SULFATE REMOVAL FROM REJECT BRINED IN INLAND DESALINATION WITH ZERO LIQUID DISCHARGE

A Thesis

by

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ABSTRACT

Sulfate is one of the most problematic ions present in reject brine in desalination systems due to its high potential of scale formation and membrane fouling; making it an obstacle in the application of zero liquid discharge. The ultra-high lime with aluminum process (UHLA) has shown to effectively remove sulfate. This research involves the study of sulfate removal from the nano-filtration unit in the zero liquid discharge system for inland desalination via a two-stage process using a calcium source to remove sulfate in the first stage and implementing the UHLA process in the second stage. The kinetics, equilibrium characteristics, and effects of different parameters on sulfate removal were studied.

Kinetics of sulfate removal was studied on both stages of the process. The observation of fast kinetics in both stages indicated that removal kinetics is not a limitation for the application of the process. Equilibrium characteristics of the UHLA process were performed which revealed efficient sulfate removal at practical ranges of lime and aluminum doses.

The effect of pH on sulfate removal in the process was studied. Results showed that sulfate removal in Stage 1 was independent of the pH of the solution while effective sulfate removal in Stage 2 was found to be above a pH of 11.

The effect of initial sulfate concentrations on sulfate removal in Stage 1 was investigated and sulfate removal was mainly controlled by calcium sulfate solubility.

The effect of initial chloride concentrations on sulfate removal in Stage 2 was evaluated and the results indicated that chloride has negligible effect on the removal of sulfate.

Experiments concerning the effect of the recycle of calcium sulfate solids in Stage 1 showed an increase of the reaction rate. In contrast, the recycle of Stage 2 dry solids into Stage 2 revealed no effect on sulfate removal.

An equilibrium model was developed to explain the equilibrium characteristics of Stage 2. It was found that a valid explanation for the chemistry of sulfate removal in Stage 2 was the formation of a solid solution consisting of ettringite and monosulfate. XRD analysis confirmed the formation of these solids.

DEDICATION

To my parents and siblings, whom I thank God every day for blessing me with.

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TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

LIST OF TABLES

1. INTRODUCTION

Over the past half century, the global need for freshwater has doubled nearly every 15 years (Abramovitz, 1996; Rosegrant et al., 2002). This increase has caused a strain on existing freshwater resources, and it has become both more challenging and more costly to acquire new freshwater resources. Tension on the world's freshwater supplies will continue to increase. The International Water Management Institute reported that approximately one-third of the world's population will reside in regions facing critical water shortage by 2025 (Rosegrant et al., 2002; Marcuss, 2005).

Desalination is the option of choice in regions with inadequate freshwater supplies where there is ample water that is unfit for use owing to its high salinity. The choice of desalination process option relies on various factors such as salinity levels in raw water, quantities of water required, and the type and cost of accessible energy (Davis and Rayman, 2006).

The demand for economical inland desalination has become a serious issue in many areas of the world where communities struggle to sustain rapidly increasing water requirements with limited freshwater resources. While freshwater sources are scarce and often difficult to obtain, many of these communities have access to unused or underused brackish water sources. The ability to affordably treat brackish water would provide relief for communities where projected water demands exceed freshwater supply (El-Said et al., 2012).

The process of desalination is not per se environmentally friendly. This is mainly due to the highly saline brine concentrate that needs to be disposed of. The waste from desalination plants is a multi-component stream, with various effects on water, deposits and marine organisms.

Inappropriate disposal of reject brine from inland plants can result in the following problems: (1) Pollution of groundwater resources that are used as feed water for desalination plants. Groundwater pollution may develop from high salinity and the existence of other unfavorable chemicals in the concentrate. (2) Inhibition of production from agricultural lands affected by the accumulation of airborne salts from dried concentrate. (3) Formation of eyesores instigated by inappropriate disposal of concentrates on neighboring land. (4) Yielding treated sewage waste unsuitable for agricultural use when a sewerage system is applied for disposal of concentrates (Khordagui, 1997).

There are four basic ways to handle brines from brackish groundwater desalination. These are: discharge to the sea, deep well injection, discharge to publicly owned treatment works, and zero liquid discharge (ZLD) systems. While the discharge of brine into the sea is not uncommon for coastal plants, it is not applicable for inland desalination plants. Deep well injection is economically unfeasible and carries with it its own problems such as potential corrosion and continuous outflow in the well casing, seismic activity which could result in well damage and consequently groundwater contamination, and well life uncertainty. When a sewerage system is applied for the disposal of concentrate high in total dissolved solids (TDS), the treated waste stream becomes improper for repeated use. Consequently, the necessity in sustaining surface and groundwater resources in addition to maximizing water recovery and minimizing waste discharge may in many cases prevent concentrate disposal by the first three approaches and promote zero liquid discharge (ZLD) as the most attractive alternative. (El-Said et al., 2012).

In ZLD, the brine stream is treated to generate desalinated water and a dry salt waste stream. As a result, the process involves no liquid discharged as waste. Most of the currently available ZLD processes treat industrial wastewater or power plant cooling water by means of thermal crystallization, evaporation ponds, or a combination of these technologies. Thermal crystallization is energy-intensive with high capital and operating costs while evaporation ponds tend to be large and are influenced by weather (Brady et al., 2005; Marcuss, 2005; El-Said et al., 2012).

The advancement of ZLD science and associated reduction of ZLD costs is of great need as it will help reduce the water shortage dilemma faced by societies worldwide struggling to maintain the rapidly increasing water requirements with restricted fresh water resources. Provided the need for ZLD and the drawbacks of existing ZLD methods, it is crucial to develop other ZLD treatment systems that deliver more reasonable concentrate management (El-Said et al., 2011).

Currently, the most economical method for desalination is reverse osmosis (RO). This process was revealed in the 1970's but was impeded by technical and cost restraints at that time. However, reverse osmosis is now gaining increasing acceptance as the process of choice for desalination of both seawater and brackish groundwater.

Unfortunately, similar to all other desalination processes, a disadvantage of this technique is the large amount of reject brine that is produced. Another major drawback for membrane systems in the treatment of brackish groundwater is the occurrence of surface membrane fouling. Membrane fouling can form due to various factors including membrane properties, solute properties, and operational parameters. However, the major limitation of membrane technology is the ability of dissolved compounds to precipitate and form solid phases when their solubility is exceeded, leading to membrane fouling (Antony et al., 2011). In most cases, water recovery in inland desalination is controlled by the presence and concentrations of scale forming chemicals.

Sulfate is present with high concentrations in brackish groundwater in Qatar and it is known as one of the major causes of RO fouling in desalination (Silva et al.,2010). While various pretreatment processes are developed for the removal of sulfate, an efficient and cost effective process is yet to be developed for sulfate removal from reject brine in order to maximize water recovery and minimize the final volumes of brine that needs to be crystalized in ZLD systems.

A promising new technology developed at Texas A&M University at Qatar is aimed at developing an economical and environmental approach for inland desalination of brackish groundwater that produces zero liquid discharge (ZLD). The practical method involves integrating applications of two-stage reverse osmosis (RO) with brine treatment processes designed to eliminate the salts that cause RO membrane fouling and, thus, inhibit water recovery from brine in the second stage. A schematic diagram of the ZLD process is shown in Figure 1.1. A Two-stage RO system has been developed and the reject brine from the first stage is further concentrated in the second stage after intermediate treatment to remove scale forming chemicals.

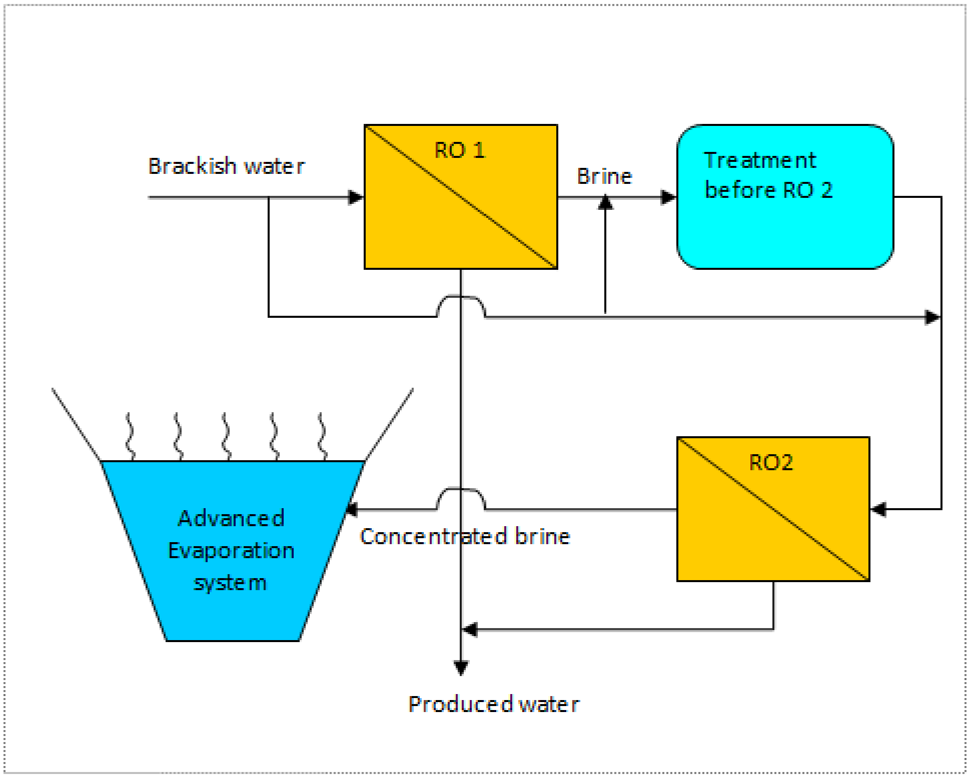

Figure 1.1 Schematic diagram of the ZLD overall process.

The technologies available for removing scale forming chemicals such as hardness, sulfate, and silica include lime softening, electrodialysis, and ion exchange. Lime softening is used for the removal of sulfate via the precipitation of gypsum ($CaSO_4 \bullet 2H_2O$). However, the amount of sulfate removed is restricted by the solubility of gypsum and, thus, makes it an inefficient sulfate removal process (INAP, 2003).

Ultra-high lime (UHL) softening is an alternative modification to the conventional lime softening. This treatment is capable of successfully removing the majority of scalants such as calcium (Ca^{2+}), magnesium (Mg^{2+}), carbonate (CO_3^{2-}), phosphate (PO_4^{3-}), and silica (SiO_2) irrespective of feed water quality. The UHL treatment concept is based on the addition of excess lime to maintain a high pH and high calcium concentration which promotes silica removal (Batchelor and McDevitt, 1984). This process, however, is not effective in removing sulfate.

Sulfate can be removed from brine before the second stage RO using nanofiltration (NF). However, NF process will result in another concentrate stream that includes very high sulfate concentration.

The ultra-high lime with aluminum (UHLA) treatment process, a modification of the UHL process, involves the addition of aluminum to enhance the removal of sulfate. The addition of aluminum as well as the high pH and calcium concentration enables the removal of sulfate by precipitation as calcium sulfoaluminate ($Ca_6Al_2(SO_4)_3(OH)_{12}$) (Abdel-Wahab & Batchelor, 2001, 2006a, 2006b, 2007). The solubility product of calcium sulfoaluminate precipitation was found to be very low. Sulfate removal through calcium sulfoaluminate precipitation revealed kinetics that was suitable enough for practical applications.

The UHLA process is valuable in the sense that it could be applied to various water treatment systems including the treatment of brine for ZLD (Abdelwahab & Batchelor, 2001, 2006a). This project will investigate sulfate removal from NF concentrate stream using a two-stage precipitation process so that this stream can be recycled back into the treatment process or bypassed to the produced water stream. The first stage of the two-stage precipitation processes involves the addition of calcium to precipitate sulfate as calcium sulfate and the second stage involves the addition of both lime and sodium aluminate to precipitate the remaining sulfate as calcium sulfoaluminate.

In order to achieve this goal, four specific objectives will be pursued and each will be associated with a specific task in the work plan. These objectives are:

1. Develop analytical and experimental procedures.
2. Develop information on the chemical equilibrium of the system and precipitate stoichiometry.
3. Study the effect of operating parameters on sulfate precipitation.
4. Develop a model for predicting chemical behavior in the treatment system.

In order to achieve the research objectives above, four tasks were carried out. The first task included demonstrating that all analytical methods performed met the goals for accuracy and precision and also included developing thorough experimental procedures. The second task involved the development of information on sulfate precipitation including identification of stoichiometric coefficients and solubility products of the solids in chemical equilibrium for the two precipitation stages in the process. The third task focused on evaluating effects of operating parameters such as process configuration, initial sulfate concentration, chloride concentration, precipitated solids recycling, and pH on sulfate removal.

In the subsequent sections, a review of literature pertinent to this study is provided, followed by the methodology followed in this research. The section that follows the methodology will provide analysis and discussions of the results obtained. Finally, conclusions and future recommendations are discussed.

2. LITERATURE REVIEW

2.1 Desalination of brackish groundwater and brine disposal

Famines, increase in population, and dry arid climates have all led to a critical growing demand for water in many parts of the world . Arid and semi-arid regions, specifically those in the Middle East and North Africa (MENA), have the world's smallest availability of water resources per capita as well as the largest rate of depletion of these resources (El-Fadel, & Alameddine, 2005). Shortage in water is also increasing in areas characterized by an arid climate with fewer than 100 mm rainfall per year (Sobhani et al., 2012). Recently, this issue has brought the focus on RO desalination of brackish water and wastewater to produce good quality water.

Desalination technology falls into two main categories: thermal processes and membrane processes. Thermal desalination (distillation) has been applied for centuries for the production of fresh water; however, large-scale municipal drinking water distillation plants initiated in the 1950s (Greenlee 2009; Roberts et al., 2010). While thermal desalination has continued to be a principal process of choice in the Middle East, the rapid development of membrane technologies in the 1960s has made them surpass thermal processes (Greenlee et al., 2009).

Underground aquifers make up a large source of freshwater supply. These aquifiers have a capacity of storing over 95% of the total existing fresh water. Overall, groundwater possesses a higher quality than surface waters. This quality is relatively consistent throughout the year which makes it simple to treat. One drawback of groundwater is that several have moderate to high amounts of dissolved solids such as calcium, magnesium, iron, sulfate, chloride, sodium, and silica, which are problematic and expensive to remove (El-said et al., 2011). In Qatar, groundwater is utilized mainly for irrigation. However, due to seawater interference, the quality of groundwater is declining. This has caused many farms to lose their business while some of their owners plan to restore them by means of inland desalination plants producing good quality water. The capability of reasonably treating brackish groundwater would relieve communities from the issues of increasing water scarcity (Abdel-wahab et al., 2011).

Brackish groundwater can be primitively brackish aquifers or groundwater that has developed brackish due to sea water intrusion or anthropogenic impacts. Brackish waters can consist of a broad range of TDS (1,000-10,000 mg/L) and are usually distinguished by low organic carbon matter and low particulate or colloidal contaminants (Greenlee et al., 2009). The chemical constituents of inland brackish waters set distinct constraints on the amount and cost of water recovery. Most inland brackish waters are enriched in calcium and reduced in sodium relative to seawater. Silica amounts are usually higher in inland brackish waters. As opposed to seawater, the principal anion in inland brackish waters tends to be sulfate instead of chloride (Brady et al., 2005).

2.2 Groundwater quality in Qatar

The State of Qatar has a very limited amount of freshwater resources. It has a total area of approximately 11493 km^2 and a current population of over 1,900,000, an increase of more than one million from 2004 (Amer, 2008; Soliman et al., 2013). With an arid climate and light winter rainfall averaging 100 mm per year, Qatar has very limited freshwater supply. It does not have surface water, and the only available and renewable customary supply of water is groundwater which is recharged by the light rainfall Qatar receives. Groundwater is mainly used in the agricultural sector. However, over-extraction of groundwater has caused deterioration in groundwater quality. There is also an imbalance between groundwater recharge and utilization. This shortage is due to several reasons. These reasons include the significant increase in population, restricted water resources, harsh climate conditions, and unproductive use of water in most of Qatari farms. Groundwater quality in Qatar is deteriorating due to seawater intrusion and deep saline water contamination. The salinity has been mostly found to increase in coastal areas (Alsharhan et al., 2001).

In Qatar, there are two major aquifers that are utilized to deliver fresh groundwater. The northern aquifer, Rus, extends beyond the central Umm er Rhaduma which is an essential aquifer throughout the Gulf area. These two aquifers maintain a salinity level which varies from 500 to 3,000 mg/l and increases near the sea succeeding 10, 000 mg/l toward the coasts (Frenken, 2009). The rate of groundwater depletion in Qatar for the year of 2005 was found to be approximately 221 million m^3 whereby most of it was used for agricultural purposes with 90% of it being highly saline brackish water. This necessitates desalination for the production of clean domestic and industrial water supply (Frenken, 2009).

Due to the potable water supply required, the proposed technology was applied to agriculture farms and rural communities in Qatar since they are the major consumers of groundwater resources facing the issue of highly saline groundwater. Figures regarding the groundwater quality in Qatar and surrounding areas were obtained through communications with several farms in the region in Um-Salal and Al-Kharara and are shown in Table 2.1 below (Abdel-wahab et al., 2011).

Table 2.1 Quality of Groundwater in Doha, Qatar (Abdel-wahab et al., 2011).

	Um-Salal Groundwater	**Al-Kharara Groundwater**
Ca^{2+}, ppm	245	254
Mg^{2+}, ppm	95.1	134
Na^{+}, ppm	576	795
SO_4^{2-}, ppm	695	691
Cl^{-}, ppm	965	1532
HCO_3^{-}, ppm	-	112
SiO_2, ppm	19.87	21.5
TDS, ppm	2833	3658
pH	7.65	7.41

As shown in Table 2.1 above, the groundwater quality in Um-Salal and Al-Kharara was found to be low when compared to the EPA standards of drinking water. Sulfate concentrations in the groundwater reached approximately 700 mg/l, an amount much higher than the EPA standards for sulfate of < 250 mg/l. In addition, the groundwater quality can be classified as very hard consisting of high calcium amounts at an average of 250 mg/l (Abdel-wahab et al., 2011).

2.3 Characteristics of reject brine

Brine can be defined as any water stream in a desalination system that possesses a higher salinity than the feed (El-Naas, 2011). It is the highly saline water in the final stage of the desalination process that is commonly disposed as wastewater. There are various types of chemicals used within the desalination process for pre-treatment and post-treatment. These chemicals consist of: sodium hypochlorite (NaOCl) which is applied for chlorination to disable bacterial growth in the desalination utility; ferric chloride ($FeCl_3$) or aluminum chloride ($ALCl_3$), which are used for the elimination of suspended substances from the water; anti-scale additives such as sodium hexametaphosphate ($NaPO_3$) which are used to inhibit the formation of scale on pipes and membranes; and acids such as sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) which are added to adjust the pH of the seawater (El-Naas, 2011). Due to the presence of these numerous chemicals at inconsistent concentrations, disposal of reject brine into water streams can affect their quality and can disrupt the aquatic life environment (El-Naas, 2011; Younos, 2005).

The characteristics of reject brine greatly rely on the nature of water fed to the system as well as the type of desalination process. In addition, they rely on the percent recovery along with the chemical additives applied (El-Naas, 2011). Standard analysis of reject brine from various desalination plants in the Arabian Gulf with various types of feed water are shown in Table 2.2 below.

Table 2.2 Characteristics of reject brine from some desalination plants in the Gulf (El-Naas, 2011).

Parameters	Abu-Fintas Doha/Qatar Seawater	Ajman BWRO[a]	Um Quwain BWRO	Qidfa I Fujairah Seawater	Qidfa II Fujairah Seawater
Temperature °C	40-44	30.6	32.4	32.2	29.1
pH	8.2	7.46	6.7	6.97	7.99
Ca, ppm	1,300-1,400	312	173	631	631
Mg, ppm	7,600-7,700	413	282	2,025	2,096
Na, ppm	NR[b]	2,759	2,315	17,294	18,293
HCO_3, ppm	3,900	561	570	159	149.5
SO_4, ppm	3,900	1,500	2,175	4,200	4,800
Cl, ppm	29,000	4,572	2,762	30,487	31,905
TDS, ppm	52,000	10,114	8,276	54,795	57,935
Total hardness, ppm	NR	NR	32	198	207
Free Cl_2, ppm	Trace	NR	0.01	NR	NR
SiO_2, ppm	NR	23.7	145	1.02	17.6

[a] Brackish water reverse osmosis

[b] Not reported

2.4 Current brine disposal options

The process of desalination involves the generation of two product streams: a clean water stream and a highly concentrated byproduct stream called brine. During desalination, the brine stream is usually disposed back into seawater in case of seawater desalination (Younus, 2005). However, this option is not present for inland desalination. Inappropriate disposal of byproduct brine from inland plants may lead to critical environmental issues. Byproduct brine can be disposed of in several ways: surface water disposal, sewage disposal, usage as irrigation water, evaporation ponds, and deep well injection (Marcuss, 2005; Danoun, 2007; Elsaid et al., 2012).

If practical, in brackish water plants, the desired disposal method is surface water disposal due to the higher costs of other alternatives. Nevertheless, surface water discharge is usually restricted to coastal RO plants since the significant quantity of pipelines required to transport concentrate from an inland desalination plant to the sea is uneconomical (Younus, 2005; Greenlee et al., 2009; Robert et al., 2010). Concentrate discharge into a combined sewer is an alternative option for brine discharge. A combined sewer transports the discharged brine to a local municipal wastewater treatment plant; some of the concentrate becomes sludge, while the rest remains dissolved and resides as part of the plant waste. High salinity can have negative effects on biological treatment processes and can violate discharge permit limits. Regional regulations, desalination plant size, and accessibility of a nearby wastewater treatment plant usually influence the practicability of this disposal alternative. Also, if the concentrate stream flow is very large or too saline, sewer disposal may not be viable (Greenlee et al., 2009).

The RO concentrate from brackish water desalination plants nearby recreational or agricultural areas can sometimes be used as irrigation water. Although this option maybe for the benefit of the desalination plant, making use of the discharge, using the discharge as irrigation may cause some issues. The use of brine for crop irrigation increases the amounts of salt to the soil and to the regional groundwater aquifers. Salt accumulation in the soil can influence crop growth, whereas the groundwater will gradually increase in salinity with time. Though a beneficial solution to concentrate disposal, the irrigation method ultimately creates the requirement for more desalination in regions that previously had fresh groundwater resources (Greenlee et al., 2009; Roberts et al., 2010).

Evaporation ponds are usually deemed to be the most common method for concentrate management but they require large space. Yet, currently, regulations have been applied to protect the regional soil and groundwater from leaching of salts or other potentially harmful chemicals coming from the evaporation ponds into the surrounding environment. Evaporation ponds have been mainly applied in the Middle East and Australia and there have been some use of them in the U.S. (Greenlee et al., 2009). Studies in the Middle East have indicated the demand for pond leakage monitoring and for improved evaporation policies. Evaporation ponds are usually limited to smaller size RO plants (less than 400 m^3 per day) (Marcuss, 2005; Greenlee et al., 2009).

Deep well injection is another option for concentrate disposal. This method involves the injection of the concentrate several hundred to thousand meters into the ground beneath the fresh water aquifers (Mickley, 2001; Marcuss, 2005). Problems that often arise from deep well injection include suitable site areas, concentrate treatment with chemicals, corrosion and leakage from the well, salt precipitation, and indefinite well lifetime. The occurrence of seismic activity could destruct the well, consequently resulting in groundwater contamination .Inappropriate disposal of brine in adjacent lands has also been found to instigate the development of eyesores (Khordagui, 1997). In addition, deep well injection has not been in practice long enough to see whether the salts will ultimately leach into fresh water aquifers overhead (Younus, 2005; Greenlee et al., 2009).

For a brackish water RO plant, each concentrate disposal method denotes a loss of water and additional plant expenses. Besides the individual drawbacks of every disposal method mentioned above, each one is uneconomical in terms of water recovery; all of the water in the concentrate is wasted throughout the disposal process. Furthermore, most of the established disposal options, excluding deep well injection, cannot be applied to large inland brackish water RO plants currently in design (Greenlee et al., 2009).

2.4.1 Environmental impacts of reject brine

Management of reject brine is one of the main environmental and financial challenges for water desalination. While there have been technological advances in the development of novel and more effective desalination processes, little progress has been made in the management of reject brine. Reject brine has often been regarded as a by-product waste that cannot be recycled and must be disposed of. Its destructive effects have been underrated despite the large amounts of chemicals and additives used in the pretreatment step of the feed (El-Naas, 2011).

Various studies have assessed the environmental effects of reject brine on soil and groundwater. Mohamed et al (2005) have reported that discharge of reject brine into unlined ponds or pits from inland desalination plants has major environmental impacts. Improper disposal of brine can potentially pollute groundwater reserves and can significantly impact subsurface soil properties if discharged by land usage (El-Naas, 2011, Mohamed et al., 2005). Studies reveal that groundwater contamination of the source reserve from brine leaching causes an increase in hardness of groundwater. Excessive salt concentrations in the reject effluent containing high amounts of sodium, chloride, and boron have the potential of reducing plant and soil productivity as well as increasing the possibility of soil salinization. It has also been reported that soil structure may become poor owing to the high salinity of the reject brine, when calcium ions are interchanged with sodium ions in the exchangeable ion complex. Consequently, this hinders the infiltration rate of water and soil aeration, thus effecting the growth of plants (Al-Faifi et al., 2010; Mohamed et al., 2005).

Other studies have emphasized the impact of reject brine conditions and concentrations on marine life. It has been reported by Sanchez-Lisazo (2008) that the elevated salinity accompanying the reject brine discharges has harmful effects on the shape and strength of sea grass (El-Naas, 2011; Sánchez-Lizaso et al., 2008).

2.5 Zero liquid discharge in treatment systems

The present alternatives for reject brine management are quite limited and have not reached a feasible solution to this environmental issue. Therefore, there is a crucial demand for the development of a novel system for the management of desalination reject brine that can be applied by coastal as well as inland desalination plants (El-Naas, 2011).

The ultimate accomplishment in brine disposal and RO recovery is to manage a process with zero liquid discharge (ZLD) and high recovery. Management of concentrate and discharge for inland desalination need to take into consideration necessary salinity and sustainability matters (Brady et al., 2005). Desalination with ZLD is applied in some areas where the brine discharge is treated to produce more desalinated water and desiccated salts. The expression 'high recovery' processing is usually used in the desalination industry to denote a second membrane stage operating on first stage brine. High recovery, however, is achievable through other technologies (Mickley, 2008). In ZLD, the majority of water is recovered as product by entirely separating the salt from water, leaving no liquid to be discharged. ZLD processing is, therefore, a subdivision of high recovery processing.

It is worth mentioning that very few high recovery facilities (as well as ZLD) exist at municipal sites due to high cost requirements. There are nearly 120 ZLD systems functioning in non-municipal sites. Primitive systems were thermal-built and used evaporators, such as brine concentrators, spray dryers or crystallizers. Current ZLD systems involve the use of integrated membrane/thermal systems. ZLD processing involves concluding stages of taking brine to solid disposal or discharge of brine in onsite evaporation ponds (Mickley, 2008).

2.5.1 Current ZLD systems

Conventional ZLD systems consist of thermal evaporators, crystallizers, brine concentrators, and spray dryers (Robert et al., 2010).

2.5.1.1 Thermal evaporators

Thermal evaporators consist of single-effect and multi-effect evaporators. Consuming steam as the source of energy, it requires approximately 1,000 BTU to evaporate one pound of water. In a single-effect evaporator, the feed is passed through a heat exchanger which evaporates the water leaving the remaining solution concentrated. The vapor is then passed through a condenser which condenses it and releases it to a water source. The concentrated solution can then be passed through additional effects. Multiple effect evaporators increase the feasibility but add to the capital cost in extra evaporator units (Mickley, 2001). A crystallizer can be added to further reduce the discharge stream to solids (Bostjancic & Ludlum, 1995).

2.5.1.2 Vapor compression evaporator systems (brine concentrators)

A vapor compression evaporator system is analogous to the single-effect evaporator except that the vapor emitted from the boiling suspension is compressed via a compressor. The pressure and saturation temperature of the vapor is increased by the compressor in order for it to be recycled back into the evaporator steam unit to be utilized as heating steam. The latent heat of vapor is used to evaporate additional water rather than being sent back to the cooling water (Mickley, 2001).

Although the majority of brine concentrators have been applied to generate cooling water, they are also used to concentrate reject brine from RO plants. About ninety percent of these concentrators are driven by a seeded slurry process that concentrates the reject to as much as 40 to 1 without the problem of scale forming in the evaporator. When integrated with crystallizers or spray dryers, brine concentrators can attain zero liquid discharge of RO concentrate regardless of the climatic surroundings (Mickley, 2001).

An electric-driven vapor compressor or process steam can be used to supply energy to the brine concentrator (Mickley, 2001). Drawbacks of brine concentrators include the utilization of high amounts of electrical energy, flow rate restrictions at the vapor compression range, and the limitation of operation of the concentrator to low brine temperature. Operation at low temperatures requires a larger heat transfer area for the heat exchanger, increasing the energy requirement and, thus, adding to the costs (Lubis & Holtzaple, 2012).

2.5.1.3 Crystallizers

Crystallizer systems have been implemented for several years to concentrate feed flow in industrial processes. Currently, as the requirement to concentrate waste waters has risen, this technology has been employed to brine reject from desalination systems, for example brine concentrate evaporators, in order to minimize wastewater to a portable solid (Juby et al., 2008). Crystallizer systems are mainly applicable in regions where the cost of construction of solar evaporation ponds is high, solar evaporation rates are poor, or deep well injection is expensive, geographically impractical, or not accepted.

Crystallizers used for wastewater disposal vary in volume from approximately 2 to 50 gpm. These systems consist of vertical cylindrical vessels that utilize heat from vapor compressors or an existing stream source (Juby et al., 2008; Mickley, 2001)

In the case of RO concentrate disposal, crystallizers are usually used alongside a brine concentrator evaporator to decrease brine concentrator blow-down to a transferable solid. Crystallizers can be utilized to concentrate RO reject immediately; however, their capital cost and energy consumption is far greater than that of a brine concentrator of similar volume (Mickley, 2001).

2.5.1.4 Spray dryers

Spray dryers offer another option to crystallizers for concentration of wastewater or brine to dry solids. Spray dryers are usually relatively more economical for smaller feed streams of less than 10 gpm (Mickley, 2001). They convert the concentrate into a dry powder of mixed solids for disposal (Tillberg, 2004).

Concentrate from the desalination plant is pumped to the drying chamber where it is dispersed into the chamber by means of a centrifugal brine atomizer. Air heated by gas, oil, or electric-powered heater heats up the drying chamber (Mickley, 2001). The concentrate is atomized inside the hot chamber where water is instantly vaporized leaving dry solids behind (Tillberg, 2004). The air is discharged to the atmosphere while the dry powder is collected in a hopper and transported to a storage facility for further relocation to a disposal site (Mickley, 2001).

Similar to crystallizers, spray dryers provide another option to evaporation ponds and deep well disposal for RO concentrate disposal. For such purposes, spray dryers are normally used with brine concentrator evaporators for feed water flows fit for 10 gpm. Spray dryers can be economical when employed directly to the concentrate stream if it ranges between 1 to 10 gpm, hence excluding the brine concentrator evaporator (Mickley, 2001).

2.5.1.5 Drawbacks of current ZLD options

A ZLD system integrated with a high recovery brackish water system can generate brine with as little as 10 mg/L TDS. ZLD systems can be applied in any geographical site and are usually well received by the local society owing to positive environmental impacts and nominal waste generation (Mickley, 2001; Greenlee et al., 2009). Even though these systems are technologically accessible, the capital cost of the system is generally higher than the cost of the desalination plant by itself (Robert et al., 2010). Furthermore, the energy necessary to acquire almost 100% recovery in a ZLD system is significantly high and usually financially infeasible, with the exclusion of small RO systems. A more economic procedure can be attained by integrating a brine concentrator system with an evaporation pond, however this concentrate disposal technique is usually a significantly expensive alternative (Greenlee et al., 2009; Mickley, 2004).Currently, attempts to decrease the cost of ZLD technology persist and bench- and pilot-scale experiments have revealed that ZLD systems can be operated to a range of water compositions and municipal requirements (Greenlee et al., 2009; Bond & Veerapaneni, 2007)

2.5.1.6 Two-stage RO process in ZLD systems

Provided the high cost associated with the existing ZLD thermal processes, it is rational to consider membrane processes for maximizing water recovery and minimizing brine volumes that is converted to dry solids by thermal processes in ZLD desalination. However, unlike treatment with thermal processes, membrane processes cannot be performed without pretreatment of the concentrate to eliminate components that would otherwise prevent membrane operation due to scale formation. High recovery in membrane processes is restricted by the ability of precipitation of scale-forming salts such as calcium sulfate, barium sulfate, and silica.

Water recovery in inland RO desalination systems in most cases is limited by the concentration of these salts in the reject brine. Therefore, before additional water can be recovered from the concentrate using second stage RO, it must be treated to minimize the precipitation potential of these salts. Consequently, the overall treatment stages of RO-based inland desalination with ZLD are as follows:

1. Membrane desalination of the feed water with a first stage RO unit
2. Intermediate brine treatment process to remove scale-forming chemicals
3. Membrane desalination of the treated brine via a secondary RO unit

It is improbable to recover all of the concentrate with a membrane process, and the unrecovered concentrate must be treated by a downstream technique such as a thermal process or solar evaporation. Thus, this option does not disregard the requirement for thermal crystallization units or evaporation ponds, but can significantly minimize the volume of brine required to be vaporized. The degree to which ZLD expenses are minimized by this technique will rely on the relative cost efficiency of Steps 2 and 3 above as opposed to transporting all of the concentrate from the first stage RO straight to thermal evaporation and crystallization.

2.6 Limitations of ZLD RO systems

The constituents of the brackish water are concentrated in the reject brine from the first stage RO by factors of 3-10 times that of the raw water, instigating membrane fouling (Ning &Troyer, 2007).

2.6.1 Scale formation and membrane fouling

Membrane fouling is a significant issue, causing a permeate flux drop, an increase in transmembrane pressure, and membrane damage. Membrane fouling can be perceived as the buildup of rejected particles on the membrane surface. RO membrane fouling consists of two constituents: external/surface and internal fouling. External fouling is affected by operating settings such as solution chemistry, temperature, quality of membrane and unit structure. Internal fouling consists of potential variations to the membrane form like membrane deterioration. External fouling is usually reversible and controllable by chemical cleaning, while internal fouling is normally irreversible. Surface fouling is a difficult incident and can be a blend of colloidal, organic, inorganic, and biofouling (Antony et al., 2011).

Inorganic fouling or scaling is denoted as precipitation or crystallization fouling and the word scale signifies adherent inorganic residues formed. Concerning high pressure membrane processes, the amount of dissolved salts are concentrated 4-10 times, relying on the operating recovery and rejection effectiveness. This leads to sparingly soluble inorganic ions such as calcium, magnesium, carbonate, sulfate, phosphate and silica to increase causing concentration polarization at the membrane surface. Concentration polarization develops when separation forms at the membrane. Consequently, the concentration of salts may surpass their limit of solubility and, therefore, precipitate on the membrane surface (Antony et al., 2011).

Scale formation has continuously been a major constraint in designing and operating RO processes as scaling leads to flux decline, membrane damage, loss of production and increase in operating costs. Several operating parameters settings such as pH, temperature, operating pressure, permeation rate, flow velocity, and existence of other salts or metal ions can effect scale development. Scale formation can be diminished by proper pretreatment procedures upstream of RO (Antony et al., 2011; Johnson, Culkin & Monroe, 2002).

Regular scale observed on RO membranes include calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4 \cdot xH_2O$), barium sulfate ($BaSO_4$), strontium sulfate ($SrSO_4$), silicates, calcium phosphate (Ca_3PO_4), and aluminosilicates (Antony et al., 2011).

2.6.2 Sulfate problem in ZLD desalination of brackish groundwater

Sulfate is found in high concentrations in brackish groundwater in Qatar. Sulfate deposits are one of the main causes of RO membrane fouling. Sulfate ions in the form of salts such as barium sulfate or calcium sulfate form scale on membranes during water recovery (Bond & Veerapaneni, 2007). Calcium sulfate is a mineral scale often precipitated from brines. This mineral scale can form crystals in solutions in three different forms which are: dehydrate (gypsum), hemihydrate and anhydrite. In RO systems, calcium sulfate is usually deposited in the form of gypsum while hemihydrate and anhydrite are frequently observed on heat exchangers and distillation units (Amjad, 1996). Although calcium sulfate scale is more soluble than other mineral scales such as $CaCO_3$, $BaSO_4$, and $SrSO_4$, once it has developed it is difficult to eradicate mechanically and is insoluble in mineral acids and other conventional solvents (CSM, 2006; Wang, 2005). The concentrate produced during reverse osmosis contains supersaturated concentrations of these soluble salts. As a result, before any additional water recovery from the concentrate is applied, the concentrate should be treated in an intermediate treatment step to eliminate the precipitation potential of sulfate (Bond & Veerapaneni, 2007).

2.7 Two-Stage RO with intermediate treatment for inland desalination with ZLD

A pilot plant demonstration unit was set up that consisted of a primary RO unit, an intermediate chemical treatment unit consisting of lime softening followed by NF, and a secondary RO unit. A schematic diagram of the ZLD system for inland desalination is shown in Figure 2.1 (Abdel-wahab et al., 2011).

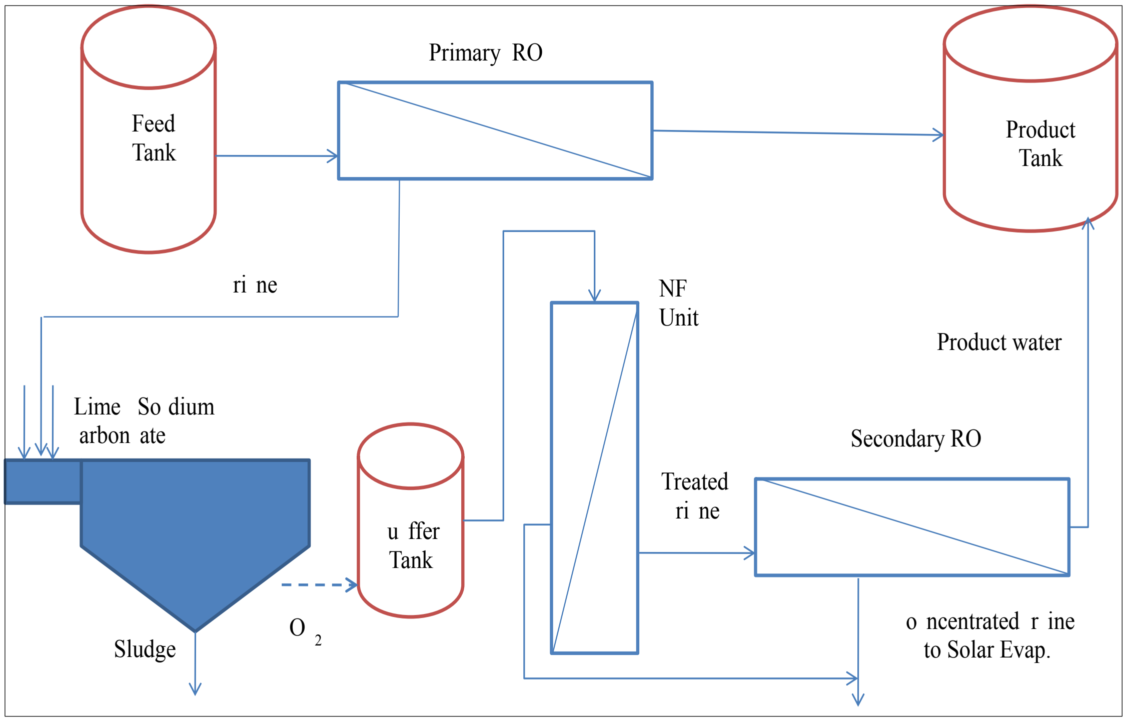

Figure 2.1 Schematic diagram of the ZLD process (Abdel-Wahab et al., 2011).

Groundwater was obtained from the Al-Kharara region in Qatar and was used as the target water to be treated. A detailed analysis of the Al-Kharara groundwater quality is presented in Table 2.3 below which show that the groundwater in Qatar is high in sulfate concentration.

Table 2.3 Groundwater quality in the region of Al-Karara.

	mM	**mg/L**
Ca^{2+}, ppm	6.35	254
Mg^{2+}, ppm	5.58	134
Na^{+}, ppm	34.6	795
SO_4^{2-}, ppm	7.19	691
Cl^{-}, ppm	43.1	1532
HCO_3^{-}, ppm	1.83	112
SiO_2, ppm	0.36	21.5
TDS, ppm	3658	
pH	7.41	

Groundwater from Al-Kharara was used as the feed for the primary RO unit in the system. The RO unit recovery was set to 75% by adjusting the upstream pressure to avoid oversaturation of sulfate-containing solids. The brine leaving the primary RO unit contains sulfate concentration of 2,726 mg/L. The brine stream leaving the primary RO unit was fed to a solid contact clarifier unit where chemical treatment with lime and soda ash/carbon dioxide was performed. The effluent from the lime softening process contains sulfate concentration of 2,661 mg/L.

After lime softening, the brine was recarbonated using carbon dioxide in order to lower the pH of the treated brine. Then the treated brine stream was fed into a NF unit in order to remove sulfate before a second stage RO unit. The reject from the NF unit contained sulfate concentration of 9,970 mg/L and it can be treated to remove sulfate and then recycled back to the lime softening unit or fed into the second stage RO unit.

The NF unit product stream was fed into a second stage RO unit to recover more water and minimize the amount of concentrate that needs to be evaporated. The concentrate leaving the second stage RO unit was minimized in the process to approximately 3-5% of the groundwater feed, a ratio much less than the brine produced from conventional RO inland desalination systems, which is approximately 20-30% of the original groundwater feed.

The purpose of this research work is to evaluate sulfate removal from the NF reject brine in order to recycle back in the process or feed it directly to the second stage RO unit after treatment.

2.8 Sulfate removal processes

There are different process alternatives that can be considered for the intermediate treatment step of brine to remove sulfate from. These processes involve the removal of sulfate through: 1) chemical treatment by precipitation, 2) membrane separation 3) ion-exchange and/or adsorption, and 4) biological treatment or a combination of these processes.

2.8.1 Chemical treatment by precipitation

Several methods have been applied for the removal of sulfate through precipitation which include: lime/limestone, barium, and ettringite precipitation.

2.8.1.1 Lime/limestone treatment

Lime or limestone is used for the removal of sulfate from Acid Rock Drainage (ARD) through the precipitation of gypsum (a SO4•2H2O). However, the extent to which sulfate concentrations are reduced is limited by the solubility of gypsum which ranges from 1500 mg/L to 2000 mg/L, subject to the composition and ionic strength of the solution. Therefore, lime or limestone precipitation can be used as a pretreatment step for waters with high sulfate concentrations (INAP, 2003). A more recent integrated lime/limestone process was established capable of partially removing sulfate in ARD. The process involves three stages as defined by Equations 2.1 to 2.4 below (Mpinga, 2009; INAP, 2003):

Stage 1: Limestone neutralization

$$CaCO_{3(s)} + H_2SO_4 + H_2O \rightarrow CaSO_4 \bullet H_2O_{(s)} + CO_{2(g)} \quad (2.1)$$

Stage 2: Gypsum crystallization

$$MgSO_4 + Ca(OH)_2 + 2H_2O \rightarrow Mg(OH)_{2(s)} + CaSO_4 \bullet H_2O_{(s)} \quad (2.2)$$

Stage 3: pH adjustment and $CaCO_3$ precipitation using CO_2

$$H_2O + CO_2 \rightarrow CO_3^{2-} + 2H^+ \quad (2.3)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3(s)} \quad (2.4)$$

Nevertheless, this process is capable of reducing sulfate concentrations in ARD to about 1200 mg/L which is still too high for surface discharge (Geldenhuys et al., 2003;INAP, 2003).

2.8.1.2 Barium salts treatment

Barium salts are used in Acid Rock Drainage (ARD) for the removal of sulfate through precipitation of barite ($BaSO_4$). Barite is very insoluble, making it a very good contender as a removal phase for the treatment of sulfate. The barium salts frequently used for sulfate treatment by precipitation include $Ba(OH)_2$, $BaCO_3$, and BaS. Sulfate is precipitated as $BaSO_4$ as displayed by Equations 2.5 to 2.7 below (INAP, 2003).

$$BaCO_{3(s)} + Ca^{2+} + SO_4^{2-} \rightarrow BaSO_{4(s)} + CaCO_3 \tag{2.5}$$

$$BaS_{(s)} + H_2SO_4 \rightarrow BaSO_{4(s)} + H_2S_{(g)} \tag{2.6}$$

$$Ba(OH)_{2(s)} + H_2SO_4 \rightarrow BaSO_{4(s)} + 2H_2O \tag{2.7}$$

Barium hydroxide and barium sulfide are both very efficient in removing dissolved sulfate throughout the whole pH range. The sulfate concentration was removed by more than 94%, leaving less than 200 mg/l in the product stream (Bosman et al., 2006). Barium carbonate is less efficient under very acidic conditions as well as neutral to highly alkaline conditions (INAP, 2003). While barium salts are very effective in removing sulfate, drawbacks include the high expense of barium salts and the environmental toxicity of barium (Bowell, 2004).

2.8.1.3 Ettringite precipitation

Sulfate can be removed from waters via ettringite precipitation. Smit & Pretorius (2000) studied sulfate removal from mine waters through a five stage process named SAVMIN. Lime is added in the first stage to raise the pH to approximately 12 in which the metals are precipitated and removed as hydroxides. The second stage involves the removal of gypsum by means of gypsum seed crystallisation. Aluminum hydroxide is then added to the supersaturated solution in the third stage to form insoluble ettringite . Subsequently, the waste stream is treated with CO_2 to reduce its pH and precipitate pure

$CaCO_3$. Finally, the ettringite slurry from the third stage is disintegrated to restore the aluminum hydroxide for recycle. This is achieved by subjecting the ettringite to a pH external to its area of stability. The subsequent aluminum hydroxide is recovered via filtration and recycled back to the third stage (INAP, 2003) (Bowell, 2004) (Smit & Pretorius, 2000). The SAVMIN process is effective in removing sulfate to less than 200 mg/L; with an initial sulfate concentration of 800 mg/L (Bowell, 2004).

The Cost Effective Sulfate Removal (CESR) process is another sulfate removal process similar to the SAVMIN process in that it removes sulfate through the precipitation of ettringite (INAP, 2003).

The first stage of the CESR process involves the addition of hydrated lime to the feed water to precipitate sulfate as gypsum. The pH is controlled at a level that inhibits the precipitation of metals and decreases the volume of metal concentrated sludge. The non-toxic gypsum sludge is isolated from the feed by filtration. An additional amount of lime is added in the second stage of the process which increases the pH of the feed to 10.5 causing the precipitation of dissolved metals as metal hydroxides. The higher pH also allows for further precipitation of gypsum. The metal –laden sludge is then removed by filtration. The third stage of the process completes the removal of sulfate via addition of lime to raise the pH to 11.5 as well as the addition of a patented reagent (obtained from the cement industry) to precipitate ettringite (INAP, 2003).

The main difference betweeen the SAVMIN and the CESR process is the patended reagent used in CESR instead of the aluminum hydroxide utilized in the SAVMIN process. The CESR process is able to reduce sulfate concentrations to less than 100 mg/L. However, contrary to SAVMIN, the CESR process does not recycle the ettringite (INAP, 2003; Brown, Barley & Wood, 2002).

2.8.2 Membrane separation

2.8.2.1 Nanofiltration

Nanofiltration (NF) is a pressure-driven membrane process with operating features between RO and ultrafiltration. The hypothetical pore size of the membrane is 1-10 nm. It has been shown that reduction of sulfate was successful using the NF system; however, a major drawback is the development of $CaSO_4$ scale on the membrane (Darbi et al., 2003). The application of NF as a stand-alone technology for the removal of sulfate in highly concentrated brine can bring about serious problems. These problems involve the accumulation of scale at the membrane surface and in the brine stream, and high osmotic pressures across the membrane. Such issues pose major technical, economic, and environmental challenges. Therefore, a pre-treatment stage before nanofiltration is required.

Bader (2008) established a process that involves the integration of NF with liquid-phase-precipitation (LPP) as an efficient pretreatment step. The process involves the separation of inorganic species from aqueous solutions by mixing the aqueous solution with an appropriate organic solvent at ambient temperature and atmospheric pressure to form certain precipitates. The selected organic solvent must be miscible with the aqueous solution and the targeted inorganic species must be sparingly soluble in the organic solvent. In addition, the selected organic solvent must have efficient physical properties such as low boiling point, high vapor pressure, high relative volatility, no azeotrope development with water .One preferable solvent for use in the LPP process is isopropylamine (Bader, 2008; 1994). The LPP application revealed that sulfate was removed with sparingly soluble cations such as calcium, barium, and strontium. After the critical scale-prone salts were removed by LPP, NF was applied to remove the remaining sulfate in the form of magnesium sulfate. However, another LPP post-treatment stage to precipitate the magnesium sulfate is required (Bader, 2008).

2.8.2.2 Electrodialysis

Electrodialysis (ED) employs direct electrical current through a stack of alternating cation and anion selective membranes. In the effluent, anions are attracted to the anode but are incapable of passing across the anion-impermeable membranes and are therefore concentrated (Bowell, 2000). Cations travel in the opposite direction and are also hindered by cation impermeable membranes. Therefore, the initial container containing the concentrated solution is reduced from salts and the treated water can be separated. Electrodialysis is significantly improved by the use of current reversal in which the anode and cathode can be regularly changed as well as the effluent and clean water channels. This process, however, is applicable only for low salinity water.

2.8.3 Ion exchange

Ion exchange (IX) is an inexpensive process that can successfully remove sulfate. The process involves the exchange of sulfate for hydroxyl or chloride ions on an anion exchange resin whereas the cations are exchanged for hydrogen on a cation exchange resin. As with RO, formation of $CaSO_4$ scale is common in conventional systems. To overcome this issue, a modified IX process was developed to treat Ca-SO_4 waters called GYPCIX) (Bowell, 2004)(INAP, 2003). The GYPCIX process consists of ion exchange resins which deploy inexpensive reagents such as lime and sulfuric acid for resin regeneration. The resins used have been constructed to target calcium and sulfate in order to reduce $CaSO_4$ amounts in effluent thus decreasing TDS and corrosion potential (Bowell, 2004)(INAP, 2003). The GYPCIX process, however, is applicable to low salinity feed waters (Schoeman & Steyn, 2001).

2.8.4 Adsorption

Adsorption is an established process that uses a solid adsorbent for the removal of dissolved sulfate from water. A common adsorbent is activated carbon which is formed from various carbonaceous sources that include coal, coke, wood, and coconut shell. The carbon source material is activated by treating it with an oxidizing gas to produce a highly porous structure with a high surface-to-volume ratio. Activated carbon exists in two different forms, granular activated carbon (GAC) and powdered activated carbon (PAC). The carbon adsorption mechanism is complex and, while the attraction is mainly physical, is a combination of physical, chemical, and electrostatic interactions amongst the activated carbon and sulfate (Salman,M.S.). Although the use of activated carbons to remove sulfate from waters is possible, it is not feasible due to their high cost and it is ineffective for waters with high sulfate concentrations (Namasivayam & Sangeetha, 2008).

Zirconium loaded adsorbents are commonly used in applications for sulfate removal, however, the rare metal zirconium is very costly. It has been reported by Cao et al. (2011) that a low cost and effective anion adsorbent for sulfate removal has been developed by converting rice straw into a strong basic anion exchanger. Batch experiments were performed and showed a high selectivity for sulfate ions. However, initial sulfate concentrations used were low, ranging from 50 to 500 mg/L (Cao et al., 2011).

2.8.5 Biological treatment

Biological sulfate removal depends on the microbial role of sulfate as an oxidant and its following reduction to hydrogen sulfides. Biological sulfate removal occurs in two steps. The first step includes sulfate reduction via sulfate reducing bacteria (SRB). The second step involves the removal of sulfide from the first step through oxidation to sulfur by means of bacteria or by precipitation through metal sulfides (i.e. bioreactors)(INAP, 2003).

Anaerobic bioreactors operate on bacterial reduction of sulfate and iron to achieve precipitation of metal sulfides. These reactions can only exist in an anaerobic reactor as the bacteria cannot withstand oxygen. The removal of sulfate was found to rely on an energy source, flow and time. The biological reduction of sulfate from industrial effluents has been reported to be an applicable process with producer gas being a dependable energy source (Bowell, 2004). This process however, is vulnerable to environmental conditions due to the relatively inflexible growth requirements of the microbes (Cao et al., 2011).

2.9 Ultra-high lime with aluminum (UHLA) process

Another process capable of removing sulfate is the ultra-high lime with aluminum (UHLA). It is an advanced alteration of ultra-high lime softening (UHL). UHL softening is a process developed as an alternative modification to the conventional lime softening. This treatment is capable of successfully removing the majority of scalants (Ca^{2+}, Mg^{2+}, CO_3^{2-}, PO_4^{3-}, and SiO_2), irrespective of feed water quality. The UHL treatment concept is based on the addition of excess lime to maintain a high pH and high calcium concentration. The process consists of a two-stage configuration, where excess lime is added to the first stage to establish a zone of high pH and high calcium concentration. In this stage, silica, magnesium, and phosphate are removed as solid precipitates. Inorganic carbon is then added in the second stage in the form of soda ash or carbon dioxide to eliminate calcium by precipitation as calcium carbonate (Batchelor et al., 1991).

The UHLA treatment process involves the addition of aluminum to enhance the removal of sulfate and chloride. Additions of aluminum as well as the high pH and calcium concentration in the first stage of the two-stage configuration enables the removal of sulfate by precipitation as calcium sulfoaluminate ($Ca_6Al_2(SO_4)_3(OH)_{12}$) (Abdel-Wahab & Batchelor, 2001, 2006a, 2006b, 2007). The solubility product of calcium sulfoaluminate precipitation was found to be very low. Sulfate removal by calcium sulfoaluminate precipitation revealed kinetics that was suitable enough for practical applications. This process was evaluated for sulfate removal from recycled cooling water. However, little information is available to support its application for removing sulfate from reject brine. Also, high sulfate concentration in the reject brine from the first stage RO in inland desalination with ZLD requires high doses of aluminum which results in high treatment costs.

A two-stage RO with intermediate brine treatment process was established at Texas A&M University at Qatar for inland desalination with zero liquid discharge. The intermediate brine treatment process involves lime softening for removing calcium and magnesium hardness and silica followed by NF for sulfate removal from brine before the second stage RO. Removal of hardness silica in the lime softening process reduces the fouling potential in the NF. The purpose of this research is to evaluate sulfate removal from the NF reject concentrate in order to recycle the reject back into the system. High sulfate concentration in the NF reject stream allows for removing the majority of it as calcium sulfate precipitate by adding a calcium source. Then the remaining sulfate is removed in a second step as calcium sulfoaluminate precipitate by adding lime and aluminum. This approach results in reducing the doses of aluminum required to remove sulfate.

Figure 2.2 depicts the two stage precipitation process in the yellow square. The first stage involves the precipitation of sulfate by the addition of calcium chloride while the second precipitates the remaining sulfate via the addition of lime and aluminum doses. After the sulfate is removed from the second stage, the treated stream is recycled back to the lime softening unit. Equations 2.8 and 2.9 below represent the two stage process.

Stage 1: $CaSO_4$ precipitation using $CaCl_2$

$Na_2SO_4 + CaCl_2 \leftrightarrow CaSO_{4(s)} + 2Na^+ + 2Cl^-$ (2.8)

Stage 2: Calcium sulfoaluminate precipitation

$6Ca^{2+} + 3SO_4^{2-} + 2Al^{3+} + 12OH^- \leftrightarrow Ca_6Al_2(SO_4)_3(OH)_{12(s)}$ (2.9)

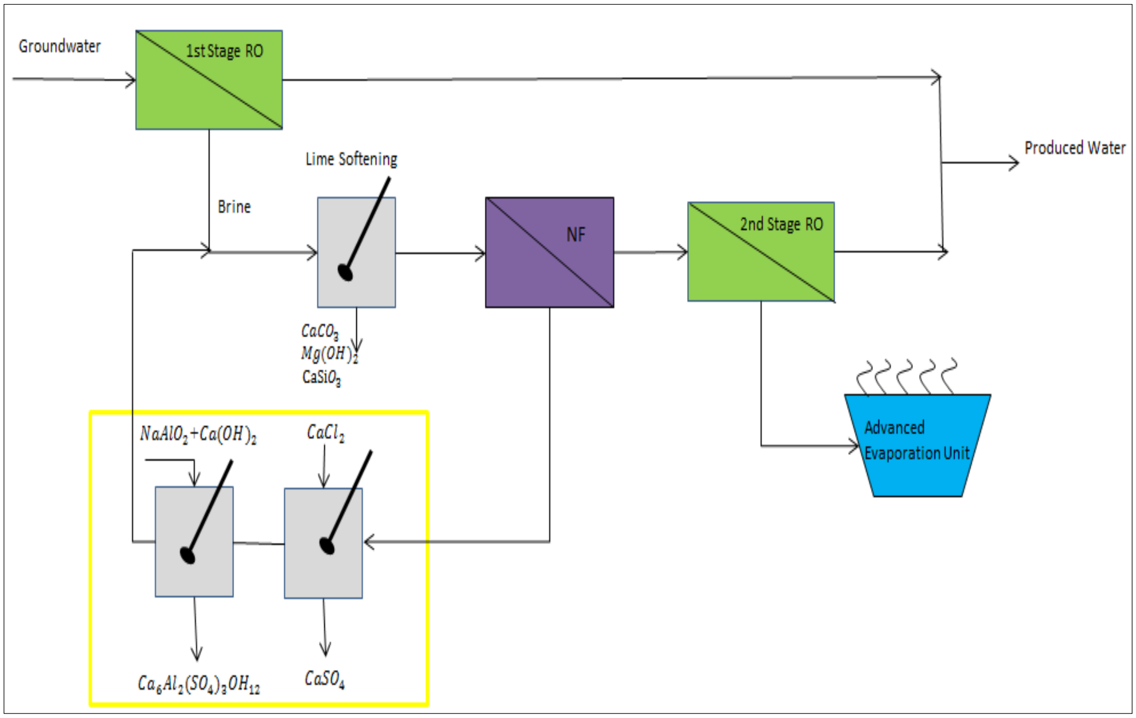

Figure 2.2 Schematic of the two-stage precipitation process of NF reject brine.

Effective removal of sulfate is essential to enable the recycle of water from the second stage of the UHLA process back to the lime softening unit. Important evidence to consider is the performance of sulfate in the chemistry of Portland cement. Under a high pH range, sulfate precipitates in cement systems in the form of calcium sulfoaluminate, commonly called ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$). Ettringite is formed when gypsum reacts with calcium and alumina present in cementitious media according to equation 2.10 below (Alvarez-Ayuso & Nugteren, 2005).

$$3Ca^{2+} + 2Al(OH)_4^- + 3CaSO_4 \bullet 2H_2O + 4OH^- + 20H_2O \leftrightarrow$$

$$3CaO \bullet Al_2O_3 \bullet 3CaSO_4 \bullet 32H_2O \qquad (2.10)$$

The stability of ettringite at equilibrium relies on adequate activities of calcium, aluminum and sulfate. The impediment of the activities of calcium or aluminum by another phase will result in the dissolution of ettringite (Chrysochoou & Dermatas, 2006).The stability of ettringite also depends on pH, temperature, and sulfate availability. It has been reported that the most favorable pH conditions for the formation and stability of ettringite are in the domain of 11 and 12.5 (McCarthy, Hassett & Bender, 1991; Chrysochoou & Dermatas, 2006). Increasing the pH above the stability range will cause the ettringite to convert to calcium hydroxide leaving behind a solution of sulfate and aluminate ions. Figure 2.3 below shows the effect of alkalinity on the stability of ettringite.

At temperatures below 50°C sulfate ettringite formation is usually favored over monosulfate. It was observed that ettringite was the only phase developed over a temperature range of 30-90°C at a sulfate-to-alumina ration of 3:1 (Clark & Brown, 2000; Chrysochoou & Dermatas, 2006). Damidot and Glasser reported from thermodynamic calculations that ettringite was stable at all times relative to the monophase at 25°C , whereas sulfate remained in the solution at low concentrations and hydrogarnet developed instead of ettringite as shown in Figure 2.3 (Damidot & Glasser, 1993; Chrysochoou & Dermatas, 2006).

In order for ettringite to develop over the monophase, the aluminum-to-sulfate ratio has to be lower than 1 (Chrysochoou & Dermatas, 2006). The availability of more aluminum than sulfate will result in sulfate developing into monosulfate while the excess aluminum exists as hydroxyl-substituted AFm phase (hydroxy-AFm). If there is a slight excess of sulfate, a mixture of monosulfate and ettringite will develop in the cement system. As the available sulfate level increases, more ettringite and less monosulfate will develop; higher amounts of sulfate will result in a mixture of ettringite and gypsum (Winter, 2009). According to Brown & Clark (2000), ettringite formation is favorable at high sulfate concentrations while at low sulfate concentrations, the monophase is preferred.

The two stage precipitation process implemented in this study will involve the precipitation of sulfate via calcium sulfate and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$). The first stage involves the removal of sulfate by the precipitation of calcium sulfate which is controlled by the solubility limit of calcium sulfate. The second stage implements the UHLA process whereby additional sulfate is removed by the precipitation of ettringite. The high amount of calcium available in the second stage as well as the high pH from the presence of lime and sodium aluminate allows the removal of sulfate via the precipitation of ettringite.

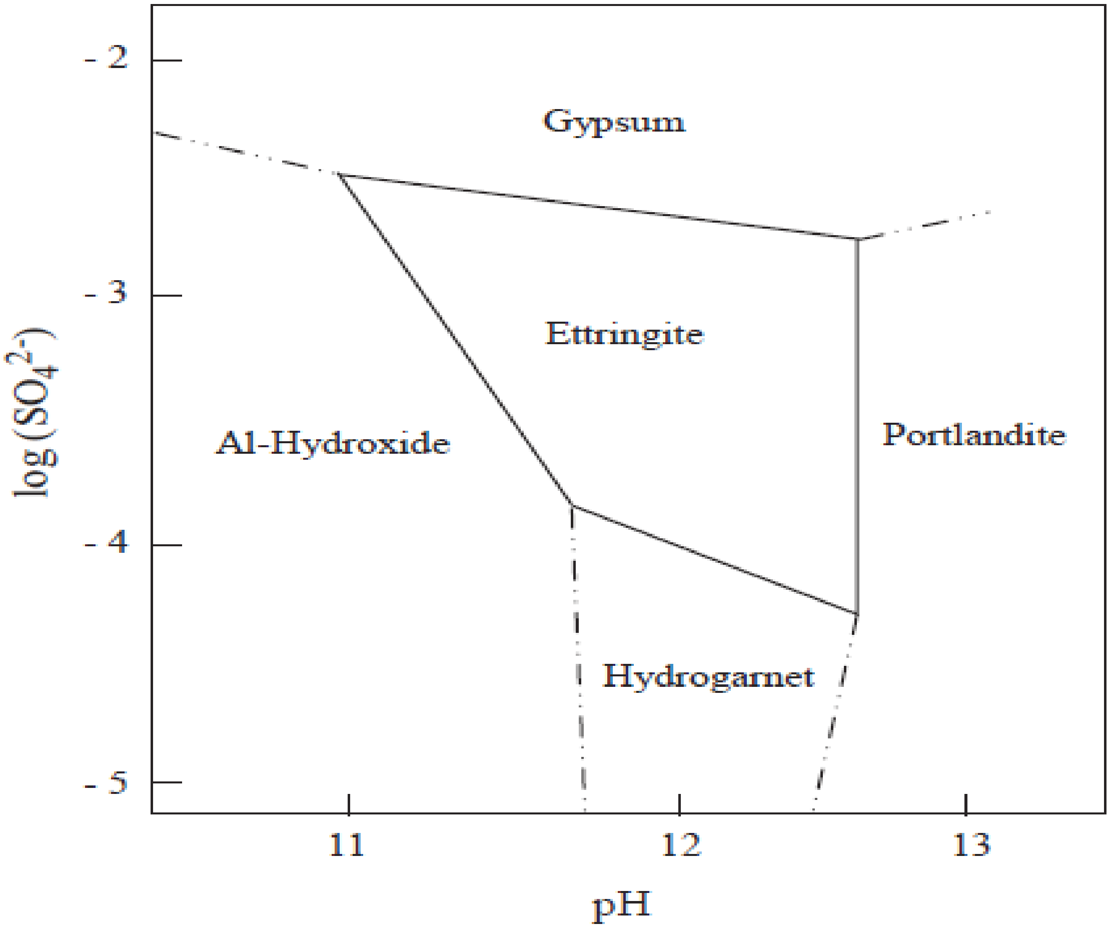

Figure 2.3 Stability of ettringite in alkaline conditions (Alvarez-Ayuso & Nugteren, 2005).

3. METHODOLOGY

3.1 Experimental plan

An experimental plan was constructed to meet the four objectives of this research. First, detailed analytical and experimental procedures were developed to study the kinetics of calcium sulfate precipitation and to obtain the reaction time required to achieve equilibrium. In addition, experimental procedures were developed to carry out equilibrium experiments.

Second, equilibrium and stoichiometry of sulfate precipitation and effects of chemical doses were investigated for two consecutive precipitation stages. The first stage involved the precipitation of sulfate by the addition of calcium chloride while the second stage involved the precipitation of the remaining sulfate by the UHLA process (lime and sodium aluminate).

Third, the effect of precipitated solids recycling on sulfate removal from brine was investigated. The solids obtained from the Stage 1 of the process were recycled back into Stage 1 and the solids from Stage 2 were recycled back into Stage 2.

Finally, the effects of important operating parameters on the efficiency of sulfate precipitation were investigated. Experiments were conducted to evaluate the effects of initial sulfate concentration, initial chloride concentration, and pH on sulfate removal.

3.2 Chemicals and reagents

The chemicals used in this research project were: sodium sulfate anhydrous (Fisher), calcium chloride (96%, Sigma Aldrich, anhydrous), calcium hydroxide (ACS), sodium aluminate (EMD), sodium hydroxide (VWR), sodium chloride (Fisher Scientific) and hydrochloric acid (37%, VWR).

All solutions were prepared with deionized water (DI water). Laboratory glassware and equipment were cleaned following standard procedure as follows: 1) soak for 24 hours in 2% laboratory detergent, 2) soak for 24 hours in water, 3) wash and rinse with DI water followed by drying. Stock solutions pertaining to sodium sulfate and calcium chloride were prepared daily by dissolving the required amount of chemical reagent in DI water. Primary standard solutions (sulfate, calcium, aluminum and chloride) used in the experiments were reagent grade chemicals (IV, Fisher). Secondary standard solutions used for development of calibration curves were prepared daily from freshly made stock solutions by dilution with DI water.

3.3 Experimental procedures

Kinetic and equilibrium experiments were performed in 250 mL high-density polyethylene (HDPE) sealed plastic bottles to act as completely mixed batch reactors. These experiments were performed in duplicates for consistency. Also, the reactors were tightly sealed after the addition of reagents and were rapidly mixed at room temperature (22-24°C).

Kinetic experiments were carried out in order to obtain the time required to reach equilibrium for sulfate removal. Initially, the experiments were conducted at an initial sulfate concentration of 96.8 mM which refers to the average concentration of brine rejected from the nano-filtration membrane. To each sample, $CaCl_2$ solution was added at a constant stoichiometric ratio of 2 to ensure the presence of enough reagent for the reaction to proceed to completion. Samples were taken at 0.5, 1, 2, 4 and 8 hours using a plastic syringe and filtered using 0.45 µm Whatman® membrane filters (VWR). The filtered samples were then acidified to a pH less than 2 and refrigerated until time of analysis.

Experiments that were conducted to investigate the effects of lime dose and aluminum dose in the second stage involved a similar experimental procedure as described above, except lime and sodium aluminate were added after filtration of 200 mL of the initial solution followed by rapid mixing until equilibrium was reached. The samples were also filtered using 0.45 µm Whatman® membrane filters (VWR), acidified to a pH less than 2 and refrigerated until time of analysis.

3.3.1 Kinetics of sulfate removal

An experiment was performed to study the kinetics of sulfate removal and to determine the time required to reach equilibrium. The original plan was to use lime as a calcium source in the first stage. However, experiments that were performed with the addition of lime to a solution of sulfate to examine the effect of lime on sulfate removal did not result in significant sulfate removal. This was because large doses of lime were required and, thus, the lime stayed insoluble in the solution. Therefore, calcium chloride was used to precipitate sulfate as calcium sulfate solids.

This stage involved conducting experiments through the addition of a solution of $CaCl_2$ to a solution of Na_2SO_4 giving a final solution with a calcium to sulfate ratio of 2:1 to ensure enough calcium is available to precipitate sulfate and that the extent of removal is not controlled by chemical doses. The experiments were performed in sealed 250 mL plastic bottles. The reactors were shaken at 200 rpm at room temperature. Filtered samples were taken and analyzed for sulfate and calcium at reaction times of 0.5, 1, 2, 4, and 8 hours.

The kinetic experiment for the second stage evaluated the effect of reaction time on sulfate removal with UHLA through the addition of lime and aluminum doses. Ratios of lime and aluminum to the initial sulfate concentration in this experiment were 100% and 67% respectively. This was chosen according to the stoichiometric ratio of lime and aluminum to sulfate in calcium sulfoaluminate, $Ca_6Al_2(SO_4)_3(OH)_{12}$. The reactors were under similar conditions as was for the first stage. Filtered samples were taken and analyzed after reaction times of 0.5, 1, 2, 4 , and 8 hours.

3.3.2 Equilibrium experiments for the effects of lime and aluminum doses on sulfate precipitation

In order to simulate the real two-stage treatment system, the source brine in the second stage was the filtrate from the first stage which involved shaking solutions with initial concentrations of 96.8 mM Na_2SO_4 and 96.8 mM $CaCl_2$ at a rate of 200 rpm at room temperature for two hours.

The second stage involved sixteen equilibrium experiments to evaluate the effects of different lime doses (0%, 100%, 200% , and 300% of initial sulfate concentration) and sodium aluminate doses (67%, 100%, 150%, and 200% of the initial sulfate concentration) on sulfate removal.. The initial sulfate concentration was approximately 23 mM and initial calcium concentration was about 24 mM in these experiments which are the final concentrations remaining after the first stage treatment. The second stage of the treatment process involved adding anhydrous lime and anhydrous sodium aluminate to 200 mL of effluent from the first stage. Table 3.1 displays the experimental conditions evaluating the effect of lime doses and aluminum doses on the removal of sulfate.

Table 3.1 Experimental conditions evaluating the effect of lime and aluminum doses on sulfate removal.

SO_4 mM (initial concentration from Stage 2)	$Ca(OH)_2$ (% of initial [SO_4] from Stage 2)	$NaAlO_2$ mM (% of initial [SO_4] from Stage 2)	No. of experiments
23	0%, 100%, 200%, 300%	67%, 100%, 150%, 200%	16

After the addition of chemical reagents, the reactors were quickly sealed in order to prevent CO_2 intrusion from the atmosphere. After the completion of the experiments, the reactors were removed from the shaker where the pH of the solutions was measured before filtration. 20 mL samples were taken using plastic syringes and instantly filtered using 0.45 μm membrane filters. The samples were then immediately acidified and stored in the refrigerator until analysis. Analysis was performed for total sulfate, total calcium, total chloride and total aluminum.

3.3.3 Effect of pH on sulfate removal

The effect of pH on the removal of sulfate in Stage 1 and 2 of the treatment process was evaluated. The influence of pH on the removal of sulfate in Stage 1 was studied at a pH range of 7 - 12. The pH was adjusted to the desired value using NaOH solution.

The influence of pH on the removal of sulfate in Stage 2 was analyzed at a pH range of 10 - 12. The pH of this stage was adjusted by adding HCl solution in the specified amounts to obtain the desired solution pH.

3.3.4 Effect of initial sulfate concentration on sulfate removal in Stage 1

Kinetic experiments were conducted to determine the effect of initial sulfate concentration on the removal of sulfate. Duplicate experiments were carried out at initial sulfate concentrations of 96.8 mM and 24.2 mM with the addition of calcium at a stoichiometric ratio of 1:1. Solutions were shaken at a rate of 200 rpm at room temperature. Samples were taken at 2, 4, and 6 hours, filtered, and analyzed for pH sulfate and calcium concentrations.

3.3.5 Effect of initial chloride concentration on sulfate removal in Stage 2

Experiments were carried out to determine the influence of initial chloride concentration on the removal of sulfate in Stage 2. Stage 1 was performed as explained previously at a Ca:SO_4 stoichiometry of 1:1. After filtration of 200 mL of the solution from Stage 1, lime and aluminum doses were added at constant ratios of 100% and 67%

to the initial sulfate concentration in Stage 2. Those ratios were selected based on results of previous experiments that examined the effect of lime and aluminum doses on sulfate removal and showed to be the most efficient and cost-effective in removing sulfate. Chloride was added in the form of sodium chloride dry salts at different doses of 300 mM and 800 mM. Solutions were shaken until equilibrium was reached, filtered , and analyzed for total concentrations of sulfate, calcium, chloride and aluminum.

3.3.6 Effect of recycle of dry solids into Stage 1 and Stage 2

The effect of recycling dry salts from Stage 1 back into the same stage was carried out. Solutions consisting of 96.8 mM Na_2SO_4 and 96.8 mM $CaCl_2$ were shaken at a rate of 200 rpm at room temperature until the equilibrium time was met. The slurry formed was placed in a centrifuge to separate the water from the salts. The salts were then dried in a vacuum drier for three days in an anaerobic. After the solids were completely dried, they were added to a solution consisting of 96.8 mM Na_2SO_4 and 96.8 mM $CaCl_2$ and shaken at a rate of 200 rpm at room temperature until the equilibrium time was met.

The effect of recycling dry salts from Stage 2 into Stage 2 was performed. The precipitated solids in Stage 2 were collected by centrifugation then dried completely at room temperature in a vacuum drier in a CO_2-free atmosphere. The dried solids were then added to the solution in Stage 2 experiments following the same procedure described above.

3.4 Analytical procedures

Analytical procedures followed standard methods acquired from the Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, WEF, 1995) as well as the equipment manual.

3.4.1 Calcium , sulfate, and chloride analysis

Ca^{2+}, SO_4^{2-}, and Cl^- were analyzed using a computerized Dionex ICS-5000 Reagent Free system with a self- regenerating suppressor, a dual pump, an eluent generator, a conductivity detector, IonPac®AS23 columns (2 x250mm), and an autosampler. The eluent used for measuring cations was methane sulfonic acid (MSA) while the eluent used for measuring anions was carbonate/bicarbonate solution. The eluent solutions were pumped through an isocratic pump at a flowrate of 0.25 mL/min. Samples from the autosampler were injected automatically into the column via a 10 µL sample loop. The analyte concentrations were calculated internally by comparing the peak area to the standard calibration curve using a standard method. Standards were prepared for calibration at concentrations of 5, 10, 20, 50 mg/L through dilution from 1000 mg/L standard solutions (Fisher, Sigma Aldrich). Subsequently, duplicate samples were analyzed in which the results matched well within 5% accuracy.

3.4.2 Aluminum

Aluminum was analyzed using a computerized ICP-OES that utilized inductively coupled plasma emitting electromagnetic radiation at an analytical wavelength of 396.152 nm with a plasma radial view. The method detection limit was 0.0049 mg/L and the linear range was from 0.0 to 100 mg/L. Aluminum concentration was measured by comparing the obtained intensities to a standard calibration curve. Standards of 10, 20, 50, and 100 mg/L were prepared for calibration by dilution of a 1000 ppm VWR aluminum standard solution. The standards and samples were analyzed in duplicates in which the results matched well within 5% accuracy.

3.4.3 pH

The pH was measured using a pH meter (SympHony SP70P) with a SympHony electrode standardized with pH 4, pH 7, pH 10, and pH 12 (VWR) buffers.

3.4.4 Classification of the precipitated solids in Stage 2

XRD analysis was performed on the dry precipitated solids from Stage 2 to identify the solid phases formed during the treatment process. The solids were allowed to precipitate following the same procedure for the equilibrium experiments using lime and aluminum doses at 100% and 67% respectively. Centrifugation of the final solution was applied to collect the solids. The solids were then dried completely at room temperature in a vacuum drier in a CO_2-free environment. The solids were scanned between 0^o and 80 ^{o} 2θ at a scan speed of 1^o/min via Rigaku Ultima V automated diffractometer using Cu radiation.

3.5 Development of an equilibrium model

A model depicting the chemical behavior occurring in the UHLA process was developed which can be used to predict the final sulfate concentration in the treated brine utilizing data on the chemical doses and initial sulfate and calcium concentrations. The solubility of the solids in the system was assumed to be controlled by precipitation. The model was carried out using the geochemical modeling software, PHREEQC

(Parkhurst and Appelo , 1999). Initial concentrations and chemical doses for every set of experiments were defined in the PHREEQC input file. Other aqueous species and solids utilized by the model were defined in the database file. The PHREEQC input files for the model are available in Appendix A.

4. RESULTS AND DISCUSSIONS

4.1. Kinetics of sulfate removal in Stage 1

A kinetic experiment was conducted to evaluate the kinetics of sulfate removal in Stage 1 by precipitation as calcium sulfate using lime as the calcium source. However results of this experiment showed that sulfate precipitation using lime was ineffective as large doses were required and, thus, some lime remained insoluble in the solution (Table 4.1).

Table 4.1 Efficiency of sulfate removal using lime.

Initial conditions			Final Concentrations			Removal Efficiency
[SO4] mM	Lime dose (mM)	pH	[SO4] mM	[Ca] mM	pH	%
99.27	123.5	6.81	68.90	Negligible	12.64	30.61

Therefore, calcium chloride was used instead of lime as a calcium source for the kinetics experiments. A solution of calcium chloride was added to a solution of sodium sulfate at calcium to sulfate ratio of 2:1 to ensure enough calcium is available to precipitate sulfate. This stoichiometric ratio was chosen since, at a Ca: SO_4 ratio of 2:1, the system will favor the formation of calcium sulfate following Le Chatelier’s principle and Equation 4.1 below.

$$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_{4\,(s)} \qquad (4.1)$$

The remaining calcium in the solution will be used as calcium source in Stage 2.

Initial sulfate concentration was set at 96.8 mM in order to simulate sulfate concentration in the NF reject brine for Qatari groundwater (Abdel-Wahab et al., 2011). Results of the kinetic experiment when calcium chloride was used are shown in Figure 4.1 and reveal that sulfate was rapidly removed, being almost complete within 2 hours. Calcium was also found to be removed in the process within a reaction time of 2 hours as can be seen in Figure 4.2. Although the results revealed a significant amount of sulfate removal, the remaining amounts were still high. This is because since the solution is oversaturated with sulfate and calcium, rapid precipitation of calcium sulfate occurs initially until it reaches the solubility of calcium sulfate at approximately 13.6 mM corresponding to this ratio of calcium to sulfate. Once the solubility limit is reached, sulfate precipitation enters a metastable region where no evident precipitation occurs for a very long period (Damons and Petersen, 2002). Therefore, it can be said that sulfate removal is controlled by the solubility of calcium sulfate in Stage 1. This designates a requirement for the addition of a second stage which induces the implementation of the UHLA process.

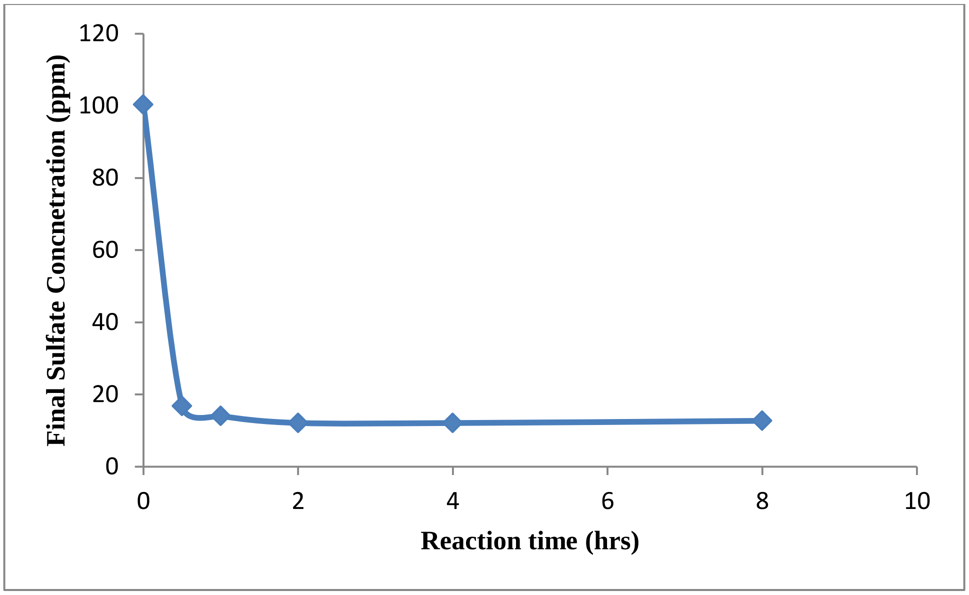

Figure 4.1 Kinetics of sulfate removal in Stage 1.

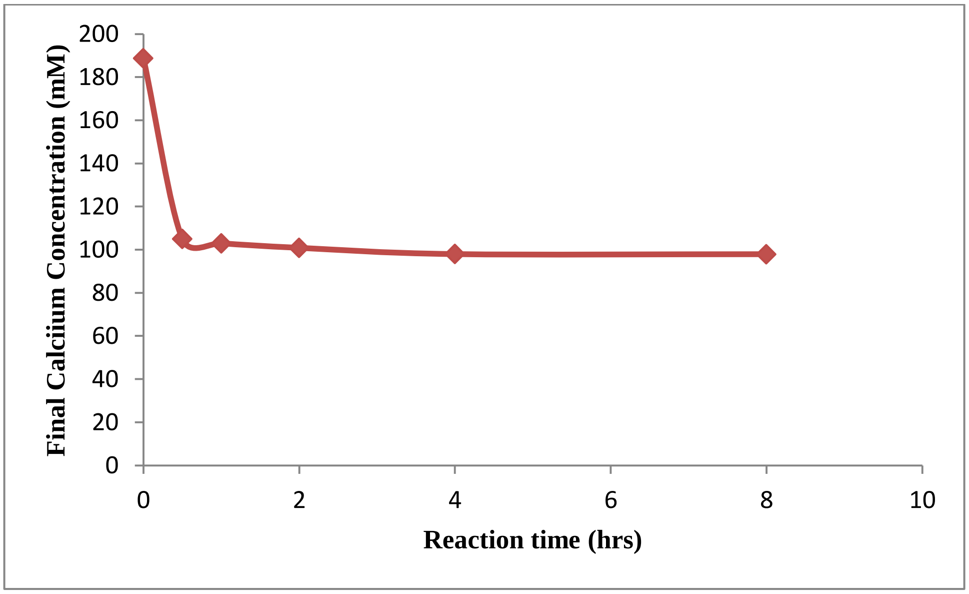

Figure 4.2 Kinetics of calcium removal in Stage 1.

4.2 Effect of calcium dose on sulfate removal in Stage 1

The effect of calcium dose on the removal of sulfate was studied at calcium to sulfate ratios of 0.5, 1, 1.5, and 2 with an initial sulfate concentration of 96.8 mM. Maximum sulfate removal was observed to be at a stoichiometric ratio of 2 as shown in Figure 4.3 below. This is due to the same reason mentioned previously. According to Le hatelier's principle the forward reaction is favored at high calcium to sulfate ratios, precipitating more calcium sulfate and, therefore, inducing more sulfate removal.

A model was developed using PHREEQC to predict the final concentrations of sulfate and calcium based on the solubility of calcium sulfate and using initial sulfate and calcium concentrations as input data to PHREEQC. Measured results shown in Figure 4.3 agreed with the predicted results from the model revealing that calcium and sulfate concentrations were mainly controlled by the precipitation of calcium sulfate.

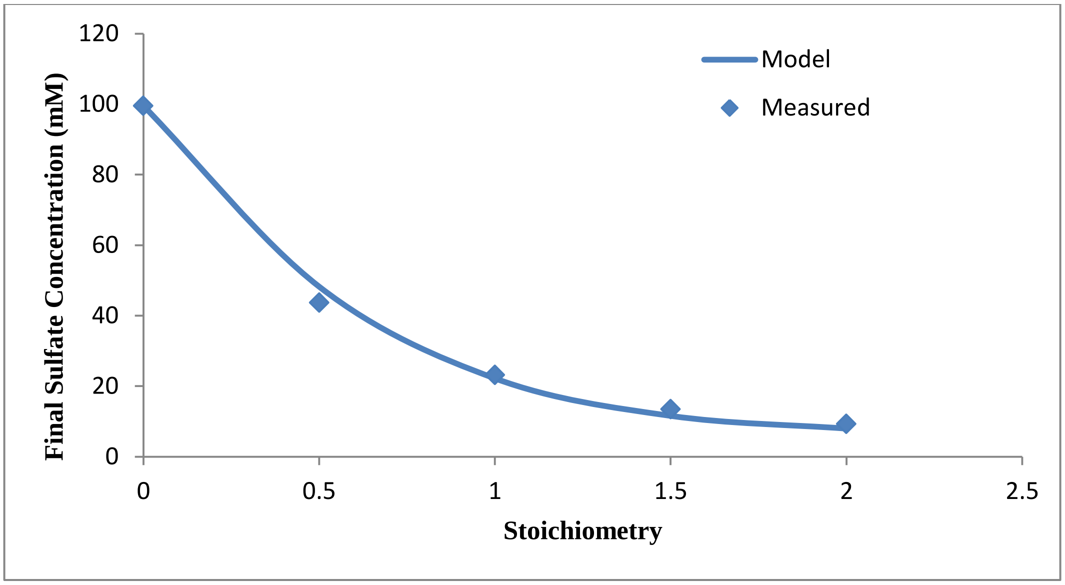

Figure 4.3 Effect of calcium doses on sulfate removal in Stage 1.

4.3 Effect of pH on sulfate removal in Stage 1

The effect of pH on the removal of sulfate in Stage 1 was investigated. A domain of pH values (7, 9, 10, 11 and 12) was studied with an initial sulfate concentration of 96.8 mM to investigate the effect of pH on sulfate removal. The stoichiometric amount of calcium chloride added to initial sulfate concentration was kept constant at 150%. The pH was adjusted by adding a solution of NaOH. Figures 4.4 and 4.5 show that pH has negligible effect on the removal of sulfate and precipitation of calcium sulfate. This hypothesis agrees with researchers that stated at a high pH range, the hydroxyls available in the solution do not influence the precipitation of calcium sulfate (Benatti et al., 2009).

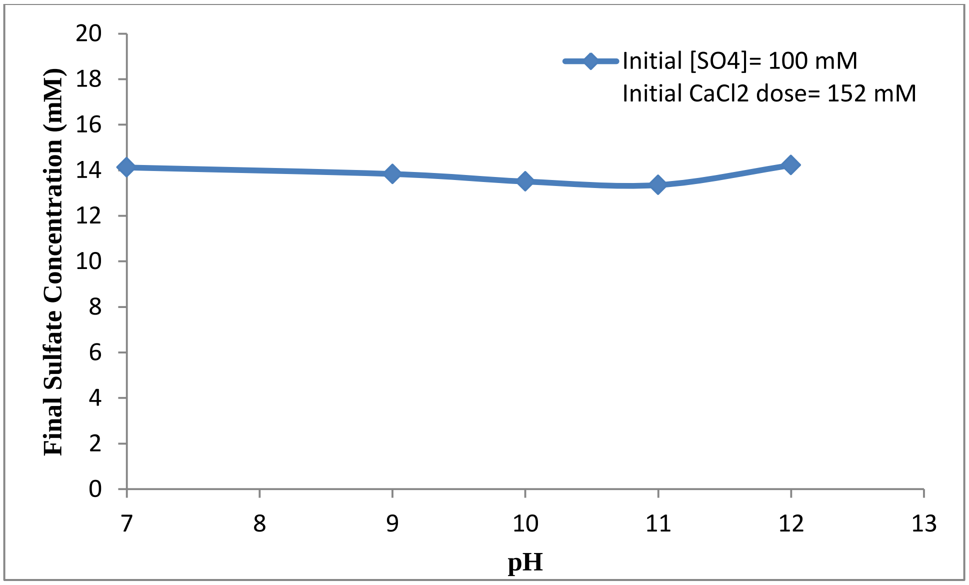

Figure 4.4 Effect of pH on sulfate removal in Stage 1.

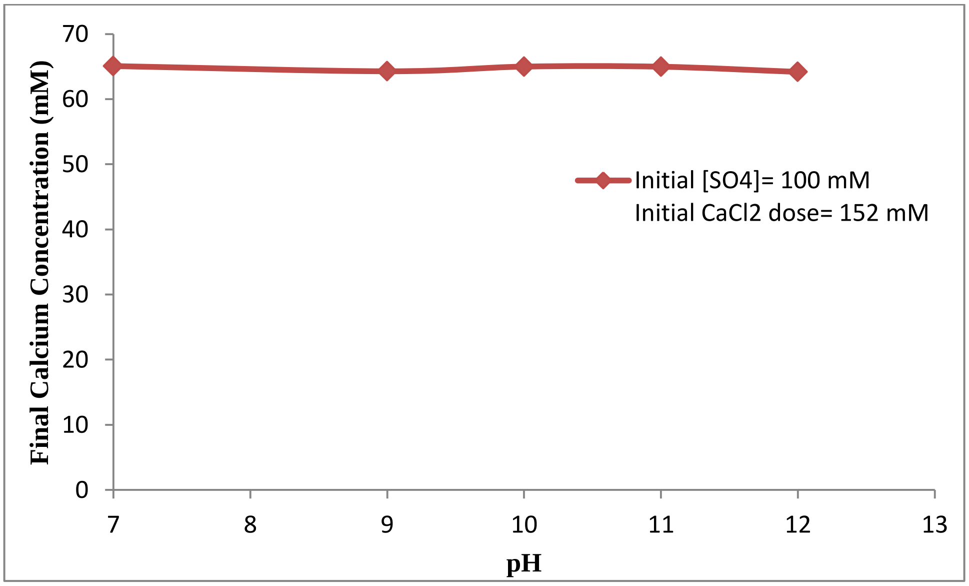

Figure 4.5 Effect of pH on calcium removal in Stage 1.

4.4 Effect of initial sulfate concentration on sulfate removal in Stage 1

Initial concentrations of sulfate (24.2 and 96.8 mM) were applied to study the influence of initial sulfate concentration on sulfate removal in Stage 1. Calcium was added as calcium chloride at a stoichiometric ratio of 100% of the initial sulfate concentration. Sulfate removal at an initial sulfate concentration of 24.2 mM was found to be low in Stage 1 as shown in Table 4.2. This is because the initial sulfate concentration was close to the solubility limit of calcium sulfate. Therefore, sulfate removal at this amount was limited by its solubility. Also, it was observed that the final sulfate concentration in this stage was still high for both initial sulfate amounts, signifying the need of a second stage to further remove sulfate.

Table 4.2 Effect of initial sulfate concentration on the removal efficiency of sulfate in Stage 1.

Initial [SO_4] in Stage 1 (mM)	24.2	96.8
[SO_4] Removal efficiency %	15.65 ± 0.1	75.3 ± 0.01
[Ca] Removal efficiency %	19.16 ± 0.01	76.0 ± 0.00

4.5 Kinetics of solids recycle in Stage 1

Experiments were carried out in Stage 1 to investigate the effect of recycling precipitated solids on the kinetics and efficiency of sulfate removal. Experiments were conducted at an initial sulfate concentration of 48.4 mM. Calcium was added at a stoichiometric ratio of 100% of the initial sulfate concentration. Samples were taken at different times starting at a reaction time of 2 hrs.

Results in Figure 4.6 show that the recycle of calcium sulfate salts back into the system accelerated the rate of sulfate removal. Sulfate concentrations were reduced down to the solubility limit of calcium sulfate within a reaction time of 2 hrs. Calcium was also found to be removed within the same reaction time down to the solubility limit of calcium sulfate (Figure 4.7). This indicates that the addition of solids enhanced the nucleation and seeding of the precipitated solids.

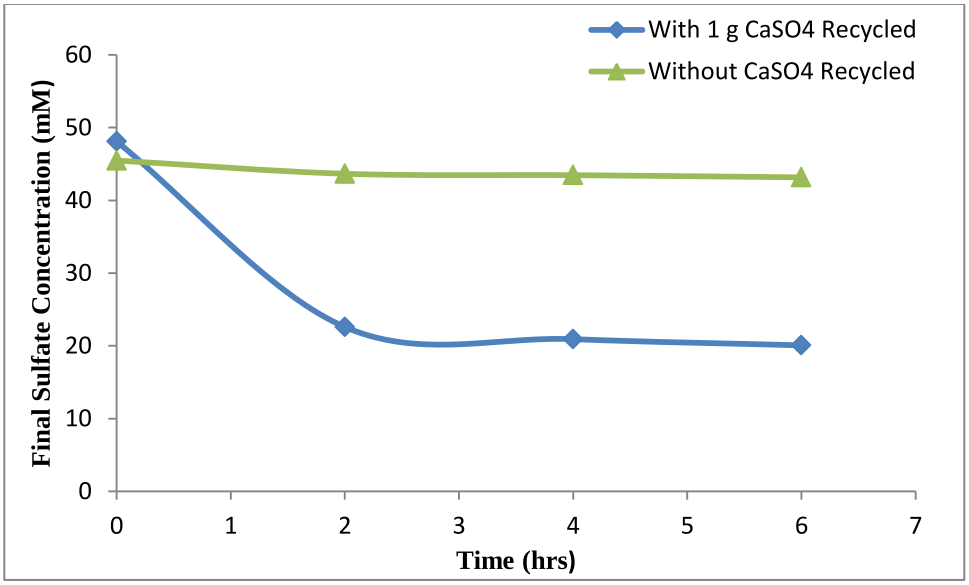

Figure 4.6 Kinetics of sulfate removal with Stage 1 calcium sulfate recycle.

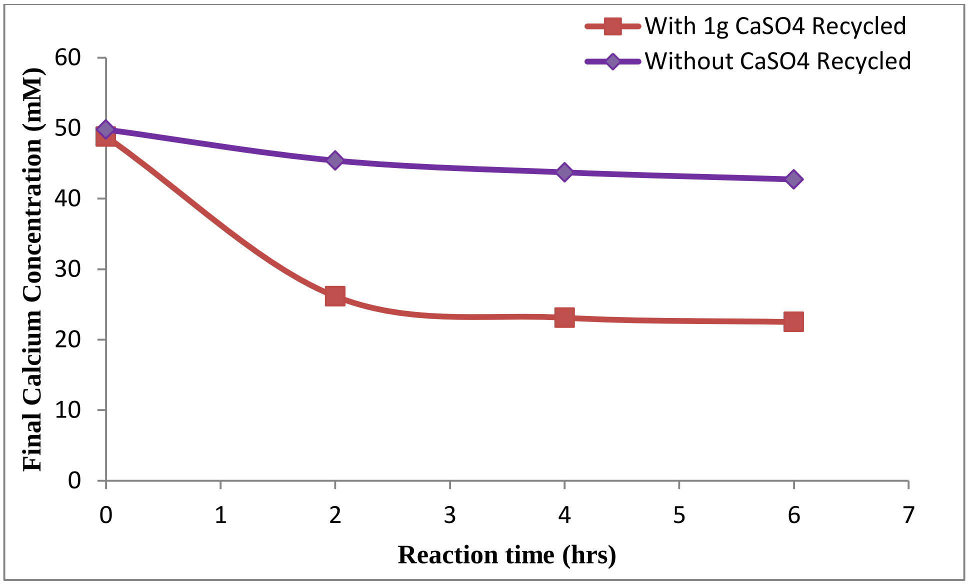

Figure 4.7 Kinetics of calcium removal with Stage 1 calcium sulfate recycle.

4.6 Kinetics of sulfate removal in Stage 2 (UHLA)

An experiment was conducted to study the kinetics of sulfate removal in the second stage in order to remove sulfate remaining in the effluent from the first stage using UHLA process. This experiment was performed by adding sodium aluminate and lime to the effluent solution from the first stage. Previous experiments showed that increasing calcium dose resulted in increasing the efficiency of sulfate removal. Based on that, an alternative is to add calcium chloride in excess in order to maximize sulfate removal in the first stage and the remaining calcium in the solution can then be used as calcium source in the second stage which will reduce the lime dose required in this stage. However, calcium chloride is more expensive than lime which prefers the use of lime as the main calcium source in the second stage. Additionally, high pH is required in the second stage for efficient sulfate removal. Therefore, in the two-stage treatment process, Stage 1 experiments were conducted with initial calcium to sulfate ratio of 1:1. Effluent from the first stage included sulfate and calcium concentrations of 21 mM and 24 mM, respectively. To ensure a sufficient amount of calcium is available for sulfate removal in the second stage, the lime dose was set to be 81.9 mM which is 300% of the initial sulfate concentration in Stage 2. Aluminum dose was set at 27.6 mM which is approximately equal to the initial sulfate concentration. Samples were taken at various times starting at a reaction time of 2 hrs. Results for the kinetic experiments are shown in Figure 4.8 and indicate that sulfate is rapidly removed and the reaction is almost complete within the first sampling time of 2 hrs. This signifies that the UHLA process could be applied effectively without being restricted by kinetics. Based on the results of these kinetic experiments, subsequent equilibrium experiments were conducted for Stage 2 using a reaction time of 2 hrs.

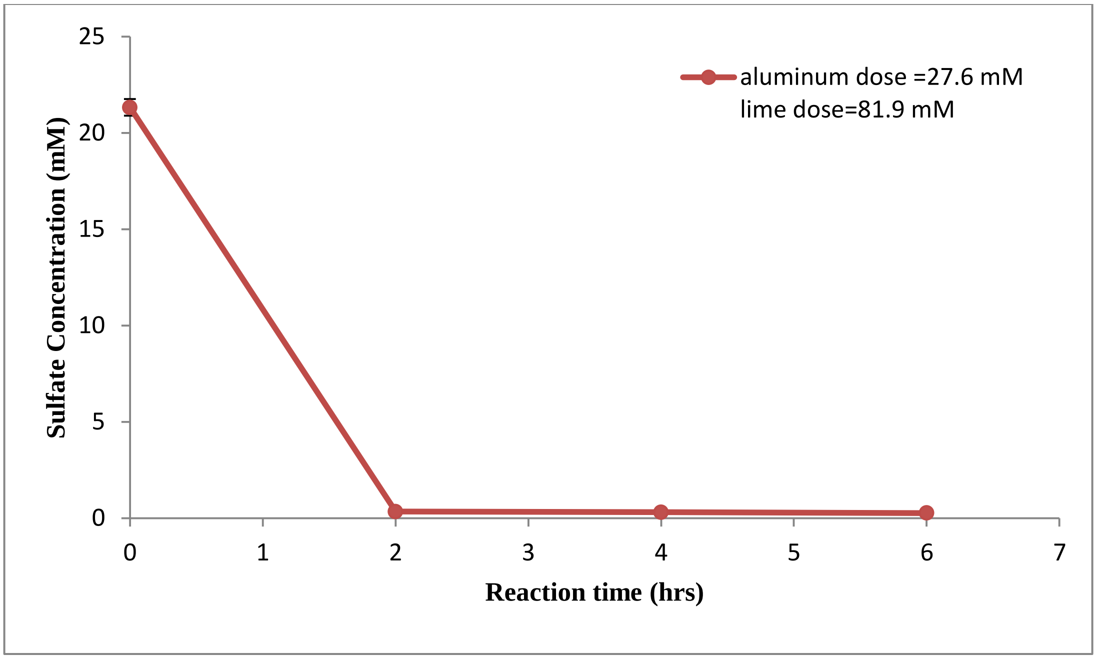

Figure 4.8 Kinetics of sulfate removal in Stage 2.

4.7 Equilibrium characteristics of sulfate removal with UHLA

Sixteen batch equilibrium experiments were performed in duplicates in order to study the effect of different lime and aluminum doses on sulfate removal using the UHLA process in Stage 2. Solutions of 96.8 mM sodium sulfate and 96.8 mM calcium chloride were used in the first stage to remove a significant amount of sulfate leaving final sulfate and calcium concentrations of 23 mM and 24 mM, respectively. Subsequently, filtered solutions of the first stage were used in the second stage and various doses of lime (0 to 54.3 mM) and sodium aluminate (0 to 41.4 mM) were added in order to evaluate equilibrium characteristics of sulfate removal in the second stage and to obtain optimum ratios of lime and aluminum doses to initial sulfate concentration.

Figure 4.9 illustrates the effect of initial calcium and sodium aluminate doses on the final sulfate concentrations. Initial calcium concentrations correspond to the calcium from the first stage plus lime added during the UHLA process. Efficient sulfate removal was detected at practical ranges of lime and sodium aluminate doses. Sulfate amounts decreased with increasing doses of lime and sodium aluminate signifying sulfate removal via precipitation of sulfate with calcium and aluminum to form Ca-Al-SO_4-OH precipitates.

From Figure 4.9, Lime and sodium aluminate stoichiometric ratios above 100% and 67% of the initial sulfate concentration in Stage 2, respectively resulted in minor additional removals compared to additional doses added. Therefore, lime and sodium aluminate doses of 26.7 mM and 18.4 mM, respectively could be adequate doses for practical applications and thus these doses were used in subsequent experiments that studied the effect of operating parameters on sulfate precipitation.

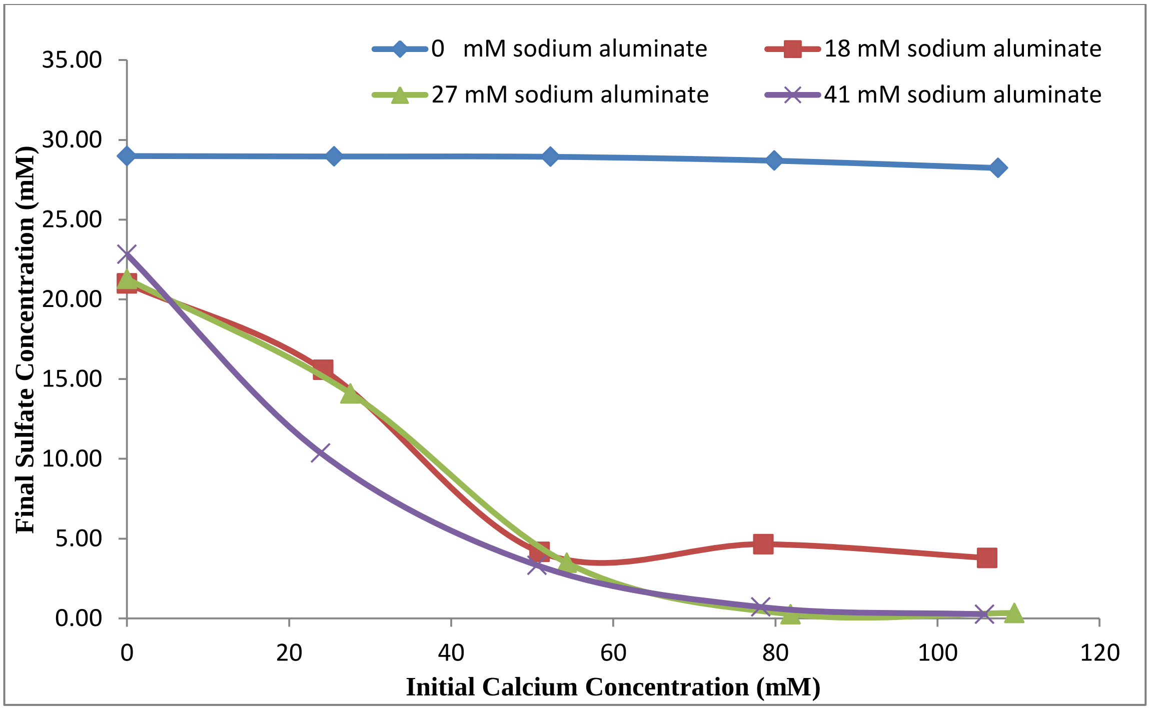

Figure 4.9 Effect of Lime and Aluminum Doses on Sulfate Removal.

4.8 Effect of pH on sulfate removal in Stage 2

The effect of pH on the removal of sulfate in Stage 2 was investigated. A domain of pH values (10, 11 and 12) was studied with stoichiometric ratios of lime and sodium aluminate of 100% and 67% of the initial sulfate concentration entering Stage 2, respectively. Results of these experiments showed that sulfate removal in Stage 2 was very dependent on the pH as can be seen in Figure 4.10. Figure 4.11 shows that calcium removal is also dependent on pH in Stage 2. Efficient sulfate and calcium removal was observed at a pH above 11. The hypothesis was made that sulfate is removed by precipitation in the form of calcium sulfoaluminate (ettringite) solid. This hypothesis agrees with literature stating that the most favorable pH conditions for the formation and stability of ettringite are in the domain of 11 and 12.5 (McCarthy, Hassett & Bender, 1991; Chrysochoou & Dermatas, 2006).

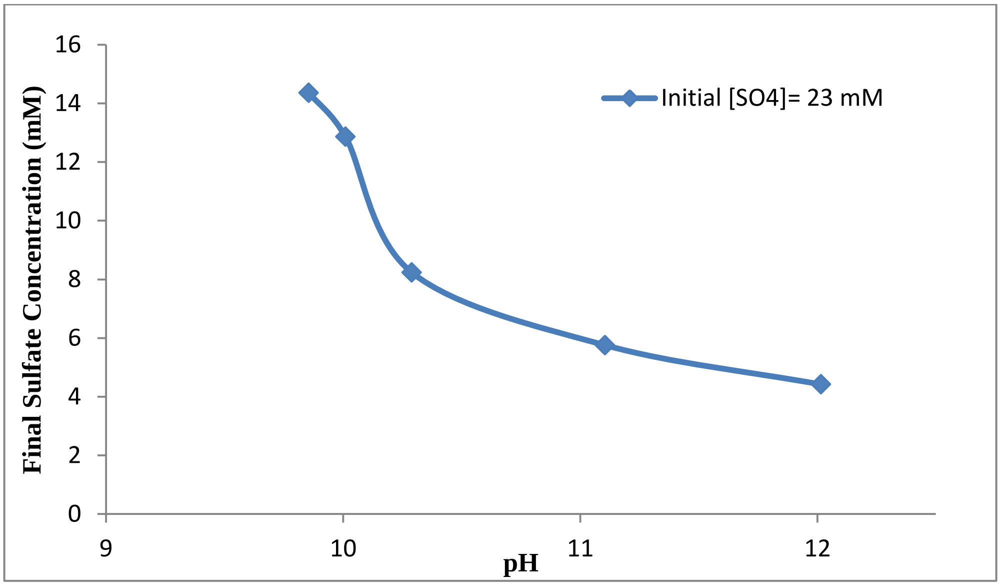

Figure 4.10 Effect of pH on the removal of sulfate in Stage 2.

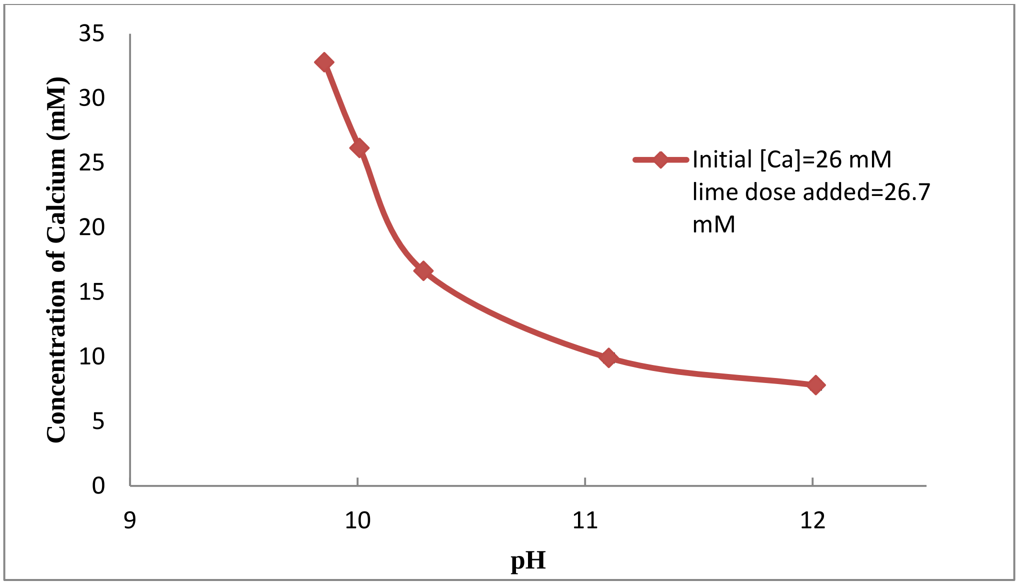

Figure 4.11 Effect of pH on the removal of calcium in Stage 2.

4.9 Effect of initial chloride concentration on sulfate removal

Three different initial concentrations of chloride (200, 500, and 1000 mM) were studied to evaluate the influence of initial chloride concentration on sulfate removal in Stage 2. Lime and sodium aluminate ratios to the initial sulfate concentration were kept constant at 100% and 67%, respectively. Results shown in Figure 4.12 indicated that sulfate removal using the UHLA process in Stage 2 was independent of the chloride concentration. This agrees with results obtained from researchers that investigated the interactions between chloride and sulfate in the UHLA process (Abdel-Wahab & Batchelor, 2006b) which indicated that calcium sulfoaluminate precipitation is more favorable than calcium chloroaluminate precipitation. Experimental results also showed that chloride had a negligible effect on the removal of calcium in Stage 2 and can be seen in Figure 4.13.

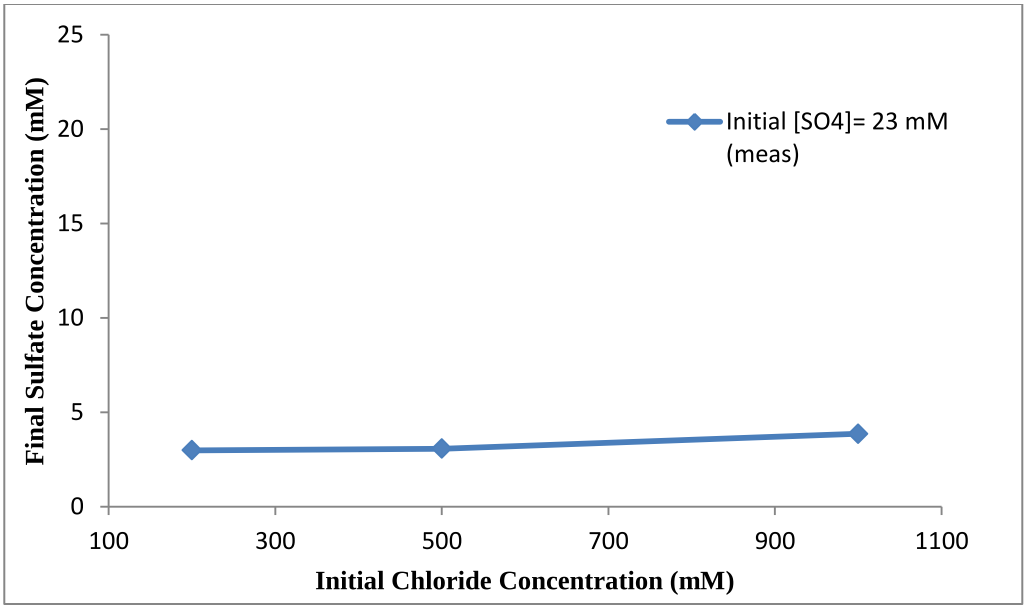

Figure 4.12 Effect of initial chloride concentration on sulfate removal.

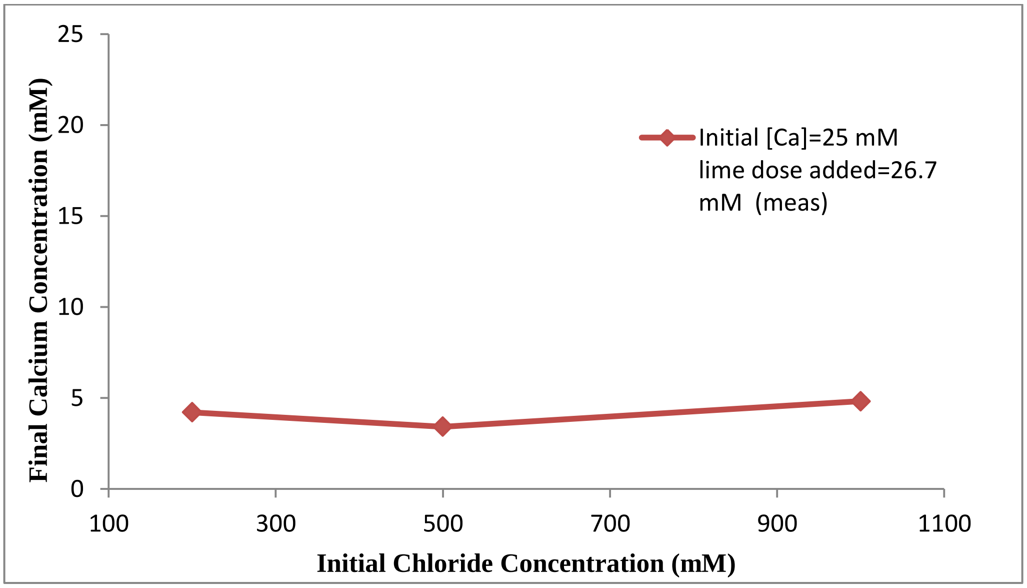

Figure 4.13 Effect of initial chloride concentration on calcium removal.

4.10 Kinetics of solids recycle in Stage 2

Experiments were carried out in Stage 2 of the process to investigate the effect of precipitated solids recycling on the kinetics and efficiency of sulfate removal. Lime and sodium aluminate ratios to the initial sulfate concentration were kept constant at 100% and 67% respectively. Solids formed in Stage 2 were dried and were recycled into Stage 2. Results in Figure 4.14 show a comparison between final sulfate concentrations with and without solids recycling and indicate that recycling precipitated solids did not enhance the rate or the efficiency of sulfate removal . This indicates that the rate of nucleation and seeding of calcium sulfoaluminate was not affected by the presence of solids in the solution.

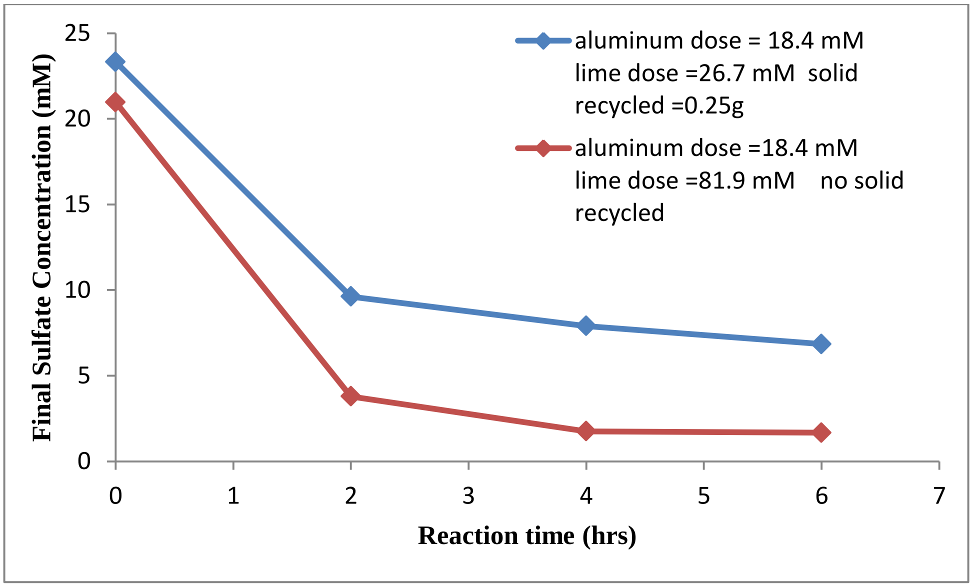

Figure 4.14 Kinetics of sulfate removal with Stage 2 solid recycle.

4.11 Equilibrium model for Stage 2

It was hypothesized that sulfate removal was primarily controlled by the formation of calcium sulfoaluminate solids ($Ca_6Al_2(SO_4)_3(OH)_{12}$) assuming the following reaction.

$6Ca^{2+} + 3SO_4^{2-} + 2Al(OH)_4^- + 12OH^- \leftrightarrow a\ {}_6Al_2(SO_4)_3(OH)_{12}(s)$ (4.2)

However, the ratios of sulfate removed to calcium and aluminum removed deviated from the theoretical ratio of the calcium sulfoaluminate solid. This indicates that another solid phase(s) or a solid solution containing more than one solid could be formed. One solid assumed to develop is monosulfate ($Ca_4Al_2(SO_4)(OH)_{12}$) and forms through the following reaction:

$4Ca^{2+} + SO_4^{2-} + 2Al(OH)_4^- + 12OH^- \leftrightarrow a\ {}_4Al_2(SO_4)(OH)_{12}(s)$ (4.3)

Other possible solids that could precipitate include gypsum, lime, gibbsite, and calcium chloroaluminate.

An equilibrium model was developed in order to understand precipitation mechanisms in Stage 2 and develop a tool that can predict final concentrations knowing initial concentrations and chemical doses in a real treatment system. The solubility products of the solid phases that could form in the system were added to the PHREEQC database and are shown in Table 4.3 below.

Table 4.3 Solubility product of solid phases that could form in the UHLA process.

Solid Name	Chemical Formula	Log (Ksp)	Reference
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}$	-43.13	Damons and Petersen (2002)
Monosulfate	$Ca_4Al_2(SO_4)(OH)_{12}$	-30.0	Damidot and Glasser (1993)
Calcium chloroaluminate	$Ca_4Al_2Cl_2(OH)_{12}$	-27.10	Bimin-Yauri and Glasser (1998)
Gibbsite	$Al(OH)_3$	-33.5	Stumm and Morgan (1996)
Gypsum	$CaSO_4 \cdot 2H_2O$	-4.58	Parkhurst and Appelo (1999)
Lime	$Ca(OH)_2$	22.81	Stumm and Morgan (1996)

Initial sulfate and calcium concentrations as well as chemical doses of lime and sodium aluminate were included in the input file of PHREEQC. Different scenarios were evaluated assuming pure solid phases and solid solution of different solid phases and the model predictions were compared with experimental data. The hypothesis assuming formation of a solid solution of calcium sulfoaluminate and monosulfate agreed well with experimental results. Final sulfate concentrations at different lime and aluminum doses were calculated using the equilibrium model and were compared to the measured values as shown in Figure 4.15 below. While the measured values agreed with the model predictions at high aluminum doses, results for the experiments conducted at the low sodium aluminate dose, 18.4 mM, deviated from the model prediction. This could be due to some lime not dissolving in the solution, thus, providing less calcium to precipitate sulfate.

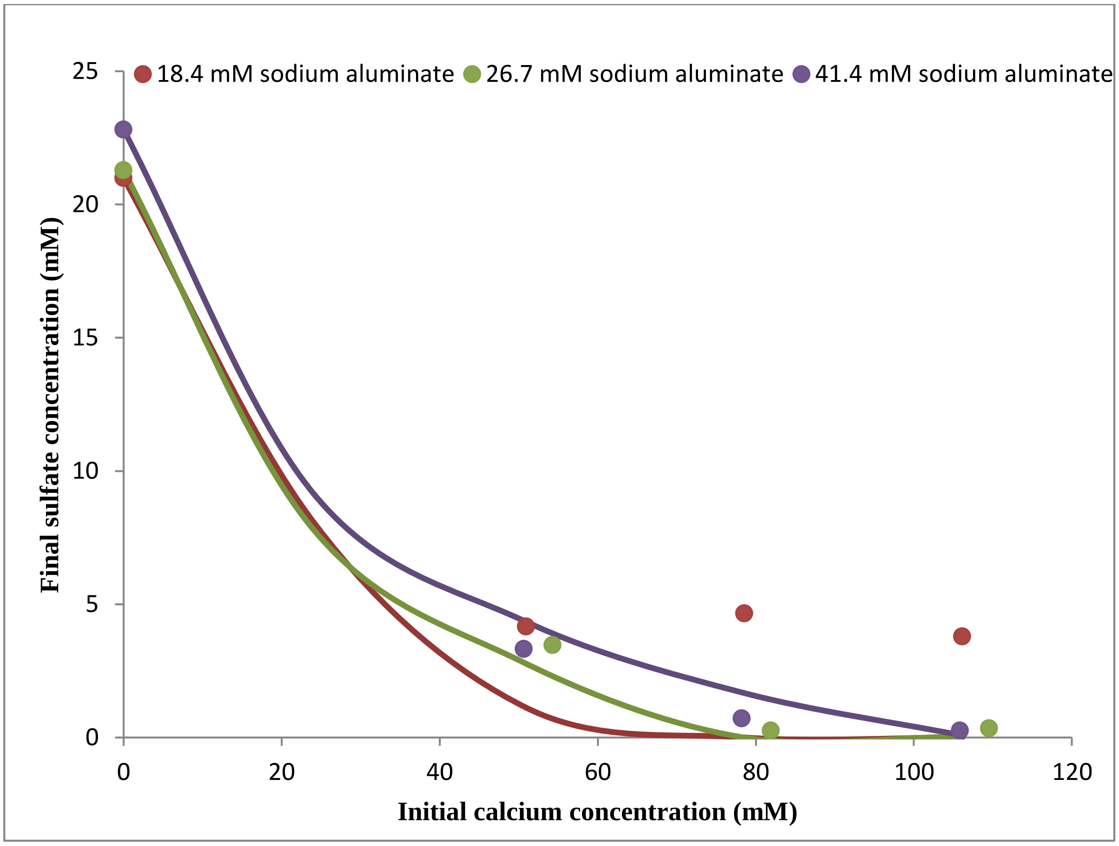

Figure 4.15 Comparison between measured and model predicted values for final sulfate concentrations in Stage 2. The dots represent measured concentrations and the lines represent model predicted concentrations.

Fractions of every solid in the solid solution were calculated corresponding to every data figure using PHREEQC. The effect of lime and aluminum doses on the development of these solids is shown in Figure 4.16. It can be seen that with increasing aluminum dose, monosulfate was found to increase while ettringite decreased. This is consistent with the sulfate to aluminum stoichiometric ratios in these solids. Monosulfate solid includes higher aluminum to sulfate ratio (2:1) than calcium sulfoaluminate (2:3). Therefore, increasing aluminum dose above the stoichiometric ratio of aluminum to sulfate in the calcium sulfoaluminate solid is neither desirable nor cost effective.

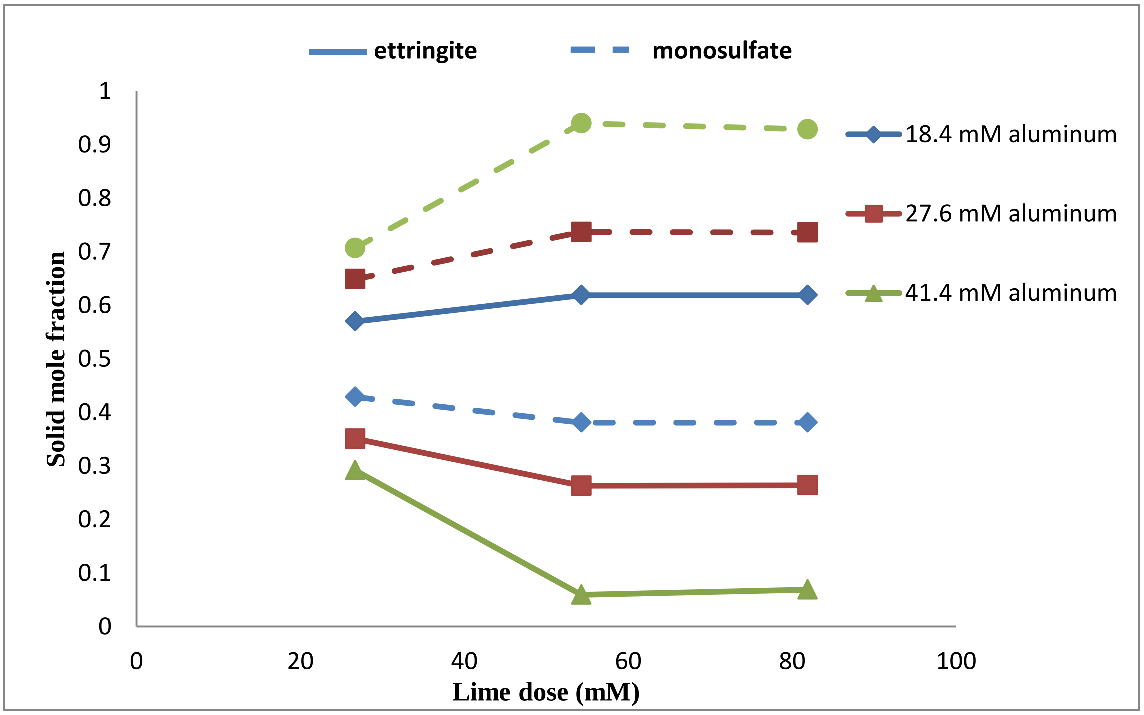

Figure 4.16 Fractions of solids in the solution in Stage 2.

Model predicted values were compared to the measured values of sulfate removal at various initial chloride concentrations in Stage 2 in Figure 4.17. Results show that the model very accurately predicted the final sulfate concentrations at different initial chloride concentrations. Similarly, the model precisely predicted the final calcium concentrations at various initial chloride concentrations in Figure 4.18.

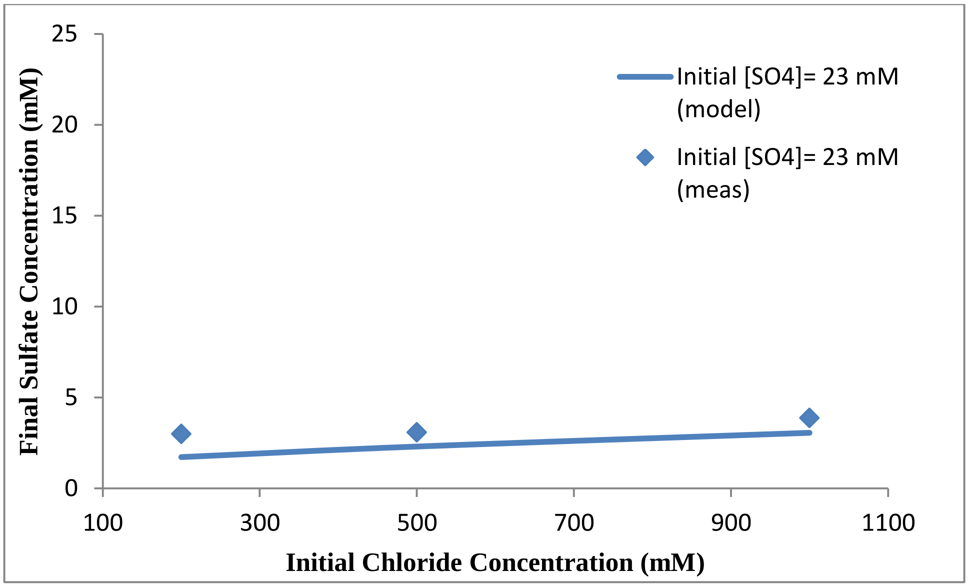

Figure 4.17 Comparison of measured and model predicted values of sulfate removal at different initial chloride concentrations.

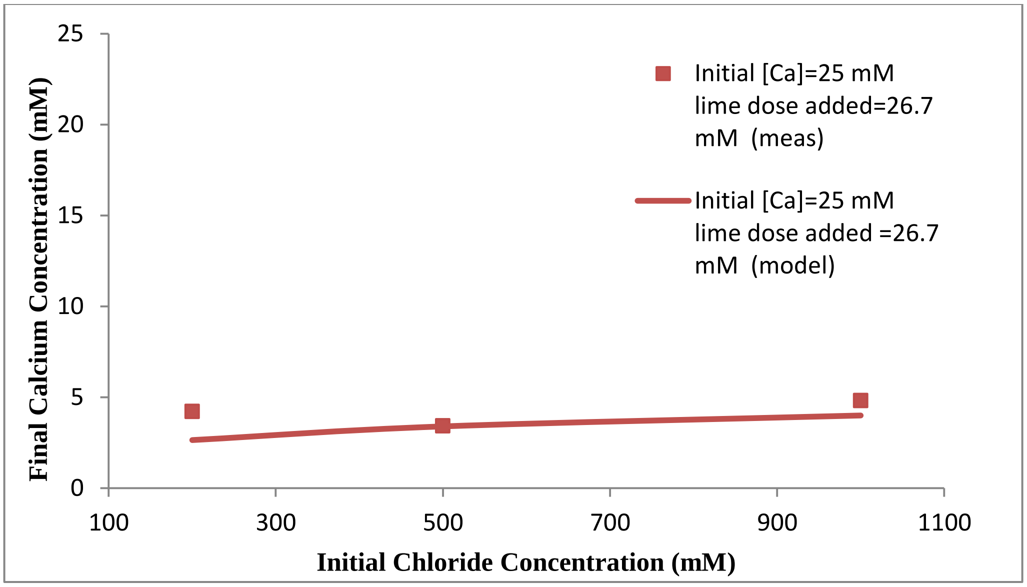

Figure 4.18 Comparison of measured and model predicted values of calcium removal at different initial chloride concentrations.

4.12 XRD analysis of Stage 2 solids

X-ray diffraction (XRD) was performed to identify the solids precipitated in Stage 2. The solids analyzed were from experiments conducted at constant lime and sodium aluminate ratios of 100% and 67% the initial sulfate concentration (26.7 and 18.4 mM respectively). The final solids were identified by comparing the peaks and the corresponding 2θ values with the standard data from the Joint ommittee on Powder Diffraction Standards (JCPDS) cards (JCPDS, 1990).

The XRD patterns shown in Figure 4.19 provide a clear indication of the presence of ettringite in the solids with two major peaks at around 8.72 and 15.42º 2θ and a third peak at around 17.9º 2θ. Monosulfate was found to be present at smaller peaks around 20.4, 22.4 and 31.2º 2θ. These results of the XRD analysis agree with the hypothesis that a solid solution of ettringite and monosulfate were formed.

XRD patterns displayed small peaks which showed the presence of lime (at 17.3, 33.5, and 46.1º 2θ), calcium chloroaluminate (at 22.6 and 31.12) and gibbsite (at 17.3, 20.08, and 44.8 º 2θ). The results obtained from the XRD analysis display the presence of the same solids that were assumed to exist by the equilibrium model which confirms the credibility of the model in portraying the means of sulfate removal by the UHLA process.

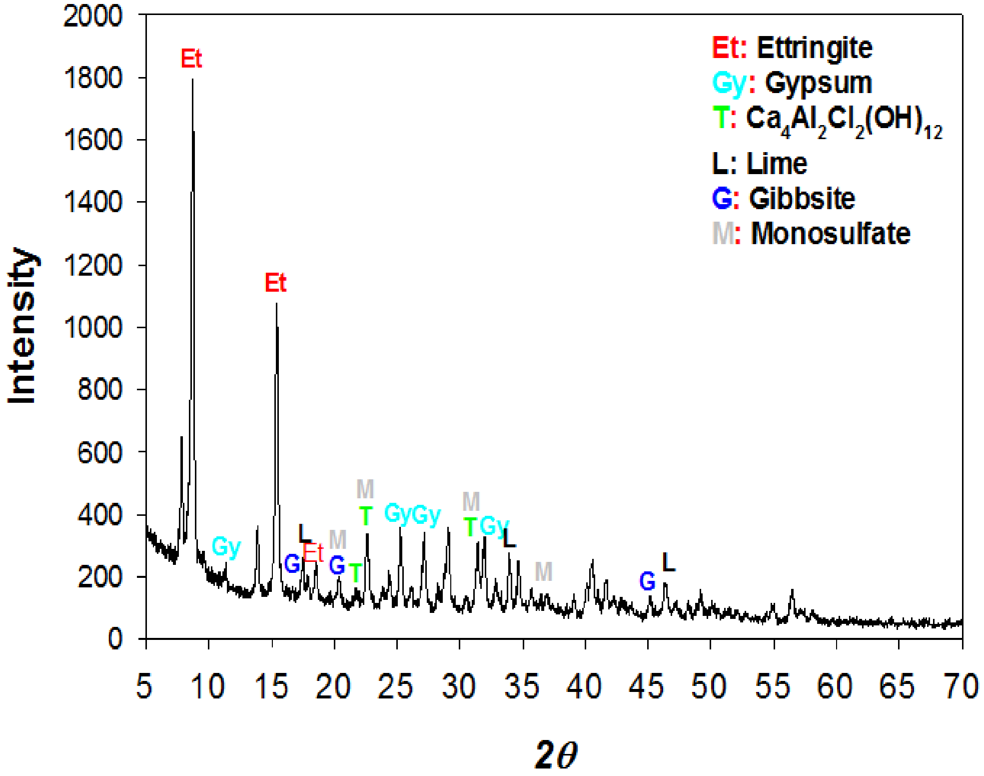

Figure 4.19 XRD patterns for the solids in Stage 2.

4.13 Techno-economic analysis of the two-stage precipitation process

The chemicals cost of the two-stage precipitation process was estimated at different initial sulfate concentrations. The chemicals cost per m^3 of NF reject brine was calculated corresponding to the amount of calcium chloride required in the first stage and lime and sodium aluminate required in the second stage. At 24 mM initial sulfate concentration and above, calcium chloride, lime, and sodium aluminate chemicals were required for treatment for the two-stage process. The calcium chloride dose was taken at a ratio of 1:1 to the initial sulfate concentration, while the lime and sodium doses were added at a ratio of 100% and 67% (26.7 mM and 18.4 mM) of the initial sulfate concentration in Stage 2 (~ 23 mM). Those ratios were selected based on results of equilibrium experiments that examined the effect of lime and aluminum doses on sulfate removal and showed to be the most cost-effective in removing sulfate. For sulfate amounts below 24.2 mM , only lime and sodium aluminate chemicals were used as the sulfate amount is low (below the calcium sulfate solubility) and the first stage treatment is not required in this case.

The prices of calcium chloride and lime were obtained from the ICIS website (include the website link) and were \$0.275/kg and \$0.065/kg, respectively. However, the price for sodium aluminate, obtained from Kirk-Othmer Encyclopedia of Chemical Technology, was at \$0.11/kg (Keller & Len, 2000). The estimated cost per m^3 of bine versus initial sulfate concentration is shown in Figure 4.20. The estimated cost is about \$3.5/m^3 for the sulfate concentration of NF reject brine of 100 mM. If the cost is calculated per cubic meter of groundwater to be treated assuming 75% recovery of the primary RO and the same recovery in the NF unit, the chemicals cost would be $ 0.219 per m^3 of groundwater fed into the system.

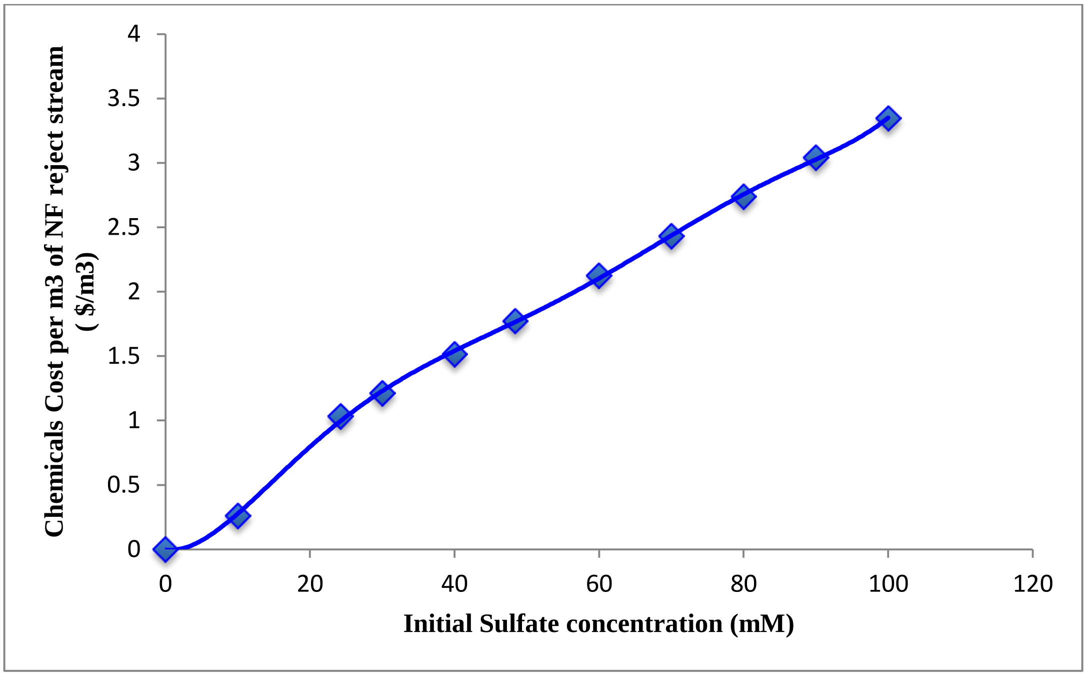

Figure 4.20 Estimated cost of the two stage process as a function of initial sulfate concentration.

5. SUMMARY AND CONCLUSION

Environmental issues caused by the improper disposal of reject brine are one of the major challenges of inland desalination, bringing about a great need for the application of zero liquid discharge. The treatment of brine streams using membrane systems for zero liquid discharge is limited by membrane fouling mainly caused by concentrate with high amounts of sulfate. Sulfate scale on membranes is very difficult to remove which necessitates a pretreatment stage for the stream before being fed into a membrane system. Previous research has shown that the ultra-high lime with aluminum (UHLA) process is capable of economically removing high amounts of sulfate regardless of the initial sulfate concentration.

A two-stage process was developed in order to provide a more economical approach through the use of less aluminum doses as well as to study its efficiency in removing sulfate from NF reject stream in the ZLD system. The process involves the removal of sulfate using a calcium source in the first stage followed by further removal of sulfate in the second stage using the UHLA technology. In order to evaluate the removal of sulfate, experiments were performed to investigate the kinetics and equilibrium specifications of sulfate removal using the two-stage process and to develop an equilibrium model for the removal of multiple elements using UHLA.

Initially, kinetic experiments were conducted on Stage 1 and Stage 2 of the two-stage process to study the kinetics of sulfate precipitation. Results revealed that sulfate removal is fast for both stages, being effectively complete within the first two hours. This indicates that kinetics is not a limitation of the application of the two-stage process.

A series of batch equilibrium experiments were conducted in Stage 1 to study the effect of operating parameters on sulfate removal. Results of these experiments showed that a significant amount of sulfate was removed. However, the remaining amounts were still high being limited by the solubility of calcium sulfate. This designates a requirement for the addition of the second stage which implements the UHLA process.

Sixteen batch equilibrium experiments were performed to study the effect of sulfate removal using the UHLA process. Solutions of 96.8 mM sodium sulfate and 96.8 mM calcium chloride were used in the first stage to remove a significant amount of sulfate. Subsequently, filtered solutions of the first stage were used with a range of doses of lime (0 to 54.3 mM) and sodium aluminate (0 to 41.4 mM). Efficient sulfate removal was detected at practical ranges of lime and sodium aluminate doses.

In order to further study the characteristics of sulfate removal using the two-stage process, experimental studies were conducted to evaluate the effect of pH, initial sulfate concentrations, initial chloride concentrations, and the recycle of solids back into the system. Results showed that sulfate removal in Stage 1 was independent of the pH of the solution while effective sulfate removal in Stage 2 was found to be above a pH of 11. Results for experiments with different initial chloride concentrations showed to have negligible effects on the removal of sulfate in the second stage of the process with UHLA.

Experiments involving the effect of solid recycle on Stage 1 revealed that the recycle of dry calcium sulfate salts from Stage 1 back into Stage 1 removed sulfate up to the calcium sulfate solubility limit. In contrast, the recycle of Stage 2 dry salts directly back into Stage 2 showed no effect on the removal of sulfate.

A model was developed to depict the chemical behavior in the UHLA process and to calculate the final sulfate concentration using data on the chemical doses and initial sulfate, calcium, and aluminum concentrations. The model was carried out using a computer program consisting of the PHREEQC geochemical modeling software. Initial concentrations and chemical doses for every set of experiments were defined in the PHREEQC input file. The model accurately predicted experimental results and can be used to predict final concentrations in practical treatment systems. Equilibrium modeling showed that the removal of sulfate was controlled by the formation of a solid solution containing ettringite and monosulfate solids.

XRD analysis for the precipitated solids in the second stage was performed and revealed the presence of the same solids assumed to be present by the equilibrium model.

Future work could be done to study the efficiency and feasibility of regenerating the precipitated solids in Stage 2 through acidification to recycle aluminum and calcium back into the system. This would make the two-stage process even more economical and favorable for industrial purposes. Other recommended future work is to apply the two-stage process on a pilot scale unit to study the effectiveness of the process as a whole. Additional research work to optimize the overall ZLD process could be done by integrating the treated stream in the current two-stage process with the lime softening process installed before the NF unit in order to use the treated stream which is high in pH and calcium concentration to substitute lime in the lime softening process.

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APPENDIX A

PHREEQC INPUT FILES

Table A.1 Input file for the Ca-Al-SO_4-OH system.

```
TITLE Batch_exp_Ca-Al-SO4-OH system

SOLUTION_S
        units   mmol/kgw
        temp    25.0

Number      pH    S(6)  Ca    Al    Cl    Na
            charge
      1     9.665 28.99 25.58 0     200   200
      2     12.50 28.99 25.58 0     200   200
      3     12.43 28.99 25.58 0     200   200
      4     12.43 28.99 25.58 0     200   200
      5     10.46 20.99 24.24 18.4  200   218
      6     11.95 20.99 24.24 18.4  200   218
      7     12.34 20.99 24.24 18.4  200   218
      8     12.52 20.99 24.24 18.4  200   218
      9     10.69 21.28 23.63 27.6  200   227
      10    11.93 21.28 23.63 27.6  200   227
      11    12.45 21.28 23.63 27.6  200   227
      12    12.56 21.28 23.63 27.6  200   227
      13    11.55 22.81 23.93 41.4  200   241
      14    12.23 22.81 23.93 41.4  200   241
      15    12.49 22.81 23.93 41.4  200   241
      16    12.67 22.81 23.93 41.4  200   241


SAVE SOLUTION 1-16
END

#Regress On

PHASES

#Unknown
      Anhydrite
            CaSO4 = Ca+2 + SO4-2
             log_k           -4.36

#Unknown
```

```
      tricalcium-hydroxyaluminate
            Ca3Al2(OH)12  = 3Ca+2 + 2Al(OH)4- + 4OH-
            log_K       -19.72

#Unknown
      tetracalcium-hydroxyaluminate
            Ca4Al2(OH)14 = 4Ca+2 + 2Al(OH)4- + 6OH-
            Log_K       -25.02
#Unknown
      Sulfoaluminate
      Ca6Al2(SO4)3(OH)12 = 6Ca+2 + 2Al(OH)4- + 3SO4-2 + 4OH-
      log_K       -43.13

#Unknown
      monosulfate
      Ca4Al2(SO4)(OH)12 = 4Ca+2 + 2Al(OH)4- + SO4-2 + 4OH-
      log_K       -30

#Unknown
        Gypsum
        CaSO4:2H2O = Ca+2 + SO4-2 + 2 H2O
        log_k           -4.580
#Unknown
        chloroaluminate
        Ca4Al2Cl2(OH)12 = 4Ca+2 + 2Al(OH)4- + 2Cl- + 4OH-
        log_k          -27.10

SOLID_SOLUTIONS 1

chlorohydroxy                 0.0   0.0
-comp   tricalcium-hydroxyaluminate   0.0 0.0
-comp   tetracalcium-hydroxyaluminate   0.0     0.0
-comp   Sulfoaluminate              0.0   0.0
-comp   monosulfate                 0.0   0.0
-comp   chloroaluminate             0.0   0.0

 EQUILIBRIUM_PHASES 1
 Ca(OH)2    0.0   0.0
 Al(OH)3    0.0 0.00
 tricalcium-hydroxyaluminate   0.0  0.0
 tetracalcium-hydroxyaluminate   0.0      0.0
 chloroaluminate    0.0 0.0
 sulfoaluminate    0.0 0.0
 monosulfate    0.0 0.0
 #aluminosilicate    0.0 0.0
 triCa    0.0 0.0
 tetCa    0.0 0.0
#carboaluminate    0.0 0.0
#Calcite 0.0 0.0
#Aragonite 0.0 0.0
#Dolomite 0.0 0.0
 #Mg(OH)2    0.0 0.0
#Mg2SiO4    0.0   0.0
```

```
 SAVE EQUILIBRIUM_PHASES 1
 USE SOLUTION none
 END

EQUILIBRIUM_PHASES 2
 Ca(OH)2    0.0   0.0267
 Al(OH)3    0.0 0.00
 tricalcium-hydroxyaluminate   0.0  0.0
 tetracalcium-hydroxyaluminate   0.0      0.0
 chloroaluminate    0.0 0.0
 sulfoaluminate    0.0 0.0
 monosulfate    0.0 0.0
 #aluminosilicate    0.0 0.0
 triCa    0.0 0.0
 tetCa    0.0 0.0
#carboaluminate    0.0 0.0
#Calcite 0.0 0.0
#Aragonite 0.0 0.0
#Dolomite 0.0 0.0
 #Mg(OH)2    0.0 0.0
#Mg2SiO4    0.0   0.0
 SAVE EQUILIBRIUM_PHASES 2
 USE SOLUTION none
 END


EQUILIBRIUM_PHASES 3
 Ca(OH)2    0.0   0.0543
 Al(OH)3    0.0 0.00
 tricalcium-hydroxyaluminate   0.0  0.0
 tetracalcium-hydroxyaluminate   0.0      0.0
 chloroaluminate    0.0 0.0
 sulfoaluminate    0.0 0.0
 #monosulfate    0.0 0.0
 #aluminosilicate    0.0 0.0
 triCa    0.0 0.0
 tetCa    0.0 0.0
#carboaluminate    0.0 0.0
#Calcite 0.0 0.0
#Aragonite 0.0 0.0
#Dolomite 0.0 0.0
 #Mg(OH)2    0.0 0.0
#Mg2SiO4    0.0   0.0
 SAVE EQUILIBRIUM_PHASES 3
 USE SOLUTION none
 END


EQUILIBRIUM_PHASES 4
 Ca(OH)2    0.0   0.0819
 Al(OH)3    0.0 0.00
 tricalcium-hydroxyaluminate   0.0  0.0
 tetracalcium-hydroxyaluminate   0.0      0.
```

```
 chloroaluminate    0.0 0.0
 sulfoaluminate    0.0 0.0
 #monosulfate    0.0 0.0
 #aluminosilicate    0.0 0.0
 triCa    0.0 0.0
 tetCa    0.0 0.0
#carboaluminate    0.0 0.0
#Calcite 0.0 0.0
#Aragonite 0.0 0.0
#Dolomite 0.0 0.0
 #Mg(OH)2    0.0 0.0
#Mg2SiO4    0.0   0.0
 SAVE EQUILIBRIUM_PHASES 4
 USE SOLUTION none
 END


TITLE  Start Dataset 1
USE SOLUTION 1
USE EQUILIBRIUM_PHASES 1
#USE SOLID_SOLUTIONS 1
END #End Dataset

TITLE  Start Dataset 2
USE SOLUTION 2
USE EQUILIBRIUM_PHASES 2
USE SOLID_SOLUTIONS 1
END #End Dataset

TITLE  Start Dataset 3
USE SOLUTION 3
USE EQUILIBRIUM_PHASES 3
USE SOLID_SOLUTIONS 1
END #End Dataset

TITLE  Start Dataset 4
USE SOLUTION 4
USE EQUILIBRIUM_PHASES 4
USE SOLID_SOLUTIONS 1
END #End Dataset

TITLE  Start Dataset 5
USE SOLUTION 5
USE EQUILIBRIUM_PHASES 1
USE SOLID_SOLUTIONS 1
END #End Dataset

TITLE  Start Dataset 6
USE SOLUTION 6
USE EQUILIBRIUM_PHASES 2
USE SOLID_SOLUTIONS 1
END #End Dataset
```

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TITLE  Start Dataset 7
USE SOLUTION 7
USE EQUILIBRIUM_PHASES 3
USE SOLID_SOLUTIONS 1
END #End Dataset

TITLE  Start Dataset 8
USE SOLUTION 8
USE EQUILIBRIUM_PHASES 4
USE SOLID_SOLUTIONS 1
END #End Dataset

TITLE  Start Dataset 9
USE SOLUTION 9
USE EQUILIBRIUM_PHASES 1
USE SOLID_SOLUTIONS 1
END #End Dataset

TITLE  Start Dataset 10
USE SOLUTION 10
USE EQUILIBRIUM_PHASES 2
USE SOLID_SOLUTIONS 1
END #End Dataset

TITLE  Start Dataset 11
USE SOLUTION 11
USE EQUILIBRIUM_PHASES 3
USE SOLID_SOLUTIONS 1
END #End Dataset

TITLE  Start Dataset 12
USE SOLUTION 12
USE EQUILIBRIUM_PHASES 4
USE SOLID_SOLUTIONS 1
END #End Dataset

TITLE  Start Dataset 13
USE SOLUTION 13
USE EQUILIBRIUM_PHASES 1
USE SOLID_SOLUTIONS 1
END #End Dataset

TITLE  Start Dataset 14
USE SOLUTION 14
USE EQUILIBRIUM_PHASES 2
USE SOLID_SOLUTIONS 1
END #End Dataset

TITLE  Start Dataset 15
USE SOLUTION 15
USE EQUILIBRIUM_PHASES 3
USE SOLID_SOLUTIONS 1
END #End Dataset
```

```
TITLE  Start Dataset 16
USE SOLUTION 16
USE EQUILIBRIUM_PHASES 4
USE SOLID_SOLUTIONS 1
END #End Dataset
```

APPENDIX B

TABULATED DATA

Table B-1 Effect of stoichiometry on the removal of sulfate in Stage 1.

	Initial Conditions		Final Conditions		
Stoichiometric ratio	SO4 (mM)	Ca (mM)	SO4 (mM)	Ca (mM)	pH
0.5	99.5	50.91	43.64	42.64	6.02
1		101.6	23.14	25.81	6.07
1.5		151.4	13.49	62.46	5.60
2		194.2	9.26	106.2	6.70

Table B-2 Kinetics of sulfate removal in Stage 1.

	Initial Conditions		Final Conditions		
Time(hr)	[SO4] (mM)	[Ca] (mM)	[SO4] (mM)	[Ca] (mM)	pH
0	100.28	188.73	100.28	188.70	7.19
0.5			16.77	104.92	4.84
1			14.02	102.96	5.05
2			12.10	100.85	4.95
4			12.08	97.95	5.89
8			12.69	97.90	7.02

Table B-3 Kinetics of sulfate removal in Stage 2.

<table>
<tr><th colspan="10">Stage 1</th></tr>
<tr><td colspan="4">Initial Conditions</td><td colspan="6">Final Concentrations</td></tr>
<tr><td colspan="2">[SO4] (mM)</td><td colspan="2">[Ca] (mM)</td><td colspan="2">Final [SO4] (mM)</td><td colspan="3">Final [Ca] (mM)</td><td>pH</td></tr>
<tr><td colspan="2">92.69</td><td colspan="2">94.68</td><td colspan="2">21.33</td><td colspan="3">24.62</td><td>6.86</td></tr>
<tr><th colspan="10">Stage 2</th></tr>
<tr><td colspan="6">Initial Conditions</td><td colspan="4">Final Concentrations</td></tr>
<tr><td>Solution No.</td><td>Time(hr)</td><td>[SO] (mM)</td><td>[Ca](mM)</td><td>Lime dose (mM)</td><td>NaAlO2 dose (mM)</td><td>[SO4] (mM)</td><td>[Ca] (mM)</td><td>[Al] (mM)</td><td>pH</td></tr>
<tr><td>8</td><td>0</td><td>21.33</td><td>24.62</td><td>81.9</td><td>18.4</td><td>20.98</td><td>25.24</td><td>18.4</td><td></td></tr>
<tr><td>8</td><td>2</td><td></td><td></td><td>81.9</td><td>18.4</td><td>3.79</td><td>24.62</td><td>0.003</td><td></td></tr>
<tr><td>8</td><td>4</td><td></td><td></td><td>81.9</td><td>18.4</td><td>1.75</td><td>22.61</td><td>0.002</td><td></td></tr>
<tr><td>8</td><td>6</td><td></td><td></td><td>81.9</td><td>18.4</td><td>1.67</td><td>22.47</td><td>0.006</td><td>12.6</td></tr>
<tr><td>12</td><td>0</td><td></td><td></td><td>81.9</td><td>27.6</td><td>21.32</td><td>24.62</td><td>27.6</td><td></td></tr>
<tr><td>12</td><td>2</td><td></td><td></td><td>81.9</td><td>27.6</td><td>0.338</td><td>15.80</td><td>0.009</td><td></td></tr>
<tr><td>12</td><td>4</td><td></td><td></td><td>81.9</td><td>27.6</td><td>0.306</td><td>14.17</td><td>0.009</td><td></td></tr>
<tr><td>12</td><td>6</td><td></td><td></td><td>81.9</td><td>27.6</td><td>0.263</td><td>13.92</td><td>0.014</td><td>12.6</td></tr>
<tr><td>16</td><td>0</td><td></td><td></td><td>81.9</td><td>41.4</td><td>21.32</td><td>24.62</td><td>41.4</td><td></td></tr>
<tr><td>16</td><td>2</td><td></td><td></td><td>81.9</td><td>41.4</td><td>0.254</td><td>8.25</td><td>0.022</td><td></td></tr>
<tr><td>16</td><td>4</td><td></td><td></td><td>81.9</td><td>41.4</td><td>0.289</td><td>9.21</td><td>0.032</td><td></td></tr>
<tr><td>16</td><td>6</td><td></td><td></td><td>81.9</td><td>41.4</td><td>0.263</td><td>8.75</td><td>0.013</td><td>12.7</td></tr>
</table>

Table B-4 Effect of pH on sulfate removal in Stage 1.

Initial Conditions		Final Concentrations		
[SO4] (mM)	[Ca] (mM)	[SO4] (mM)	[Ca] (mM)	pH
99.84	152.23	14.12	65.07	7.23
		13.84	64.27	9.17
		13.51	64.99	9.84
		13.35	64.97	10.93
		14.22	64.18	11.92

Table B-5 Effect of pH on sulfate removal in Stage 2.

<table>
<tr><td colspan="6">Stage 1</td></tr>
<tr><td colspan="2">Initial Conditions</td><td colspan="4">Final Concentrations</td></tr>
<tr><td>[SO4] (mM)</td><td>[Ca] (mM)</td><td>[SO4] (mM)</td><td colspan="2">[Ca] (mM)</td><td>pH</td></tr>
<tr><td>100.09</td><td>96.36</td><td>23.15</td><td colspan="2">25.81</td><td>6.91</td></tr>
<tr><td colspan="6">Stage 2</td></tr>
<tr><td colspan="2">Initial Conditions</td><td colspan="3">Final Concentrations</td><td></td></tr>
<tr><td>[SO4] (mM)</td><td>[Ca] (mM)</td><td>[SO4] (mM)</td><td>[Ca] (mM)</td><td>[Al] (mM)</td><td>pH</td></tr>
<tr><td rowspan="5">23.15</td><td rowspan="5">25.81</td><td>14.36</td><td>32.77</td><td>1.57</td><td>9.86</td></tr>
<tr><td>12.86</td><td>26.15</td><td>2.09</td><td>10.01</td></tr>
<tr><td>8.23</td><td>16.63</td><td>1.34</td><td>10.29</td></tr>
<tr><td>5.76</td><td>9.90</td><td>11.13</td><td>11.11</td></tr>
<tr><td>4.42</td><td>7.79</td><td>0.02</td><td>12.02</td></tr>
</table>

Table B-6 Effect of initial sulfate concentrations on sulfate removal in Stage 1.

Initial Conditions		Final Concentrations		
SO4 (mM)	Ca (mM)	Final [SO4] (mM)	Final [Ca] (mM)	Final pH
22.7118	24.32784	19.15842	19.66467	6.89
45.48651	49.79266	43.16696	45.38922	6.23
98.16571	95.93513	23.30174	24.50948	6.63

Table B-7 Effect of initial chloride concentrations on sulfate removal in Stage 2.

Stage 1					
Initial Conditions			Final Concentrations		
[SO4] (mM)	[Ca] (mM)	[Cl] (mM)	[SO4] (mM)	[Ca] (mM)	pH
98.17	95.94	235.29	23.30	24.51	5.82

Stage 2									
Initial Conditions					Final Concentrations				
[SO4] (mM)	[Ca] (mM)	[Cl] (mM)	Lime dose (mM)	$NaAlO_2$ (mM)	[SO4] (mM)	[Ca] (mM)	[Cl] (mM)	[Al] (mM)	pH
23.30	24.51	235.29	26.70	18.40	2.99	4.21	179.84	0.05	11.96
		535.29	26.70	18.40	3.07	3.42	503.49	0.12	11.82
		1035.3	26.70	18.40	3.86	4.82	1090.6	0.07	11.72

Table B-8 Effect of recycle of Stage 1 solids into Stage 1.

	Initial Conditions		Final Concentrations		
Time (hrs)	[SO4] (mM)	[Ca] (mM)	[SO4] (mM)	[Ca] (mM)	pH
0	48.12	48.80	48.12	48.80	
2			22.59	26.14	6.01
4			20.92	23.11	5.98
6			20.07	22.50	5.91

Table B-9 Effect of recycle of Stage 1 solids into Stage 2.

Stage 1				
Initial Conditions		Final Concentrations		
[SO4] (mM)	[Ca] (mM)	[SO4] (mM)	[Ca] (mM)	pH
99.03	93.37	23.33	22.35	7.3
Stage 2				
Initial Conditions		Final Concentrations		
[SO4] (mM)	[Ca] (mM)	[SO4] (mM)	[Ca] (mM)	pH
23.33	22.35	23.33	22.35	
		9.62	3.34	11.125
		7.91	2.56	11.67
		6.85	2.37	11.83

Table B-10 Measured results for effect of lime doses and aluminum doses on sulfate removal in Stage 2.

	Initial Conditions				Final Concentrations		
Exp No.	lime dose (mM)	NaAlO2 dose (mM)	Initial [SO4] (mM)	Initial [Ca] (mM)	[SO4] (mM)	[Ca] (mM)	[Al] (mM)
1	0	0	28.99	25.58	28.96	25.33	0.00
2	26.7	0			28.94	48.88	0.00
3	54.3	0			28.69	49.51	0.00
4	81.9	0			28.24	50.41	0.00
5	0	18.4	20.99	24.24	15.58	12.38	5.96
6	26.7	18.4			4.16	2.72	0.48
7	54.3	18.4			4.65	21.84	0.00
8	81.9	18.4			3.79	24.62	0.00
9	0	27.6	21.28	23.63	14.10	8.59	9.62
10	26.7	27.6			3.47	0.66	7.30
11	54.3	27.6			0.26	8.60	0.01
12	81.9	27.6			0.34	15.80	0.01
13	0	41.4	22.8127	23.93	10.36	1.05	9.28
14	26.7	41.4			3.33	0.60	17.86
15	54.3	41.4			0.71	0.92	11.19
16	81.9	41.4			0.25	8.25	0.02

Table B-11 Model results for effect of lime doses and aluminum doses on sulfate removal in Stage 2.

	Initial Conditions				Final Concentrations		
Solution no.	lime dose (mM)	NaAlO2 dose (mM)	Initial [SO4] (mM)	Initial [Ca] (mM)	[SO4] (mM)	[Ca] (mM)	[Al] (mM)
1	0	0	28.99	25.58	17.33	20.39	0
2	26.7	0			16.94	37.48	0
3	54.3	0			16.94	37.48	0
4	81.9	0			16.94	37.48	0
5	0	18.4	20.99	24.24	8.00	3.31	1.83
6	26.7	18.4			1.12	3.46	0.19
7	54.3	18.4			0.00	16.78	0.00
8	81.9	18.4			0.00	16.78	0.00
9	0	27.6	21.28	23.63	7.95	1.42	4.26
10	26.7	27.6			2.86	0.80	6.45
11	54.3	27.6			0.03	10.77	0.01
12	81.9	27.6			0.02	13.64	0.00
13	0	41.4	22.8127	23.93	9.19	0.66	8.45
14	26.7	41.4			4.38	0.47	14.33
15	54.3	41.4			1.69	0.55	3.96
16	81.9	41.4			0.09	9.88	0.01