

CHLORIDE SALTS REMOVAL BY NON PLANTED CONSTRUCTED
WETLANDS RECEIVING SYNTHETIC BRINES FROM
BELLE PLAINE POTASH MINING

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Abstract

Four pilot-scale constructed wetlands (CWs) were employed to study the fate and transport of the two dominant chloride salts (NaCl and KCl) receiving the synthetic brine. The characteristics of the brine solution are made up with a 10:1 concentration ratio between NaCl and KCl based on data obtained from Belle Plaine potash mine site. The multi-layer soils were designed to function as a main salt filtering component comprising of Regina Clay (grain size <0.002 mm), Brick Sand (grain size <4.75 mm) and sharp gravels (grain size between 6.3-19.1 mm) despite the clay layers contained a poor compact condition ($D_b = 1.4$, <1.6 g/cm³). The volume of void space in the compacted clay was reduced to approximately half the natural state following application of pressure (4,505 cm³ to 2,743 cm³). The CW systems were operated by the 16-day format (batch 1-3) and the 4-day format (batch 4). During the 16-day format experiments, the best K⁺ removal rate was recorded on Cell2 as 92.1±63.4% (4.6±5.3mg/l) while Cell 4 contributed the maximum removal of Na⁺ and Cl⁻ as 44.8±76.7% (53.2±92.4mg/l) and 50.5±109.6% (85.3±184.3.4mg/l). In the 4-day format operation, the chloride breakthrough curve was discovered in all treatment CW cells, excluding the control. Moreover, the curve stated at less than 6 hours ($C/C_0 > 0.05$) and approximately reached the break point ($C/C_0 > 0.95$) after passing 48 hours. Then the clay media was exhausted and lost its ability to remove Cl⁻. However, the study was not able to determine the breakthrough curves in neither Na⁺ nor K⁺ cases during batch experiment 4 due to unidentified ending points on both cations.

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List of Abbreviations

AEC	Anion Exchange Capacity
AMD	Acid Mine Drainage
ASTM	American Society for Testing and Materials
BOD ₅	5-day Biochemical Oxygen Demand
C/C ₀	Relative Concentration Ratio
C _c	Coefficient of Curvature
CEC	Cation Exchange Capacity
Cl ⁻	Chloride Ion
COD	Chemical Oxygen Demand
C _u	Coefficient of uniformity
CW	Constructed Wetland
d ₁₀ , d ₃₀ , d ₆₀	Grain Diameter Corresponding to 10%, 30%, 60% Passing
DI Water	Deionised Water
EIS	Environmental Impact Statement
FWS	Free Water Surface
GP	Poorly Graded Gravels
GSD	Grain Size Distribution
GW	Well Graded Gravels
ISEs	Ion Selective Electrodes
K ⁺	Potassium Ions
n	Number of Sample
Na ⁺	Sodium Ion

NFC	Nelson Farm Clay
r	Correlation coefficient
sd	Standard Deviation
se	Standard Error
SP	Poorly Graded Sand
SSF	Subsurface Flow Wetland
t_{df}	Degree of Freedom
TDS	Total Dissolved Solids
TMA	Tailings Management Area
TRC	Technical Review Committee
TSS	Total Suspended Solids
U.S. EPA	United States Environmental Agency

1. Introduction

During massive growth in an exploration for petroleum reserves in Saskatchewan during the 1940s, significant potash seams were incidentally discovered in 1943, a number of companies drilling oil wells discovered extensive potash reserves. Approximately, 107 billion metric tonnes of KCl (67.41 billion metric tonnes of K₂O) of discovered ore deposits beneath the southern Prairie areas in Saskatchewan were reported by the government in 1973 (Stone, 2008). These massive potash ore deposits were formed by the evaporation of the ancient inland sea since the middle Devonian period (MacKenzie, 2003). Much of the potash is deposited at shallow levels (from 400 - 800 m) and can be accessed by conventional mining methods. Other portions of the deposits deep (> 1,500 m underground) and are extracted using a solution mining approach.

Saskatchewan is the world's leading potash producer operating seven conventional potash mines and two solution potash mines (Stone, 2008). The potash mining industries are not only the most valuable business contributing stability to Saskatchewan's economy, but also constitute more than a thousand jobs available for local people.

Typically, more than a million tonnes of chloride salt solution (NaCl) and hot water have been applied during an ore extraction process in a potash solution mine. Those are converted to millions tonnes of excess brine by the end of mining process. For instance, the average amount of excess brine at the Belle Plaine site was reported between 3.3 - 4.6 million m³/year (MDH Engineering Solution Corp., 2009). Due to The Saskatchewan Environmental Assessment Act, brine slurries and solutions are not permitted to discharge into any natural water resources.

The migration of brine from the waste management area through aquifers is considered as the primary environmental concern for Saskatchewan's potash mines (Reid & Getzlaf, 2004). High concentration of excessive brine leads to create a hypo-osmotic condition to aquatic life by increasing salt ions concentration in surrounding environment. Therefore, water and nutrients diffuse out from the aquatic life cells via an osmosis process (Environment Canada, 2010). Another word, the hypo-osmotic is the movement of water from an area of low concentration of solute into higher solute concentration area. The impact of extreme chloride concentration in drinking water resources conveys undesirable tastes to water and causes corrosion in the distribution system (Health Canada, 1997).

The most popular brine disposal method, deep well injection, currently in use was initially developed in Saskatchewan in 1964 (MacKenzie, 2003). Using the deep well injection disposal method, brine solution is not only being untreated, but is also left underground for long-term storage. Challenges related to deep well injection include potential negative impacts of natural disasters such as earthquakes that could cause brine leak through natural cracks into aquifers and operator errors that can lead to failure of the technique or the longevity of the storage. Regardless, the method is most appropriately defined as bulk brine disposal method, not a brine treatment method, that may have unintended negative impacts on surrounding environments.

The fate and transport of the two dominant chloride salts (NaCl and KCl) most through constructed multi-layer soils in brine storage facilities is investigated in this thesis. The characteristics of the synthetic brine solution are based on data obtained from Belle Plaine potash mine site, since authentic samples were not available.

1.1 Research Objectives

The current research was undertaken to quantify salt movement, focusing on sodium (Na), potassium (K), and chlorine (Cl), through a constructed multi-layer soil filtration system typical of those designed for use in potash mining tailings ponds. The constructed cells were composed of Regina Clays to simulate regional conditions relevant to south Saskatchewan potash mining locations. Synthetic tailings pond water was prepared in the laboratory to quantify salts uptake, movement, and transport through the multi-layer constructed cells.

The specific objectives for this research included:

- (1) To identify salt concentrations of sodium(Na^+), potassium(K^+) and chlorine(Cl^-) ions relevant for potash tailings pond water and produce a synthetic mixture for analyses;
- (2) To determine aqueous removal rates of the three target salt ions from a synthetic aqueous sample simulating potash mine tailings water using Regina clay as an adsorptive material in the event that its effectiveness as an environmental barrier is lost;
- (3) To conduct at least 3 bench-scale experiments including observations and analyses of salt concentrations, conductivity, pH, total dissolved solids (TDS), and salinity in both aqueous influent and effluent samples; and
- (4) To quantify the removal capacity of Regina clay for the three targeted salt ions commonly occurring in potash tailings pond water.

2. Literature Review

2.1 Saskatchewan's Potash

The term potash commonly refers to the short form description for the muriate of potash (MOP) and its scientific name, potassium oxide (K_2O). The potash ore that is deposited 1-3km below the ground surface, sylvinite, refers to sylvite-bearing rock consisting of a mixture of sylvite (KCl) and halite (NaCl). Within the ore deposit, clay, anhydrite, dolomite crystals, carnallite ($KCl \cdot MgCl_3 \cdot 6H_2O$) and kieserite ($MgSO_4 \cdot H_2O$) impurities are also found (Halabura & Hardy, 2007).

Potash products that are mined and marketed are reported based on the KCl unit, while K_2O is used as a purity measure to classify the quality or grade of the potash product. Sylvinite containing more than 30% K_2O with a bright and translucent pinkish-orange color represents high grade, while a low grade ore contains 23-27% K_2O and is a dusky brownish red color.

2.2 Geology of Saskatchewan's Potash Deposits

Saskatchewan's potash-bearing bed was formed by the evaporation of an ancient inland sea in the Prairie Evaporite formation during the Middle Devonian period nearly four million years ago (Figure 2.1). The Elk Point Basin, the first cycle in the Middle Devonian age consists of Ashem and Winnipegosis Formation, while the Prairie Evaporite refers to the sylvinite bed deposit. Although the Dawson Bay and Souris River Formations are also represented in the second and third cycles of the Middle Devonian period, potash deposits are not found here due to lack of intensity and regularity of the evaporation process (Fuzesy, 1982).

The potash deposits in the Elk Point Basin are divided in ascending order as: Esterhazy Member, White Bear Member, Belle Plaine Member and Patience Lake Member. Each Member consists of one or more beds of interceded and has an average thickness of about 7 m (Fuzesy, 1982). The Elk Point Basin lies within and beneath Saskatchewan and parts of Manitoba, North Dakota, and northeast Montana. The subsurface depth and distribution of potash deposits is dependent on local geology, geography and climate. For instance, the sylvinite beds underground near Prince Albert (central), SK are located at depths between 400-800 m, near Belle Plaine, SK (south) at approximately 1,500 m, and between 1,700-3,650 m in north eastern Montana and North Dakota. Figure 2.2 provides an overview of the Prairie Evaporite potash deposit in the Elk Point Basin.

2.3 Belle Plaine Potash Mine

2.3.1 General Information

The Belle Plaine Potash mine is located approximately 45 km west of Regina in south-central Saskatchewan (Figure 2.3). The ore deposits are located at more than 1,500 m below ground surface, requiring a solution mining technique for extraction of the potash from the deposit. The mine site includes the minefield, product refinery, tailings management area (TMA), production ponds, disposal wells, administration offices, and various storage and maintenance buildings.

According to the Technical Review Comments (TRC) from the Ministry of Environment's Environmental Assessment Branch, the Belle Plaine mine site has a current mining capacity of 2.27 million tonnes per year, which is expected to increase to 4.81 million tonnes by the end of 2020 (Saskatchewan Ministry of Environment, 2009). Based on injection volumes reported between the year of 2000 and 2005, the

total brine injection volume was calculated between 3.3-4.6 million m³/year (MDH Engineering Solution Corp, 2009).

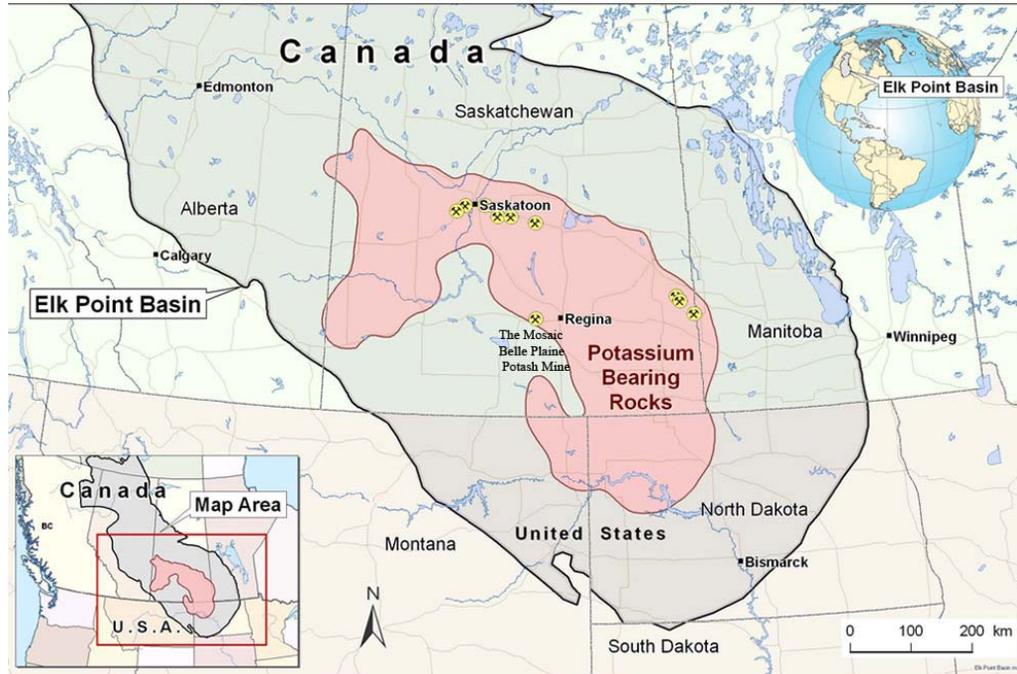


Figure 2.4 Prairie Evaporite Potash Deposit in Elk Point Basin (source: Canada Potash Corporation, 2014)

2.3.2 Solution Mining Technology

At the Belle Plaine potash mine, the extraction process takes place at a number of cluster sites. According to the Environmental Impact Statement (EIS), the proposed Belle Plaine Expansion includes 37 cluster sites across the mine with each cluster creating as many as 14 cavities (MDH Engineering Solution Corp, 2009). To access the sylvinitic bed containing the mixture of KCl and NaCl, a pair of wells is drilled to a depth of 1,585 m to facilitate inflow and extraction activities. Water is injected via one well and the brine is returned to the surface via the second. Normally, these activities, referred to as cavity development, require up to 4-5 years to achieve the desired size and shape of production cavity.

Once the cavity is fully saturated and turned into fractured rubble (collapsible zone), the recycle-brine from the refinery, containing hot NaCl salt, is injected to dissolve KCl from the collapsible potash bed. The saturated raw potash ore solution is recovered and extracted to the surface then transported to the raw feed storage tank, the refinery and the production ponds via the networks of underground pipelines. Figure 2.5 provides an overview of the production process at Belle Plaine solution mine.

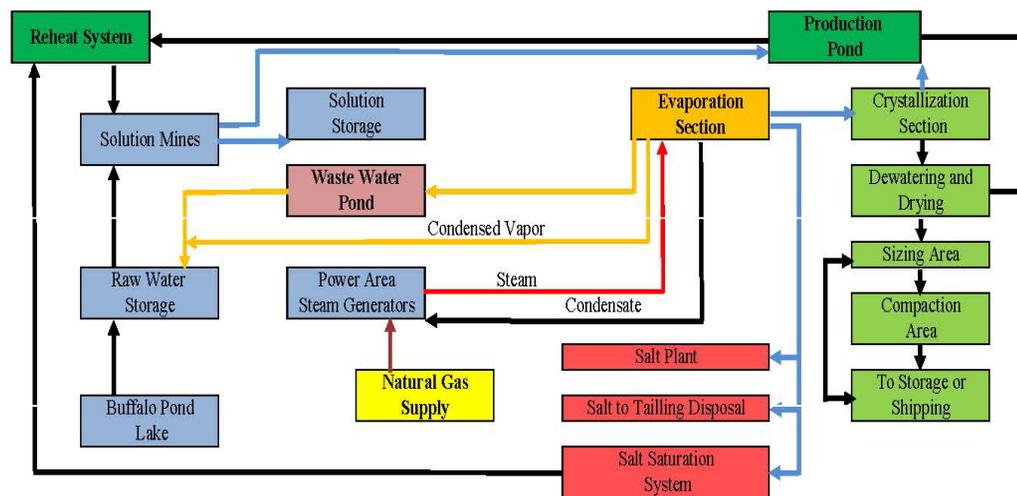


Figure 2.5 Flow Chart for Production Process at Belle Plaine (source: MDH Engineering Solution Corp, 2009)

The two main systems used to extract the ore slurry from the raw feed include evaporation and crystallization processes and the production pond technique. In the evaporation and crystallization processes, solution ore is transported to a quadruple set of evaporators to produce an enriched KCl solution. The overflow solution from the evaporators is thickened so that it contains none of NaCl or other impurities found in the original raw feed solution. The thickened solution is crystallized as KCl slurry

through a series of seven cooling crystallizers. The KCl slurry is washed and dried prior to transportation to the sizing area.

The production pond consists of impounded brine and control structures, a sump structure, pump houses and piping. Here, the solution ore from the raw feed storage precipitates as KCl slurry under ambient temperature conditions in the production ponds. To achieve the required product purity, KCl is separated from the precipitated slurry by dredging with a cold leach circuit. Then, it is dried and transported to the sizing area for classification.

The Belle Plaine potash mine annually produces 1.5 and 1.1 million tonnes of potash products via produced from the evaporation and crystallization process and production pond (MDH Engineering Solution Corp, 2009).

2.3.3 Excess Brine Disposal Methods

Approximately 12,000 dam³ of raw water are required to sustain the existing solution mining processes (MDH Engineering Solution Corp, 2009). From that allocation, more than 3 million m³/ year of brines are generated, mostly during the cavity development stage. Excess brines are transported to the brine pond located in a tailing management area (TMA) after they are no longer required in the various extraction and purification activities within the mine site. At the Belle Plaine mine, deep well injection technology is employed to dispose of large quantities excess brine. In 2008, 2.63 million tonnes of salt and 42 dams³ of brine mound were produced and injected (MDH Engineering Solution Corp, 2009). To maintain adequate freeboard and flood storage in the TMA, the volume of excess brine must be carefully monitored and controlled.

According to the EIS for the proposed Belle Plaine Expansion, two deep injection disposal wells have been drilled into the Winnipeg and Deadwood Formation at depths between 2,040 and 2,210 m below the surface. Here, the average brine injection volume is between 3.3 and 4.6 million m³/ year based on data for 2000 to 2005(MDH Engineering Solution Corp, 2009).

Other waste products resulting from the solution mining process, including salt tailings and insoluble solids (silts and clay), also require environmental management infrastructure, monitoring, and controls.

2.4 Deep Well Injection

Deep injection well technology is used to pump liquid waste underground into a deep rock formation by use of high pressure. According to the United States Environmental Protection Agency (U.S. EPA, 2012b), injection wells can be classified into five classes (Figure 2.6). For the purpose of solution mining wastewaters, class II injection wells are recommended. The results of research and monitoring programs indicate that injection wells constitute a safe method to protect and prevent surface and ground water resources contamination from fluid waste migration (U.S. EPA, 2012a).

With the application of high pressures at depth, structural damages may occur in the deep rock formations leading to technology failures or migration of wastes (Lustgarten, 2012). Failures in the structure of injection wells may occur inside of the wells themselves. Although injection wells are constructed using high quality stainless steel, the appearance of internal holes and cracks is possible. Alternatively, there may be connections and fissures that connect shallow geological formations with deeper geology, which may be affected or become worsened by the application of

high pressured. In the field, careful operation is required to ensure that the maximum high pressure allowance is not exceeded. Additionally, alteration and movement of the deep rock formation can occur due to natural disasters, such as an earthquake. Although the risk of this technology failure is minimal, leaked fluid migration may occur due to any one or combination of these three reasons.

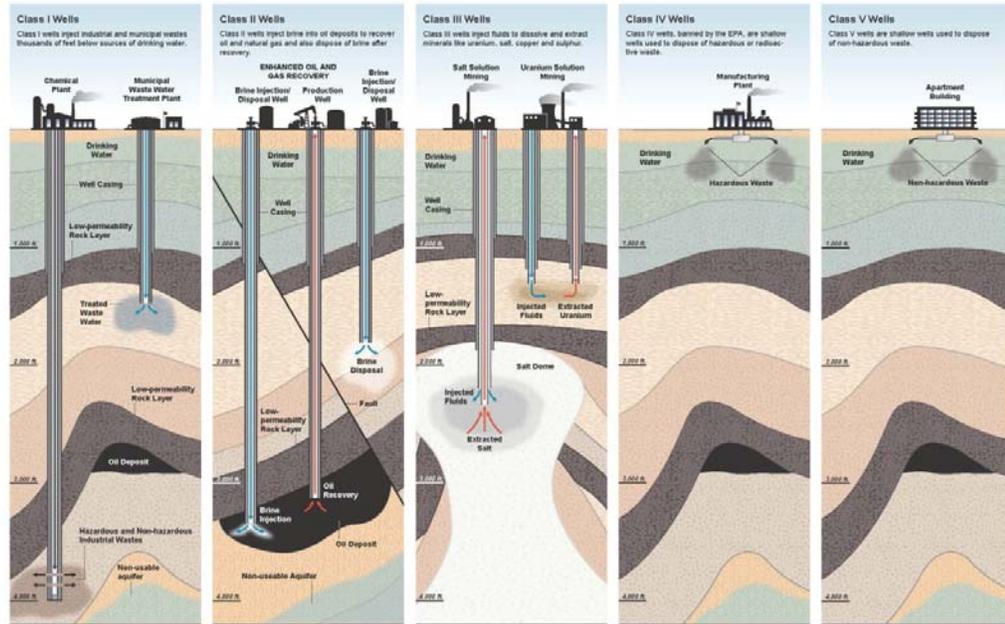


Figure 2.6 Classes of Deep Injection Wells (source: U.S. EPA, 2012b)

Liquid waste migrations have been reported in areas located near deep well injection sites in Runnels County, Texas (Paine et al., 1999; Lustgarten, 2012), an isolated agricultural area in Chico, Texas and the internal site area of Unit Petroleum Company in southern Louisiana (Lustgarten, 2012). Significant impacts were reported in those instances, leading to contamination of water resources related to seepage of liquid waste.

2.5 Brine and Environmental Issues

The failures of deep injection wells and subsurface formations to contain brine and other liquid wastes can lead to serious environmental consequences. Environmental issues such as water resources and soils contamination, imparted change to natural geology, and harm to biotic systems including plants, wildlife and humans can occur due to brine migration from disposal wells.

Increased soil salinity creates problems for agricultural production due to retention of salt in soils, inability of many plants to grow under higher salt conditions, and uptake in the agricultural products themselves (Parida & Das, 2005). Many commercially viable cropped plants cannot fully develop under high salinity conditions due to a hypo-osmotic condition, causing water and nutrients diffuse out from the plant cells to the surrounding environment. In fact, the hypo-osmotic is the movement of water from an area of low concentration of solute into higher solute concentration area. Large concentrations of cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) and anions (Cl^- , SO_4^{2-} , HCO_3^-) that commonly occur in injected, or otherwise disposed of, brine solutions are toxic to plants, leading to the overall impact of dramatically reduced crop productivity (Todorova et al., 2013).

In addition to agricultural productivity challenges, the accumulation and seepage of subsurface liquid wastes can affect or change the geology of the immediate disposal area. According to Lustgarten (2012), the seepage of leaked fluid waste through natural cracks, as associated with impacts of pressure, hydraulic friction, and temperature, has the potential to change the properties of a rock formation. Large amounts of injected and disposed waste fluids over time can also promote formation of new rock types such as an anthropogenic "plastic rocks" that

have been observed in relation to accumulation of plastic waste in Kamilo Beach, Hawaii (Corcoran et al., 2014).

2.6 Constructed Wetlands

Constructed wetlands (CW) are designed, passive biology treatment systems that can be implemented for treatment or polishing of a wide variety of wastewaters. Generally, the two most common types of constructed wetlands are free water surface (FWS) and subsurface flow (SSF) wetlands. Constructed wetlands consist of a constructed pond, populated with wetland plants, media, a bed system and a water distribution system (inlet and outlet). Although CW systems were initially developed to treat organic compounds and suspended solids, most modern CW designs focus on wastewater pollution control in municipal applications (Morari & Giardini, 2009), agricultural and dairy facilities (Dordio & Carvalho, 2013)(Healy et al., 2007), fermented food production (Kantawanichkul, 2009), and pulp and paper mills (Abira, 2008).

Typically, CWs are most effective for the removal of total suspended solids (TSS), oxygen demand (BOD₅ and COD), nitrogen- and phosphorous-based compounds, metals, hydrocarbons and pathogens (Kadlec, 2009). Because of the combination of physical and chemical removal process, such as filtration, settling, precipitation, volatilization and adsorption, along with biological treatment mechanisms, various types of wastewaters can be successfully treated to discharge quality in CW systems (Kadlec, 2009). However, wastewater characterized by high concentrations of ammonia and pesticides can lead to poor treatment efficiencies in CW systems due to biological sensitivities to these toxic chemicals (Pa et al., 1995).

Since their initial application to industrial activities, CWs have been purposefully designed and implemented for treatment and reduction of acid mine drainage (AMD) and tailings produced by a wide variety of mining industries. AMD normally consists of acidity, iron, manganese, aluminum, sulfate and trace metals, CW systems can be designed to remove these contaminants via the combination of physical, chemical and biological processes described earlier. Specifically, settling, precipitation, absorption, ion exchange, biodegradation, and plant uptake mechanisms are essential for treatment of AMD.

Seasonal impacts due to changing weather conditions can produce instability and inconstant removal efficiency in CW systems primarily due to biological systems sensitivity to temperature deviations (Kadlec, 2009). In summer months, weather conditions offer appropriate environments for wetland plants to uptake contaminants and grow. Likewise, microorganisms trend to operate at higher metabolic rates under warm climate conditions, particularly when a constant source of nutrients is available. Thus, the ability of CW systems to effectively remove pollutants is higher in summer than winter seasons. Under cold weather conditions, CWs lose heat and may become ice-covered, causing reduced oxygen availability. To prevent the entire system from freezing, the water level underneath the iced surface functions as an insulation (Kennedy & Mayer, 2002). The insulation layer prevents heat loss and maintains a low level of biological activity to support ongoing wastewater treatment.

Constructed wetlands not only constitute efficient wastewater treatment facilities, but can also reduce flood risks, conserve natural resources and develop wildlife habitats. Although large land areas are required to establish CW systems, the costs of construction, operation and maintenance are considered less expensive when compared to other engineered treatments. In fact, CW treatment processes mainly

consume energy from natural resources such as solar power and biophysical energy (Kennedy & Mayer, 2002).

In addition to challenges with timely and effective cold weather wastewater treatment efficacy (Werker et al., 2002), CW systems are less likely to produce consistent long term treatment performance and require extended treatment times to produce an equivalent wastewater discharge quality as compared with most conventional wastewater treatment designs. Other concerns include potentially lethal build up of trace metals concentrations in aquatic plants and soils/sediments of CWs (Kennedy & Mayer, 2002).

2.7 Regina Clay

Engineered soils in CW systems function as both top soils and liner soils. Top soils provide essential nutrient sources for wetland plants to uptake contaminants and grow. Liner soils are not only recommended for protection of groundwater contamination, but also as a site for enhanced cation exchange capacity (CEC).

For the purposes of this study, the focus is liner soils and, in particular, Regina Clays, which are commonly used as liners and environmental barriers in design due to the predominance of these soils in the natural environment.

According to several researchers, natural clay soils are commonly used to prepare a compacted liner for various applications (Kang & Shackelford, 2010). For instance, clay was employed as an engineered compacted clay liner for the SaskPower CWs located in Estevan, SK. According to the Saskatchewan Power Corporation & Lakshman (1994), the CW system was designed to treat sewage with the maximum capacity of 7,500 m³/d and 5-9 days of hydraulic retention time. Cattails and bulrushes were introduced as the primary aquatic plants responsible for

biological uptake in the system. The results indicate measurable increases in the amounts of Na^+ and Ca^{2+} in both species of plant tissues. With the enhanced microbial metabolism and physical and chemical removal mechanisms, the Estevan SaskPower CW system was also reported to achieve significant removal of Mg^{2+} and Cl^- .

Similarly, the Saskatchewan Ministry of Agriculture recommends heavy clay soil as the best soil texture group for use in manure storage pond liners at intensive livestock operations (Saskatchewan Ministry of Agriculture, 2008). Due to the very low hydraulic conductivity of heavy clay, which is about 0.2 cm/hr, there is significant capacity to prevent seepage from both solid and liquid manure.

The benefits of Regina Clay as a liner material were further reported in the EIS for the Regina Landfill Expansion proposal in terms of preventing groundwater contamination due to landfill leachate migration (AMEC, 2009). The City of Regina plans to use Regina Clay to prepare a soil liner layer in a single composite liner system; Regina Clays are also used as the daily cover material for the landfill expansion project.

Since clays have a high CEC, they can serve as effective salt filters (McKelvey & Milne, 1962). According to McKelvey and Milne's research (1962), by combining compacted bentonite clay and shale into a clay membrane to removal salt ions from a NaCl solution, it was possible to effectively removal salt ions. In their experiment, outflow was collected and the change in normality between inflow and outflow considered as salt filtering ability. The results indicated salt ions removal by ion exchange, with bentonite clay (0.94 N) exhibiting a higher capacity to remove salt ions than shale (0.092N). The researchers also emphasized that the salt filtering

ability could be increased when porosity was reduced due to low permeability (McKelvey & Milne, 1962).

Kang & Shackelford (2010) conducted complementary research with compacted Nelson Farm Clay (NFC) specimens used as a barrier to receive a prepared KCl solution. The study compared membrane efficiency, expressed by difference between initial and final KCl concentration, between natural compacted NFC and compacted NFC modified with 5% (dry weight) sodium bentonite. The results showed that the modified NFC, with 11% specimen volume decrease and 97.3% membrane efficiency, contributed higher salt removal efficiency than unmodified NFC, with 2 % of volume decrease and <1.4% membrane efficiency (Kang & Shackelford, 2010). Therefore, they suggested that salt filtration performance could be enhanced when reduced the size of pore spaces by compacting the clay filter samples.

Based on these and several examples of successful implementation of compacted clays in industrial, agricultural and municipal facilities, it may be considered that compacted clay can be use as a membrane to restrict the migration of chloride salt ions.

3. Materials and Methods

3.1 Soils

Regina Clay, coarse sands and medium angular rocks were three different types of soils selected to function as natural media in order to remove salt ions from a synthetic brine sample solution within this research.

Regina Clay was collected from a house construction site in Harbour Landing, the new developing residential area is located in south of Regina, in June 2012 (Figure 3.1.).

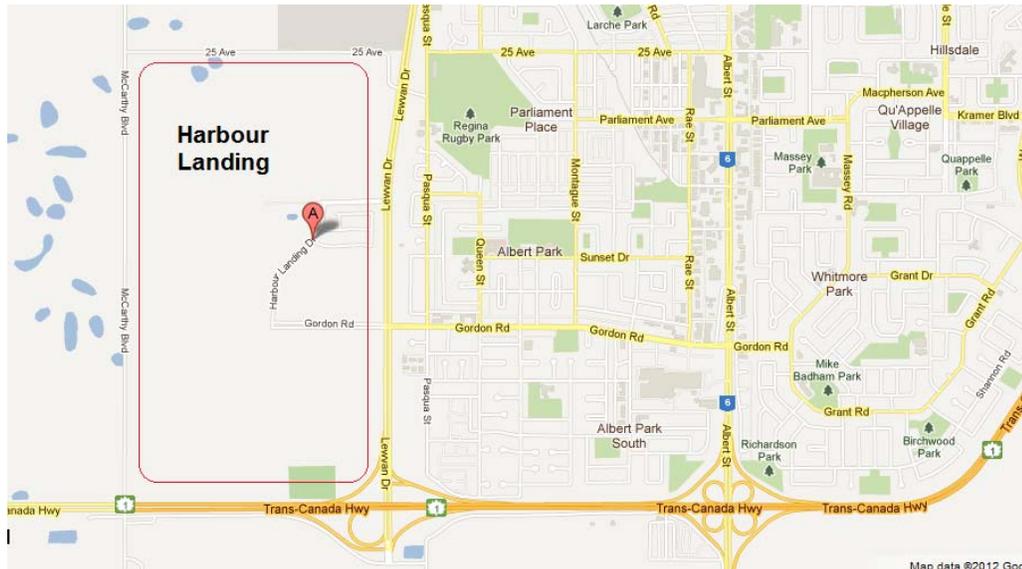


Figure 3.1 Harbour Landing Site Map (source: Google Map)

During the foundation building stage, the housing site was an open-cut pit of approximately 1.3m depth below the ground surface. The clay sample was collected from the surface of a waste clay mound near the pit.

The samples were collected as 60 kg wet samples that were stored in three rectangular plastic containers. The wet clay samples were stored at constant

temperature at 25°C in the Water Analysis Laboratory at the University of Regina until they were completely dried. Approximately 3 kg of the wet clay were selected to evaluate the sample's geotechnical parameters in the Geotechnical Testing Laboratory at the University of Regina (Dr. Azam's laboratory).

Sands and gravels were purchased from Waxy's Bobcat, a local landscaping supplier located in Regina, SK in 2012. The sand layer was designed to perform as the second salt filter layer, and to provide flow path for effluent water. The sand sample was prepared from Brick Sand which is well known as Sharp or River Sand, and is commonly used for building purposes, typically containing a mixture of fine gravels.

The sand sample was initially graded by using sieve size 4 (4.75mm) in order to take all sizes of gravels out before performing the sieve analysis test. Due to the high ability of water transition, the sand layer was primary designed not only to provide drainage system, but it also functions as the second salt filter layer.

Likewise, the gravel layer which also provided the last layer of salt filtration, especially to enhance quality of final effluent was built up by crushed rocks. Although the majority of gravel sample was medium angular rocks, there are various appearances of very fine particles to larger rocks. It was very important to achieve the uniformly graded aggregate due to obtain internal lock supporting from the angular gravel characteristic, and to provide drainage area. Therefore, the gravel sample was graded by sieve size 19.1mm ($\frac{3}{4}$ "') and 6.3mm ($\frac{1}{4}$ "'), so the designated particle size for the gravel sample was ranged between 6.3-19.1mm.

3.2 Soil Physical Properties

The geotechnical index properties of each soil layer were quantified using several different types of ASTM standard methods.

Grain size distribution (GSD), moisture content, and porosity (η) were taken from each individual soil within this study. However, only Regina Clay was additionally tested for consistency limits. The bulk density (D_b) and particle density (D_p) were determined in order to obtain the clay porosity value.

3.2.1 Grain Size Distribution

The ASTM Standard Test Method for Particle-Size Analysis of Soils (D422-63) was used to determine GSD for each soil sample. A hydrometer analysis method was applied on Regina Clay due to its particle size finer than 0.075 mm. Unlike the clay, the GSD of sand and gravel samples were determined by sieve analysis method. The results of this GSD curve production is provided for the three samples (Figure 3.2).

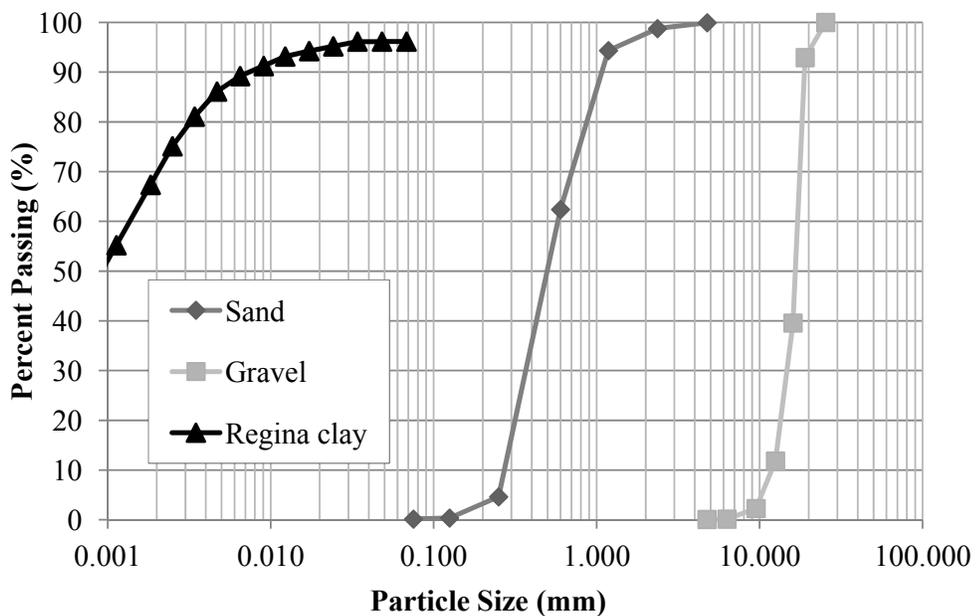


Figure 3.2 Grain size distribution curve of soil samples

3.2.2 Bulk Density

Soil bulk density (D_b) is the ratio of the mass of dry soil to the unit volume of solids and pore spaces. The measurement of bulk density for all samples was performed using the core method.

3.2.3 Particle Density

Particle density (D_p) is expressed as the mass of dry solid particle per the volume of the solids which regardless pore spaces and water. The particle density of each soil samples was determined by the core method.

3.2.4 Porosity

Porosity (η) is the ratio of the volume of soil pores to the total soil volume, and it can be expressed as:

$$Porosity = 1 - \frac{D_b}{D_p}$$

Equation 3.1

Equation 3.1 presents porosity (η) can be determined via the relationship between the bulk density (D_b) and particle density (D_p).

3.2.5 Atterberg Limits

Atterberg limits which is also known as the limits of consistency include liquid limit (LL), plastic limit (PL) and shrinkage limit (SL). Only the liquid and plastic limits were conducted in this study using the ASTM Standard Test Methods for Liquid Limit, Plastic Limit, and Plasticity Index of Soils (D4318-10).

3.3 Synthetic Brine Solution

Sodium chloride (NaCl) and potassium chloride (KCl) are two dominant salts found in the brine solution at the Belle Plaine potash solution mine site. According to the Environment Impact Statement for the Mosaic Belle Plaine Expansion, the concentration of NaCl is approximately ten times greater than that of KCl in the brine (MDH Engineering Solution Corp., 2009). The average concentration of NaCl and KCl measured at eight monitor wells located around the salt tailings ponds at the Belle Plaine facility were 30,000mg/L and 3,000mg/L, respectively. Hence, the ratio of these two major brine solution salts is 10:1 of NaCl:KCl.

Due to design methods intended to minimize chemicals use and simplify industry processes, one liter of the synthetic brine solution was diluted to contain 150mg NaCl/L and 15mg KCl/L. In fact, these concentrations were assigned as the average brine concentrations for this study. Synthetic brine was prepared to serve two purposes, including (1) creation controlled experimental conditions for direct comparison and (2) limited to no access to authentic brine from the mine site.

The one liter of the synthetic influent solution for laboratory experiments was prepared from 300mg of NaCl GR ACS, 30mg of KCl GR ACS and 1liter of deionized (DI) water. Likewise, 5L of the synthetic influent contained 1.5g of NaCl GR ACS, 0.15g of KCl GR ACS and 5L of DI water. For the purposes of this study, the potential influences of salinity generated from CaCl_2 and MgCl_2 due to low concentrations in the brine solution at the Belle Plaine site were ignored.

The influent synthetic brine solutions were prepared in three salt concentrations plus one blank solution comprising pure deionised water and used as a reference solution. The influent synthetic brine solutions were identified as C1, C2, C3, and C4.

In these experiments, the C4 solution represents the highest risk brine concentration, at two times greater than the average concentration. Consequently, one liter of the C4 solution contained 300mg NaCl and 30mg KCl. In contrast, the minimum B2 solution was designed to address the possibility of the lowest concentration by creating a solution two times diluted from the average. Hence, 75mg NaCl and 7.5mg KCl were required to synthesize the C2 solution. The average, or C3, synthetic influent solution contained 150mg NaCl/L and 15mg KCl/L. The preparation details for creation of the 5L influent solutions are presented in Table 3.1.

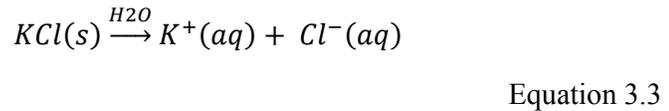
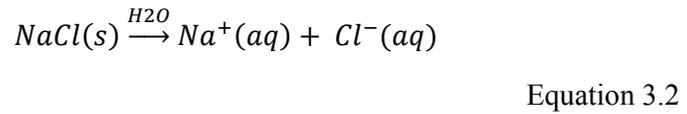
Table 3.1 The series of the synthetic brine portions

Brine Concentration (C)	NaCl (mg/L)	KCl (mg/L)	NaCl:KCl Ratio	Types of Risk
1	0	0	0	None
2	75	7.5	10:1	Lightest Load
3	150	15	10:1	Average Load
4	300	30	10:1	Shock Load

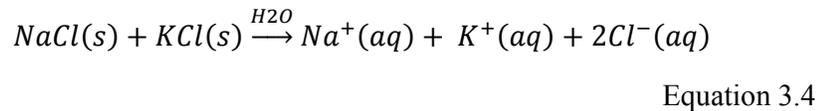
All salt neat chemicals were placed with DI water a 20L plastic cylinder container and rapidly stirred using a half meter clear vinyl tube to achieve complete mixing. Four plastic containers were used to separately mix each individual concentration. All chemical solutions including the synthetic brines were prepared with DI water and a 4 digit scale employed to measure all chemicals masses used in the experiments.

Theoretically, both NaCl and KCl are strong electrolytes due to their extremely high solubility in water. Therefore, the salt crystal structures are completely

dissociated by the polar water molecular when they are dissolved into water. In fact, the sodium ions (Na^+), potassium ions (K^+) and chloride ions (Cl^-) are released as free ions in the solution. The dissociation of each individual chloride salt is represented by Equation 3.2 and Equation 3.3.



Therefore, the dissociation equation of the mixture between two ionic salts in deionised water can be expressed as follows:



According to Equation 3.3, the concentrations of Na^+ and K^+ in each influent solution should be directly relative to the initial concentrations provided in Table 3.1 while the Cl^- concentration should amount to the total concentration sourced from the two chloride salt compounds.

For example, the average B3 brine solution mathematically contains 82.5mg Cl^- , of which 75mg Cl^- was sourced from NaCl and 7.5mg Cl^- from KCl. Similarly, 75mg Na^+ and 7.5mg K^+ are contained in that same B3 aqueous solution. Thus, the concentrations of the three anticipated salt ions as measured using ion selective electrodes (ISEs) Cl-800, K-800, R-503/D and Type 10 205 3064 Na^+ Electrode purchased from WTW reflect the chemical purity of the compounds used as well as the efficiency of dissociation reactions occurring in the creation of the brine solutions. Comparisons between theoretical and laboratory data (mean value

calculating from batch 1 to 3) for concentrations of Na⁺, K⁺ and Cl⁻ in the influent solutions, including standard deviations, are provided in Table 3.2.

Table 3.2 Salt ions concentration in the influent synthetic brine solution, theoretical versus ISEs results

Brine		[Na ⁺]			[K ⁺]			[Cl ⁻]		
Solutions		(mg/L)			(mg/L)			(mg/L)		
Influent	Eq.	Na ⁺ ISE	sd	Eq.	K ⁺ ISE	sd	Eq.	Cl ⁻ ISE	sd	
1	0.0	1.9	1.3	0.0	0.4	0.3	0.0	1.0	0.7	
2	37.5	28.1	6.7	3.8	4.9	0.8	41.3	38.6	1.9	
3	75.0	56.9	12.8	7.5	8.2	0.5	82.5	81.2	0.9	
4	150.0	117.8	22.8	15.0	17.3	1.6	165.0	171.6	4.6	

The laboratory data were collected from the starting point in each batch experiment and also represented the average values amongst the first, second and third batches of experiments.

3.4 Experimental Cell Design

Experimental cells were designed as a non-plug flow construed wetland based on the theory of subsurface and vertical flow wetland treatment. Moreover, the study also intended to simulate the experiment cells as tailing ponds, so the application of Bio plants was not required within this research. Basically, all pilot scale cells included a cell tubes, multi-layers soil, effluent storages and drainage pipes including a seepage collecting system as described in Figure 3.3.

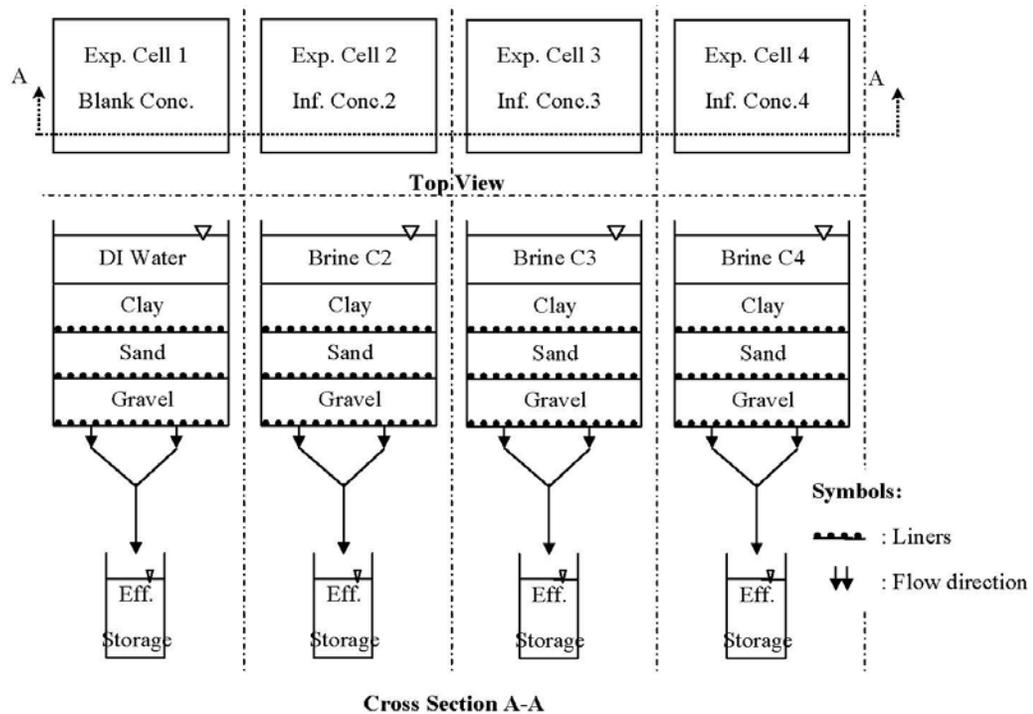


Figure 3.3 Experimental cells drawings

There were four identical experimental cells built to study salt ions reduction on four influent concentrations. Each pilot scale cell was designed and constructed using a clear plastic container known commercially as a 48liter Sterilite. The cell tube size which is controlled by the internal dimension of the container was 61.9cm x 38.4cm x 29.8cm (length x width x height). Indeed, the experimental cells were identified as Cell1, Cell2, Cell3, and Cell4 referring to the treatment units of the control, minimum, average, and maximum concentrations, respectively.

Two circular holes were fitted on the bottom of each cell tube by a drill gun in order to permit drainage (diameter about 1.27mm ($\frac{1}{2}$ ")). To avoid creaking of the plastic container during the process of drain holes creation, only two holes were adequate. If one got clogged, the effluent was able to flow out via the other. The drainage holes position and installation details were shown in Figure 3.4. Each

experiment cell was placed on two wooden laboratory stools, and the space between both drain holes was left to install the seepage flow collection system. Two discharge spouts with diameter of 1.27mm were modified from a plastic insert reducer approximately,



Figure 3.4 Position of the two main discharge pipes

1.27mm x 2.54 mm (diameter x diameter), and installed into the provided holes. To prevent leaking, the internal and external surface of the contacted area between the fittings and the container were sealed by GE Silicone II Sealant, Kitchen & Bath. It was essential to leave all cells to dry in the room temperature for one night to obtain completed dry condition for the sealant.

The weed block fabric was placed under each soil layer functioning as a geosynthetic liner. For sand and gravel layer, the fabric liner was cut in 60cm x 50cm (length x width) rectangular size while the one used in the clay layer was 95cm x 65cm (length x width). The extra area of the liner applied on clay gave more handling

space in the process of compacted clay installation. The geo-synthetic liner not only contributed water permeable ability to the soil layer, but also minimized the migration of soil particles for the top layer to lower layers.

The multi-layer soils simulating a constructed or/and tailing pond design consisted of three soil layer as the details given in Table 3.3.

Table 3.3 Multi-layer soils information

Layers	Soils	Sizes	Conditions	Mass	Thickness
		(mm)		(kg)	(cm)
Top	Regina Clay	Less than 0.075	Dry	10	5
Middle	Brick Sand	Less than 4.75	Dry	16	5
Bottom	Crushed Rocks	6.3 to 19	Dry	11.5	5

The three media layer installation started from building up the bottom layer after first liner was placed in a cell tank. The 11.5kg of dry graded angular gravels ranging in size from 6.3-19mm (retained at sieve size ¼”) were gently placed into the tank, beginning with all corners, sides and center as shown in Figure 3.5. To achieve the desired surface level, a bubble level ruler was employed to create the gradient slope which runs down from the edges to center of the tank. After a gravel layer achieved the well graded surface, geo-synthetic fabric was placed on top.

The second layer was built up with 16kg of dry graded coarse sand (passed sieve size 4). After the tank was filled with the sand, it was compacted by using a round metal soil sample container. The bubble level ruler was also used to ensure the sand layer was a well graded surface as shown in Figure 3.6.



Figure 3.5 Building of the bottom layer

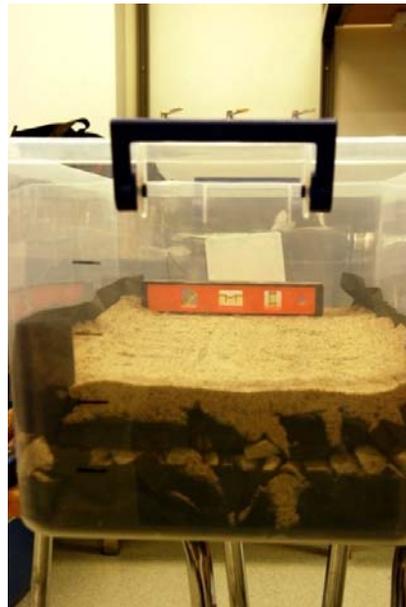


Figure 3.6 Completed sand layer installation

The construction of the top clay layer differed from the previous layer in terms of sample preparation and cell installation. The dry Regina Clay sample was weight 10kg using a typical one digit scale meter, and was initially mixed with 2.5 liters of

DI water in the plastic container. Then the moisten sample was gently transferred on the laboratory cart which contained the geo-synthetic fabric along with a 33.5cm x 53cm (length x width) rectangular wooden frame on top by using a mortar spatula.

The compaction was applied by using a round rubber hammer after the frame was filled full with the moisten clay. When the height of the clay layer was approximately 5cm thick, the compacting process was stopped (Figure 3.7). A marble roller pin was used to create a well graded surface and fine levelling was achieved by using the level ruler.



Figure 3.7 Compaction process

Finally, the wooden frame was removed from the clay sample, and the experimental cell was transferred into the cell tank by lifting up the edges of the extra spaced of the geo-synthetic liner.

Lateral seepage flow occurred from gaps around the cell tank was prevented by watering the top surface and drawing a line around the tanks as shown in Figure 3.8.



Figure 3.8 The prevention of lateral seepage

The seepage flow collecting system conveyed the drainage water from the main drainage pipes which consisted of three pieces of 30cm clear vinyl pipes (internal diameter 15.9mm) and ½” plastic 3-way fitting pipe. The two vinyl pipes were connected to the drainage pipes by steel hose clamps while the other ends were joined with the 3-way pipe. The last pipe conducted for water to the effluent storage. Five liter glass bottles were applied as an effluent storage for each individual experimental cell.

The example of completed experimental cells installation is presented in the Figure 3.9.



Figure 3.9 two examples of completed experimental cells

3.5 Experiment Operating and Sampling

The experiment operation was designed and conducted based on batch scale test. The experiment was run by 3 identical batch systems plus one special test that effluent samples were observed every 6 hours during 4 days. The batch tests were identified as B1, B2, B3, and B4 referring to the batch 1, batch 2, batch 3 and the special batch 4 respectively. All details of the experiment operating and sampling are explained in the Table 3.4.

The B1, B2, and B3 were regularly operated by for 16 days sampling effluent water every 24 hours. Once the experiment had started, 5litters of the influent water were poured into each cell based on four designated salt concentrations everyday for the 13 days (called as treatment stage). In the 14th-16th operational day, 5litters of deionised water were fed in all cells in order to create a cleaning stage. The negative charges on the clay surface could be recharged by water via the action of breaking alumina layer in clay structure (Holtz, 2011). Therefore, clay became being fresh

again after passed the cleaning period. The collection of effluent water was took place after 24 hours. To achieve the accuracy and preciseness of the sampling time, a digital clock stop was employed as a time recorder.

Table 3.4 Batch Experiment Operating

Batch	Cells	Operation Days		Eff.Sampling		Total
(B)	(unit)	Syn. Brine Feeding	Cleaning Stage	Sampling	Format	Samples
1	4	1st - 13th	14th - 16th	1	per 1day	64
2	4	1st - 13th	14th - 16th	1	per 1day	64
3	4	1st - 13th	14th - 16th	1	per 1day	64
4	4	1st-4th	n/a	1	per 6 hrs	64

To prepare the multi soil layer for the next batch, the cleaning stage started from day 14th to the end of experiment, by adding 5litters of DI water instead of the synthetic brine solution into all treatment units. The cleaning stage was to restore the equivalent salt filter ability to the clay layer. Therefore, 64 samples of the effluent water were collected from four treatment units for 16 operational days.

The B4 testing, the design came from the laboratory data of three regular batch experiments, was created to take a closer look at the ability of salt reduction of the clay media via a breakthrough curve. The results from the three previous batch experiments firmly showed that the majority of the salt concentration in effluent samples significantly changed during the first four days. After that, the trend data were likely to be constantly until the end of the batch experiments. To obtain the breakthrough curve, the effluent samples were collected at every 6 hrs for 4 days without performing the cleaning stage. Indeed, the effluent samples were observed

for four times per day. Therefore, the B4 contributed 64 samples of the effluent water from the 4 operational days. The influent synthetic brine solutions and a number of treatment units that were applied in the B4 were identically the same as the regular batch system in term of the concentration and quantity.

All effluent samples obtained from B1, B2, B3 and B4 were transferred from the 5litter glass storage bottle to acid-washed 500ml glass beakers and analyzed immediately for the three introduced salt concentrations. The excess amounts were stored in 125ml and 250ml plastic Nalgene bottles to achieve the room temperature ensuring that any future testing could be accomplished. All deviations between influent and effluent quality were attributed to chemical and physical soil interactions within the experimental cells.

3.6 Water Quality Analyses

All influent and effluent samples of the synthetic brine solution were not only focused on the most critical parameters such as Cl^- , Na^+ , and K^+ , but other essential attributes such as pH, conductivity and total dissolved solid (TDS) were also tested. In addition, the study applied all the mentioned water quality analyses to all influent and effluent samples including pre- and post- treatment. The influent samples were tested only one time at the first day of each batch experiment. The pre-treatment samples were tested for once a day in batch experiment 1-3, and 4 times a day in batch experiment 4. Therefore, there were 4 samples of influent and 64 samples of effluent in each batch. The laboratory took place at the wet chemical laboratory (RIC 445) which is located in the Research and Innovation Center (RIC).

3.6.1 Ion-selective Electrodes (ISEs)

A WTW pH/ION 3400i meter, Cl-800 and K-800 selective electrodes were employed to measure Cl⁻ and K⁺ concentrations. Specially, Na⁺ concentrations were determined using the duo probes between a Type 10 205 3064 Na⁺ Electrode and a R-503/D reference electrode along with the pH/ION 3400i meter. To obtain the accuracy results from the Na ion-selected probe (a glass membrane censor type), the additional reference was required. The calibration solution of the three electrodes were biweekly prepared from a WTW sodium standard solution 10g/L Na⁺ (NaCl) and a WTW potassium standard solution 10g/L K⁺ (KCl). All ion-selective electrodes, the pH meter and the WTW standard solution were purchased from Hoskin Scientific, Vancouver, Canada.

3.6.2 pH

An Eco Testr pH2 (Fisher Scientific, Edmonton, Canada) calibrated with VWR pH buffer standard solutions pH 4, 7 and 10 was applied to determined pH in the study.

3.6.3 Conductivity, Salinity, and Total Dissolved Solid

Conductivity, salinity and total dissolved solid (TDS) were measured by an ExStik II model EC500 multi-electrode probe (Fisher Scientific, Edmonton, Canada). Extech Conductivity Standard solutions 84 µS, 1413 µS and 12880 µS a long with a Rinse Solution (pH 103-RS-20ml pouch) were used to calibrate the meter. The room temperature was also observed with the ExStik probe.

3.6.4 Alkalinity

According to Standard methods for the examination of water and waste water (Eaton et al., 1998) alkalinity was analyzed based on the total alkaline titration

method (2320 B. Titration Method) to estimate the amount of bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and hydroxide (OH^-) concentrations.

All samples were collected from the experimental cells on a regular basis to identify trends and time to initial breakthrough. Table 3.5 notes the timing for samples analysed in the batch experiments.

Table 3.5 Water Quality Analyses

Time		Testing	Inff. Samples				Eff. Samples from Cells				Equipments &	Remarks
(min)	(hr)		C1	C2	C3	C4	Cell1	Cell2	Cell3	Cell4	Methods	
0	0	Collecting Effl.Samples	n/a	n/a	n/a	n/a	y	y	y	y	500 ml glass beakers	y, yes
15	0.25	pH, Cond., S, TDS	y	y	y	y	y	y	y	y	Eco Testr pH2 & ExStik	n/a, not applicable
45	0.75	Alkalinity	y	y	y	y	y	y	y	y	Titration Method	
60	1	Chloride ion, Cl-	y	y	y	y	y	y	y	y	pH/ION 3400i meter & Cl 800	
120	2	Potassium ion, K+	y	y	y	y	y	y	y	y	pH/ION 3400i meter & K 800	
180	3	Sodium ion, Na+	y	y	y	y	y	y	y	y	pH/ION 3400i meter Na+ Electrode & R-503/D	
240	4	Closing Daily Testing										

3.7 Data Analysis

The primary laboratory data were compiled using an Excel spreadsheet version Microsoft Office 2007 for all basic mathematic calculations. The trend data were plotted on time-sequence figures to illustrate changes in all parameters over time.

The statistical software named an IBM SPSS Statistics version 20 was applied to analyze the data for essential descriptive statistics along with multiple comparison and correlation parameters. The secondary data acquired from the Excel spreadsheet was initially tested for normal distribution mean (z curve and histogram), variance, standard deviation, standard error based, p-value and correlation (r) based on 95% confidence interval. If the data were indicated as a non-parametric data, alternative statistical tests such non parametric mean (t-table), Spearman's rho correlation test and Kruskal-Wallis independent samples test were applied. Otherwise the normal data were analysed via t-test, One-Way ANOVA test, post hoc multiple comparison (Tukey and Duncan tests) and Pearson correlation test.

The significant of means comparison at for both parametric and non-parametric data sets 95% confidence interval were imparted via a p-value. Also, the correlative results between a pair, or group of data were shown as a r-value and plotted as trend lines via a graph function within this program.

4. Results and Discussion

The full scale CW systems were performed to test the chloride salts removal abilities receiving the synthetic brine solutions in fall semester 2013. In particular, the first demo system testing was operated for 25 days in August 2013. The purposes were mainly to practice installing the multi-soil layers and working with ion selective electrodes (ISEs). Then the full scale experiments were conducted in between October to December 2013. The information on geotechnical properties of soils and characteristic of synthetic brine solutions will be presented in this chapter. Secondly, the laboratory results on all parameters (Na^+ , K^+ , Cl^- , conductivity, TDS, salinity, pH, temperature and alkalinity) will be discussed. Finally, the last section provides the results of break through curves on chloride salt ions.

4.1 Geotechnical Properties of Soils

The geotechnical properties of Regina Clay samples, as measured and calculated in this research, are summarized in

Table 4.1. The data include presentation of the relevant parameters between both natural and compacted conditions, as well as those data prepared and presented by (Ito, 2009). Bulk density (D_b) was measured to be 0.84g/cm^3 and 1.40g/cm^3 while particle density (D_p) was 2.09g/cm^3 and 2.21g/cm^3 for natural and compacted samples, respectively. The measured bulk density did not meet the criteria for achieving compacted conditions ($D_b > 1.6\text{g/cm}^3$) due to limited instrumental options

for applying heavier pressures on the clay sample in the experimental cells without cracking of plastic containers.

Table 4.1 Geotechnical properties of Regina Clay

Properties	Units	Conditions			Test Methods
		Natural	Compacted	0-1.5 m Depth*	
		Mean±se (n=2, t _{df} =12.71)			
Ave. Bulk Density	g/cm ³	0.8 ± 0.3	1.4 ± 1.6	-	Core Method
Ave. Particle Density	g/cm ³	2.1 ± 0.2	2.2 ± 1.2	-	Core Method
Porosity		0.60	0.37	-	Eq.3.1
Bed Volume	cm ³	4,504	2,742	-	Eq.4.1
Liquid Limit	%	74.5	n/a	76.9	D4318-10
Plastic Limit	%	28.3	n/a	27.1	D4318-10
Plastic Index	%	46.3	n/a	49.8	LL-PL

*data reported from Ito (2009)

These indicate that the volume of void space in the compacted clay was reduced to approximately 40% of its natural state following application of pressure.

$$\eta = \frac{V_v}{V_T} = \frac{BV}{V_T}$$

Equation 4.1

Bed volumes (BV) of natural and compacted clay samples were determined via the relationship between Porosity (η) and the total volume of clay layer (V_T) as stated in the Equation 4.1.

The measured liquid limit (w_l), plastic limit (w_p) and plastic index (I_p) for the clay sample were 74.53%, 28.28% and 46.25%, respectively. Excluding a shrinkage limit, the measured Atterberg limits are corresponding with Ito's (2009) work at the depth 0-1.5m of Regina Clay. Due to the massive amount of specific surface area of the clay particles, high capacity of water adsorption and retention of the clay sample was expected from the clay samples containing high value of liquid and plastic limits along with plastic index (Ito, 2009).

Figure 4.1 provides the information on GSD curve for all three selected materials including the reference data. Based on one-time performance of hydrometer testing, the GSD curve of clay sample was compared to another research in order to insure the quality of obtained data. In fact, the reference data not only provided particle size of Regina Clay at depth 0 to 1.5m below the ground surface, but also showed the comparison in term of uniformity of clay particle size between these two researches outcomes. The clay sample characterized 95% of its grain size smaller than 0.075 mm, and contained 70% portion of material finer than 0.002 mm.

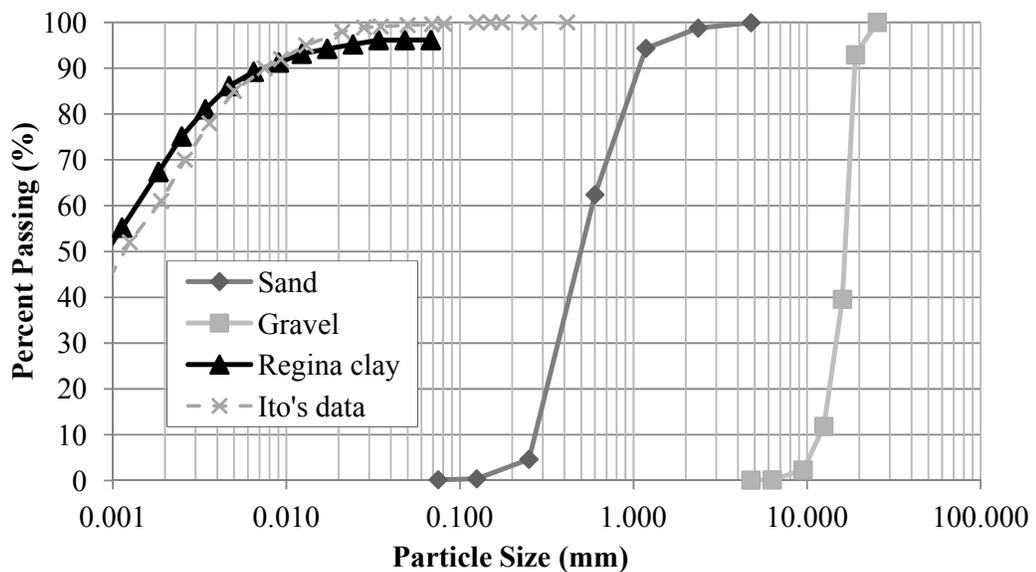


Figure 4.1 Grain size distribution curve of soil samples

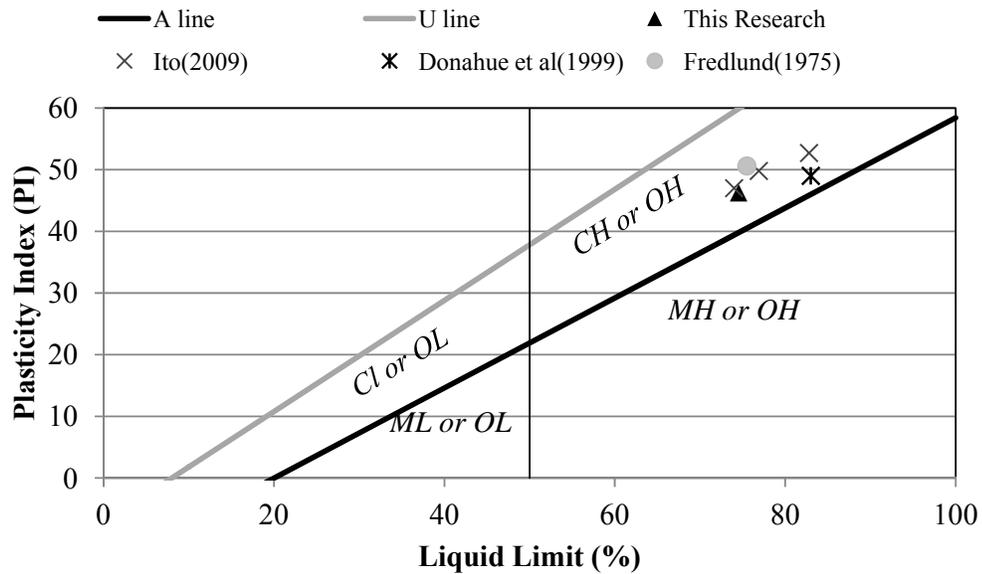


Figure 4.2 Simple Plasticity Chart (modified from Ito, 2009). Where nCl or CL= low plasticity clay, CH=high-plasticity clay, OH=high plasticity organic soil, OL=, MH=high plasticity silt, ML=low plasticity silt.

The plasticity chart of the clay sample along with relative works on Regina Clay such as Ito (2009), Donahue et al (1999) and (Fredlund, 1975) is presented in Figure 4.2. According to the Unified Soil Classification System (USCS), the clay sample was classified as CH (highly plastic clay).

$$C_u = \frac{d_{60}}{d_{10}}$$

Equation 4.2

$$C_c = \frac{(d_{30})^2}{(d_{60})(d_{10})}$$

Equation 4.3

The coefficient of uniformity (C_u) and coefficient of curvature (C_c) for sand and gravel samples corresponding to 10%, 30% and 60% passing (d_{10} , d_{30} and d_{60}) in Figure 4.1. In fact, C_u and C_c were determined using Equation 4.2 and Equation 4.3.

Based on the GSD graph, the sand sample characterized $d_{10} = 0.27$, $d_{30} = 0.38$ and $d_{60} = 0.60$ mm, and the coefficient factors C_u and C_c were determined to be 2.22 and 0.89, respectively. According to Hoffmann et al.(2011), the recommended d_{10} of sand applying as a substrate in subsurface flow CWs should range between 0.1-0.4mm. The filter bed could be degraded its performance if sand sample contained d_{10} coarser than 0.4mm, For the gravel samples, d_{10} , d_{30} and d_{60} were read as 12.0, 15.5 and 18.0 mm, respectively with a $C_u = 1.50$ and $C_c = 1.11$ respectively. Apparently, gravels contained higher value of both coefficients than sands due to greater grain diameter sizes.

According to the ASTM Standard Practice for Classification of Soils for Engineering Purposes (D2487-06), poorly graded sands (SP) ranges between $C_u < 6$ and/or $1 > C_c > 3$ while the criteria $C_u < 4$ and/or $1 > C_c > 3$ are suggested for poorly graded gravels (GP). Therefore, both sand and gravel samples were classified to be poorly (uniformly) graded aggregates. Another word, only selected grain particle sizes retained among the two soil samples.

4.2 Synthetic Brine Characteristics

The characteristics of the synthetic brine fed into all experimental cells during the first, second and third batch experiments are presented in Table 4.2. Although, all cells daily received 5litters of the synthetic brine for 13 days, the samples of influent water were observed only once at the beginning of each batch experiment.

The influent qualities were extremely high in term of electrolyte ion concentrations with very light amount of alkalinity. The ion of electrolyte trend directly relates to the NaCl:KCl ratio which are higher from the first to the forth experimental cells. In fact, those ratios were calculated from the mean values of Na⁺, K⁺ and Cl⁻ from Cell2 to Cell4 in the first three phases. The values from control cell in all batch experiments were neglected with in this calculation. Moreover, electrolyte ions contribute high concentration of conductivity, salinity and total dissolve solid (TDS).

Table 4.2 Characteristics of synthetic brine fed into all cells during the batch experiment 1-3. All data provided mean values with standard errors based on 95% confidential interval (n =3 and t_{df} = 4.303).

Parameters		Batch 1 - 3			
		<i>16 days format</i>			
Chemical Statistical		Cell 1	Cell 2	Cell 3	Cell 4
Na ⁺ mg/l	range	2.0 - 1.7	28.4 - 27.6	59.3 - 55.3	121.3 - 115.8
	sd	0.2	0.5	2.1	3.1
	Mean±se	1.9 ± 0.4	28.1 ± 1.1	56.9 ± 5.2	117.8 ± 7.6
K ⁺ mg/l	range	0.5 - 0.3	5.7 - 3.4	9.3 - 6.3	20.4 - 14.2
	sd	0.1	1.3	1.6	3.1
	Mean±se	0.4 ± 0.3	4.9 ± 3.2	8.2 ± 4.0	17.3 ± 7.8
Cl ⁻ mg/l	range	1.5 - 0.4	42.6 - 35.5	86.8 - 76.6	176.0 - 164.5
	sd	0.6	3.7	5.2	6.2
	Mean±se	1.0 ± 1.4	38.6 ± 9.1	81.2 ± 12.8	171.6 ± 15.4
Cond. µS/cm	range	18.0 - 11.5	192.1 - 182.1	369.0 - 355.5	732.5 - 712.0
	sd	3.6	5.4	7.5	11.8
	Mean±se	13.8 ± 9.0	188.3 ± 13.5	364.2 ± 18.7	725.7 ± 29.4
Salinity ppm	range	11.5 - 6.0	96.1 - 91.0	184.0 - 177.5	366.0 - 355.5
	sd	2.8	2.8	3.8	5.6
	Mean±se	8.8 ± 6.8	94.2 ± 6.9	181.8 ± 9.3	361.8 ± 13.9
TDS mg/l	range	12.6 - 8.0	134.4 - 127.4	258.0 - 248.5	512.5 - 498.0
	sd	2.5	3.8	5.5	8.4
	Mean±se	9.7 ± 6.3	131.8 ± 9.5	254.8 ± 13.6	507.7 ± 20.8
Temp. °C	range	21.1 - 19.7	21.1 - 20.3	20.7 - 20.2	20.9 - 20.0
	sd	0.7	0.4	0.3	0.5
	Mean±se	20.4 ± 1.7	20.8 ± 1.0	20.5 ± 0.7	20.5 ± 1.2
pH	range	7.4 - 6.3	7.0 - 6.4	6.8 - 6.4	6.7 - 6.4
	sd	0.6	0.3	0.2	0.2
	Mean±se	6.7 ± 1.5	6.7 ± 0.7	6.6 ± 0.4	6.5 ± 0.5
Alkalinity mg/l as	range	4.0 - 4.0	6.0 - 6.0	10.0 - 6.0	10.0 - 8.0
	sd	0.0	0.0	2.3	1.2
CaCO ₃	Mean±se	4.0 ± 0.0	6.0 ± 0.0	7.3 ± 5.7	9.3 ± 2.9

Table 4.3 Characteristics of the synthetic brine fed into the batch experiment 4

Parameters	Batch 4			
	<i>4days format</i>			
	Cell 1	Cell 2	Cell 3	Cell 4
Na ⁺ , mg/l	1.8	22.8	51.0	111.3
K ⁺ , mg/l	0.5	3.3	6.1	14.7
Cl ⁻ , mg/l	1.2	36.6	83.2	188.3

Parameters		Batch 1 - 3			
		<i>16 days format</i>			
Chemical	Statistical	Cell 1	Cell 2	Cell 3	Cell 4
Na ⁺ mg/l	range	2.0 - 1.7	28.4 - 27.6	59.3 - 55.3	121.3 - 115.8
	sd	0.2	0.5	2.1	3.1
	Mean±se	1.9 ± 0.4	28.1 ± 1.1	56.9 ± 5.2	117.8 ± 7.6
K ⁺ mg/l	range	0.5 - 0.3	5.7 - 3.4	9.3 - 6.3	20.4 - 14.2
	sd	0.1	1.3	1.6	3.1
	Mean±se	0.4 ± 0.3	4.9 ± 3.2	8.2 ± 4.0	17.3 ± 7.8
Cl ⁻ mg/l	range	1.5 - 0.4	42.6 - 35.5	86.8 - 76.6	176.0 - 164.5
	sd	0.6	3.7	5.2	6.2
	Mean±se	1.0 ± 1.4	38.6 ± 9.1	81.2 ± 12.8	171.6 ± 15.4
Cond. µS/cm	range	18.0 - 11.5	192.1 - 182.1	369.0 - 355.5	732.5 - 712.0
	sd	3.6	5.4	7.5	11.8
	Mean±se	13.8 ± 9.0	188.3 ± 13.5	364.2 ± 18.7	725.7 ± 29.4
Salinity ppm	range	11.5 - 6.0	96.1 - 91.0	184.0 - 177.5	366.0 - 355.5
	sd	2.8	2.8	3.8	5.6
	Mean±se	8.8 ± 6.8	94.2 ± 6.9	181.8 ± 9.3	361.8 ± 13.9
TDS mg/l	range	12.6 - 8.0	134.4 - 127.4	258.0 - 248.5	512.5 - 498.0
	sd	2.5	3.8	5.5	8.4
	Mean±se	9.7 ± 6.3	131.8 ± 9.5	254.8 ± 13.6	507.7 ± 20.8
Temp. °C	range	21.1 - 19.7	21.1 - 20.3	20.7 - 20.2	20.9 - 20.0
	sd	0.7	0.4	0.3	0.5
	Mean±se	20.4 ± 1.7	20.8 ± 1.0	20.5 ± 0.7	20.5 ± 1.2
pH	range	7.4 - 6.3	7.0 - 6.4	6.8 - 6.4	6.7 - 6.4
	sd	0.6	0.3	0.2	0.2
	Mean±se	6.7 ± 1.5	6.7 ± 0.7	6.6 ± 0.4	6.5 ± 0.5
Alkalinity mg/l as	range	4.0 - 4.0	6.0 - 6.0	10.0 - 6.0	10.0 - 8.0
	sd	0.0	0.0	2.3	1.2
CaCO ₃	Mean±se	4.0 ± 0.0	6.0 ± 0.0	7.3 ± 5.7	9.3 ± 2.9

Table 4.3 shows the synthetic brine qualities fed into all operational cells during the batch 4. In term of salts and chloride ions concentration, there was no significant difference ($p < 0.05$) between the 16 and 4 day formats and between cells with different batch operation.

Due to effluent sampling collected in every 6 hrs, influent water qualities that were daily fed in 5liters were measured only one time at the starting point in order to

confirm and define breakthrough curves in the salts compounds. Therefore, only Na^+ , K^+ and Cl^- concentrations were observed within this batch experiment.

4.3 Ionic of salt compounds removal: Batch 1-3

4.3.1 Sodium Ion (Na^+)

Table 4.4 presents average Na^+ concentration and its unimpressive percent removal results in outflow throughout the first three batch experiments. Removing of Na^+ was not occurred at any treatment days (day 1st-13th) in a control cell showing as negative mean values. The reduction of sodium ions was observed in Cell2, Cell3 and Cell4. The concentration of Na^+ was significantly reduced between the first three days of the treatment process as shown in Figure 4.3.

Cell2, the maximum removal rate was found as $32.6 \pm 85.8\%$. Another word, the CW system had ability to removed 9.1 ± 24 mg/l of Na^+ out from the initial concentration (28.1 ± 1.1 mg/l).

Cell 3, the deduction rate of Na^+ concentration ranged between $16.2 \pm 14.9\%$ - $33.6 \pm 102.8\%$ along with 19.25 ± 58.4 mg/l of the highest removal result from the influent concentration (56.90 ± 5.2 mg/l). In fact, the plotted line was likely to be a positive parabola shape at the first four days, and a declined straight line shown the ability of Na^+ reduction was slightly decreased.

Likely in Cell4, the plotted line indicated the best performance of Na^+ reduction occurred on the first four days. In addition, Cell4 contributed between 20.3 ± 27.5 mg/l ($17.3 \pm 24\%$) - 53.2 ± 92.4 mg/l ($44.8 \pm 76.7\%$) of Na^+ removal from the mean initial concentration (117.77 ± 7.6 mg/l) recorded on the first treatment day.

In the cleaning stage (day 14th-16th), Na⁺ concentration decreased in the control and treatment cells because of feeding in DI water caused Na⁺ concentration to be diluted.

Based on 144 samples of three experimental cell excluding the control data, statistical data revealed no significantly different ($p < 0.05$) in term of Na⁺ removal efficiency between all treatment cells due to obtained p-value as 1.00 and 0.97 via Turkey HSD and Duncan post hoc tests, respectively. However, all treatment cells had significantly higher ability to remove Na⁺ when compared to the control cell ($p = 0.00$). Although standard error bars which are shown in Figure 4.3 are likely wide in range, positive mean value indicates that sodium ion has potential to be removed in higher concentration ratio of the synthetic influent.

Table 4.4 Mean values with standard errors of outflow Na⁺ concentration and removal efficiency based on at 95% confidential interval (n =3 and t_{df} = 4.303). The brine feeding stage started from 1st to 13th while the cleaning state ranged between 14th to the end. In addition, all experimental data were corrected per the controls.

Treatment Time (Day)	Mean±se Na ⁺ outflow, mg/l				Mean±se Na ⁺ removal efficiency, %			
	<i>Batch 1-3 (16 days format)</i>							
	Cell 1	Cell 2	Cell 3	Cell 4	Cell 1	Cell 2	Cell 3	Cell 4
Start point	1.9 ± 0.4	28.1 ± 1.1	56.9 ± 5.2	117.8 ± 7.6	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
1	10.0 ± 13.0	19.0 ± 24.7	37.6 ± 57.0	64.5 ± 87.1	-422.3 ± 577.7	32.6 ± 85.8	33.6 ± 102.8	44.8 ± 76.7
2	10.0 ± 13.4	22.2 ± 23.3	40.2 ± 44.8	69.4 ± 84.5	-423.9 ± 590.8	21.2 ± 80.6	29.2 ± 81.3	40.7 ± 74.5
3	9.7 ± 13.5	23.0 ± 17.9	44.9 ± 25.0	90.2 ± 72.0	-408.4 ± 604.4	18.1 ± 61.5	20.7 ± 47.8	23.0 ± 65.1
4	10.2 ± 18.6	24.5 ± 24.9	43.1 ± 14.0	86.5 ± 36.1	-429.3 ± 851.5	13.0 ± 86.2	24.1 ± 27.9	26.3 ± 34.7
5	10.1 ± 18.9	23.8 ± 17.1	43.4 ± 4.7	89.7 ± 14.2	-419.3 ± 865.9	15.5 ± 58.5	23.7 ± 10.9	23.7 ± 16.7
6	10.2 ± 20.1	21.8 ± 6.0	44.2 ± 3.6	90.9 ± 15.1	-424.2 ± 926.6	22.3 ± 18.7	22.3 ± 3.3	22.8 ± 11.9
7	9.0 ± 15.7	22.3 ± 7.1	46.2 ± 4.4	93.9 ± 19.2	-365.8 ± 715.3	20.6 ± 23.6	18.8 ± 11.7	20.3 ± 17.1
8	8.7 ± 15.0	23.2 ± 6.2	47.5 ± 2.6	93.2 ± 36.1	-349.8 ± 679.5	17.2 ± 21.7	16.4 ± 12.0	20.9 ± 31.4
9	8.6 ± 14.7	22.4 ± 4.2	46.9 ± 3.7	93.4 ± 21.5	-342.9 ± 666.6	20.1 ± 14.2	17.4 ± 12.1	20.6 ± 18.6
10	8.2 ± 13.9	21.9 ± 2.4	46.9 ± 0.6	97.5 ± 30.0	-323.8 ± 632.0	22.1 ± 7.9	17.5 ± 7.6	17.3 ± 23.9
11	7.6 ± 13.0	22.3 ± 3.2	47.6 ± 4.9	96.8 ± 34.4	-293.9 ± 589.7	20.3 ± 14.2	16.2 ± 14.9	17.8 ± 29.9
12	7.9 ± 15.4	21.1 ± 2.0	46.1 ± 4.0	95.4 ± 32.0	-309.1 ± 704.8	24.7 ± 10.2	18.8 ± 12.4	19.0 ± 26.6
13	8.0 ± 16.3	20.8 ± 3.9	46.3 ± 5.3	94.3 ± 34.9	-311.9 ± 750.2	25.9 ± 16.8	18.6 ± 12.5	19.9 ± 29.7
14	7.0 ± 12.3	16.6 ± 7.8	38.6 ± 5.0	90.4 ± 21.4	-263.9 ± 556.8	41.0 ± 25.5	32.0 ± 14.4	23.2 ± 17.2
15	7.0 ± 12.0	11.8 ± 9.9	28.8 ± 12.3	76.7 ± 12.2	-262.1 ± 541.0	58.1 ± 34.1	49.3 ± 24.4	34.8 ± 9.4
16	6.3 ± 8.3	9.3 ± 6.2	21.6 ± 5.8	56.2 ± 4.6	-231.1 ± 360.0	67.1 ± 21.0	61.9 ± 12.8	52.3 ± 1.0

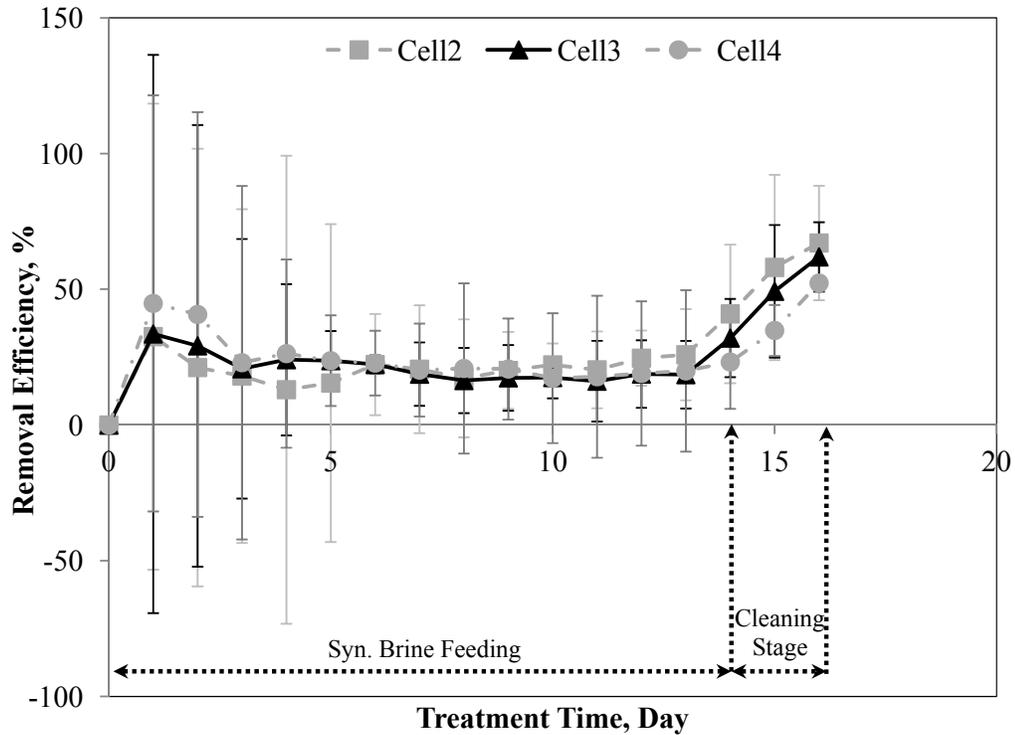


Figure 4.3 The efficiency of Na⁺ removal recorded on Cell2, Cell3 and Cell4 during 3 batch experiments. The data from control cell was ignored due to extremely dissimilar data range.

4.3.2 Potassium Ion (K⁺)

Disregarding the control cell, the removal efficiency of K⁺ showing as positive values in Table 4.5 was taken place among treatment cells. Figure 4.4 shows all graphic lines represented the relationship between the average percentage removal of K⁺ and date of experiment.

Cell2, the K⁺ concentration was reduced between 3.2±4.8mg/l (60.8±70%) - 4.6±5.2 mg/l (92.1±63.4 %). The plotted line was tended to be a positive inclined straight line indicated the removal efficiency increasing for the start point to the twelfth treatment day before slightly decreasing on the last day of the treatment process (day 13th).

Cell3, the plotted line representing the percent K^+ removal tended to be a straight line with a few drops. The drops referred to less performance of the K^+ reduction so higher amount of K^+ concentration was observed, and the percent removal were decreased. The highest removal rate was noted as $80.6 \pm 32.2\%$, so about 6.7 ± 5.5 mg/l was removed from its mean initial concentration (8.20 ± 4 mg/l), respectively.

Cell4, the maximum removal rate was recorded as $87.6 \pm 28.3\%$ referring to 15.3 ± 10.8 mg/l of K^+ was deducted from its initial concentration. In contrast, the lowest K^+ removal was observed as 80.8 ± 27.4 or 13.9 ± 6.8 mg/l out of its mean initial concentration (17.3 ± 7.80 mg/l). The percentage removal of K^+ plotted line was a straight line generally steady over a period of experiment. There was not significantly changed after the first experimental day.

In terms of cell performance comparisons, all treatment cells had significantly higher ability to remove K^+ when compared to the control cell ($p = 0.00$). However, there were no significantly difference ($p < 0.05$) in term of K^+ removal efficiency between all treatment cells. The p-values obtained from the multiple comparisons with Turkey HSD and Duncan post hoc tests were 0.99 and 0.81, respectively. The results were determined based on 48 samples of each experimental cell.

Table 4.5 Mean values with standard errors of outflow K⁺ concentration and removal efficiency based on at 95% confidential interval (n =3 and t_{df} = 4.303). The brine feeding stage started from 1st to 13th while the cleaning state ranged between 14th to the end. In addition, all experimental data were corrected per the controls.

Treatment Time (Day)	Mean±se K ⁺ outflow, mg/l				Mean±se K ⁺ removal efficiency, %			
	<i>Batch 1-3 (16 days format)</i>							
	Cell 1	Cell 2	Cell 3	Cell 4	Cell 1	Cell 2	Cell 3	Cell 4
Start point	0.4 ± 0.3	4.9 ± 3.2	8.2 ± 4.0	17.3 ± 7.8	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
1	2.1 ± 2.5	1.2 ± 3.8	1.5 ± 2.1	2.1 ± 3.5	-391.9 ± 629.6	68.1 ± 115.7	80.6 ± 32.2	87.1 ± 23.2
2	1.7 ± 1.6	1.7 ± 1.6	2.0 ± 1.3	2.7 ± 3.9	-333.7 ± 667.5	60.8 ± 70.0	76.2 ± 9.1	82.7 ± 30.4
3	1.9 ± 2.0	1.2 ± 2.0	1.8 ± 1.2	2.6 ± 3.3	-366.5 ± 720.7	70.0 ± 68.8	77.5 ± 16.7	84.1 ± 23.7
4	2.3 ± 2.9	1.1 ± 0.9	1.9 ± 1.1	2.6 ± 3.0	-470.4 ± 941.2	75.2 ± 39.8	76.7 ± 6.8	83.8 ± 21.2
5	1.7 ± 2.4	1.2 ± 1.1	2.1 ± 0.8	2.8 ± 3.2	-338.1 ± 859.3	72.1 ± 45.2	74.0 ± 10.3	83.3 ± 21.4
6	2.4 ± 4.1	0.5 ± 1.5	1.8 ± 2.1	2.1 ± 5.0	-521.1 ± 1326.7	90.4 ± 25.2	77.8 ± 22.3	87.6 ± 28.3
7	2.0 ± 1.5	1.1 ± 1.7	2.5 ± 1.8	2.6 ± 4.8	-384.9 ± 545.9	75.8 ± 38.9	67.8 ± 28.5	84.2 ± 28.0
8	2.6 ± 3.3	0.3 ± 3.1	1.7 ± 3.4	2.2 ± 6.3	-539.5 ± 922.5	92.1 ± 63.4	78.2 ± 44.3	86.8 ± 35.9
9	1.7 ± 1.4	1.1 ± 0.5	2.4 ± 0.4	2.7 ± 3.4	-321.9 ± 600.6	75.0 ± 32.7	69.3 ± 18.6	85.0 ± 18.2
10	1.9 ± 0.8	0.6 ± 1.9	1.9 ± 2.2	2.2 ± 4.3	-348.7 ± 393.1	85.1 ± 51.0	75.9 ± 30.5	87.5 ± 24.4
11	1.4 ± 0.5	1.0 ± 0.7	2.3 ± 1.0	2.9 ± 3.4	-237.9 ± 323.1	76.5 ± 30.1	71.5 ± 10.1	83.6 ± 15.7
12	1.3 ± 1.0	0.7 ± 0.2	1.9 ± 0.6	2.5 ± 3.5	-222.8 ± 423.1	85.0 ± 17.0	76.8 ± 11.7	85.7 ± 19.0
13	1.3 ± 0.8	1.0 ± 1.3	2.6 ± 1.2	3.4 ± 5.0	-226.3 ± 383.8	77.3 ± 38.8	67.4 ± 15.6	80.8 ± 27.4
14	1.7 ± 1.8	0.6 ± 1.8	1.5 ± 2.4	2.8 ± 5.2	-301.9 ± 421.1	85.5 ± 44.6	80.4 ± 29.1	83.8 ± 29.6
15	1.6 ± 1.5	0.5 ± 0.8	1.5 ± 1.2	2.7 ± 3.9	-283.5 ± 605.4	90.6 ± 12.8	82.2 ± 7.8	85.1 ± 20.6
16	1.8 ± 1.7	0.0 ± 1.8	0.9 ± 1.0	1.8 ± 2.0	-318.6 ± 461.0	97.8 ± 35.4	88.6 ± 14.0	89.7 ± 6.7

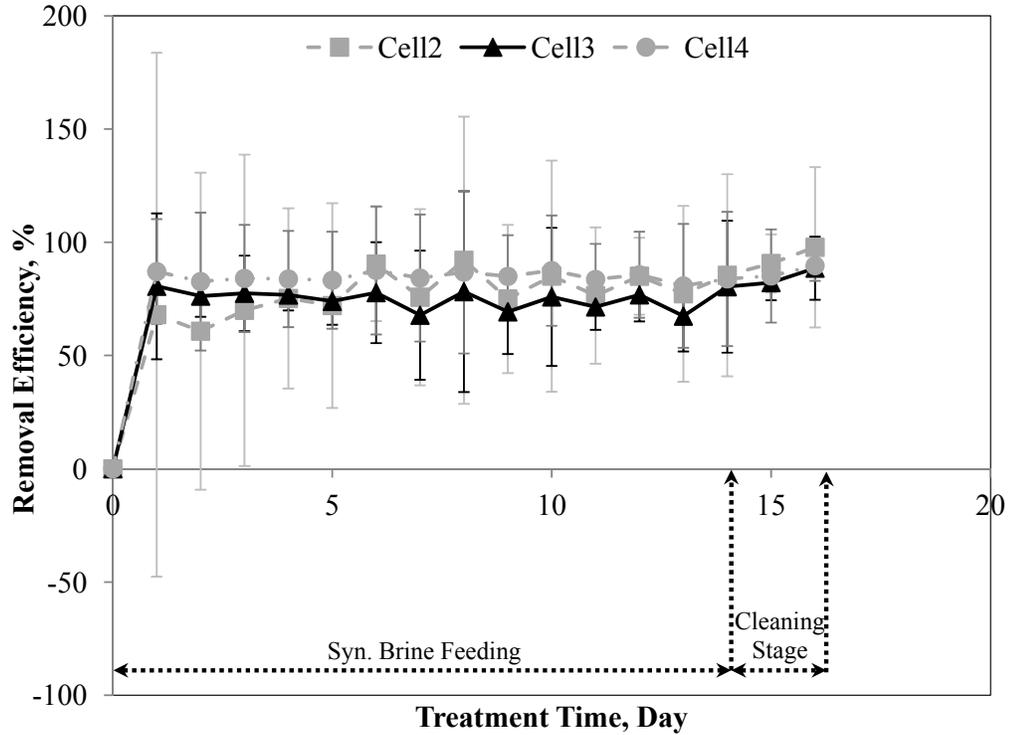


Figure 4.4 K^+ removal efficiency recorded on Cell2, Cell3 and Cell4 during 3 batch experiments. The data from control cell was ignored due to extremely dissimilar data range.

4.3.3 Chloride Ion (Cl^-)

Table 4.6 shows average Cl^- concentration and its percent removal efficiencies in outflow measured from the first three batch experiments. The Cl^- concentration reduction was not occurred within the control cell when compared to its initial concentration showing as higher values in mg/l unit. In facts, the control cell data set was really unrelated to the others, so its trend line was not display in Figure 4.5.

The maximum Cl^- removal mean values were recorded on the second operational day as $45.1 \pm 86.6\%$, $41.9 \pm 132.2\%$ and $50.5 \pm 109.6\%$ for Cell2, Cell3 and Cell4, respectively. In another word, $16.6 \pm 31.3 \text{ mg/l}$, $32.3 \pm 106.3 \text{ mg/l}$ and 85.3 ± 184.3

mg/l of Cl^- were eliminated for the initial concentrations. Significantly, the ability to remove Cl^- for all treatment cells was occurred only in the first four treatment days, and it continuously reduced until the end of treatment day (day 13th) shown as the positive and negative plotted trend lines in Figure 4.5. In fact, all trend lines similarly characterized in the same shape during treatment and cleaning stages.

Statistically, multiple comparisons with Turkey HSD and Duncan post hoc tests for 144 samples of 3 experimental cells indicated no significant difference in terms of Cl^- reduction between all treatment cells due to obtained greater p-values than 0.05. However, all treatment cells had significantly higher ability to remove Cl^- when compared to the control cell ($p=0.00$).

Table 4.6 Mean values with standard errors of outflow Cl⁻ concentration and removal efficiency based on at 95% confidential interval (n =3 and t_{df} = 4.303). The brine feeding stage started from 1st to 13th while the cleaning state ranged between 14th to the end. In addition, all experimental data were corrected per the controls.

Treatment Time (Day)	Mean±se Cl ⁻ outflow, mg/l				Mean±se Cl ⁻ removal efficiency, %			
	<i>Batch 1-3 (16 days format)</i>							
	Cell 1	Cell 2	Cell 3	Cell 4	Cell 1	Cell 2	Cell 3	Cell 4
Start point	1.0± 1.4	38.6± 9.1	81.2± 12.8	171.6± 15.4	0.0± 0.0	0.0± 0.0	0.0± 0.0	0.0± 0.0
1	4.1± 9.3	22.0± 39.9	48.9± 118.0	86.2± 195.0	-650.0± 2540.3	45.1± 86.6	41.9± 132.2	50.5± 109.6
2	4.6± 8.7	31.5± 19.4	59.2± 62.8	104.7± 166.0	-673.4± 2482.7	19.0± 30.0	27.9± 65.7	39.5± 92.3
3	3.3± 2.4	36.3± 2.2	76.5± 23.3	134.6± 70.6	-385.9± 1148.5	5.2± 25.5	5.7± 27.9	21.6± 38.4
4	3.0± 1.1	39.8± 22.6	71.2± 3.5	143.7± 55.9	-311.2± 835.8	-2.5± 33.1	12.0± 17.1	16.3± 30.5
5	2.3± 4.4	42.4± 22.8	80.1± 12.2	173.9± 13.7	-288.9± 1183.8	-9.5± 39.5	0.8± 30.2	-1.4± 2.1
6	2.1± 3.3	38.6± 5.4	82.1± 14.2	177.1± 14.8	-219.4± 739.0	-0.7± 26.3	-1.7± 32.7	-3.3± 12.1
7	2.1± 3.2	35.9± 11.9	85.4± 17.5	173.6± 49.4	-181.8± 550.2	5.7± 51.1	-5.8± 36.8	-1.4± 33.7
8	1.4± 1.5	36.7± 12.1	85.5± 33.8	179.2± 41.4	-105.5± 428.9	3.5± 51.5	-6.2± 55.4	-4.7± 30.2
9	1.4± 1.6	38.1± 20.3	87.6± 39.1	184.6± 51.8	-83.4± 294.8	-0.7± 73.9	-8.9± 62.5	-7.9± 37.8
10	2.4± 3.1	44.3± 8.6	92.1± 16.4	184.2± 52.0	-231.7± 664.9	-15.8± 46.3	-14.1± 37.4	-7.6± 36.9
11	2.1± 2.0	40.5± 10.2	88.8± 21.3	186.6± 52.2	-167.7± 430.8	-5.9± 38.4	-9.9± 38.2	-8.9± 32.9
12	1.9± 1.3	41.1± 17.1	92.5± 39.4	194.1± 77.9	-155.8± 464.8	-8.4± 67.1	-15.0± 64.7	-13.4± 48.8
13	1.9± 0.8	41.7± 16.8	89.5± 34.1	191.9± 84.3	-158.0± 485.6	-9.8± 64.9	-11.1± 56.0	-12.0± 50.2
14	2.1± 1.5	21.8± 6.2	70.4± 31.7	174.6± 90.9	-161.0± 393.1	43.4± 15.2	12.7± 47.3	-2.0± 55.2
15	1.6± 0.5	13.1± 19.0	38.4± 49.7	113.1± 64.0	-111.4± 360.7	64.8± 57.7	52.1± 63.8	33.9± 38.2
16	2.0± 2.0	8.2± 12.5	23.1± 33.8	72.2± 77.4	-138.2± 299.4	78.1± 37.4	71.1± 43.2	57.7± 46.8

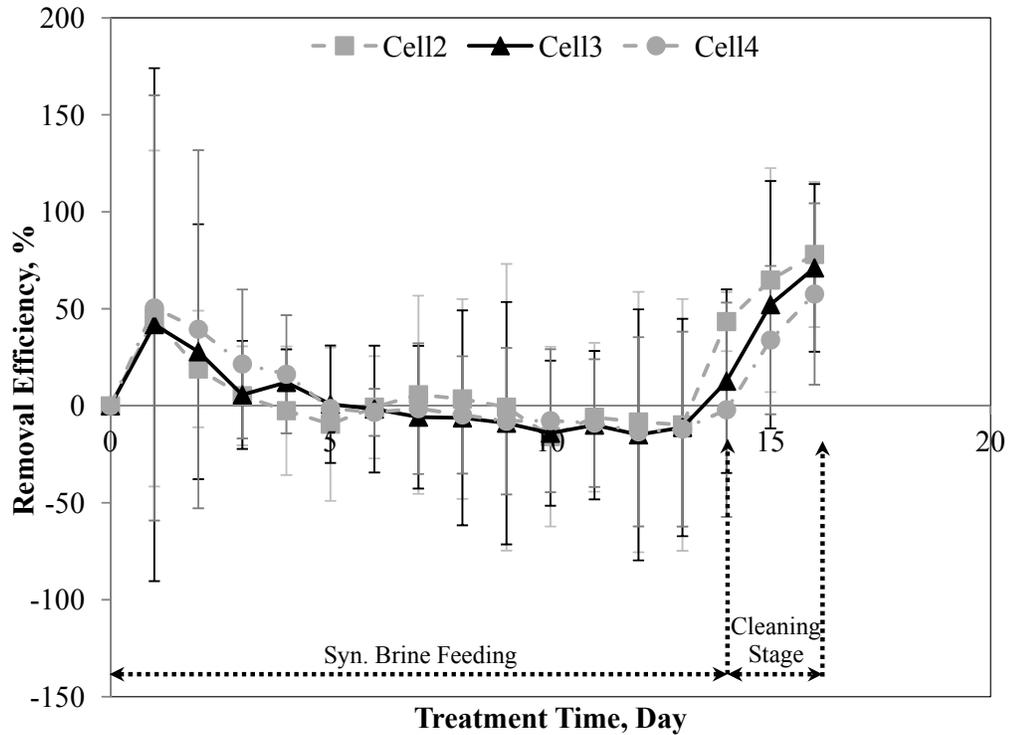


Figure 4.5 The efficiency of Cl⁻ removal recorded on Cell2, Cell3 and Cell4 during 3 batch experiments. The data from control cell was ignored due to extremely dissimilar data range.

4.3.4 Correlation between Na⁺, K⁺, and Cl⁻ Removal Efficiencies

Figure 4.6 shows that higher concentration of Na⁺ concentration tended to be reduced when K⁺ removal efficiency increased. Specially, Na⁺ concentration started to be eliminated during 50% to 100% of K⁺ removal efficiency, shown as positive values on a vertical axis. Based on 117 samples of three experimental cell excluding the control and all data from the cleaning stage, the statistical comparison with Spearman's rho test revealed significant correlation between Na⁺ and K⁺ within every cells during all batch experiments at 95% confidence interval (p=0.00) along with the correlation coefficient (r) equal to 0.57.

Figure 4.7 shows a scatter chart plotted between two pairs of Na^+ versus Cl^- and K^+ versus Cl^- based on their removal efficiencies. The amount of Na^+ concentration was mostly started to decreased before the process of Cl^- removal occurred. After the Cl^- removal efficiency was lifted, a greater amount of Na^+ concentration was expected to eliminate. According to the Spearman's rho test, the relationship between Na^+ and Cl^- removal efficiency was significant at 95% confidence interval ($p=0.00$, $n=117$) along with the coefficient (r) equal to 0.41.

Likely, the statistical data based on 117 samples indicated significant correlation ($p =0.00$) between K^+ and Cl^- removal efficiencies with coefficient (r) equal to -0.6. In another word, the ability of K^+ removal directly related to the percentage removal of Cl^- . Indeed, the amount of K^+ concentration was mainly removed before the process of Cl^- reduction took place, displayed as positive values on a vertical axis in Figure 4.7. Although, the Cl^- removal efficiency increased, the K^+ reduction process was slightly increased, and tended to stabilize.

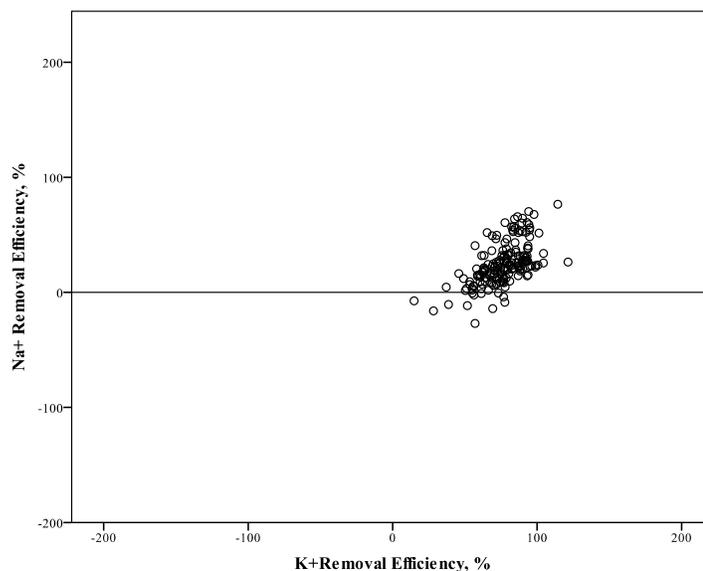


Figure 4.6 Correlation between Na^+ and K^+ removal efficiencies in all cells during 3 batch experiments ($n = 192$)

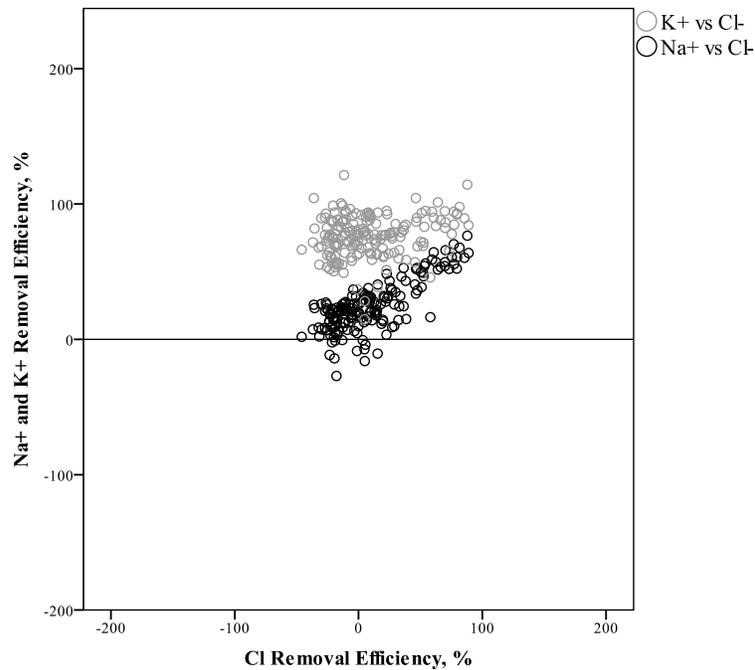


Figure 4.7 Correlation between two pairs of Na^+ versus Cl^- and K^+ versus Cl^- based on their removal efficiencies in all cells during 3 batch experiments ($n = 192$)

4.4 Electrolytes' Parameters: Batch 1-3

4.4.1 Conductivity

The conductivity sampling outcomes measured by an ExStik II model EC500 are given in

Table 4.7 as a mean value with a standard error. It shows the increase of conductivity concentration in effluent samples. As water passed through the clay media, amounts of positive and negative charged ions which are naturally sourced within clay structure were released as electrolytes via ion-exchange process of clay minerals. The changes of concentration occurred after the first operational day, and trended to maintain their levels until the end of experiment. This is indicated by an inclined

straight line in the conductivity concentration as shown in Figure 4.8. Additionally, the conductivity was increased since the 1st day, and retained its values throughout the brine feeding stage. In Cell4, conductivity slightly decreased from the 1st day. Then it was raised up during the 2nd-4th and mentioned its values until entering to the cleaning stage. The average effluent conductivity concentration were $283.2 \pm 13.8 \mu\text{S/cm}$, $272 \pm 21.9 \mu\text{S/cm}$, $497.6 \pm 25.5 \mu\text{S/cm}$ and $781.6 \pm 40.8 \mu\text{S/cm}$ with a maximum of $323.3 \pm 497.2 \mu\text{S/cm}$, $320.2 \pm 406.8 \mu\text{S/cm}$, $576.2 \pm 650.4 \mu\text{S/cm}$ and $922.2 \pm 1827.8 \mu\text{S/cm}$ respectively for the control, Cell2, Cell3, and Cell4. The error bars showing in the graph indicated standard error of each individual data.

Table 4.7 Mean values with standard errors of conductivity concentration in outflow at 95% confidential interval (n =3 and $t_{df} = 4.303$). In addition, all experimental data were corrected per the controls.

Treatment Time (Day)	Mean±se Conductivity outflow, $\mu\text{S/cm}$			
	<i>Batch 1-3 (16 days format)</i>			
	Cell 1	Cell 2	Cell 3	Cell 4
Start point	13.8 ± 9.0	188.3 ± 13.6	364.2 ± 18.7	725.7 ± 29.4
1	305.6 ± 395.8	319.3 ± 442.0	545.9 ± 905.5	694.4 ± 1968.1
2	317.2 ± 409.1	284.4 ± 280.6	558.6 ± 723.7	820.4 ± 2165.4
3	297.8 ± 357.4	319.9 ± 408.6	576.2 ± 650.4	922.2 ± 1827.8
4	323.3 ± 497.2	320.2 ± 406.8	530.4 ± 492.3	894.6 ± 1319.8
5	301.4 ± 513.2	313.6 ± 278.6	517.8 ± 299.7	876.1 ± 969.4
6	302.2 ± 553.1	270.0 ± 185.6	494.1 ± 186.5	784.8 ± 554.7
7	266.1 ± 424.8	286.4 ± 240.2	501.1 ± 238.6	775.3 ± 469.8
8	265.8 ± 465.1	278.5 ± 211.0	496.7 ± 191.9	756.0 ± 387.6
9	271.2 ± 430.9	254.3 ± 150.7	469.5 ± 152.4	755.0 ± 385.3
10	274.1 ± 511.5	223.8 ± 88.6	452.3 ± 69.8	748.3 ± 211.5
11	242.5 ± 436.2	246.5 ± 150.8	470.2 ± 87.4	747.2 ± 265.9
12	251.7 ± 504.9	217.5 ± 139.3	443.3 ± 27.3	707.3 ± 117.2
13	263.0 ± 558.4	201.7 ± 127.0	412.6 ± 55.5	679.1 ± 70.5
14	226.1 ± 411.1	183.6 ± 202.5	370.6 ± 102.1	637.8 ± 29.4
15	229.6 ± 391.2	119.0 ± 220.0	251.2 ± 13.0	481.7 ± 32.5
16	201.6 ± 260.1	90.8 ± 244.7	197.1 ± 104.2	323.9 ± 94.3

Figure 4.9 illustrates the wide range of average outflow salinity data comparing within cells, batch experiments and initial concentrations. During the first batch, increase in concentration of conductivity was outstanding in all experimental cells. This caused extreme errors in the mean values showing in

Table 4.7. The outflow concentration was expected to increase from the initial concentrations. However, Cell4 effluent contributed greater capability to transmit electrical current (1033.8 μ S/cm) than Cell3 (571 μ S/cm), Cell2 (321.4 μ S/cm) and the control (468.8 μ S/cm).

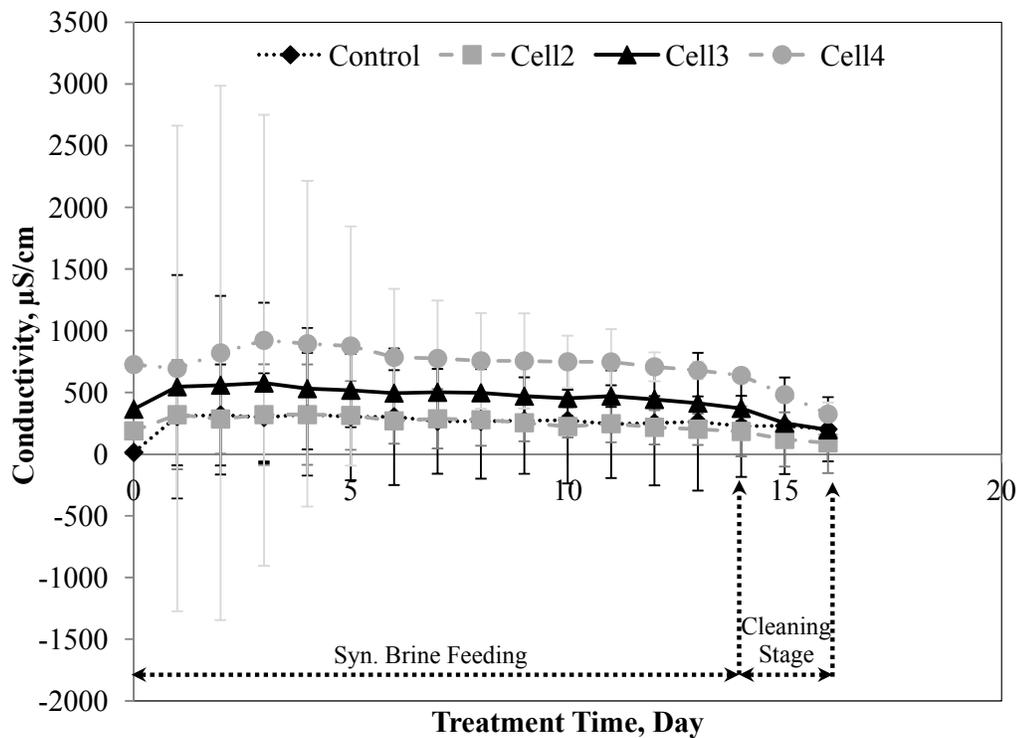


Figure 4.8 Variation in outflow conductivity concentration results based on 16 operational days

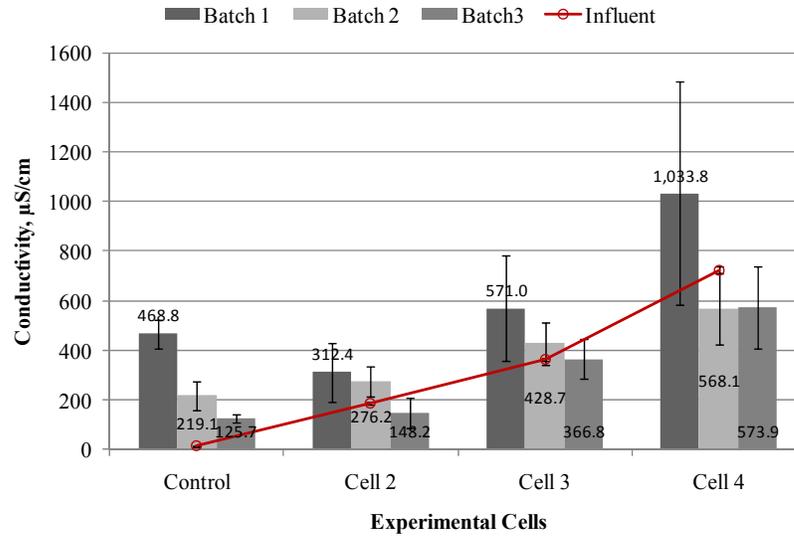


Figure 4.9 Conductivity results showing as average values along with standard deviation (n = 3 and 16 for each influent and effluent data, respectively)

4.4.2 Total Dissolved Solid (TDS)

Table 4.8 gives TDS results in effluents base on daily bias. The average outflow concentrations were collected on the control, Cell2, Cell3, and Cell4 as $197.5 \pm 9.8 \text{mg/l}$, $190.8.2 \pm 15 \text{mg/l}$, $347.2 \pm 17.5 \text{mg/l}$ and $548.4 \pm 27.7 \text{mg/l}$, respectively. Also, the control and Cell2 contributed a max of $226 \pm 347.8 \text{mg/l}$ and $224 \pm 284.8 \text{mg/l}$ of TDS while Cell3 and Cell4 gave $403.7 \pm 456.5 \text{mg/l}$ and $645.2 \pm 1280 \text{mg/l}$ as their highest concentrations. Similarly, the variation of conductivity, amount of TDS started to increase in all experimental cells since day one indicated by a positive steep line in the TDS concentration as displayed in Figure 4.10. Additionally, the long range shown by the error bars represents elevated value of standard error.

Table 4.8 Mean values with standard errors of TDS concentration in outflow at 95% confidential interval (n =3 and $t_{df} = 4.303$). In addition, all experimental data were corrected per the controls.

Treatment Time (Day)	Mean±se TDS outflow, mg/l			
	<i>Batch 1-3 (16 days format)</i>			
	Cell 1	Cell 2	Cell 3	Cell 4
Start point	9.6 ± 6.3	131.8 ± 9.4	254.8 ± 13.6	507.7 ± 20.8
1	213.6 ± 276.7	223.4 ± 309.1	382.1 ± 634.1	500.4 ± 1439.8
2	221.8 ± 286.0	199.1 ± 196.5	390.9 ± 506.1	573.4 ± 1514.1
3	208.3 ± 249.4	223.7 ± 286.1	403.1 ± 456.5	645.2 ± 1280.0
4	226.0 ± 347.8	224.0 ± 284.8	371.0 ± 343.9	624.5 ± 917.5
5	210.8 ± 358.7	219.4 ± 195.3	344.1 ± 278.5	612.9 ± 679.3
6	211.1 ± 386.4	189.1 ± 131.1	345.9 ± 131.4	549.2 ± 389.1
7	186.0 ± 297.1	200.4 ± 168.3	350.4 ± 167.7	542.4 ± 328.5
8	185.6 ± 324.9	195.1 ± 148.6	347.7 ± 135.2	529.1 ± 272.0
9	189.5 ± 301.2	177.8 ± 105.5	328.5 ± 107.2	528.3 ± 270.2
10	184.6 ± 367.1	163.4 ± 89.1	323.4 ± 61.1	530.8 ± 135.5
11	169.7 ± 305.1	172.2 ± 105.8	329.0 ± 61.7	522.7 ± 185.8
12	176.1 ± 353.3	151.8 ± 97.1	309.9 ± 19.5	494.9 ± 82.7
13	184.0 ± 390.6	141.0 ± 88.1	288.2 ± 38.8	474.9 ± 49.3
14	158.1 ± 287.2	128.5 ± 141.6	259.1 ± 72.3	447.4 ± 17.1
15	160.5 ± 273.0	83.5 ± 153.8	175.7 ± 8.4	336.0 ± 18.7
16	140.8 ± 180.9	63.6 ± 171.8	137.9 ± 74.2	226.7 ± 66.8

Figure 4.11 presents, the first batch results obviously differ from the other two groups. The results are shown as average outflow concentration. The effluents contained higher amount of TDS concentration than the initial concentrations. For all cells, the highest averaged outflow TDS concentration was noted on Cell4 as 726mg/l while Cell3, Cell2 and the control contributed as 399.7mg/l, 218.7mg/l, and 327.7mg/l of TDS, respectively.

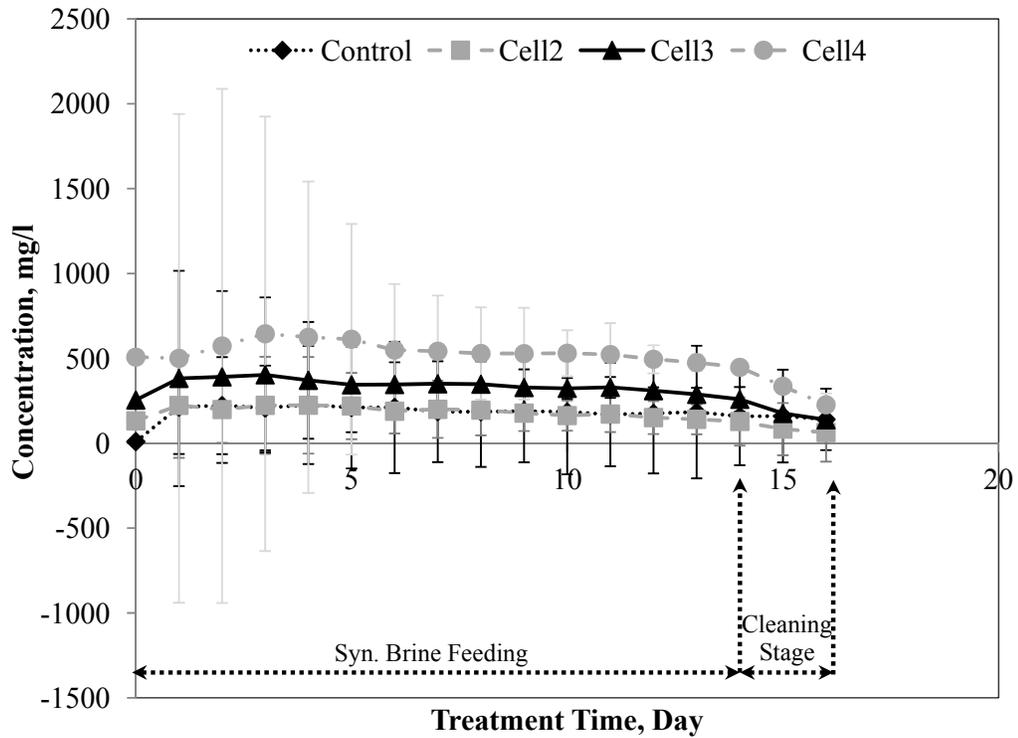


Figure 4.10 Variation in outflow TDS concentration results based on 16 operational days

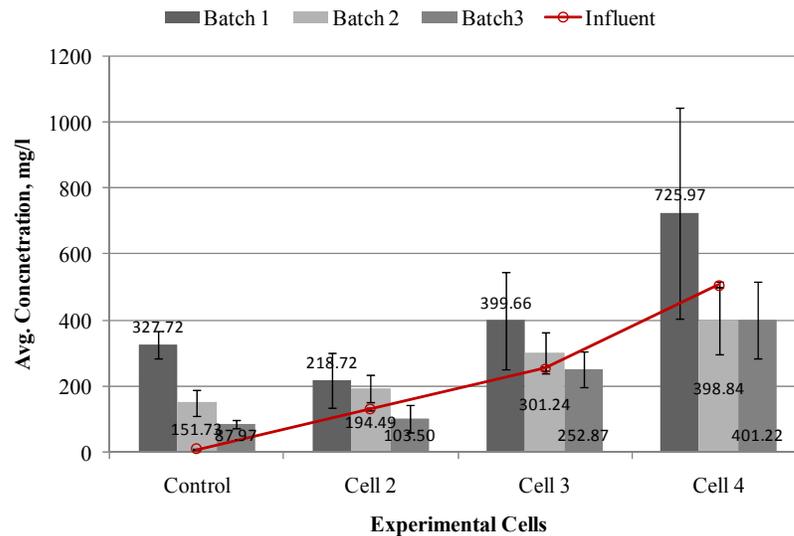


Figure 4.11 TDS results showing as average values along with standard deviation (n = 3 and 16 for each influent and effluent data, respectively)

4.4.3 Salinity (*S*)

Similar to conductivity and TDS, salinity concentration was increased in effluent samples. It indicated that the effluent contained greater amount of total concentration of dissolved salts than the influent. The mean values of outflow salinity concentration along with standard errors were given in Table 4.9. The average concentrations were measured as 141.5 ± 6.9 mg/l with a maximum of 161.5 ± 94 and 136 ± 11 mg/l with a maximum of 161.6 ± 209.8 respectively for the control and Cell2. Likely, Cell3 and Cell4 contributed 248.7 ± 12.7 mg/l with a maximum of 287.9 ± 325.8 and 391.2 ± 20 mg/l with a maximum of 460.2 ± 9.11 mg/l of salinity, respectively. This increased concentration took place at the first days and it was indicated by an inclined line in the salinity concentration as shown in Figure 4.12. Moreover, the long length of error bar represents high value of standard errors.

Similar to conductivity and TDS results, Figure 4.13 shows the diversity of data sets within three batch experiments. The averaged outflow results indicate the first batch data sets have higher salinity concentration than the data sets from batch 2 and 3. Within the first batch, Cell4 contained the greater amount of total dissolved salts (518.1 mg/l) than Cell 3 (285.5 mg/l), Cell2 (156.4 mg/l) and the control (234.2 mg/l). For all experimental cells, outflow TDS concentration was expected to increase from the initial concentrations.

Table 4.9 Mean values with standard errors of salinity concentration in outflow at 95% confidential interval (n =3 and $t_{df} = 4.303$). In addition, all experimental data were corrected per the controls.

Treatment Time (Day)	Mean±se Salinity outflow, ppm			
	<i>Batch 1-3 (16 days format)</i>			
	Cell 1	Cell 2	Cell 3	Cell 4
Start point	8.8 ± 6.9	94.1 ± 6.8	181.8 ± 9.3	361.8 ± 13.9
1	152.8 ± 198.2	159.6 ± 220.3	272.9 ± 452.5	354.2 ± 1015.2
2	158.6 ± 204.6	142.1 ± 140.4	279.1 ± 361.8	410.1 ± 1083.1
3	148.8 ± 178.4	159.7 ± 204.9	287.9 ± 325.8	460.2 ± 911.0
4	161.5 ± 248.7	161.6 ± 209.8	265.0 ± 245.7	447.3 ± 659.9
5	150.4 ± 256.5	156.9 ± 139.8	258.9 ± 150.4	438.1 ± 485.2
6	150.9 ± 276.5	135.2 ± 93.3	247.2 ± 93.2	392.3 ± 278.1
7	133.0 ± 212.1	143.1 ± 120.4	250.4 ± 120.0	387.6 ± 235.0
8	132.8 ± 232.7	139.2 ± 105.8	248.2 ± 95.6	377.9 ± 194.0
9	135.4 ± 215.2	126.9 ± 75.3	234.7 ± 76.2	377.4 ± 193.3
10	137.0 ± 255.8	111.7 ± 44.6	226.1 ± 34.8	373.9 ± 105.7
11	121.2 ± 217.8	123.0 ± 74.8	235.0 ± 43.9	373.4 ± 132.4
12	125.7 ± 252.1	108.6 ± 69.4	221.4 ± 14.1	353.8 ± 58.9
13	131.3 ± 278.5	100.7 ± 62.8	206.4 ± 27.7	339.6 ± 34.7
14	113.0 ± 205.2	91.6 ± 100.9	185.2 ± 51.1	318.7 ± 15.0
15	114.7 ± 195.3	59.4 ± 109.5	125.6 ± 5.9	240.8 ± 15.9
16	100.6 ± 129.4	45.5 ± 122.7	98.7 ± 52.7	161.9 ± 47.0

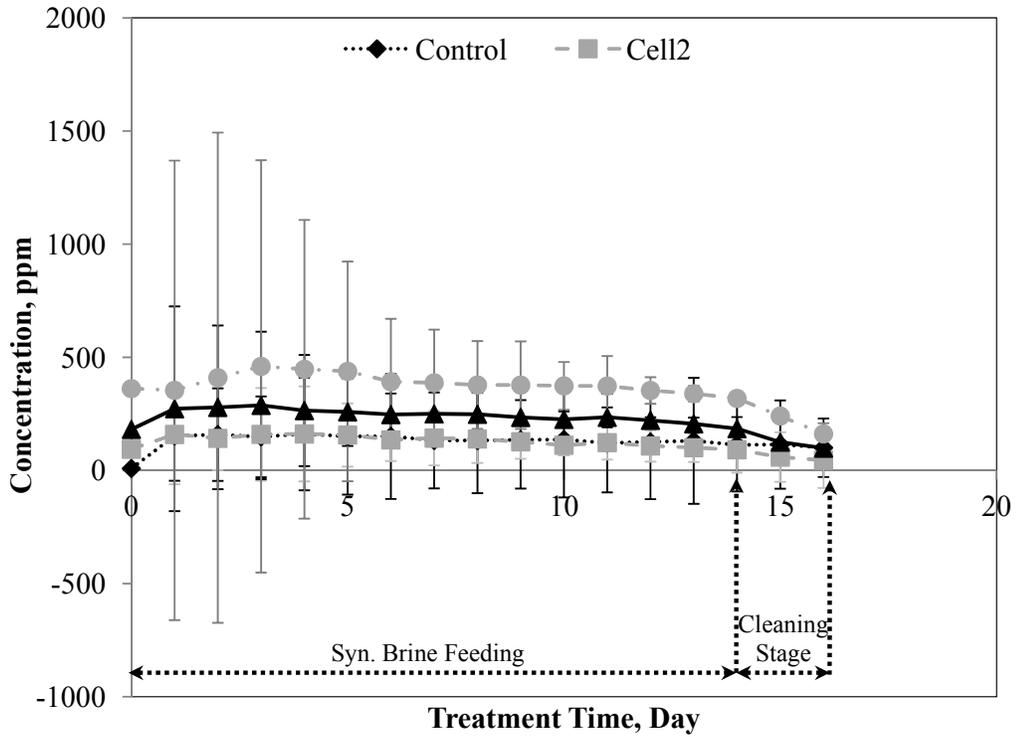


Figure 4.12 Variation in outflow salinity concentration results based on 16 days

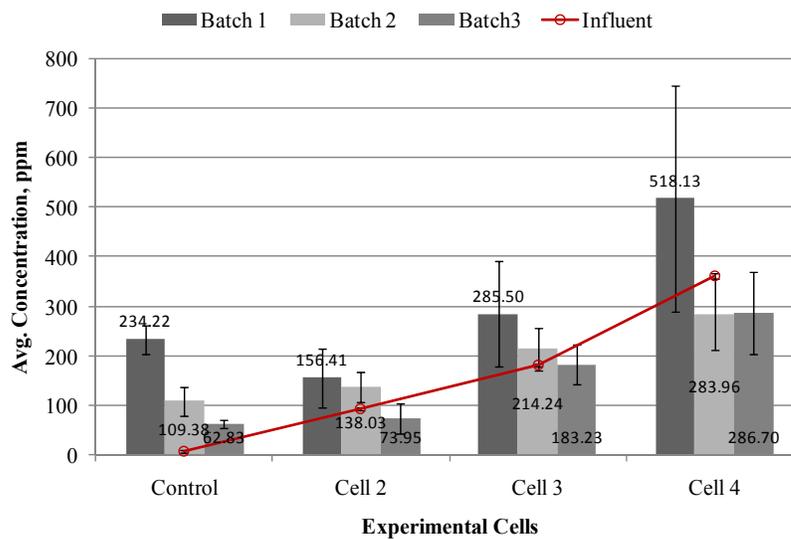


Figure 4.13 Salinity results showing as average values along with standard deviation (n = 3 and 16 for each influent and effluent data, respectively)

4.4.4 Correlation between Conductivity, TDS and Salinity

Based on 144 samples including all experimental cells throughout three batch operations, multiple comparisons with Spearman's rho test confirmed correlation between these three parameters was very highly significant ($p=0.00$, $r=1.00$). Figure 4.14 indicates the positive direct relationship within each pairs of input parameters. This means, the capability of water to conduct electricity directly depends on the amount of total dissolved solids (TDS) and concentration of total dissolved salt ions. Moreover, total dissolved solids contribute higher electrical conductivity values than only the total dissolved salts due to carrying more positive and negative charged ions.

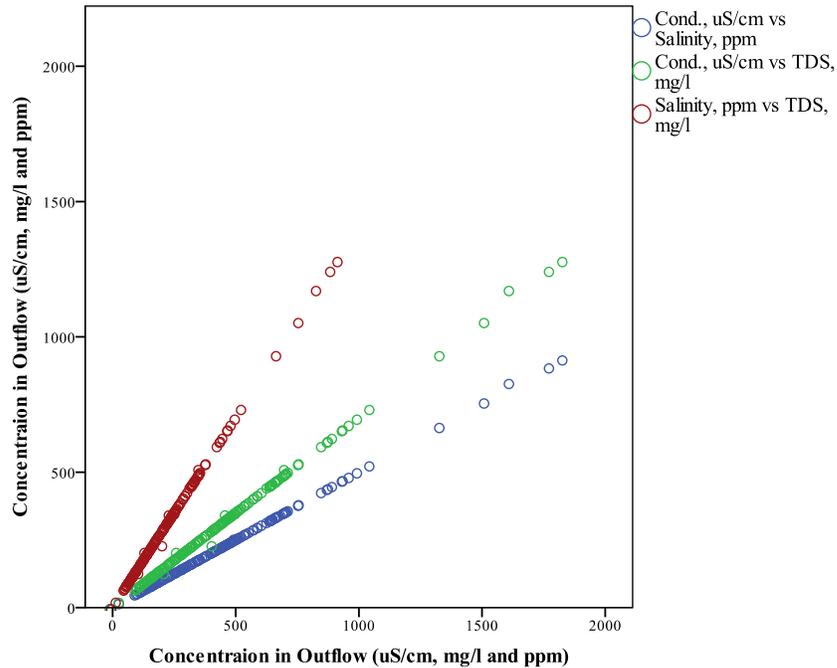


Figure 4.14 Correlation between outflow conductivity, TDS and salinity concentrations in all cells during 3 batch experiments (n = 192)

4.5 pH: Batch 1-3

Table 4.10 gives outflow pH results base on 16 experimental days. The synthetic brines had pH range of 6.5-6.7 while an initial pH value was measured as 6.7 in the

control. The alteration of pH value in all cells was increased since the first day and it was reached at pH of 8.00 before entering to the cleaning stage as shown in Figure 4.15. Due to ionizing of alkali salts (NaCl and KCl) in water and minerals in clay media, the amount of hydroxide ions (OH⁻) decrease the concentration of hydrogen ion (H⁺).

Table 4.10 Mean values with standard errors of pH concentration in outflow at 95% confidential interval (n =3 and t_{df} = 4.303)

Treatment Time (Day)	Mean±se pH outflow			
	<i>Batch 1-3 (16 days format)</i>			
	Cell 1	Cell 2	Cell 3	Cell 4
Start point	6.7 ± 1.5	6.7 ± 0.7	6.6 ± 0.4	6.5 ± 0.5
1	8.1 ± 0.7	7.8 ± 0.5	7.7 ± 0.8	7.9 ± 0.8
2	8.1 ± 0.8	7.9 ± 0.4	7.8 ± 0.6	7.9 ± 0.8
3	7.9 ± 0.8	7.9 ± 0.6	7.8 ± 0.6	7.8 ± 0.7
4	7.8 ± 1.1	7.8 ± 0.8	7.9 ± 0.4	7.9 ± 0.8
5	8.0 ± 0.6	7.9 ± 0.4	7.8 ± 0.6	7.9 ± 0.4
6	8.2 ± 1.2	7.9 ± 0.6	7.9 ± 0.7	7.9 ± 0.7
7	7.9 ± 0.5	8.0 ± 0.5	8.0 ± 0.2	7.9 ± 0.3
8	8.1 ± 0.2	7.9 ± 0.2	7.9 ± 0.1	7.9 ± 0.3
9	8.1 ± 0.3	8.0 ± 0.3	7.9 ± 0.3	8.0 ± 0.5
10	8.0 ± 0.3	8.0 ± 0.3	7.9 ± 0.3	8.0 ± 0.1
11	8.2 ± 0.3	8.1 ± 0.0	8.0 ± 0.1	8.0 ± 0.1
12	8.0 ± 0.4	8.1 ± 0.3	8.0 ± 0.3	8.0 ± 0.3
13	8.2 ± 0.2	8.1 ± 0.1	8.0 ± 0.1	8.1 ± 0.2
14	8.2 ± 0.1	8.1 ± 0.4	8.1 ± 0.2	8.0 ± 0.3
15	8.0 ± 0.3	8.0 ± 0.5	8.0 ± 0.4	8.1 ± 0.3
16	8.2 ± 0.4	8.2 ± 0.4	8.2 ± 0.3	8.4 ± 0.4

The average outflow pH ranges were measured as 8.2 -7.8, 8.2-7.8, 8.2- 7.73 and 8.4- 7.8, respectively for the control, Cell2, Cell3, and Cell4. The data also indicated that the effluent pH (near neutral) has possibility to meet discharge limits as defined by the Saskatchewan Draft Discharge and Discovery Reporting Standard for environmental discharge (Saskatchewan Ministry of Environment, 2011). Only the

discharge limit on soils (pH=6) was suggested in the Saskatchewan discharge standard while information were required in order to specified the pH limits on sediments, groundwater and surface water.

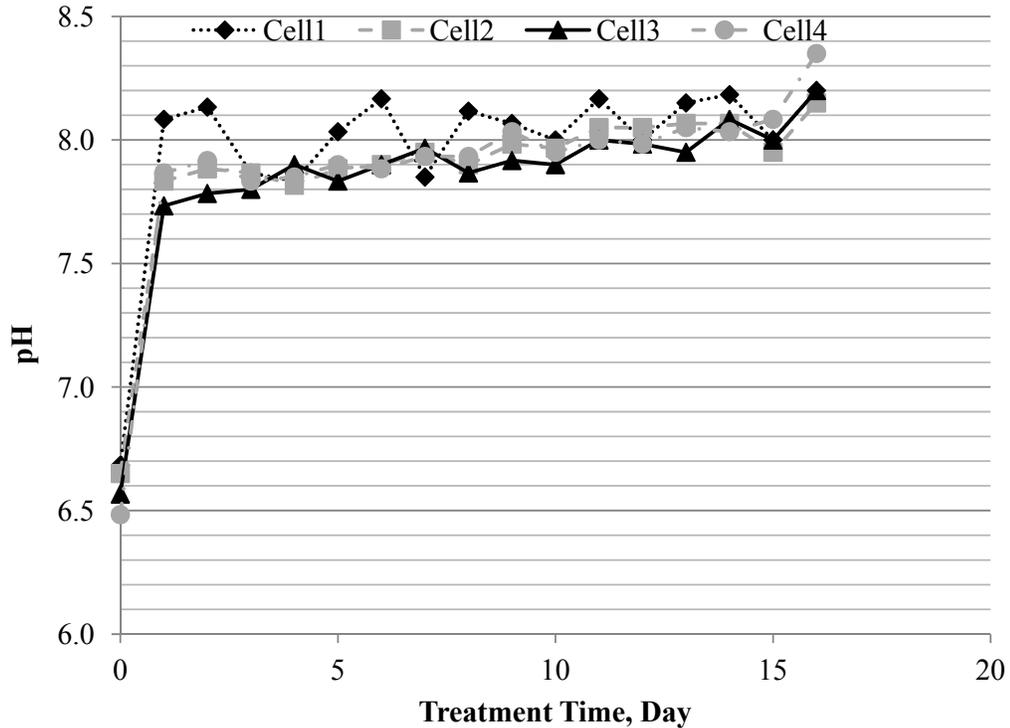


Figure 4.15 Variation in outflow pH concentration results based on 16 days

4.6 Temperature: Batch 1-3

Temperature was designed to set at 20-23°C (ambient temperature in the laboratory) and monitored in all samples as a control parameter. As given in Table 4.11, there was slightly changed in between the influent and effluent samples. The overall temperature ranged between 19.5 -20.1°C. Figure 4.16 shows that outflow temperature randomly altered throughout the entire experiment. Since the set of effluent samples in each day could not be performed the temperature measurement at the same time, the change might be caused by the ambient environments.

Table 4.11 Mean values with standard errors of temperature concentration in outflow at 95% confidential interval (n =3 and $t_{df} = 4.303$)

Treatment	Mean±se Temperature outflow, °C			
Days	Batch 1-3 (16 days format)			
	Cell 1	Cell 2	Cell 3	Cell 4
Start point	20.43 ± 1.74	20.75 ± 0.99	20.52 ± 0.68	20.53 ± 1.17
1	20.10 ± 1.18	19.85 ± 1.30	19.72 ± 0.93	19.87 ± 0.83
2	19.93 ± 1.98	19.87 ± 2.02	19.75 ± 2.38	19.88 ± 2.08
3	20.05 ± 0.97	19.83 ± 0.90	19.75 ± 0.76	19.85 ± 0.90
4	20.03 ± 1.11	19.97 ± 1.60	19.88 ± 1.11	19.88 ± 1.33
5	19.92 ± 1.29	19.77 ± 1.41	19.63 ± 1.36	19.63 ± 1.36
6	19.80 ± 0.97	19.75 ± 0.75	19.67 ± 0.81	19.75 ± 1.06
7	20.08 ± 0.63	19.92 ± 0.71	19.90 ± 0.75	19.83 ± 0.92
8	19.53 ± 0.56	19.60 ± 0.66	19.67 ± 0.52	19.67 ± 0.52
9	19.80 ± 0.45	19.70 ± 0.54	19.77 ± 0.83	19.67 ± 0.64
10	19.60 ± 0.65	19.52 ± 0.44	19.53 ± 0.63	19.48 ± 0.75
11	19.80 ± 0.45	19.73 ± 0.72	19.67 ± 0.59	19.65 ± 0.45
12	19.67 ± 1.50	19.50 ± 1.79	19.55 ± 2.09	19.52 ± 1.86
13	19.73 ± 0.38	19.62 ± 0.26	19.60 ± 0.25	19.63 ± 0.26
14	19.90 ± 0.50	19.75 ± 0.65	19.75 ± 0.57	19.72 ± 0.61
15	19.97 ± 0.68	19.77 ± 0.75	19.73 ± 0.72	19.73 ± 0.61
16	19.75 ± 0.45	19.68 ± 0.50	19.65 ± 0.78	19.78 ± 0.88

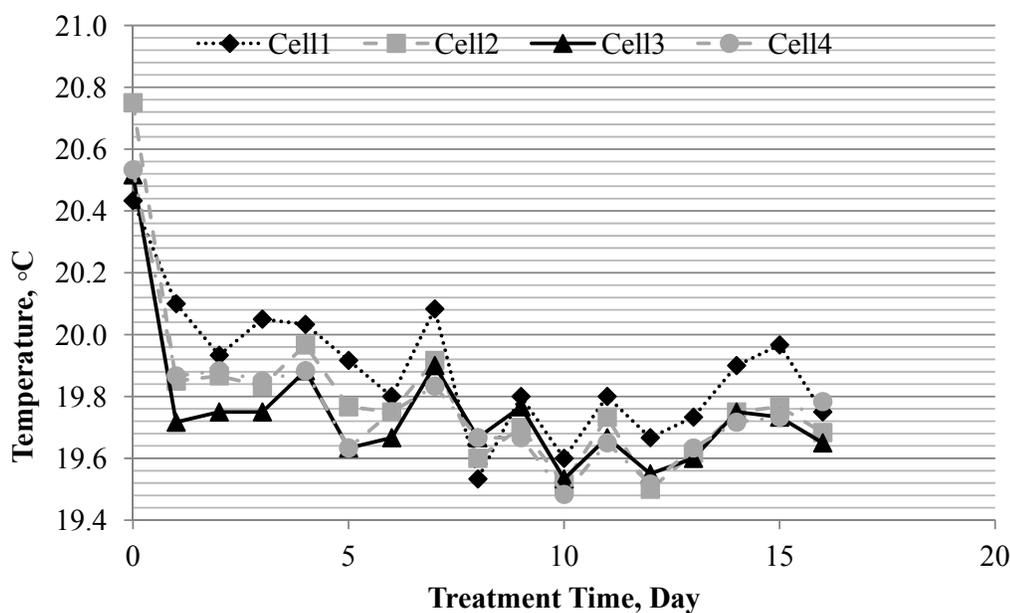


Figure 4.16 Variation in outflow temperature concentration results based on 16 days

4.7 Alkalinity: Batch 1:3

The everyday means values of outflow alkalinity concentration along with standard errors were given in Table 4.12. Obviously, the results drastically increased in the first day after the synthetic brines were fed into all cells. Dissolved salt ions (Na^+ and K^+) along with all ions in clay were released when water moved through the experimental cells causing the concentration of alkalinity to increase. The average concentrations were measured as $37.5 \pm 0.9 \text{ mg/l}$ with a maximum of $40 \pm 12.4 \text{ mg/l}$ and $38.6 \pm 0.7 \text{ mg/l}$ with a maximum of $40 \pm 6.2 \text{ mg/l}$ according to the control and Cell 2. Likely, Cell 3 and Cell 4 contributed $37.69 \pm 1.28 \text{ mg/l}$ with a max of 40.00 ± 0.00 and $43.79 \pm 3.48 \text{ mg/l}$ with a max of $56.67 \pm 14.34 \text{ mg/l}$ of salinity, respectively.

Unsurprisingly, Figure 4.17 indicates all data series shown negative removal efficiency, meaning no significant activities of alkalinity reduction. However, some minimum changes in alkalinity concentration did randomly occur in all cells during this study period.

Table 4.12 Mean values with standard errors of outflow alkalinity concentration and removal efficiency calculated at 95% confidential interval (n =3 and t_{df} = 4.303). The operational stage started from 1st to 11th while the cleaning state ranged between 14th to the end.

Treatment	Mean±se Alkalinity outflow, mg/L as CaCO₃				Mean±se Alkalinity removal efficiency, %			
Days	<i>Batch 1-3 (16 days format)</i>							
	Cell 1	Cell 2	Cell 3	Cell 4	Cell 1	Cell 2	Cell 3	Cell 4
Start point	4.00 ± 0.00	6.00 ± 0.00	7.33 ± 5.74	9.33 ± 2.87	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
1	36.67 ± 14.34	40.00 ± 0.00	38.33 ± 7.17	55.00 ± 32.86	-816.67 ± 358.58	-566.67 ± 0.00	-450.00 ± 338.92	-504.17 ± 512.47
2	40.00 ± 24.84	40.00 ± 24.84	40.00 ± 0.00	56.67 ± 14.34	-900.00 ± 621.08	-566.67 ± 414.06	-477.78 ± 382.49	-508.33 ± 35.86
3	38.33 ± 18.97	38.33 ± 7.17	38.33 ± 7.17	51.67 ± 18.97	-858.33 ± 474.36	-538.89 ± 119.53	-450.00 ± 338.92	-454.17 ± 125.50
4	36.67 ± 14.34	36.67 ± 14.34	35.00 ± 12.42	41.67 ± 7.17	-816.67 ± 358.58	-511.11 ± 239.06	-405.56 ± 393.54	-350.00 ± 124.22
5	40.00 ± 0.00	40.00 ± 0.00	40.00 ± 0.00	40.00 ± 0.00	-900.00 ± 0.00	-566.67 ± 0.00	-477.78 ± 382.49	-333.33 ± 143.43
6	38.33 ± 7.17	40.00 ± 0.00	40.00 ± 0.00	40.00 ± 0.00	-858.33 ± 179.29	-566.67 ± 0.00	-477.78 ± 382.49	-333.33 ± 143.43
7	36.67 ± 14.34	38.33 ± 7.17	38.33 ± 7.17	40.00 ± 0.00	-816.67 ± 358.58	-538.89 ± 119.53	-461.11 ± 454.21	-333.33 ± 143.43
8	35.00 ± 12.42	36.67 ± 14.34	38.33 ± 7.17	40.00 ± 0.00	-775.00 ± 310.54	-511.11 ± 239.06	-450.00 ± 338.92	-333.33 ± 143.43
9	38.33 ± 14.34	38.33 ± 7.17	40.00 ± 0.00	40.00 ± 0.00	-858.33 ± 358.58	-538.89 ± 119.53	-477.78 ± 382.49	-333.33 ± 143.43
10	35.00 ± 12.42	36.67 ± 14.34	33.33 ± 7.17	35.00 ± 12.42	-775.00 ± 310.54	-511.11 ± 239.06	-377.78 ± 293.76	-279.17 ± 176.58
11	35.83 ± 12.93	39.00 ± 4.30	33.33 ± 14.34	44.33 ± 12.75	-795.83 ± 323.22	-550.00 ± 71.72	-366.67 ± 143.43	-376.67 ± 100.40
12	37.33 ± 6.25	38.33 ± 7.17	38.33 ± 7.17	41.67 ± 7.17	-833.33 ± 156.30	-538.89 ± 119.53	-450.00 ± 338.92	-350.00 ± 124.22
13	38.83 ± 8.46	38.83 ± 8.46	36.67 ± 7.17	43.33 ± 7.17	-870.83 ± 211.38	-547.22 ± 140.92	-422.22 ± 262.96	-366.67 ± 71.72
14	36.67 ± 7.17	40.00 ± 0.00	40.00 ± 0.00	42.67 ± 6.25	-816.67 ± 179.29	-566.67 ± 0.00	-477.78 ± 382.49	-360.00 ± 89.57
15	38.33 ± 7.17	40.00 ± 0.00	41.67 ± 7.17	43.33 ± 18.97	-858.33 ± 179.29	-566.67 ± 0.00	-494.44 ± 310.77	-362.50 ± 82.16
16	35.00 ± 12.42	40.00 ± 0.00	40.00 ± 0.00	51.67 ± 7.17	-775.00 ± 310.54	-566.67 ± 0.00	-477.78 ± 382.49	-458.33 ± 156.30

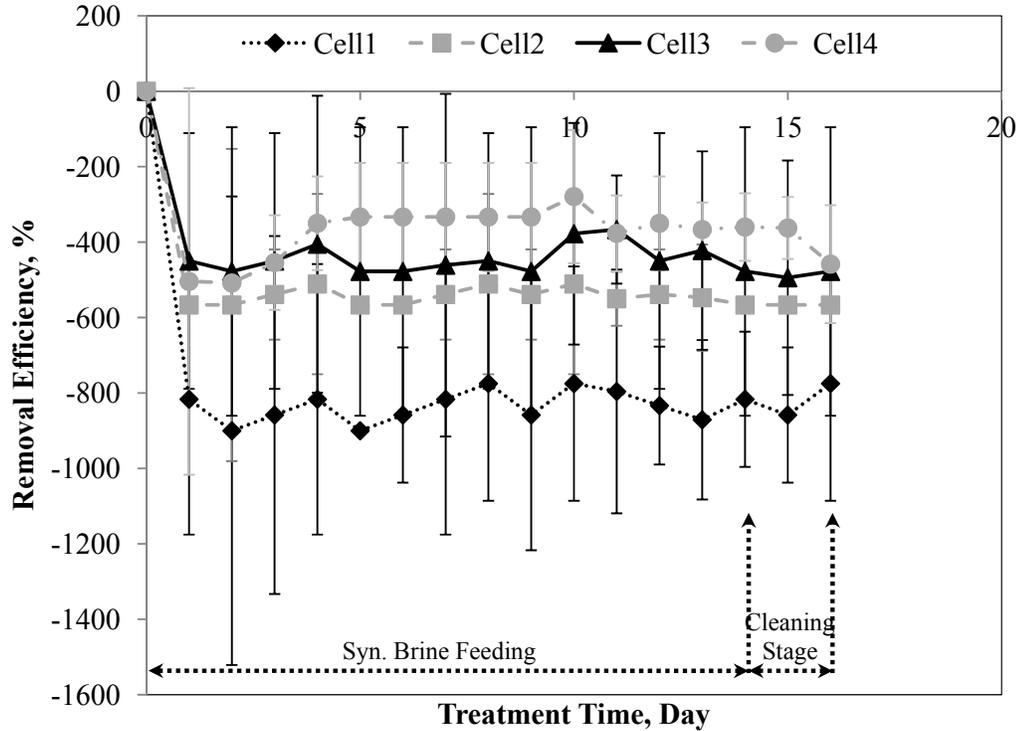


Figure 4.17 Variation in outflow alkalinity concentration results based on 16 days

4.8 Chloride Salts Breakthrough Curves (BC): Batch 4

Chloride in the brine was considered the main component which sources of dissolved salt compounds.

4.8.1 Chloride (Cl) removal period

According to the lab data shown in Table 4.6 and Figure 4.5, chloride elimination process was occurred within only the first 4 days, and it decreased with longer treatment time. Specially, first day of each batch experiments contributed the highest chloride removal efficiencies. Therefore, the chloride removal was predicted to limit in between 1st-4th day. To confirm this assumption, the lab results were considered and divided into 4 groups based on average chloride outflow concentrations as displayed in Figure 4.18.

The chloride mostly decreased in all treatment cells during the prediction period indicated in Figure 4.18(b) by the spaces between the influent concentration line and the chloride concentration columns. Although the 1st batch data conveyed out completely different messages, the 2nd and 3rd batch data sets still proved appearance of chloride reduction occurred in this predicted period. In fact, the 3rd batch experiment contributed the best chloride reduction. In between treatment cells, Cell4 gave better removal efficiency (48.6%, 83.4mg/l) than Cell3 (39.7%, 32.3mg/l) and Cell2 (26.9%, 10.4mg/l).

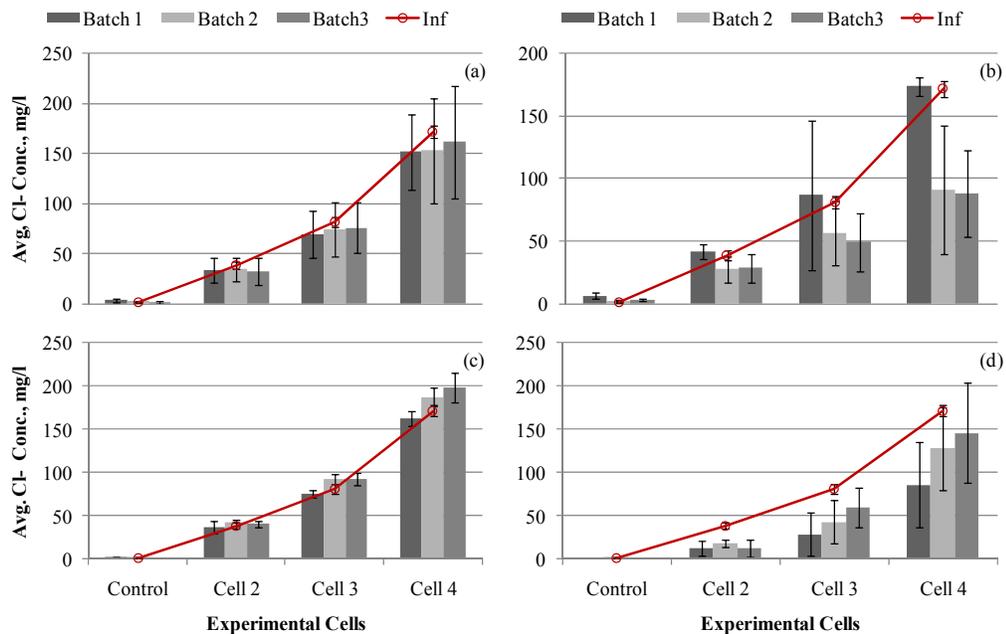


Figure 4.18 Chloride outflow results were shown as average values along with standard deviation. (a), (b), (c) and (d) represented overall 16 days (n=16), 1st-4th day (n=4), 5th-13th day (n=9) and cleaning periods (n=3), respectively.

Furthermore, the data showing in Figure 4.18(c) supports that chloride removal process was limited in the first 4 days indicated by chloride concentration bars were higher than the influent line. The chloride removal efficiency was not

counted in the cleaning stage (Figure 4.18(d)) because the reduction was diluted by deionised water rather than coming from treatment cells performances.

4.8.2 Sodium (Na^+) and Potassium (K^+) removal period

Figure 4.19(a) presents that the third batch experiment leads to a reduction of Na^+ . The best Na^+ removal efficiencies were noted on Cell4 at 42% (49.3mg/l) which is higher than Cell3 (42.6%, 24.2mg/l) and Cell2 (42%, 11.8mg/l). The ability of Na^+ removal was not limited on the first 4 days. Although outflow concentration increased, Figure 4.19(b) still proves that all treatment cells were able to eliminate sodium ions until the end of steady period. This was indicated by the gaps between the influent line and the concentration columns.

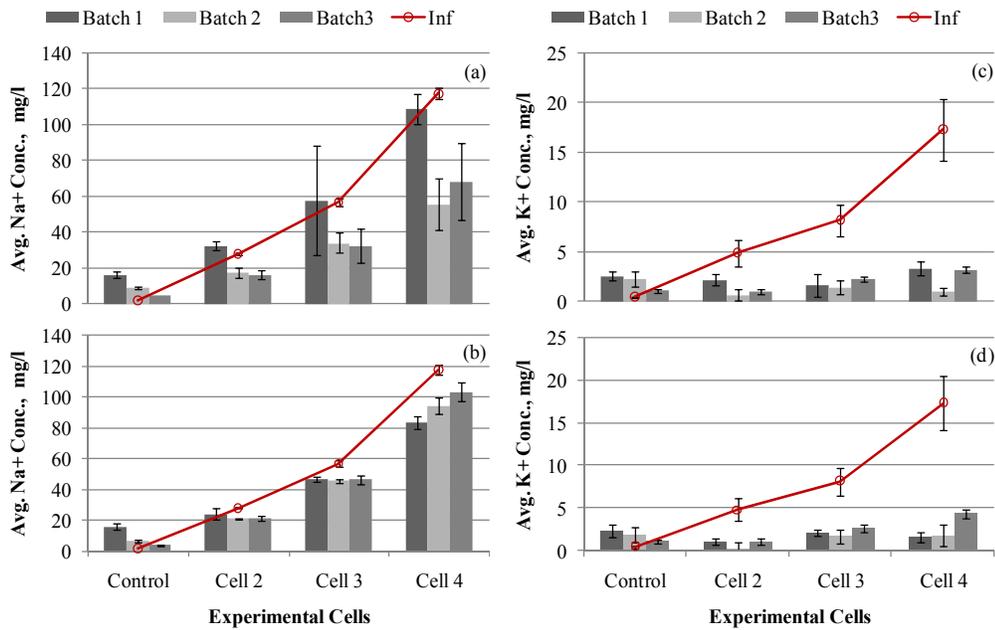


Figure 4.19 Na^+ and K^+ outflow results were shown as average values along with standard deviation. The data in (a) and (c) referred to the 1st-4th day (n=4) while the 5th-13th day (n=9) were labelled as (b) and (d).

Similar to Na^+ , Figure 4.19(c) and (d) show that all treatment cells was able to remove K^+ during in both stages. Therefore, the breakthrough curve should not occur in this study period. The best K^+ reduction rate were measured as 94.3% (16.3mg/l), 82.5% (6.7mg/l) and 87.3% (4.3mg/l) respectively for Cell4, Cell3 and Cell2. Finally, the results in each batch and each cell contained less diversity between samples indicated by very narrow error bars.

4.8.3 Chloride Salts Breakthrough Curves

Figure 4.20 shows relationship between relative concentrations of chloride (C/C_0) and treatment time. C_0 represent initial concentration while C is effluent concentration at each observation times. The breakthrough is assumed to take place when the effluent concentration equals to 5% of the influent value, and the absorption bed ability will be exhausted when the effluent concentration reaches 95% of the initial value (Metcalf & Eddy, 2003).

The chloride breakthrough started at less than 6 hours (0.25 day) in all treatment cells indicated by the breakthrough line was raised higher than 0.05 of chloride concentration on the C/C_0 axis. For each cells, Cell2 consumed only 1.2 hours (0.05 day) to launch the absorption process while Cell3 and Cell4 was about to occur in the same time at 3.6 hours (0.15 day). The breakthrough trended to occur faster in the synthetic brine with very low initial concentration.

In term of the clay exhaustion, the brine samples with higher concentrate of chloride took longer time to reach the end of breakthrough (at 0.95 on the C/C_0 axis). The ending points were found at 52.8 hours (2.2 days), 67.2 hours (2.8 days) and 75.6 hours (3.15 days) respectively for Cell2, Cell3 and Cell4. After passing the break points, all treatment cells were lost their ability to remove chloride. To support this,

the C/C_0 concentration s were increased up to 1.0 and remained steady until the last day meaning the effluent concentrations were now higher than of their initial values.

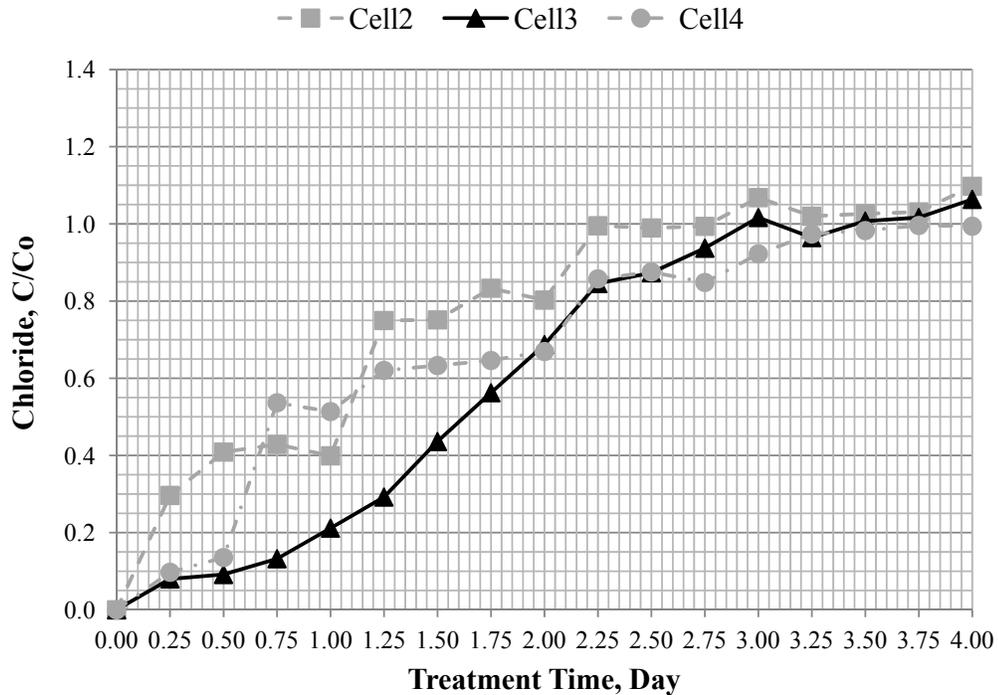


Figure 4.20 Chloride breakthrough curves (data collected from batch 4)

Figure 4.21 indicates that the clay media started to absorb Na^+ at about 1.2 hours (0.05 day) after the brine samples were fed into all treatment cells. The process occurred earlier in Cell2 while it was occurred at almost the same time in Cell3 and Cell4. During the first 6 hours (0.25 day), the C/C_0 ratios dramatically changed in higher values indicated by steep inclined line on the x axis. The ending points were not observed in any cells even though the CW system had operated to reach the last day. Therefore, the Na^+ breakthrough curves could not be addressed during this batch experiment. The clay media contributed a faster absorption rate in the brine samples

with low Na^+ concentration. In fact, the break points were possibility assumed to happen more rapidly in the samples containing less concentrate of Na^+ .

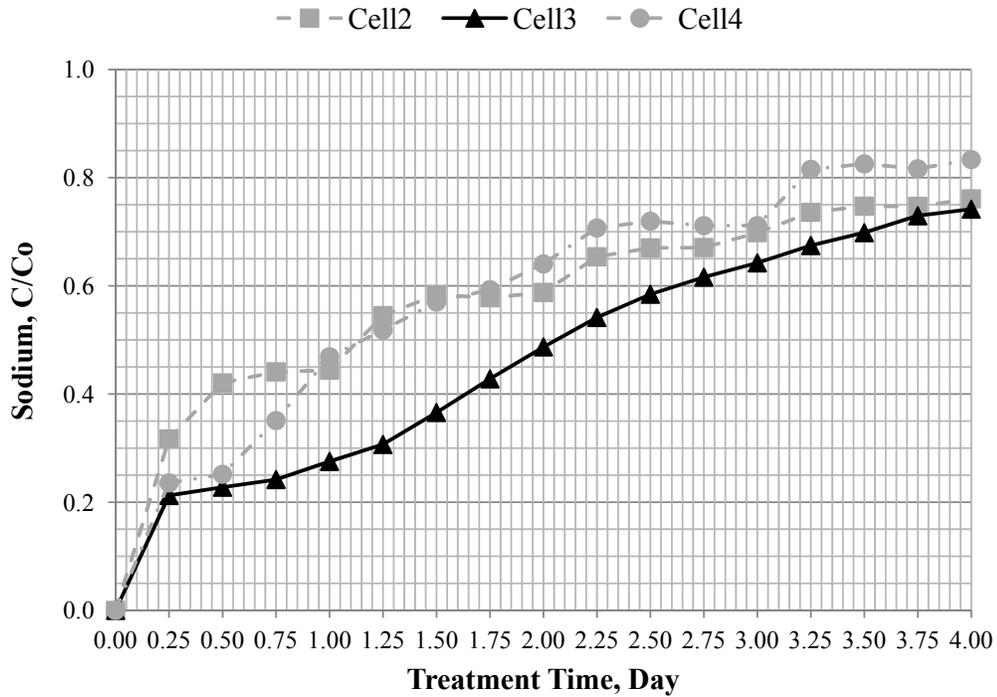


Figure 4.21 Variation of sodium ions in batch experiment 4

Similarly, Figure 4.22 presents variation of K^+ during the four day format experiment without any appearances of breakthrough curves. However, the start points did take place at around 1.2 hours (0.05 day) in all treatment cells. Like to Na^+ results, the alteration of C/C_0 concentration was drastically increasing during the first 6 hours (0.25 day). It also kept developing until the last experimental day. At the last day, the C/C_0 ratios were monitored as 0.32, 0.46 and 0.4 respectively for Cell2, Cell3 and Cell4. The C/C_0 line shown the possibility to reach the break point in Cell3, and it was found highest when compared to Cell2 and Cell4. However, those final ratio values were not able to reach 95% of their initial concentration, so the break

point did not occur. In addition, the speed of K^+ absorption rate directly related to the concentrate of K^+ in the influent samples.

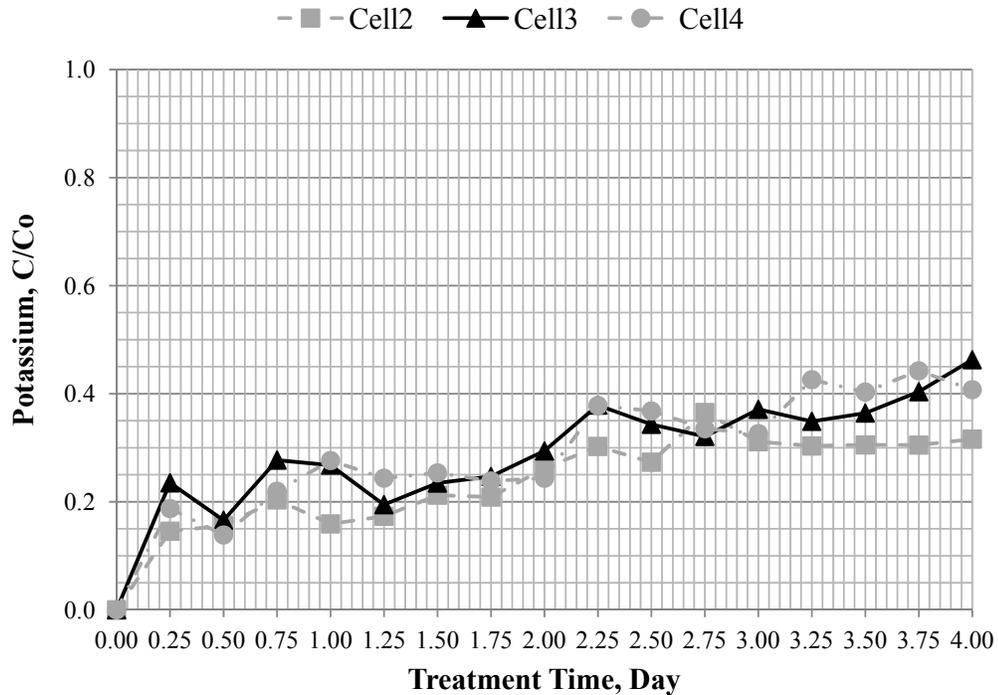


Figure 4.22 Variation of potassium ions in batch experiment 4

4.9 Summary of Observations

1. The bulk density (D_b) was measured in compacted clay samples as 1.40 g/cm^3 , and it did not meet the criteria for compacted condition ($D_b > 1.6 \text{ g/cm}^3$). The volume of voids space in the compacted clay was reduced to approximately half the natural state following application of pressure. ($4,505 \text{ cm}^3$ reduced to $2,743 \text{ cm}^3$).
2. The measured liquid limit (w_l), plastic limit (w_p) and plastic index (I_p) for the clay sample were 74.53 %, 28.28% and 46.25%, respectively. These data are similar to Ito's work at the depth 0 to 1.5 m for Regina Clay.

3. The sand sample characterized $d_{10} = 0.27$, $d_{30} = 0.38$ and $d_{60} = 0.60$ mm, and the coefficient factors C_u and C_c were determined to be 2.22 and 0.89, respectively. For the gravel samples, d_{10} , d_{30} and d_{60} were obtained as 12.0, 15.5 and 18.0 mm, correspondingly while the parameter $C_u = 1.50$ and $C_c = 1.11$.
4. During the 16-day format experiments, the best K^+ removal rate was recorded on Cell2 as $92.1 \pm 63.4\%$ ($4.6 \pm 5.3 \text{ mg/l}$) while Cell 4 contributed the maximum removal of Na^+ and Cl^- as $44.8 \pm 76.7\%$ ($53.2 \pm 92.4 \text{ mg/l}$) and $50.5 \pm 109.6\%$ ($85.3 \pm 184.3 \text{ mg/l}$).
5. During the first 4 days in batch experiment 4, the start points of chloride breakthrough ($C/C_0 > 0.05$) were found at less than 6 hours and it took approximately 48 hours to reach the break points ($C/C_0 > 0.95$). After that, all treatment cells lost their ability to remove chloride ions.

5. Conclusions and Recommendations

5.1 Conclusions

1. Synthetic brine qualities were high in term of Cl^- , Na^+ , conductivity, TDS and salinity concentrations, but contained low level amount of K^+ and alkalinity. Temperature was recorded as room temperature while pH was measured as natural value.
2. Effluent qualities were high in overall parameters along with room temperature and natural pH values.
3. Non-vegetated constructed wetland system achieved higher chloride salt ions removal efficiency when the concentration ratio of $\text{NaCl}:\text{KCl}$ in the synthetic brine was increased. The order of removal efficiency within the operational cells was $\text{Cell4} > \text{Cell3} > \text{Cell2} > \text{control cell}$.
4. The best cations removal efficiency was found nearly 92% on K^+ . Also, the K^+ removal rate staying high throughout the period of brine feeding. The maximum removal on Na^+ was recorded as 45%, and its removal rate dropped down during the first three days. Although the quantity of a positive charged ion on both Na^+ and K^+ are equal, the K^+ removal rate was 2 times higher than Na^+ . Due to the lyotropic series ($\text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+ > \text{H}^+$), cations carry great level of positive charged ions along with containing large atomic size are likely to be attracted and absorbed by the negative charge surface of smectite clay (Bergaya, Lagaly, & Vayer, 2006). If the degree of their valences are equal, the larger ion size contributed stronger substitution power (Holtz, 2011). In fact, the ionic radius of K^+ , are reported as 1.38\AA and 1.51\AA in the structures of an alumina (octahedral) and a silica (tetrahedral) structures respectively, are

bigger than Na^+ (1.02Å in alumina layer and 1.18 in silica layer) (Giese, 2002). In conclusion, the fresh clay surface were full with the amount of negative charges, so amount of Na^+ and K^+ were mostly removed at the first experimental day. Then the negative charges on clay surface became limited, K^+ took priority to bond to an ion-exchange site. Na^+ removal process was still occurred from the remaining negative charges. Therefore K^+ removal rate stayed high while Na^+ was decreasing.

5. The maximum removal efficiency was found 51% on Cl^- , and its removal rate was decreasing. None of Cl^- was eliminated after passed the 4th operational day. Mostly, the amount of Cl^- was dramatically reduced at the first day by forming insoluble salt compounds with available cations and precipitating at the clay surface (Bergaya et al., 2006). In additional, very few were removed by anion exchange process due to clay naturally containing very low anion exchange capacity (AEC) (Bergaya et al., 2006). When the available cations and AEC were limited and became depleted, the rate of forming and precipitating of salt compounds was reduced and stopped after passed the 4th day. Then, amount of free Cl^- were accumulated in the clay solution, and they were expected to leaching out by the influent water. Therefore, effluent samples collected from the 5th-13th day were found high in term of Cl^- concentration.
6. During the cleaning stage, deionised water not only washed out all residual salt ions from the CW system, but the clay was also refilled the negative charges on clay surface. Another word, clay became being fresh again after passed the cleaning stage. Due to the weakness of Van der Waals' forces of the silica sheet, hydrogen ion (H^+) from water can enter to the edge of silica layers

which is located on top of the alumina layer in the 2:1 structure of smectite, and make hydrogen bonding with groups of oxygen or hydroxyl (Holtz, 2011). The separation and defection of silica layer are occurred. This action known as broken edge releases plenty of negative charges to the clay surface due to the incomplete structural formation of silica sheet. In addition, the clay mineral itself has ability to recharge the negative charges on the surface by substitution of cations in the alumina layer. The process increases the negative charges when the new cations that were replaced in contain less valences than the current cations (Holtz, 2011).

7. Clay use as an adsorptive material can remove pollutants via adsorption, precipitation and ion exchange process.
8. Batch experiment 4 provided breakthrough curve (BC) for Cl^- , but not $\text{N}^{\text{a}+}$ and K^+ due to unidentified ending points on both cations.
9. Due to the short-circuiting and preferential flow from the edges of operational cells, the ending point of chloride breakthrough curve was much faster than theoretically calculated.

5.2 Recommendations for Future Work

1. The measurement of ions should be conducted with an Ion Chromatography (IC) instead of using the ISE probes due to inconstant outcomes and laboratory time consuming.
2. To meet the compaction criteria ($D_b > 1.6 \text{ g/cm}^3$), new solutions are required in order to apply pressure on clay samples. Compacting with a rubber hammer and a marble rolling pin contributed insufficient pressure load. Alternatively,

building cell cases with new materials that are stronger than plastic containers leads no concerns of structure failures in the process of compaction.

3. The pre and post treated natural and compacted clay samples require to measure and record cation exchange capacity (CEC) for each treatment cell and batch experiment.
4. The CW systems should be designed in the circular column instead of rectangular shape if the experiment focuses on series of synthetic brine concentrations or a range of clay thickness. The experiment is conducted by small scales of clay sample and influent volume. Although it contributes less specific surface than a rectangular shape, the clay sample preparation are likely to achieve the compaction condition.
5. To achieve high salt ions removal rate in outcomes, the clay thickness should be increased due to CEC direct related with amount of clay.
6. To obtain accurate outflow results especially for the chloride breakthrough curve, the solutions to prevent short-circuiting or preferential flow that occurred from the edge around the operational cell needs to be found.
7. In large scale use, the CW systems should be assigned as the secondary treatment which requires a pre and post treatment process. Depending on influent volume, the CW systems can operate by a rotation system with at least 3 treatment units. While the two units are receiving brine at the same time, the one is standby for a cleaning stage. Alternatively, feeding chemicals to adjust an ion balance in the system is another option to recovery the negative charges to the clay. However, the information on types and quantities of the chemicals is required to reveal by next studies.

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