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Belbase, Shashidhar, <u>Evaluation of the Effectiveness of Zeolite Treatment in Remediation of Impacts of Coalbed Natural Gas Coproduced Water on Soil</u>, Master of Science, Department of Civil and Architectural Engineering, August, 2011.

Abstract

This research study examined the impact of high sodicity CBNG coproduced water on a soil's hydraulic characteristics (infiltration), chemical properties in relation to sodium adsorption ratio (SAR), electrical conductivity (EC), and pH, and the subsequent impact on these properties by the use of Bear River (BR) zeolite. A batch adsorption isotherm study revealed that the adsorption of sodium (Na^+) was determined by the type of anions associated with Na^+, indicating that bicarbonate (HCO_3^-) had a more positive impact than Cl^- ions on the adsorption of Na^+. Fitting this with the Langmuir and Freundlich models revealed that the coefficients of Na^+ adsorption were higher for HCO_3^- than Cl^-. An adsorption kinetics study indicated that adsorption of Na^+ by BR-zeolite was an inverse function of particle size, with smaller particles having greater adsorption capacities. The greatest efficiency was found with the particle size 1.3–1.5 mm which removed about 72% of the Na^+ in the first 30 minutes of reaction compared to 59% with the zeolite particle size 2.0-2.5 mm. The SAR was also reduced from 30 to below 10 $(mol/m^3)^{1/2}$ in the first 30 minutes of batch reaction. Both a laboratory columns study and a field experiment of a falling head permeameter infiltration test indicated that the negative impact of infiltration through soil in CBNG coproduced water can be at last partially mitigated by BR-zeolite.

There was a significant difference in the infiltration of CBNG coproduced water through boreholes with zeolite and without zeolite at the 95% confidence level ($p=6.87*10^{-7}<0.05$ for phase I and $p=2.76*10^{-6}<0.05$ for phase II). An analysis of influent and effluent water from the column study and the post-treatment analysis of soil saturated paste extracts from the 0-5, 5-15, 15-30, 55-65, and 95-105 cm intervals below the boreholes, revealed BR

zeolite reduced the SAR and the EC of soil and water. By reducing the potential harmful impacts of high concentrations of Na^+ in CBNG water on the physicochemical properties of soil and groundwater, it is possible that a Ca^{2+} and Mg^{2+} rich zeolite lining at the bottom of an infiltrated containment pond can enhance the beneficial use of coproduced water for groundwater recharge and other possible uses. It can be concluded from this study that a BR-zeolite treatment of CBNG water can be an effective method for mitigating the harmful impacts caused by high Na^+ concentration on the physicochemical characteristics of soil and water.

EVALUATION OF THE EFFECTIVENESS OF ZEOLITE IN REMEDIATION OF
IMPACTS OF COALBED NATURAL GAS COPRODUCED WATER ON SOIL

By

Shashidhar Belbase

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CHAPTER 1

ISSUES AND CONCERNS ASSOCIATED WITH COALBED NATURAL GAS COPRODUCED WATER IN THE POWDER RIVER BASIN OF WYOMING

Context of Coalbed Natural Gas (CBNG) Coproduced Water

Where does the huge amount of CBNG coproduced water in the Powder River Basin (PRB) of Wyoming and Montana end up? What are the quality issues with the CBNG coproduced water? What effects do these waters have on soil, water, and the environment? What are the current management and treatment practices? These are some of the key questions and concerns that arise when we think about issues associated with CBNG coproduced water.

CBNG production involves extracting natural gas from coalbeds by depressurizing coal seams through removing coal aquifer water. The lower hydraulic pressure allows the CBNG gas to desorb from coal. The desorbed gas is collected and used as an energy source (Brinck et al., 2008; DeBruin et al., 2004). Commercial production of CBNG in the Northern Appalachian Basin began in the 1930s and from the San Juan Basin during the early 1950s (DOE, 2008). The economic significance of CBNG resources was first realized in the 1970s and early 1980s when the Bureau of Mines (BM), Department of Energy (DEO), Gas Research Institute (GRI), and oil and gas operators made a rigorous effort to demonstrate the commercial production of CBNG in the United States (Ayers, 2002). In the Wyoming PRB, CBNG production began in earnest with a small number of gas wells in 1987.

According to a report of the DOE, the number of gas wells in the PRB reached 13,600 by 2004, with projected number of wells to reach 20,900 by the end of 2010 (DOE, 2008). This number has been estimated to be around 30,000 at present. The Powder River coalfield within the PRB of Wyoming and Montana is the largest coal resources in the United States

(Stearns et al., 2005). A rapid expansion of CBNG production wells in the PRB has substantially increased the amount of CBNG coproduced water in the area. Between 1987 to 2004, the amount of water produced was 467 million cubic meters as compared to 36.8 billion cubic meters of natural gas during the same period (DOE, 2008). The amount of water produced from the CBNG wells in the PRB has been a concern to all stakeholders. It is estimated that approximately 600 million cubic meters of CBNG coproduced water will be produced by 2029 from now (Johnston et al., 2008). A major issue associated with CBNG production is about what to do with the large volume of CBNG coproduced water. The management of this water is a major environmental concern for both public and private stakeholders (Johnston et al., 2008).

One of the major issues with disposal of CBNG coproduced water is the water quality. Much of the CBNG produced water has a high concentration of sodium (Na^+) relative to calcium (Ca^{2+}) and magnesium (Mg^{2+}). The relative concentration of Na^+ is measured in terms of the sodium adsorption ratio (SAR). Produced water with a high SAR can leach Ca^{2+} out from the soil, and destroy the soil structure through the dispersion of clay particles (Payne, 2004). Payne (2004) further stated that the SAR is an indicator of the hazards associated with the ion-exchange complex reaction of CBNG coproduced water within the soil. Water from the CBNG wells in the PRB is mostly dominated by Na^+ and bicarbonate (HCO_3^-) ions. This water has a maximum pH 9.2, EC 5.0 dS/m, and SAR 70.0 $(mol/m^3)^{1/2}$ (Ganjegunte et al., 2005; Jackson & Reddy, 2007; Vance et al., 2008). An SAR is the ratio of Na^+ ion concentration to Ca^{2+} and Mg^{2+} ions. Here, Na^+ is considered a detrimental element in the CBNG coproduced water that can be replaced by Ca^{2+} and Mg^{2+} ions, both of which are considered beneficial elements in the water needed to maintain soil quality. Generally, an SAR value of 7 to 18 indicates a medium hazard from Na^+, a high hazard between 18 and 26, and very high hazards above 26 (Fetter, 2001). The hazard of Na^+

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not only destroys the soil structure, but also it affects the absorption of water by plants (Warrance et al., 2001).

Since the surface applied CBNG coproduced waters must pass through the topsoil, salinity and sodicity usually controls the rate of water entry into the soil (Minhas et al., 1994). The physical and chemical characteristics of the topsoil play a significant role in the infiltration of discharged CBNG coproduced water. It is challenging to maintain the controls (environment) in the field for the soils characterization against the permeability hazards of salinity and sodicity. Therefore, characterization of the soils against permeability hazards is done mostly under laboratory conditions with saline solutions applied to identically prepared soils. Threshold values of electrolyte content in relation to exchangeable sodium percentage (ESP) derived from such laboratory studies have been used to diagnose soil permeability hazards that vary in texture, clay mineralogy, salt release characteristics, organic matter and pH (Bresler et al., 1982; Shainberg & Letey, 1984).

Fate of CBNG Coproduced Water

One of the primary issues regarding CBNG coproduced water is its proper management. A large quantity of water produced from CBNG wells is disposed of into natural creeks, rivers, surface lands, containment ponds, or re-injected into deep aquifers. Some of this water is also utilized, or re-used, for beneficial purposes such as irrigation, wetlands, water supplies, and fisheries. Disposal choice depends in large part on the composition of the water (USGS, 2000). The major parameters determining the quality of the water include total dissolved salts (TDS), pH, concentrations of dissolved cations and anions, and dissolved organics and gases. Disposal or reuse options are also dependent upon the cost of treatment. The reuse of this water has to meet federal and state standards. If it is too costly to treat the water, then the water can be disposed of either by reinjection into subsurface

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(deep or swallow aquifers) or by surface discharge into containment ponds, wetlands, and rivers or creeks assuming that it meets the federal and state regulations.

As it is a way to conserve valuable water and reduce costs, treatment of the produced water for beneficial use has a significant appeal in most of the arid regions in the western United States, including the PRB. The challenge is to identify and develop a less complicated and more cost effective CBNG coproduced water treatment technology (Hightower, 2001).

Chemistry of CBNG Coproduced Water

One of the PRB CBNG coproduced water issues is associated with its water chemistry that is a potential regional environmental threat. Most of the water produced from CBNG wells in the PRB is dominated by Na^+ and HCO_3^- ions, with pH ranging from 6.8 to 9.2, electrical conductivity (EC) from 0.4 to 5.0 dS/m, and sodium adsorption ratio (SAR) from 5.0 to 70.0 $(mol/m^3)^{1/2}$ (Ganjegunte et al., 2005; Jackson & Reddy, 2007; Rice et al., 2000; Vance et al., 2008).

The measure of total dissolved salts (TDS) in CBNG coproduced water is termed salinity. The total amount of dissolved Na^+ present in the produced water is termed sodicity. CBNG coproduced water chemistry is highly variable throughout the PRB (Sessoms et al., 2002) in that the produced water is generally rich in sodium bicarbonate ($NaHCO_3$) and the region's surface water is found to be rich in calcium (Ca^{2+}). When the produced water is exposed to the atmosphere, and is discharged to the surface or applied in irrigation, $NaHCO_3$ undergoes the following reaction:

$$NaHCO_3 \longrightarrow Na^+ + CO_3^{2-} + H^+ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 1.1$$

$$Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \longrightarrow CaCO_3 (s) + MgCO_3 (s) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 1.2$$

The free carbonate in the water is available to bind with Ca^{2+} and Mg^{2+} in the surface water or the soil to form $CaCO_3$ and $MgCO_3$ solids. Precipitation of Ca^{2+} and Mg^{2+} from surface water, or the soil, increases the ratio of Na^+ over Ca^{2+} and Mg^{2+} thereby increasing

the sodicity or SAR of the water and soil (Sessoms et al., 2002). High sodic and saline water affect not only a soil's physical, chemical, and biological characteristics, but it also has a deleterious impact on the water and land ecosystems.

The acidity or basicity characteristic of a soil solution is measured by pH, which is the measure of activity of hydrogen ions (H^+) in a solution. A pH value is expressed in a logarithmic scale. Therefore, the hydrogen ion activity in a solution is defined as a negative logarithm of hydrogen ion activity in a solution. It is expressed like $pH = -\log_{10} (H^+)$. In practice, the pH measure gives the hydrogen ion activity in the solution rather than H^+ concentration.

There is less impact on the soil's pH through the disposal of CBNG produced water in the PRB in comparison to other parameters such as SAR and EC. However, the continuous disposal of CBNG produced water on surface soil that is exposed to the atmosphere for a longer time can also impact the bicarbonate component of the CBNG coproduced water thereby releasing carbon dioxide gas that reduces the pH of the water, and thus reducing the pH of the soil (equations 1.3 and 1.4) which again may balance high pH caused by Na^+.

$NaHCO3^- \longrightarrow Na^+ + H^+ + CO_3^{2-}$………………………………………………1.3

$2H^+ + CO_3^{2-} \longrightarrow H_2O + CO_2$…………………………………………………1.4
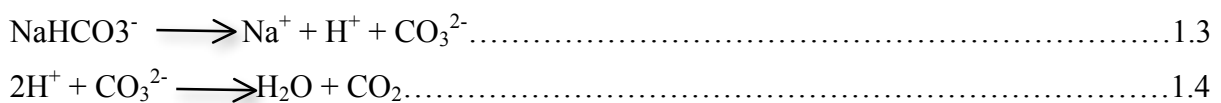
Howat (2000) states that the pH values of a soil influence several soil characteristics such as weathering, soil structure, humification, biotic activities, mobilization of nutrients, and ion exchange. Soil pH change can affect the chemicals in the soil as well as any physical and biological activities. Upon discharge, the average pH of CBNG coproduced water in the PRB is between 7.0 to 7.5, and increases up to 8.0 thereafter due to a cation exchange with the soil. A pH of 9 generally reduces the growth of most plants, and it is fatal to some species (Sessoms et al., 2002). Tisdale et al. (1993) reported that high concentration of Na^+, combined with low concentrations of salts, causes soil aggregates to breakdown, reducing the pore size of the aggregates, increasing bulk density, and finally leading to a decrease in the

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total porosity. During wetting, soil dispersion occurs due to excess Na^+ ions which are unable to bind the soil particles together into stable aggregates. Upon drying of the soil, a hard crust forms on the exposed surface that may cause poor aeration, and inhibits plant growth (Hayward & Bernstein, 1958). The CBNG coproduced water chemistry is, therefore, associated with dissolved constituents such as TDS, organics, gases, and pH, all of which have a significant impact on soil and water characteristics as a result of either disposal or reuse.

Impact of Sodicity and Salinity on Soil Physical, Chemical and Biological Properties

Impact on Soil Physical Properties

Various studies (e.g., Abu-Sharer et al., 1987; Agassi et al., 1981; Beletse et al., 2008; Ganjegunte et al., 2005; Johnston et al., 2008; McNeal & Coleman, 1966; McNeal, 1968; Pearson et al. 2003; Sumner, 1993; Vance et al., 2008) have discussed the impact of water salinity on the physical characteristics of soil. Soil aggregate, stability, soil water retention, porosity, bulk density, solid density, coagulation and flocculation, and soil texture are important parameters associated with the physical characteristics of soils. Salinity and sodicity of CBNG coproduced water used for irrigation has a significant effect on soil characteristics.

Soil particles such as sand, silt, clay minerals, and organic matter bind together to form aggregates that are the basic structural units of soil. Soil aggregates have different strengths that withstand stressors due to water and air flow, root growth, micro and macro organisms' movement, and other physical phenomena such as temperature and pressure. The structural stability of soil plays a very important role in growth of plants and other micro faunal communities. High salinity causes fine particles in the soil to bind together into aggregates. This process is beneficial in terms of soil aeration, root penetration and growth, but it can be toxic to plants due to the presence of excess ions (Beletse et al., 2008).

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Multivalent cations such as Ca^{2+}, Mg^{2+}, Al^{3+} etc., help to form soil particle flocculates in the form of soil aggregates enhancing porosity. However, elevated salinity adversely affects the ability of plants to uptake water in order to facilitate biochemical processes in plants such as photosynthesis (Vance et al., 2008).

Sodium has an adverse effect on soil aggregation and stabilization. The presence of excess Na^+ disperses clay particles by weakening the forces that bind the clay particles, ultimately causing them to disrupt due to the separation and expansion caused by the swelling and dispersion of clay in soil (Abu-Sharer et al., 1987; Ganjegunte et al., 2005; Johnston et al., 2008; Pearson et. al., 2003; Sumner, 1993). Finally, the dispersion of clay particles causes the plugging of soil pores reducing soil permeability. The repeated wetting and drying of soil creates a cement-like solid structure that causes surface crusting. According to Johnston et al. (2008), elevated sodicity in irrigation water adversely affects a soil's structure, thereby affecting water infiltration, nutrient supply, and aeration.

The harmful effects of Na^+ salts on soil properties are well recognized. This is generally linked with high Na^+ levels for increased erosion and runoff (Ghadiri et al. 2004). Ghadiri et al. (2004) conducted a study to evaluate the effect of soil salinity and sodicity on soil erodibility and sediment transport. They concluded that there was a decrease in soil aggregate stability with a concomitant increase in the dispersion rates as a result of increasing sodicity. The high salinity and sodicity made the upper part of the soil crust hard, and then upon drying the soil cracked due to brittleness of the soil aggregates thus causing destruction in the soil structure (Agassi et al., 1981). The process of swelling and slaking, the dispersion and movement of clay causing pore blockage, are known to reduce permeability in soils (Payne, 2004). Oster and Schroer (1979) and Agassi et al. (1985) showed infiltration to be more sensitive to water quality than hydraulic conductivity. Unsaturated hydraulic conductivity has also been shown to be quite sensitive to sodicity and salinity. In most of the

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studies, the effects of water quality have been investigated under laboratory conditions. Very few attempts have been conducted to relate hydraulic properties of soils under actual field conditions. Our attempt is to fulfill this need by conducting infiltration study in the field scale.

The common effect of soil texture and soil structure is called tilth; tilth reveals how easily the plant roots can penetrate the soil. Good soil tilth indicates that there is sufficient water and air being transported to the roots of plants, and other microbes in the soil for plant life to flourish. Macropores are responsible for the permeation of water and air into the soil, and is responsible, over time, for the soil's water retention. Salinity and sodicity of CBNG coproduced water greatly impacts soil tilth. High salinity and sodicity causes deterioration of soil structure, soil stability, water and air transportation characteristics, and soil surface sealing, resulting in reduced infiltration, increased erosivity, impaired aeration, and finally poor tilth (Hadas, 1997). The presence of a high Na^+ concentrations in soils causes the soil to be dispersed, and then it is further compacted by rain or irrigated water thus reducing soil porosity. The cultivation of crops is made very difficult in such soil due to poor air and water movement.

Levy et al. (2005) examined the effects of ESP, fast wetting, and leaching using distilled water or saline water, and the effect on the hydraulic conductivity of 60 Israeli soils' wetting rate, ESP, and water salinity. The study revealed that there was an adverse impact of sodicity on the hydraulic conductivity of the soil samples that had been subjected to fast wetting combined with leaching that strongly depended on the soils' textures. Both the hydraulic conductivity and relative hydraulic conductivity were predominantly affected by water salinity (EC) and soil ESP (Crescimanno et al., 1995; Levy et al., 2005).

In their study Agassi et al. (1981, 1985) concluded that infiltration rates were sensitive to the sodicity of the soil and the electrical conductivity of the applied water. Their

observations suggested that crust formations were the result of the physical dispersion of soil aggregates impacted by the action of raindrops and a chemical dispersion that depends on a soil's ESP and the applied water's EC. Their study showed that there was a detrimental effect of sodicity on plant available water in the soil.

Impact on Soil Chemical Properties

Various literature has discussed the impact of salinity and sodicity on the chemical characteristics of the soil by changing soil pH, ESP, CEC, nutrient cycling such as carbon (C), nitrogen (N), phosphorus (P), and sulphur (S) cycling in the soil over time. Soil salinity and sodicity affects nutrient cycling. Carbon, N, P, S and micronutrient cycles are greatly affected by the content of soluble salts of Ca^{2+}, Mg^{2+}, K^+, and Na^+. High salinity and sodicity is detrimental to nutrient cycling in soil. Wong (2007) reported that soil organic carbon (SOC) level is a function of C inputs, which is mostly dominated by plant litter and rhizodeposition within the soil, and then the losses of C by leaching, erosion, and heterotrophic respiration. These changes in carbon biomass inputs, or organic matter accumulation in the soil, this will most likely alter these levels of SOC in the soil as a result of increasing salinity and sodicity (Wong, 2007).

Wong et al. (2004) claimed that increasing soil salinity and sodicity affects C dynamics within the soil, because soil C level is dependent inputs and losses. Wong et al. (2004) reported that where salination and sodication occurs, soil C stores are most likely depleted as organic matter which solubilizes, and provides substrate for the microbial population in the soil. During this process, plant inputs of C in the soil decreases due to effect on growth caused by excess Na^+ in the soil (Wong et al., 2004). Wong et al. (2004) emphasized that increase in salinity and sodicity may cause an increase dissolved organic

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carbon by dissolving organic matter in the soil initially providing a substrate for soil microbial population.

Salinity and sodicity also affects the cycling of N. Rao et al. (2002) report that production of legumes is harshly reduced in salt-affected soils. This might be associated with their ability to form and maintain N-fixing sites such as nodules which is damaged by both salinity and sodicity (Rao et al., 2002). When N-fixing is affected by salinity and sodicity, it also affects the N cycle in the soil by limiting bacterial nitrification and denitrification. Keith et al. (2009) conclude that water with Na^+ levels in typical Montana CBNG produced water is high enough to degrade the soil physical and chemical properties making the soil completely unsuitable for the growth of plants.

Impact on Soil Biological Properties

Application of high sodicity (SAR>12 $(mol/m^3)^{1/2}$) and salinity (EC>2 dS/m) CBNG coproduced water used for irrigation and other purposes has been found to have detrimental effects on the biological characteristics of the soil (Pearson, 2003). Pearson claims that biological activities of various organisms in the soil are affected by the saltiness and sodicity of the water. The saltiness and sodicity of water changes the amount of water in the soil that is available to plants (Pearson, 2003). Pearson (2003) reports that the presence of soluble salts in the soil makes water move from a lesser salt concentration to a greater salt concentration. This movement of water from a lower salt concentration to a higher salt concentration may cause plant roots to exert more pressure to pull water from the higher salinity region into the plant roots. The presence of the high concentration of salts may lower the amount of water actually available to the plants despite total amount of water in the root zone. This shows that higher salinity in the soil can decrease plant available water in the soil, and can cause plant stress (Pearson, 2003).

In less tolerant plants, higher salinity (EC> 10 dS/m) causes plant cell dehydration, reduced plant growth, and possibly death. Crop growth and yield may be reduced by soil ECs of 4 dS/m or more. Very sensitive crops, like some chilies, may be affected at an EC of 3 dS/m or more. At EC values of 16 dS/m or more, the yields of nearly all crops are affected. The negative symptoms of high soil salinity on crops are stunted growth, cupping of leaves, coloring of leaves to brown on the brittle tips, then the leaf margins, and finally the degradation of whole leaves (Anjum et al, 2005; Williams, 2008).

According to Marschner (1986), plant growth is affected by the presence of Na^+ salts. Marschner (1986) stated that this effect can be seen when the SAR exceeds a value of 15 $(mol/m^3)^{1/2}$ and the EC exceeds a value of 4 dS/m. Sodic soils affect the growth of plants as it adversely affects nutrient and water availability to plants. Phosphate is available at pH 6 to 7 while micronutrients like iron, manganese, zinc, copper, and cobalt are less available to plants at pH above 7. High Na^+ concentrations in irrigation water may result in soil crusting and a decrease in soil permeability. The lower soil permeability may cause the soil to be more degraded in terms of soil fertility and cultivation. Development of saline and sodic conditions due to poor soil drainage can add to poor physical, chemical, and biological properties (Williams, 2008).

Rietz and Haynes (2003) conducted a study on a Zimbabwean sugar estate to observe the effects of irrigation induced soil salinity and sodicity on microbial activity. They found a significant negative exponential relationship between the EC and microbial biomass C, the percentage of organic carbon present as microbial biomass. They found a negative correlation between SAR and ESP with the soil microbial biomass C. They also noticed that mineralizable N measured by aerobic incubation also found to be negatively correlated to EC and SAR. Their study indicated an increasing salinity and sodicity in the soil resulted in a smaller and more stressed microbial community. The exponential relationships with EC

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demonstrate a highly detrimental effect, suggesting that even a small increase in salinity had a negative impact on the microbial community (Rietz & Haynes, 2003).

A study conducted by Yuan et al. (2007) supported the above results of Rietz and Haynes (2003) on the effects of higher salinity and sodicity on microbial biomass. The effects of salinity on the size, activity, and the community structure of soil microorganisms affected arid soils showing a significant, but negative exponential relationship between EC and microbial biomass C. Yuan et al. (2007) further maintained that the percentage of SOC present as microbial biomass, microbial biomass N, the rate of ammonification, and potentially mineralizable nitrogen were negatively correlated to the electrical conductivity of the soil. The exponential relationships with EC demonstrated the highly detrimental effect that soil salinity had on microbial communities (Yuan et al. 2007).

Why CBNG Coproduced Water is Problematic?

The emergence of CBNG development as an economically viable source of methane extraction has resulted in the rapid expansion of CBNG development in the PRB in Wyoming (Rice et al., 2000; Stearns et al., 2005). There is a rapid increase in the demand that CBNG be a clean energy source. Large volumes of saline and sodic water being pumped out from the CBNG coal seams through producing wells have become a problem to the gas producers, government agencies, landowners, and to the environment in general. This water has the potential to harm irrigation sources, streams, agricultural ponds, riparian plant communities, aquatic resources, wildlife and farm habitats, and biodiversity and sustainability due to high sodicity levels (Stearns et al., 2005). The direct discharge of high sodicity CBNG coproduced waters (SAR > 13 $(mol/m^3)^{1/2}$) to the land's surface poses potential negative effects to the immediate environment. Some of the CBNG coproduced waters contain high salinity at

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numerous sites, and this has resulted in the swelling and dispersion of clay soils characteristics of those found in the PRB of Montana and Wyoming (Stearns et al., 2005).

When high sodic CBNG coproduced water is continuously used for irrigation purposes, the soil turns out to be highly sodic. Upon drying, the soil suffers due to poor soil-water relations caused by its decreasing permeability, reduced soil infiltration capacity, and the formation of soil surface crusts (Bauder, 2002). The degradation of soil due to high sodicity further affects SOC levels resulting in deteriorating vegetation growth and hence, decreasing plant biomass inputs and lower levels of organic matter accumulation in the soil (Wong, 2007). The discharged CBNG coproduced water has a serious impact on the transient or permanent streams and rivers in the PRB (The National Academy of Sciences, 2010). As a result, this changes surface water chemistry and other areas of CBNG production in the US. The National Academy of Sciences (2010) report unveils widespread adverse effects of CBNG coproduced water on indigenous organisms and vegetation. Some of these effects include degradation of soil and water qualities.

CBNG Coproduced Water Treatment and Management in the PRB

Different methods are being used to manage CBNG coproduced water in the PRB, Wyoming, and the choice of a method depends upon the water quality and the quantity to be managed. Some of the water management methods are direct surface discharge (with or without pretreatment), discharge into infiltration impoundments, containment of produced water in impoundments (negligible infiltration), land application (irrigation), and deep well injection (Fort Union Formation below the coal zone) (BLM, 2002).

Soils in dry and semi-arid regions, like the PRB, often contain high amounts of exchangeable Na^+, which if found, in amounts excessive to Ca^{2+} (SAR > 13), can have deleterious effects on soil physical properties (Mosaddeghi et al., 2008; Quirk & Schofield, 1955). Both salinity and sodicity influence how soils respond to wetting and interactions

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between the two must be examined in order to assess irrigation water suitability. In general, the flocculating effect of increasing soil EC counteracts the physically deleterious effect of an elevated SAR. Thus, salinity could reduce the negative effects of sodicity on a soil's physical properties and soil structures (Mosaddeghi et al., 2008). Non-saline sodic waters will disperse particles, and or aggregates, and result in the breakdown of soil structure (Ayers and Westcott, 1985; Curtin et al., 1994). As soil salinity increases, the high salt concentration causes the flocculation of soil domains and the persistence of soil structural stability.

In deep injection, the produced water is returned to subsurface, into the deep geologic units where the CBNG injection wells are completed (BLM, 2002). This method assumes that all injection wells will be completed in the Fort Union sandstone area below the coal zone or lower injection zones, and that all injections will occur underneath the coal units developed for CBNG (BLM, 2002). Current methods used for handling CBNG coproduced water in the PRB are discharge into surface water systems, infiltration impoundments, containment impoundments, land application, and shallow and deep injection. Discharges are permitted by the Wyoming Department of Environmental Quality (WDEQ) under National Pollutant Discharge Elimination System (NPDES) permit (BLM, 2002).

Zeolite linings at the bottom of evaporation impoundment ponds can help to reduce the sodicity of the infiltered water in the subsurface and increase the infiltration rate due to the soil's stability and flocculation. Bentonite linings form a clay layer at the bottom of evaporation impoundment ponds thereby reducing the infiltration of the produced water into the subsurface helping to prevent the potential leaching of salts from the soil. With the application of Ca^{2+} and Mg^{2+} rich zeolite to treat the CBNG coproduced water in the PRB, both evaporation and infiltration can be applied effectively at a lower cost compared to other advanced treatment techniques such as membrane technology, ion-exchange, and other physical processes such as freeze thaw and mechanical evaporation (Huang & Natrajan,

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2006). Prior studies revealed that a metric ton (1000 kg) of Ca-WY-Zeolite could treat about 60,000 L of CBNG coproduced water to lower SAR from 30 to an acceptable level of 10 (Zhao et al., 2008, 2009). Zeolite is a naturally occurring mineral that can be mined and processed at a cost that is less than other chemicals used for the treatment of CBNG coproduced water. Additionally, the application of zeolite in the evaporation impoundment ponds can reduce the treatment cost of the produced water.

Purpose and Objective of the Study

The purpose of this research study was to assess the effectiveness of Bear River (BR) zeolite in mitigating the harmful effects of CBNG coproduced water when applied to soil. The objectives of this study were to:

(1) Study the impact of sodium in CBNG coproduced water on the infiltration through subsoil,

(2) Evaluate the effect of BR zeolite for the remediation of the effect that CBNG coproduced water has on soils,

(3) Conduct a lab test and a field test in order to evaluate the effectiveness of BR zeolite treatment of CBNG coproduced water treatment, and measure its impact on physicochemical characteristics of soil.

Chapter Outline

The study contains four chapters with a general introduction, specific lab experiments and field research, and summary and conclusion.

Chapter 1

This chapter deals with a general introduction of CBNG coproduced water, issues related to CBNG coproduced water, its impact on soil physical, chemical, and biological characteristics, and treatment practices. This chapter includes purpose and objective of the study.

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Chapter 2

In chapter two, I have discussed adsorption isotherms, adsorption kinetics, and a column study using simulated CBNG coproduced water and BR zeolite. These studies were conducted in the laboratory at University of Wyoming.

Chapter 3

Chapter three includes field test of infiltration of CBNG coproduced water through boreholes with and without zeolite. Chapter 3 also includes soil extract analysis for pH, EC, and SAR of the soil taken from the field test site to a depth of 1.8 m from the bottom of each borehole.

Chapter 4

In this chapter, I have summarized the study with a brief conclusion and recommendations for further study.

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CHAPTER 2

EFFECTS OF COALBED NATURAL GAS COPRODUCED WATER ON SOIL USING
BEAR RIVER ZEOLITE: A BATCH ADSORPTION, KINETICS AND COLUMN STUDY

Abstract

Batch-scale sorption kinetic and isotherm studies were conducted to evaluate both the adsorption rate of Bear River (BR) zeolite for sodium (Na^+) using surrogate coalbed natural gas (CBNG) coproduced water with a sodium adsorption ratio (SAR) of 30 $(mol/m^3)^{1/2}$, and the effects of bicarbonate (HCO_3^-) and chloride (Cl^-) anions on the adsorption of Na^+. The batch adsorption isotherm study showed that the adsorption of sodium (Na^+) by zeolite followed the Langmuir adsorption model with the maximum adsorption of Na^+ by BR zeolite to be 18 and 21 mg Na^+ per gram BR zeolite with 0.0006 and 0.0012 L/mg Langmuir coefficients (K_L), and Freundlich coefficients (Kf) being 0.08 and 0.29 in NaCl and $NaHCO_3$ solutions, respectively. This clearly indicated that sorption of Na^+ was higher for HCO_3^- than for Cl^- as anions associated with Na^+. The adsorption kinetics study showed that the sorption of Na^+ was an inverse function of the size of zeolite particles and resulted in greater adsorption for smaller particles. Removal efficiency was found to be the highest (72%) for the smallest particle size (1.3–1.5 mm) compared to 59% for the largest particle size (2.0–2.5 mm) within the experimental conditions. Use of zeolite in the columns studies reduced the infiltration rate of tap water (SAR=1.9 $(mol/m^3)^{1/2}$ and electrical conductivity (EC)=0.2 dS/m) due to physical resistance of the zeolite particles from the top of the soil. However, during the first three days after the application of CBNG coproduced water (SAR=17.7$(mol/m^3)^{1/2}$ & EC=1.6 dS/m), the infiltration rate for columns with zeolite was higher than for the columns without zeolite indicating a positive impact of zeolite into the infiltration of CBNG coproduced water through the soil columns. The findings of these studies suggest that BR zeolite can be used as a possible treatment media for the remediation of potential harmful impacts associated with CBNG coproduced water in the soil and surface/ground water quality.

Introduction

A rapid expansion of coalbed natural gas (CBNG) production in the Powder River Basin (PRB) has increased the amount of water produced in the area with increasing impacts on the region's natural environment. From 1987 to 2004, the amount of coproduced water was 467 million cubic meters (16.5 billion cubic feet) as compared to 36.8 billion cubic meters (1.3 trillion cubic feet) of natural gas during the same period (DOE, 2008). The amount of water coproduced in the PRB from CBNG wells has become a concern for all the stakeholders. Approximately 600 million cubic meters (21.2 billion cubic feet) of CBNG coproduced water will be produced by 2029 (Johnston et al., 2008), and management of this water will be a major environmental concern for both public and private stakeholders.

A major issue associated with CBNG coproduced water is the potential surface and groundwater quality problems that are due to the disposal of the water without any treatment. Much of the CBNG coproduced water has a high sodium adsorption ratio (SAR>12 $(mol/m^3)^{1/2}$), and a high specific electrical conductivity (EC>2 dS/m). The presence of sodium (Na^+) in the water causes a common ion exchange reaction in the soil by replacing calcium (Ca^{2+}) with Na^+. The displaced Ca^{2+} is carried away by the water resulting in a high Na^+ concentration in the soil which can destroy the soil's structure by the dispersion of clay particles (Payne, 2004). Payne (2004) further stated that the SAR value is an indicator of hazards that are associated with the ion-exchange complex reaction of CBNG coproduced water and soil. The change in SAR values of discharged produced water from well to well may bring variations in the region's soil chemistry as a result of the surface discharge of CBNG coproduced water. Generally, a SAR value from 7 to 18 $(mol/m^3)^{1/2}$ indicates medium hazards from Na^+, a SAR value between 18 and 26 $(mol/m^3)^{1/2}$ high hazards, and a SAR value above 26 $(mol/m^3)^{1/2}$ very high hazards (Fetter, 2001). The surface application of Na^+

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can both destroy soil structure as well as reduce the absorption of water by plants (Warrance et al., 2001).

When CBNG coproduced water passes through topsoil the rate of water infiltration is controlled by soil and water salinity and sodicity (Minhas et al., 1994). The physical and chemical characteristics of the topsoil play a significant role in the infiltration of CBNG coproduced waters. It is a challenge to maintain the controls (e.g., environmental factors) on the soil with respect to the permeability hazards of salinity and sodicity at the field scale. Therefore, characterization of soils for potential permeability hazards is done primarily under laboratory conditions with saline, and/or sodic solutions applied to identically prepared soils (Minhas et al., 1994). Threshold laboratory values of the electrolyte content in relation to the exchangeable sodium percentage (ESP) that are derived from such studies have been used to diagnose the permeability hazards of soils that vary in texture, clay mineralogy, salt release characteristics, organic matter, and pH (Bresler et al., 1982; Pratt & Suarez, 1990; Quirk, 1971; Shainberg & Letey, 1984). Water from CBNG wells in the PRB is often dominated by Na^+ and HCO_3^- ions. The pH values range from 6.8 to 9.2; EC ranges from 0.4 to 5.0 dS/m; and SAR ranges from 5.0 to 70.0 $(mol/m^3)^{1/2}$ (Ganjegunte et al., 2005; Jackson & Reddy, 2007; Vance et al., 2008).

The relative concentration of Na^+ ions with respect to Ca^{2+} and Mg^{2+} ions in water is known as SAR. Here, Na^+ is considered to be a detrimental element in the CBNG coproduced water that can be replaced by Ca^{2+} and Mg^{2+} ions, which are considered beneficial elements in water for maintaining soil quality. The value of SAR is determined using the equation:

$$SAR \ (mol/m^3)^{1/2} = [Na^+]/([Ca^{2+}]+[Mg^{2+}])^{1/2} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 2.1$$

Where $[Na^+]$, $[Ca^{2+}]$ and $[Mg^{2+}]$ are the concentrations in mol/m^3 of respective ions in CBNG coproduced waters and/or soil solutions.

The salinity of produced water or soil solutions is a property related to the amount of

dissolved salts contained in these waters. The electrical conductivity (EC) is the most common measure of salinity. It generally indicates the ability of an aqueous solution to transmit an electric current. It is commonly expressed in units of millisiemens per meter (mS/m) or decisiemens per meter (dS/m). The higher the salinity or saltier the water, the greater the EC, hence the degree of salinity can be determined by measuring EC.

The purpose of this research study was to assess the effectiveness of Bear River (BR) zeolite in remediating the effects of CBNG coproduced water when applied to soil. The findings of this study can be helpful for designing CBNG coproduced water treatment ponds in the PRB, and can be used as a foundation for further research seeking to find beneficial uses for managing and treating CBNG coproduced water. The specific objectives of this research study were to evaluate the influence of BR zeolite on the sorption of Na^+, examine the impact of HCO_3^- and Cl^- ions in the adsorption of Na^+, and to examine the effect of zeolite on infiltration of CBNG coproduced water through soil columns.

Materials and Methods

Bear River (BR) Zeolite

St. Cloud Mining in New Mexico states that the most commercially valuable and dynamic property of zeolite is its cation exchange capacity (CEC). Generally, a cation exchange occurs when two or more positively charged compounds (compound ions) or elements (simple ions) exchange their relative places on a negatively charged host (simple or compound ions) (St. Cloud Mining, 2010). Natural zeolites are hydrated aluminosilicates of alkaline and alkaline-earth metals and mostly they consist of analcime, chabazite, clinoptilolite, erionite, ferrierite, haulandite, laumontite, mordenite, and phillipsite (Zhao et al., 2008). BR zeolite is a brand of zeolite mined, processed, packaged, and sold by Bear River Zeolite Company at Preston, Idaho. BR zeolite has an overall surface area of 24.9 m^2/g, bulk density is 881 – 991 kg/m^3, and mineral composition is 85% clinoptilolite. It has a CEC

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ranging from 1.5 to 1.8 meq/g. The chemical composition of BR zeolite in terms of major cations is 3.5% potassium (K^+), 1.6% of Ca^{2+} and less than 0.5% of Na^+. This zeolite has the ability to release beneficial ions (Ca^{2+} and Mg^{2+}) while capturing and binding less desirable ion (Na^+). A characteristic that makes it an ideal zeolite is the selective adsorption of Na^+ from the CBNG coproduced water.

Surrogate CBNG Coproduced Water

Surrogate CBNG coproduced water was synthesized in the lab by dissolving a mixture of $NaHCO_3$, KCl, Na_2SO_4, $NaCl$, $CaCl_2\text{-}2H_2O$, $MgCl_2\text{-}6H_2O$ and $(C_2H_5O)_4Si$ in de-ionized (DI) water with concentrations as shown in Table 2.1. The concentrations (mol/m^3) of the major anions and cations for the synthetic CBNG coproduced water are shown in the Table 2.2. The simulated water had an SAR of about 30 $(mol/m^3)^{1/2}$, EC 1.6 dS/cm and pH 9.2. For the purpose of identification, this stock CBNG coproduced water was labeled type I synthetic CBNG coproduced water. Another lot of synthetic CBNG coproduced water was prepared with tap water and labeled type II synthetic CBNG coproduced water.

Table 2.1: Composition of synthetic CBNG coproduced water

Chemical Species	Concentration (g/m^3)
$NaHCO_3$	1391
KCl	4.77
Na_2SO_4	14.80
$NaCl$	63.54
$CaCl_2.2H_2O$	36.68
$MgCl_2.6H_2O$	20.92
$(C_2H_5O)_4Si$	34.66

Table 2.2 Concentration of major cations and anions in synthetics CBNG coproduced water using DI Water (Zhao et al., 2008)

Cations	Concentration of Cations (mol/m^3)	Anions	Concentration of Anions (mol/m^3)
Na^+	17.85	HCO_3^-	16.56
K^+	0.06	Cl^-	1.86
Ca^{2+}	0.250	SO_4^{2-}	0.10
Mg^{2+}	0.10		

Table 2.3: Concentration of major cations in synthetic CBNG coproduced water using tap water

Major Cation Species	From Chemicals (mol/m^3)	From Tap Water (mol/m^3)	Total (mol/m^3)
Na$^+$	17.85	1.78	19.63
Ca^{2+}	0.25	0.55	0.8
Mg^{2+}	0.10	0.33	0.43
SAR	30.17 (mol/m^3)$^{1/2}$	1.9 (mol/m^3)$^{1/2}$	17.70 (mol/m^3)$^{1/2}$

Due to the presence of cations such as Na$^+$, K$^+$, Ca^{2+}, and Mg^{2+} in the tap water, the concentration of cation species was different for simulated CBNG coproduced water using DI water (type I) and tap water (type II). The species concentration of different cations and anions in the simulated CBNG coproduced water were determined in terms of mol/m^3, and tabulated as shown in the Table 2.2. The value of SAR in the synthetic CBNG coproduced water prepared by using DI water (type I) was 30 (mol/m^3)$^{1/2}$ but it was 17.7 (mol/m^3)$^{1/2}$ when prepared by using tap water (type II). This difference can be attributed to the presence of Ca^{2+} and Mg^{2+} (Table 2.3) in the tap water. The cation and anion concentrations were compared in terms of charge (equivalence) and they were found to be balanced both in terms of mole/m^3 or equivalent/m^3.

Degassing Water

Both tap water and the type II synthetic CBNG coproduced water were degassed in order to prevent gas bubbles from forming in the soil columns. Gas bubbles are problematic because they prevent the efficient flow of water through the soil columns. A sand column of approximately 1 m high and 10 cm diameter was used for degassing the water. A continuous supply of helium gas was sparged through the sand column from the bottom while tap water or synthetic CBNG coproduced water was passed down through the sand column from the top. Helium, which has a lower partial pressure than air, was used to strip the air from the water. During the column study experiments, the degassed tap water was collected in a reservoir tank of 113 L and it was used to supply water to the soil columns.

Adsorption Isotherm Study

The Na^+ adsorption isotherm study was performed using BR zeolite with $NaHCO_3$ and NaCl solutions. The BR zeolite was sieved in order to get a sample of 1.5-2.0 mm uniform particle size. A liter of stock solutions of each $NaHCO_3$ (18.26 g) and NaCl (12.72 g) were prepared with initial Na^+ concentrations of 5000 mg/L. Solution triplicates of 40; 30; 20; 15; 10; and 5 ml were mixed with 0; 10; 20; 25; 30; and 35 ml of DI water, respectively, to make 40 ml solutions with concentrations of sodium 5,000; 3,750; 2,500; 1,875; 1,250; and 625 mg/L, respectively. Each solution was poured into 50 ml plastic bottles containing 5 g of BR zeolite. Each bottle was then tightly capped and placed on a mechanical rotator (Barnsted Thermolyne LABQUAQE^R, Shaker Rotisserie, and Model No. 4152110). To reach equilibration, these bottles were rotated at 60 rpm for a period of two days (48 hours) at ambient temperature (22^0C). The supernatant solutions were then filtered into 40 ml test tubes using disc filters (SFCA/PF, 0.20 µm). The filtrate samples were stored in a refrigerator at 4^0C until they were analyzed for Na^+ concentrations.

Adsorption Kinetics Study

A Na^+ adsorption kinetics study was conducted on four different zeolite size fractions (1.3–1.5, 1.5-1.7, 1.7-2.0, and 2.0-2.5mm) using a batch equilibration technique (Zhao et al., 2008, 2009). Twenty grams of the BR zeolite from each particle size group were placed in separate 500 ml beakers and 500 ml of synthetic CBNG coproduced water (type I) was added to each of them. At 60 rpm at ambient temperature (22^0 C), the mixtures were stirred using a mechanical stirrer (PHIPPS & BIRD, Model No. 300). Samples of 1 ml aliquots of the solution were collected at 0; 30; 60; 120; 180; 300; 420; and 660 minutes using a 10 ml syringe (BD M 7938) with disc filter (SFCA/PF, 0.20 µm) attached. Adding DI water, samples were diluted to 25 ml, and stored in a refrigerator at 4^0C until where they would later be used for analysis of Na^+, Ca^{2+}, and Mg^{2+} concentrations.

Columns Study

A column study was conducted to evaluate the effect of CBNG coproduced water on flow rates through soil columns with and without zeolite. The soil for this experiment was collected from the field study area near the University of Wyoming Research and Extension Center at Sheridan, Wyoming. During construction of the boreholes for the field study, the soil was collected from the surface to a depth of 1.8 m, was packed in a polyethylene bag, stored in a laboratory at room temperature, and composited prior to its use in the columns study. The soil was then sieved with a 1.32 cm pore size screen (USA Standard Sieve, Serial # 00344). Six transparent polyvinyl chloride (PVC) columns with a height of 50 cm and a diameter of 5 cm were used for the construction of the soil columns. A wire gauge screw and synthetic filter were placed at the bottom of each column. A mass of 250 g of the sieved soil was gently poured into each column. To avoid the formation of air bubbles, degassed tap water was passed up through the bottom of each soil column. The columns were connected to the inlet tubes from a water reservoir tank (A in Figure 2.1). The column experimental data was acquired by flushing the major cations (Na^+, Ca^{2+}, and Mg^{2+}) in tap water and simulated CBNG coproduced water through soil columns with and without zeolite. The effluent was collected using 100 ml graduated cylinders. The column schematic is shown in figure 2.1.
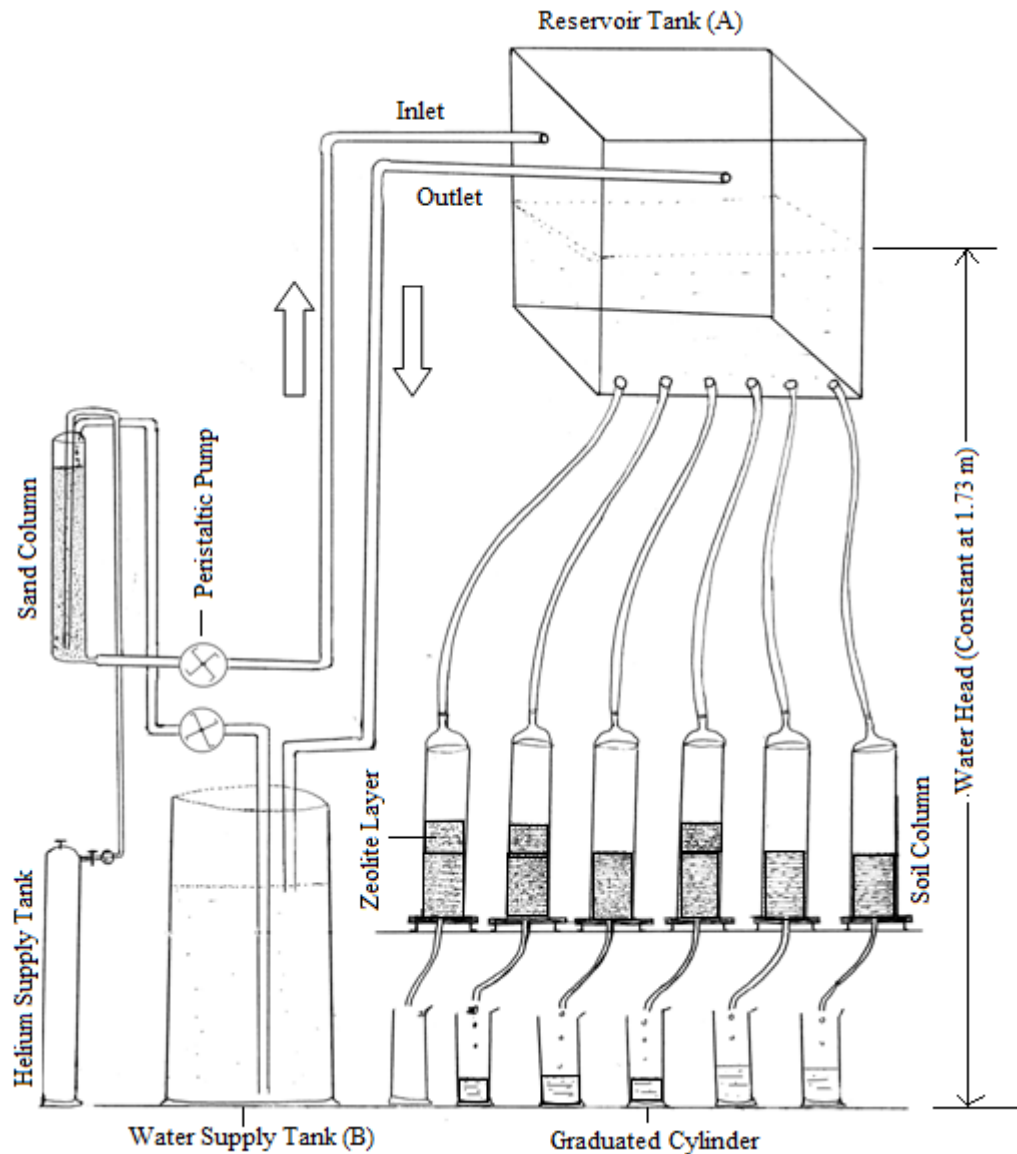
Figure 2.1: Schematic of the column apparatus including de-aeration and a constant head of water supply to the soil columns with and without zeolite (not in scale)

By balancing the flow of water to and from the reservoir tank, a constant head of 1.73 m was maintained. The reservoir overflow was collected in a 190 L water supply tank located at ground level. Water was constantly circulated through the degassing sand column to the reservoir tank using a peristaltic pump. For 24 hours, the columns were operated to allow the soil to settle in the columns. Three columns (C3, C5 & C6) out of the six columns were randomly selected for the application of zeolite, and the remaining columns were used without zeolite. Approximately 200 g of unseived BR zeolite was poured into each column to

form a 4 cm layer of zeolite above the soil. The flow of tap water through the columns was resumed. In on hour intervals, the volume of effluent water passed through each column was recorded six times a day. Average daily rates were calculated in ml/s. To stabilize the flow rates the experiment was continued with tap water for a period of 18 days. The reservoir and water supply tank were emptied, and filled with simulated CBNG coproduced water (type II). The columns were leached with the CBNG coproduced water for a period of two weeks.

It has been reported that a mass of 1000 kg of BR zeolite (14X40) can treat approximately 60,000 L of CBNG coproduced water by reducing the water SAR from 30 to below 10 $(mol/m^3)^{1/2}$ (Zhao et al., 2008). Based on this information, a mass of 200 g BR zeolite can treat 12000 ml of CBNG coproduced water to reduce its SAR from 30 to below 10. However, this process is water specific, and it may not be the same for all CBNG coproduced water with SAR value 30 $(mol/m^3)^{1/2}$. With the same SAR value, there can be different concentrations of Na^+ relative to Ca^{2+} and Mg^{2+} in the CBNG coproduced water that makes a difference in how much water can be treated by a certain mass of BR zeolite.

Triplicate samples were collected from the influent tap water, simulated CBNG coproduced water (type II) and columns effluent prior to the application of CBNG coproduced water through the columns. At the start of applying the CBNG coproduced water through the soil columns, effluent samples were collected in triplicate on the third, seventh, and 14th days. The EC value was measured using an electrical conductivity meter (OAKTON, Serial No. 31569), and pH was measured using a pH meter (Fisher Scientific). These water samples were labeled and stored in a refrigerator for an analysis of the concentration of Na^+, Mg^{2+}, and Ca^{2+}.

Chemical Analysis

The samples of water from the batch adsorption isotherm, adsorption kinetics, influent and effluents of the columns studies were used for an analysis of major cations. The cations

Na$^+$, Ca^{2+}, and Mg^{2+} were analyzed using Inductively Coupled Plasma (ICP) Spectroscopy (Thermo Jarrell Ash, Model P300). These analyses were done in the Geochemistry and Soil Science Laboratories at the University of Wyoming.

Statistical Analysis

Two equal samples t-test was applied to compare the mean flow rates through the soil columns to evaluate if the difference was significant at 95% confidence level.

Results and Discussion

Adsorption Isotherm

Adsorption of Na$^+$ (mg/g) on BR zeolite is shown for different equilibrium concentration (mg/L) of Na$^+$ in NaHCO$_3$ and NaCl solutions (Figure 2.2). The graph indicates that the sorption of sodium in BR zeolite was higher for the NaHCO$_3$ solution than the NaCl solution for all initial concentrations of Na$^+$ 5,000; 3,750; 2,500; 1,875; 1,250; and 625 mg/L. The rate of adsorption by absorbate is higher for higher concentration of Na$^+$ in the absorbent indicating more cation exchanges between the solution (NaHCO3 and NaCl) and the solid absorbent (zeolite). This also indicates that greater the exchangeable cation (Na$^+$) density in the solution greater is the chances of replacing the lightly held cations (Ca^{2+} and Mg^{2+}) from the surfaces of solid (that is zeolite in this case).

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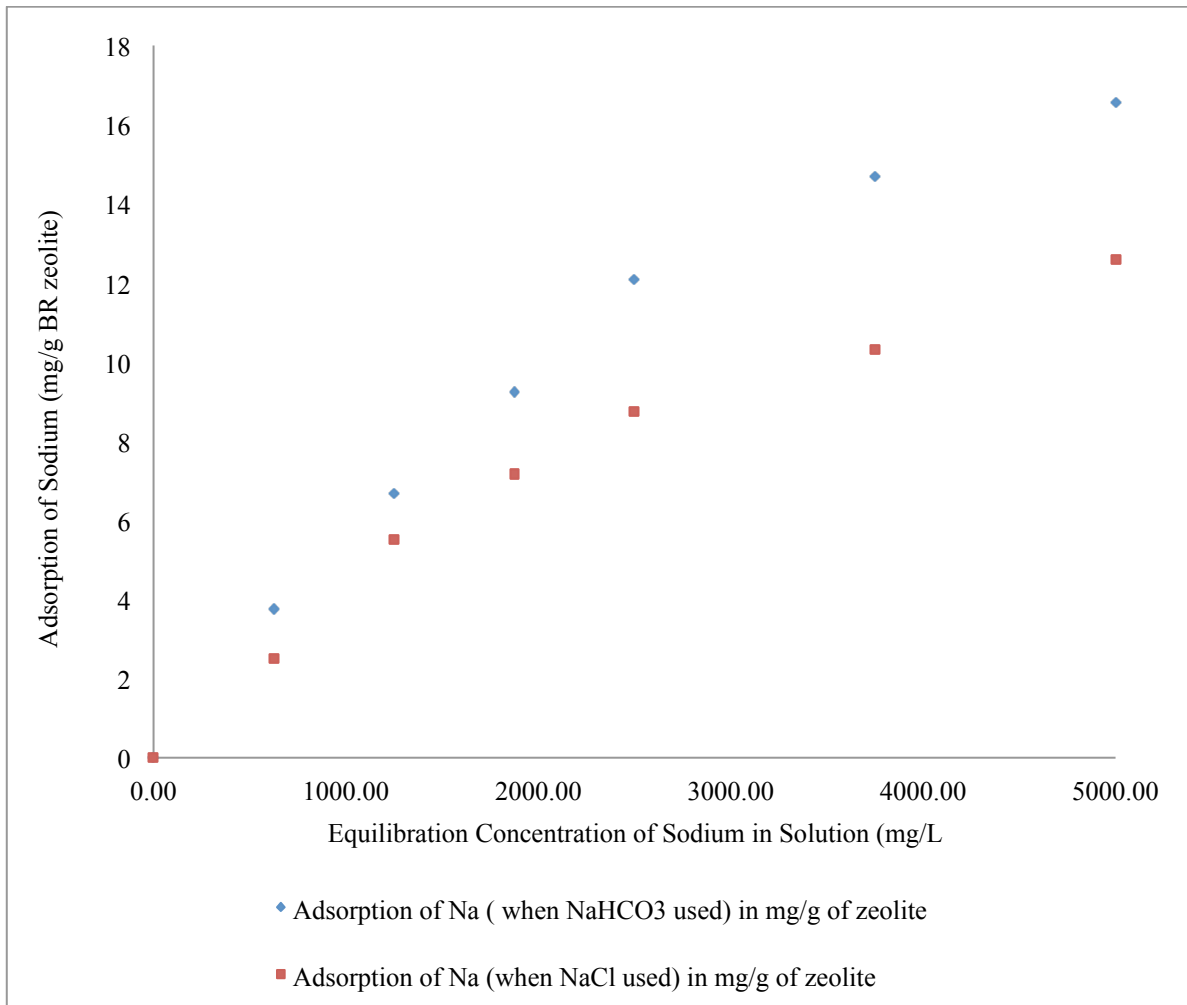
Figure 2.2: Sorption of Na$^+$ by BR zeolite at different equilibrium concentrations in 48 hours for NaHCO$_3$ and NaCl solutions

The adsorption curves in the Figure 2.2 revealed that adsorption on BR zeolite for NaHCO$_3$ and NaCl solutions could be well described by using the Langmuir equation 2.2:

$$q = \frac{q_{max} KC}{1 + KC}$$ 2.2

Where q is the sodium adsorbed (mg/g), q$_{max}$ is the maximum adsorption capacity (mg/g) of the solid phase, K is the Langmuir constant and C is the concentration (mg/L) of sodium in the solution at equilibrium. By rearranging the equation, equation 2.3 is obtained:

$$\frac{C}{q} = \frac{1}{K q_{max}} + \frac{C}{q_{max}}$$ 2.3

By plotting C/q vs. C, the slope of the line ($1/q_{max}$) can be used to determine q_{max} and the intercept $1/(Kq_{max})$, which can be used to determine K (Zhao et al., 2008). From the lines in the figure 2.3, the values of q_{max}, K and R^2 were calculated using their slopes and y-intercepts as in table 2.4.
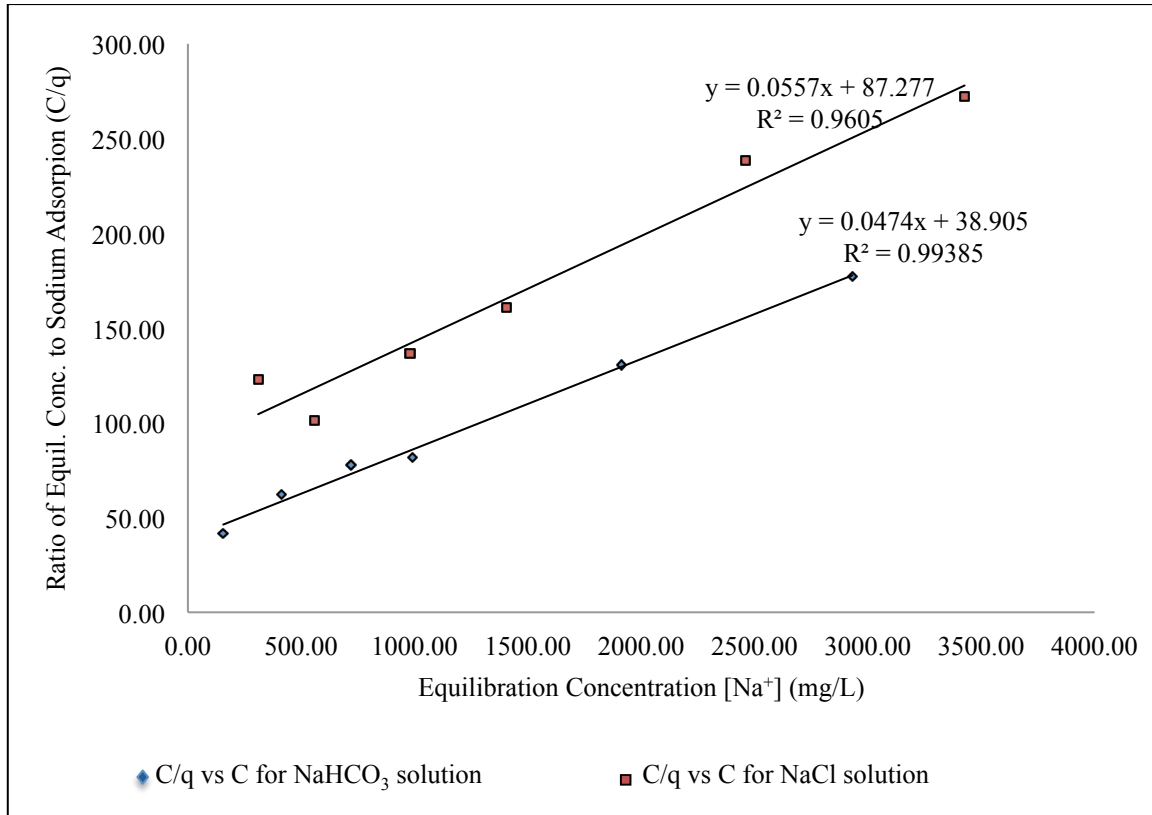
Figure 2.3: Langmuir Adsorption Isotherm models for adsorption of Na^+ by BR zeolite from $NaHCO_3$ and NaCl solutions at different equilibration concentrations

Table 2.4: Maximum adsorption of sodium, Langmuir Coefficients and R squared values

Reaction	q_{max} (mg/g)	K	R^2
BR zeolite with $NaHCO_3$	21	0.0012	0.99
BR zeolite with NaCl	18	0.0006	0.96

By fitting the Freundlich model for the adsorption of Na^+ by BR zeolite at different equilibration concentrations the adsorption isotherm can be studied. The Freundlich equation is represented by equation 2.4:

$X/m = K_f C_e^{1/n}$ …………………………………………………………………………….2.4

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Where X is mass (mg) of absorbate, m is mass of absorbent (g), K_f is Freundlich coefficient, C_e is the equilibrium concentration (mg/L) and $1/n$ is a constant. This equation is converted into a linear form in order to plot the graphs to determine K_f and n as in equation 2.5:

Log (X/m) = Log (K_f) + $1/n$ Log (C_e) ………………………………………………………………2.5

Fitting the Freundlich equation Log (X/m) vs Log (C_e), slope $(1/n)$ and y-intercept [Log (K_f)] were used to determine the value of n and K_f.

Table 2.5: Freundlich constants n, K_f, and R squared values

Reaction	n	K_f	R^2
BR zeolite with $NaHCO_3$	1.93	0.29	0.96
BR zeolite with NaCl	1.64	0.08	0.92

Both the Langmuir and Freundlich adsorption coefficients of BR zeolite were greater for the $NaHCO_3$ solution than the NaCl solution. The larger adsorption coefficients and maximum adsorption (q_{max}) for $NaHCO_3$ can be attributed to the precipitation of Ca^{2+} due to the formation of $CaCO_3$ and its release from zeolite to the solution. The formation of CO_2 that changes pH of the solution may contribute for a favorable condition to desorb more Ca^{2+} and Mg^{2+} from the zeolite resulting into more adsorption of Na^+ in the exchange sites.

The cation exchange reaction of Na^+ with zeolite is shown in equations 2.6-2.11 as follows:

NaCl $\longleftrightarrow$ Na^+ + Cl^- …………………………………………………………………………….......2.6

$2Na^+$ + Ca-Zeolite $\longleftrightarrow$ Ca^{2+} + Na_2-Zeolite ……………………………………2.7

Ca^{2+} + 2 Cl^- $\longleftrightarrow$ $CaCl_2$ (soluble) …..……………………………… 2.8

$NaHCO_3$ $\longleftrightarrow$ Na^+ + HCO_3^-…………………………………………………………......2.9

$2Na^+$ + Ca-Zeolite $\longrightarrow$ Ca^{2+}+ Na_2-Zeolite ……………………………...............2.10

Ca^{2+} + 2 HCO_3^- $\longrightarrow$ $CaCO_3$ (solid) $\downarrow$ + H_2O+CO_2 ..……………………………..2.11
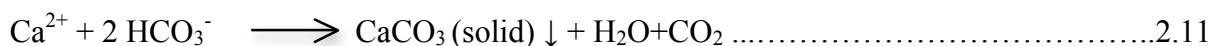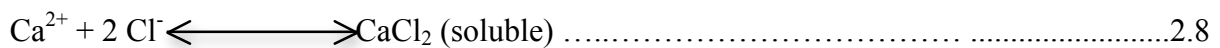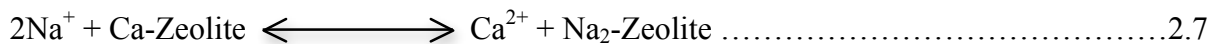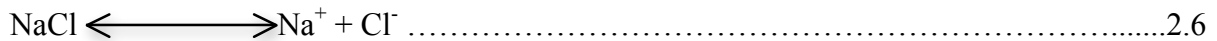
The ion exchange reactions (equation 2.7 & 2.10) continue until they reach an equilibrium state. This equilibrium is reached earlier in case of the NaCl solution because the

concentration of Ca^{2+} in the solution (desorbed from the zeolite) increases with time, and does not precipitate (equations 2.7 & 2.8). However, a part of the Ca^{2+} desorbed from the zeolite in the presence of $NaHCO_3$ can precipitate out (equations 2.9, 2.10 & 2.11) keeping the concentration of Ca^{2+} solution lower in its dissolved form, and shifting the equilibrium towards the right. In these reactions zeolite behaves as an adsorbent in the ion-exchange process, and the exchange reaction at the zeolite/$NaHCO_3$ and zeolite/NaCl solution interface was drastically affected by the physicochemical properties which may have influenced the mobility of the ions (Critter & Airoldi, 2003).

Adsorption Kinetics

For the surrogated CBNG coproduced water-I the effect of particle size on the removal rate of zeolite is shown in figure 2.4.
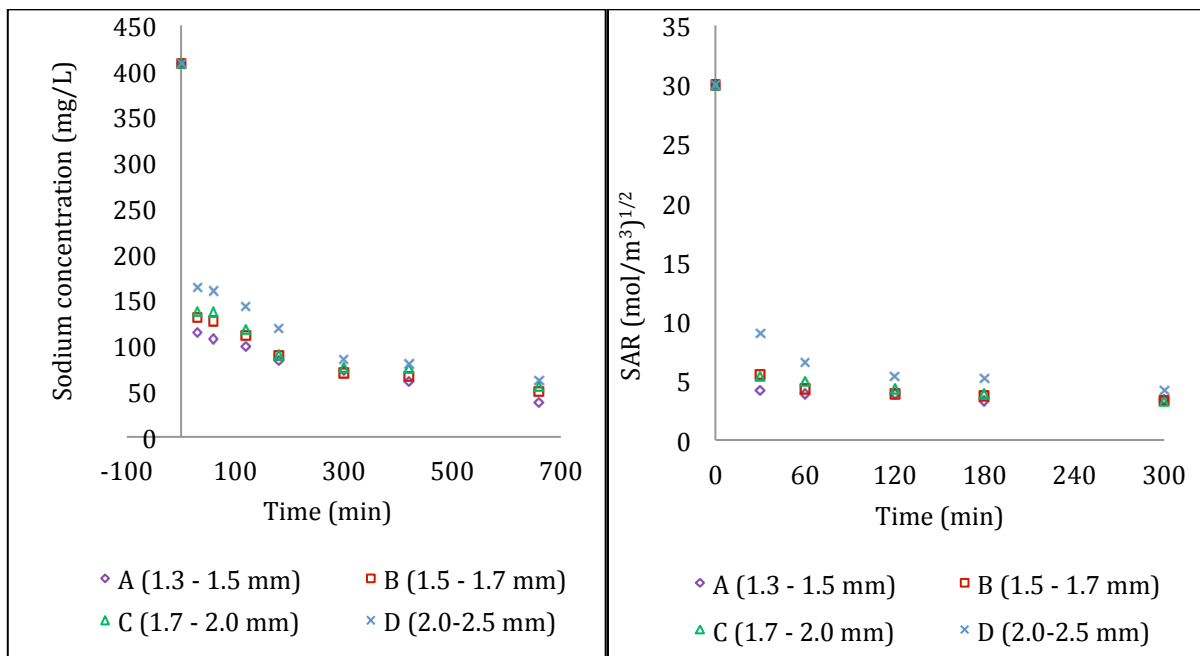
Figure 2.4: Change of Na^+ concentration (mg/L) with time (min) for particle sizes 1.3–1.5, 1.5–1.7, 1.7–2.0, and 2.0–2.5 mm of BR zeolite.

Figure 2.5: Change of Sodium Adsorption Ratio $(mol/m^3)^{1/2}$ with time (min) for BR zeolite particle sizes 1.3–1.5 mm, 1.5–1.7 mm, 1.7–2.0 mm, and 2.0–2.5 mm

It was observed that for all the particle sizes examined, the rate of Na^+ removal was higher for the first 30 minutes, and after that the rate decreased (Huang & Natrajan, 2006). It

was also found that there were greater removal rates of Na^+ with smaller sized zeolite particles. The greatest efficiency was found with the particle size 1.3–1.5 mm which removed about 72% of sodium in the first 30 minutes of reaction (Table 2.6).

Table 2.6: Percentage removal of Na^+ by BR zeolite from the CBNG coproduced water in the first 30 minutes

Particle size	1.3 – 1.5 mm	1.5 – 1.7 mm	1.7 – 2.0 mm	2.0 – 2.5 mm
% removal in first 30 min	72	68	66	59

Table 2.7: Change in the CBNG coproduced water's SAR by the different BR zeolite particle sizes in the first 30 minutes.

Particle size	1.3 – 1.5 mm	1.5-1.7 mm	1.7 – 2.0 mm	2.0 – 2.5 mm
Initial SAR	30.0	30.0	30.0	30.0
SAR in first 30 min	4.2	5.5	5.4	9.0

The SAR was also reduced from 30 to below 10 $(mol/m^3)^{1/2}$ in the first 30 minutes of reaction. In the same time period, the SAR values reduced to 4.2, 5.5, 5.4 and 9.0 $(mol/m^3)^{1/2}$ for the zeolite particle sizes 1.3-1.5, 1.5-1.7, 1.7-2.0, and 2.0- 2.5 mm, respectively (Figure 2.5 & table 2.7). The differences in the SAR for different particle sizes can be attributed to the difference in their surface area per unit mass of zeolite. Due to a large number of micro and macro pores that can adsorb more solute particles, smaller particles have a larger surface area in a unit mass of zeolite. The presence of macro pores may help to explain the rapid Na^+ uptake observed in the kinetic study (Huang and Natrajan, 2006). The adsorption process depends upon the available surface area for contact (Critter & Airoldi, 2003), and refers to the accumulation of matters (here Na^+) in the solid/aqueous solution interface.

Zhao et al. (2008) stated that in porous materials, such as zeolites, the majority of reactive sites are on internal surfaces. They further stated that diffusional resistance to mass transport within larger particle-sized zeolites is generally higher than that of smaller particle-sized zeolites, with some internal surfaces of the larger particles not utilized for adsorption.

Columns Study

Average flow rates (ml/s) of de-aired tap water and CBNG coproduced water through the soil columns with and without zeolite layers are plotted in Figure 2.6.
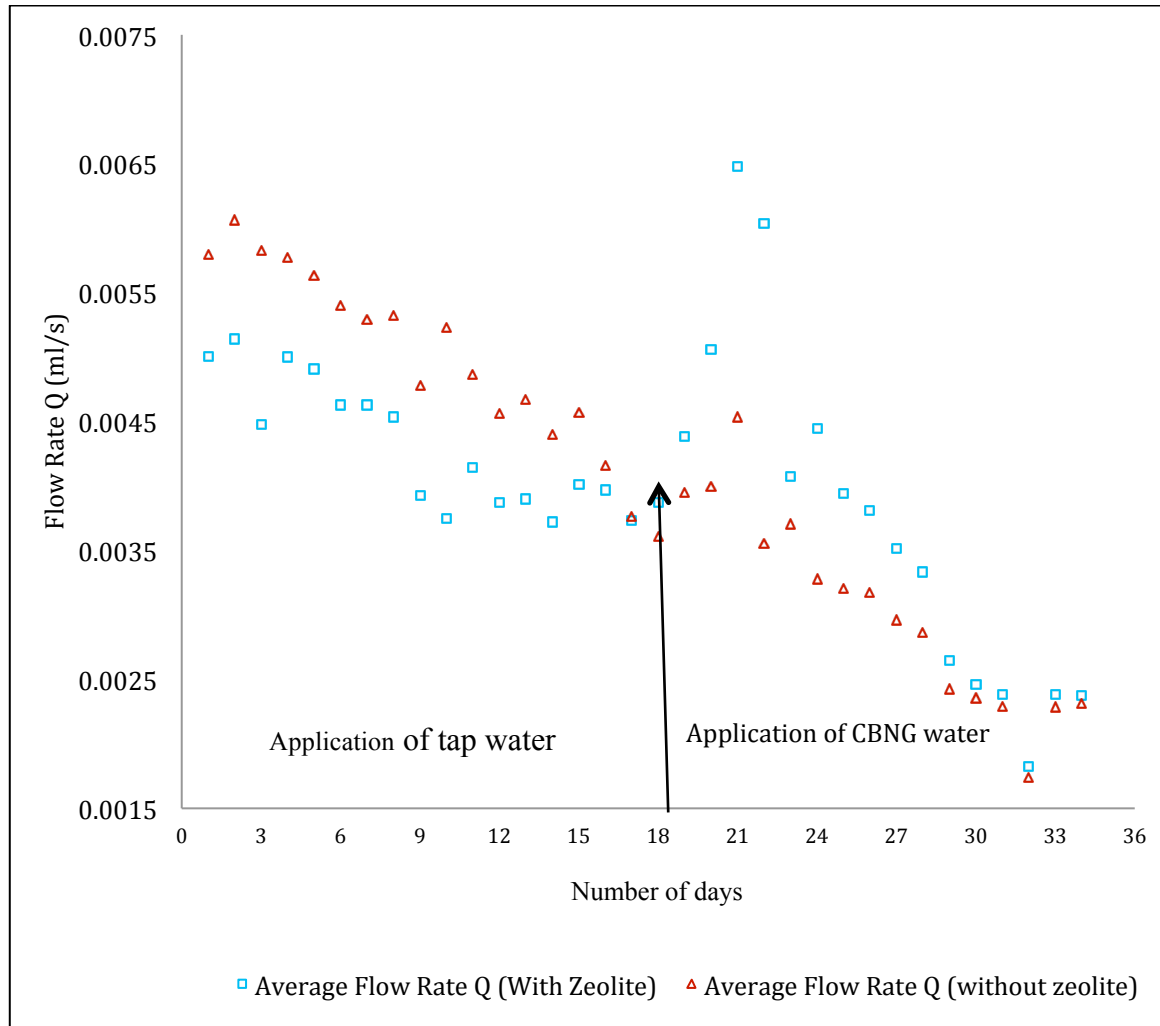
Figure 2.6: Average flow rates for the columns with and without the zeolite layer as a function of time

The graph in the Figure 2.6 shows that, in the first 16 days, the flow rates of de-aired tap water for columns with zeolite were lower than that for columns without zeolite. The flow rates were very close to each other on the 17th and 18th day. Then on the 18th day, the tap water was switched to CBNG coproduced water (type II). This resulted in an increase in the average flow rates for a period of three days. On the third day, the maximum flow rate was 562 ml/day (0.0065 ml/s) for columns with zeolite, and 389 ml/day (0.0045 ml/s) for the

columns without zeolite. The flow rates (ml/s) then began to decrease again, and by the end

of the experiment, the average flow rates for the columns with and without zeolite were

almost similar (Figure 2.6).
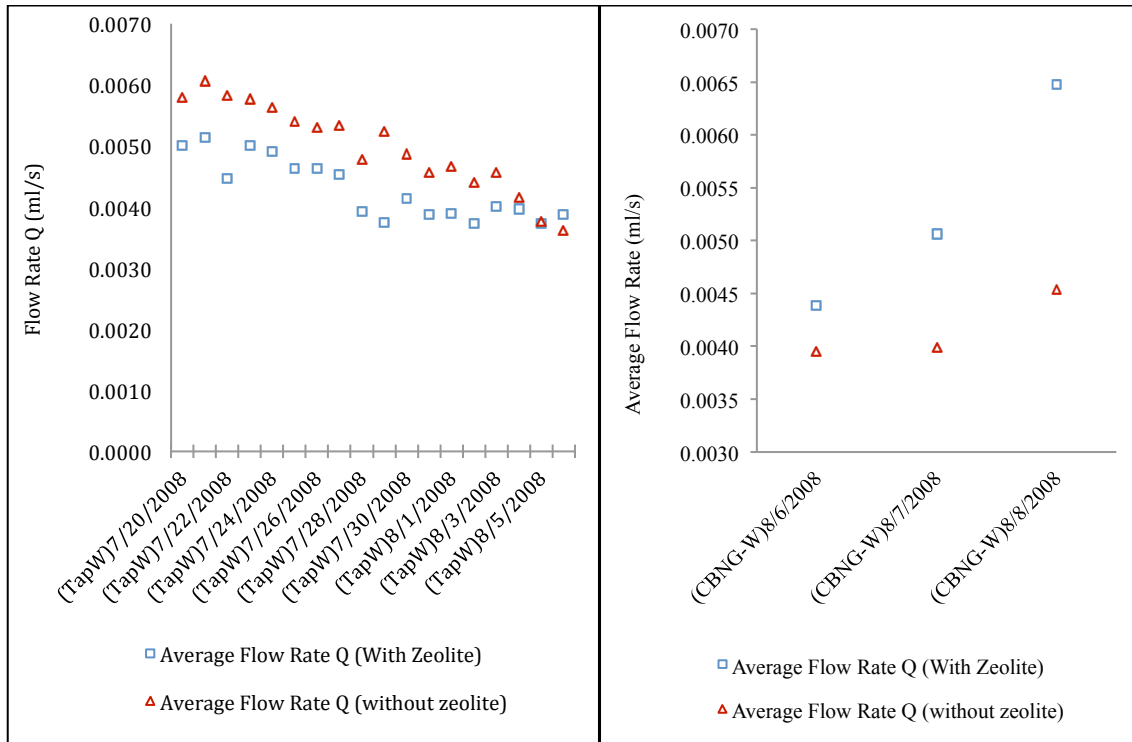
Figure 2.7: Flow rates of tap water through columns with and without zeolite layer over time

Figure 2.8: Flow Rates of CBNG coproduced water through columns with and without zeolite for first three days of an application of CBNG coproduced water

Figure 2.7 shows the average flow rates for the columns with and without zeolite

during the initial phase of the study when tap water was used. The time series plot for flow

rate shows that the flow gradually decreases. The difference in the average flow rates through

columns with and without zeolite for tap water is significant at 95% confidence level

($p=1.28*10^{-6}<0.05$). There was greater variability in the flow rates of tap water through

columns without zeolite than columns with zeolite ($\sigma_{without\ zeolite} =62.6 > \sigma_{with\ zeolite}=43.03$ in

ml/day). This result suggests that the finer particles within the columns are re-depositing

throughout the columns. A lower average flow rate through the columns with zeolite than

those without zeolite may have been caused by very fine zeolite particles mixing with coarse

particles thereby reducing the porosity of the zeolite lining and soil columns. This result is similar to that of Al-Busaidi et al. (2008) when they stated that the infiltration rate of soil was negatively affected by zeolite as the fine particles, and micro pores of zeolite slowed the percolation of water in the soil.

The graph in the Figure 2.8 shows the average flow rates (ml/s) of the CBNG coproduced water for the first three days of operation. Interestingly, immediately following the introduction of the CBNG coproduced water the average flow rates through the columns increased. These results suggest that the CBNG coproduced water altered the soil and the zeolite medium within the columns in a manner that increased their permeability, and that this effect was enhanced for those columns containing zeolite. This may have been the result of a high rate of cation exchange between the Na^+ ions in the CBNG coproduced water and the Ca^{2+} and Mg^{2+} ions in the zeolite leading to a higher concentration of Ca^{2+} and Mg^{2+} passing through the columns, thus increasing the salinity. High salinity causes fine particles in the soil to bind together into aggregates (Beletse et al., 2008) thereby increasing porosity.

An increase in the average flow rates during the first three days of the CBNG coproduced water application was also observed for the columns without zeolite (Figure 2.6 & 2.8). However, the magnitude of the increase was less than that observed for columns with zeolite. The possible reason for the increase in the flow rates through columns without a zeolite layer might be that the tap water used contained Ca^{2+} and Mg^{2+} ions (Table 2.3), and to the long run the soil may have been enriched with these ions increasing the aggregation of the soil resulting in enhanced infiltration.

Highly charged cations such as Ca^{2+}, Mg^{2+}, Al^{3+} etc., help to form flocculates of soil particles in the form of soil aggregates that enhance porosity (Vance et al., 2008). A mass of 200 g of BR zeolite can treat about 12000 ml of CBNG coproduced water with a SAR 30, and reduce it to below 10 $(mol/m^3)^{1/2}$ (Zhao et al., 2008). The maximum flow rates of CBNG

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coproduced water on the first, second, and the third days were, respectively, 380, 441, and 562 ml/day. The amount of water infiltered in the first three days was 1383 ml (<12000ml). The infiltration through the columns decreased after three days because the elevated levels of exchangeable Na^+ had adverse impacts on the soil structure and caused reductions in water infiltration rates, aggregate stability, clay dispersion, and the swelling of expandable clays (Saurez et al., 2008). The difference between the average flow rates of CBNG coproduced water through columns with and without zeolite was statistically significant at 95% confidence level ($p=1.28*10^{-6}<0.05$) with greater standard deviation for columns with zeolite than columns without zeolite ($\sigma_{with\ zeolite} = 117.7 > \sigma_{without\ zeolite} = 66.97$ in ml/day).

Mass Loading of Na^+

Cumulative mass loading of Na^+ through columns with and without zeolite was calculated by using the cumulative flow of water (ml) with time (days) and influent concentration of Na^+ of tap water (41 mg/L) and simulated CBNG water (286 mg/L). Maximum sorption capacities of BR zeolite for Na+ were 18 mg/g and 21 mg/g for NaCl and $NaHCO_3$ solutions, respectively, from Langmuir model fitting. This showed that 200 g of BR zeolite could adsorb 3600–4200 mg of Na^+ from a solution containing Na^+.

The mass loading indicates that soil columns with zeolite have less Na^+ loading capacity in the fist 18 days when tap water was leached through the columns. But, the mass loading (mg) increased and remained higher for the columns with zeolite than for the columns without zeolite when CBNG coproduced water was leached through them. By the end of the experiment, total amount of Na^+ leached (inputs) were 1735 and 1520 mg through columns with and without zeolite, respectively. In the same period of time, the columns were leached by 177 and 196 mg of Ca^{2+} and 96 and 97 mg of Mg^{2+} with and without zeolite, respectively, as inputs with influents. The mass of Na^+ that came out with effluents (as output) were approximately 775 and 1,011 mg through columns with and without zeolite,

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respectively. At the same time, the concentrations of Ca^{2+} and Mg^{2+} respectively were 244

and 121 mg for columns with zeolite and 231 and 94 mg for columns without zeolite. The

difference in the mass of Na^+ and zeolite impacts in percent are shown in the following table

(Table 2.8).

Table 2.8: Mass Loading of Na^+ through Soil Columns

Experimental conditions		Na^+ (mg)
Influent	Columns with zeolite	1735
	Columns without zeolite	1520
Effluent	Columns with zeolite	775
	Columns without zeolite	1011
Adsorbed/desorbed	Columns with zeolite	960
	Columns without zeolite	509
Zeolite capacity (200 g)		3600-4200
Impact of zeolite		23-27%

There was 55% of Na^+ mass adsorbed by the columns with zeolite utilizing 23-27% of

sodium adsorption capacity of the BR zeolite (Table 2.8). The flow rate seem be exhausted in

the graph (Figure 2.6) by the end of experiment not because of enough Na^+ exchanges by

zeolite (or clay in the soil), but it might have been affected by other factors such as the

presence of Ca^{2+} and Mg^{2+} while leaching out the Na^+.

Chemical Analysis of Water

Measurement of SAR. Results from an analysis of water samples for the concentration

of Na^+, Mg^{2+}, and Ca^{2+} were used to determine the trend of SAR values for the columns with

and without zeolite before and after the application of CBNG coproduced water (Figure 2.9).

Figure 2.9: SAR values for columns with and without zeolite before and after an application of CBNG coproduced water

Table 2.9: SAR values of influent and effluents from the columns with and without zeolite

SAR $(mol/m^3)^{1/2}$ of Influent		SAR $(mol/m^3)^{1/2}$ of Effluent Tap Water (in 18 days)		SAR $(mol/m^3)^{1/2}$ of Effluent CBNG coproduced water (in 2 days)	
Tap Water	Surrogated CBNG coproduced water	Columns without zeolite	Columns with zeolite	Columns without zeolite	Columns with zeolite
1.9	17.7	6.80	0.90	8.30	3.90

Just prior to the application of CBNG coproduced water (Table 2.9) the average effluent SAR values for columns with and without a zeolite layer for tap water were 0.9 and 6.8 $(mol/m^3)^{1/2}$, respectively. The SAR values for the influent tap water and simulated CBNG coproduced water were 1.9 and 17.7 $(mol/m^3)^{1/2}$, respectively. When CBNG coproduced water was applied the SAR of the effluent of the CBNG coproduced water was reduced to 8.3 in 2 days and to 9.2 in 14 days for the columns without zeolite. For columns with zeolite after the application of CBNG coproduced water the SAR value of CBNG coproduced water was

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reduced from 17.7 to 3.9 $(mol/m^3)^{1/2}$ in 2 days and from 17.7 to 4.5 $(mol/m^3)^{1/2}$ in 14 days. This result shows that SAR values of effluents decrease as a result of the zeolite application. The decrease in SAR may have resulted from the sorption of Na^+ ions in the CBNG coproduced water by the BR zeolite in the soil above the soil columns.

The SAR for influent tap water was 1.9 $(mol/m^3)^{1/2}$ and the effluent from columns without zeolite was 6.80 $(mol/m^3)^{1/2}$. This increase in the SAR values for effluent tap water through columns without zeolite might have resulted from either the addition (leaching) of Na^+ from the soil or the soil's adsorption of Ca^{2+} or Mg^{2+} that was present in the tap water or possibly, both might have occurred. There was a significant decrease (from 17.7 to 3.9 $(mol/m^3)^{1/2}$) in the SAR of the CBNG coproduced water when passed through soil columns with zeolite compared to decrease (from 17.7 to 8.3 $(mol/m^3)^{1/2}$) when passed through the columns without zeolite. It is possible that the reduction in the SAR of influent CBNG coproduced water which passed through the columns without zeolite resulted from the soil's adsorption of Na^+. Further research is required to confirm the soil cation exchange capacity (CEC).

Measurement of EC. Figure 2.10 presents (in graphical form) an analysis of the data obtained from the measure of EC. As shown, EC for the influent tap water was 0.2 dS/m, and simulated CBNG coproduced water was 1.6 dS/m (Table 2.10). When passing tap water for 18 days the effluents from columns with and without zeolite had ECs 0.9 and 1.2 dS/m, respectively. Two days after the application of CBNG coproduced water through the columns, the ECs average value for the columns with zeolite was 1.1 dS/m and without zeolite was 1.5 dS/m. In the next seven days, these values changed to 1.2 and 1.6 dS/m, respectively, for columns with and without zeolite. This shows evidence that over time there was an increase in the EC of effluent CBNG coproduced water after passing through soil columns without zeolite. This increase in the CBNG coproduced water EC suggests that the

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soil columns with and without zeolite became exhausted and that the effluent contained a
high concentration of Na^+.
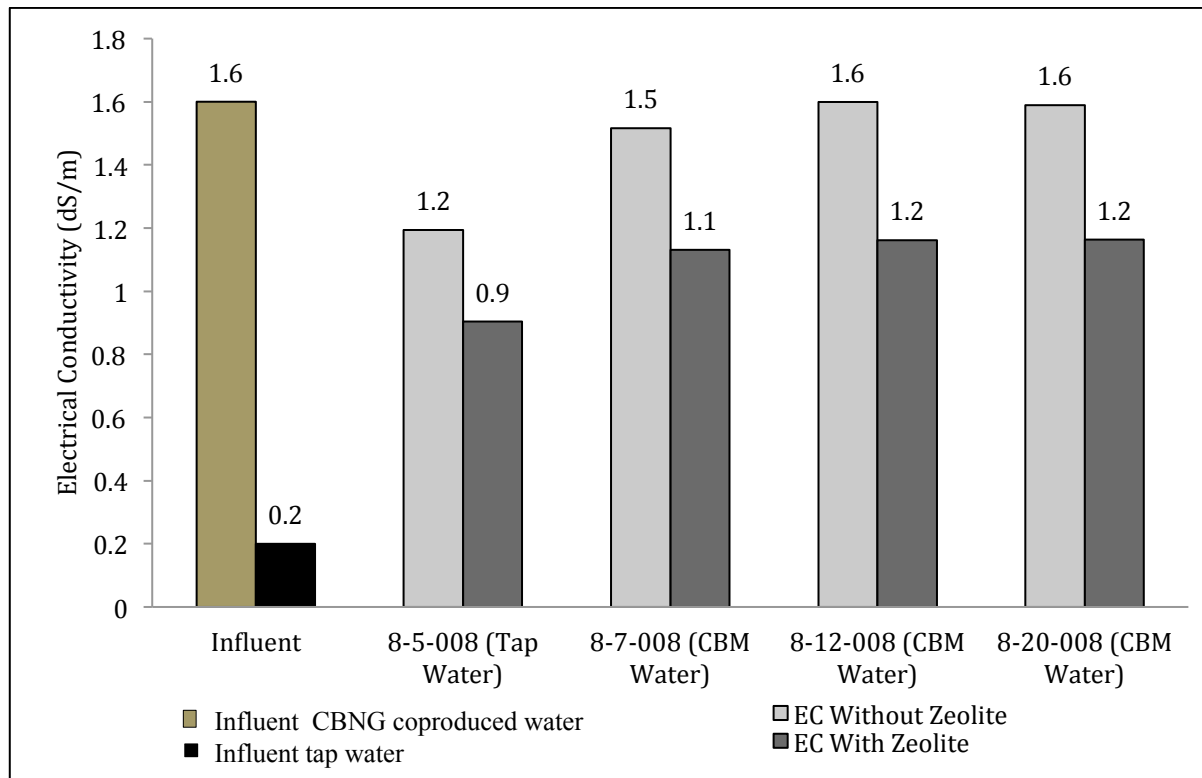
Figure 2.10: Measure of EC for columns with and without zeolite before and after an
application of CBNG coproduced water

Table 2.10: EC values of influent and effluents from the columns with and without zeolite

EC (dS/m) of Influent		EC (dS/m) of Effluent Tap Water (in 18 days of operation)		EC (dS/m) of Effluent CBNG coproduced water (in 2 days of operation)	
Tap Water	Surrogated CBNG coproduced water	Columns without zeolite	Columns with zeolite	Columns without zeolite	Columns with zeolite
0.2	1.6	1.2	0.9	1.5	1.1

Although, over time, there was an increase in the EC of effluents from the columns
both with and without zeolite, after passing CBNG coproduced water through them (Fig
2.10), the EC values for the effluents from the columns without zeolite were higher than
those for the columns with zeolite. The difference in the EC from the columns both with and
without zeolite revealed that there was a reduction in the concentration of the cation species

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after passing through the columns with zeolite indicating that there was an adsorption of Na^+ by the zeolite. Also, it was noticed that there was an increase in EC from 0.2 dS/m (influent) to 1.2 dS/m (effluent) when tap water passed through the soil columns without the zeolite. This increase in EC when passing through the soil columns without zeolite showed that there was an increase in cations in the effluent samples due to a leaching of salts from the soil. An increase in EC was relatively lower for columns with zeolite than the columns without zeolite. This difference could be due to a complex cation exchange of Na^+ that was present in the tap water with Ca^{2+} and Mg^{2+} present in the zeolite.

Measurement of pH. A measurement of pH values of influent tap water, simulated CBNG coproduced water, and effluents from the columns with and without zeolite were taken. These values were plotted in graph (Figure 2.11).
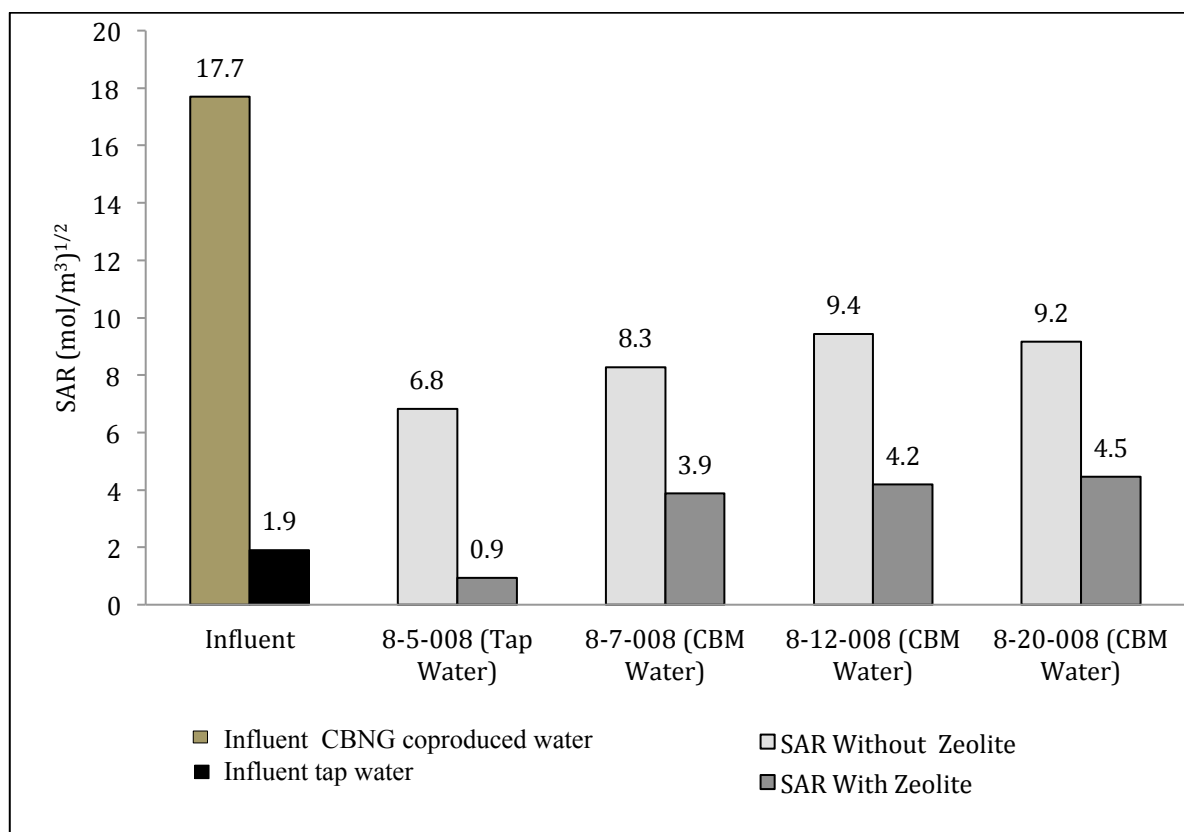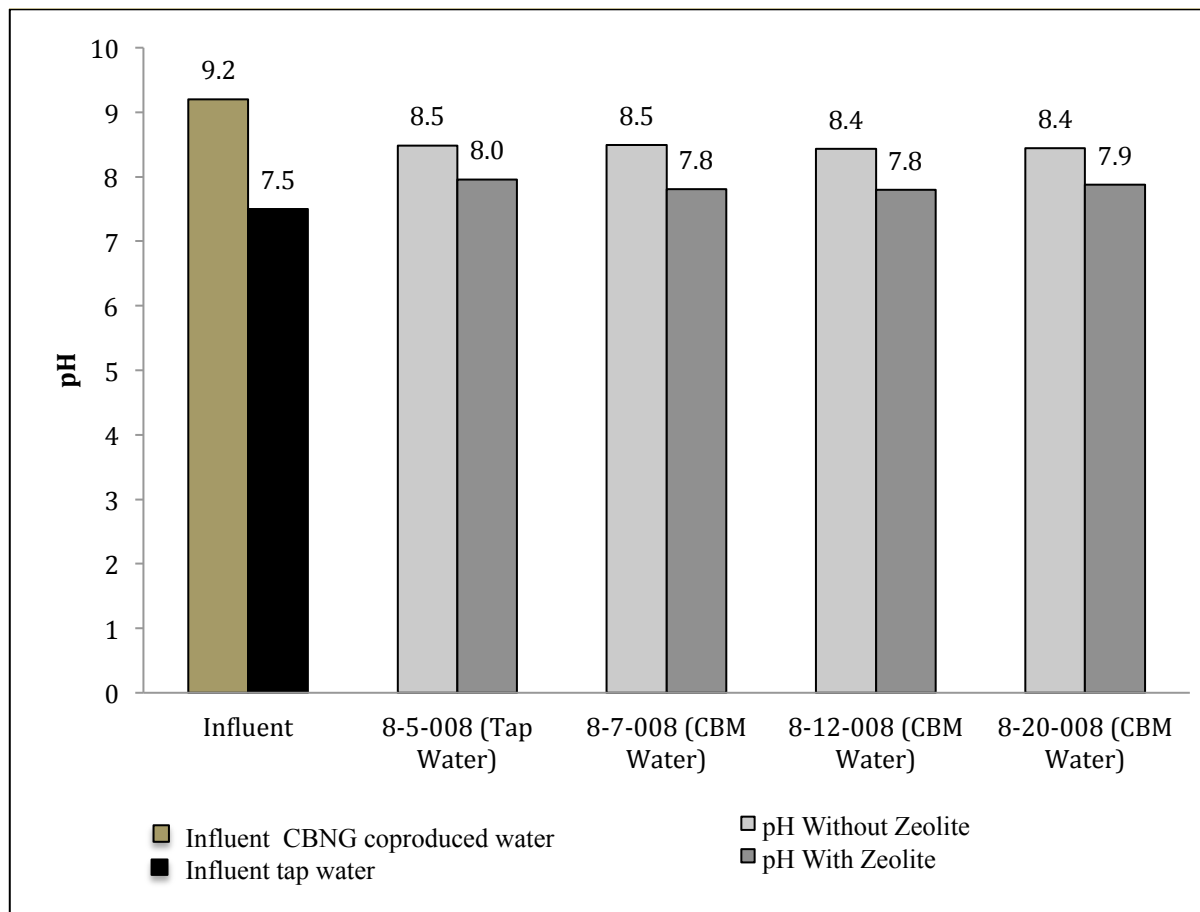

Figure 2.11: Measure of pH for columns with and without zeolite before and after application of CBNG coproduced water

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Table 2.11: pH values of influent and effluents from the columns with and without zeolite

pH of Influent		pH of Effluent Tap Water (in 18 days)		pH of Effluent CBNG coproduced water (in 2 days)	
Tap Water	Surrogated CBNG coproduced water	Columns without zeolite	Columns with zeolite	Columns without zeolite	Columns with zeolite
7.5	9.2	8.5	8.0	8.5	7.8

Figure 2.11 shows that the pH for columns without zeolite was 8.5 for effluent tap water, and after an application of CBNG coproduced water it was again found to be 8.5 indicating there was no impact on pH. However, in two days, the pH for columns with zeolite was 8.0 for effluent tap water and 7.8 for CBNG coproduced water. The pH values for tap water influent was 7.5, and the effluent pH was 8.5 indicating that there might be leaching of some cations increasing the pH while they passed through the soil columns without zeolite (Table 2.11). In two days, the pH value of influent CBNG coproduced water was 9.2, and it was reduced to 7.8 and 8.5 after passing through columns with and without zeolite. The pH value for effluent CBNG coproduced water passing through the columns without zeolite (8.5) was higher than that (7.8) for columns with zeolite. This data indicate that it may be possible that the presence of zeolite in the soil columns, as opposed to those without zeolite, increased the Na^+ adsorption, and it caused a slight decrease in the pH value of the effluents. This difference does not seem to be significant as they are very close for columns with and without zeolite, and for both tap water and CBNG coproduced water.

Conclusion

The Langmuir adsorption isotherm model showed the maximum Na^+ adsorption (q_{max}) of BR zeolite was 21 and 18 mg Na^+/g of BR zeolite for $NaHCO_3$ and NaCl solutions respectively with an initial concentration of sodium being 5,000 mg/L. The sorption coefficients (K_L and K_f) were higher for $NaHCO_3$ than for the NaCl solution. This could be due to precipitation of $CaCO_3$ reducing the concentration of Ca^{2+} in the solution and the pH.

The adsorption kinetics study showed that the adsorption of Na^+ by BR zeolite is an inverse function of the size of the zeolite particles. The percentages of Na^+ removal were 72%, 68%, 66%, and 59% for zeolite particles sizes 1.3-1.5, 1.5-1.7, 1.7–2.0, and 2.0–2.5 mm respectively in the first 30 minutes of the reaction indicating that the smaller a particle's size the greater efficiency of Na^+ removal by the zeolite. The reason for this may be that the surface area available for sorption per unit mass of zeolite is higher for smaller sized particles. The SAR values were reduced from 30 to 4.2, 5.5, 5.4, and 9.0 $(mol/m^3)^{1/2}$ for zeolite particle sizes 1.3-1.5, 1.5-1.7, 1.7-2.0, and 2.0- 2.5 mm, respectively, in the first 30 minutes. These results also indicate that the zeolite with the smallest particle size (1.3–1.5 mm) reduced, in the first 30 minutes of reaction, the SAR values most effectively, reducing it from 30 to 4.2 $(mol/m^3)^{1/2}$.

After application of the CBNG coproduced water (SAR = 17.7 $(mol/m^3)^{1/2}$ and EC = 1.2 dS/m) for the first three days the flow rates increased through the columns with and without zeolite. The trend of flow rates revealed that the rate of change (increase) of flow rates (slopes) for the columns with zeolite was approximately three times higher than that for the columns without zeolite. This indicated that the flow rates increased through the columns with zeolite more rapidly than that for columns without zeolite due to cation exchange reaction of Na^+ in the CBNG coproduced water with Ca^{2+} and Mg^{2+} ions in the zeolite thereby increasing the salinity of the effluent. The release of the divalent cations during cation exchange reaction helped in the aggregation of clay particles in the soil columns thus increasing the porosity of the soil that increased flow rates (Beletse et al., 2007).

During the first two days, the influent CBNG coproduced water SAR was 17.7 $(mol/m^3)^{1/2}$ while soil column effluent with zeolite (SAR =3.9 $(mol/m^3)^{1/2}$) was less than the SAR of effluent CBNG coproduced water (SAR = 8.3 $(mol/m^3)^{1/2}$) through columns without zeolite. In the same period, the EC value was 1.6 dS/m for influent CBNG coproduced water,

whereas the effluent ECs were 1.1 and 1.5 dS/m, respectively, for columns with and without zeolite. In the first two days of passing CBNG coproduced water through the columns, the pH of influent CBNG coproduced water was 9.2, but the values for the effluents through columns with and without zeolite were 7.8 and 8.5, respectively thus mitigating the high pH of CBNG coproduced water.

Results from the adsorption isotherm, adsorption kinetics, and the columns studies showed that BR zeolite can be applicable for the mitigation of the CBNG coproduced water's harmful effects (due to high SAR values) on both the chemical and physical characteristics of soil and water.

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CHAPTER 3

EFFECTS OF COALBED NATURAL GAS COPRODUCED WATER ON SOIL USING
BEAR RIVER ZEOLITE: A FIELD SCALE TREATMENT AND POST TREATMENT
ANALYSIS

Abstract

This field study aimed to examine the effects of coalbed natural gas (CBNG) coproduced water on soil using Bear River (BR) zeolite, and it was also accompanied by post field treatment analysis of soil pH, electrical conductivity (EC), and sodium adsorption ratio (SAR). This test utilized 12 open boreholes, each installed to a depth of approximately 1.8 m. Each borehole was lined with a 3.0 m long, 15 cm diameter schedule 40 PVC pipe and fitted with automatic data logging pressure transducers for collecting and measuring, water level data over time. An 8 cm thick layer of BR zeolite was placed into the bottoms of six boreholes; the remaining six boreholes were not amended. Tap water from the city of Sheridan, Wyoming (SAR $1.47(mol/m^3)^{1/2}$, EC 1.00 dS/m) was used to fill six of the boreholes (three with zeolite and three without). CBNG coproduced water (SAR 27.00 $(mol/m^3)^{1/2}$, EC 1.90 dS/m) from a nearby CBNG outfall filled the remaining six boreholes (three with zeolite and three without).

In the field test, BR zeolite was found to mitigate the effect that high SAR values (SAR $=27$ $(mol/m^3)^{1/2}$) of the coproduced water had on the soil's hydraulic behavior (infiltration). At the end of two months, during which time Phase I and Phase II of the field tests were completed, it was found that there were changes in the infiltration rates. In Phase I the infiltration rate in the boreholes with CBNG coproduced water and zeolite was approximately four times that of the boreholes with CBNG coproduced water and no zeolite. In Phase II the infiltration rate of CBNG coproduced water through boreholes with zeolite was nearly ten times that of the control (boreholes without zeolite). This higher rate in phase II was not due to increase in filtration of CBNG coproduced water through the boreholes with zeolite but it was due to reduced infiltration of CBNG coproduced water through the controls (bore holes without zeolite). There was no significant difference in the infiltration of city tap water through boreholes without zeolite at 95% confidence level in phases I and II. There was a significant difference in the infiltration of CBNG coproduced water through boreholes with zeolite and without zeolite at 95% confidence level both in phases I and II indicating significant impact of sodium in infiltration of CBNG coproduced water through soil and also impact of BR zeolite treatment on the infiltration of the water. At the depths 0-5, 5-15, 15-30, 55-65 and 95-105 cm, respectively, post-treatment field test soil analysis revealed that the values of SAR for boreholes with CBNG coproduced water and zeolite were less than the SAR for the boreholes with CBNG coproduced water but no zeolite, thus mitigating the high SAR with BR zeolite. The SAR values decreased with depth while EC value increase with increasing depth in general. This increase in EC value indicated that there were greater amount of soluble salts with depths due to leaching of such salts from the upper subsoil layers.

Introduction

Due to high water-pressure in aquifers, some subsurface coalbeds hold natural gas that is fixed to coal surfaces. By pumping out the water from the coalbeds, water pressure is lowered, which facilitates the release of the CBNG from the coal for extraction and its use as an energy source. Large amounts of water are pumped out from the coalbeds during this process. The release of the CBNG coproduced water is managed through treatment, disposal, storage, or reuse, and is subject to compliance with federal and state regulations. In the Powder River Basin (PRB) of Wyoming and Montana, the chemical characteristics of CBNG coproduced water is influenced by salinity and sodicity can vary significantly from one discharge point to another. This has raised serious concerns with respect to irrigation and land-applied disposal of CBNG coproduced water in the region (National Academy of Sciences, 2010).

The high salinity of CBNG coproduced water can impact the chemico-physical properties of the soil (Stearns et al., 2005). Soil aggregate stability, soil water retention, porosity, bulk density, solid density, coagulation and flocculation, and soil texture are important parameters associated with the physical characteristics of soils. Soil particles such as sand, silt, clay minerals, and organic matter are bound together to form aggregates that are the basic structural units of soil (Bandel & Meisinger, 2002). Soil aggregates have different strengths that bear stress due to water and air flow, root growth, micro and macro organisms' movement and other physical phenomena such as temperature and pressure. The structural stability of soil plays a very important role in growth of plants and other micro faunal communities. High salinity causes fine particles in the soil to bind together into aggregates, and this process is beneficial in terms of soil aeration, root penetration and root growth, but it can be toxic to plants due to the presence of excess ions (Beletse et al., 2008). Highly charged cations such as Ca^{2+}, Mg^{2+}, Al^{3+} etc. help to form flocculates of soil particles in the form of

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soil aggregates. This may increase the porosity, but elevates salinity and affects the ability of plants to uptake water and to enhance the biochemical processes of plants (Vance et al., 2008).

Sodium (Na^+) has an adverse effect on soil aggregation and stabilization. The presence of excess Na^+ disperses clay particles by weakening the forces that bind the clay particles, ultimately causing them to disrupt due to the separation and expansion that is caused by swelling and the dispersion of clay in soil (Abu-Sharar et al., 1987; Ganjegunte et al., 2005a; Johnston et al., 2008; Pearson, 2003; Sumner, 1993). The dispersion of clay particles causes the plugging of soil pores thus reducing a soil's permeability. The repeated wetting and drying some of soils can forms a cement-like solid structure that causes surface crusting. According to Johnston et al. (2008), elevated sodicity in irrigation water adversely affects the water infiltration, the nutrient supply, and soil aeration.

The arrangement of soil particles such as clay, silt, sand and organic matters that form aggregates are known as soil structure. Soil structure represents how soil particles are bound together and how much free space (voids) there are among the particles. These voids or spaces among the aggregates determine a soil's porosity. Soil porosity plays an important role in the transportation of water, air and other solute particles through the soil. The harmful effects of sodium on soil properties are well recognized, and high Na^+ concentrations have been associated to an increase in erosion and runoff (Ghadiri et al., 2004). Ghadiri et al. (2004) conducted a study to determine the effect of soil salinity and sodicity on soil erodibility and sediment transport. They concluded that there was a decrease in soil aggregate stability with a concomitant increase in the dispersion rates as a result of increasing sodicity. High salinity and sodicity can cause soil crusting. Upon drying, the soil cracks due to the brittleness of the soil aggregates thus causing destruction in the soil structure that can lead to limited plant growth.

The common effect of soil texture and soil structure is called tilth. Tilth demonstrates how easily plant roots can penetrate the soil. Good soil tilth provides enough water and air to the plant roots and the microbes that live in the soil. The macropores are responsible for a soil's infiltration of water and air and over time these pores are responsible for a soil's water retention (Whitening et al., 2009). The salinity and sodicity of CBNG coproduced water greatly impacts the soil's tilth. High salinity and sodicity cause the deterioration of a soil's structure, stability, water adsorption, air transportation characteristics, and soil surface sealing. This deterioration results in a soil's reduced ability to infiltrate water, increasing erosivity, impaired aeration, and finally poor tilth (Hadas, 1997). The presence of high Na^+ concentrations in the soil causes the soil to be dispersed, and then it is compacted by rain or irrigated water thus reducing the soil's porosity. In such soil, cultivation of crops is made very difficult due to poor air and water movement through the soil.

Levy et al. (2005) concluded that depending on a soil's texture, there was a strong adverse impact of sodicity on soil hydraulic conductivity when soils had been subjected to fast wetting combined with leaching. Both the hydraulic conductivity and relative hydraulic conductivity of the soil were predominantly affected by water salinity (EC) and soil ESP. To better understand and simulate field conditions, this study suggested that the dependence of a soil's hydraulic conductivity on salinity, sodicity, and the rate of wetting should not be considered independently, but simultaneously.

The emergence of CBNG development as an economically viable source of methane (i.e., natural gas) has resulted in the rapid growth of the CBNG sources in the Powder River Basin (PRB) of Wyoming (Stearns et al., 2005). There has been a rapid increase in the demand of CBNG as a clean energy source which has played a role in the quick development of CBNG production wells in the PRB that has increased the amount of produced water in the area. From 1987 to 2004, CBNG coproduced water amounted to 467 million cubic meters

(16.5 billion cubic feet) as compared to, during the same time period, 36.8 billion cubic meters (1.3 trillion cubic feet) of natural gas (DOE, 2008). The amount of water produced from the CBNG wells in the PRB is a concern for all stakeholders. Approximately 600 million cubic meters of CBNG coproduced water will be produced by 2029 (Johnston et al., 2008), and management of this water will be a major environmental concern for both public and private stakeholders.

The large volume of saline and sodic water pumped out from the coal seams of CBNG-producing wells raises concerns for gas producers, governmental agencies, landowners, and for the environment in general. This water has the potential to harm irrigation sources, streams, agricultural ponds, riparian plant communities, aquatic resources, wildlife and farm habitats, and biodiversity and sustainability (Stearns et al., 2005). The direct discharge of the CBNG coproduced waters to the land surface poses potential negative effects for the environment that comes in immediate contact with CBNG development. Coproduced CBNG waters contain high salinity at numerous sites, and this has resulted in the swelling and dispersion of clay soils characteristics of those found in Montana and Wyoming (Stearns et al., 2005).

"The CBNG coproduced water has impacted PRB drainage in the central and western part of the PRB where most CBNG coproduced water goes to evaporation-infiltration ponds, or is discharged directly to surface drainage" (DOE, 2008, p. 2). When issues of CBNG coproduced water in the PRB develop, the water's chemistry becomes a primary factor for a potential environmental threat in the region. The CBNG coproduced water from the CBNG wells in the PRB is mostly dominated by sodium (Na^+) and bicarbonate (HCO_3^-) ions with pH ranging from 6.8 to 9.2, electrical conductivity (EC) from 0.4 to 5.0 dS/m, and sodium adsorption ratio (SAR) from 5.0 to 70.0 $(mol/m^3)^{1/2}$ (Ganjegunte, 2005a & 2005b; Jackson & Reddy, 2007; Vance et al., 2008). In order to avoid permanent damage to the

fragile PRB ecosystems, it is now essential to treat the CBNG produced water that has a high concentration of Na^+ before it is used for irrigation, and discharge into natural drainage (Ganjegunte et al., 2005a, b).

The major purpose of this study was to evaluate the effectiveness of BR zeolite in remediation of effects associated with CBNG coproduced water when applied to soil. The objective of this study was to evaluate how the sodium present in CBNG coproduced water impacts infiltration of the water through subsoil and how zeolite treatment impacts infiltration of the water. The study also aimed to study how the SAR, EC, and pH of the soil were affected by zeolite-treated CBNG coproduced water as it infiltrated through the subsurface environment.

<div align="center">**Materials and Methods**</div>

Bear River (BR) Zeolite

St. Cloud Mining in New Mexico states that the cation exchange capacity (CEC) of zeolite is most important property for water treatment. Generally, cation exchange occurs in the soil or water when two or more positively charged compounds (compound ions) or elements (simple ions) exchange takes place on a negatively charged solid (St. Cloud Mining, 2010). Zeolites are hydrated aluminosilicates of alkaline and alkaline-earth metals, and mostly consist of analcime, chabazite, clinoptilolite, erionite, ferrierite, haulandite, laumontite, mordenite, and phillipsite (Zhao et al., 2008). Bear River (BR) zeolite is a brand of zeolite mined, processed, packed, and sold by Bear River Zeolite Company at Preston, Idaho and has an average surface area of 24.9 square meter per gram, bulk density is 881 – 991 kg/m^3 (55-60 pounds per cubic feet), and its mineral composition is 85% clinoptilolite. It has a cation exchange capacity ranging from 1.5 to 1.8 meq/g and a chemical composition of 3.47% potassium, 1.6% calcium, and less than 0.5% of sodium (U.S. Antimony Corporation, 2009).

CBNG coproduced water and Tap Water

For the field study, CBNG coproduced water with SAR = 27 $(\text{mol/m}^3)^{1/2}$, EC=1.9 dS/m, and pH = 8.5 came from a nearby CBNG coproduced water discharge outfall, was used for infiltration through boreholes both with and without zeolite. Triplicate samples of this water were collected in 20 ml test tubes and stored in a refrigerator at 4^0 C. The water samples were tested for the major cations (Na^+, Ca^{2+}, Mg^{2+}), EC, and pH.

Tap water with SAR=1.47 $(\text{mol/m}^3)^{1/2}$, EC = 1 dS/m), and pH = 8.0 from the city of Sheridan, Wyoming was used for infiltration through boreholes both with and without zeolite. Triplicate samples of this water were collected in 20 ml test tubes and stored in a refrigerator at 4° C. The water samples were used for analysis of the major cations (Na^+, Ca^{2+}, Mg^{2+}), EC, and pH.

Field Research Site

A field site located at the University of Wyoming Sheridan Research and Extension Center was established on September 4, 2007. Located inside a fenced area adjacent to the UW Research and Extension Center, this site provided easy access to and from the town of Sheridan and the CBNG coproduced water discharge outfall (Pennaco Energy Outfall # 005) located along Wyarno Road (Figure 3.1).

The specific location of the field study was latitude approximately at 44.84° N and longitude approximately 106.84° W. Climate of the region for the months of June, July, and August had an average temperatures of 17.0°, 21.0° and 20.5° C, respectively, and the precipitation of 5.8 cm, 2.8 cm, and 2.0 cm, respectively (http://www.weatherbase.com/weather/). Munn and Arneson (1998) report that the default soil mapping unit for the PRB landscape is a complex of Haplocalcids and Haplargids with Mollisols on favorable sites. This semi-arid region has many CBNG wells, CBNG coproduced water discharge outfalls, and discharge ponds.

Figure 3.1: Google satellite map of field research site near UW Research and Extension Center, Sheridan, WY.

Construction of Infiltration Boreholes

Construction of infiltration boreholes began on June 11, 2008 at the field experiment site near the University of Wyoming Research and Extension Center in Sheridan, Wyoming. A private drilling company was hired and it drilled 12 boreholes in three rows (four to a row) that were 8 m apart from each other. Boreholes were at a depth of 1.8 m with a diameter that was slightly greater than 15cm (Figure 3.2 A). Polyvinyl chloride (PVC) schedule 40 pipes that were about 3 m long and 15 cm diameter were inserted into the boreholes up to the depth of 1.8 m keeping 1.2 m above the ground surface level (Figure 3.2 B & C) in order to prevent the infiltration of water along the side walls of the boreholes. Outside the PVC pipes, the boreholes were sealed with bentonite in order to prevent the movement of the pipes due to wind or storm, and to minimize, in case of rainfall, the inflow of surface runoff into the boreholes.

Out of the twelve boreholes, six were randomly selected to receive a zeolite lining added to their bottoms. Approximately 3000 grams of BR zeolite was added to the selected boreholes. At the bottom of the boreholes, the zeolite layer formed a permeable reactive barrier of approximately 8-10 cm thickness. This amount of zeolite can treat about 180 L of

CBNG coproduced water, and possibly reduce an SAR from 30 to below 10 (Zhao et al., 2008). The remaining six boreholes that were without a zeolite layer served as controls. Automatic data logging pressure transducers (In-Situ Level TROLL 500) were calibrated, and used to install falling head permeameters in all the boreholes at their bottoms to measure, over time, the depth of water levels. At the research site, a separate pressure transducer was attached to one of the pipes from the outside (above the ground level) to record the ambient temperature and barometric pressure.
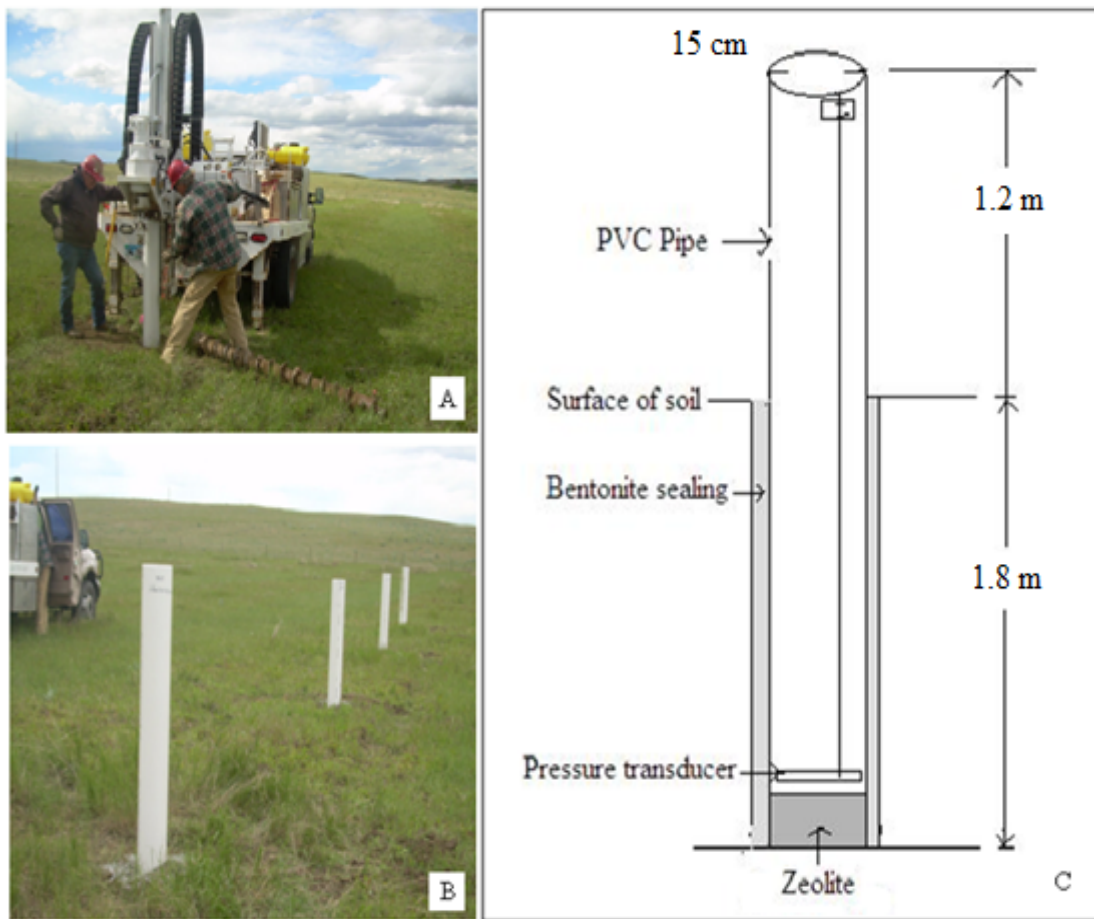
Figure 3.2: A. Drilling of boreholes, B. Lining of scheduled 40 PVC pipes into the boreholes, C. Schematic of each borehole for the field experiment

In Phase I on June 12, 2008, six of the boreholes (three with zeolite and three without zeolite) were filled with CBNG coproduced water (SAR = 27 $(mol/m^3)^{1/2}$, EC=1.9 dS/m) from a nearby CBNG coproduced water discharge outfall, and the other six boreholes (three with zeolite and three without zeolite) were filled with city tap water (SAR=1.47

$(mol/m^3)^{1/2}$, EC = 1.00 dS/m) from Sheridan. Each borehole contained about 53 L of water. Four experimental conditions were triplicated and established: (1) city tap water and no zeolite, (2) CBNG coproduced water and zeolite, (3) city tap water and zeolite, and (4) CBNG coproduced water with no zeolite. Each borehole with a permeameter was categorized within the four experimental conditions, and was labeled to identify the experimental conditions (Figure 3.3 & Table 3.1). The boreholes were covered at the top with synthetic tape to prevent the addition of water from rainfall, and to reduce evaporation of water from inside the boreholes. On July 9, 2008, in Phase II, the experiment site was revisited in order to refill the respective boreholes with tap water and CBNG coproduced water as done in Phase I. At the same time, triplicate 20 ml tap water and CBNG coproduced water samples were collected and stored in a refrigerator. These water samples were used for a concentration analysis of Na^+, Ca^{2+}, and Mg^{2+} ions, and to measure EC and pH.
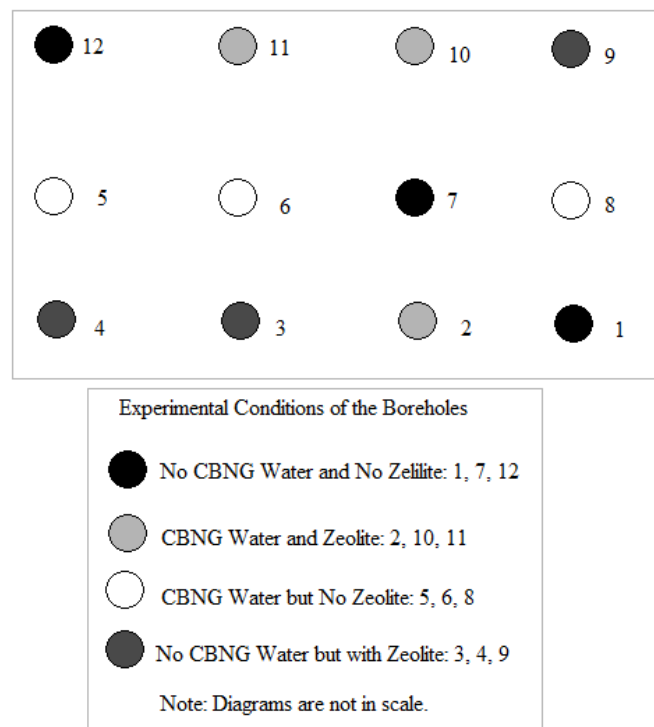
Figure 3.3: Relative positions of boreholes with different experimental conditions (not in scale)

Table 3.1: Experimental conditions in the field research

Boreholes	Experimental Conditions	
	CBNG coproduced water	Zeolite
BH1	No	No
BH2	Yes	Yes
BH3	No	Yes
BH4	No	Yes
BH5	Yes	No
BH6	Yes	No
BH7	No	No
BH8	Yes	No
BH9	No	Yes
BH10	Yes	Yes
BH11	Yes	Yes
BH12	No	No

Collection of Intact Soil Core Samples

On the final day of the field experiment, August 22, 2008, the data logging pressure transducers were retrieved from the bottom of each borehole. The PVC linings of the boreholes were taken out, and the site was decommissioned. With the help of the drilling machine, intact soil cores were collected from the bottoms of each of the boreholes in 1.2 m long by 5 cm diameter polyethylene pipes. In order to prevent the loss of moisture from the soil, the soil cores were sealed. Soils taken from the bottom of the boreholes were separated into depth samples representing 0-5, 5-15, 15-30, 55-65, and 95-105 cm.

Preparation of Saturated Soil Extraction

Soils from the different depths were stored in air tight ziplock plastic bags. The soil from each section was composited before preparing saturated paste extracts. About 100 g of the composited soils was placed into a waterproof cup. Deionized (DI) water while stirring until the sample was saturated and the surface became shiny like mercury (USDA Handbook

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60, 1954). The saturated pastes were left to equilibrate for 24 hours. After 24 hours, the saturated pastes were extracted using vacuum suction filtration (Figure 3.4). From each section's soil solution, a 1 ml sample solution was diluted to 25 ml with DI water. This process was repeated on each soil depth from the core's sections. Altogether there were 60 samples for the 12 cores. The diluted samples were labeled and preserved in the refrigerator at 4^0 C. These solutions were used for an analysis of the concentrations of Na^+, Ca^{2+}, and Mg^{2+} ions. The pH and EC were measured using samples from the original (undiluted) paste extracts.
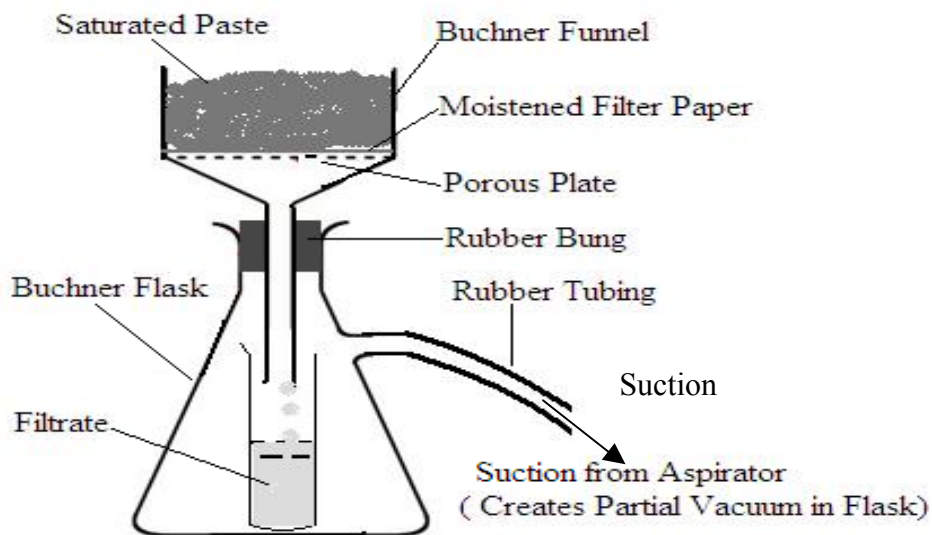
Figure 3.4: Soil solution extraction from a saturated paste

Analysis of Saturated Soil Extraction

Inductively coupled plasma (ICP) spectroscopy (Thermo Jarrell Ash, Model P300), was used to analyze the solution for concentrations for the major cations Na^+, Ca^{2+}, and Mg^{2+}. Measurement of EC was taken directly from the electrical conductivity meter (OAKTON, Serial No. 31569), and measurement of pH was taken using the pH meter (Fisher Scientific) (Vance et al., 2008; Zhao et al., 2008, 2009).

Two equal samples t-test was applied to compare the mean flow rates through the boreholes to evaluate if the difference (if any) was significant at 95% confidence level. Bivariate correlations between SAR and EC, EC and pH, and SAR and pH were also used for analysis and discussion of results.

Results and Discussion

Infiltration through Boreholes

For each experimental condition, the water levels in the boreholes were a function of time. The daily (12:00 noon) water levels (m) in the boreholes and amount of water infiltered through boreholes with different experimental conditions were plotted over time (days) for Phases I and II (Figure 3.5).
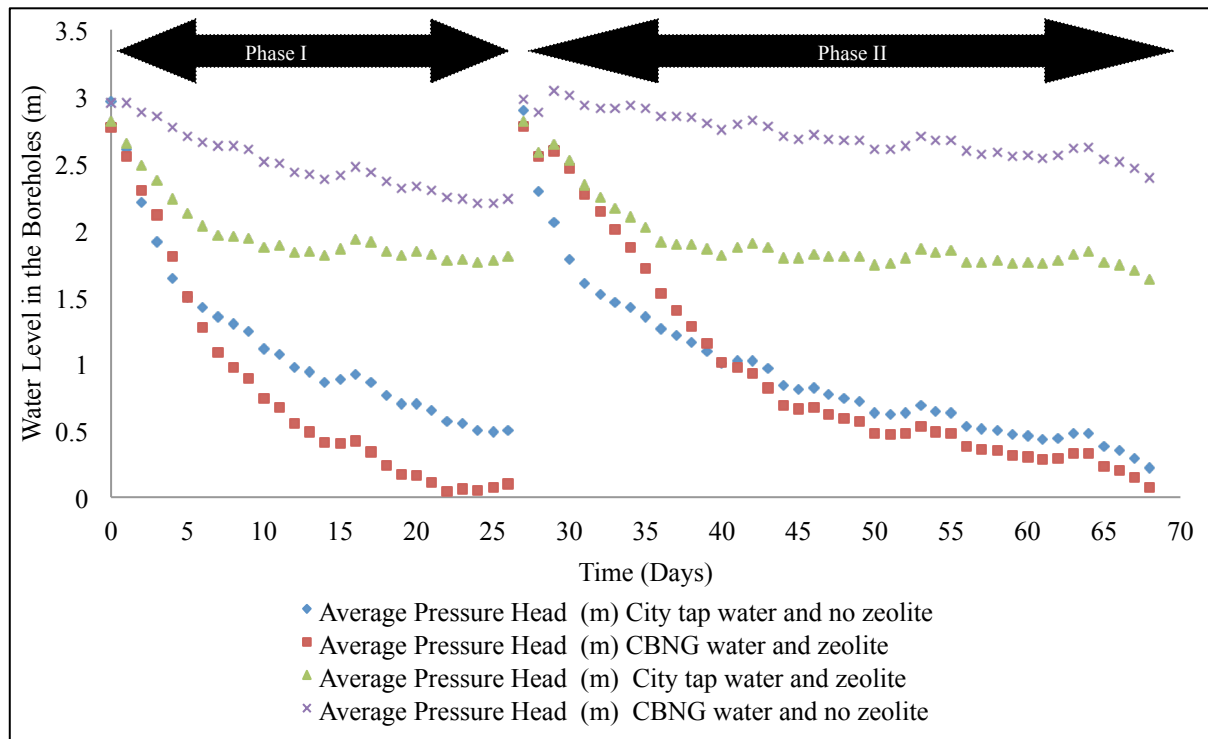
Figure 3.5: Daily water levels (m) in boreholes of different experimental conditions over time (days). The number of experimental days from 1-27 constituted phase I and 28-68 constituted phase II.

The graphs for the water levels (m) over time (days) in the Figure 3.5 shows that the water level decreased at a faster rate from the boreholes with CBNG coproduced water and zeolite and city tap water and no zeolite than those boreholes with CBNG coproduced water but no zeolite and city tap water but zeolite. The cumulative volume of water infiltered through the boreholes indicating that infiltration through boreholes with tap water and no zeolite and boreholes with CBNG coproduced water and zeolite are greater than other two experimental conditions (boreholes with tap water and zeolite and boreholes with CBNG coproduced water and no zeolite). The decrease in water levels (m) or infiltration of water (L) was very slow in the boreholes with CBNG coproduced water but no zeolite compared to other experimental conditions both in Phase I and II. This clearly indicated the detrimental impact of Na^+ present in the CBNG coproduced water on infiltration through the subsurface soil. The average daily volume of water infiltered through boreholes with CBNG coproduced water and zeolite were greater than through the boreholes with CBNG water and no zeolite both in phases I and II (Table 3.2) indicating that positive impact of BR zeolite on infiltration of CBNG coproduced water through the subsoil.

Mass Loading of Na^+

Cumulative mass loadings of Na^+ through boreholes with and without zeolite were calculated by using the cumulative flow of water (L) with time (days) and influent concentration of Na^+ city tap water (15 mg/L) and CBNG coproduced water (300 mg/L) and it was plotted in line graphs (Figure 3.6). Maximum sorption capacities of BR zeolite for Na+ were 18 mg/g and 21 mg/g for NaCl and NaHCO3 solutions, respectively from Langmuir model fitting (in Chapter 2). This showed that 3,000 g of BR zeolite used at the bottom of the boreholes could adsorb 5,4000 – 63,000 mg (from Langmuir maximum sorption capacity, p. 35) of Na^+ from a water containing NaCl or $NaHCO_3$ solution or mixture of both. Throughout the period of field experiment, the maximum loading of Na^+ were 559 mg; 1,312 mg; 6,936

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mg; and 28,500 mg for boreholes with city tap water and zeolite, city tap water and no zeolite, CBNG coproduced water and no zeolite, and CBNG coproduced water and zeolite, respectively (Figure 3.6). The BR zeolite adsorption capacity (54,000–63,000 mg for 3,000 g of zeolite) was higher than the total amount of sodium leached (28,484 mg) through the boreholes with CBNG water and zeolite, the water level curves (Figures 3.5) for this condition were going down rapidly with cumulative infiltration going up indicating enhancement of infiltration through those boreholes. This also indicates that greater is the infiltration rate, greater is the mass loading rate and greater is the amount of water that can be treated by the application of BR zeolite. However, there might be other influencing factors in the infiltration of the CBNG coproduced water through the boreholes with zeolite such as zeolite particle size, soil chemistry, and chemistry of the CBNG water in terms of other cations except Na^+.

Table 3.2: Mass loading of Na^+ through boreholes

Experimental conditions		Na^+ (mg)
City tap water	Boreholes with zeolite	559
	Boreholes without zeolite	1312
CBNG coproduced water	Boreholes with zeolite	28500
	Boreholes without zeolite	6936
Zeolite capacity (3000 g)	From Langmuir model	54000-63000
Impact of zeolite	Mass of Na^+ that was possibly absorbed by the zeolite	50% (approximately)

Table 3.2 indicates that mass loading of Na^+ through boreholes with CBNG coproduced water and zeolite (28500 mg) was greater than the mass loading through boreholes with CBNG water and no zeolite (6936 mg). The maximum amount of sodium loaded through the boreholes with CBNG coproduced water and zeolite about 50% of the total sorption capacity of the BR zeolite utilized in the borehole. The mass loading of Na^+ through the boreholes with different experimental conditions are shown in the Figure 3.6.
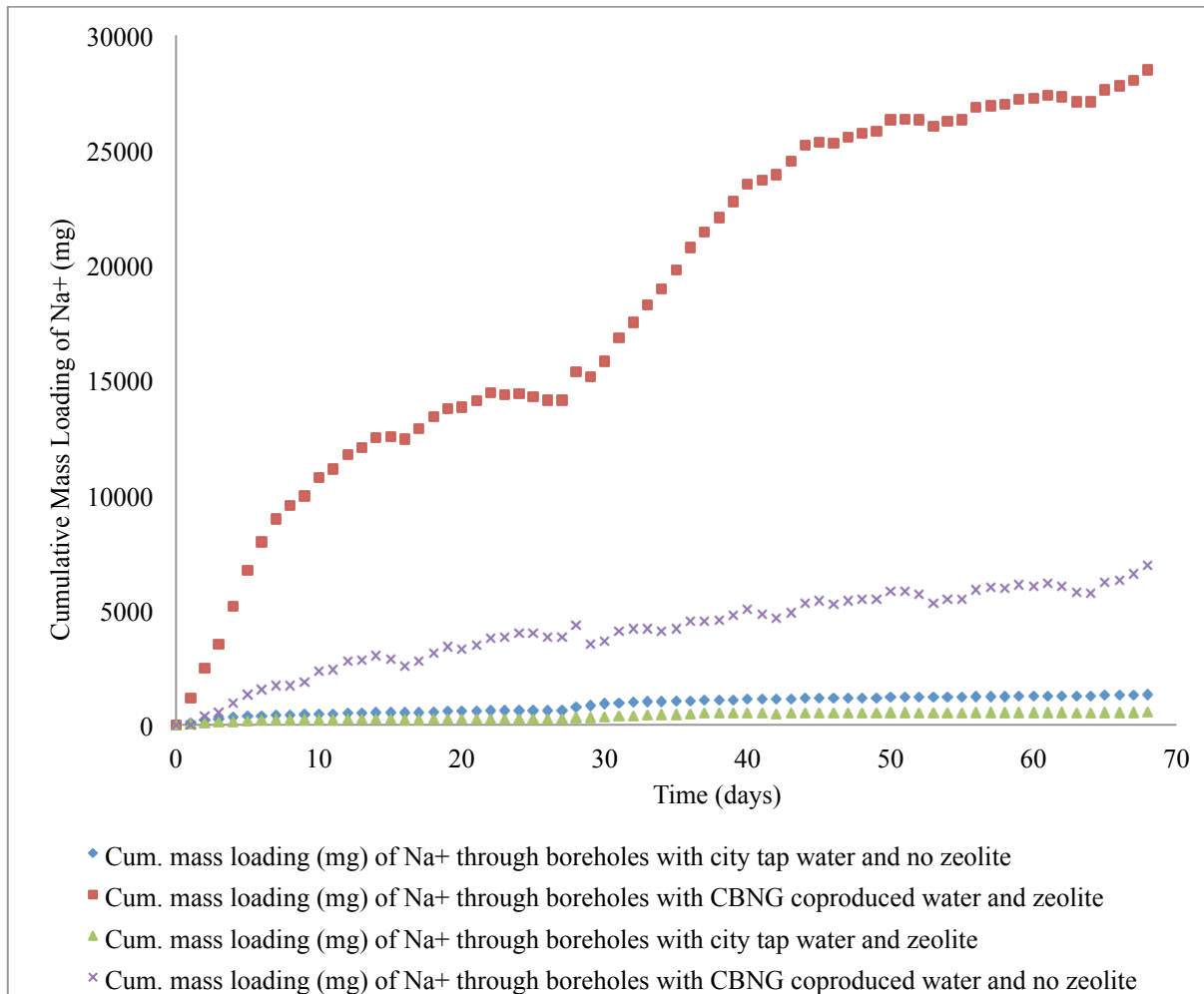
Figure 3.6: Cumulative mass loading (mg) of Na$^+$ through boreholes of different experimental conditions over time (days)

Impact of sodium on infiltration. The results of water levels (m) over time (days) are represented by the line graphs in Figures 3.6, 3.7, 3.8, and 3.9. By comparing Phases I and II these results lead to a discussion on the impact of sodium ions that are present in the CBNG coproduced water, and its infiltration through soil under different experimental conditions.
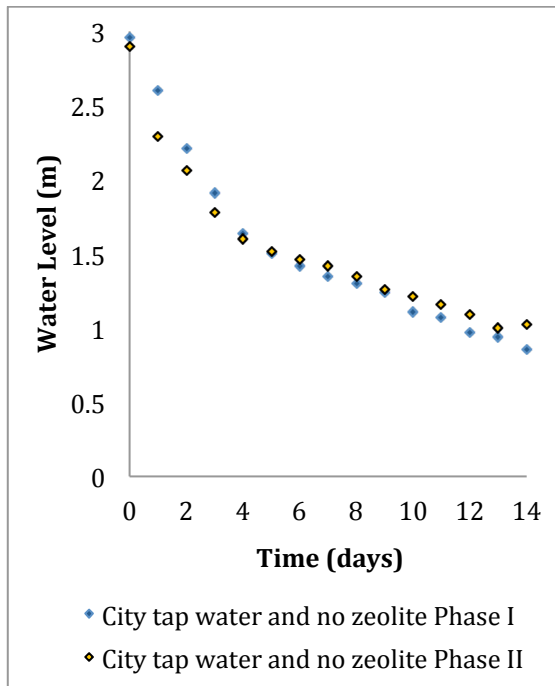
Figure 3.7: Water levels in boreholes with city tap water and no zeolite over time for the first two weeks of phases I and II.
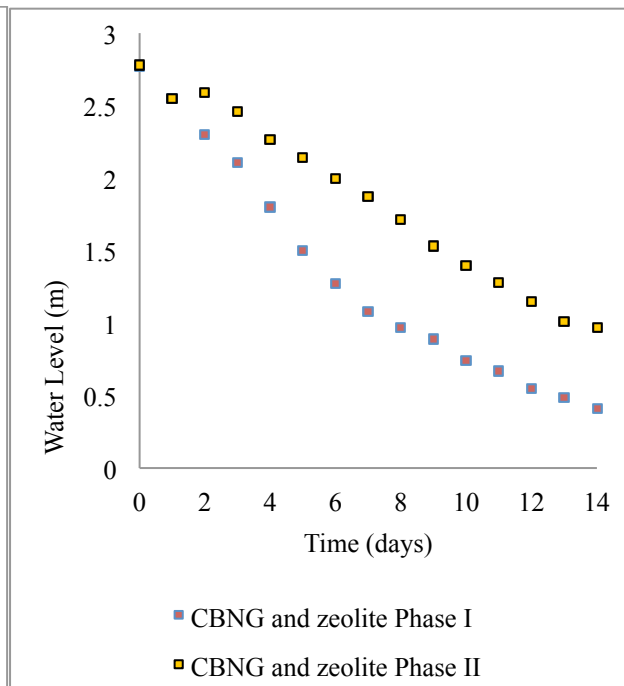
Figure 3.8: Water levels in boreholes with CBNG coproduced water and zeolite over time for the first two weeks of phases I and II.

During the first two weeks (Figure 3.7) in Phases I and II, the water levels in the boreholes with city tap water and no zeolite had similar daily water levels indicating that during that period of time the infiltration of water through the boreholes in Phases I and II did not change significantly. There was no significant difference in the average water levels in the boreholes with city tap water and no zeolite at 95% level of confidence ($p=0.93>0.05$) for infiltration in the two phases. The water levels in the boreholes with CBNG coproduced water and zeolite was lower in Phase I than in Phase II at each point in time. This indicates that infiltration rate was decreasing in Phase II compared to Phase I (Figure 3.8). There was a significant difference in the water levels (heads) in the first two weeks of experiments in boreholes with CBNG coproduced water and zeolite in phases I and II at 95% level of confidence ($p=1.35*10^{-6}<0.05$). There was about 3000 g of zeolite in each of the boreholes with zeolite that could treat about 180 L of water thereby reducing the SAR value from 30 to below 10 $(mol/m^3)^{1/2}$ (Zhao et al., 2008). However, the capability of the zeolite to treat

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CBNG coproduced water depends not only on the reaction time, but also on the soil's chemistry underneath the surface soil. During the infiltration of CBNG coproduced water, the SAR value might not have been reduced to 10 at a time. The excess sodium from the CBNG coproduced water should have been leached down into the soil in Phase I as that impacted, and controlled the rate of water entry into the soil in Phase II (Minhas et al., 1994).
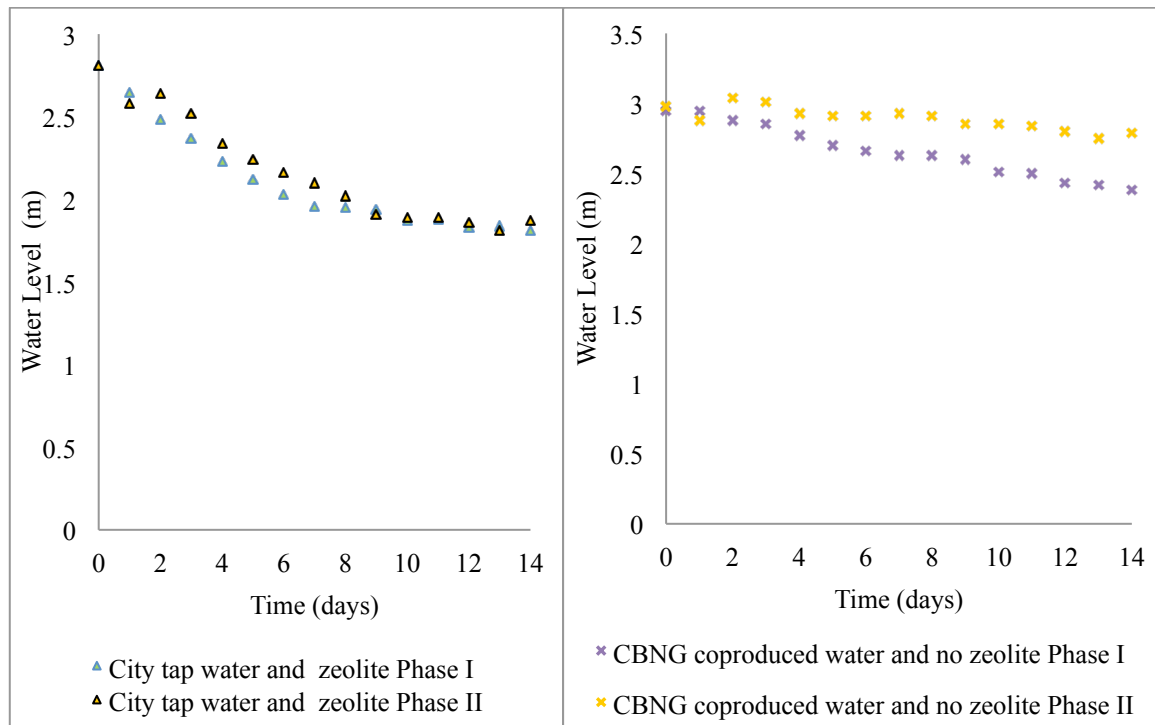
Figure 3.9: Water levels in the boreholes with city tap water and zeolite over time for the first two weeks of phases I and II

Figure 3.10: Water levels in the boreholes with CBNG coproduced water and no zeolite over time for the first two weeks of phases I and II

The water levels in the boreholes with city tap water but zeolite were almost similar in Phases I and II (Figure 3.9). This indicates that there was a minimal difference with the infiltration of tap water due to effect of zeolite in both Phases I and II. The possible reason that infiltration rate did not change much in the Phase II may be that the tap water (SAR = 1.47 $(mol/m^3)^{1/2}$) has a less relative concentration of sodium impacting the soil's physical and chemical characteristics that could alter infiltration of water. Paired sampled t-test showed that the difference was significant in the two phases for the boreholes with city tap water but

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with zeolite at 95% level of confidence (p=0.009<0.05). At all points in time, the water levels in the boreholes with CBNG coproduced water but no zeolite were higher in Phase II as compared to Phase I, and this difference was statistically significant at 95% level of confidence ($p=6.73*10^{-6}<0.05$). This indicates that there was a decrease in the infiltration of the CBNG coproduced water through the subsoil in Phase II possibly due to impact of the high sodium concentration that might have leached into the soil in Phase I thereby impacting the infiltration in Phase II (Minhas et al., 1994, Zhao et al., 2008). Higher SAR values (SAR = 8.3 $(mol/m^3)^{1/2}$) of the soil for the boreholes with CBNG coproduced water and but not zeolite at the upper layer 0–5 cm compared to SAR = 6.4 $(mol/m^3)^{1/2}$ for the boreholes with CBNG coproduced water and zeolite at the same depth shows that there was more leaching of sodium from the boreholes with CBNG coproduced water but no zeolite into the soil that might have possibly reduced the infiltration rate (Figure 3.10).

Impact of zeolite on infiltration. The results of water levels (m) with time (days) are represented in line graphs (Figures 3.11 & 3.12) for the discussion of infiltration comparing different experimental conditions for the first two weeks in Phase I and II. The water levels in the boreholes were found to be impacted by the application of zeolite. In both Phases I and II for the first two weeks, the water levels in the boreholes with CBNG coproduced water but no zeolite were greater than the water levels in the boreholes with CBNG coproduced water and zeolite. The results of water levels in the boreholes in Phase I (Figure 3.11) indicated that the infiltration (loss of water) from the boreholes with CBNG coproduced water and zeolite (79% in 14 days) was approximately four times that for boreholes with CBNG coproduced water but no zeolite (19% in 14 days).
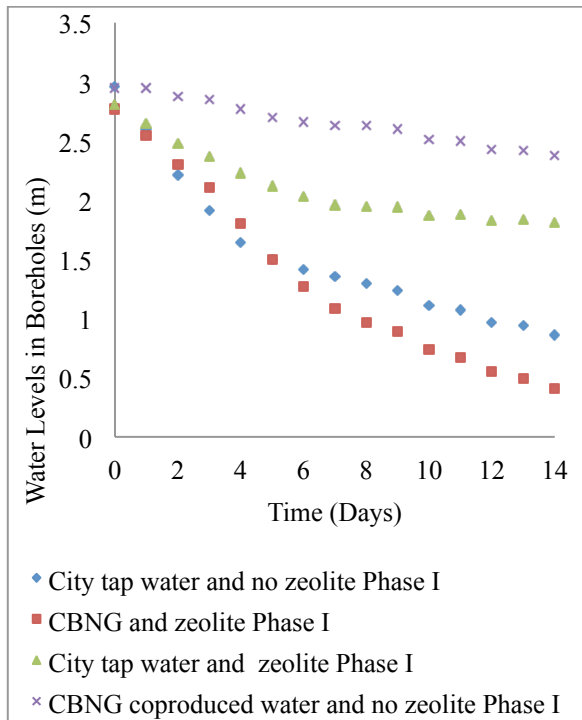
Figure 3.11: Water levels in boreholes of different experimental conditions over time for first two weeks of phase I
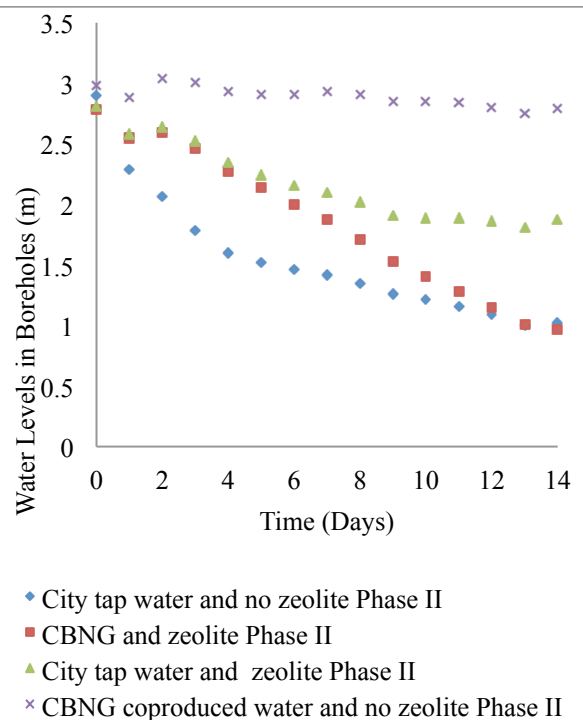
Figure 3.12: Water levels in boreholes of different experimental conditions over time for first two weeks of phase II

There was a loss of water from the boreholes with CBNG coproduced water and zeolite of 60% (32 L), which was approximately, 10 times the loss of water by 6% (3.3 L) from the boreholes with CBNG coproduced water but no zeolite as in Phase II during the same period of time. This indicates that there was greater rate of infiltration in the boreholes in Phase I as compared to Phase II. However, the proportionate difference was greater for the two experimental conditions in Phase II as compared to Phase I (10 times > 4 times) although the absolute difference was greater in Phase I (32 L > 28.7 L). In both Phases I and II (Figure 3.11 & 3.12) and at all points in time for two weeks, the water levels in the boreholes with city tap water and zeolite were higher than the water levels in the boreholes with city tap water and no zeolite. This indicates that there was a negative impact from the zeolite with the infiltration of the tap water, possibly due to the clogging of soil pores by small zeolite particles thereby reducing the porosity of the soil's upper layer (Al-Busaidi et al., 2008).

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The cation exchange capacity of BR zeolite can thus be utilized to exchange sodium ions from the CBNG coproduced water that has calcium and magnesium ions present in the zeolite thereby mitigating the harmful impact of the sodium concentration in the produced water used on soil. This characteristic of the BR zeolite can be utilized in the zeolite lining of containment ponds from which treated water can be infiltered into the swallow aquifers. The zeolite lining using BR zeolite can enhance the infiltration rate, and it can improve the quality of ground water by controlling the amount of sodium that is passed into this water. Zeolite, being largely deposited throughout the western US, incurs low mining costs, and provides a high capacity to cation exchange thereby reducing the CBNG coproduced water treatment cost, and enhancing the beneficial use of the CBNG coproduced water by reducing the SAR to an acceptable level (Zhao et al., 2008).

Post Treatment Soil Analysis

Post treatment field test soil analysis for SAR, EC and pH values are summarized in the following Table 3.3. The application of zeolite in the boreholes with CBNG coproduced water changed the SAR values at all depths for boreholes with CBNG coproduced water, and in reverse order, this might have a subsequent effect on the EC depth values with very little change in pH depth values. In preparation for a discussion of the results in the next section the SAR, EC, and pH values with different experimental conditions are presented in comparable graphs.

Mass loadings and concentrations of major cations with depth: We can observe the mass loading of major cations (Na^+, Ca^{2+}, & Mg^{2+}) and their concentrations with depth in Figures 3.13, 3.14, 3.15, 3.16, 3.17, 3.18, 3.19, and 3.20. These graphs show the impact of amount of mass loading of Na^+ on concentration of the ions in the soil at different depths.

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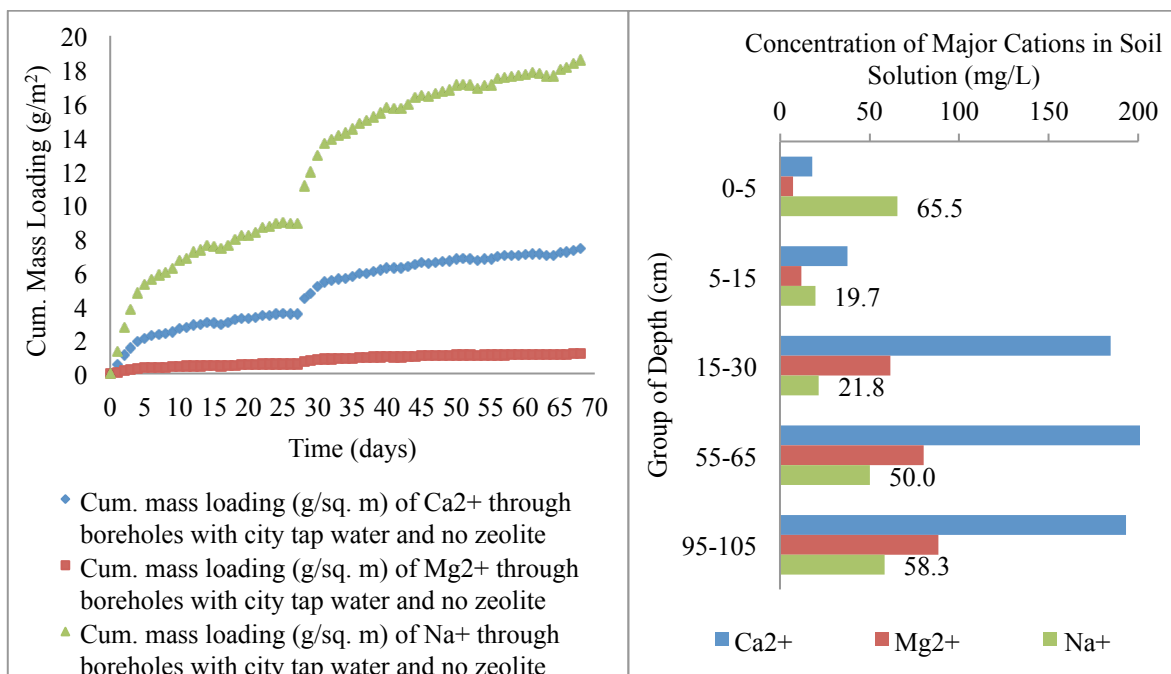
Figure 3.13: Mass loading (g/m^2) of Ca^{2+}, Mg^{2+}, and Na$^+$ through boreholes with city tap water and no zeolite

Figure 3.14: Concentration (mg/L) of Ca^{2+}, Mg^{2+}, and Na$^+$ in solutions from different depth for boreholes with city tap water and no zeolite
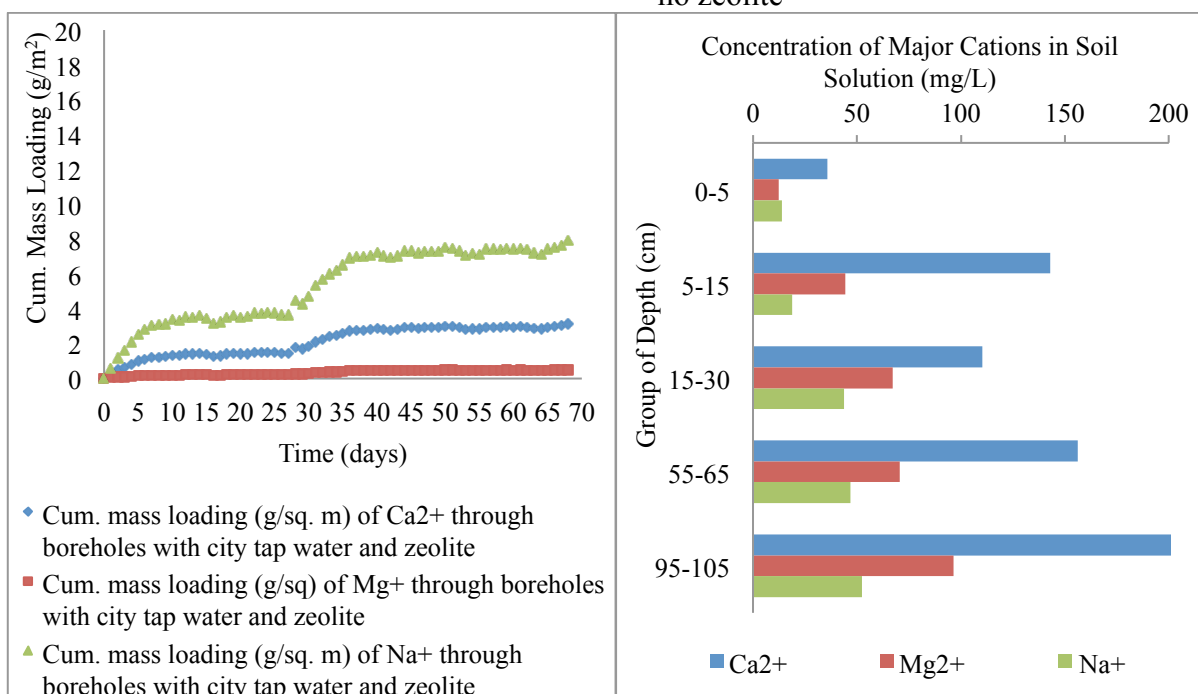
Figure 3.15: Mass loading (g/m^2) of Ca^{2+}, Mg^{2+}, and Na$^+$ through boreholes with city tap water and zeolite

Figure 3.16: Concentration (mg/L) of Ca^{2+}, Mg^{2+}, and Na$^+$ in solutions from different depth for boreholes with city tap water and zeolite

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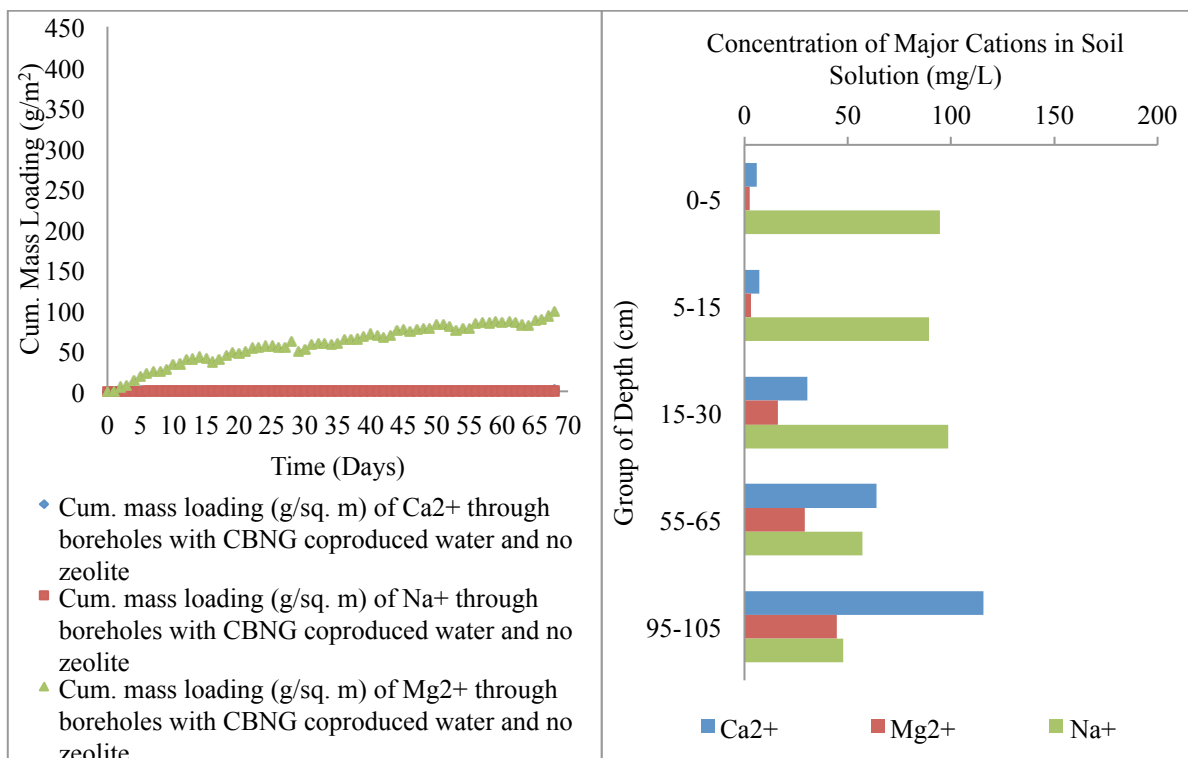
Figure 3.17: Mass loading (g/m^2) of Ca^{2+}, Mg^{2+}, and Na$^+$ through boreholes with CBNG coproduced water and no zeolite

Figure 3.18: Concentration (mg/L) of Ca^{2+}, Mg^{2+}, and Na$^+$ in solutions from different depth for boreholes with CBNG coproduced water and no zeolite
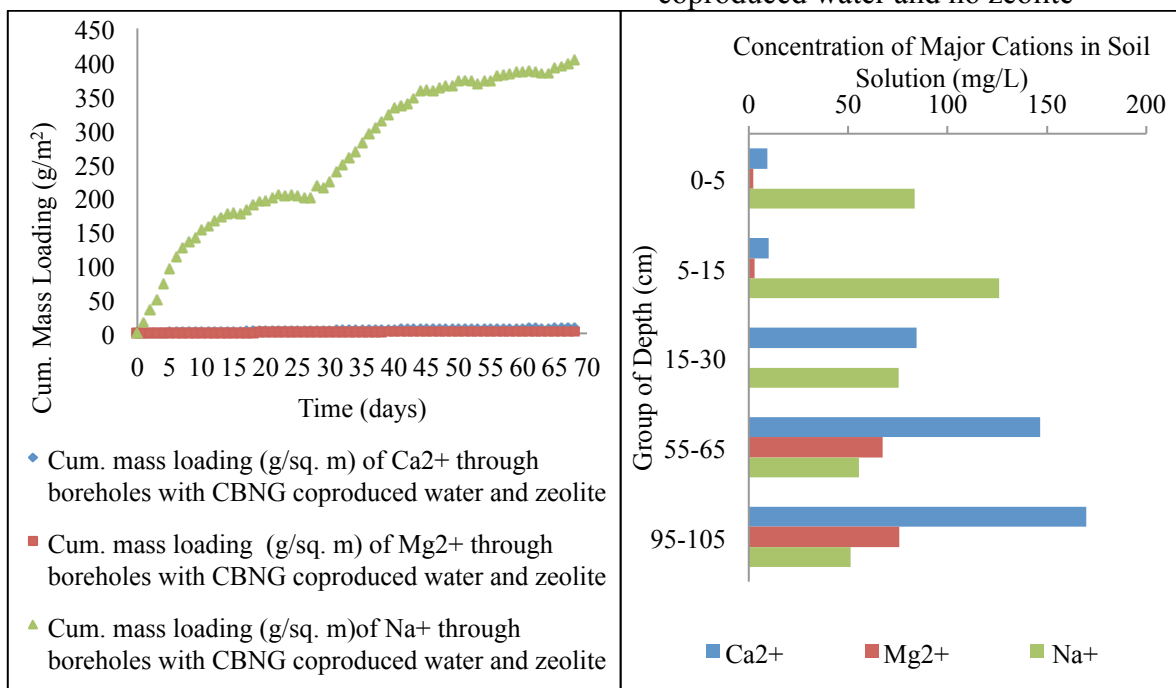
Figure 3.19: Mass loading (g/m^2) of Ca^{2+}, Mg^{2+}, and Na$^+$ through boreholes with CBNG coproduced water and zeolite

Figure 3.20: Concentration (mg/L) of Ca^{2+}, Mg^{2+}, and Na$^+$ in solutions from different depth for boreholes with CBNG coproduced water and zeolite

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We can see the impact of mass loading of Na^+, Ca^{2+} and Mg^{2+} on the concentration of these ions on the upper layer of soil below the boreholes. The concentration of Na^+, Ca^{2+} and Mg^{2+} are increasing with depth for boreholes with tap water (both with and without zeolite) indicating that there was no influence of mass loading of these cations from the tap water (Figures 3.13, 3.14, 3.15, & 3.16). Actually, the maximum total mass loadings of Na^+ were 18 and 8 mg/m^2 for boreholes with tap water and without and with zeolite, and this did not have much impact on the concentration of Na^+ at the upper soil layer. The concentration of Ca^{2+} and Mg^{2+} are increasing with depth for boreholes with CBNG coproduced water (both with and without zeolite) indicating that there is a little or no influence of mass loading of these cations from the infiltration of CBNG coproduced water. However, there is greater impact of mass loading of Na^+ on the concentration of this ion at the upper soil layer in the boreholes with CBNG coproduced water (both with and without zeolite) (Figures 3.17, 3.18, 3.19, & 3.20). The total mass loading of Na^+ (403 mg/m^2) is greater for the boreholes with CBNG coproduced water and zeolite (Figure 3.19) than it (93 mg/m^2) is for the boreholes with CBNG coproduced water and no zeolite (Figure 3.17) indicating a greater impact of the later case on the Na^+ concentration on the upper layers of the soil (up to 15-30 cm) compared to the first case. Lesser mass loading of Na^+ for CBNG coproduced water has greater impact on Na^+ concentrations at upper soil layer.

Analysis of SAR, EC, and pH with depth. The result of analysis of SAR, EC and pH of soil solutions from different depth are presented in Table 3.3. Bivariate correlation of SAR, EC and pH were determined. It was found that there were moderate negative correlation between SAR and EC ($r = -0.62$) and EC and pH ($r = -0.68$), whereas there was a strong positive correlation between SAR and pH ($r = 0.96$). These correlations match with the direction of change of the values of these parameters (SAR and pH decreasing with depth whereas EC increasing with depth).

Table 3.3: Case summaries of experimental conditions

Experimental Conditions		Experimental Results		
Treatment	Depth (cm)	SAR $(mol/m^3)^{1/2}$	EC (dS/m)	pH
CBNG coproduced water but no zeolite	0 - 5	8.3	0.9	7.4
	5 - 15	7.4	0.9	7.3
	15 - 30	5.8	1.3	7.1
	55 - 65	1.6	1.4	6.3
	95 - 105	1.1	1.6	6.1
CBNG coproduced water and zeolite	0 - 5	6.4	0.8	7.3
	5 - 15	8.8	1.1	7.3
	15 - 30	2.9	1.4	6.9
	55 - 65	1.0	1.9	6.1
	95 - 105	0.8	2.2	6.1
City tap water but zeolite	0 - 5	0.6	0.7	6.3
	5 - 15	0.5	1.4	6.3
	15 - 30	0.9	1.9	6.2
	55 - 65	0.8	2.2	6.3
	95 - 105	0.8	2.3	6.3
City tap water and no zeolite	0 - 5	3.1	1.6	6.6
	5 - 15	0.8	1.2	6.3
	15 - 30	0.5	1.7	6.2
	55 - 65	0.8	2.2	6.2
	95 - 105	0.9	2.3	6.2

SAR with depth. The most important aspect of CBNG produced water from the deeper coal seams is the significant increase in the SAR of soil and groundwater (Ganjegunte et al., 2005a, b). An analysis of saturated soil extractions taken from the cation concentrations Na^+, Ca^{2+}, and Mg^{2+} were used for the calculation of SAR values. The SAR soil depth values are shown bar diagrams (Figure 3.21).
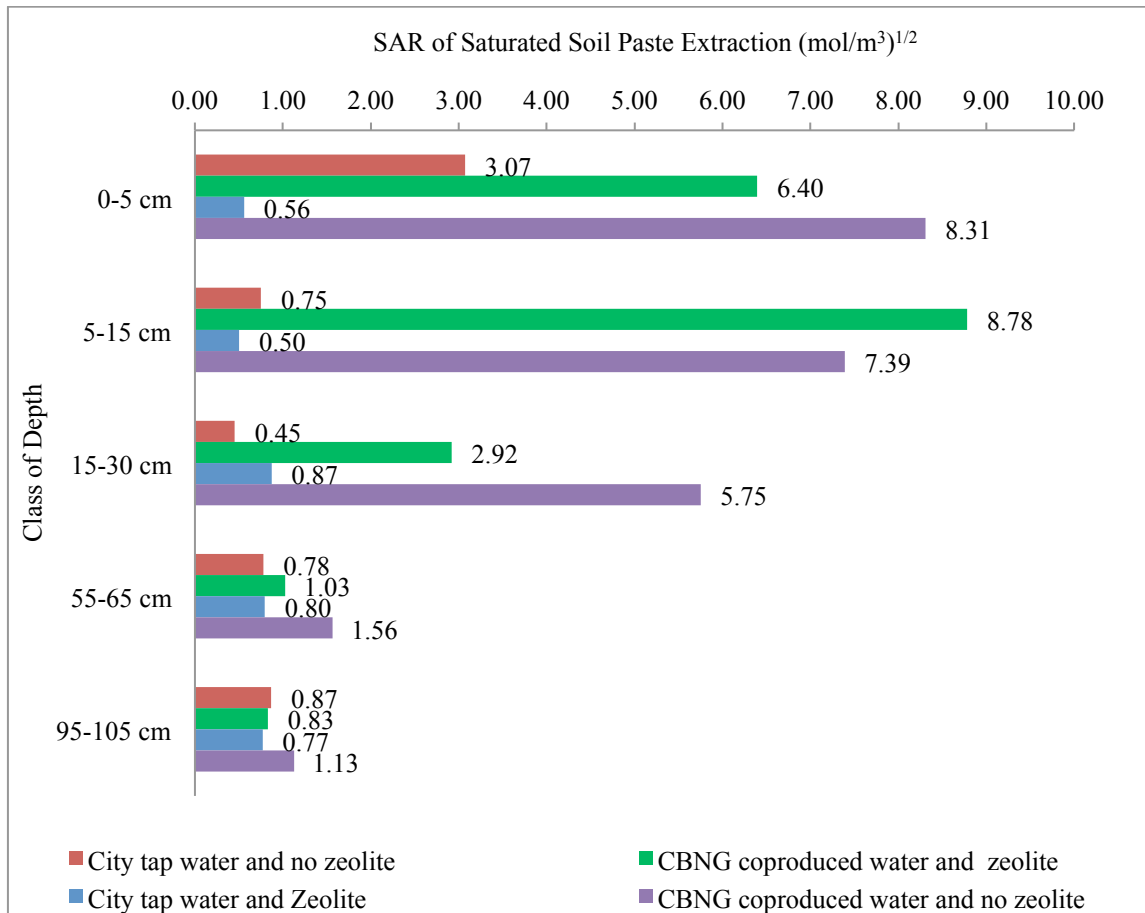
Figure 3.21: Distribution of SAR of soil solutions depth values for boreholes under different experimental conditions

Figure 3.21 shows that boreholes SAR values under all experimental conditions decreased with increasing depth (Ganjegunte et al., 2004) except for the boreholes with CBNG coproduced water and zeolite, which the SAR value at a depth of 5-15 cm (SAR = 8.8 $(mol/m^3)^{1/2}$) is greater than that at the depth of 0-5 cm (SAR = 6.4 $(mol/m^3)^{1/2}$). The saturated paste extraction SAR values indicate that the upper 0-15 cm soil horizon is more sodic than the soil below (Ganjegunte et al., 2004). The greater SAR near the surface (0–5 cm) shows that sodium is build up in this part of the soil due to the cation exchange of infiltered CBNG coproduced water with the soil (Burrow et al., 2002; Ganjegunte et al., 2004). A comparison of SAR depth values showed that the SAR values for the boreholes with CBNG coproduced water but no zeolite were higher than that for boreholes with CBNG coproduced water and zeolite except at 5-15 cm.

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The soil analysis results revealed that the SAR values were 6.4, 8.8, 2.9, 1.0, and 0.8 $(mol/m^3)^{1/2}$ for the boreholes with CBNG coproduced water and zeolite, and the SAR values were 8.3, 7.4, 5.8, 1.6, and 1.1 $(mol/m^3)^{1/2}$ for the boreholes with CBNG coproduced water but no zeolite at the depths of 0-5, 5-15, 15-30, 55-65, and 95-105 cm respectively. These results indicate that there might be more sodium retention due to sodium adsorption at the upper profile of the soil. The SAR values were mitigated by zeolite to some extent because at a 0-5 cm depth, the soil solution SAR was 6.4 $(mol/m^3)^{1/2}$ for the soils from boreholes with CBNG coproduced water and zeolite, whereas this value was 8.3 $(mol/m^3)^{1/2}$ for the boreholes with CBNG coproduced water but no zeolite. It is unknown why the SAR value for the soil solution from the boreholes with CBNG coproduced water and zeolite increased at the depth 5–15 cm. One possible reason for this increase in SAR at this depth may be that the soil already had a higher concentration of sodium in this layer compared to the upper layer of 0–5 cm thus making the total relative concentration of sodium ions higher (SAR = 8.8 > 6.4 $(mol/m^3)^{1/2}$). At 0-5, 5-15, 15-30, 55-65, and 95-105 cm (Table 3.6), the SAR values for the boreholes with CBNG coproduced water but no zeolite decreased with increasing depths (SAR=8.3, 7.4, 5.8, 1.6, and 1.1 $(mol/m^3)^{1/2}$. This result may indicate that most of the sodium ions were adsorbed into the soil at the upper profiles causing a further decrease in the infiltration of CBNG coproduced water in Phase II of the infiltration experiment.

EC with depth. Measurements of the soil solutions electrical conductivity (EC) presented in a bar diagrams (Figure 3.22).
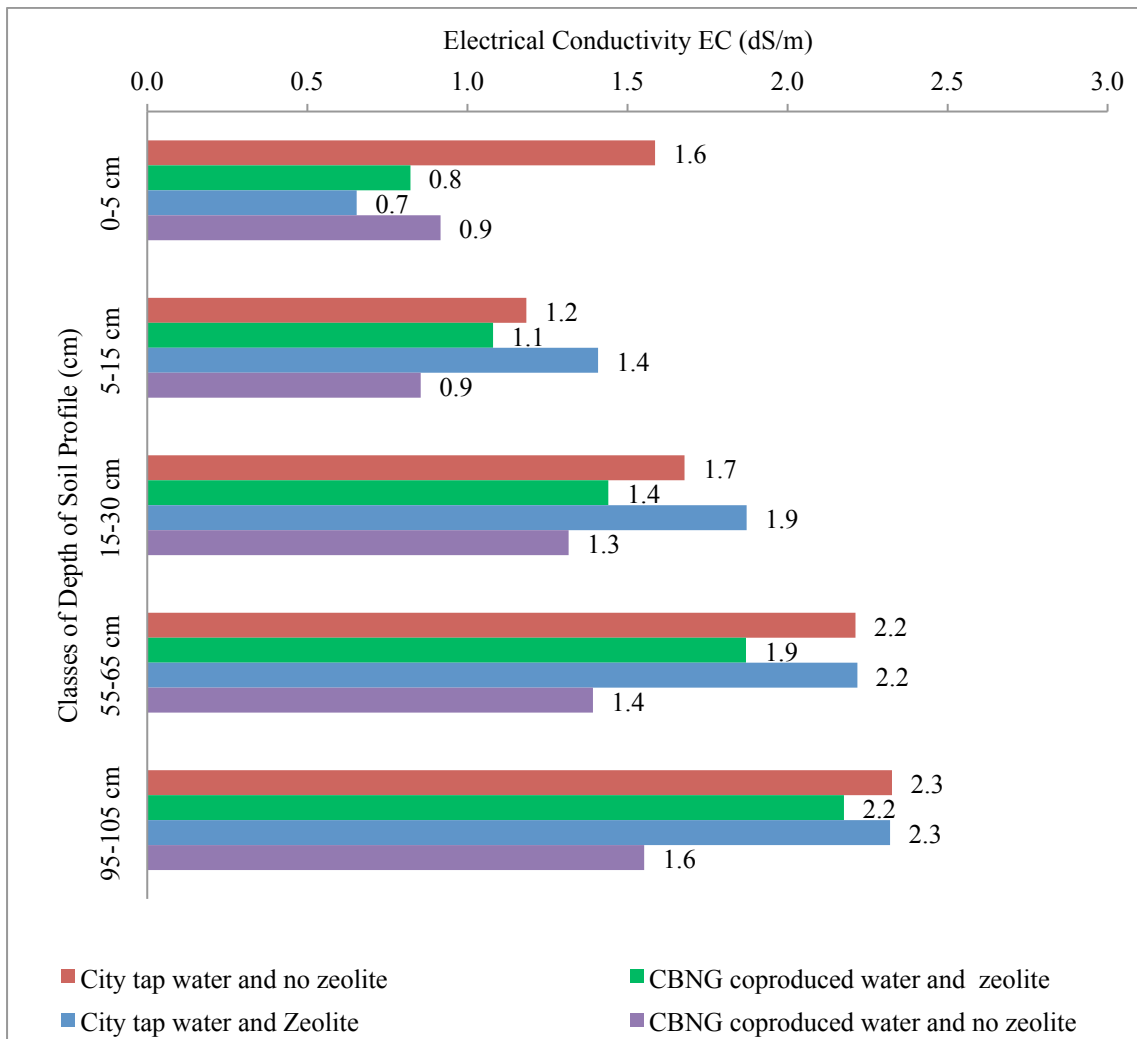
Figure 3.22: Distribution of EC of soil solutions depth values for boreholes under different experimental conditions

The results of EC with depth in Figure 3.22 showed that the measure of ECs boreholes soil solutions under all experimental condition increased with increasing depth except for the boreholes with city tap water and no zeolite from the depths of 0-5 to 5-15 cm in which EC decreased from 1.6 dS/m to 1.2 dS/m. These results are contradictory to those reported Ganjegunte et al. (2004). The possible reason for an increasing EC with greater depth could be that more salts from the upper soil leached down during the infiltration of the CBNG coproduced water. The measure of EC from CBNG coproduced water and from tap

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water were 1.9 dS/cm and 0.1 dS/m, respectively. At the depth of 0-5 cm, soil solution EC for boreholes with city tap water and no zeolite, and city tap water and with zeolite were 1.6 dS/m and 0.7 dS/m, respectively, indicating that BR zeolite reduced the EC within this soil profile. The EC of the tap water (0.1 dS/m) measurement was less than the EC (1.6 dS/m) for soil solutions from the boreholes with city tap water and no zeolite. The reason for the greater EC soil solutions at the 0-5 cm depth for boreholes with city tap water and no zeolite compared with tap water can be attributed to the salts present in the soil that increased the total amount of the soluble salts.

The measure of the soil solutions ECs (1.1, 1.4, 1.9, and 2.2 dS/m) for boreholes with CBNG coproduced water and zeolite were greater than the ECs (0.9, 1.3, 1.4, and 1.6 dS/m) for boreholes with CBNG but no zeolite at depths 5-15, 15-30, 55-65, and 95-105 cm, respectively. However, the EC at 0-5 cm was lower for boreholes with CBNG coproduced water and zeolite (0.8 dS/m) than in boreholes with CBNG coproduced water and no zeolite (0.9 dS/m) (Table 3.6). This result indicates that there was a reduction in EC at 0-5 cm soil due to application of zeolite when CBNG coproduced water was applied. At depths greater than 5 cm, the reason for the greater EC values for soil extracts from the boreholes with CBNG coproduced water and zeolite compared to the EC for soil extracts from the boreholes with CBNG coproduced water but no zeolite may be due to the leaching of salts to greater depths from the upper soil profile, but this needs further research to identify the actual cause. Another interesting result is that the measures of ECs for the boreholes with city tap water and no zeolite were greater at all depths compared to the boreholes with CBNG coproduced water but no zeolite (Figure 3.22).

These results indicate that the application of CBNG coproduced water reduced the EC of the soil. The cause for the reduction of EC values when CBNG coproduced water was applied may be that the sodium from the CBNG coproduced water was adsorbed in the soil

due to an ion exchange with clay particles. If the CBNG coproduced water *is reach in* NaHCO$_3$, it may change Ca^{2+} and Mg^{2+} salts in the soil to form insoluble carbonates thus reducing the amount of soluble salts in the soil. Hence, this may reduce the EC values of the soil. An increasing EC with increasing depth can be attributed to the increase in the concentration of soluble salts in the soil due to the leaching of soluble salts from the upper layers of the soils to the lower depths of the soil.

   *pH with depth.* The measure of soil solutions pH were analyzed with depth of soil profiles and the results are presented in graph (Fig 3.23).
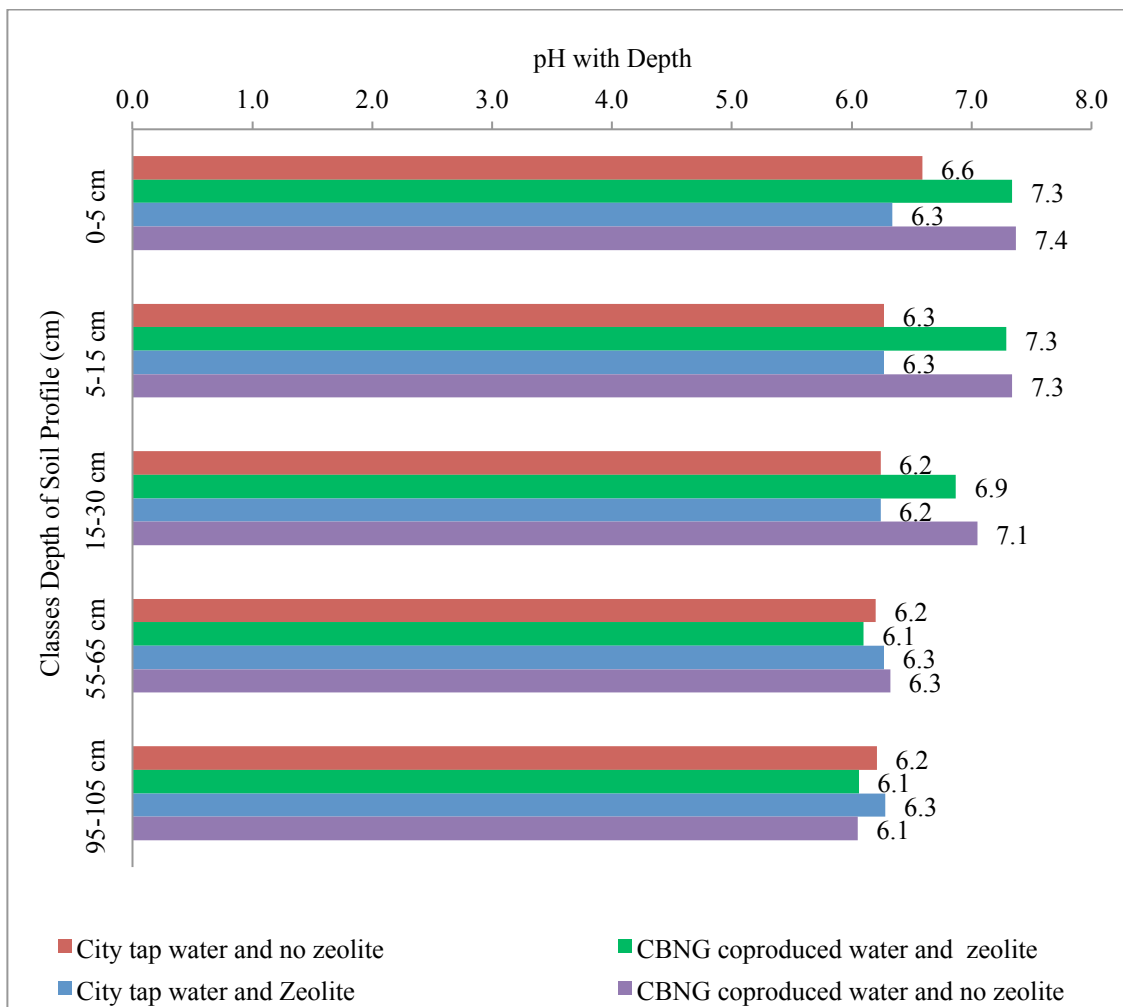
Figure 3.23: Distribution of pH of soil solutions depths values for boreholes under different experimental conditions

The distribution of soils pH depth values shows that there was a slight decrease in pH with increasing depth. The measure of pH in the field using CBNG coproduced water and tap water were 8.9 and 7.5, respectively. The pH of the soil solutions in boreholes with city tap water and no zeolite, and city tap water with zeolite were 6.6 and 6.3, respectively, at the depth of 0-5 cm. This indicates a loss of tap water pH (7.5) when it passed through the soil at 0-5 cm (pH = 6.6). The loss was greater for the soils that came from the boreholes with zeolite (pH = 6.3) indicating that zeolite can reduce a soil's pH and remediate the harmful impact of high pH due to high sodium concentrations.

The bar graph in Figure 3.23 shows that the soil solutions pH values are less affected with increasing depth. At 0-5, 5-15, 15-30, 55-65, and 95-105 cm, respectively, the pH for soils from boreholes with CBNG coproduced water and zeolite (7.3, 7.3, 6.9, 6.1, and 6.1) were slightly less than or equal to the pH values (7.4, 7.3, 7.1, 6.3, and 6.1) for soils from boreholes with CBNG coproduced water but no zeolite. Again, the slight decrease in soil solutions pH values from boreholes with CBNG coproduced water and zeolite compared to the pH values for soil solutions from the boreholes with CBNG coproduced water and no zeolite can be attributed to the application of BR zeolite indicating a positive impact of zeolite in the remediation of high pH due to high sodium concentrations.

Conclusion

The results of the field test on the infiltration of CBNG coproduced water, with and without BR zeolite amendments suggest that BR zeolite could mitigate the effect that high SAR values (SAR =27 $(mol/m^3)^{1/2}$) had on the coproduced water on a soil's hydraulic behavior. The water levels in the boreholes with city tap water and no zeolite were similar in Phases I and II indicating that the infiltration of tap water through the boreholes in Phases I and II did not change significantly. There was no significant difference in the average infiltration at 95% confidence level (p=0.93 > 0.05) for the first two weeks through the

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boreholes with tap water and no zeolite in phases I and II. The possible reason for this may be that the tap water had a less relative concentration of Na^+, and there was little to no impact on the soil. However, there was a statistically significant difference between the water level for the infiltration of city tap water through boreholes with zeolite in phase I and II at 95% confidence level indicating a negative impact of zeolite on infiltration of the tap water.

The water levels in the boreholes with CBNG coproduced water and zeolite was lower in Phase I than in Phase II at each point in time. This indicated that infiltration rate decreased in Phase II compared to Phase I due to presence of high sodium concentrations in the soil with sorption capacity decreasing in phase II and leaking of more Na^+ to the subsoil through the zeolite layer. There was a significant difference in the infiltration of CBNG coproduced water through boreholes with and without zeolite both in phases I and II at 95% level of confidence ($p=6.87*10^{-7}<0.05$ for phase I and $p=2.76*10^{-6}<0.05$ for phase II). There was about 3000 g of zeolite in each of these boreholes that could treat about 180 L of water in order to reduce the SAR value from 30 to below 10 (Zhao et al., 2008). However, it is possible that the during infiltration of the CBNG coproduced water, the SAR value was not reduced to 10 at a time, and more sodium could have leached down into the soil thereby controlling the rate of water entry into the soil (Minhas et al., 1994).

At all points in time, the water levels in the boreholes with CBNG coproduced water but no zeolite were higher in Phase II than in Phase I. This indicated that there was a decrease in the infiltration of the CBNG coproduced water through the subsoil due to the impact of a high Na^+ concentration leached into the soil in Phase I that possibly impacted the infiltration in Phase II (Minhas et al, 1994; Zhao et al., 2008). The infiltration of CBNG coproduced water through boreholes with zeolite was much higher compared to it through the boreholes without zeolite indicating a positive impact of BR zeolite in enhancing the infiltration of CBNG coproduced water through the soil.

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Post treatment field test of soil revealed that SAR and pH values decreased with depth while the EC increased. At the depths 0-5, 5-15, 15-30, 55-65, and 95-105 cm respectively, the SAR values were 6.4, 8.8, 2.9, 1.0, and 0.8 $(mol/m^3)^{1/2}$ for the boreholes with CBNG coproduced water and zeolite, and the SAR values were 8.3, 7.4, 5.8, 1.6, and 1.1 $(mol/m^3)^{1/2}$ for the boreholes with CBNG coproduced water and no zeolite indicating that there was a positive effect of zeolite at each layer of soil except at 5-15 cm thus by mitigating impact of high SAR in the soil. The SAR values showed that the general trend for SAR values decreased with increasing depth for soils below the boreholes. At the depths 0-5, 5-15, 15-30, 55-65, and 95-105 cm, respectively, the EC values were 0.8, 1.0, 1.4, 1.9, and 2.2 dS/m for the boreholes with CBNG coproduced water and zeolite, and the EC values were 0.9, 0.9, 1.3, 1.4, and 1.6 dS/m for the boreholes with CBNG coproduced water but no zeolite indicating that the zeolite treatment was effective only at the upper soil layer 0–5 cm to mitigate the EC slightly. The distribution of ECs showed that the general trend for EC was increasing with increasing depth of the soil. The pH values decreased slightly with increasing depths for boreholes with CBNG coproduced water and zeolite, and for those without zeolite. There was almost no impact of zeolite treatment on the pH values of soil extracts for boreholes with CBNG coproduced water and zeolite compared to the boreholes with CBNG water and no zeolite. The results from the field test on the infiltration of CBNG coproduced water, and the post treatment soil analysis of SAR, EC, and pH revealed that a zeolite treatment can be a viable method and a simple technology to mitigate the effects that high sodicity CBNG coproduced water has on a soil's physicochemical properties. However, further research is necessary to conclusively confirm the effective use of BR zeolite as a way to mitigate the impact of CBNG coproduced water for higher EC at an increasing depth below 5 cm, and at a higher SAR at the depth of 5-15 cm.

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CHAPTER 4

SUMMARY, CONCLUSION, AND RECOMMENDATIONS

Summary of the Study

The purpose of this research study was to assess the effectiveness of Bear River (BR) zeolite in mitigating the harmful effects of CBNG coproduced water when applied to soil. The objectives of this study were to evaluate the BR zeolite treatment of CBNG coproduced water with the purpose of enhancing its beneficial use, to evaluate the effect of BR zeolite for the remediation of the harmful effect that CBNG coproduced water has on soils, to conduct a lab test and a field test in order to evaluate the effectiveness of BR zeolite as a CBNG coproduced water treatment, and to measure its impact on physicochemical characteristics of soil.

An adsorption isotherm study was performed using BR zeolite with $NaHCO_3$ and NaCl solutions with concentrations of sodium 5,000; 3,750; 2,500; 1,875; 1,250; and 625 mg/L. A Na^+ adsorption kinetics study was conducted on four different zeolite size fractions (1.3–1.5, 1.5-1.7, 1.7-2.0, and 2.0-2.5mm) using a batch equilibration technique (Zhao et al., 2008, 2009) using synthetic CBNG coproduced water (SAR = 30 $(mol/m^3)^{1/2}$). A column study was conducted to evaluate the effect of synthetic CBNG coproduced water (SAR =17.7 $(mol/m^3)^{1/2}$) on flow rates through soil columns with and without zeolite. Then, a field experiment was conducted utilizing 12 infiltration boreholes (six with zeolite and six without zeolite) each fitted with an automatic water level data logging pressure transducer (In-Situ Level TROLL 500) at the bottom. Sheridan city tap water (SAR=1.47 $(mol/m^3)^{1/2}$, EC = 1.00 dS/m, and pH = 8.00) and CBNG coproduced water (SAR = 27.00 $(mol/m^3)^{1/2}$, EC=1.90 dS/m, and pH = 8.50) from a nearby CBNG coproduced water discharge outfall were used for infiltration through boreholes both with and without zeolite. The city tap water and the

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CBNG coproduced water were refilled into the boreholes after a month. Intact soil cores were collected from the bottoms of each of the boreholes in 1.2 m long by 5 cm diameter polyethylene pipes. The soils taken from the bottom of the boreholes were separated into depth samples representing 0-5, 5-15, 15-30, 55-65, and 95-105 cm. Saturated paste extracts were obtained from soils from each of these depths for analysis of Na^+, Ca^{2+}, and Mg^{2+} ion concentrations, EC, and pH. A two samples t-test was applied to compare the mean flow rates through the soil columns and water levels in the boreholes to evaluate the differences (if any) existed at 95% confidence level in phases I and II.

The batch adsorption isotherm study showed the adsorption of Na^+ by BR zeolite to be 18 and 21 mg Na^+ per gram BR zeolite with 0.0006 and 0.0012 L/mg Langmuir coefficients (K_L), and Freundlich coefficients (Kf) being 0.08 and 0.29 in NaCl and $NaHCO_3$ solutions, respectively. The adsorption kinetics study showed that the sorption of Na^+ was an inverse function of the size of zeolite particles and resulted in greater adsorption for smaller particles. Removal efficiency was found to be the highest (72%) for the smallest particle size (1.3–1.5 mm) compared to 59% for the largest particle size (2.0–2.5 mm) within the experimental conditions. Use of zeolite in the columns studies reduced the infiltration rate of tap water (SAR=1.90 $(mol/m^3)^{1/2}$ and electrical conductivity (EC)=0.20 dS/m) due to physical resistance of the zeolite particles from the top of the soil. However, during the first three days after the application of CBNG coproduced water (SAR=17.70 $(mol/m^3)^{1/2}$ & EC=1.60 dS/m), the infiltration rate for columns with zeolite was higher than for the columns without zeolite indicating a positive impact of zeolite into the infiltration of CBNG coproduced water through the soil columns.

The results of field test showed that BR zeolite was found to mitigate the effect that high SAR values (SAR =27 $(mol/m^3)^{1/2}$) of the coproduced water had on the soil's hydraulic behavior. At the end of two months, during which time Phase I (the first month of

experiment) and Phase II (the second month of the experiment) of the field tests were completed, it was found that there were changes in the infiltration rates. In Phase I, the infiltration rate in the boreholes with CBNG coproduced water and zeolite was approximately four times that of the boreholes with CBNG coproduced water and no zeolite. In Phase II, the infiltration rate of CBNG coproduced water through boreholes with zeolite was nearly ten times that of the control (boreholes without zeolite). At the depths 0-5, 5-15, 15-30, 55-65 and 95-105 cm, post-treatment field test soil analysis revealed that the values of SAR for boreholes with CBNG coproduced water and zeolite were less than the SAR for the boreholes with CBNG coproduced water but no zeolite, thus mitigating the high SAR with BR zeolite. At the depths 0-5, 5-15, 15-30, 55-65, and 95-105 cm respectively, the SAR values were 6.4, 8.8, 2.9, 1.0, and 0.8 $(mol/m^3)^{1/2}$ for the boreholes with CBNG coproduced water and zeolite, and the SAR values were 8.3, 7.4, 5.8, 1.6, and 1.1 $(mol/m^3)^{1/2}$ for the boreholes with CBNG coproduced water and no zeolite indicating that there was a positive effect of zeolite at each layer of soil except at 5-15 cm thus by mitigating impact of high SAR in the soil. The SAR values decreased with depth while EC value increase with increasing depth in general. At the depths 0-5, 5-15, 15-30, 55-65, and 95-105 cm, respectively, the EC values were 0.8, 1.0, 1.4, 1.9, and 2.2 dS/m for the boreholes with CBNG coproduced water and zeolite, and the EC values were 0.9, 0.9, 1.3, 1.4, and 1.6 dS/m for the boreholes with CBNG coproduced water but no zeolite indicating that the zeolite treatment was effective only at the upper soil layer 0–5 cm to mitigate the EC slightly. However, there was almost no mitigation of high pH value of the soil extract for boreholes with CBNG coproduced water with zeolite compared to the pH values for boreholes with CBNG coproduced water and no zeolite.

Conclusion of the Study

Findings from both the lab and the field studies concluded that by reducing the potential impacts of high concentrations of Na^+ in CBNG coproduced water on the

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physicochemical properties of soil and groundwater, it is possible that a Ca^{2+} and Mg^{2+} rich zeolite lining at the bottom of an infiltrated containment pond can enhance the beneficial use of coproduced water for groundwater recharge and other possible uses. A BR-zeolite treatment of CBNG coproduced water can be an effective method for mitigating the harmful impacts caused by high Na^+ concentration on the physicochemical characteristics of soil and water with zeolite lining at the bottom of infiltration-evaporation containment ponds.

Recommendations for further Study

Following are the recommendations for further study:

1. The lab studies (adsorption isotherm, adsorption kinetic, and column studies) were limited to adsorption of sodium by BR zeolite and potential impact of Na^+ on the infiltration through soil columns with and without zeolite. Further study is recommended for the evaluation of effectiveness of different kinds of zeolite in mitigating impacts of high concentration of Na^+ on soil and water.

2. The field study was limited to infiltration of city tap water and CBNG coproduced water through boreholes with and without zeolite within an area of 350 square meters. Further study is recommended that covers a wider range of the study area in the PRB in Wyoming incorporating both boreholes and evaporation/infiltration ponds.

3. This study did not analyze the cost associated with zeolite treatment of CBNG coproduced water. Therefore, a further study is recommended for cost evaluation of zeolite treatment of CBNG coproduced water in the PRB.

4. This study did not evaluate the impact on ground water quality due to surface or subsurface disposal of CBNG coproduced water with and without zeolite treatment. Therefore, a further study is recommended for monitoring and evaluation of swallow ground water quality as a result of direct surface or subsurface disposal of CBNG coproduced water with and without zeolite treatment.

APPENDIX- A

Data for Flow Rates of Tap Water and Simulated CBNG Water in Column Study

Application of Water	Date	Average Flow Rate (ml/s) through Soil Columns with Zeolite	Average Flow Rate (ml/s) through Soil Columns without Zeolite
Application of Tap Water through Soil Columns	7/20/2008	0.0050	0.0058
	7/21/2008	0.0051	0.0061
	7/22/2008	0.0045	0.0058
	7/23/2008	0.0050	0.0058
	7/24/2008	0.0049	0.0056
	7/25/2008	0.0046	0.0054
	7/26/2008	0.0046	0.0053
	7/27/2008	0.0045	0.0053
	7/28/2008	0.0039	0.0048
	7/29/2008	0.0038	0.0052
	7/30/2008	0.0041	0.0049
	7/31/2008	0.0039	0.0046
	8/1/2008	0.0039	0.0047
	8/2/2008	0.0037	0.0044
	8/3/2008	0.0040	0.0046
	8/4/2008	0.0040	0.0042
	8/5/2008	0.0037	0.0038
	8/6/2008	0.0039	0.0036
Application of Simulated CBNG Water through Soil Columns	8/6/2008	0.0044	0.0039
	8/7/2008	0.0051	0.0040
	8/8/2008	0.0065	0.0045
	8/8/2008	0.0060	0.0036
	8/9/2008	0.0041	0.0037
	8/10/2008	0.0044	0.0033
	8/11/2008	0.0039	0.0032
	8/12/2008	0.0038	0.0032
	8/13/2008	0.0035	0.0030
	8/14/2008	0.0033	0.0029
	8/15/2008	0.0026	0.0024
	8/16/2008	0.0025	0.0024
	8/17/2008	0.0024	0.0023
	8/18/2008	0.0018	0.0017
	8/19/2008	0.0024	0.0023
	8/20/2008	0.0024	0.0023

APPENDIX-B

Data for SAR from Concentrations of Major Cations in Influent and Effluents in Column Study

Water samples			Column	CA MG/L Diluted	MG MG/L Diluted	NA MG/L Diluted	CA MG/L Corrected	MG MG/L Corrected	NA MG/L Corrected	SAR $(mol/m^3)^{1/2}$
Influent	Tap water	s1		0.88	0.31	1.65	22.00	7.75	41.25	1.92
		s2		0.90	0.32	1.59	22.50	8.00	39.75	1.83
		s3		0.88	0.32	1.66	22.00	8.00	41.50	1.92
	CBNG water	s1		0.23	0.33	11.07	5.75	8.25	276.75	17.23
		s2		0.22	0.35	11.39	5.50	8.75	284.75	17.47
		s3		0.23	0.34	11.87	5.75	8.50	296.75	18.28
Effluent Tap Water	8/5/2008	No zeolite	c1	0.36	0.41	5.79	9.00	10.25	144.75	7.79
		No zeolite	c2	0.51	0.52	3.87	12.75	13.00	96.75	4.53
		zeolite	c3	1.29	0.98	1.35	32.25	24.50	33.75	1.09
		No zeolite	c4	0.59	0.30	6.17	14.75	7.50	154.25	8.13
		zeolite	c5	1.05	0.95	1.19	26.25	23.75	29.75	1.01
		zeolite	c6	1.46	1.05	0.91	36.50	26.25	22.75	0.70
Effluent CBNG Water	8/7/2008	No zeolite	c1	0.28	0.30	6.34	7.00	7.50	158.50	9.87
		No zeolite	c2	0.32	0.28	6.86	8.00	7.00	171.50	10.63
		zeolite	c3	1.01	0.53	3.62	25.25	13.25	90.50	3.62
		No zeolite	c4	0.62	0.54	3.85	15.50	13.50	96.25	4.29
		zeolite	c5	0.41	0.42	3.95	10.25	10.50	98.75	5.15
		zeolite	c6	1.34	0.67	3.25	33.50	16.75	81.25	2.85
	8/12/2008	No zeolite	c1	0.70	0.31	6.65	17.50	7.75	166.25	8.29
		No zeolite	c2	0.57	0.29	7.12	14.25	7.25	178.00	9.54
		zeolite	c3	1.22	0.52	3.83	30.50	13.00	95.75	3.65
		No zeolite	c4	0.27	0.29	6.60	6.75	7.25	165.00	10.45
		zeolite	c5	0.37	0.42	4.15	9.25	10.50	103.75	5.52
		zeolite	c6	0.55	0.63	3.12	13.75	15.75	78.00	3.39
	8/20/2008	No zeolite	c1	0.90	0.31	6.54	22.50	7.75	163.50	7.55
		No zeolite	c2	0.53	0.27	6.69	13.25	6.75	167.25	9.29
		zeolite	c3	0.59	0.51	4.26	14.75	12.75	106.50	4.88
		No zeolite	c4	0.27	0.27	6.57	6.75	6.75	164.25	10.65
		zeolite	c5	0.47	0.40	4.26	11.75	10.00	106.50	5.49
		zeolite	c6	1.20	0.61	3.26	30.00	15.25	81.50	3.01

APPENDIX C

Data for Electrical Conductivity and pH of Influent and Effluents in Column Study

	Exp. Conditions	Columns	Sample id	EC dS/m	pH	Avg EC	Avg pH
tap water			1	0.22	7.48	0.22	7.51
			2	0.23	7.53		
			3	0.22	7.51		
CBNG water			4	1.61	9.01	1.62	9.21
			5	1.62	9.50		
			6	1.63	9.12		
8/5/2008	zeolite	c1	7	1.37	8.68	1.19	8.49
	zeolite	c2	8	1.07	8.45		
	no zeolite	c3	9	0.96	8.20	0.90	7.96
	zeolite	c4	10	1.14	8.33		
	no zeolite	c5	11	0.86	7.88		
	no zeolite	c6	12	0.90	7.80		
8/7/2008	zeolite	c1	13	1.51	8.44	1.52	8.49
	zeolite	c2	14	1.54	8.70		
	no zeolite	c3	15	1.23	7.50	1.13	7.81
	zeolite	c4	16	1.51	8.34		
	no zeolite	c5	17	1.13	8.26		
	no zeolite	c6	18	1.03	7.67		
8/12/2011	zeolite	c1	19	1.59	8.58	1.60	8.43
	zeolite	c2	20	1.61	8.12		
	no zeolite	c3	21	1.30	7.20	1.16	7.80
	zeolite	c4	22	1.60	8.60		
	no zeolite	c5	23	1.14	8.18		
	no zeolite	c6	24	1.04	8.02		
8/20/2008	zeolite	c1	25	1.56	8.52	1.59	8.44
	zeolite	c2	26	1.59	8.20		
	no zeolite	c3	27	1.20	7.40	1.16	7.87
	zeolite	c4	28	1.62	8.60		
	no zeolite	c5	29	1.16	8.10		
	no zeolite	c6	30	1.12	8.12		

APPENDIX-D

Data from Adsorption of Isotherm Study

Initial Con. (a) of Na^+	Final Con. (b) of Na+ ($NaHCO_3$ used)	Final Con. (c) Of Na^+ (NaCl used)	Adsorption of Na^+ ($NaHCO_3$ used) = (a-b)/1000*(40/5)	Adsorption of Na^+ (NaCl used) = (a-c)/1000*(40/5)	Percent Adsorption of Na^+ (NaHCO3 used)	Percent Adsorption of Na^+ (NaCl used)
Mg/L	Mg/L	Mg/L	Mg of Na^+/g Zeolite	Mg of Na^+/g Zeolite	%	%
5000.00	2931.72	3426.62	16.55	12.59	41.37	31.47
3750.00	1913.97	2460.71	14.69	10.31	48.96	34.38
2500.00	989.50	1406.99	12.08	8.74	60.42	43.72
1875.00	719.82	978.59	9.24	7.17	61.61	47.81
1250.00	415.72	559.78	6.67	5.52	66.74	55.22
625.00	155.85	309.91	3.75	2.52	75.06	50.41

Data from Adsorption Kinetics Study

Sample id	Time (min)	#	Na$^+$	Mg^{2+}	Ca^{2+}	Na$^+$	Mg^{2+}	Ca^{2+}	SAR
			1 ml diluted to 25 ml			Corrected concentrations			
			ppm	ppm	ppm	mol/m^3	mol/m^3	mol/m^3	(mol/m^3)$^{1/2}$
	0.00								30.00
A1	30.00	1	6.69	0.17	3.22	7.27	0.18	2.01	4.91
B1	30.00	2	6.53	0.12	2.46	7.10	0.13	1.54	5.50
C1	30.00	3	6.49	0.15	2.87	7.05	0.15	1.79	5.06
D1	30.00	4	8.18	0.12	1.35	8.89	0.13	0.84	9.03
A2	60.00	5	5.84	0.16	3.31	6.34	0.16	2.07	4.25
B2	60.00	6	6.33	0.23	3.70	6.88	0.24	2.32	4.30
C2	60.00	7	5.84	0.16	3.29	6.34	0.16	2.05	4.26
D2	60.00	8	7.98	0.16	2.58	8.68	0.17	1.61	6.51
A3	120.00	9	4.94	0.16	2.80	5.37	0.16	1.75	3.88
B3	120.00	10	5.57	0.19	3.62	6.05	0.20	2.26	3.86
C3	120.00	11	4.88	0.17	3.27	5.30	0.18	2.04	3.56
D3	120.00	12	7.13	0.18	3.02	7.75	0.19	1.89	5.39
A4	180.00	13	4.18	0.15	2.78	4.54	0.15	1.73	3.31
B4	180.00	14	3.43	0.13	2.51	3.73	0.13	1.57	2.86
C4	180.00	15	3.48	0.12	2.34	3.79	0.13	1.47	3.00
D4	180.00	16	5.90	0.16	2.20	6.42	0.16	1.38	5.17
A5	300.00	17	2.63	0.09	1.72	2.86	0.10	1.07	2.64
B5	300.00	18	2.88	0.11	1.90	3.13	0.11	1.19	2.74
C5	300.00	19	3.76	0.13	2.36	4.09	0.13	1.48	3.23
D5	300.00	20	4.25	0.12	1.75	4.62	0.13	1.10	4.17
A6	420.00	21	3.45	0.11	1.68	3.75	0.12	1.05	3.46
B6	420.00	22	3.28	0.11	2.04	3.56	0.11	1.28	3.02
C6	420.00	23	3.75	0.11	1.98	4.07	0.12	1.24	3.49
D6	420.00	24	3.99	0.13	1.69	4.33	0.14	1.05	3.96
A7	660.00	25	2.90	0.34	2.13	3.15	0.36	1.33	2.42
B7	660.00	26	2.47	0.08	1.53	2.68	0.09	0.96	2.63
C7	660.00	27	2.77	0.08	1.55	3.01	0.09	0.97	2.93
D7	660.00	28	3.08	0.09	1.50	3.35	0.09	0.94	3.30

Note: A = 1.3 – 1.5 mm, B = 1.5 – 1.7 mm, C = 1.7 – 2.0 mm, and D = 2.0 – 2.5 mm

APPENDIX-F

Data for Water Levels in the Boreholes in Field Experiment

Phases	Time Days	Average Pressure Head (m) City tap water and no zeolite	Average Pressure Head (m) CBNG water and zeolite	Average Pressure Head (m) City tap water and zeolite	Average Pressure Head (m) CBNG water and no zeolite
Phase I	0	2.96	2.77	2.81	2.95
	1	2.60	2.55	2.65	2.95
	2	2.21	2.30	2.48	2.88
	3	1.91	2.11	2.37	2.85
	4	1.64	1.80	2.23	2.77
	5	1.50	1.50	2.12	2.70
	6	1.42	1.27	2.03	2.66
	7	1.35	1.08	1.96	2.63
	8	1.30	0.97	1.95	2.63
	9	1.24	0.89	1.94	2.60
	10	1.11	0.74	1.87	2.51
	11	1.07	0.67	1.88	2.50
	12	0.97	0.55	1.83	2.43
	13	0.94	0.49	1.84	2.42
	14	0.86	0.41	1.81	2.38
	15	0.88	0.40	1.86	2.41
	16	0.92	0.42	1.93	2.47
	17	0.86	0.34	1.91	2.43
	18	0.76	0.24	1.84	2.36
	19	0.70	0.17	1.81	2.31
	20	0.70	0.16	1.84	2.33
	21	0.65	0.11	1.82	2.30
	22	0.57	0.04	1.77	2.24
	23	0.55	0.06	1.78	2.23
	24	0.50	0.05	1.76	2.20
	25	0.49	0.07	1.77	2.20
	26	0.50	0.10	1.80	2.23
Phase II	27	2.90	2.78	2.81	2.98
	28	2.29	2.55	2.58	2.88
	29	2.06	2.59	2.64	3.04
	30	1.78	2.46	2.52	3.01
	31	1.60	2.27	2.34	2.93
	32	1.52	2.14	2.24	2.91
	33	1.46	2.00	2.16	2.91
	34	1.42	1.87	2.10	2.93

Data for Water Levels in the Boreholes in Field Experiment

Phase	Time Days	Average Pressure Head (m) City tap water and no zeolite	Average Pressure Head (m) CBNG water and zeolite	Average Pressure Head (m) City tap water and zeolite	Average Pressure Head (m) CBNG water and no zeolite
Phase II	35	1.35	1.71	2.02	2.91
	36	1.26	1.53	1.91	2.85
	37	1.21	1.40	1.89	2.85
	38	1.16	1.28	1.89	2.84
	39	1.09	1.15	1.86	2.80
	40	1.00	1.01	1.81	2.75
	41	1.02	0.97	1.87	2.79
	42	1.02	0.93	1.90	2.82
	43	0.96	0.82	1.87	2.78
	44	0.84	0.69	1.79	2.70
	45	0.81	0.66	1.79	2.68
	46	0.82	0.67	1.82	2.71
	47	0.77	0.62	1.80	2.68
	48	0.74	0.59	1.80	2.67
	49	0.72	0.57	1.80	2.67
	50	0.63	0.48	1.74	2.60
	51	0.62	0.47	1.75	2.60
	52	0.63	0.48	1.79	2.63
	53	0.69	0.53	1.86	2.70
	54	0.64	0.49	1.83	2.67
	55	0.63	0.48	1.85	2.67
	56	0.53	0.38	1.76	2.59
	57	0.51	0.36	1.76	2.57
	58	0.50	0.35	1.77	2.58
	59	0.47	0.31	1.75	2.55
	60	0.46	0.30	1.76	2.56
	61	0.43	0.28	1.75	2.54
	62	0.44	0.29	1.77	2.56
	63	0.48	0.33	1.82	2.61
	64	0.48	0.33	1.84	2.62
	65	0.38	0.23	1.76	2.53
	66	0.35	0.20	1.74	2.51
	67	0.29	0.15	1.70	2.46
	68	0.22	0.07	1.63	2.39

APPENDIX-G

Cumulative Infiltrated Water through Boreholes in the First Two Weeks in Field Experiment

Time (days)	No CBNG & No Zeolite Phase I (Vol. in L)	No CBNG & No Zeolite Phase II (Vol. in L)	CBNG and Zeolite Phase I (Vol. in L)	CBNG and Zeolite Phase II (Vol. in L)	No CBNG but Zeolite Phase I (Vol. in L)	No CBNG but Zeolite Phase II (Vol. in L)	CBNG but no Zeolite Phase I (Vol. in L)	CBNG but no Zeolite Phase II (Vol. in L)
0	0	0	0	0	0	0	0	0
1	25.434	43.0965	15.543	16.2495	11.304	16.2495	0	7.065
2	52.9875	63.585	46.629	26.1405	33.912	22.608	5.652	-5.652
3	74.1825	83.367	60.0525	35.325	41.6835	31.086	7.7715	-3.5325
4	93.258	96.084	81.954	48.7485	51.5745	43.803	13.4235	2.1195
5	103.149	101.736	103.149	57.933	59.346	50.868	18.369	3.5325
6	108.801	105.975	119.3985	67.824	65.7045	56.52	21.195	3.5325
7	113.7465	108.801	132.822	77.0085	70.65	60.759	23.3145	2.1195
8	117.279	113.7465	140.5935	88.3125	71.3565	66.411	23.3145	3.5325
9	121.518	120.105	146.2455	101.0295	72.063	74.1825	25.434	7.7715
10	130.7025	123.6375	156.843	110.214	77.0085	75.5955	31.7925	7.7715
11	133.5285	127.17	161.7885	118.692	76.302	75.5955	32.499	8.478
12	140.5935	132.1155	170.2665	127.8765	79.8345	77.715	37.4445	11.304
13	142.713	138.474	174.5055	137.7675	79.128	81.2475	38.151	14.8365
14	148.365	137.061	180.1575	140.5935	81.2475	77.0085	40.977	12.0105

APPENDIX-H

Data of Post-Field Experiment Soil Analysis for SAR with Depth

Boreholes	Depths (cm)	Ca^{2+} Mg/L Diluted	Mg^{2+} Mg/L Diluted	Na^+ Mg/L Diluted	Ca^{2+} mM/L Corrected	Mg^{2+} mM/L Corrected	Na^+ mM/L Corrected	SAR $(mol/m^3)^{1/2}$
BH1	0-5	0.81	0.38	5.47	0.51	0.40	5.95	6.26
	5-15	0.95	0.39	1.10	0.59	0.41	1.20	1.20
	15-30	1.76	0.80	1.05	1.10	0.83	1.14	0.82
	55-65	4.71	1.85	1.93	2.94	1.93	2.10	0.95
	95-105	8.14	3.31	2.31	5.09	3.45	2.51	0.86
BH2	0-5	0.38	0.11	2.11	0.24	0.11	2.29	3.87
	5-15	0.37	0.12	4.30	0.23	0.13	4.67	7.83
	15-30	1.20	0.50	2.74	0.75	0.52	2.98	2.64
	55-65	9.92	4.20	2.61	6.20	4.38	2.84	0.87
	95-105	10.24	4.21	2.59	6.40	4.39	2.82	0.86
BH3	0-5	0.99	0.40	0.66	0.62	0.42	0.72	0.71
	5-15	0.81	0.40	0.84	0.51	0.42	0.91	0.95
	15-30	2.16	1.16	1.77	1.35	1.21	1.92	1.20
	55-65	8.95	3.84	2.15	5.59	4.00	2.34	0.75
	95-105	9.46	4.23	2.19	5.91	4.41	2.38	0.74
BH4	0-5	2.58	0.81	0.56	1.61	0.84	0.61	0.39
	5-15	6.81	2.37	0.82	4.26	2.47	0.89	0.34
	15-30	10.18	4.37	2.52	6.36	4.55	2.74	0.83
	55-65	6.08	2.89	1.88	3.80	3.01	2.04	0.78
	95-105	10.84	5.26	2.45	6.78	5.48	2.66	0.76
BH5	0-5	0.24	0.11	3.94	0.15	0.11	4.28	8.33
	5-15	0.27	0.10	3.42	0.17	0.10	3.72	7.12
	15-30	0.48	0.21	3.53	0.30	0.22	3.84	5.33
	55-65	1.32	0.56	2.11	0.83	0.58	2.29	1.93
	95-105	1.22	0.50	1.71	0.76	0.52	1.86	1.64
BH6	0-5	0.30	0.10	3.67	0.19	0.10	3.99	7.39
	5-15	0.41	0.20	2.93	0.26	0.21	3.18	4.67
	15-30	2.86	1.60	2.76	1.79	1.67	3.00	1.61
	55-65	3.17	1.43	2.44	1.98	1.49	2.65	1.42
	95-105	5.33	2.15	2.14	3.33	2.24	2.33	0.99

Boreholes	Depths (cm)	Ca^{2+} Mg/L Diluted	Mg^{2+} Mg/L Diluted	Na^+ Mg/L Diluted	Ca^{2+} mM/L Corrected	Mg^{2+} mM/L Corrected	Na^+ mM/L Corrected	SAR $(mol/m^3)^{1/2}$
BH7	0-5	0.90	0.33	1.90	0.56	0.34	2.07	2.17
	5-15	1.71	0.57	0.84	1.07	0.59	0.91	0.71
	15-30	10.29	2.95	0.64	6.43	3.07	0.70	0.23
	55-65	9.89	4.16	1.92	6.18	4.33	2.09	0.64
	95-105	9.08	4.81	2.80	5.68	5.01	3.04	0.93
BH8	0-5	0.18	0.08	3.75	0.11	0.08	4.08	9.21
	5-15	0.20	0.08	4.36	0.13	0.08	4.74	10.38
	15-30	0.31	0.14	5.53	0.19	0.15	6.01	10.31
	55-65	3.19	1.51	2.32	1.99	1.57	2.52	1.34
	95-105	7.34	2.70	1.88	4.59	2.81	2.04	0.75
BH9	0-5	0.74	0.27	0.46	0.46	0.28	0.50	0.58
	5-15	9.54	2.54	0.59	5.96	2.65	0.64	0.22
	15-30	0.90	2.53	0.97	0.56	2.64	1.05	0.59
	55-65	3.72	1.73	1.59	2.33	1.80	1.73	0.85
	95-105	4.41	2.08	1.64	2.76	2.17	1.78	0.80
BH10	0-5	0.39	0.08	4.42	0.24	0.08	4.80	8.40
	5-15	0.25	0.07	2.98	0.16	0.07	3.24	6.77
	15-30	0.27	0.09	2.14	0.17	0.09	2.33	4.54
	55-65	5.68	2.88	2.38	3.55	3.00	2.59	1.01
	95-105	4.13	2.23	1.84	2.58	2.32	2.00	0.90
BH11	0-5	0.35	0.08	3.50	0.22	0.08	3.80	6.92
	5-15	0.59	0.15	7.83	0.37	0.16	8.51	11.75
	15-30	8.68	2.72	4.17	5.43	2.83	4.53	1.58
	55-65	2.01	0.99	1.67	1.26	1.03	1.82	1.20
	95-105	6.01	2.66	1.72	3.76	2.77	1.87	0.73
BH12	0-5	0.47	0.16	0.49	0.29	0.17	0.53	0.78
	5-15	1.88	0.46	0.42	1.18	0.48	0.46	0.35
	15-30	10.09	3.64	0.92	6.31	3.79	1.00	0.31
	55-65	9.55	3.63	2.15	5.97	3.78	2.34	0.75
	95-105	5.95	2.50	1.88	3.72	2.60	2.04	0.81

APPENDIX-I

Data of Post-Field Experiment Soil Analysis for EC and pH with Depth

Boreholes	Sample id	Depth (cm)	EC (dS/m)	pH	Borehole	Sample id	Depth (cm)	EC (dS/m)	pH
BH1	1	0 - 5	1.535	6.56	BH7	1	0 - 5	0.662	6.46
	2	5-15	0.62	6.13		2	5-15	0.771	6.41
	3	15-30	0.907	6.63		3	15-30	1.97	6.12
	4	55-65	1.999	6		4	55-65	2.36	6.5
	5	95-105	2.19	6.14		5	95-105	2.62	6.33
BH2	1	0 - 5	0.604	6.5	BH8	1	0 - 5	0.933	7.22
	2	5-15	1.159	7.58		2	5-15	1.014	8.25
	3	15-30	1.253	7.02		3	15-30	1.369	8.36
	4	55-65	2.86	5.61		4	55-65	1.589	6.53
	5	95-105	2.72	5.63		5	95-105	1.95	6.16
BH3	1	0 - 5	0.547	5.91	BH9	1	0 - 5	0.319	6.49
	2	5-15	0.543	6.45		2	5-15	1.79	6.24
	3	15-30	1.296	6.23		3	15-30	1.68	6.16
	4	55-65	2.43	6.66		4	55-65	1.663	6.16
	5	95-105	2.51	6.52		5	95-105	1.792	6.1
BH4	1	0 - 5	1.097	6.53	BH10	1	0 - 5	1.089	8.3
	2	5-15	1.89	6.12		2	5-15	0.758	7.26
	3	15-30	2.64	6.34		3	15-30	0.61	7.22
	4	55-65	2.56	5.98		4	55-65	1.66	6.15
	5	95-105	2.66	6.22		5	95-105	1.972	6.22
BH5	1	0 - 5	0.959	6.99	BH11	1	0 - 5	0.772	7.21
	2	5-15	0.774	6.9		2	5-15	1.321	7.03
	3	15-30	0.91	6.8		3	15-30	2.46	6.38
	4	55-65	0.97	6.12		4	55-65	1.094	6.55
	5	95-105	0.857	6.09		5	95-105	1.84	6.32
BH6	1	0 - 5	0.856	7.9	BH12	1	0 - 5	2.56	6.75
	2	5-15	0.776	6.88		2	5-15	2.16	6.26
	3	15-30	1.67	6		3	15-30	2.16	6.97
	4	55-65	1.618	6.3		4	55-65	2.28	6.1
	5	95-105	1.85	5.9		5	95-105	2.17	6.16

APPENDIX-J

Major Cation Concentrations in Field CBNG Coproduced Water and City Tap Water

	Samples	Ca2+ (mg/L)	Mg2+ (mg/L)	Na+ (mg/L)
City Tap Water	1	5.70	0.90	14.24
	2	5.75	0.93	14.79
	3	5.79	0.92	14.34
Average		5.75	0.92	14.46
CBNG Coproduced Water	1	5.50	2.25	299.00
	2	5.50	2.25	303.75
	3	5.55	2.25	296.50
Average		5.52	2.25	299.75