	309	292	357	545	321	436	350	2 610	5 161
Cl	1 384	22.1	21.0	25.7	39.2	38.3	31.3	25.1	203	419
Total	10 654 **	516	468	548	841	525	751	586	4 248 **	8 710 **

* Mass calculated from Table 6.2 and shown here as a representative example of values for all ions reported in this table

mass Na = (58.7 g/1000 g) x 2 538 mg = 149 mg

** Mass balance (10 654 mg versus 4 248 mg + 8 710 mg = 12 958 mg) reflects relative accuracy with which seven successive fractions of precipitate were acquired, collected and analysed

The number of moles of each ion removed from each of the two real-world water samples was calculated from the previous two tables and is listed in Table 6.5. The mass of each ion removed was within experimental error surprisingly constant for the seven different fractions of precipitate collected, so that either the average or the total of the seven values could be used in calculating the corresponding number of moles for the purpose of determining various mole ratios. A representative example of the calculation of the number of moles is given as a footnote to Table 6.5.

Table 6.5 Number of moles of each ion removed from TRO and EDR brine waste water samples

↓Sample Ion →	**Na**	**Mg**	**K**	**Ca**	**Sr**	**SO_4**	**Cl**
$TRO_{average}$ (mmol)	2.26*	0.040	0.019	0.318	0.011	1.16	0.937
$TRO_{total1-7}$ (mmol)	15.8**	0.279	0.136	2.23	0.075	8.13	6.54
$EDR_{average}$ (mmol)	7.18	0.656	0.006	0.565	0.010	3.88	0.817
$EDR_{total1-7}$ (mmol)	50.3	4.61	0.039	3.97	0.068	27.2	5.73

* mass of Na (from Table 6.3) = (51.9 ± 12.4) mg

mol Na = 51.9×10^{-3} g / 22.99 g mol^{-1} = 2.26×10^{-3}

** total mass of Na taken over 7 fractions = 363 mg (from Table 6.3)

mol Na = 363×10^{-3} g / 22.99 g mol^{-1} = 15.8×10^{-3}

calculations above identical for EDR except data taken from Table 6.4

The number of moles of sodium and sulfate ion in the ice-salt mixtures is significantly higher than for the other ions. Moreover, the Na:SO_4 molar ratio for both TRO and EDR brine waste water is approximately 2:1, suggesting removal of Na_2SO_4 in large quantities. It was shown in the previous section that a large amount of sodium sulfate could be removed effortlessly from a synthetically prepared eutectic solution of this salt.

The amount of calcium and chloride removal from solution is also relatively high, but the Ca:Cl molar ratios do not suggest precipitation of any known inorganic species. The TRO and EDR precipitates have Na:Cl, Ca:SO_4 and Ca:Cl molar ratios of approximately 2½:1 and 9:1, 3½:1 and 7:1, and 1:3 and

1:1½, respectively, none of these being indicative of any known salt formed. The Mg:Cl molar ratio for the EDR precipitate is close to 1:1, but the value is meaningless in terms of the formation of a known compound. It is possible that ions are removed as a combination of sodium chloride, sodium sulfate, calcium chloride and magnesium chloride, the formation of which might be assisted by the common ion effect. Moreover, heavy metal ions like nickel, iron, zinc, manganese and copper are also present in low concentrations in the waste water samples obtained from industry. Their presence may assist in the removal of calcium, chloride and sulfate ion as $FeCl_3$, $ZnCl_2$, $CuCl_2$, $NiSO_4$, $MnSO_4$, $FeSO_4$, $ZnSO_4$ and $CuSO_4$, to name a few possibilities.

Table 6.6 Concentration of ions in stock solution of real-world samples before and after fractional crystallisation

Sample →	**TRO brine**		**EDR brine**	
	Before	**After**	**Before**	**After**
↓ Ion (mg/L) Mass (g) →	1 113	463	1 170	455
Na	1 400	2 308	3 200	6 000
Mg	39	41	420	531
K	130	30	35	7
Ca	500	400	660	323
Sr	42	29	31	19
SO_4	10 148	4 365	3 576	11 344
Cl	731	1 377	1 183	921

The stock solution of each of the two real-world water samples was analysed (Section 3.2.3) for the various ions after the 7-step fractional crystallisation since the mother liquid from each fraction was returned to the stock solution in the cooling bath. The initial and residual concentration of the various ions are listed in Table 6.6. The concentration of sodium and chloride ion in the TRO brine waste water almost doubled and the concentration of sodium, magnesium and sulfate ion in the EDR brine waste water increased while the concentration of all other ions decreased. These results indicate that eutectic freeze crystallisation can be used to either concentrate or dilute ions in solution as preparation for further process steps. The simple experimental set-up/design and high amounts of inorganic salts that can be removed easily from solution render eutectic freeze crystallisation a preferred technique for mineral and water processing.

References Chapter 6

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CHAPTER 7

EVALUATION AND FUTURE PERSPECTIVE

Nothing has such power to broaden the mind as the ability to investigate systematically and truly all that comes under your observation in life.

Marcus Aurelius

In this chapter the study is evaluated by considering the extent to which the objectives could be achieved. A few prospects to address shortcomings of this study are also given.

7.1 Achievements versus Objectives

In this study the viability of targeted precipitation, supercritical water treatment and eutectic freeze crystallisation as alternative methods for inorganic salt removal from synthetically prepared and complex real-world waste water samples from the petroleum industry was duly proven, in fulfilment of the first two objectives stated in the introductory chapter.

The achievements with each of these techniques as applied to the selected water samples are briefly evaluated in the next three subparagraphs as required by the third objective in the motivation to this study:

Two targeted precipitations were performed in an attempt to remove sulfate and chloride ion from synthetic and real-world solutions in which the molar ratios Al:SO_4:Ca and Cl:Al:Ca were adjusted to 2:3:6 and 1:1:2, respectively, to facilitate precipitation of selected target compounds. The removal of sulfate ion was quite successful (up to 88%) from simple synthetic solutions containing only the three relevant species (Al, SO_4 and Ca), but from the more complex real-world solutions lower yields of precipitated sulfate (50% for TRO and 75%

for EDR) were obtained and a problem of redissolution with time was encountered. Chloride ion removal from synthetic solutions increased from 28% to 60% by shifting the Cl:Al:Ca molar ratio from 1:1:2 to 1:1½:3, but from the industrial brines disappointingly low chloride ion recovery (25% for TRO, 12% for EDR) was achieved.

The Al:SO_4:Ca and Cl:Al:Ca molar ratios of both synthetic and real-world solutions subjected to subcritical and supercritical water conditions were preadjusted to the same values as those selected for targeted precipitation. The removal of sulfate ion from synthetic solutions was equally successful (up to 80% at both subcritical and supercritical conditions) as targeted precipitation, but resolvation as a result of competition with other ions for hydrating water molecules caused high yields to decrease substantially over time. A vast difference in the amount of removed sulfate was observed at subcritical and supercritical water conditions respectively, with yields increasing from 100 mg/L (3%) to 1000 mg/L (28%) for TRO and from 50 mg/L (1%) to 3500 mg/L (35%) for EDR on changing from subcritical to supercritical conditions. Large amounts of sodium (450 mg/L or 31% for TRO, 1 300 mg/L or 41% for EDR) and calcium (450 mg/L or 85% for TRO, 600 mg/L or 90%) precipitated in addition to sulfate at supercritical water conditions. Chloride ion removal was disappointingly low and never exceeded 15% for synthetic and 8% for real-world solutions.

Eutectic freeze crystallisation was used successfully in successive fractionations to remove fairly large amounts of simple inorganic salts, such as Na_2SO_4 (67%) and Na_2CO_3 (31%), from preprepared eutectic solutions. Application of the technique to industrial waste water samples in seven successive fractionations led to collective removal of 20% of sulfate and 18% of chloride content of TRO and 60% of sulfate and 15% of chloride content of EDR waste water samples. The removal of ions in successive steps resulted in a continuously changing composition of the mother liquid, rendering the technique feasible for concentrating or diluting waste stream components.

The chosen analytical techniques proved to be suitable for the quantitative analysis of selected anions/cations, in accordance with the fourth objective. The techniques included simple ($AgNO_3$) and complexometric (EDTA) titrations for the analysis of all synthetically prepared samples and more elaborate instrumental analysis (ICP-MS for anions, IC for cations) of industrial TRO and EDR brine samples. SEM was used to a limited extent to examine the morphology of the precipitates obtained from TRO and EDR samples subjected to supercritical water conditions. The acquired data was processed using standard routines for statistics and graphics in a commercially available software package [1].

Finally, this study contributed in a more or lesser degree to all other general objectives stated in the introductory chapter. Good cooperation was established between the partners (North-West University and Sasol Secunda) and individuals (supervisor, learner, research assistant and industrial manager) involved, i.a. by virtue of a postgraduate bursary, financial support, scheduled visits and access to real-world sampling). The thrust of the study was to make a contribution to the field of industrial waste water treatment for the sake of mineral recovery and water restoration. The approach was to identify, to apply and to evaluate less known or novel methods of waste water treatment in order to expand knowledge in this field and to possibly enhance the capability of industry to help conserve water as a scarce resource. The inclusion of a method based on supercritical technology demonstrated its applicability to industrial processes and its relevance to the issues of green chemistry and sustainable development through the use of environmentally benign supercritical fluids.

7.2 Prospects versus Shortcomings

The delimitation of this project allowed three less known methods of waste water treatment to be investigated. There are, however, more methods to pursue in future studies. One possibility is hydrothermal precipitation [2, 3], which is based on an inverse solubility-temperature relationship at hyperatmospheric conditions and exclusion of any precipitating agent.

Two major constituents of waste water from a petroleum industry, next to an abundancy of sodium and calcium ions, are chloride and sulfate ions. The hazardous nature of these two ions explains why there was an emphasis on removing these species from waste water samples by the methods pursued in this study. Chloride ion was not sufficiently removed by any of the applied methods, and other options (ion-exchange, silver ion based targeted precipitation, etc.) need to be considered.

The analyses in this study were restricted to filtrates and none of the precipitates were analysed. A thorough analysis of the precipitates obtained from the TRO and EDR brines in this study could complement the existing results, eliminate some guesswork as to what compounds are formed and assist in interpreting the observed tendencies. The analysis of precipitates requires other analytical techniques (XD, XRF, SEM), the exposure to which would add to the expertise of the learner involved.

The development and application of supercritical technology need to be considered a priority in future. The technology is still largely unexplored and industry should be encouraged to think imaginatively about its feasibility in an industrial plant where resources like heat and pressure are readily available.

References Chapter 7

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